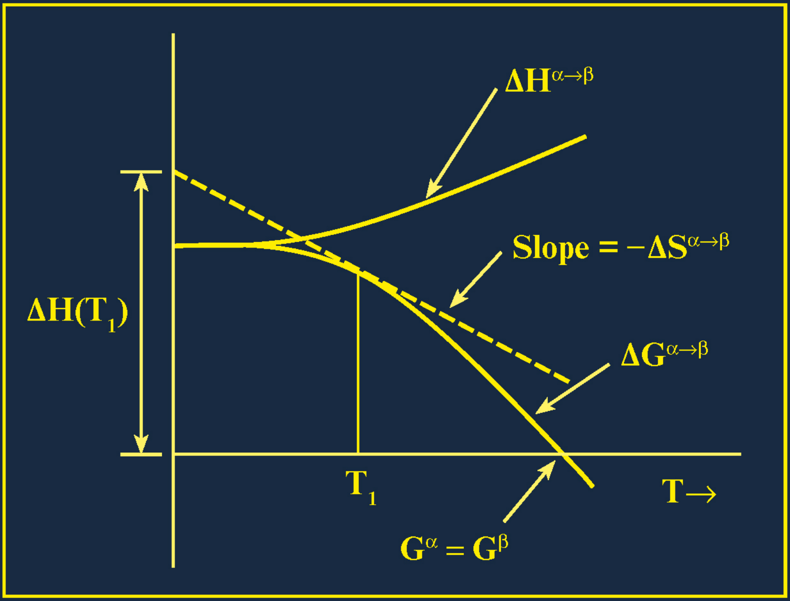
Introduction to the THERMODYNAMICS OF MATERIALS

SIXTH EDITION



David R. Gaskell
David E. Laughlin

CRC Press
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Dedication

Grandchildren are the crown of the aged.

(Proverbs 17:6)

Sadie, Gabe, Rowan, Sawyer, Ramona,
Adam, Charlie, Astrid, and Reuben.

The LORD bless you … and may you
(also) see your children's children.

(Psalm 128:5ff.)

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Contents

Part I
Thermodynamic Principles

Chapter 3

Chapter 4

Part II
Phase Equilibria

Part III
Reactions and Transformations of Phases

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Preface

In preparing this new edition, I have endeavored to retain the substance of the previous five editions while adding some flavors of my own. These additions are ones which reflect my research interests (in magnetism and phase transformations) and are also relevant to current materials science students. Additions to this book include the role of work terms other than P-V work (e.g., magnetic work), along with their attendant aspects of entropy, Maxwell relations, and the role of such applied fields on phase diagrams. Also, there is an increased emphasis on the thermodynamics of phase transformations. These topics are sprinkled throughout the text, and an entirely new chapter (Chapter 15) has been included which collects specific thermodynamic applications to the study of phase transformations. To make the agreed-upon deadline for the manuscript, other potential changes remain on my computer. Perhaps they will see the light of day in the seventh edition!

The text is written for undergraduate materials science students and can be utilized by materials-related graduate students who have not taken such a course in their undergraduate studies. It has been more than 40 years since I used the first edition of the text when teaching my first class in thermodynamics at Carnegie Mellon University. I also used the text in the mid-1990s in several summer school classes on thermodynamics at CMU. Experience makes me aware that it is impossible to make it through the entire text in a one-semester course. In this edition, I have divided the book into three sections. I suggest that at least the first section (“Thermodynamic Principles”) and as much as possible of the second section (“Phase Equilibria”) be included in a one-semester undergraduate course. The third section (“Reactions and Transformations”) can make its way into other courses of the curriculum that deal with oxidation, energy, and phase transformations.

This author is well aware of the rise of computational materials science and the need for computational thermodynamics in such courses. I consider this text a prerequisite for any course that utilizes the computational methods of thermodynamics: one should not compute what one does not understand!

I acknowledge the continual support of my family, especially my wife Diane, who has been very patient over the years with my excursions to my study in preparation for lectures, often on weekends! All of my students have been helpful in so many ways over the years of teaching and research. My former student Dr. Jingxi Zhu is especially thanked for help with the proof reading of several chapters. For nearly twenty years I have had the benefit of collaboration and friendship with Prof. Michael McHenry with whom I have taught magnetic materials classes in which thermodynamics has played a major role. Lastly, I acknowledge my long friendship with Prof. William A. Soffa of the University of Virginia for countless discussions and learning sessions on topics relevant to thermodynamics, magnetism, phase transformations, as well as the history and philosophy of science. I hope that he has learned at least half as much from me as I have from him.

I count it a privilege to produce the sixth edition of Gaskell's *Thermodynamics*, some 4 years after David's death. May the text continue to train materials students well in the basics of thermodynamics.

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Postscript: Typographical errors enter thermodynamics books at an alarming rate. There is a Web site for this text https://www.crcpress.com/product/isbn/9781498757003 and on it will be a list of typos. Please feel free to send me any that you find. Send all typos to Gaskell.Laughlin@gmail.com.

Authors

David R. Gaskell received a BSc in metallurgy and technical chemistry from the University of Glasgow, Scotland, and a PhD from McMaster University, Hamilton, ON. Dr. Gaskell's first faculty position was at the University of Pennsylvania, where he taught from 1967 to 1982 in metallurgy and materials science. In 1982, he was recruited at the rank of professor by Purdue University, West Lafayette, IN, where he taught until 2013. During Dr. Gaskell's career, he served as a visiting professor at the National Research Council of Canada, Atlantic Regional Laboratory, Halifax, NS (1975–1976), and as a visiting professor at the G. C. Williams Co-operative Research Centre for Extraction Metallurgy, in the Department of Chemical Engineering, University of Melbourne, Australia (1995). He also held a position during his sabbatical in Australia as a visiting scientist at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Clayton, Victoria. Dr. Gaskell authored the textbooks *Introduction to Metallurgical Thermodynamics*, *Introduction to the Thermodynamics of Materials*, and *Introduction to Transport Phenomena in Materials Engineering.*

David E. Laughlin is the ALCOA Professor of Physical Metallurgy in the Department of Materials Science and Engineering of Carnegie Mellon University (CMU), Pittsburgh, PA, and also has a courtesy appointment in the Electrical and Computer Engineering Department. He was the principal editor of *Metallurgical and Materials Transactions* from 1987 to 2016. David is a graduate of Drexel University, Philadelphia, PA (1969), and the Massachusetts Institute of Technology, Cambridge, MA (1973). He is a fellow of the Minerals, Metals and Materials Society (TMS), an honorary member of the American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME), and a fellow of ASM International. He is also the recipient of several CMU awards for teaching and research excellence and was named a distinguished scientist of the TMS Electronic, Magnetic and Photonic Materials Division. He has authored more than 400 technical publications in the field of phase transformations, physical metallurgy, and magnetic materials, has been awarded 12 patents and has edited or coedited seven books, including the fifth edition of *Physical Metallurgy.*

PART I

Thermodynamic Principles

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CHAPTER 1

Introduction and Definition of Terms

1.1 INTRODUCTION

The term *thermodynamics* is related to the two Greek words *therme* and *dynamikos*, which translate into English as “heat” and “power” (or “movement”), respectively. Thermodynamics is the physical science that focuses on the relationship between energy and work as well as the equilibrium states and variables of systems that are being investigated. Importantly, thermodynamics defines heat and identifies it as the process in which energy is transferred from one region to another down a temperature gradient. In this text, we will mainly use the phrase *thermal energy* to identify this form of energy transfer, but sometimes the word *heat* will be used. Thermodynamics deals with the *conservation* of energy as well as the *conversion* of the various forms of energy into each other or into work. Thermodynamics is concerned with the behavior of and interactions between portions of the universe denoted as *systems* and those portions of the universe called the *surroundings* or the *environment*. The system is that part of the universe we wish to investigate in detail, and the surroundings is that part of the universe outside the system which may interact with it by exchanging energy or matter. The system may perform work on the surroundings or have work performed on it by the surroundings. The boundary or wall between the system and the surroundings is what allows such interactions. In what we will call *simple thermodynamic systems*, the surroundings interacts with the system only via pressure and temperature changes. The composition remains constant in simple systems.

It is convenient to characterize systems by the kinds of interactions that are allowed between them and their surroundings.

1. *Isolated systems*: In these systems, no work is done on or by the system. In addition, energy or matter may not enter or leave it. Thus, the energy of these systems remains constant, as does the overall composition. Isolated systems are therefore unaffected by changes in the surroundings.
2. *Closed systems*: These are systems which may receive (or give off) energy from (or to) the surroundings. The boundaries are called *diathermal*; that is, they allow thermal energy to transfer through them into or out of the system. However, the

boundaries are impermeable to matter; hence, the amount of matter is constant in these systems.

3. *Open systems*: These are systems which can exchange both energy and matter with the surroundings. Neither the energy nor the composition of these systems need remain constant. The boundaries are both permeable and diathermal.

The boundaries or walls of the system are classified as follows:

- *Adiabatic*: No thermal energy can pass through.
- *Diathermal*: Thermal energy can pass through.
- *Permeable*: Matter can pass through.
- *Impermeable*: Matter cannot pass through.
- *Semipermeable*: Some components are able to pass through, while others are not.

It is evident that when evaluating a system, it is important that its interactions with the surroundings be either known or determined.

The macroscopic property of systems called *temperature* is a distinguishing aspect of the subject of thermodynamics. Temperature is not utilized in the mechanical description of matter (mass, velocity, momentum, etc.) encountered in introductory physics courses. The discovery that mechanical energy could be *converted* to thermal energy (via friction) was an important early step in the development of thermodynamics. Later, the conversion of thermal energy into mechanical work, or other forms of energy, became a focus of classical thermodynamics. This will be discussed in the introduction to the First Law of Thermodynamics in Chapter 2.

The system may be a machine (heat engine) or a device (transducer) of interest to us. In the study of the thermodynamics of materials, the system is usually composed of matter, which is anything that has mass and occupies space. Matter has a given temperature, pressure, and chemical composition, as well as physical properties such as thermal expansion, compressibility, heat capacity, viscosity, and so on. A central aim of applied thermodynamics is the determination of the effect of the surroundings on the equilibrium state of a given system. Since the surroundings interacts with the system by transferring or receiving various forms of energy or matter with it, another focus of applied thermodynamics is the establishment of the relationships which exist between the equilibrium state of a given system and the influences which have been brought to bear on it.

1.2 THE CONCEPT OF STATE

A fundamental concept in thermodynamics is that of the thermodynamic *state*. If it were possible to know the masses, velocities, positions, and all modes of motion (translational, rotational, etc.) of all of the constituent particles in a system, this knowledge would serve to describe the *microscopic state* of the system, which, in turn, would determine, in principle, all of the thermodynamic variables of the system that can be measured (energy, temperature, pressure, etc.). For systems with macroscopic dimensions, this would entail more than 10^{24} coordinates, which is clearly an impossible task. In the absence of such detailed knowledge as is required to determine the microscopic state of the system, classical thermodynamics begins with a consideration of the variables of the system, which, when determined, completely define the *macroscopic state* of the system; that is, when all of the thermodynamic variables are fixed, then the macroscopic state of the system is fixed and is said to be in equilibrium. It is found that when the values of a small number of thermodynamic variables are fixed, the values of the rest of the thermodynamic variables are also fixed. Indeed, when a *simple system* such as a given quantity of a substance of fixed composition is being considered, the fixing of the values of two of the thermodynamic variables fixes the values of the rest of the thermodynamic variables. Thus, only two thermodynamic variables are independent, which, consequently, are called the *independent thermodynamic variables* of the system. All of the other variables are *dependent variables*. The thermodynamic state of such a system is thus uniquely determined when the values of the two independent variables are fixed. This has been called the *Duhem* postulate*. There are situations, however, when more independent variables are needed—for example, when thermodynamic fields other than temperature and pressure are present. Such fields include electric or magnetic fields.

The values of the thermodynamic variables of a system are not functions of the history of the system; that is, they are independent of the path over which the process has taken the system in changing it from its previous state to its present state. These thermodynamic variables are thus *intrinsic* to the state of the system. Such thermodynamic variables are functions of state and can be expressed as *exact differentials*[†] of their dependent variables. There are, of course, times when the system has properties which do depend on its history; these properties are commonly called *extrinsic* properties. They are not equilibrium properties of the system; given time, they may change. It should be noted that some of these extrinsic properties can be manipulated to produce materials with optimum characteristics.

Consider the volume, V, of 1 mole of a pure gas. The value of the volume is dependent on the values of the pressure, P, and temperature, T, of the gas. The relationship between the dependent variable V and the independent variables P and T can be expressed as

$$V = V(P,T) \tag{1.1}$$

In a three-dimensional diagram, the coordinates of which are volume, pressure, and temperature, the points in V-P-T space which represent the equilibrium states of existence of the system lie on a surface. This is shown in Figure 1.1 for 1 mole of a simple gas. Fixing the values of any two of the three variables fixes the value of the third variable of the system when it is in equilibrium.

Consider a process which changes the state of the gas from state 1 to state 2. This process causes the volume of the gas to change by

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* Pierre Maurice Marie Duhem (1861–1916).

[†] See Appendix B for a discussion of exact differential equations.

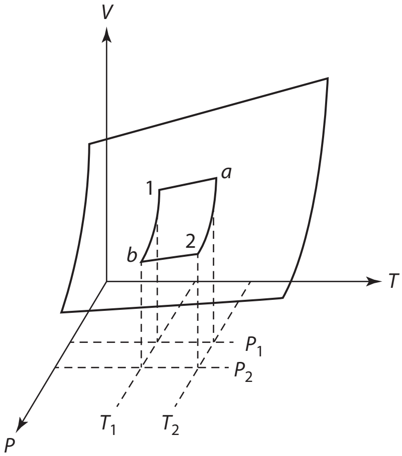

Figure 1.1 The equilibrium states of existence for 1 mole of gas in *V*-*P*-*T* space, shown to lie on a surface.

$$\Delta V = V_2 - V_1$$

The process could proceed along many different paths on the *V*-*P*-*T* surface, two of which, 1 → *a* → 2 and 1 → *b* → 2, are shown in Figure 1.1. Consider the path 1 → *a* → 2. The change in volume is

$$\Delta V = \Delta V_{1\to a} + \Delta V_{a\to 2}$$

$$\Delta V = \left(V_a - V_1\right) + \left(V_2 - V_a\right)$$

$$\Delta V = V_2 - V_1$$

where:

1 → *a* occurs at the constant pressure, P_1
a → 2 occurs at the constant temperature, T_2

We can express these changes as

$$\Delta V_{1\to a} = V_a - V_1 = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT$$

and

$$\Delta V_{a\to 2} = V_2 - V_a = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

Thus,

$$\Delta V_{1\to 2} = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_{T_2} dP \tag{1.2}$$

Similarly, for the path 1 → b → 2:

$$\Delta V_{1\to b} = V_b - V_1 = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_{T_1} dP$$

and

$$\Delta V_{b\to 2} = V_2 - V_b = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial P} \right)_{P_2} dT$$

Hence,

$$\Delta V_{1\to 2} = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_{P_2} dT \tag{1.3}$$

Equations 1.2 and 1.3 must yield the same value of $\Delta V_{1\to 2}$. In the limit of infinitesimal change in volume, these equations yield the complete differential of Equation 1.1:

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT \tag{1.4}$$

The change in volume caused by changing the state of the gas from state 1 to state 2 depends only on the volumes at states 1 and 2 and is independent of the path taken by the gas between the states. This is because the volume of the gas is a *state function* and Equation 1.4 is an exact differential of the volume, which is a thermodynamic state variable.

The partial differentials which relate the change in volume to changes in the intensive thermodynamic variables (P and T) are related to the properties of the gas—namely,

$\beta_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P} \right)_T$, the isothermal compressibility with dimensions of P^{-1}

and

$\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T} \right)_P$, the coefficient of thermal expansion with dimensions of T^{-1}

Thus, the complete differential of Equation 1.4 can be written as

$$dV = \alpha V dT - \beta_T V dP$$

This equation can be easily integrated over the ranges in T and P, where β_T and α are assumed to be constant.

1.3 EXAMPLE OF EQUILIBRIUM

In Figure 1.1, the equilibrium states of the system are shown to lie on a surface in V-P-T space. This means that equilibrium exists at unique combinations of P and T such that P and T satisfy the equation for the $V(P,T)$ surface.

A particularly simple system is illustrated in Figure 1.2. In this figure, 1 mole of a gas is shown to be contained in a cylinder by a movable piston. The system is at equilibrium when

1. The pressure exerted *by* the gas *on* the piston equals the pressure exerted *by* the piston *on* the gas.
2. The temperature of the gas is the same as the temperature of the surroundings (provided that thermal energy can be transferred through the boundary of the cylinder; that is, the boundaries of the cylinder are diathermal).

The state of the gas is thus fixed, and equilibrium occurs as a result of the establishment of a balance between the tendency of the external influences acting on the system to cause a change in the system (i.e., the temperature and pressure) and the tendency of the system to resist such a change. Fixing the pressure of the gas at P_1

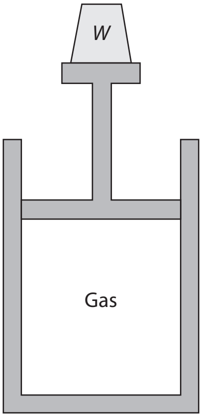

Figure 1.2 One mole of a gas is shown to be contained in a cylinder by a piston. The walls of the cylinder are diathermal, and *W* is the mass that is exerting pressure on the gas.

and T_1 determines the state of the system and hence fixes the volume at the value V_1. If, at constant temperature, by a suitable increase in the weight placed on the piston, the pressure exerted on the gas is increased to P_2 (Figure 1.1), the resulting imbalance between the pressure exerted by the gas and the pressure exerted on the gas causes the piston to move into the cylinder. This process decreases the volume of the gas and hence increases the pressure of the gas which it exerts on the piston until equalization of the pressures is restored. As a result of this process, the volume of the gas decreases from V_1 to V_b. Thermodynamically, the isothermal change of pressure from P_1 to P_2 changes the state of the system from state 1 (characterized by P_1, T_1) to state b (characterized by P_2, T_1), and the volume, as a dependent variable, decreases from the value V_1 to V_b. This shows that work was performed on the gas by the piston.

If the pressure exerted by the piston on the gas is maintained constant at P_2 and the temperature of the surroundings is raised from T_1 to T_2, the consequent temperature gradient across the cylinder wall causes the transfer of thermal energy from the surroundings into the gas. The increase in the temperature of the gas at the constant pressure P_2 causes the expansion of the gas, which pushes the piston out of the cylinder. When the gas is uniformly at the temperature T_2, the volume of the gas is V_2. Again, thermodynamically, the increasing of the temperature from T_1 to T_2 at the constant pressure P_2 changes the state of the system from state b (P_2, T_1) to state 2 (P_2, T_2), and the volume as a dependent variable increases from V_b in the state b to V_2 in the state 2. In this case, work was performed on the piston by the expanding gas. Since volume is a state function, the final volume V_2 would be the same if the state were first changed from 1 to a and then from a to 2.

1.4 THE EQUATION OF STATE OF AN IDEAL GAS

The pressure–volume relationship of a gas at constant temperature was determined experimentally in 1660 by Robert Boyle (1627–1691), who found that, at constant T,

$$P \propto \frac{1}{V}$$

This is known as *Boyle's law*. Similarly, the volume–temperature relationship of a gas at constant pressure was determined experimentally in 1787 by Jacques-Alexandre-Cesar Charles (1746–1823). This relationship, which is known as *Charles' law*, is that, at constant pressure,

$$V \propto T$$

Thus, in Figure 1.1, which is drawn for 1 mole of a gas, sections of the V-P-T surface drawn at constant T produce rectangular hyperbolae which asymptotically approach the P and V axes in a P versus V plot, and sections of the surface drawn at constant P produce straight lines in a V versus T plot. These sections are shown in Figure 1.3a and b.

In 1802, Joseph-Luis Gay-Lussac (1778–1850) observed that the thermal coefficient of what were called *permanent gases* was a constant. Previously, we noted that the coefficient of thermal expansion, α, is defined as the fractional increase of the volume of the gas, with the change in temperature at constant pressure; that is,

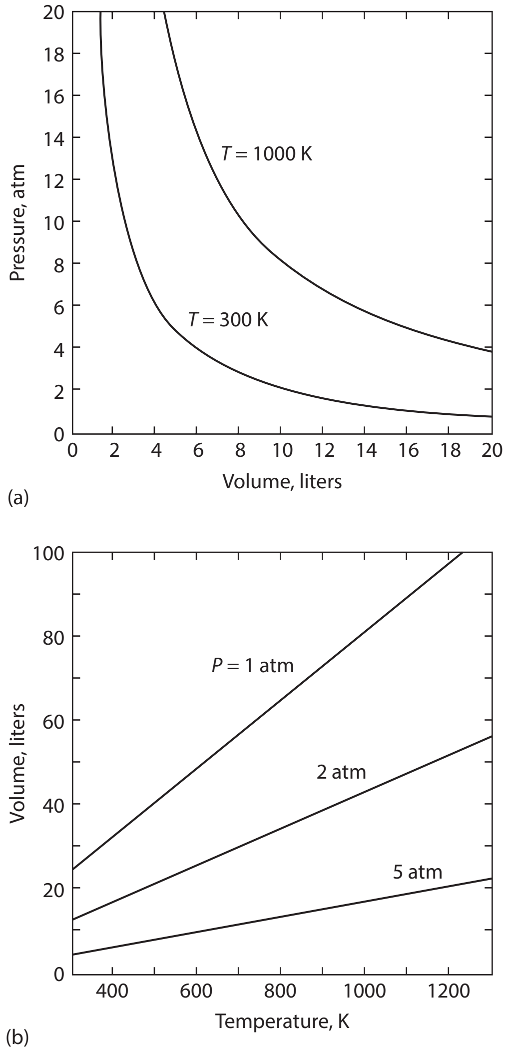

Figure 1.3 (a) The variation, with pressure, of the volume of 1 mole of ideal gas at 300 and 1000 K. (b) The variation, with temperature, of the volume of 1 mole of ideal gas at 1, 2, and 5 atm.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1.5}$$

where V is the volume of 1 mole of the gas at 0°C. Gay-Lussac obtained a value of $1/267$ for α, but more refined experimentation by Henri Victor Regnault (1810–1878) in 1847 showed α to have the value $1/273$. Later, it was found that the accuracy with which Boyle's and Charles' laws describe the behavior of different gases varies from one gas to another. Generally, gases with lower boiling points obey the laws more closely than do gases with higher boiling points. It was also found that the laws are more closely obeyed by all gases as the pressure of the gas is decreased. It was thus found convenient to invent a hypothetical gas which obeys Boyle's and Charles' laws exactly *at all temperatures and pressures*. This hypothetical gas is called the *perfect* or *ideal gas*, and it has a value of $\alpha = 1/273.15$.

The existence of a finite coefficient of thermal expansion therefore sets a limit on the thermal contraction of the ideal gas; that is, since $\alpha = 1/273.15$, then the fractional decrease in the volume of the gas, per degree decrease in temperature, is $1/273.15$ of the volume at 0°C. Thus, at −273.15°C, the volume of the gas would be zero, and hence the limit of temperature decrease, −273.15°C, is the absolute zero of temperature. This defines an absolute scale of temperature called the *ideal gas temperature scale*, which is related to the arbitrary Celsius scale by the equation

$$T\ (\text{degrees absolute}) = T\ (\text{degrees Celsius}) + 273.15$$

A combination of Boyle's law:

$$P_0V(T,P_0) = PV(T,P)$$

and Charles' law:

$$\frac{V(P_0,T_0)}{T_0} = \frac{V(P_0,T)}{T}$$

where:

P_0 = standard pressure (1 atmosphere [atm])

T_0 = standard temperature (273.15 degrees absolute)

$V(P,T)$ = volume at pressure P and temperature T

gives

$$\frac{PV}{T} = \frac{P_0V}{T_0} = \text{constant} \tag{1.6}$$

From Avogadro's (Lorenzo Avogadro, 1776–1856) hypothesis, the volume per gram-mole* of all ideal gases at 0°C and 1 atm pressure (termed *standard temperature and pressure* [STP]) is 22.414 liters. Thus, the constant in Equation 1.6 has the value

$$\frac{P_0V_0}{T_0} = \frac{1\ \text{atm} \cdot 22.414\ \text{liters}}{273.15\ \text{K} \cdot \text{mole}} = 0.082057 \frac{\text{liter} \cdot \text{atm}}{\text{degree} \cdot \text{mole}}$$

This constant is given the symbol R, the *gas constant*, and, being applicable to all ideal gases, it is a universal constant. Equation 1.6 can thus be written as

$$PV = RT \tag{1.7}$$

which is the equation of state for 1 mole of ideal gas. Equation 1.7 is also called the *ideal gas law*. Because of the simple form of its equation of state, the ideal gas is used extensively as a system in thermodynamic discussions.

The existence of an absolute temperature scale shows that different systems can be assigned a single-valued function to designate the *intensity* of its thermal energy. The Zeroth Law of Thermodynamics can be stated as follows: if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C. Thus, all three systems must have the same absolute temperature, and therefore, the temperature of a system is a thermodynamic intensive state variable. If the temperature gradient between two systems is equal to zero, the systems are in thermal equilibrium. If the temperature gradient is nonzero, there is a tendency for energy to transfer from the high-temperature system to the low-temperature system, commonly called *heat transfer*. We will see that temperature is a measure of the energy of the particles which compose the system.

1.5 THE UNITS OF ENERGY AND WORK

The unit liter·atm occurring in the units of R is an energy term. Work is done when a force moves a body through a distance. Work and energy have the dimensions force·distance. Pressure is force per unit area; hence, work and energy can have the dimensions pressure·area·distance, or pressure·volume. The unit of energy in SI is the joule, which is the work done when a force of 1 newton moves a distance of 1 meter. Liter·atm are converted to joules as follows:

$$1\ \text{atm} = 101{,}325\ \frac{\text{newtons}}{\text{meters}^2}$$

---

* A gram-mole (g-mole or mole) of a substance is the mass of Avogadro's number of molecules of the substance expressed in grams. Thus, a g-mole of O_2 has a mass of 32 g, a g-mole of C has a mass of 12 g, and a g-mole of CO_2 has a mass of 44 g.

Multiplying both sides by liters (10^{-3} meters^3) gives

$$1 \text{ liter} \cdot \text{atm} = 101.325 \text{ newton} \cdot \text{meters} = 101.325 \text{ joules}$$

Thus,

$$R = 0.082057 \ \frac{\text{liter} \cdot \text{atm}}{\text{degree} \cdot \text{mole}}$$

$$R = 8.3144 \ \frac{\text{joules}}{\text{degree} \cdot \text{mole}}$$

Other forms of work, such as magnetic and electrical, and their conversions will be discussed as they arise in the course of the text.

1.6 EXTENSIVE AND INTENSIVE THERMODYNAMIC VARIABLES

Thermodynamic state variables are either *extensive* or *intensive*. Extensive variables have values which depend on the size of the system, whereas values of intensive variables are independent of the size of the system. Volume is an extensive variable, and temperature and pressure are intensive variables. The values of extensive variables, expressed per unit volume or unit mass of the system, have the characteristics of intensive variables; for example, the volume per unit mass (specific volume) and the volume per mole (molar volume) are variables whose values are independent of the size of the system. For a system of n moles of an ideal gas, the equation of state is

$$PV' = nRT$$

where V' is the total volume of the system. Per mole of the system, the equation of state reduces to Equation 1.7:

$$PV = RT$$

where V, the molar volume of the gas, equals V'/n. The molar volume of an ideal gas at Standard Temperature Pressure (STP) is 22.414 liters.

1.7 EQUILIBRIUM PHASE DIAGRAMS AND THERMODYNAMIC COMPONENTS

Of the several ways to graphically represent the equilibrium states of the existence of a system, the *constitution* or *equilibrium phase diagram* is the most popular and convenient. The complexity of a phase diagram is determined primarily by the number of *components* which occur in the system, where components are chemical species of fixed composition. The simplest components are chemical elements

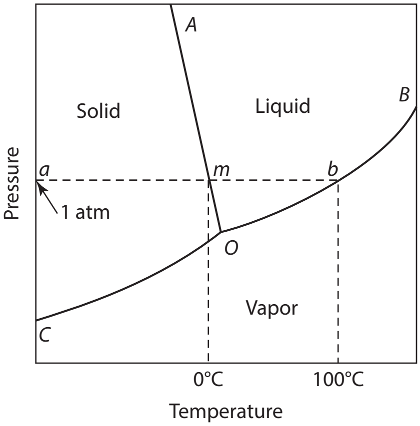

Figure 1.4 Schematic representation of part of the pressure–temperature equilibrium phase diagram for H_2O. The melting point is designated as *m* and the boiling point as *b*.

and stoichiometric compounds. Systems are primarily categorized by the number of components which they contain—for example, one-component (unary) systems, two-component (binary) systems, three-component (ternary) systems, four-component (quaternary) systems, and so on.

The phase diagram of a one-component system with only two independent state variables is a two-dimensional representation of the dependence of the equilibrium state, with the two independent variables as the coordinate axes. Pressure and temperature are normally chosen as the two independent variables. Figure 1.4 shows a schematic representation of part of such a phase diagram for H_2O. The full curves in Figure 1.4 divide the diagram into three areas, designated solid, liquid, and vapor. If a quantity of pure H_2O is at some temperature and pressure which is represented by a point *within* the area *AOB*, the equilibrium state of the H_2O is a liquid. Similarly, within the area *COA* and below the *COB curve*, the equilibrium states are, respectively, the solid and vapor states of water. When the equilibrium state lies within one of these regions, it is said to be *homogeneous*; that is, it consists of only one phase of water.

If the state of existence lies on a curve, the equilibrium state consists of two phases. On the curve *AO*, the liquid and solid H_2O coexist in equilibrium with one another. States such as these are called *heterogeneous*. For now,* we define a *phase* as being a finite volume in the physical system within which the thermodynamic variables are uniformly constant; that is, they do not experience any abrupt change in passing from one point in the volume to another.

The curve *AO* represents the simultaneous variation of *P* and *T* required for the maintenance of the equilibrium between solid and liquid H_2O, and thus represents the influence of pressure on the melting temperature of ice. Similarly, the curves *CO* and *OB* represent the simultaneous variations of *P* and *T* required, respectively, for the maintenance of the equilibrium between solid and vapor H_2O and between liquid

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* See the introduction to chapter 15 for a more precise definition of phase.

and vapor H_2O. The curve *CO* is thus the variation, with temperature, of the saturated vapor pressure of solid ice or, alternatively, the variation, with pressure, of the sublimation temperature of water vapor. The curve *OB* is the variation, with temperature, of the saturated vapor pressure of liquid water or, alternatively, the variation, with pressure, of the dew point of water vapor. The three two-phase equilibrium curves meet at the point *O* (the triple point), which thus represents the unique values of *P* and *T* required for the establishment of the three-phase (solid + liquid + vapor) equilibrium.

The path *amb* indicates that if a quantity of ice is heated at a constant pressure of 1 atm, melting occurs at the state *m*, which, by definition, is the normal melting temperature of ice. Boiling occurs at the state *b*, which is the normal boiling temperature of water.

We have seen that phases may be solids, liquids, or gases. Gases are single-phase solutions and, hence, are homogeneous phases. Liquids may be homogeneous and single phase or they may divide into regions of different composition and therefore be composed of two or more phases. Likewise, solids may be single phase or may also be composed of more than one phase. It is common to call a metal composed of more than one component an alloy. Alloys may be single phase or multiphase. A single-phase crystalline alloy consists of two or more components distributed randomly on a single crystal structure. Such single-phase alloys are called *solid solutions*.

If the system contains two components, a composition axis must be included and, consequently, the complete diagram is three-dimensional, with the coordinates composition, temperature, and pressure. In most cases of condensed phases, however, it is sufficient to present a binary phase diagram as a constant-pressure section of the three-dimensional diagram. The constant pressure chosen is normally 1 atm, and the coordinates are composition and temperature. Figure 1.5, which is a typical simple binary phase diagram, shows the phase relationships occurring in

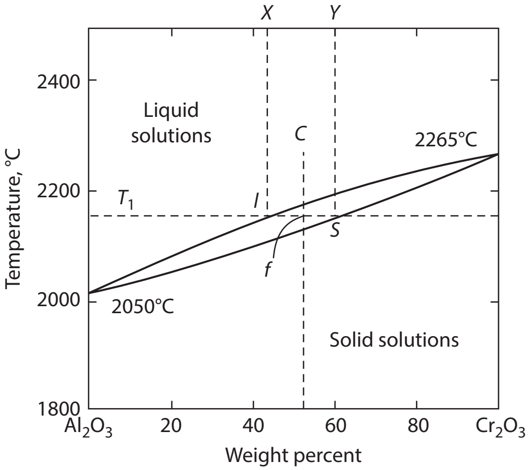

Figure 1.5 The temperature composition equilibrium phase diagram for the system Al_2O_3–Cr_2O_3 at a constant pressure of 1 atm.

the system Al_2O_3–Cr_2O_3 at 1 atm pressure. This phase diagram shows that, at temperatures below the melting temperature of Al_2O_3 (2050°C), solid Al_2O_3 and solid Cr_2O_3 are completely miscible in all proportions and form a solid solution. This can occur because Al_2O_3 and Cr_2O_3 have the same crystal structure (corundum, space group $R\bar{3}c$) and the Al^{3+} and Cr^{3+} ions are of similar size. The Al^{3+} and Cr^{3+} ions are considered to be randomly distributed on the c sites of the space group $R\bar{3}c$. At temperatures above the melting temperature of Cr_2O_3 (2265°C), liquid Al_2O_3 and liquid Cr_2O_3 are completely miscible in all proportions and form a liquid solution.

This diagram thus contains areas of complete solid solubility and complete liquid solubility, which are separated from one another by a two-phase area in which solid and liquid solutions coexist in equilibrium with one another. For example, at the temperature T_1, the Al_2O_3–Cr_2O_3 system of composition between X and Y exists as a two-phase system comprising a liquid solution of composition l in equilibrium with a solid solution of composition s. The relative proportions of the two phases present in equilibrium depend only on the overall composition of the system in the range X–Y and are determined by the lever rule, as follows:

> For the overall composition C at the temperature T_1, the fraction of solid in equilibrium at T_1 is given as lC/lS and the fraction of liquid is given as CS/lS where the numerator and denominators of the expressions are the length of the cords denoted on the phase diagram.

Because the only requirement of a component is that it has a fixed composition, the designation of the components of a system is somewhat arbitrary. In the system Al_2O_3–Cr_2O_3, the obvious choice of the components is Al_2O_3 and Cr_2O_3. However, the most convenient choice is not always as obvious, and the general arbitrariness in selecting the components will be discussed later when dealing with other oxide phase diagrams.

1.8 LAWS OF THERMODYNAMICS*

Sometimes, thermodynamics is summarized by stating its laws, which can be treated either as experimentally determined facts of nature or as axioms from which other thermodynamic relationships can be derived. We have seen that the so-called Zeroth Law introduces us to the important intensive thermodynamic variable temperature, T, which is a measure of the thermal intensity of a material and allows the determination of thermal equilibrium. The other three laws are summarized in the following subsections and will be the subject of study throughout the text.

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* A very good summary of the Laws of Thermodynamics is found in Peter Atkins, *The Laws of Thermodynamics: A Very Short Introduction*, Oxford University Press, Oxford, UK, 2010.

1.8.1 The First Law of Thermodynamics

The First Law not only states that the energy of the universe is *conserved* but it also posits that the various forms of energy (e.g., thermal, electrical, magnetic, and mechanical) can be *converted* into other forms of energy. When first delineated, it was the fact that thermal energy (heat) could be converted to mechanical work that was of special interest (heat engines). This law also defines an important extensive thermodynamic state function called the *internal energy*, U, of the system under investigation.

1.8.2 The Second Law of Thermodynamics

Although the Second Law is the one that often gets the most attention in popular discussions of science, it is often incorrectly understood! Care must be taken in applying the law by delineating the system and the surroundings. This law allows us to make important predictions of the direction in which a system will evolve with time during spontaneous processes, if other important caveats are taken into account. The Second Law introduces another important extensive thermodynamic state function called *entropy*, S. A short version of the Second Law is that the entropy of the universe never decreases.

1.8.3 The Third Law of Thermodynamics

In its boldest form, the Third Law states that when a system which is in complete internal equilibrium approaches the absolute zero in temperature, all of the aspects of its entropy approach zero. Sometimes, the Third Law is stated as follows: a system can never be taken to the absolute zero in temperature. This is also called the *unattainability principle*.

The Laws of Thermodynamics will be discussed in the following chapters and applied to the thermodynamic stability of systems in later chapters of the text.

1.9 SUMMARY

1. In thermodynamics, the universe is divided into the system (that part of the universe of interest to us) and the surroundings. There are several kinds of walls between the system and the surroundings, and each type gives rise to a system with specific characteristics.
2. In thermodynamics, the equilibrium of the system is of interest in that, if it is known, one can determine if the state of the system will change and in which direction such a change would go.
3. The state of a simple system is determined by its temperature and pressure, the two intensive independent variables of the system.

4. Other thermodynamic variables are functions of pressure and temperature, and graphs may be plotted which display the equilibrium states of the system as a function of the independent variables.
5. The Zeroth Law of Thermodynamics introduces the intensive variable temperature, T.
6. The First Law of Thermodynamics states that the energy of the universe is constant, shows that different forms of energy may be converted into one another, and introduces the extensive thermodynamic variable internal energy, U.
7. The Second Law of Thermodynamics defines which processes may occur spontaneously and introduces the extensive thermodynamic variable entropy, S. The entropy of the universe can never decrease.
8. The Third Law of Thermodynamics states that all aspects of entropy approach the value of zero as the temperature of the system approaches zero, if the system is in complete internal equilibrium.

1.10 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 1

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Alloy
Boundaries: adiabatic/diathermal/permeable/semipermeable
Boyle's law
Charles' law
Coefficient of thermal expansion
Components
Conservation of energy
Conversion of energy
Energy/work
Equilibrium phase diagram
Exact differentials
Extensive/intensive thermodynamic variables
Gas constant, R
Homogeneous/heterogeneous systems
Ideal gases/ideal gas law
Independent/dependent thermodynamic variables
Isolated/closed/open systems
Isothermal compressibility
Laws of Thermodynamics
Microscopic/macroscopic thermodynamic variables
Solid/liquid solutions
System/surroundings
Thermodynamic field variables
Thermodynamic state

Thermodynamic state functions
Thermodynamic state variables
Triple point
Vapor pressure
V-*P*-*T* space

1.11 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Figure 1.1 shows the volume versus pressure and temperature plot for 1 mole of an ideal gas. How would the plot change for 2 moles of an ideal gas? How would it change for *n* moles?

Solution to Qualitative Problem 1

The surface would be shifted up to double the volume at every point. The slopes and curvatures of the surface at $2V_i$ remain the same as those at V_i.

For *n* moles, the surface shifts up at every point by $n\ V_i$—again, with the slopes and curvatures remaining the same.

Qualitative Problem 2

Obtain simplified expressions for β_T and α of an ideal gas.

Solution to Qualitative Problem 2

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \text{ but } V = \frac{RT}{P} : \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} :$$

$$\beta_T = \left(-\frac{1}{V}\right)\cdot\left(-\frac{RT}{P^2}\right) = \frac{1}{P}$$

and

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \text{ but } V = \frac{RT}{P} : \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} :$$

$$\alpha = \frac{1}{V}\cdot\frac{R}{P} = \frac{1}{T}$$

1.12 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Consider 1 mole of an ideal gas. Using a *y* axis of pressure and an *x* axis of temperature, plot the variations of pressure with temperature for volumes of 11.2 liters, 22.4 liters, and 44.8 liters. Use ranges of pressure and temperature consistent with Figure 1.3.

Solution to Quantitative Problem 1

States of constant volume can be calculated using the ideal gas law ($PV' = nRT$). The following table summarizes the calculations. The plot is found in Figure 1.6.

	Pressure (atm)		
Temperature (K)	***V* = 11.2 liters**	***V* = 22.4 liters**	***V* = 44.8 liters**
300	2.20	1.10	0.55
400	2.93	1.47	0.73
500	3.66	1.83	0.92
600	4.40	2.20	1.10
700	5.13	2.56	1.28
800	5.86	2.93	1.47
900	6.59	3.30	1.65
1000	7.33	3.66	1.83
1100	8.06	4.03	2.01
1200	8.79	4.40	2.20
1300	9.52	4.76	2.38

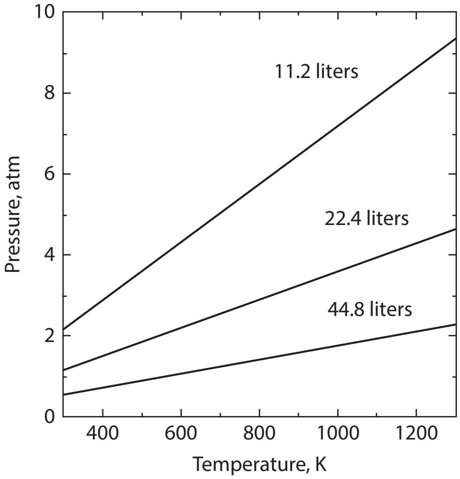

Figure 1.6 Pressure temperature plots for 1 mole of an ideal gas at three different volumes.

Quantitative Problem 2

A rock with a mass of 10 lb falls 100 ft from a cliff to the floor of a canyon. What is the change in potential energy (ΔPE) of the rock?

Solution to Quantitative Problem 2

$$1 \text{ lb} = 0.4536 \text{ kg; thus, } 10 \text{ lb} = 4.536 \text{ kg}$$

$$1 \text{ in} = 2.54 \text{ cm; thus, } 1 \text{ m} = 100 \text{ cm and } 1 \text{ ft} = 12 \text{ in; therefore, } 100 \text{ ft} = 30.48 \text{ m}$$

$$\Delta PE = mg\Delta h$$

$$\Delta PE = (4.536 \text{ kg})(9.81 \text{ m/s}^2)(-30.48 \text{ m})$$

$$= -1356 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$$

$$1 \text{ N} = 1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-1} \text{ and } 1 \text{ J} = 1 \text{ N} \cdot \text{m}$$

$$\Delta PE = -1356 \text{ J}$$

PROBLEMS

1.1* The plot of $V = V(P,T)$ for a gas is shown in Figure 1.1. Determine the expressions of the two second derivatives of the volume of this plot (*note*: the principle curvatures of the surface are proportional to these second derivatives).

What are the signs of the curvatures? Explain.

1.2* The expression for the total derivative of V with respect to the dependent variables P and T is

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Substitute the values of β_T and α obtained in Qualitative Problem 2 into this equation and integrate them to obtain the equation of state for an ideal gas.

1.3* The pressure temperature phase diagram in Figure 1.4 has no two-phase areas (only two-phase curves), but the temperature composition diagram in Figure 1.5 does have two-phase areas. Explain.

1.4* Calculate the value of the ratio α/β_T for an ideal gas in terms of its volume.

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* New problem in this edition.

CHAPTER 2

The First Law of Thermodynamics

2.1 INTRODUCTION

The First Law of Thermodynamics is sometimes thought to be merely an extension to the Law of Conservation of Energy, which was discovered in the late seventeenth century for mechanical systems. It is, however, much more! The First Law introduces the important thermodynamic state variable *internal energy*, *U* (also called a *thermodynamic potential*), and the law posits that energy may be converted from one of its forms to another form. Furthermore, the law introduces the important concept that the transfer of thermal energy (heat) is a different kind of energy than that which is done during a process of *work*. First, we start with a review of basic mechanics.

Kinetic energy is conserved in a frictionless system of interacting rigid elastic bodies. A collision between two of these bodies results in a transfer of kinetic energy from one to the other; the work done by the one equals the work done on the other. The total kinetic energy of the system is unchanged as a result of the collision. If the kinetic system is in the influence of a gravitational field, then the sum of the kinetic and potential energies of the bodies is constant. Changes of position of the bodies in the gravitational field, in addition to changes in the velocities of the bodies, do not alter the total dynamic energy of the system. As the result of possible interactions, kinetic energy may be *converted* to potential energy and vice versa, but the sum of the two remains constant. If, however, friction occurs in the system, then with continuing collision and interaction among the bodies, the total dynamic energy of the system *decreases* and thermal energy is produced. It is thus reasonable to expect that a relationship exists between the dynamic energy *dissipated* and the thermal energy *produced* as a result of the effects of friction.

The establishment of such a relationship laid the foundations for the development of the thermodynamic method. As a subject, this has now gone far beyond simple considerations of the interchange of energy from one form to another—for example, from dynamic energy to thermal energy. The development of thermodynamics from its early beginnings to its present state was achieved as the result of the *invention* of convenient thermodynamic *functions of state*. In this chapter, the first two of these thermodynamic functions—the *internal energy*, *U*, and the *enthalpy*, *H*—are introduced.

2.2 THE RELATIONSHIP BETWEEN HEAT AND WORK

The relationship between heat (thermal energy) and work was suggested in 1798 by Count Rumford (aka Sir Benjamin Thomson, 1753–1814), who, during the boring of cannons at the Munich Arsenal, noticed that the heat, q, produced during the boring was roughly proportional to the work, w, performed during the boring. This suggestion was novel, as hitherto, heat had been regarded as being an invisible fluid called *caloric*, which resided between the constituent particles of a substance. In the caloric theory of heat, the temperature of a substance was considered to be determined by the quantity of caloric gas which it contained. It was thought that when two bodies of differing temperature were placed in contact with one another, they came to an intermediate common temperature as the result of caloric flowing between them. Thermal equilibrium was thought to be reached when the pressure of caloric gas in the one body equaled that in the other.

Some 40 years would pass before the relationship between heat and work was placed on a firm quantitative basis, as the result of a series of experiments carried out by James Prescott Joule (1818–1889). Joule conducted experiments in which work was performed in a certain quantity of adiabatically* contained water, and he then measured the resultant increase in the temperature of the water. He observed that a direct proportionality existed between the work done and the resultant increase in temperature and that the same proportionality existed no matter what means were employed in the work production. Methods of work production used by Joule included:

1. Rotating a paddle wheel immersed in the water
2. An electric motor driving a current through a coil immersed in the water
3. Compressing a cylinder of gas immersed in the water
4. Rubbing together two metal blocks immersed in the water

This proportionality between the work performed and the rise in temperature gave rise to the notion of a *mechanical equivalent of heat*, and for the purpose of defining this figure it was necessary to define a unit of thermal energy. This unit is the *calorie* (or *15° calorie*), which is the quantity of thermal energy needed to be transferred to 1 gram of water to increase the temperature of the water from 14.5°C to 15.5°C. On the basis of this definition, Joule determined the value of the mechanical equivalent of heat to be 0.241 calories per what we now call a *joule* (J). The presently accepted value is 0.2389 calories (15° calories) per joule. Rounding this to 0.239 calories per joule defines the *thermochemical calorie*, which, until the introduction in 1960 of SI units, was the traditional energy unit used in thermochemistry.

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* An adiabatic vessel is one which is constructed in such a way as to prohibit, or at least minimize, the passage of thermal energy through its walls. The most familiar example of an adiabatic vessel is the *Dewar flask* (known more popularly as a *thermos flask*). Thermal energy transmission by conduction into or out of this vessel is minimized by using double glass walls separated by an evacuated space, and a rubber or cork stopper. Thermal energy transmitted by radiation is minimized by using highly polished mirror surfaces.

From the preceding discussion, it is seen that the transfer of thermal energy, q, and the performance of work, w, are *processes* which occur on or to a system and are not intrinsic to the system; that is, they are not variables of the system. When performed on a system they do, however, change the properties of the system.

2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

From Joule's experiments, it can be said that "the change of a body inside an adiabatic enclosure from a given initial state to a given final state involves the same amount of work by whatever means the process is carried out."[*] The statement is a preliminary formulation of the First Law of Thermodynamics, and in view of this statement, it is necessary to define some function which depends only on the *internal state* of a body or system. Such a function is U, the internal energy. We will see that the internal energy is related to the system's capacity to do work. Internal energy is best introduced by means of comparison with more familiar concepts.

When a body of mass m is lifted in a gravitational field from height h_1 to height h_2, the work w done on the body is given by

$$\begin{aligned} w &= \text{force} \times \text{distance} \\ &= mg \times (h_2 - h_1) \\ &= mgh_2 - mgh_1 \\ &= \text{potential energy at position } h_2 - \text{potential energy at position } h_1 \end{aligned}$$

Since the potential energy of the body of given mass m depends only on the position of the body in the gravitational field, it is seen that the work done on the body is dependent only on its final and initial positions and is independent of the path taken by the body between the two positions—that is, between the two states. U is that potential.

Similarly, the application of a force f to a body of mass m causes the body to accelerate according to Newton's law:

$$f = ma = m\frac{dv}{dt}$$

where the acceleration a equals dv/dt. The work done on the body is thus obtained by integrating

$$dw = f\ dl$$

where dl is the distance that the force moves the body.

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[*] Kenneth Denbigh, *The Principles of Chemical Equilibrium*, Cambridge University Press, Cambridge, UK, 1971.

$$\therefore \quad dw = m\frac{dv}{dt}dl = m\frac{dl}{dt}dv = mv\ dv$$

Integration gives

$$\begin{aligned} w \quad &= \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 \\ &= \text{the kinetic energy of the body at velocity } v_2 \text{ (state 2)} \\ &\quad - \text{the kinetic energy of the body at velocity } v_1 \text{ (state 1)} \end{aligned}$$

> Again, the work done on the body is the difference between the values of a function of the state of the body and is *independent of the path* taken by the body between the states. In this case, the change in U is equal to the change in the kinetic energy of the system.

In the case of work being done on an adiabatically contained body of constant potential and kinetic energy, the pertinent function which describes the state of the body, or the change in the state of the body, is the internal energy, U. Thus, the work done on (or by) an adiabatically contained body equals the change in the internal energy of the body; that is, the work equals the difference between the value of U in the final state and the value of U in the initial state. In describing work, we will use the convention that assigns a negative value to work done *on* a body and a positive value to work done *by* a body. This convention arises because we often consider only the work done to be PdV work. When a gas expands, and hence does work against an external pressure, the integral $\int_1^2 PdV$, which is the work performed *by* the system, is a positive quantity. Thus, the internal energy must decrease. For an adiabatic process in which work w is done on the gas, as a result of which its state moves from A to B.

$$w = -\left(U'_B - U'_A\right)$$

If work w is done on the body, then $U'_B > U'_A\ (w < 0)$, and if the body itself performs work, then $U'_B < U'_A\ (w < 0)$.[*]

In Joule's experiments, the change in the state of the adiabatically contained water was measured as an increase in the temperature of the water. The same increase in temperature, and hence the same change of state, could have been produced by placing the water in thermal contact with a source that was hotter than the water, allowing energy to flow down the temperature gradient into the water. In describing the transfer of thermal energy, we will use the convention that assigns a negative value to thermal energy which transfers *out* of a body (an exothermic process) and

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[*] The prime in U' indicates the total internal energy of the system. U is the internal energy per mole.

a positive value to thermal energy which transfers *into* a body (an endothermic process). Hence,

$$q = \left(U'_B - U'_A\right)$$

Thus, when energy transfers into the body due to a thermal gradient, q is a positive quantity and $U'_B > U'_A$, whereas, if energy transfers out of the body due to a thermal gradient, $U'_B < U'_A$ and q is a negative quantity. See Figure 2.1 for a schematic description of the sign conventions for heat and work used in the text.

It is now of interest to consider the change in the internal energy of a body which simultaneously performs work and absorbs thermal energy. Consider a body, initially in the state A, which performs work, w, and absorbs energy, q, via a thermal gradient, and, as a consequence, moves to the state B. The absorption of q *increases* the internal energy of the body by the amount q, and the performance of work w by the body *decreases* its internal energy by the amount w. Thus, the total change in the internal energy of the body, $\Delta U'$, is

$$\Delta U' = U'_B - U'_A = q - w \tag{2.1}$$

This equation summarizes the First Law of Thermodynamics for a system of fixed composition. The equation shows that while the internal energy of the system has changed by an amount $(q - w)$, the energy of the surroundings has changed by $-(q - w)$. Thus, the total energy of the universe (system plus surroundings) is unchanged.

For an infinitesimal change of state, Equation 2.1 can be written as a differential:

$$dU' = \delta q - \delta w \tag{2.2}$$

Notice that the left-hand side of Equation 2.2 gives the value of the increment in an already existing property of the system, whereas the right-hand side has no corresponding interpretation. U', the total internal energy, is an extensive state variable (function) of the system, which means that the integration of dU' between two states gives a value which is independent of the path taken by the system between the two

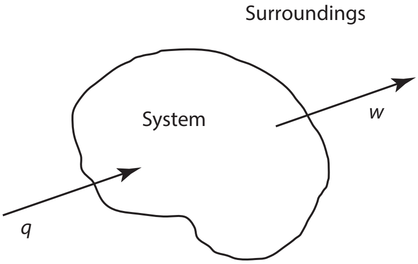

Figure 2.1 Schematic showing the sign convention for the work, w (positive), done by the system and energy transferred as heat, q, added to the system.

states. Such is not the case when δq and δw are integrated. The thermal and work effects, which involve energy in transit, depend on the path taken between the two states, as a result of which the integrals of δw and δq cannot be evaluated without knowledge of the specific path. This is illustrated in Figure 2.2. Here, the value of $U_2' - U_1'$ is independent of the path taken between state 1 (P_1V_1) and state 2 (P_2V_2). However, the work done by the system, which is given by $w = \int_{V_1}^{V_2} PdV$ (the area under the curve between V_1 and V_2) varies, depending on the path. In Figure 2.2 the work done in the process 1 → 2 via c is less than that done via b, which, in turn, is less than that done via a. From Equation 2.1, it is seen that the δq must also depend on the path, and in the process 1 → 2, more thermal energy is absorbed by the system via a than is absorbed via b, which, again in turn, is greater than the heat absorbed via c. In Equation 2.2, use of the symbol d indicates a differential element of a state function or state variable, the integral of which is independent of the path. The use of the symbol δ indicates a small change of some quantity which is not a state function. In Equation 2.1, note that the algebraic sum of two quantities, neither of which individually is independent of the path, gives a quantity which is independent of the path.

In the case of a *cyclic process* which returns the system to its initial state—for example, the process 1 → 2 → 1 in Figure 2.2—the change in U as a result of this process is zero; that is,

$$\Delta U' = \int_1^2 dU' + \int_2^1 dU' = (U_2' - U_1') + (U_1' - U_2') = 0$$

The vanishing of a cyclic integral $\oint dU' = 0$ is a property of a state variable.

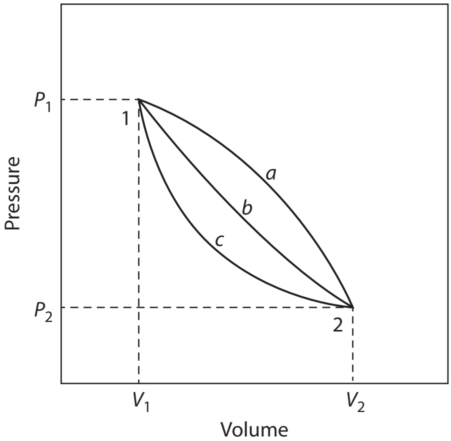

Figure 2.2 Three process paths taken by a fixed quantity of gas in moving from the state 1 to the state 2, showing that the work performed by the gas during expansion depends on the path traversed during the process.

In Joule's experiments, where $(U'_2 - U'_1) = -w$, the process was adiabatic ($q = 0$), and thus, the path of the process was specified.

Since U' is an extensive thermodynamic state variable, for a simple system consisting of a given amount of substance of fixed composition, the value of U' is fixed once any two thermodynamic variables (the independent variables) are fixed. If temperature and volume are chosen as the independent variables, then

$$U' = U'(V', T)$$

The complete differential U' in terms of the partial derivatives gives

$$dU' = \left(\frac{\partial U'}{\partial T}\right)_{V'} dT + \left(\frac{\partial U'}{\partial V'}\right)_{T} dV'$$

It should be noted that if the system is open to changes in the number of moles of the substance, this equation is rewritten to include such changes:

$$dU' = \left(\frac{\partial U'}{\partial T}\right)_{V',n} dT + \left(\frac{\partial U'}{\partial V'}\right)_{T,n} dV' + \left(\frac{\partial U'}{\partial n}\right)_{T,V'} dn$$

(Here we are assuming the system to be composed of but one chemical component.)

Since the state of a closed system is fixed when the two independent variables are fixed, it is of interest to examine those processes which can occur when the value of one of the independent variables is maintained constant and the other is allowed to vary. In this manner, we can examine processes in which the volume V' is maintained constant (isochore or isometric processes), the pressure P is maintained constant (isobaric processes), or the temperature T is maintained constant (isothermal processes). We can also examine adiabatic processes in which $\delta q = 0$.

2.4 CONSTANT-VOLUME PROCESSES

If the volume of a *simple system* is maintained constant during a process, then the system does no work ($\int P dV' = 0$), and from the First Law, Equation 2.2,

$$dU' = \delta q_v \tag{2.3}$$

where the subscript v indicates constant volume. Integration of Equation 2.3 gives

$$\Delta U' = q_v$$

for such a process. This shows that the increase or decrease in the internal energy of the closed system equals, respectively, the thermal energy absorbed or rejected by the system during the constant-volume process. If thermal energy enters the system, the internal energy of the system increases. For this process,

$$\left(dU'\right)_V = \left(\frac{\partial U'}{\partial T}\right)_{V'} dT = \delta q_V$$

The thermodynamic property $(\partial U'/\partial T)_{V'}$ is the constant-volume heat capacity of the system (see Section 2.6).

2.5 CONSTANT-PRESSURE PROCESSES AND THE ENTHALPY, *H*

If the pressure is maintained constant during a process which takes the system from state 1 to state 2, then the work done by the closed system is given as

$$w = \int_{V_1}^{V_2} PdV = P\int_{V_1}^{V_2} dV = P\times(V_2 - V_1)$$

and the First Law gives

$$U'_2 - U'_1 = q_p - P(V_2 - V_1)$$

where the subscript P indicates constant pressure. Rearrangement gives

$$\left(U'_2 + PV_2\right) - \left(U'_1 + PV_1\right) = q_p$$

Since the expression $(U' + PV')$ contains only thermodynamic state variables, the expression itself must be a thermodynamic state variable. This is called the *enthalpy*, H', of the system; that is,

$$H' \equiv U' + PV' \tag{2.4}$$

Hence, the total derivative of the enthalpy is

$$dH' = dU' + PdV' + V'dP$$

and at constant pressure,

$$dH' = dU' + PdV'$$

Integrating, we obtain

$$\Delta H' = H'_2 - H'_1 = q_P \tag{2.5}$$

Thus, the enthalpy change during a constant-pressure process is equal to the thermal energy admitted to or withdrawn from the system during the process.

Suppose we need to know the enthalpy change, ΔH, for the oxidation of BCC iron (α) into solid hematite.

$$2\text{Fe}(\alpha) + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$$

Tables do not show the value of ΔH for this reaction. However, the molar values of ΔH for the following reactions are found in the tables:

$$3\text{Fe}(\alpha) + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \qquad \Delta H_1$$

$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 \qquad \Delta H_2$$

Since enthalpy is a thermodynamic state variable, the value of its change from one state to another is independent of the path of the reaction. Thus, if we add two-thirds of the reaction

$$3\text{Fe}(\alpha) + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \quad \Delta H_1$$

to one-third of the reaction

$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 \quad \Delta H_2$$

we get

$$2\text{Fe}(\alpha) + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$$

and

$$\Delta H = \frac{2}{3}\Delta H_1 + \frac{1}{3}\Delta H_2$$

This use of equivalent reactions is a direct consequence of the First Law of Thermodynamics and the path independency of enthalpy changes. It is called *Hess' law of constant heat summation* (Germain Hess, 1802–1850) and is commonly used in thermochemistry.

2.6 HEAT CAPACITY

Before discussing the adiabatic and isothermal processes, it is convenient to introduce the concept of *heat capacity*. The heat capacity, C, of a system is the ratio of the thermal energy added to or withdrawn from a system of fixed composition to the resultant change in the temperature of the system. Thus,

$$C \equiv \frac{q}{\Delta T}$$

or, if the temperature change is made vanishingly small, then

$$C \equiv \frac{\delta q}{dT}$$

The concept of heat capacity is only used when the addition of thermal energy to or withdrawal of thermal energy from the system produces a temperature change; the concept is not used when a phase change is involved. For example, if the system is a mixture of ice and water at 1 atm pressure and 0°C, then the addition of heat simply melts some of the ice and no change in temperature occurs. In such a case, the heat capacity, as defined, would be infinite.

Note that if a system is in a state 1 and the absorption of a certain quantity of thermal energy by the system increases its temperature from T_1 to T_2, then the statement that the final temperature is T_2 is insufficient to determine the final state of the system. This is because the system has two independent variables, and so one other variable, in addition to the temperature, must be specified in order to define the state of the system. This second independent variable could be varied in a specified manner or could be maintained constant during the change. The latter possibility is the more practical, and so the addition of thermal energy to a simple system to produce a change in temperature is normally considered at either constant pressure or constant volume. In this way, the path of the process is specified, and the final state of the system is known.

Thus, the heat capacity at constant volume, C_v, and the heat capacity at constant pressure, C_p, are defined as

$$C_v \equiv \left(\frac{\delta q}{dT}\right)_V$$

$$C_p \equiv \left(\frac{\delta q}{dT}\right)_P$$

From Equations 2.3 and 2.5,

$$C_v = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U'}{\partial T}\right)_V \quad \text{or} \quad dU' = C_v dT \tag{2.6a}$$

$$C_p = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{\partial H'}{\partial T}\right)_P \quad \text{or} \quad dH' = C_p dT \tag{2.6b}$$

The heat capacity is dependent on the size of the system and is therefore an *extensive* property. However, in normal usage, it is more convenient to use the heat capacity per unit quantity of the system. Thus, the specific heat of the system is the heat capacity per gram at constant P (or constant V), and the molar heat capacity is the heat capacity per mole at constant pressure or at constant volume. Thus, for a system containing n moles,

$$nc_p = C_p$$

and

$$nc_v = C_v$$

where c_p and c_v are the *molar values* of the heat capacity.

It is to be expected that, for any substance, c_p will be of greater magnitude than c_v. If it is required that the temperature of a system be increased by a certain amount, then, if the process is carried out at a constant volume, all of the thermal energy added to the system is used to raise the temperature of the system. However, if the process is carried out at constant pressure, then, in addition to raising the temperature by the required amount, the thermal energy added is required to provide the work necessary to expand the system at the constant pressure. This work of expansion against the constant pressure per degree of temperature increase is calculated as

$$\frac{PdV'}{dT} \text{ or } P\left(\frac{\partial V'}{\partial T}\right)_P$$

and hence, it might be expected that

$$c_p - c_v = P\left(\frac{\partial V}{\partial T}\right)_P \tag{2.7}$$

For 1 mole of an ideal gas, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

and thus, $c_p - c_v = R$.

For any gas, the difference between c_p and c_v is calculated as follows:

$$c_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

and

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Hence,

$$c_p - c_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

but

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

and therefore,

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

Hence,

$$\begin{aligned} c_p - c_v &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \end{aligned} \tag{2.8}$$

The two expressions for $c_p - c_v$ (Equations 2.7 and 2.8) differ by the term

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial U}{\partial V}\right)_T$$

In an attempt to evaluate the term

$$\left(\frac{\partial U}{\partial V}\right)_T$$

for gases, Joule performed an experiment which involved filling a copper vessel with a gas at some pressure and connecting this vessel via a stopcock to a similar but evacuated vessel. The two-vessel system was immersed in a quantity of adiabatically contained water and the stopcock was opened, thus allowing the free expansion of the gas into the evacuated vessel. After this expansion, Joule could not detect any change in the temperature of the system. Since the system was adiabatically contained and no work was performed, then from the First Law,

$$\Delta U = 0$$

and hence,

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0$$

Thus, since $dT = 0$ (experimentally determined) and dV is not 0, the term

$$\left(\frac{\partial U}{\partial V}\right)_T$$

must be zero. Joule thus concluded that the internal energy of a gas is a function only of temperature and is independent of the volume (and hence pressure). Consequently, for a gas

$$c_p - c_v = P\left(\frac{\partial V}{\partial T}\right)_P$$

However, in a more critical experiment performed by Joule and Thomson, in which an adiabatically contained gas of molar volume V_1 at the pressure P_1 was throttled through a porous diaphragm to the pressure P_2 and the molar volume V_2, a change in the temperature of the gas was observed, which showed that, for real gases,

$$\left(\frac{\partial U}{\partial V}\right) \neq 0$$

Nevertheless, if

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

then, from Equation 2.8,

$$c_p - c_v = P\left(\frac{\partial V}{\partial T}\right)_P$$

and since, for 1 mole of ideal gas, $PV = RT$, we obtain as before

$$c_p - c_v = R$$

The reason Joule did not observe a temperature rise in the original experiment was that the heat capacity of the copper vessels and the water was considerably greater than the heat capacity of the gas, and thus, the small heat changes which actually occurred in the gas were absorbed in the copper vessels and the water. This decreased the actual temperature change to below the limits of the available means of temperature measurement at that time.

In Equation 2.8, the term

$$P\left(\frac{\partial V}{\partial T}\right)_P$$

represents the work done by the system per degree rise in temperature in expanding against the constant external pressure P acting on the system. The other term in Equation 2.8—namely,

$$\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

represents the work done per degree rise in temperature in expanding against the internal cohesive forces acting between the constituent particles of the substance. As will be seen in Chapter 8, an ideal gas is a gas consisting of noninteracting particles, and hence, the atoms or molecules of an ideal gas can be separated from one another without the expenditure of work. Thus, for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

equals zero, and since

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V \neq 0$$

(where α is the volume thermal expansion coefficient) in the preceding equation, the term

$$\left(\frac{\partial U}{\partial V}\right)_T$$

equals zero for an ideal gas.

In real gases the internal pressure contribution is very much smaller in magnitude than the external pressure contribution; but in liquids and solids, in which the interatomic forces are considerable, the work done in expanding the system against the external pressure is insignificant in comparison with the work done against the internal pressure. Thus, for liquids and solids the term

$$\left(\frac{\partial U}{\partial V}\right)_T$$

is very large.

Heat capacities can be used in conjunction with the First Law of Thermodynamics to calculate enthalpy changes of reactions as a function of temperature. Consider the solidification of 1 mole of a liquid to a solid at its equilibrium freezing temperature T_2 (Figure 2.3). The value of its enthalpy of freezing (or solidification) is seen to be

$$H_S(T_2) - H_L(T_2) < 0$$

since thermal energy leaves the substance and enters the surroundings (exothermic). This value is the negative of the length of the cord $\overline{ad}$ in Figure 2.3. If the liquid is supercooled to a temperature of T_1, the enthalpy change for freezing is seen now to be $H_S(T_1) - H_L(T_1)$. This value can be calculated as follows:

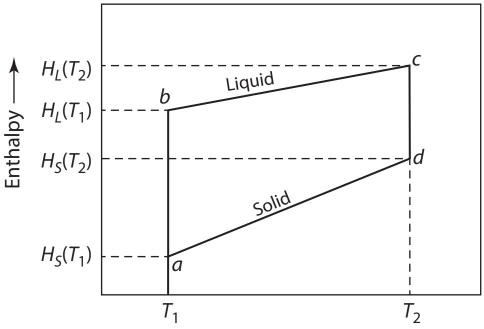

Figure 2.3 Enthalpy vs. temperature plots for 1 mole of a solid and liquid, showing that the enthalpy of transformation depends on temperature if the heat capacities differ. T_2 is the equilibrium solidification temperature.

$$\text{The enthalpy of the liquid at } T_1 = H_L(T_2) + \int_{T_2}^{T_1} c_P^L dT = H_L(T_2) + c_P^L(T_1 - T_2)$$

$$\text{The enthalpy of the solid at } T_1 = H_S(T_2) + \int_{T_2}^{T_1} c_P^S dT = H_S(T_2) + c_P^S(T_1 - T_2)$$

$$\text{Thus, } H_S(T_1) - H_L(T_1) = H_S(T_2) - H_L(T_2) + \int_{T_2}^{T_1} (c_P^S - c_P^L) dT$$

which is equal to the negative of the length of the cord $\overline{ba}$. This value is more negative (more thermal energy leaving the system: more exothermic) than that at T_2because the temperature dependence of the enthalpy of the solid is greater than that of the liquid. The temperature dependence of the enthalpy is the heat capacity! The change in the enthalpy as a function of temperature can be written as

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta c_P$$

when the heat capacities vary linearly with temperature.

2.7 REVERSIBLE ADIABATIC PROCESSES

During a *reversible process* in which the state of a gas is changed, gas never leaves the equilibrium surface shown in Figure 1.1. Consequently, during a reversible process, the gas passes through a continuum of equilibrium states, and the work

w is given by the integral $\int_{V_1}^{V_2} PdV$. In a *reversible adiabatic process*, $q = 0$, and thus, from the First Law, $dU = -\delta w$.

Consider a system comprising 1 mole of an ideal gas. From Equation 2.6a,

$$dU = c_v dT$$

and, for a reversible adiabatic process,

$$dU = -\delta w = -PdV$$

Thus,

$$c_v dT = -PdV$$

Since the system is 1 mole of ideal gas, then

$$P = \frac{RT}{V}$$

and hence,

$$c_V dT = -\frac{RT}{V} dV$$

Integrating between states 1 and 2 gives

$$c_v \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

or

$$\left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^{R}$$

or

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{c_V}}$$

For an ideal gas, it has been shown that $c_p - c_v = R$. Thus, $(c_P/c_V) - 1 = R/c_V$, and if we set $c_P/c_V = \gamma$, then $R/c_V = \gamma - 1$, and hence,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

From the ideal gas law,

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Thus,

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

and hence,

$$P_2V_2^{\gamma} = P_1V_1^{\gamma} = PV^{\gamma} = \text{constant} \tag{2.9}$$

This is the relationship between the pressure and the volume of an ideal gas undergoing a reversible adiabatic process (Figure 2.4). For an ideal gas, since

$$c_P = \frac{5}{2}R \text{ and } c_V = \frac{3}{2}R$$

we see that

$$\gamma = \frac{5}{3}$$

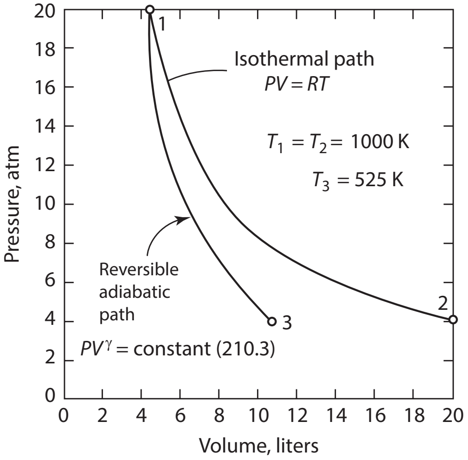

Figure 2.4 Comparison of the process path taken by a reversible isothermal expansion of one mole an ideal gas with the process path taken by a reversible adiabatic expansion of an ideal gas between an initial pressure of 20 atm and a final pressure of 4 atm.

2.8 REVERSIBLE ISOTHERMAL PRESSURE OR VOLUME CHANGES OF AN IDEAL GAS

From the First Law,

$$dU' = \delta q - \delta w$$

and for an isothermal process, $dT = 0$ and $dU' = 0$ for an ideal gas.

Therefore, $\delta w = \delta q = PdV = RT\ dV/V$ per mole of gas.

Integrating between the states 1 and 2 gives

$$w = q = RT \ln\left(\frac{V_2}{V_1}\right) = RT \ln\left(\frac{P_1}{P_2}\right) \tag{2.10}$$

Thus, for an ideal gas, an *isothermal* process is one of constant internal energy, during which the work done by the system equals the thermal energy absorbed by the system, both of which are given by Equation 2.10.

The plots of pressure versus volume for a reversible isothermal process and for a reversible adiabatic process are shown in Figure 2.4. It is seen that, for a given decrease in pressure, the work done by the *reversible isothermal* process (which is equal to the area under the curve) exceeds that done by the reversible adiabatic process. This difference is due to the fact that during the isothermal process, thermal energy is absorbed by the system in order to maintain constant temperature, whereas during the adiabatic process, no thermal energy is admitted to the system. During the *isothermal expansion*, the internal energy of the gas remains constant, but during the *adiabatic expansion*, the internal energy decreases by an amount equal to the work done by the gas.

Example

For the reversible isothermal path shown in Figure 2.4, Equation 2.10 gives the work done by the gas as

$$w = RT \ln\left(\frac{P_1}{P_2}\right) = 8.3144 \times 1000 \times \ln\left(\frac{20}{4}\right) = 13.38 \text{ kJ}$$

For the reversible adiabatic path, the area under the curve is obtained as follows. Since PV^γ = constant = 210.3 and

$$\gamma = \frac{c_P}{c_V} = \frac{5/2\,R}{3/2\,R} = \frac{5}{3}$$

then

$$w = \int P dv = 210.3 \times \int \frac{dV}{V^{5/3}}$$

The volume of the gas in the state 3 is obtained from Equation 2.9 as $V_3 = (210.4/4)^{3/5} = 10.78$ liters, and the volume in the state 1 is $V_1 = (210.3/20)^{3/5} = 4.10$ liters. Thus,

$$\begin{aligned} w \quad &= 210.3 \times \left(-\frac{3}{2}\right) \times \left(V_3^{-2/3} - V_1^{-2/3}\right) \\ &= 210.3 \times (-1.5) \times \left(10.78^{-2/3} - 4.10^{-2/3}\right) = 58.4 \; l \cdot \text{atm} = 5.92 \text{ kJ} \end{aligned}$$

Alternatively, since $q = 0$, $w = -\Delta U = c_v \ (T_3 - T_1) = -1.5 \times 8.3144 \times (525 - 1000) = 5.92$ kJ

Thus more work is performed during the isothermal process that during the adiabatic process.

2.9 OTHER FORMS OF WORK

Up to this point, we have only used *PdV* work in the First Law. We called these systems *simple systems*. There are, of course, other kinds of work that may be performed on or by a system. Here, we present three additional kinds of work that we will utilize in later chapters of the text. To include other forms of work, the First Law can be written as

$$dU' = \delta q - \sum \delta w_i$$

It is important to remember that in this equation, each of the terms δw_i is the work done *by* the system.

2.9.1 Magnetic Work on a Paramagnetic Material

The work done *on* a material by an external magnetic field is given by

$$\delta w' = -V\mu_0 \; \mathcal{H} \, d\boldsymbol{M}$$

$$w' = -V\mu_0 \int_{M_1}^{M_2} \mathcal{H} \, d\boldsymbol{M}$$

$\boldsymbol{M}$ and $\boldsymbol{\mathcal{H}}$ have units of amp/m, μ_0 the permittivity of vacuum has units of N/amp^2, and V is in units of m^3. The units of work in this equation are in joules. Both $\boldsymbol{\mathcal{H}}$ and $\boldsymbol{M}$ are axial vectors.

The First Law therefore becomes

$$dU' = \delta q - \sum \delta w_i = \delta q - PdV + V\mu_0\boldsymbol{\mathcal{H}}\, d\boldsymbol{M}$$

For an adiabatic process at constant volume,

$$\left(dU'\right)_{q,V} = V\mu_0\boldsymbol{\mathcal{H}}\, d\boldsymbol{M}$$

Thus, under the specified conditions, the internal energy, U', of the paramagnetic material increases when an applied magnetic field increases its magnetization. Thus, the system is capable of doing more work, since some of the internal energy is available to perform work.

2.9.2 Electrical Work on a Dielectric Material

The work done *on* a dielectric material by an external electric field is given by

$$\delta w' = -V\boldsymbol{E}d\boldsymbol{D}$$

$$w' = -V\int_{D_1}^{D_2} \boldsymbol{E}d\boldsymbol{D}$$

where $\boldsymbol{E}$ is the electric field intensity (N/coul) and $\boldsymbol{D}$ is electric displacement (coul·m/m^3). The units of work are in joules. Both $\boldsymbol{E}$ and $\boldsymbol{D}$ are *polar* vectors.

The First Law in this case therefore becomes

$$dU' = \delta q - \sum \delta w_i = \delta q - PdV + V\boldsymbol{E}d\boldsymbol{D}$$

For an adiabatic process at constant volume,

$$\left(dU'\right)_{q,V} = V\boldsymbol{E}d\boldsymbol{D}$$

Thus, under the specified conditions, the internal energy, U, of the dielectric material increases if an applied electric field increases its displacement field.

2.9.3 Work to Create or Extend a Surface

The reversible work done in *creating* a new surface (in joules) of area A is given as

$$\delta w' = -\gamma dA$$

γ having units of J/m^2 and A having units of m^2. The surface energy, γ, is a scaler. For liquids, the surface energy is isotropic; for solids, the surface energy has a symmetry that is at least that of the point symmetry of the solid. The First Law now becomes

$$dU' = \delta q' - \sum \delta w_i = \delta q' - PdV' + \gamma dA$$

For an adiabatic process at constant volume,

$$\left(dU'\right)_{q,V} = \gamma dA$$

Thus, under the specified conditions, the total energy of the system increases when new surface area is created.

In the text to this point, we have ignored the surface energy of a material. Our implicit assumption has been that the volume terms are much larger than the surface terms, and hence, the surface terms may be neglected. Surface terms need to be included when the surface-to-volume ratio is not negligible, such as is the case for small particles.

A related quantity of work is the reversible work necessary to *increase* the surface area by *stretching* it with a stress σ. This work is given as

$$\delta w' = -\sigma dA$$

Surface stress is a second-rank tensor, with units of N/m. For a liquid, the surface stress, σ, is isotropic and is numerically equal to the surface energy, γ, which is positive. This is not necessarily the case for crystalline solids, where the surface stress may take on positive or negative values.

2.10 SUMMARY

1. The establishment of the relationship between the work done on or by a system and the thermal energy entering or leaving the system is facilitated by the introduction of the thermodynamic function U, the internal energy.
2. U is a function of state, and thus, the difference between the values of U in two states depends only on the states and is independent of the process path taken by the system in moving between the states.
3. The relationship between the internal energy change, the work done, and the thermal energy absorbed per mole by a system of fixed composition in moving from one state to another is given as $\Delta U = q -$ w, or, for an increment of this process, $dU = \delta q - \delta w$. This relationship summarizes the First Law of Thermodynamics.
4. The internal energy of an isolated system ($\delta q = 0$ and $\delta w = 0$) is constant.
5. The integrals of δq and δw can only be obtained if the process path taken by the system in moving from one state to another is known. Process paths which are convenient for consideration include
    a. Constant-volume processes (isochoric) in which $\int \delta w = \int PdV = 0$, if only PdV work is possible.

   b. Constant-pressure processes (isobaric) in which $\int \delta w = P \int dV = P\Delta V$ if only PdV work is possible.
   c. Constant-temperature (isothermal) processes.
   d. *Adiabatic* processes in which $q = 0$. For adiabatic processes, the work needed to take the system from $U' = U_1'$ to $U' = U_2'$ is independent of the path.
6. For a constant-volume process in a simple system, $w = 0$ and $\Delta U' = q_v$. The definition of the constant-volume molar heat capacity as

$$c_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

   (which is an experimentally measurable quantity) facilitates the determination of the change in U resulting from a constant-volume process, since $\Delta U = \int_{T_1}^{T_2} c_v dT$.
7. Consideration of constant-pressure processes is facilitated by the introduction of the thermodynamic function H; the enthalpy for 1 mole is defined as $H \equiv U + PV$. Since the expression for H contains only functions of state, H is also a function of state, and thus, the difference between the values of H in two states depends only on the states and is independent of the path taken by the system in moving between them.
8. For a constant-pressure process, $\Delta H = \Delta U + P\Delta V = (q_p - P\Delta V) + P\Delta V = q_p$. The definition of the constant-pressure molar heat capacity as

$$c_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

   (which is an experimentally measurable quantity) facilitates the determination of the change in H as the result of a constant-pressure process, since $dH = \int_{T_1}^{T_2} c_p dT$.
9. For an ideal gas, the internal energy U' is a function only of temperature.
10. $c_p - c_v = R$ for an ideal gas.
11. The process path of an ideal gas undergoing a reversible adiabatic change of state is described by PV^γ = constant, where $\gamma = c_P/c_V$. During an adiabatic expansion, since $q = 0$, the decrease in the internal energy of the system equals the work done by the system.
12. Since the internal energy of an ideal gas is a function only of temperature, the internal energy of an ideal gas remains constant during an isothermal change of state. Thus, the thermal energy which enters or leaves the gas as a result of the isothermal process equals the work done by or on the gas, with both quantities being given by

$$w = q = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right)$$

13. Only the differences in the values of U and H between two states—that is, the values of ΔU and ΔH—can be measured. The absolute values of U and H in any given state cannot be determined.
14. Other work terms include the work done on a material by the application of an external magnetic field or by an electric field. Also, the creation of new surface must be done by doing work on the material. A generalized First Law can be written as

$$dU' = \delta q - \sum \delta w_i$$

where $\sum \delta w_i$ is the total work done by the system.

2.11 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 2

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Adiabatic process
Calorie
Conservation of energy
Cyclic process
Electric work
Enthalpy of melting/freezing
Enthalpy, H
First Law of Thermodynamics
Heat (thermal energy)
Heat capacity
Hess' law of constant heat summation
Internal energy, U
Isobaric process
Isochoric process
Isothermal process
Kinetic energy/potential energy
Magnetic work
Mechanical equivalent of heat
Process
Reversible processes
Specific/molar heat capacity
Surface energy/work
Thermodynamic state variable (function)
Work

2.12 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

One mole of an ideal gas at a pressure of 1 atm and temperature of 273 K is expanded to twice its volume at constant pressure.

a. In terms of P and V_1 and V_2 how much work was performed? Was the work performed on the gas or by the gas? Explain.
b. If two moles of an ideal gas at the same initial pressure and temperature were to double its volume under constant pressure, how much work would be performed on or by the gas? Compare the value with that in part (a).
c. In either case (a) or (b), does the temperature increase or decrease? Explain.

Solution to Qualitative Problem 1

a. The work is performed *by* the gas and equals $P\Delta V = P(V_2 - V_1) = P\,V_1$.
b. The starting volume for this part of the problem is $2V_1 = V_2$. This doubles to $4V_1$. Thus, the work performed by 2 moles of the gas is $2PV_1$, twice that of part (a) of the problem.
c. The temperature increases in both cases. Take case (a):

$P_1V_1 = RT_1$ and $P_2V_2 = RT_2$, but $P_2 = P_1$ and $V_2 = 2V_1$.
Thus, $T_2 = 2T_1$. The temperature increases.

Why does the temperature increase? In order to expand at constant pressure, more energy must be given to the gas to keep the pressure from decreasing.

Qualitative Problem 2

A magnetic field $\boldsymbol{\mathcal{H}}$ is applied to a material with a positive susceptibility χ. Assume $\boldsymbol{M} \,//\, \boldsymbol{\mathcal{H}}$ and that the $\boldsymbol{M}$ versus $\boldsymbol{\mathcal{H}}$ plot is linear with a slope χ (Figure 2.5a).

a. Determine the work done when $\boldsymbol{\mathcal{H}}$ varies from zero to $\boldsymbol{\mathcal{H}} = \boldsymbol{\mathcal{H}}_f$.
b. Sketch the area on the $\boldsymbol{\mathcal{H}}$–$\boldsymbol{M}$ plot that corresponds to the work done on the material.
c. The product of $V\mu_0, \boldsymbol{M}_f \cdot \boldsymbol{\mathcal{H}}_f$, is an energy. Subtract your answer in part (a) from the value $\boldsymbol{M}_f \cdot \boldsymbol{\mathcal{H}}_f$. What is this energy?

Solution to Qualitative Problem 2

a. $$w = V\mu_0 \int_0^{M_f} \boldsymbol{\mathcal{H}}\, d\boldsymbol{M} = V\mu_0 \int_0^{M_f} \frac{\boldsymbol{M}}{\chi}\, d\boldsymbol{M} = \frac{V\mu_0 M_f^2}{2\chi} = \frac{V\mu_0 M_f \boldsymbol{\mathcal{H}}_f}{2}$$

b. Refer to Figure 2.5b.
c. This is the work that the moments, $\boldsymbol{M}$, performed against the applied magnetic field, $\boldsymbol{\mathcal{H}}$, in resisting magnetization. Since this was a reversible and linear process, the work is equal to in magnitude and opposite in sign to the work applied to the material.

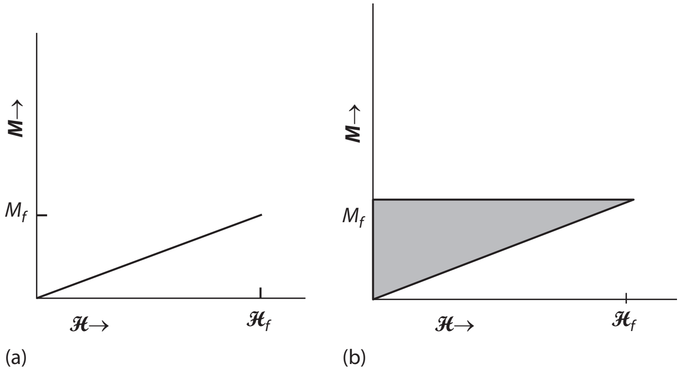

Figure 2.5 (a) Schematic showing $\boldsymbol{M}$ vs. $\boldsymbol{\mathcal{H}}$ plot for a material under the applied magnetic field. (b) Plot of Figure 2.6a, showing work done on the material as the shaded region.

2.13 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem

Ten liters of a monatomic ideal gas at 25°C and 10 atm pressure are expanded to a final pressure of 1 atm. The molar heat capacity of the gas at constant volume, c_v, is 3/2 R and is independent of temperature. Calculate the work done, the heat absorbed, and the change in U and in H for the gas if the process is carried out

- Isothermally and reversibly
- Adiabatically and reversibly

Having determined the final state of the gas after the reversible adiabatic expansion, verify that the change in U for the process is independent of the path taken between the initial and final states by considering the process to be carried out as

- An isothermal process followed by a constant-volume process
- A constant-volume process followed by an isothermal process
- An isothermal process followed by a constant-pressure process
- A constant-volume process followed by a constant-pressure process
- A constant-pressure process followed by a constant-volume process

Solution to Quantitative Problem

The size of the system must first be calculated. From consideration of the initial state of the system (the point a in Figure 2.6),

$$n = \text{the number of moles} = \frac{P_a V_a}{RT_a} = \frac{10\times 10}{0.08206\times 298} = 4.09$$

a. *The isothermal reversible expansion*. The state of the gas moves from a to b along the 298-degree isotherm. Along any isotherm, the product PV is constant:

$$V_b = \frac{P_a V_a}{P_b} = \frac{10\times 10}{1} = 100 \text{ liters}$$

For an ideal gas undergoing an isothermal process, $\Delta U = 0$, and hence, from the First Law,

$$q = w = \int_a^b P dV = nRT\int_a^b \frac{dV}{V} = 4.09\times 8.3144\times 298\times \ln\frac{100}{10}\text{ J}$$

$$= 23.3 \text{ kJ}$$

Thus, in passing from the state a to the state b along the 298-degree isotherm, the system performs 23.3 kJ of work and absorbs 23.3 kJ of heat from the constant-temperature surroundings.

Since for an ideal gas, H is a function only of temperature, $\Delta H'_{(a\rightarrow b)} = 0$; that is,

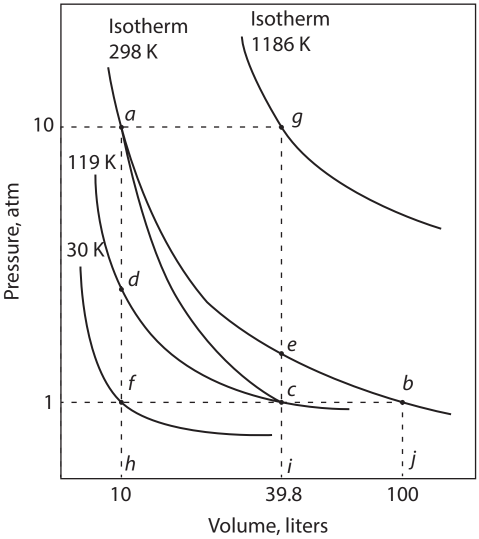

Figure 2.6 The five process paths considered in the numerical problem.

$$
\begin{aligned}
\Delta H_{(a\to b)} &= \Delta U_{(a\to b)} + (P_bV_b - P_aV_a) = (P_bV_b - P_aV_a) \\
&= nRT_b - nRT_a = nR(T_b - T_a) = 0
\end{aligned}
$$

b. *The reversible adiabatic expansion*. If the adiabatic expansion is carried out reversibly, then during the process the state of the system is, at all times, given by PV^γ = constant, and the final state is the point c in the diagram. The volume V_c is obtained from $P_aV_a^\gamma = P_cV_c^\gamma$ as

$$
V_c = \left(\frac{10\times 10^{5/3}}{1}\right)^{3/5} = 39.8 \text{ liters}
$$

and

$$
T_c = \frac{P_cV_c}{nR} = \frac{1\times 39.8}{4.09\times 0.08206} = 119 \text{ degrees}
$$

The point c thus lies on the 119-degree isotherm. As the process is adiabatic, $q = 0$, and hence,

$$
\begin{aligned}
\Delta U_{(a\to)} &= -w = \int_a^c nc_v dT = nc_v(T_c - T_a) \\
&= 4.09\times 1.5\times 8.3144\times(119 - 298) \text{ J} \\
&= -9.13 \text{ kJ}
\end{aligned}
$$

The work done by the system as a result of the process equals the decrease in the internal energy of the system = 9.13 kJ.

i. *An isothermal process followed by a constant-volume process* (the path $a \rightarrow e \rightarrow c$; that is, an isothermal change from a to e, followed by a constant-volume change from e to c).

$$\begin{aligned} \Delta U'_{(a\rightarrow e)} &= 0, \text{ as this is an isothermal change of state} \\ \Delta U'_{(e\rightarrow c)} &= q_v (\Delta V = 0, \text{ and hence, } w = 0) \\ &= \int_e^c nc_v dT \end{aligned}$$

and as the state e lies on the 298-degree isotherm, then

$$\Delta U'_{(e\rightarrow c)} = \quad 4.09 \times 1.5 \times 8.3144 \times (119 \quad 298)\,\text{J} = \quad 9.13\text{ kJ}$$

Thus,

$$\Delta U'_{(a\rightarrow c)} = \Delta U'_{(a\rightarrow e)} + \Delta U'_{(e\rightarrow c)} = -9.13\text{ kJ}$$

ii. *A constant-volume process followed by an isothermal process* (the path $a \rightarrow d \rightarrow c$; that is, a constant-volume change from a to d, followed by an isothermal change from d to c).

$$\begin{aligned} \Delta U'_{(a\rightarrow d)} &= q_v (\Delta V = 0, \text{ and hence, } w = 0) \\ &= \int_a^d nc_v dT, \text{ and as the state d lies in the 119-degree isotherm, then} \\ \Delta U'_{(a\rightarrow d)} &= 4.09 \times 1.5 \times 8.3144 \times (119 - 298)\text{ J} = -9.13\text{ kJ} \\ \Delta U'_{(d\rightarrow c)} &= 0, \text{ as this is an isothermal process, and hence,} \\ \Delta U'_{(a\rightarrow c)} &= \Delta U'_{(a\rightarrow d)} + \Delta U'_{(d\rightarrow c)} = -9.13\text{ kJ} \end{aligned}$$

iii. *An isothermal process followed by a constant-pressure process* (the path $a \rightarrow b \rightarrow$ c; that is, an isothermal change from a to b, followed by a constant-pressure change from b to c).

$$\begin{aligned} \Delta U'_{(a\rightarrow d)} &= 0, \text{ as this process is isothermal} \\ \Delta U'_{(b\rightarrow c)} &= q_p - w, \text{ and as } P_b = P_c, \text{ then } w = P_b(V_c - V_b) \\ &= \int_b^c nc_p dT - P_b(V_c - V_b) \end{aligned}$$

Since $c_v = 1.5\,R$ and $c_p - c_v = R$, then $c_p = 2.5\,R$; and as 1 liter atm equals 101.3 J,

$$\begin{aligned} \Delta U'_{(b\rightarrow c)} &= [4.09 \times 2.5 \times 8.3144 \times (119 - 298)] \\ &\quad -[1 \times (39.8 - 100) \times 101.3]\text{ J} \\ &= -15.2 + 6.1 = -9.1\text{ kJ} \end{aligned}$$

Thus,

$$\Delta U'_{(a\to c)} = U'_{(a\to b)} + U'_{(b\to c)} = -9.1 \text{ kJ}$$

iv. *A constant-volume process followed by a constant-pressure process* (the path $a \to f \to c$; that is, a constant-volume change from a to f, followed by a constant-pressure change from f to c).

$$\begin{aligned}\Delta U'_{(a\to f)} &= q_v (V_a = V_f, \text{ and hence, } w = 0)\\ &= \int_a^f nc_v dT\end{aligned}$$

From the ideal gas law,

$$T_f = \frac{P_f V_f}{nR} = \frac{1\times 10}{4.09\times 0.08206} = 30 \text{ degrees}$$

That is, the state f lies on the 30-degree isotherm. Thus,

$$\begin{aligned}\Delta U'_{(a\to f)} &= 4.09\times 1.5\times 8.3144\times(30-298)\text{joules} = -13.67 \text{ kJ}\\ \Delta U'_{(f\to c)} &= q_p - w = \int_f^c nc_p dT - P_f(V_c - V_f)\\ &= [4.09\times 2.5\times 8.3144\times(119-30)] - [1\times(39.8-10)\times 101.3] \text{ J}\\ &= +7.57 - 3.02 \text{ kJ}\end{aligned}$$

Thus,

$$\begin{aligned}\Delta U'_{(a\to c)} &= \Delta U'_{(a\to f)} + \Delta U'_{(f\to c)} = 13.67 + 7.57 - 3.02\\ &= -9.12 \text{ kJ}\end{aligned}$$

v. *A constant-pressure process followed by a constant-volume process* (the path $a \to g \to c$; that is, a constant-pressure step from a to g, followed by a constant-volume step from g to c).

$$\Delta U'_{(a\to g)} = q_p - \text{w}$$

From the ideal gas law,

$$T_g \frac{P_g V_g}{nR} = \frac{10\times 39.8}{4.09\times 0.08206} = 1186 \text{ degrees}$$

and hence, the state g lies on the 1186-degree isotherm. Thus,

$$\begin{aligned}\Delta U'_{(a\to g)} &= [4.09\times 2.5\times 8.3144\times(1186-298)] \text{ J}\\ &\quad -[10\times(39.8-10)\times 101.3] \text{ J}\\ &= 75.5 - 30.2 \text{ kJ}\\ \Delta U'_{(g\to c)} &= q_v = 4.09\times 1.5\times 8.3144\times(119-1186) \text{ J}\\ &= -54.4 \text{ kJ}\end{aligned}$$

Thus,

$$\begin{aligned}\Delta U'_{(a\to c)} &= \Delta U'_{(a\to g)} + \Delta U'_{(g\to c)} = 75.5 - 30.2 - 54.4\\ &= -9.1 \text{ kJ}\end{aligned}$$

The value of $\Delta U'_{(a\to c)}$ is thus seen to be independent of the path taken by the process between the states *a* and *c*.

The change in enthalpy from a to c (Figure 2.6). The enthalpy change is most simply calculated from the consideration of a path which involves an isothermal portion, over which $\Delta H' = 0$, and an isobaric portion, over which $\Delta H' = q_p = \int nc_p dT$. For example, consider the path $a \to b \to c$.

$$\begin{aligned}\Delta H'_{(a\to b)} &= 0\\ \Delta H'_{(b\to c)} &= q_p = nc_p(T_c - T_b)\\ &= 4.09\times 2.5\times 8.3144\times(119-298) \text{ J}\\ &= -15.2 \text{ kJ}\end{aligned}$$

and hence,

$$\Delta H'_{(a\to c)} = -15.2 \text{ kJ}$$

or alternatively

$$\begin{aligned}\Delta H'_{(a\to c)} &= \Delta H'_{(a\to c)} + (P_cV_c - P_aV_a)\\ &= -9.12 \text{ kJ} + [(1\times 39.8 - 10\times 10)\times 101.3] \text{ J}\\ &= -9.12 - 6.10 = -15.2 \text{ kJ}\end{aligned}$$

in each of the paths (i) to (v), the heat and work effects differ, although in each case the difference $q - w$ equals –9.12 kJ. In the case of the reversible adiabatic path, $q = 0$, and hence, $w = +9.12$ kJ. If the processes (i) to (v) are carried out reversibly, then

- For path (i), $q = -9.12$ + the area *aeih*
- For path (ii), $q = -9.12$ + the area *dcih*
- For path (iii), $q = -9.12$ + the area *abjh* – the area *cbji*
- For path (iv), $q = -9.12$ + the area *fcih*
- For path (v), $q = -9.12$ + the area *agih*

PROBLEMS

2.1 An monatomic ideal gas at 300 K has a volume of 15 liters at a pressure of 15 atm. Calculate

a. The final volume of the system
b. The work done by the system
c. The heat entering or leaving the system
d. The change in the internal energy
e. The change in the enthalpy when the gas undergoes
    i. A reversible isothermal expansion to a pressure of 10 atm
    ii. A reversible adiabatic expansion to a pressure of 10 atm

The constant-volume molar heat capacity of the gas, c_v, has the value 1.5 R.

2.2 One mole of a monatomic ideal gas, in the initial state $T = 273$ K, $P = 1$ atm, is subjected to the following three processes, each of which is conducted reversibly:

a. A doubling of its volume at constant pressure,
b. Then a doubling of its pressure at constant volume,
c. Then a return to the initial state along the path $P = 6.643 \times 10^{-4}V^2 + 0.6667$.

Calculate the heat and work effects which occur during each of the three processes.

2.3 The initial state of a quantity of monatomic ideal gas is $P = 1$ atm, $V = 1$ liter, and $T = 373$ K. The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V. This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of V and the total work done on or by the gas.

2.4 Two moles of a monatomic ideal gas are contained at a pressure of 1 atm and a temperature of 300 K; 34,166 J of heat are transferred to the gas, as a result of which the gas expands and does 1216 J of work against its surroundings. The process is reversible. Calculate the final temperature of the gas.

2.5 One mole of N_2 gas is contained at 273 K and a pressure of 1 atm. The addition of 3000 J of heat to the gas at constant pressure causes 832 J of work to be done during the expansion. Calculate

a. The final state of the gas
b. The values of ΔU and ΔH for the change of state
c. The values of c_v and c_p for N_2

Assume that nitrogen behaves as an ideal gas, and that the change of state is conducted reversibly.

2.6 Ten moles of monatomic ideal gas, in the initial state $P_1 = 10$ atm, $T_1 = 300$ K, are taken round the following cycle:

a. A reversible change of state along a straight line path on the P-V diagram to the state $P = 1$ atm, $T = 300$ K
b. A reversible isobaric compression to $V = 24.6$ liters
c. A reversible constant-volume process to $P = 10$ atm

How much work is done on or by the system during the cycle? Is this work done on the system or by the system?

2.7 One mole of an monatomic ideal gas at 25°C and 1 atm undergoes the following reversibly conducted cycle:

a. An isothermal expansion to 0.5 atm, followed by
b. An isobaric expansion to 100˚C, followed by
c. An isothermal compression to 1 atm, followed by
d. An isobaric compression to 25˚C

The system then undergoes the following reversible cyclic process:

a. An isobaric expansion to 100˚C, followed by
b. A decrease in pressure at constant volume to the pressure P atm, followed by
c. An isobaric compression at P atm to 24.5 liters, followed by
e. An increase in pressure at constant volume to 1 atm

Calculate the value of P which makes the work done on the gas during the first cycle equal to the work done by the gas during the second cycle.

2.8* One mole of a monatomic ideal gas at standard temperature and pressure (STP) undergoes the following three processes:

a. At constant pressure, the temperature is doubled.
b. At constant temperature the pressure is doubled.
c. The gas is returned to STP via a constant-volume process.

Calculate ΔU, ΔH, Q, and W for each of the steps.

2.9* Paramagnetic salts often obey the Curie relation:

$$\frac{M}{\mathcal{H}} = \frac{\text{constant}}{T} = \frac{C}{T}$$

Obtain an expression for the work needed to change the magnetization from $M = 0$ to M = M of such a material. Assume that the field and the magnetization are parallel.

2.10* One mole of a monatomic ideal gas is taken on the path A → B → C → D → A, as shown in Figure 2.7. All paths are reversible.

- $A \rightarrow B$ is a reversible isothermal expansion of the gas.
- $B \rightarrow C$ is a reversible adiabatic expansion of the gas.
- $C \rightarrow D$ is a reversible isothermal compression of the gas.
- $D \rightarrow A$ is a reversible adiabatic compression of the gas.

a. Derive expressions for ΔU, q, and w during each step in terms of V_a, V_b, V_c, V_d, t_1, t_2, and R. Determine the sign of each.
b. Determine the values of $\sum(w_i)$, $\sum(q_i)$, and $\sum(\Delta U_i)$ in terms of V_a, V_b, V_c, V_d, t_1, t_2, and R. Determine the sign of each.

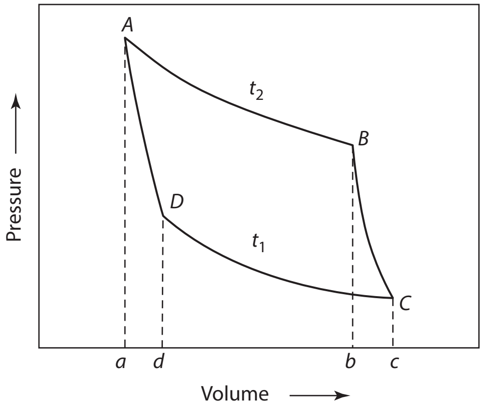

Figure 2.7 A cycle for one mole of a monatomic ideal gas with two isothermal paths and two adiabatic paths. The area enclosed by *ABCD* is the work done by the gas during the cycle.

2.11* The change in enthalpy when 1 mole of solid water (ice) is melted at 273 K is 6008 J.

a. Calculate the change in enthalpy when ice is melted at 298 K. Is this process possible at 1 atm?
b. Calculate the change in enthalpy when supercooled water solidifies at 260 K.
c. Sketch the H versus T plot for both solid and liquid water.

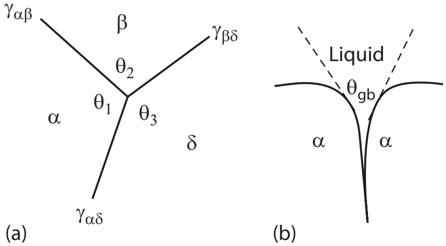

Figure 2.8 (a) Three phases meeting at a point, showing the angles between their surfaces. (b) A grain boundary groove showing the equilibrium groove angle.

For this problem, take the heat capacity of liquid water to be 75.44 J/K and that of solid water to be 38 J/K over the range in temperatures of the problem. The enthalpy of liquid water at 298 K may be arbitrarily set equal to zero.

2.12* Three phases, α, β, and δ meet as shown in Figure 2.8a, forming three interphase interfaces—namely, α/β, α/δ, and β/δ. It can be shown that the following holds.

$$\frac{\gamma_{\alpha/\beta}}{\sin\theta_3} = \frac{\gamma_{\alpha/\delta}}{\sin\theta_2} = \frac{\gamma_{\beta/\delta}}{\sin\theta_1}$$

Using this equation, determine the equation that relates the grain boundary grooving angle θ_{gb} to the interface energy $\gamma_{\alpha/L}$ and the grain boundary energy $\gamma_{\alpha/\alpha}$ (Figure 2.8b).

APPENDIX 2A: Note on the Sign Convention of δ*w*

There are two sign conventions in the literature for the work term in the First Law. One convention is that work done by the system is considered positive, and therefore, since the internal energy, U, decreases, for $\delta q = 0$, we have

$$dU = -\delta w \ (\text{convention } i)$$

This is the convention used in this text.

The other convention is that work done on the system is positive work, and therefore, the internal energy of the system increases when positive work is performed (for $\delta q = 0$):

$$dU = +\delta w \ (\text{convention } ii)$$

In thermodynamic discussions which deal mainly with gases, the first convention is the best one to use. This is because when the system is a gas and pressure is applied

---

* New problem in this edition.

to it, the gas contracts ($V_2 < V_1$). This means that the internal energy of the gas changes (for $\delta q = 0$) as

$$dU = -PdV = -P\left(V_2 - V_1\right) > 0$$

This convention is based on the fact that pressure applied to a gas is defined as positive, and therefore, the volume of the gas decreases.

The internal energy of the gas must decrease if the gas does work.

Using this convention, for work terms caused by the application of external magnetic fields or stress fields, the work term on the system is negative work. For example, we write

$$dU = \delta q - \delta w = \delta q - \left(-V\mu_0 \boldsymbol{H} d\boldsymbol{M}\right) = \delta q + V\mu_0 \boldsymbol{H} d\boldsymbol{M}$$

which shows that magnetic work done on the system increases the internal energy, as expected.

For stress, this is taken care of since the equivalent stress to hydrostatic pressure is a compressive stress:

$$P = -\frac{1}{3}\begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{pmatrix}$$

which is defined as negative stress, tensile stress being positive.

CHAPTER 3

The Second Law of Thermodynamics

3.1 INTRODUCTION

In Chapter 2, it was seen that when a system undergoes a change of state, the consequent change in the internal energy of the system is dependent only on the initial and final states and is equal to the algebraic sum of the thermal energy, q, and work, w, effects. Two questions now arise.

1. What magnitudes may the q and w effects have?
2. What criteria govern these magnitudes?

Two extreme cases related to the first question can occur.

- $w = 0$ and $q = \Delta U'$
- $q = 0$ and $w = -\Delta U'$

But if $q \neq 0$ and $w \neq 0$, a third question arises.

3. Is there a definite limit to the amount of work which the system can do during its change of state?

The answers to these questions require an examination of the *nature* of the processes which affect q and w. This examination, which is made in this chapter, identifies two types of processes (*reversible* and *irreversible* processes) and introduces a state function called the *entropy* (S).

The concept of entropy will be introduced from two different starting points. In Sections 3.2 through 3.8, entropy will be seen as a *quantification* of the degree of irreversibility of a process. In Sections 3.10 through 3.14, it will be seen that, as a result of an examination of the properties of reversibly operated heat engines, there naturally develops a quantity which has all the properties of a thermodynamic state function. This state function is the entropy. These findings lead to a statement of the Second Law of Thermodynamics, which, together with the other laws of thermodynamics lay the foundation for the thermodynamic method of describing the behavior of matter to be discussed in the text.

3.2 SPONTANEOUS OR NATURAL PROCESSES

A system left to itself will do one of two things: it may remain in the state in which it happens to be or it may change of its own accord to some other state. That is, if the system is initially in equilibrium with its surroundings, then, left to itself, it will remain in this equilibrium state. On the other hand, if the initial state is not the equilibrium state, the system will spontaneously* (i.e., without any external influence) move toward its equilibrium state. The equilibrium state is a state of rest (at least at the macroscopic level), and thus, once at equilibrium, a system will only move away from equilibrium if it is acted on by some external agency. Even then, the combined system, comprising the original system and the external agency, is simply moving toward the equilibrium state of the new combined system. A process which involves the spontaneous movement of a system from a nonequilibrium state to an equilibrium state is called a *natural* or *spontaneous* process. Since such a process cannot be reversed without the application of an external agency which leaves a permanent change in this agency, such a process is said to be *irreversible*. The terms *natural*, *spontaneous*, and *irreversible* are synonymous in this context.

The mixing of gases and the transfer of energy down a temperature gradient are common examples of natural processes.

- If the initial state of a system consisting of two gases A and B is that in which gas A is contained in one vessel and gas B is contained in a separate vessel, then, when the vessels are connected to one another, the system *spontaneously* moves to the equilibrium state in which the two gases are completely mixed; that is, the composition of the gas mixture is uniform throughout the volume which the gas occupies.
- If the initial state of a two-body system is that in which one body is at one temperature and the other body is at another temperature, then, when the bodies are placed in thermal contact with one another, a spontaneous process occurs in which energy is transferred from the hotter to the colder body. The equilibrium state is reached when both bodies attain a common uniform temperature.

In both of these examples, the reverse process (the unmixing of the gases and the transfer of thermal energy up a temperature gradient) will never occur spontaneously, and in both thermal examples, common experience allows the equilibrium states to be predicted without any knowledge of the criteria for equilibrium. However, in more complex systems, the equilibrium state may not be able to be predicted from common experience, and thermodynamic criteria governing equilibrium must be established before a calculation of the equilibrium state can be made.

The determination of the equilibrium state is of prime importance in thermodynamics, since knowledge of this state for any materials system will allow the determination of the direction in which any change of state will proceed from any starting or initial state. For example, knowledge of the equilibrium state of a chemical reaction system such as

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* In thermodynamics, a *spontaneous change* does not imply anything about the rate of change of the system, only that there is no energetic barrier to its occurrence.

$$A + B = C + D$$

will afford knowledge of whether, from any initial state, which would be some mixture of A, B, C, and D, the reaction will proceed from right to left or from left to right. Also, knowledge of the extent to which the reaction will proceed before equilibrium is reached can be attained.

If a system undergoes a spontaneous process involving the performance of *work* and the transfer of thermal energy, then, as the process continues, during which time the system approaches its equilibrium state, the capacity of the system for further spontaneous change decreases, as does its capacity to do further work. Once equilibrium is reached, the *capacity of the system* for doing further work is exhausted. In the initial nonequilibrium state of an isolated system (a system of constant internal energy), some of the energy of the system is available for doing useful work, and when the equilibrium state is reached, as a result of the completion of a spontaneous process, none of the energy of the system is available for doing further spontaneous useful work, even though the total energy of the system has not decreased. Thus, as a result of the spontaneous process, the energy of the system has become degraded, in the sense that energy, which was available for doing useful work, is now in a form which is not available for external purposes. Sometimes, this is referred to as the *dissipation* of energy.

3.3 ENTROPY AND THE QUANTIFICATION OF IRREVERSIBILITY

Two distinct types of spontaneous processes are

1. The conversion of work into thermal energy—that is, the *degradation* of mechanical energy to thermal energy (heat)
2. The transfer of thermal energy down a temperature gradient

If an irreversible process is one in which the energy of the system undergoing the process is degraded, then the possibility that the extent of degradation can differ from one process to another suggests that a *quantitative measure* of the extent of degradation, or degree of irreversibility, can be developed.

The existence of processes which exhibit differing degrees of irreversibility can be illustrated as follows. Consider the weight–heat reservoir system shown schematically in Figure 3.1. This system consists of a weight–pulley arrangement which is coupled to a constant-temperature heat reservoir. The system is at equilibrium when an upward force acting on the weight exactly balances the downward force, W, of the weight. If the upward force is removed, the equilibrium is upset and the weight spontaneously falls, performing work, which is converted, by means of a suitable system of paddle wheels, into thermal energy, which enters the constant-temperature heat reservoir. Equilibrium is reattained when the upward force acting on the weight is replaced, and the net effect of this process is that mechanical energy is converted to thermal energy.

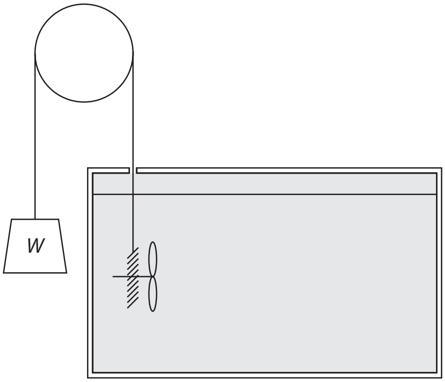

Figure 3.1 A weight–pulley–heat reservoir arrangement in which the work done by the falling weight is degraded to thermal energy, which appears in the heat reservoir.

Lewis and Randall* considered the following three processes:

1. The heat reservoir in the weight–heat reservoir system is at the temperature T_2. The weight is allowed to fall, performing work, w, and the thermal energy produced, q, enters the heat reservoir.
2. The heat reservoir at the temperature T_2 is placed in thermal contact with another heat reservoir at a lower temperature T_1, and the same thermal energy, q, is allowed to be transferred from the reservoir at T_2 to the reservoir at T_1.
3. The heat reservoir in the weight–heat reservoir system is at the temperature T_1. The weight is allowed to fall, performing work, w, and the thermal energy produced, q, enters the reservoir.

Each of these processes is *spontaneous* and hence *irreversible*, and therefore, degradation occurs in each of them. However, since process 3 is the sum of processes 1 and 2, the degradation occurring in process 3 must be greater than the degradation occurring in each of the processes 1 and 2. Thus, it can be said that process 3 is more irreversible than either process 1 or process 2. An examination of the three processes indicates that both the amount of thermal energy transferred, q, and the temperatures between which this energy is transferred are important in defining a quantitative scale of irreversibility. In the case of comparison between process 1 and process 3, the quantity q/T_2 is smaller than the quantity q/T_1, which is in agreement with the conclusion that process 1 is less irreversible than process 3. The quantity q/T can thus be taken as a measure of the degree of irreversibility of the process, and the value of q/T is the increase in entropy occurring as a result of the process. Thus, when the weight–heat reservoir system undergoes a spontaneous process

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* G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer, 3rd ed., McGraw-Hill, New York, 1995, p. 78.

which causes the absorption of thermal energy q at the constant temperature T, the entropy produced by the system, $\Delta S'$, is given by

$$\Delta S' = \frac{q}{T} > 0 \tag{3.1}$$

This value is larger in the case of the lower-temperature reservoir. The increase in entropy caused by the process is thus a measure of the degree of irreversibility of the process.

3.4 REVERSIBLE PROCESSES

Since the degree of irreversibility of a process is path dependent, it should be possible for the process to be conducted in such a manner that the degree of irreversibility is minimized. The ultimate of this minimization is a process in which the degree of irreversibility is zero and in which no degradation of energy occurs. This limit, which the behavior of real systems can be made to approach, is called a *reversible* process. If a process is reversible, then the concept of spontaneity is no longer applicable. Recall that spontaneity occurs as a result of the system moving, of its own accord (i.e., no external influences), from a nonequilibrium state to an equilibrium state. Thus, if the spontaneity is removed, it is apparent that, at all times *during* the process, the system is at equilibrium. A reversible process, then, is one during which the system is never away from equilibrium. A reversible process which takes the system from the state A to the state B is one in which the process path passes through a continuum of equilibrium states. Such a path is, of course, an idealization, but it is possible to conduct an actual process in such a manner that it is virtually reversible. Such an actual process (sometimes called a *quasi-static* process) is one which proceeds under the influence of an infinitesimally small driving force, such that, during the process, the system is never more than an infinitesimal amount from equilibrium. If, at any point along the path, the small external influence is removed, then the process ceases; if the direction of the small external influence is reversed, then the direction of the process is reversed.

Reversible and natural processes are illustrated in the following section.

3.5 ILLUSTRATION OF REVERSIBLE AND IRREVERSIBLE PROCESSES

In this section, we will compare two processes: the isothermal reversible expansion of an ideal gas and the free expansion of an ideal gas. These two processes have in common that the temperature of the gas remains constant. Since the gas is ideal, the internal energy of the gas does not change for either process, since the temperature does not change. However, the processes differ in that, in the reversible case, work is performed *by* the gas during its expansion, but no work is performed by the gas during the free expansion. We will see that, in the reversible case, the entropy of the universe (system plus surroundings) remains constant ($\Delta S'_{\text{total}} = 0$), while in the irreversible case (free expansion), the entropy of the universe increases ($\Delta S'_{\text{total}} > 0$).

3.5.1 The Reversible Isothermal Expansion of an Ideal Gas

Let us consider the reversible isothermal expansion of 1 mole of a monatomic ideal gas from the state (V_A,T) to the state (V_B,T), where $V_B > V_A$ (Figure 3.2). The gas is placed in thermal contact with a heat reservoir* at the temperature T, and by slowly reducing the weight on the piston by removing one grain of sand at a time, the pressure exerted by the gas is only infinitesimally greater than the instantaneous pressure exerted by the piston on the gas. The state of the gas thus lies, at all times, on a section at the constant temperature T of the V-P-T surface (Figures 1.1 and 1.3a), and hence, the gas passes through a continuum of equilibrium states in going from the state (V_A,T) to the state (V_B,T). Since the gas is never out of equilibrium, the process is reversible.

From the First Law,

$$\Delta U = q - w$$

We have seen that the internal energy of an ideal gas depends only on its temperature. Hence, $\Delta U = 0$, and thus, $q = w$; that is, the work done by the expanding gas on

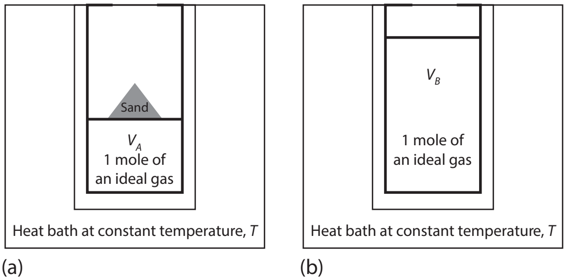

Figure 3.2 (a) One mole of a confined ideal gas being held at V_A by a mass of sand. (b) The mass of sand is removed and the new volume if the gas is V_B.

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* The pertinent feature of a constant-temperature heat reservoir is that it experiences only heat effects and neither performs work nor has work performed on it. The *ice calorimeter*, which comprises a system of ice and water at 0°C and 1 atm pressure, is an example of a simple constant-temperature heat reservoir. Thermal energy transferring into or out of this calorimeter at 0°C is measured as the change occurring in the ratio of the amount of ice to that of water present as a result of the thermal energy flow. Since the molar volume of ice is larger than that of water, the change in this ratio is measured as a change in the total volume of ice plus water in the calorimeter. Strictly speaking, if thermal energy flows out of the calorimeter, freezing some of the water, the volume of the system increases, and hence, the calorimeter does, in fact, perform the work of expansion against the atmospheric pressure. However, the ratio of the work done in expansion to the corresponding thermal energy leaving the system is small enough that the work effects may be neglected.

the piston equals the thermal energy transferred from the constant-temperature heat reservoir into the gas.

We calculate the work done as

$$w_{\text{rev}} = \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{RTdV}{V} = RT\ln\frac{V_B}{V_A}$$

Since $V_B > V_A$, w_{rev} is a positive quantity, in accordance with the fact that work is done *by* the gas. The transfer of thermal energy from the reservoir to the gas (at constant internal energy) causes a change in the entropy of the gas:

$$\Delta S_{\text{gas}} = S_B - S_A = \frac{q_{\text{rev}}}{T} = \frac{w_{\text{rev}}}{T} = R\ln\frac{V_B}{V_A}$$

which is also a positive quantity. The change in the entropy of the reservoir is given by

$$\Delta S_{\text{heat reservoir}} = -\frac{q}{T} = -\Delta S_{\text{gas}} = R\ln\frac{V_A}{V_B} < 0$$

The total change in the entropy (gas plus heat reservoir) can be written as

$$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} = 0 \tag{3.2}$$

For the reversible process, the total change in entropy of the universe is zero: no entropy has been produced.

3.5.2 The Free Expansion of an Ideal Gas

We now consider the free expansion (i.e., expansion against zero atmospheric pressure) of 1 mole of an ideal gas from V_A to V_B. We have seen in Chapter 2 that the free expansion of an ideal gas is also isothermal. Thus, the final state of the free expansion is the same as the state of the isothermal reversible expansion process (i.e., both states have the same V and T). In this case, however, no work is done by the gas against the piston, since the weight on the piston is rapidly removed. Thus, $\Delta U = 0$ and $w = 0$, which by the First Law means that $q = 0$ as well. Since entropy is a state function, the change of entropy of the gas for the free expansion must be the same as that for the isothermal expansion.

$$\Delta S_{\text{gas}} = S_B - S_A = R\ln\frac{V_B}{V_A}$$

Also, since no thermal energy leaves the heat reservoir, $\Delta S_{\text{reservoir}} = 0$ The total change in the entropy (gas plus heat reservoir) for the free expansion is

$$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} = \Delta S_{\text{gas}} = R \ln \frac{V_B}{V_A} \tag{3.3}$$

In the case of free expansion, there is no decrease in entropy of the heat reservoir, since no thermal energy was absorbed by the ideal gas, since it did no work. Thus, for the free expansion process, the entropy of the universe increases ($\Delta S_{\text{total}} > 0$).

3.6 FURTHER DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE EXPANSION

We now look at the processes from the point of view of the thermal energy that was transferred from the heat reservoir to the gas and the work that was performed by the gas. For the reversible isothermal expansion case, $q_{\text{rev}} = w_{\text{max}}$. This process yields the maximum amount of work that can be performed by the gas during isothermal expansion. The reversible process also yields the most amount of thermal energy that can be transferred to the gas from the heat reservoir. The total change in entropy of the universe is zero.

For the case of the free expansion of the gas, we have seen that $w = q = 0$.

Overall, it can be seen that the work performed in the preceding two cases of the isothermal expansion of an ideal gas varies between 0 for free expansion (isothermal) and w_{max} for reversible isothermal expansion; that is,

$$0 \le w \le w_{\text{max}}$$

We also see that

$$0 \le q \le q_{\text{rev}}$$

This means that

$$0 \le \Delta S_{\text{total}} \le \frac{q_{\text{rev}}}{T}$$

$\Delta S_{\text{total}} = 0$ when the process is reversible. $\Delta S_{\text{total}} > 0$ when the process is irreversible. The maximum value of ΔS_{total} occurs for the completely irreversible free expansion case.

It is important to note that the difference in entropy between the final and initial states of the gas is independent of whether the process is conducted reversibly or irreversibly. In going from state A to state B,

$$\Delta S = S_B - S_A = \frac{q}{T} + \Delta S_{\text{irr}} \tag{3.4a}$$

$$= \frac{q_{\text{rev}}}{T} \tag{3.4b}$$

Equation 3.4b indicates that, since the change in entropy can be determined only by the measurement of thermal energy transferred reversibly at the temperature T, then entropy changes can be measured only for reversible processes, in which case the measured thermal energy transferred is q_{rev} and $\Delta S_{\text{irr}} = 0$.

3.7 COMPRESSION OF AN IDEAL GAS

3.7.1 Reversible Isothermal Compression

Consider the reversible isothermal compression of 1 mole of an ideal gas from the state (V_B,T) to the state (V_A,T) (Figure 3.2). The gas is placed in thermal contact with a heat reservoir at the temperature T, and, by adding one grain of sand at a time to the top of the piston, the gas is compressed slowly enough that, at all times during its compression, the pressure exerted on the gas is only infinitesimally greater than the instantaneous pressure of the gas, P_{inst}, where $P_{\text{inst}} = RT/V_{\text{inst}}$. The state of the gas thus lies, at all times, on a section at the constant temperature T of the V-P-T surface (Figures 1.1 and 1.3a), and hence, the gas passes through a continuum of equilibrium states in going from the state (V_B,T) to the state (V_A,T). Since the gas is never out of equilibrium, the process is reversible and no degradation of energy occurs. Entropy is not *created* during this process. Entropy is transferred from the gas to the heat reservoir, where it is measured as the thermal energy entering divided by the temperature T. Since the compression is conducted isothermally, $\Delta U = 0$; thus, the work done on the gas is equal to the thermal energy withdrawn from the gas; that is,

$$w_{\max} = q_{\text{rev}}$$

where

$$w_{\max} = \int_{V_B}^{V_A} PdV = \int_{V_B}^{V_A} \frac{RTdV}{V} = RT \ln \frac{V_A}{V_B}$$

Since $V_B > V_A$, $w_{\max}$ is a negative quantity, in accordance with the fact that work is done on the gas. The transfer of thermal energy from the gas to the reservoir causes a change in the entropy of the gas:

$$\Delta S_{\text{gas}} = \frac{q_{\text{rev}}}{T} = \frac{w_{\max}}{T} = R \ln \frac{V_A}{V_B}$$

which is also a negative quantity. Since there is no change in the total entropy during the reversible compression, the change in the entropy of the reservoir is given by

$$\Delta S_{\text{heat reservoir}} = -\Delta S_{\text{gas}} = R\ln\frac{V_B}{V_A} > 0$$

3.8 THE ADIABATIC EXPANSION OF AN IDEAL GAS

Consider the reversible adiabatic expansion of 1 mole of an ideal gas from the state (P_A,T_A) to the state (P_B,T_B), where $P_B < P_A$. For the process to be reversible, it must be conducted slowly enough that, at all times, the state of the gas lies on its V-P-T surface. As has been shown in Chapter 2, this condition, together with the condition that $q = 0$ (an adiabatic process), dictates that the process path across the V-P-T surface follows the curve PV^γ = constant. Since the process is reversible, no degradation of energy occurs, and, since the process is adiabatic, no thermal energy transfer occurs. The change in the entropy of the gas is therefore zero. Consequently, all states of an ideal gas lying on a PV^γ = constant curve are states of equal entropy (cf. all states of an ideal gas lying on a $PV = RT$ curve are states of equal internal energy). A reversible adiabatic process is thus an *isentropic* process. During a reversible adiabatic expansion, the work done by the gas, $w_{\max}$, equals the decrease in the internal energy of the gas; that is,

$$\Delta U = -w_{\max}$$

We can write the following for the reversible process:

$$w = \int_{V_A}^{V_B} PdV \text{ and } PV^\gamma = \text{constant (call it K)}$$

$$w = K\int_{V_A}^{V_B} V^{-\gamma}dV = \left.\frac{KV^{-\gamma+1}}{(-\gamma+1)}\right]_{V_A}^{V_B} = \left.\frac{PV}{(-\gamma+1)}\right]_{P_AV_A}^{P_BV_B} = \frac{R(T_B-T_A)}{1-\gamma}$$

$$w = \frac{3}{2}R(T_A-T_B)$$

Since the work done by the gas is positive, $T_B < T_A$; that is, the gas cools. The change in the internal energy can be calculated as

$$\Delta U = \int_{T_A}^{T_B} c_v dT = \frac{3}{2}R(T_B-T_A) = -w$$

which is negative. The internal energy of the gas decreased by the amount of work that the gas performed.

The gas has now returned to its original equilibrium state (P_A,T_A). If the pressure exerted on the gas is now suddenly decreased from P_A to P_B, then the state of the gas moves off the *V*-*P*-*T* surface, and, being out of equilibrium, the expansion occurs irreversibly and the degradation of energy occurs. Since the gas is contained adiabatically, the thermal energy produced by the energy degradation remains in the gas, and thus, the final temperature of the gas after an irreversible expansion is greater than the temperature T_B of the reversible adiabatic expansion. Thus, the final state of a gas after an irreversible adiabatic expansion from P_A to P_B differs from the final state after a reversible expansion from the same initial to the same final pressures. The irreversible adiabatic expansion does not follow the path PV^γ = constant. The entropy produced in the gas due to the irreversible process is the difference in entropy between the final and initial states, and the final state itself is determined by the degree of irreversibility of the process. That is, for a given decrease in pressure ($P_A \rightarrow P_B$), the more irreversible the process, the more thermal energy produced in the gas by degradation, the higher the final temperature and internal energy, and the greater the increase in entropy. Thus, during an irreversible adiabatic expansion, the work done by the gas still equals the decrease in the internal energy of the gas (as is required by the First Law), but the decrease in U is less than that in the reversible expansion from P_A to P_B, due to the production of thermal energy in the gas as the result of degradation.

3.9 SUMMARY STATEMENTS

The following points have emerged from the discussion so far.

1. Entropy is a thermodynamic state variable (function).
2. Entropy is not created when a system undergoes a reversible process; entropy is transferred from one part of the system/surroundings to another part.
3. The total entropy of the universe increases when an irreversible process occurs.
4. For all processes, we can write $\Delta S'_{\text{system}} = q/T + \Delta S'_{\text{irr}}$ and $q \leq q_{\text{rev}}$.
5. For all processes, the entropy of the universe increases or stays the same. The total entropy of the universe never decreases.

3.10 THE PROPERTIES OF HEAT ENGINES

Traditionally, the concept of entropy as a thermodynamic state function is introduced by considering the behaviors and properties of heat engines. A heat engine is a device which converts thermal energy (heat) into work. It is interesting to note that steam engines were in operation for a considerable number of years before the reverse process—that is, the conversion of work into thermal energy—was investigated by

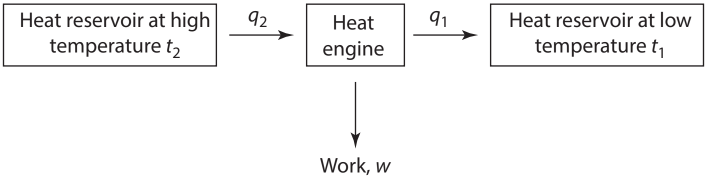

Figure 3.3 Schematic representation of the working of a heat engine.

Rumford in 1798. In the operation of a heat engine, *some* of the energy that has been transferred from a high-temperature heat reservoir is converted into work, with the remainder of the energy being transferred to a low-temperature heat reservoir. The process is shown schematically in Figure 3.3. Treating the engine as the system, the First Law gives

$$\Delta U' = q_2 - q_1 - w$$

Consider the steam engine, which is a typical example of a heat engine. In a steam engine, superheated steam is passed from the boiler (the high-temperature heat reservoir) to the cylinders, where the steam performs work by expanding against the pistons (the engine). As a result of this expansion, the temperature of the steam decreases, and at the end of the piston stroke, the spent steam is exhausted to the atmosphere (the low-temperature heat reservoir). A flywheel returns the piston to its original position, thus completing the cycle and preparing for the next working stroke.

The efficiency of a heat engine is given by

$$\text{Efficiency} = \eta = \frac{\text{work obtained}}{\text{energy input}} = \frac{w}{q_2}$$

The factors governing the efficiency of this process were explained in 1824 by Carnot (Nicolas Léonard Sadi Carnot, 1796–1832), who considered the cyclic process illustrated in Figure 3.4.

In the step $A \rightarrow B$, thermal energy q_2 is isothermally and reversibly transferred from a heat reservoir at the temperature t_2 to a thermodynamic substance, as a result of which the thermodynamic substance isothermally and reversibly expands from the state A to the state B and performs work w_1 equal to the area $ABba$.

In the step $B \rightarrow C$, the thermodynamic substance undergoes a reversible adiabatic expansion from the state B to the state C, as a result of which its temperature decreases to t_1, and it performs work equal to the area $BCcb$.

In the step $C \rightarrow D$, energy q_1 is isothermally and reversibly transferred from the thermodynamic substance to a heat reservoir at the temperature t_1. Work w_3, equal to the area $DCcd$, is done on the substance.

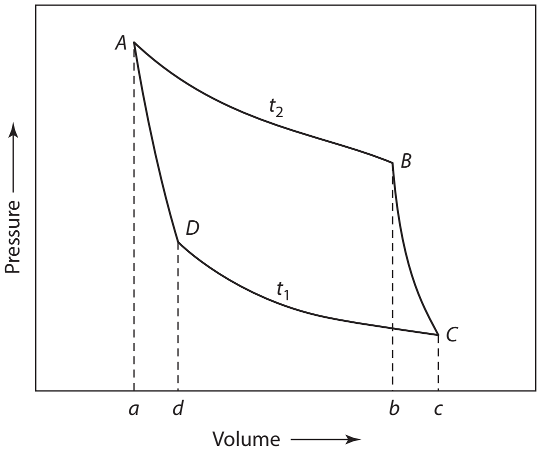

Figure 3.4 A pressure vs. volume depiction of a Carnot cycle.

In the step D → A, the substance is reversibly and adiabatically compressed, during which its temperature increases from t_1 to t_2, and work w_4, equal to the area *ADda*, is done on the substance.

During this *cyclic process*, which has returned the thermodynamic substance to its initial state, the substance has performed the work $w = w_1 + w_2 - w_3 - w_4$ (equal to the area *ABCD*) and has absorbed thermal energy $q = q_2 - q_1$. For a cyclic process, $\Delta U' = 0$, and thus, from the First Law,

$$\sum q_i = \sum w_i$$

Thus,

$$q_2 - q_1 = \sum w_i \equiv w$$

The efficiency of this cyclic process (which is known as a *Carnot cycle*) is given by

$$\text{Efficiency} = \eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}$$

This equation shows that in this idealized Carnot cycle (all processes assumed to be reversible), the efficiency is less than unity for finite values of q_1, the dissipated energy.

The consequence of all of the steps in the cyclic process having been conducted reversibly is illustrated in the following discussion. Consider a second engine working with a different substance, again between the temperatures t_1 and t_2, and let this second engine be *more* efficient than the first one. This greater efficiency could be obtained in either of two ways:

1. The same amount of thermal energy, q_2, is withdrawn from the heat reservoir at t_2, and *more work*, w', is obtained from it than was obtained from the first engine; that is, $w' > w$. Thus, the second engine rejects less thermal energy, q_1', to the cold reservoir at t_1 than does the first engine; that is, $q' < q$.
2. The same work is obtained by withdrawing less thermal energy, q_2', from the heat reservoir at t_2; that is, $q_2' < q_2$. Thus, less thermal energy, q_1', is rejected into the heat reservoir at t_1; that is, $q_1' < q_1$.

Consider now that the second engine is run in the forward direction, and the first engine is run in the reverse direction; that is, it acts as a *heat pump*. Then, from (1), for the second engine run in the forward direction, $w' = q_2 - q_1'$. For the first engine run in the reverse direction, $-w = -q_2 + q_1$. The sum of the two processes is

$$(w' - w) = (q_1 - q_1')$$

that is, an amount of work $(w' - w)$ has been obtained from a quantity of thermal energy $(q_1 - q_1')$ without any other change occurring. Although this conclusion does not contravene the First Law of Thermodynamics, it is contrary to human experience. Such a process corresponds to *perpetual motion of the second kind*; that is, heat is converted to work without leaving a change in any other body. (Perpetual motion of the first kind is the creation of energy from nothing.)

From (2), for the second engine run in the forward direction, $w = q_2' - q_1'$. For the first engine run in the reverse direction, $-w = -q_2 + q_1$. The sum of the two processes is

$$q_2' - q_2 = q_1 - q_1' = q$$

that is, an amount of thermal energy at the lower temperature has been transferred to a higher temperature without any other change occurring. This corresponds to the *spontaneous transfer of thermal energy* up a temperature gradient and is thus even more contrary to human experience than is perpetual motion of the second kind.

The preceding discussion gives rise to the following two preliminary formulations of the Second Law of Thermodynamics:

1. It is impossible, by means of a cyclic process, to transfer thermal energy from a hot reservoir and convert it to work without, in the same process, transferring thermal energy to a cold reservoir. This is known as the *principle of Kelvin and Planck* (Lord Kelvin, aka William Thomson, 1824–1907, and Max Karl Ernst Ludwig Planck, 1858–1947).
2. It is impossible to transfer thermal energy from a cold to a hot reservoir without, in the same process, converting a certain amount of work to thermal energy. This is the *principle of Clausius* (Rudolf Julius Emanuel Clausius, 1822–1888).

These two statements are equivalent to each other: if one of them can be shown to be false, the other one must also be false.

3.11 THE THERMODYNAMIC TEMPERATURE SCALE

The foregoing discussion suggests that all reversible Carnot cycles operating between the same upper and lower temperatures must have the same efficiency—namely, the maximum possible. This maximum efficiency is independent of the working substance and is a function only of the working temperatures t_1 and t_2. Thus,

$$\text{Efficiency} = \eta = \frac{q_2 - q_1}{q_2} = f'(t_1, t_2) = 1 - \frac{q_1}{q_2}$$

or

$$\frac{q_1}{q_2} = f(t_1, t_2)$$

Consider the Carnot cycles shown in Figure 3.5. The two cycles operating between t_1 and t_2, and between t_2 and t_3, are equivalent to a single cycle operating between t_1 and t_3. Thus,

$$\frac{q_1}{q_2} = f(t_1, t_2)$$

$$\frac{q_2}{q_3} = f(t_2, t_3)$$

and

$$\frac{q_1}{q_3} = f(t_1, t_3)$$

So,

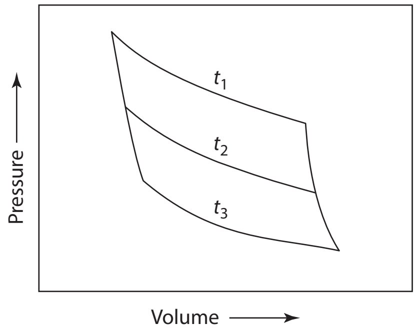

Figure 3.5 Carnot cycles operating between t_1 and t_2, t_1 and t_3, and t_2 and t_3.

$$\left(\frac{q_1}{q_3}\right)\times\left(\frac{q_3}{q_2}\right) = \frac{f(t_1,t_3)}{f(t_2,t_3)} = \frac{q_1}{q_2} = f(t_1,t_2)$$

Since $f(t_1,t_2)$ is independent of t_3, then $f(t_1,t_3)$ and $f(t_2,t_3)$ must be of the form

$$f(t_1,t_3)=\frac{F(t_1)}{F(t_3)}$$

and

$$f(t_2,t_3)=\frac{F(t_2)}{F(t_3)}$$

that is, the efficiency function $f(t_1,t_2)$ is the quotient of a function of t_1 alone and t_2 alone. Thus,

$$\frac{q_1}{q_2}=\frac{F(t_1)}{F(t_2)}$$

Kelvin took these functions to have the simplest possible form—namely, T_1 and T_2. Thus,

$$\frac{q_1}{q_2}=\frac{T_1}{T_2}$$

In which case the efficiency of a Carnot cycle is

$$\text{Efficiency} = \frac{q_2-q_1}{q_2}=\frac{T_2-T_1}{T_2}=1-\frac{T_1}{T_2} \tag{3.5}$$

This defines an *absolute thermodynamic scale of temperature* which is independent of the working substance. It is seen that the zero of this temperature scale is that temperature of the cold reservoir which makes the Carnot cycle 100% efficient.

The absolute thermodynamic temperature scale (or Kelvin scale) is identical to the ideal gas temperature scale discussed in Chapter 1. This can be demonstrated by considering 1 mole of ideal gas to be the working substance in a Carnot cycle. Referring to Figure 3.4,

State A to state B. Reversible isothermal expansion at t_2:

$$\Delta U = 0$$

and from Equation 2.10,

$$q_2 = w_1 = Rt_2 \ln\left(\frac{V_B}{V_A}\right)$$

State B to state C. Reversible adiabatic expansion:

$$q = 0$$

and from Equation 2.6a,

$$w_2 = -\Delta U = -\int_{t_2}^{t_1} c_v dT$$

State C to state D. Reversible isothermal compression at t_1:

$$q_1 = w_3 = Rt_1 \ln\left(\frac{V_D}{V_C}\right)$$

State D to state A. Reversible adiabatic compression:

$$q = 0$$

$$w_4 = -\int_{t_1}^{t_2} c_v dT$$

The total work done on the gas = $w = w_1 + w_2 + w_3 + w_4$

$$= Rt_2 \ln\left(\frac{V_B}{V_A}\right) - \int_{t_2}^{t_1} c_v dT + Rt_1 \ln\left(\frac{V_D}{V_C}\right) - \int_{t_1}^{t_2} c_v dT$$

The thermal energy transferred from the hot reservoir $= q_2 = Rt_2 \ln\left(\frac{V_B}{V_A}\right)$.

It can be shown (see Problem 3.7) that

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

and thus,

$$w = R(t_2 - t_1)\ln\left(\frac{V_B}{V_A}\right)$$

Finally,

$$\text{Efficiency} = \eta = \frac{w}{q_2} = \frac{(t_2 - t_1)}{t_2} = 1 - \frac{T_1}{T_2}$$

which is equivalent to Equation 3.5. Thus, the absolute thermodynamic temperature scale is the same as the ideal gas temperature scale.

3.12 THE SECOND LAW OF THERMODYNAMICS

The equation

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

can be written as

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \tag{3.6}$$

Any cyclic process can be broken down into a number of Carnot cycles, as shown in Figure 3.6. In going around the cycle *ABA* in a clockwise direction, the work done by the system equals the area enclosed by the path loop. This loop can be roughly approximated by a number of Carnot cycles as shown, and for the zigzag paths of these cycles, from Equation 3.6,

$$\Sigma \frac{q_i}{T_i} = 0$$

where the thermal energy being transferred into the system is positive and the thermal energy being transferred out of the system is negative. The zigzag path of the Carnot cycles can be made to coincide with loop *ABA* by making the Carnot cycles smaller and smaller, and in the limit of coincidence, the summation can be replaced by a cyclic integral; that is,

$$\oint \left(\frac{\delta q_i}{T} \right)_{\text{rev}} = 0$$

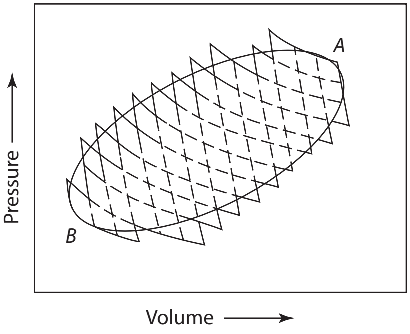

Figure 3.6 A cyclic process broken down into a large number of Carnot cycles.

The vanishing of the cyclic integral indicates that the integral is an exact differential of some function of state of the system. This function is the entropy, S, and for the case of a reversible process, we can write

$$dS' = \frac{\delta q}{T} \tag{3.7}$$

where δq is the infinitesimal thermal energy transferred into (or out of) the system at temperature T. Thus, if thermal energy is transferred into the system, the entropy of the system increases.

For the loop ABA,

$$\oint dS' = 0 = \int_A^B dS' + \int_B^A dS' = (S_B - S_A) + (S_A - S_B) = 0$$

It is to be emphasized that q in Equation 3.7 is the reversible thermal energy increment, and thus, Equation 3.7 should be written properly as

$$dS' = \frac{\delta q_{\text{rev}}}{T} \tag{3.8}$$

Recall that this expression was derived from the consideration of Carnot cycles, in which all operations are conducted reversibly.

The application of Equation 3.6 to a reversibly operated heat engine, in which q_2 is withdrawn from a constant-temperature source at T_2, work w is performed, and q_1 is rejected into a constant-temperature heat sink at T_1, shows that the decrease in the entropy of the high-temperature source, q_2/T_2, equals the increase in the entropy of the heat sink, q_1/T_1; that is, $\Delta S'_{\text{total}} = 0$, which is a consequence of the fact that the process is conducted reversibly.

The Second Law of Thermodynamics can thus be stated as follows:

1. The incremental change in entropy dS' of a system into which (or out of which) thermal energy has been reversibly added (or expelled) is given as $dS' = \delta q_{rev}/T$, and the function S is a state function of the system.
2. The entropy of a system in an adiabatic enclosure can never decrease.
    - The entropy increases during an irreversible process.
    - The entropy remains constant during a reversible process.
    - The entropy remains constant if the system was initially in equilibrium.

From (2), it is seen that, for an infinitesimal change of state of an adiabatically contained system,

$$\sum dS'_i \geq 0 \tag{3.9}$$

that is, the sum of the incremental changes in entropy of all i parts of the system which are in thermal contact with each other is zero if the infinitesimal change of state is reversible and is greater than zero if the infinitesimal change of state is irreversible. Equation 3.9 can be converted to an equality by writing

$$\sum_i dS_i' = dS_{\text{irr}}' \tag{3.10}$$

where dS_{irr}' is the total entropy created in the given incremental irreversible process.

3.13 MAXIMUM WORK

For a change of state from A to B, the First Law gives

$$U_B' - U_A' = q - w$$

In Section 3.1, three questions were raised concerning this law. The third question was,

> *Is there a definite limit to the amount of work which the system can do during its change of state?*

As we indicated in Section 3.1, the First Law gives no indication of the allowed magnitudes of q and w in the given process. We have seen in the preceding discussion that, although the values of q and w can vary depending on the degree of irreversibility of the path taken between the state A and B, the Second Law sets a definite limit on the maximum amount of work which can be obtained from the system during a given change of state and, hence, sets a limit on the quantity of thermal energy which the system may absorb. For an infinitesimal change of state, Equation 3.4a can be written as

$$dS_{\text{system}}' = \frac{\delta q}{T} + dS_{\text{irr}}'$$

and, from the First Law,

$$\delta q = dU_{\text{system}}' + \delta w$$

Thus,

$$dS_{\text{system}}' = \frac{dU_{\text{system}}' + \delta w}{T} + dS_{\text{irr}}'$$

or

$$\delta w = TdS'_{\text{system}} - dU'_{\text{system}} - TdS'_{\text{irr}}$$

and finally,

$$\delta w \le TdS'_{\text{system}} - dU'_{\text{system}} \tag{3.11}$$

If the temperature remains constant throughout the process (and equal to the temperature of the reservoir supplying heat to the system), then the integration of Equation 3.11 from state A to state B gives

$$w \le T\left(S'_B - S'_A\right) - \left(U'_B - U'_A\right)$$

and since U and S are functions of state, then w cannot be greater than a certain amount, $w_{\max}$, the work which is obtained from the system when the process is conducted reversibly; that is,

$$w_{\max} = T\left(S'_B - S'_A\right) - \left(U'_B - U'_A\right)$$

This work, $w_{\max}$, corresponds to the absorption of the maximum heat, q_{rev}, and is the most work that can be performed during the change of state.

Since entropy is a state function, then, in undergoing any specific change of state from A to B,

> *The change in the entropy of the system is the same whether the process is conducted reversibly or irreversibly.*

The preceding discussion indicates that *it is the* heat effect *which is different* in the two cases; that is, if the process involves the absorption of thermal energy and is conducted reversibly, then the thermal energy absorbed, q_{rev}, is greater than the thermal energy which would have been absorbed if the process had been conducted irreversibly. As has been seen, when 1 mole of an ideal gas is isothermally and reversibly expanded from state A to state B, energy q, where

$$q = RT \ln \frac{V_B}{V_B}$$

is reversibly transferred from the heat reservoir to the gas, and the increase in the entropy of the gas, $S_B - S_A$, equals $R \ln V_B / V_B$. The entropy of the thermal reservoir decreases by an equal amount and, therefore, entropy is not created; that is, $\Delta S_{\text{irr}} = 0$. However, if the mole of gas is allowed to expand freely from P_A to P_B (as in Joule's experiment discussed in, Section 2.6), then, since the gas performs no work, no thermal energy is transferred from the reservoir to the gas, and there is no change in the entropy of the reservoir. Since entropy is a state function, the value of $S_B - S_A$ is independent of the process path, and hence, the entropy created,

ΔS_{irr}, equals $S_B - S_A$, which equals $R\ln V_B/V_B$. This entropy is created as a result of the degradation of the work which would have been performed by the gas had the expansion not been carried out against zero pressure. This degraded work equals $w_{\max}$ as well as q_{rev}.

The free expansion therefore represents the limit of complete irreversibility, during which all of the *potential* work is degraded because of the increase in volume of the gas. The degraded potential work in the gas accounts for the increase in the entropy of the gas. For the isothermal expansion of 1 mole of ideal gas from the state A to the state B, the value of ΔS_{irr} is

$$0 \le \Delta S_{\text{irr}} \le R\ln\frac{V_B}{V_B}$$

$\Delta S_{\text{irr}} = 0$ for a reversible isothermal expansion and $\Delta S_{\text{irr}} = R\ln V_B/V_B$ for a free expansion. The value of ΔS_{irr} is thus shown to depend on the degree of irreversibility of the process.

3.14 ENTROPY AND THE CRITERION FOR EQUILIBRIUM

At the beginning of this chapter, it was stated that a system, left to itself (i.e., no interactions with the surroundings, an isolated system), would either remain in the state in which it happened to be or would *spontaneously* change (that is, without any outside influence) to some other state. If the system is initially at equilibrium, then it will remain at equilibrium, and if it is not initially in equilibrium it will change to its equilibrium state. This *spontaneous* process is, by definition, irreversible, and the movement of the system from its initial nonequilibrium state to its final equilibrium state is accompanied by an increase in the entropy of the system. The attainment of the equilibrium state coincides with the entropy reaching a *maximum value*, and hence, for such systems, entropy can be used as a criterion for determining the equilibrium state.

In an *isolated* system of constant internal energy, U, and constant volume, V, equilibrium is attained when the entropy of the system is at maximum, consistent with the fixed values of U and V. Consider the chemical reaction

$$A + B = C + D$$

occurring in an adiabatic enclosure at constant volume. Starting with A and B, the reaction will proceed from left to right as long as the entropy of the system is thereby increased; or, conversely, starting with C and D, the reaction will proceed from right to left, again provided that the entropy of the system is thereby increased. Figure 3.7 shows a possible variation of entropy with the extent of reaction. It is seen that a point is reached along the reaction coordinate at which the entropy of the system has its maximum value. This is the equilibrium state of the system, since

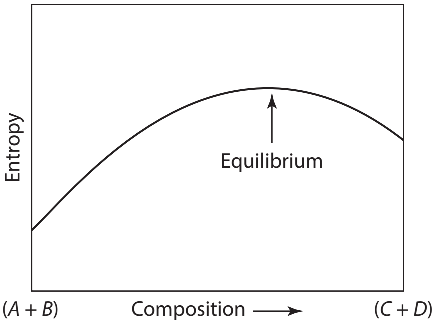

Figure 3.7 Schematic representation of the entropy of a closed system containing $A + B + C + D$ as a function of the extent of the reaction $A + B = C + D$ at constant internal energy and volume.

further reaction in either direction would decrease the entropy and, hence, will not occur spontaneously. This concept will be utilized when we discuss the reactions of gases in Chapter 11.

3.15 THE COMBINED STATEMENT OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

For an incremental change in the state of a closed simple system, the First Law of Thermodynamics gives

$$dU' = \delta q - \delta w$$

and, if the process occurs reversibly, the Second Law of Thermodynamics gives

$$dS' = \frac{\delta q}{T} \text{ or } \delta q = TdS'$$

For a simple system,

$$\delta w = PdV'$$

A combination of the two laws gives the equation

$$dU' = TdS' - PdV' \tag{3.12}$$

Restrictions on the application of Equation 3.12 are

1. That the system is closed—that is, does not exchange matter with its surroundings during the process
2. That work due to change in volume is the only form of work performed by the system

Equation 3.12 relates the dependent variable of the system, U, to the independent variables, S and V; that is,

$$U' = U'(S', V')$$

The total differential of U' is written as

$$dU' = \left(\frac{\partial U'}{\partial S'}\right)_V dS' + \left(\frac{\partial U'}{\partial V'}\right)_S dV' \tag{3.13}$$

A comparison of Equations 3.12 and 3.13 shows that

$$\text{Temperature} = T = \left(\frac{\partial U'}{\partial S'}\right)_V$$

$$\text{Pressure} = P = -\left(\frac{\partial U'}{\partial V'}\right)_S$$

The particularly simple form of Equation 3.12 stems from the fact that, in considering variations in U as the dependent variable, the "natural" choice of independent variables is S and V. The consideration of S as the dependent variable and U and V as the independent variables—that is,

$$S' = S'(U', V')$$

gives

$$dS' = \left(\frac{\partial S'}{\partial U'}\right)_V dU' + \left(\frac{\partial S'}{\partial V'}\right)_U dV' \tag{3.14}$$

Rearranging Equation 3.12 as

$$dS' = \frac{dU'}{T} + \frac{PdV'}{T}$$

and comparing it with Equation 3.14 shows that

$$\left(\frac{\partial S'}{\partial U'}\right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S'}{\partial V'}\right)_U = \frac{P}{T} \tag{3.15}$$

From this equation, it can be seen that increasing the internal energy of the system at constant volume increases its entropy, since $1/T > 0$ (Figure 3.8). The curvature of the S versus U plot is negative.

$$\left(\frac{\partial^2 S'}{\partial U'^2}\right)_V = -\frac{1}{T^2}\frac{\partial T}{\partial U'} < 0$$

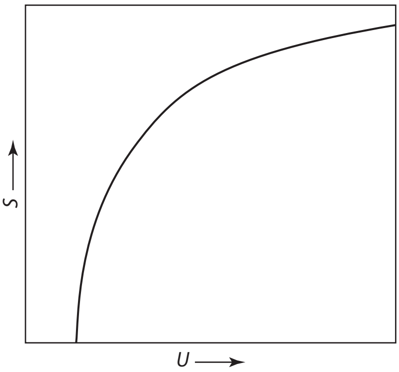

Figure 3.8 Plot of entropy vs. internal energy. Note that as U approaches its minimum value, S also approaches its minimum value.

Also, since $P/T > 0$, increasing the volume increases the entropy of a system at constant U. The plot of S versus V is similar to the one of S versus U: S increases with V and the plot has negative curvature.

It can also be seen that as T approaches zero, U approaches its minimum value, as does the entropy (more on this in Chapter 6, when the Third Law of Thermodynamics is discussed).

There is no need to have a δq transfer of energy to have entropy increase! This type of entropy is related to the increase of the *space the system occupies*. We will call this *configurational entropy* to distinguish it from so-called thermal entropy.

The further development of thermodynamics is a consequence of the fact that S and V (or S and P) are an inconvenient pair of independent variables. In considering a real system, considerable difficulty would be encountered in arranging the state of the system such that, simultaneously, it has the required entropy and occupies the required volume. It would be much better to have temperature and pressure or temperature and volume be the two independent variables. In Chapter 5, we will introduce other thermodynamic state functions that will be of help to our study of thermodynamics.

In the next chapter, we will give a more physical description of entropy.

3.16 SUMMARY

1. The process paths taken by a system undergoing a change of state can be classified into two types: *reversible* and *irreversible*.
   - When the change in the state of the system occurs as the result of the application of a finite driving force, the process proceeds irreversibly, and the degree of irreversibility of the process increases with the increasing magnitude of the driving force.

- For a process to occur reversibly, the driving force must be infinitesimal, and thus, a reversible process proceeds at an infinitesimal rate. The system is imagined to move through a continuum of equilibrium states during a reversible process.

2. When a system undergoes a change of state, during which it performs work and absorbs thermal energy, the magnitudes of the quantities w and q are maxima (w_{max} and q_{rev}), respectively, when the change of state occurs reversibly. For an irreversible path between the two states, less work is performed by the system, and correspondingly less thermal energy is absorbed.
3. There exists a state function called entropy, S, which can be written as

$$dS' = \frac{\delta q_{\text{rev}}}{T}$$

when δq_{rev} enters (or leaves) the system. The difference between the entropy in state B and that in state A is thus

$$\Delta S' = S'_B - S'_A = \int_A^B \frac{\delta q_{\text{rev}}}{T}$$

4. If, in moving between the two states, the temperature of the system remains constant, the change in the entropy of the system is $\Delta S' = q_{\text{rev}}/T$ where q_{rev} is the thermal energy absorbed or given off by the system in moving *reversibly* between the two states.
5. If q_{rev} is provided by a constant-temperature heat reservoir at the temperature T, the entropy of the reservoir decreases by the amount q_{rev}/T as a result of the system moving from A to B. The entropy of the combined system plus heat reservoir is thus unchanged as a result of the *reversible process*; entropy has simply been transferred from the heat reservoir to the system.
6. If the change in the state of a system from A to B were carried out *irreversibly*, then less thermal energy, q ($q < q_{\text{rev}}$), would be withdrawn from the heat reservoir by the system. Thus, the magnitude of the decrease in the entropy of the reservoir would be smaller (equal to q/T). However, since entropy is a state function, the change in entropy of the gas, $S'_B - S'_A$, is independent of the process path, and thus, $\Delta S'_{\text{system}} + \Delta S'_{\text{heat reservoir}} > 0$. Entropy has been created as a result of the occurrence of an irreversible process. The entropy created is termed $\Delta S'_{\text{irr}}$.
7. In the general case, $S'_B - S'_A = q/T + \Delta S'_{\text{irr}}$, and as the degree of irreversibility increases, the thermal energy, q, withdrawn from the heat reservoir decreases and the magnitude of $\Delta S'_{\text{irr}}$ increases.
8. The increase in entropy, due to the occurrence of an irreversible process, arises from the degradation of the energy of the system, wherein some of the internal energy, which is potentially available for the doing of useful work, is degraded.
9. A process occurring in an adiabatically contained system of constant volume (i.e., a system of constant U' and V') will proceed irreversibly with a consequent production of entropy until the entropy is *maximized*. The attainment of maximum entropy is the criterion for equilibrium. Thus, the entropy of an adiabatically contained

system can never decrease; it increases as the result of an irreversible process and remains constant at its maximum value during a reversible process.

10. A combination of the First and Second Laws of Thermodynamics gives, for a closed system which does no work other than the work of expansion against a pressure, $dU = TdS - PdV$. U is thus the natural choice of dependent variable for S and V as the independent variables.

3.17 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 3

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Adiabatic expansion of gas
Carnot cycle
Constant-temperature heat reservoir
Dissipation of energy
Driving force
Efficiency of engine
Entropy
Equilibrium state
Heat engine
Irreversible processes
Isentropic process
Isothermal expansion of gas
Maximum work
Natural processes
Nonequilibrium state
Perpetual motion
Principle of Clausius
Principle of Kelvin and Planck
Quasi-static process
Reversible processes
Second Law of Thermodynamics
Spontaneous processes

3.18 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

A heat engine is operating in a Carnot cycle: all processes are reversible (Figure 3.4). For each of the processes, obtain expressions for the change in entropy of the engine and the change in entropy of the surroundings after one cycle. Assume one mole of an ideal monatomic gas.

Solution to Qualitative Problem 1

The values of q for each process can be found in Section 3.11.

The engine:

1. For the reversible isothermal expansion process from A to B:

$$\Delta S_{\text{engine}} = \frac{q_2}{T_2} = R\ln\left(\frac{V_B}{V_A}\right)$$

2. For the reversible adiabatic expansion process from B to C:

$$\Delta S_{\text{engine}} = 0, \text{ since } q = 0$$

3. For the reversible isothermal compression process from C to D:

$$\Delta S_{\text{engine}} = \frac{q_1}{T_1} = R\ln\left(\frac{V_D}{V_C}\right)$$

4. For the reversible adiabatic compression process from D to A:

$$\Delta S_{\text{engine}} = 0, \text{ since } q = 0$$

The total change in entropy of the engine is therefore

$$\Delta S_{\text{engine}}^{\text{total}} = R\ln\left(\frac{V_B}{V_A}\right) + R\ln\left(\frac{V_D}{V_C}\right) = 0, \text{ since } \frac{V_B}{V_A} = \frac{V_D}{V_C} \qquad \text{(see Problem 3.7)}$$

For each of the processes, the change in entropy of the surroundings is the negative of that for the engine. Thus, $\Delta S_{\text{surroundings}}^{\text{total}} = 0$.

Thus, for the Carnot cycle, $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounds}} = 0$.

Qualitative Problem 2

Draw the entropy versus temperature diagram for the Carnot cycle depicted in Figure 3.4.

Solution to Qualitative Problem 2

Start by choosing a position in the temperature–entropy space for that of state A.

1. The first process is an isothermal ($dT = 0$) increase in entropy from state A to B.
2. The second process is a constant entropy decrease in temperature from state B to C.
3. The third process is an isothermal decrease in entropy from state C to state D.
4. The last process is a constant entropy increase in temperature from state D to state A.

Be sure you understand the sign of each of the changes in temperature and entropy (Figure 3.9).

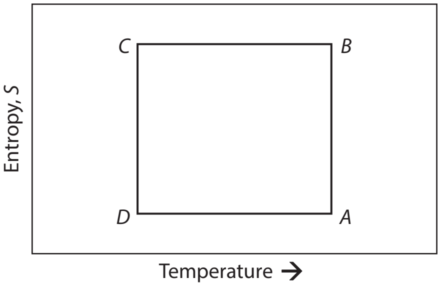

Figure 3.9 The temperature entropy diagram for the Carnot cycle of Figure 3.4.

3.19 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Five moles of a monatomic ideal gas are contained adiabatically at 50 atm pressure and 300 K. The pressure is suddenly released to 10 atm, and the gas undergoes an irreversible expansion, during which it performs 4000 J of work.

a. Show that the final temperature of the gas after the irreversible expansion is greater than that which the gas would attain if the expansion from 50 to 10 atm had been conducted reversibly.
b. Calculate the entropy produced as a result of the irreversible expansion.

Given: The constant-volume molar heat capacity of the gas, c_v, has the value 1.5 R.

Solution to Quantitative Problem 1

a. In the initial state 1:

$$V_1' = \frac{nRT_1}{P_1} = \frac{5 \times 0.08206 \times 300}{50} = 2.46 \text{ liters}$$

If the adiabatic expansion from 50 to 10 atm is carried out reversibly, then the process path follows PV^{γ} = constant, and in the final state 2:

$$V_2' = \left(\frac{P_1 V_1^{\gamma}}{P_2}\right)^{1/\gamma} = \left(\frac{50 \times 2.46^{5/3}}{10}\right)^{3/5} = 6.47 \text{ liters}$$

and

$$T_2 = \frac{P_2 V_2}{nR} = \frac{10 \times 6.47}{5 \times 0.08206} = 158 \text{ K}$$

For the irreversible process, which takes the gas from the state 1 to the state 3, as $q = 0$:

$$\Delta U' = -w = -4000 = nc_v\left(T_3 - T_1\right) = 5\times 1.5\times 8.3144\times\left(T_3 - 300\right)$$

and hence, $T_3 = 236$ K, which is higher than T_2.

b. As the irreversible expansion from state 1 to state 3 was conducted adiabatically, no thermal energy was transferred into the system, and hence, the difference between the entropy at state 3 and the entropy at state 1 is the entropy created, $\Delta S'_{\text{irr}}$, as a result of the irreversible process. This difference in entropy can be calculated by considering any reversible path from state 1 to state 3. Consider the reversible path $1 \rightarrow a \rightarrow 3$ shown in Figure 3.10, which is a reversible decrease in temperature from 300 to 236 K at constant volume, followed by a reversible isothermal expansion from V'_a and V'_3.

For a reversible constant-volume process,

$$\delta q_v = nc_v dT = TdS'$$

or

$$dS' = \frac{nc_v dT}{T}$$

the integration of which, from state 1 to state a, gives

$$S'_a - S'_1 = nc_v \ln\frac{T_a}{T_1} = 5\times 1.5\times 8.3144\times \ln\frac{234}{300} = -15.0 \text{ J/K}$$

For the reversible isothermal expansion from state a to state 3, as $\Delta U' = 0$:

$$q = w = nRT\ln\frac{V'_3}{V'_a}$$

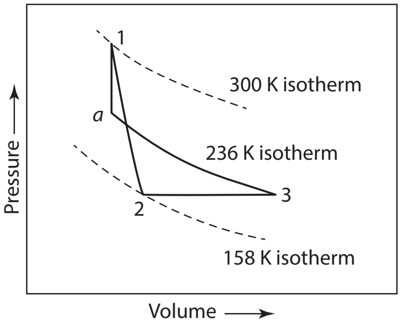

Figure 3.10 The process paths considered in Example 1.

where

$$V_3' = \frac{nRT_3}{P_3} = \frac{5 \times 0.08206 \times 236}{10} = 9.68 \text{ liters}$$

and thus,

$$S_3' - S_a' = \frac{q}{T} = nR \ln \frac{V_3'}{V_a'} = 5 \times 8.3144 \ln \frac{9.68}{2.46} = 57.8 \text{ J/K}$$

The entropy created during the irreversible expansion is thus

$$S_3' - S_1' = -15.0 + 57.0 = 42.0 \text{ J/K}$$

Alternatively, the state of the gas could be changed from 1 to 3 along the path 1 → 2 → 3. As the reversible adiabatic expansion from state 1 to state 2 is isentropic:

$$S_3' - S_1' = S_3' - S_2'$$

and, for the reversible isobaric expansion from state 2 to state 3:

$$\delta q_p = nc_p dT = TdS'$$

or

$$dS' = \frac{nc_p dT}{T}$$

the integration of which, from state 2 to state 3, gives

$$S_3' - S_2' = 5 \times 2.5 \times 8.3144 \times \ln \frac{236}{158} = 42.0 \text{ J/K}$$

which, again, is the entropy created by the irreversible adiabatic expansion of the gas from state 1 to state 3.

Quantitative Problem 2

At a pressure of 1 atm, the equilibrium melting temperature of lead is 600 K, and at this temperature, the latent heat of melting of lead is 4810 J/mole.

Calculate the entropy produced when 1 mole of supercooled liquid lead spontaneously freezes at 590 K and 1 atm pressure.

Given: The constant-pressure molar heat capacity of liquid lead, as a function of temperature, at 1 atm pressure is given by

$$c_{p(l)} = 32.4 - 3.1 \times 10^{-3} T \text{ J/K}$$

and the corresponding expression for solid lead is

$$c_{p(s)} - 23.56 + 9.75\times10^{-3}T \text{ J/K}$$

Solution to Quantitative Problem 2

The entropy produced during the irreversible freezing of the lead equals the difference between the change in the entropy of the lead and the change in the entropy of the constant-temperature heat reservoir (at 590 K) caused by the process.

First, calculate the difference between the entropy of 1 mole of solid lead at 590 K and 1 mole of liquid lead at 590 K. Consider the processes illustrated in Figure 3.11.

1. Step $a \rightarrow b$: 1 mole of supercooled liquid lead is heated from 590 to 600 K at 1 atm pressure.
2. Step $b \rightarrow c$: 1 mole of liquid lead is solidified reversibly at 600 K (the equilibrium melting or freezing temperature is the only temperature at which the melting or freezing process can be conducted).
3. Step $c \rightarrow d$: 1 mole of solid lead is cooled from 600 to 590 K at 1 atm pressure.

Since entropy is a state function,

$$\Delta S_{(a\rightarrow d)} = \Delta S_{(a\rightarrow b)} + \Delta S_{(b\rightarrow c)} + \Delta S_{(c\rightarrow d)}$$

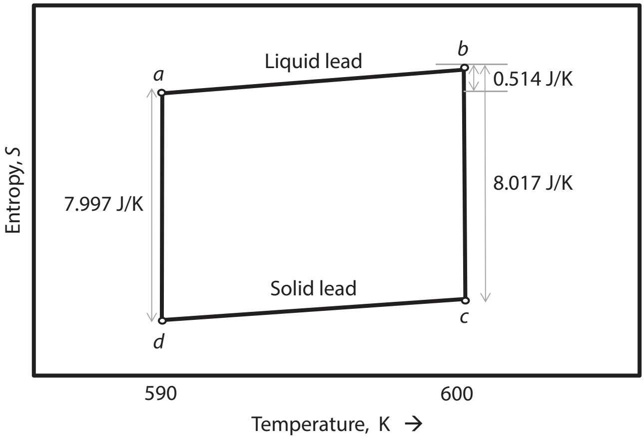

Figure 3.11 The changes of state examined in Quantitative Problem 2 depicted in an entropy vs. temperature diagram.

Step a → b

$$\begin{aligned}\Delta S_{(a\to b)} &= \int_a^b \frac{\delta q_{\text{rev}}}{T} = \int_a^b \frac{\delta q_p}{T} = \int_{590\text{K}}^{600\text{K}} \frac{c_{p,\text{Pb}(l)}dT}{T}\\ &= \int_{590\text{K}}^{600\text{K}} \left(\frac{32.4}{T} - 3.1\times 10^{-3}\right) dT\\ &= 32.4 \ln \frac{600}{590} - 3.1\times 10^{-3} \times (600-590) = +0.514 \text{ J/K}\end{aligned}$$

Step b → c

$$\begin{aligned}\Delta S_{(b\to c)} &= \frac{q_{\text{rev}}}{T} = \frac{q_p}{T} = \frac{\text{latent heat of freezing}}{\text{equilibrium freezing temperature}}\\ &= -\frac{4810}{600} = -8.017 \text{ J/K}\end{aligned}$$

Step c → d

$$\begin{aligned}\Delta S_{(c\to d)} &= \int_c^d \frac{\delta q_{rev}}{T} = \int_c^d \frac{\delta q_p}{T} = \int_{600\text{K}}^{590\text{K}} \frac{c_{p,\text{Pb}(s)}dT}{T}\\ &= \int_{600\text{ K}}^{590\text{K}} \left(\frac{23.6}{T} + 9.75\times 10^{-3}\right) dT\\ &= 23.6 \ln \frac{590}{600} + 9.75\times 10^{-3}(500-600) = -0.494 \text{ J/K}\end{aligned}$$

Thus,

$$\Delta S_{(a\to d)} = +0.514 - 8.017 - 0.494 = -7.997 \text{ J/K}$$

Consider the thermal energy entering the constant-temperature heat reservoir at 590 K. As the thermal energy is transferred at constant pressure, $q_p = \Delta H$, where ΔH is the difference between the enthalpies of states *d* and *a*. As *H* is a state function,

$$\begin{aligned}\Delta H_{(a\to d)} &= \Delta H_{(a\to b)} + \Delta H_{(b\to c)} + \Delta H_{(c\to d)}\\ \Delta H_{(a\to b)} &= \int_a^b c_{\text{p,Pb}(l)}dT = \int_{590\text{K}}^{600\text{K}} \left(32.4 - 3.1\times 10^{-3}\right) dT\\ &= 32.4 \times (600-590) - \frac{3.1\times 10^{-3}}{2}(600^2 - 590^2) = 306 \text{ J}\\ \Delta H_{(b\to c)} &= -4810 \text{ J}\\ \Delta H_{(c\to d)} &= \int_c^d c_{\text{p,Pb}(s)}dT = \int_{600\text{K}}^{590\text{K}} (23.6 + 9.75 \times 10^{-3})dT\\ &= 23.6(590-600) + \frac{9.75 \times 10^{-3}}{2}(590^2 - 600^2) = -294 \text{ J}\end{aligned}$$

Thus,

$$\Delta H_{(a-d)} = -4799 \text{ J}$$

and so, the heat reservoir absorbs 4799 J of thermal energy at 590 K. Consequently,

$$\Delta S_{\text{heat reservoir}} = \frac{4799}{590} = 8.134 \text{ J/K}$$

Thus, the entropy created is

$$\Delta S_{\text{irr}} = -7.994 + 8.134 = 0.137 \text{ J/K}$$

An examination shows that the lower the temperature of the irreversible freezing of the supercooled liquid, the more irreversible the process and the larger the value of ΔS_{irr}.

PROBLEMS

3.1 The initial state of 1 mole of a monatomic ideal gas is $P = 10$ atm and $T = 300$ K. Calculate the change in the entropy of the gas for

a. An isothermal decrease in the pressure to 5 atm
b. A reversible adiabatic expansion to a pressure of 5 atm
c. A constant-volume decrease in the pressure to 5 atm

3.2 One mole of a monatomic ideal gas is subjected to the following sequence of steps:

a. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.
b. The gas is next heated reversibly to 400 K at constant volume.
c. The gas is reversibly expanded at constant temperature until its volume is again tripled.
d. The gas is finally reversibly cooled to 300 K at constant pressure.

Calculate the values of q and w and the changes in U, H, and S.

3.3 One mole of a monatomic ideal gas undergoes a reversible expansion at constant pressure, during which the entropy of the gas increases by 14.41 J/K and the gas absorbs 6236 J of thermal energy. Calculate the initial and final temperatures of the gas. One mole of a second monatomic ideal gas undergoes a reversible isothermal expansion, during which it doubles its volume, performs 1729 J of work, and increases its entropy by 5.763 J/K. Calculate the temperature at which the expansion was conducted.

3.4 Calculate the change in the enthalpy and the change in entropy when 1 mole of SiC is heated from 25°C to 1000°C. The constant-pressure molar heat capacity of SiC varies with temperature as

$$c_p = 50.79 + 1.97 \times 10^{-3} T - 4.92 \times 10^{6} T^{-2} + 8.20 \times 10^{8} T^{-3} \text{ J/mole} \cdot \text{K}$$

3.5 One mole of copper at a uniform temperature of 0°C is placed in thermal contact with a second mole of copper which, initially, is at a uniform temperature of 100°C. Calculate the temperature of the 2-mole system, which is contained in an adiabatic enclosure, when thermal equilibrium is attained. Why is the common uniform temperature not exactly 50°C? How much thermal energy is transferred, and how much entropy is produced by the transfer? The constant-pressure molar heat capacity of solid copper varies with temperature as

$$c_p = 22.64 + 6.28 \times 10^{-3} T \text{ J/mole} \cdot \text{K}$$

3.6 A reversible heat engine, operating in a cycle, withdraws thermal energy from a high-temperature reservoir (the temperature of which consequently decreases), performs work w, and rejects thermal energy into a low-temperature reservoir (the temperature of which consequently increases). The two reservoirs are, initially, at the temperatures T_1 and T_2 and have constant heat capacities C_1 and C_2, respectively. Calculate the final temperature of the system and the maximum amount of work which can be obtained from the engine.

3.7* In deriving the equation for the efficiency of a Carnot engine in Section 3.11, it was stated that $V_B/V_A = V_C/V_D$. Show that this equality is valid.

3.8* This problem picks up from Problem 2.11. Use data from that problem for this one.

a. Calculate the change in entropy at 273 K for the freezing of water.
b. Calculate the change in entropy for the freezing of water at 260 K.

3.9* Calculate the work performed by the Carnot cycle shown in Figure 3.4 using the *T-S* diagram of Figure 3.9.

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* New problem in this edition.

CHAPTER 4

The Statistical Interpretation of Entropy

4.1 INTRODUCTION

Classical thermodynamics is *phenomenological*; that is, it deals with matter as it appears to our senses. In this regard, we use our senses to describe the properties of matter such as pressure, volume, and temperature. Classical thermodynamics does not delve into the more fundamental aspect, of what does matter consist? In this chapter, we will use the understanding of matter consisting of atoms and molecules and introduce the use of statistics to the approach of the topic of thermodynamics. This starting place moves us from the realm of classical thermodynamics to statistical thermodynamics. Our excursion will be brief, but it is hoped that it will give the reader a better physical understanding of entropy.

In Chapter 3, the introduction of entropy as a thermodynamic state function was facilitated by the realization that there exist possible and impossible spontaneous processes, and by the examination of the thermal energy and work effects occurring during these processes. From the formal statements of the Second Law of Thermodynamics, as developed from classical thermodynamics arguments, it is difficult to assign a *physical significance* or a *physical quality* to entropy. In this respect, entropy differs from internal energy in spite of the fact that, within the scope of classical thermodynamics, both properties are extensive thermodynamic functions of the state of a system. The ready acceptance of the First Law of Thermodynamics in the nineteenth century, after its enunciation, was due to the easily understood physical significance of internal energy, whereas the lack of a corresponding understanding of entropy caused the acceptance of the Second Law of Thermodynamics to be slower. A more physical interpretation of entropy had to await the development of statistical thermodynamics and the subsequent development of quantum mechanics.

4.2 ENTROPY AND DISORDER ON AN ATOMIC SCALE

Gibbs (Josiah Willard Gibbs, 1839–1903) described the entropy of a system as being its "mixed-up-ness."* We can understand this concept of mixed-up-ness to be applied at the atomic or molecular level; that is, the more "mixed up" the constituent particles of a system, the larger is the value of its entropy. For example, in the crystalline solid state, most of the constituent particles are confined to vibrating about their regularly arrayed positions, whereas in the liquid state, confinement of the particles to specific sites is absent. The particles are relatively free to wander through the communal volume occupied by the liquid. The arrangement of the particles in the crystalline solid state is thus said to be more ordered than that of the liquid state, or alternatively, is less mixed up than that of the liquid state. As a consequence, the configurational entropy of the liquid state can be understood to be greater than that of the solid crystalline state. Similarly, the atomic or molecular disorder in the gaseous state is greater than that in the liquid state, since, in the gaseous state, there is more volume in which the molecules are free to move. Thus, the entropy of the gaseous state is greater than that of the liquid state.

This qualitative understanding of entropy correlates with phenomena on a macroscopic level. For example, the transformation of a solid to a liquid at its equilibrium melting temperature, T_m, requires that the substance absorb a quantity of thermal energy, q, called the *enthalpy of melting*. The entropy of the substance being melted is thus understood to be increased. Indeed, if the melting process is conducted at constant pressure:

$$\Delta S'_{\text{melting}} = \frac{\Delta H'_{\text{melting}}}{T_m}$$

The increase in the entropy of the substance which accompanies melting correlates with the corresponding increase in the degree of disorder of the configurational states of its constituent particles.

Care must be taken, however, in using the concept of mixed-up-ness. An isolated supercooled liquid increases its entropy when it spontaneously transforms to a crystal, since the process is an irreversible one. But a crystal is certainly less mixed up than a liquid! How can the entropy of the substance increase? This apparent anomaly exists because we have focused on only one of the aspects of entropy—namely, the configurational aspect. If we include in our examination the influence of the enthalpy of freezing (the thermal energy released during freezing), it is seen that this release of energy increases the temperature of the isolated system, resulting in a concomitant increase in the thermal entropy of the system. This increase in thermal entropy is greater than that of the decrease in configurational entropy during the liquid-to-crystal transformation. This shows that all aspects of the entropy of a system must be

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* *The Collected Works of J. W. Gibbs*, Vol. 1, Yale University Press, New Haven, CT, 1928, unpublished fragments.

considered when evaluating changes in a system, just as all aspects of the energy of a system must be taken into account when applying the First Law of Thermodynamics.

If the transformation from liquid to solid occurs isothermally at the equilibrium melting temperature of the substance, T_m, then the increase in the degree of disorder of the heat reservoir equals the decrease in the degree of disorder of the substance, and the total degree of disorder of the combined system plus heat reservoir is unchanged. Consequently, the entropy of the combined system is unchanged as a result of the equilibrium freezing process; entropy has been transferred from the substance to the heat reservoir. The equilibrium melting or freezing temperature of a substance can thus be defined as that temperature at which no change in the entropy of the substance plus heat reservoir occurs as a result of the phase change. Only at this temperature are the solid and liquid in equilibrium with one another, and hence, only at this temperature can the phase change occur reversibly, with no net increase of entropy.

4.3 THE CONCEPT OF MICROSTATE

In classical thermodynamics, the *state* of a single-component isolated system, which in this chapter is denoted as its *macrostate*, is fixed with the knowledge of two of its thermodynamic variables, usually considered to be the intensive thermodynamic variables of pressure and temperature. However, when we consider the atomic and molecular makeup of the system, there are many more possible configurations of the constituents which give rise to the same macrostate of the system. Each constituent has three coordinates for its position and three coordinates for its momentum. In addition, there is an enormous number of constituents in real systems, of the order of 10^{24} for a mole of particles. Statistical thermodynamics considers the various ways that the total number of constituents, N, can be configured in the systems we encountered in the first three chapters, namely:

1. Isolated systems, where $S' = S'(U',V',N)$ or $U' = U'(S',V',N)$
2. Closed systems in equilibrium with a heat bath, where $S' = S'(T,V',N)$
3. Open systems, where $S' = S'(T,V',\mu)$

When considering such systems, special names have been given in the statistical approach to thermodynamics—namely, the microcanonical, canonical, and grand-canonical formalisms, respectively. In this brief introduction to statistical thermodynamics, we will consider the microcanonical (isolated) cases.

The development of a quantitative relationship between entropy and the degree of mixed-up-ness requires quantification of the term *degree of mixed-up-ness*, and this can be obtained from a consideration of elementary statistical thermodynamics. Statistical thermodynamics postulates that the equilibrium state of a system is simply the most probable of all of its possible (i.e., accessible) microstates. Therefore, statistical thermodynamics is concerned with

- The determination of the most probable microstate
- The criteria governing the most probable microstate
- The properties of this most probable microstate

Both Boltzmann (Ludwig Eduard Boltzmann, 1844–1906) and Gibbs found it convenient to examine the distribution of energies among the particles of the system by placing the energy of the particles into discrete *compartments*. This changed the distribution of energy of the particles from being a continuous function of state to a discrete function and therefore made it more convenient to perform various statistical operations (averages, RMS deviations, etc.) on the system of interest. This method turned out to be similar (but not identical) to the one used by quantum theory, which was developed several decades later. A postulate of quantum theory is that, if a particle is confined to move within a given fixed volume, then its energy is quantized; that is, the particle may only have certain discrete values of energy, which are separated by *forbidden energy bands*. For any given particle, the spacing between the quantized values of energy (the allowed energy levels) decreases as the volume available to the movement of the particle increases. This identifies another aspect of the entropy of a system—namely, the degree of spread in the distribution of the particles among its possible energy levels. This spread can be considered the degree of mixed-up-ness of the occupied energy levels of the particles in the system and is related to the system's thermal entropy.

4.4 THE MICROCANONICAL APPROACH

4.4.1 Identical Particles on *Distinguishable* Sites with Different Assigned Energies

The effect of the quantization of energy and its resulting distribution can be illustrated by considering a hypothetical system comprising a perfect crystal in which all of the distinguishable sites are occupied by *identical* particles. The characteristics of the particles and the crystal structure determine the quantization of the allowed energy levels, in which the lowest energy level, or the ground state, is designated ε_0, and the succeeding levels of increasing energy are designated ε_1, ε_2, ε_3, and so on. The crystal contains n particles and has the fixed energy U' and fixed volume V'. The system is therefore considered to be an *isolated* one: neither energy nor particles can enter or leave the system. Statistical thermodynamics asks the following questions:

- In how many ways can the n particles be distributed over the available energy levels such that the total energy of the crystal (i.e., U') remains the same?
- Of the possible distributions, which is the most probable?

Consider that the crystal contains three identical particles which are located on three distinguishable lattice sites A, B, and C. Suppose, for simplicity, that the quantization is such that the energy levels are equally spaced, with the ground level being taken as $\varepsilon_0 = 0$, the first level $\varepsilon_1 = u$, the second level $\varepsilon_2 = 2u$, and so on, and let the total energy of the system be $U' = 3u$. This system has three possible distributions, as shown in Figure 4.1.

a. All three particles on level 1
b. One particle on level 3, and the other two particles on level 0
c. One particle on level 2, one particle on level 1, and one particle on level 0

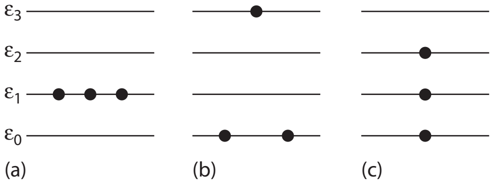

Figure 4.1 The distributions of particles among energy levels in a system of constant energy.

These distributions are now examined to determine how many distinguishable arrangements (complexions or microstates) they individually contain.

- *Distribution a*. There is only one microstate of this distribution, since the interchange of the particles among the three sites does not produce a different microstate.
- *Distribution b*. Any of the three distinguishable sites can be occupied by any of the three particles of energy $3u$, and the remaining two sites are each occupied by a particle of zero energy. Since the interchange of the particles of zero energy does not produce a different arrangement, there are three microstates in distribution *b*.
- *Distribution c*. Any of the three distinguishable sites can be occupied by the particle of energy $2u$. Either of the two remaining sites can be occupied by the particle of energy $1u$, and the single remaining site is occupied by the particle of zero energy. The number of distinguishable microstates in distribution *c* is thus $3 \times 2 \times 1 = 3! = 6$.

These arrangements are shown in Figure 4.2. The 10 arrangements are the 10 microstates of the system. Since each of the microstates have the same energy, they correspond to one macrostate of the system.

The concept of macrostate lies within the domain of classical thermodynamics. The macrostate is fixed when the values of the independent variables are fixed. In the

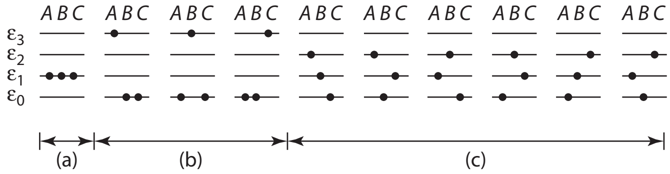

Figure 4.2 Illustration of the complexions or microstates within distributions of particles among energy levels in a system of constant energy.

preceding example, the system was considered to be isolated; that is, the values of U, V, and N are fixed (the constancy of volume is required in order that the quantization of the energy levels can be determined), and hence, the macrostate of the system is fixed. With respect to the occupancy of the microstates within any macrostate, in view of the absence of any reason to the contrary, it is assumed that *each of the microstates is equally probable*, and thus, the probability of observing the preceding system in any one of its 10 possible microstates is 1/10. However, the ten microstates occur in three distinct distributions, and hence, the probability that the system occurs

- In distribution a is 1/10
- In distribution b is 3/10
- In distribution c is 6/10

Distribution c is thus the *most probable*. The physical significance of these probabilities can be viewed in either of two ways:

1. If it were possible to make an instantaneous observation of the system, the probability of observing an arrangement in distribution c would be 6/10.
2. If the system were observed over a finite interval of time, during which the system rapidly changed from one microstate to another, the fraction of time which the system spends in all of the arrangements in distribution c would be 6/10.

As the total energy of the system and the number of particles which it contains increase, the number of distinguishable microstates also increases, and, for given values of U', V', and N, these microstates still correspond to a single macrostate. Similarly, the number of possible distributions increases, and in real systems—for example, 1 mole of a system which contains 6.023×10^{23} particles—the number of arrangements within the most probable distribution is very much larger than the number of arrangements in all of the other distributions ($\Omega \approx \Omega_{\max}$). Thus, the most probable microstate is considered to be *the* equilibrium state in the macrosystem, and the total number of possible arrangements, Ω, is set equal to the number of microstates with maximum probability, $\Omega_{\max}$. Since the equilibrium state in a closed system is the one of greatest entropy, the entropy, S', varies with Ω:

$$S' \sim \Omega \tag{4.1}$$

Hence, the entropy of an isolated system is calculated from the microstates which maximize the spread of the particles among the energy levels. From the preceding simplified example, the maximum entropy occurs when occupied energy levels of the particles are the most spread out (see Figure 4.2 (c)).

4.4.2 Configurational Entropy of Differing Atoms in a Crystal

In the preceding discussion, the entropy was considered in terms of the number of ways that the energy of identical but distinguishable particles could be distributed.

The entropy was seen to be greatest when the occupancy of the energy levels was broadly distributed. The degree of mixed-up-ness corresponded to the spread of the distribution. Entropy can also be considered in terms of the number of ways in which particles themselves can be distributed in space, and this consideration gives rise to the concept of *configurational entropy* mentioned briefly in Section 4.1.

Consider two crystals, one containing white atoms and the other containing gray atoms. Assume that there is no difference in the energy of white/white, white/gray, and gray/gray bonds. When the two crystals are placed in physical contact with one another, a *spontaneous process* occurs in which the white atoms diffuse into the crystal of the gray atoms and the gray atoms diffuse into the crystal of the white atoms.* Since this process is spontaneous, entropy must be produced. If the system is isolated, it is predicted that equilibrium will be reached when the entropy of the system reaches a maximum value, which would be when the diffusion processes have occurred to the extent that all concentration gradients in the system have been eliminated. This is the mass transport analog of the heat transfer case, in which heat flows irreversibly between two bodies until the temperature gradients have been eliminated (see Section 3.2).

Consider the two crystals to be composed of four white atoms and four gray atoms, as shown in Figure 4.3, which shows the initial arrangement of the atoms. Assume the crystals are held at the same temperature and volume. As stated previously, we assume that there are no energetically favored bonds.

If the partition is removed, the atoms are able to rearrange themselves by diffusion. We seek to determine the most probable state of the system; that is, where will the atoms reside with respect to the position of the barrier after equilibrium is attained (i.e., how many gray atoms will be on the left side and how many will be on the right side of the system)?

The use of combinatorics allows us to calculate the number of distinguishable ways in which this arrangement can be realized. Recall that the number of ways that N atoms can be arranged into two groups of n atoms each is given as

$$\Omega = \frac{N!}{n! \cdot (N-n)!} \tag{4.2}$$

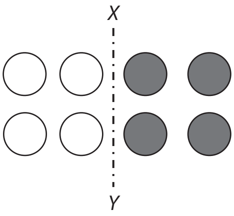

Figure 4.3 Representation of a crystal of white atoms in contact with a crystal of gray atoms.

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* We ignore the mechanism of diffusion in this discussion.

First, consider the number of possible distributions of white atoms on the left side:

1. Four white atoms on the left: $\Omega_{4,0} = (4\times3\times2/4!\cdot 0!) = 1$ (in which the notation indicates four white atoms on the left of *XY* and none on the right).
2. Three white atoms on the left: $\Omega_{3,1} = (4!/3!\cdot 1!) = 4$ (the "missing" white atom could be in any of the four sites).
3. Two white atoms on the left: $\Omega_{2,2} = (4!/2!\cdot 2!) = 6$.
4. One white atom on the left: $\Omega_{1,3} = (4!/1!\cdot 3!) = 4$ (the one white atom could be on any of the four sites).
5. No white atoms on the left: $\Omega_{0,4} = (4!/0!\cdot 4!) = 1$.

For each of these distribution of white atoms there is a corresponding set of distribution of gray atoms on the right side:

1. For case 1, all gray atoms are on the right side: $\Omega_{0,4} = (4!/0!\cdot 4!) = 1$ (in which the notation indicates four gray atoms on the right of *XY* and none on the left).
2. For case 2, three gray atoms are on the right side: $\Omega_{1,3} = (4!/1!\cdot 3!) = 4$ (the "missing" gray atom could be on any of the four sites).
3. For case 3, two gray atoms are on the right side: $\Omega_{2,2} = (4!/2!\cdot 2!) = 6$.
4. For case 4, one gray atom is on the right side: $\Omega_{3,1} = (4!/3!\cdot 1!) = 4$.
5. For case 5, no gray atoms are on the right side: $\Omega_{4,0} = (4!/4!\cdot 0!) = 1$.

Now consider the number of ways that each of the preceding configurations can be made. Starting with all white atoms on the left and all gray atoms on the right, clearly there is only one way for this to occur, which can be found as $\Omega_{4,0}\cdot\Omega_{0,4} = 1$.

Next, consider three white atoms on the left and one gray atom on the right: This is case 2, so there are four ways to obtain the configuration on the left. There are also four ways to arrive at that corresponding configuration (three gray atoms and one white atom) on the right. Thus, there are 16 ways of distributing one gray atom on the left and one white atom on the right. This can be found as $\Omega_{3,1}\cdot\Omega_{1,3} = 16$.

The case of two white atoms on the left and two gray atoms on the right is given as $\Omega_{2,2}\cdot\Omega_{2,2} = 36$. The rest can be found by symmetry:

- One white atom on the left and three gray atoms on the right is the same as three white atoms on the left and one gray atom on the right; $\Omega_{1,3}\cdot\Omega_{3,1} = \Omega_{3,1}\cdot\Omega_{1,3} = 16$.
- No white atoms on the left can only be done one way.

These results are summarized in the following table:

Atoms on Left of Partition	**Atoms on Right of Partition**	**No. of Ways (Complexions)**
4 white	4 gray	1
3 white/1 gray	3 gray/1 white	16
2 white/2 gray	2 gray/2 white	36
1 white/3 gray	1 gray/3 white	16
4 gray	4 white	1

Thus, the total number of spatial configurations available to the system is 1 + 16 + 36 + 16 + 1 = 70, which is the number of distinguishable ways in which four atoms of one color and four atoms of the other color can be arranged on eight sites; that is,

$$\text{Number of ways} = \frac{8!}{4!4!} = 70$$

If, as before, it is assumed that each of these configurations is equally probable, then the probability of finding the system in the arrangements 4:0 or 0:4 is 1/70, the probability of arrangements 3:1 or 1:3 is 16/70, and the probability of arrangement 2:2 is 36/70. Arrangement 2:2 is thus the most probable and thus corresponds to the equilibrium state, in which the concentration gradients have been eliminated. Again, it is seen that the maximization of Ω maximizes the entropy under consideration (configurational).

The most likely arrangement of atoms would be to have two gray atoms and two white atoms on both sides of the permeable partition. But other arrangements are possible, and since there is no energetic difference between the various microstates, all are equally probable. However, since there are 36 microstates with equal numbers of gray and white atoms on either side, that macrostate would be most probable. Once again, the most probable case is the one with the greatest configurational entropy for the given energy. Statistical thermodynamics thus does not determine with absolute certainty what the final arrangement will be, but only that which is the most probable configuration and the most likely to be observed. Again, it is emphasized that for large systems, there is negligible chance for the system to be found away from its maximum Ω.

In the preceding case, the increase in entropy occurs as a result of the increase in the number of spatial configurations which become available to the system when the crystals of A and B are placed in contact with one another. The increase in the entropy of the system arises from an increase in its configurational entropy, S_{conf}. It must be kept in mind that this is for the case where there is no energetically favored bonds between or among the particles of the system. If, for example, the white/gray bond energy was much greater than the white/white and gray/gray bond energy, the system may have to remain as shown in Figure 4.3 in order to keep the total energy of the system constant.

The mixing process can be expressed as

$$A + B(\text{unmixed}) \rightarrow A + B(\text{mixed}) \text{ at constant } U, V, \text{ and } n$$

that is,

$$\text{state } 1 \rightarrow \text{state } 2$$

$$\begin{aligned}\Delta S'_{\text{conf}} = S_{\text{conf}(2)} - S_{\text{conf}(1)} &= k_B \ln \Omega_{\text{conf}(2)} - k_B \ln \Omega_{\text{conf}(1)} \\ &= k_B \ln\left(\frac{\Omega_{\text{conf}(2)}}{\Omega_{\text{conf}(1)}}\right)\end{aligned}$$

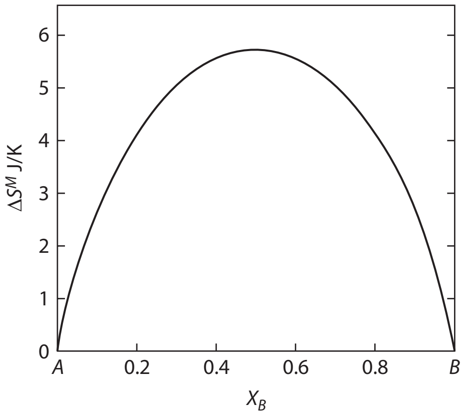

Figure 4.4 The molar configurational entropy of mixing for a binary solution with no preference for any type of bonds. The maximum value is R ln 2.

and, if n_a atoms of A are mixed with n_b atoms of B, then

$$\Omega_{\text{conf}(2)} = \frac{(n_a + n_b)!}{n_a!n_b!} \quad \text{and} \quad \Omega_{\text{conf}(1)} = 1$$

Thus,

$$\Delta S'_{\text{conf}} = k_B \ln \frac{(n_a + n_b)!}{n_a!n_b!} \tag{4.3}$$

If we consider X_A and X_B to be the mole fraction of A atoms and the mole fraction of B atoms, the expression can be reduced to

$$\Delta S_{\text{conf}} = R\left[X_A \ln X_A + X_B \ln X_B\right]$$

for 1 mole of atoms (see Qualitative Problem 1a in this chapter). This equation gives the configurational entropy of a binary system containing two distinguishable kinds of atoms. It is plotted in Figure 4.4. The maximum configurational entropy of mixing can be seen to occur when equal numbers of the two kinds of atoms are mixed together to form a (solid) solution.

4.4.3 Configurational Entropy of Magnetic Spins on an Array of Atoms

As a final example, consider a collection of magnetic spins in a paramagnet i.e., one in which the spins are randomly placed on the atoms. The spins may take values of ±½. The spins will be called *up* and *down* spins for convenience, even though they do not have a direction in space.

If there is no external magnetic field applied and if the interaction energy between the spins (also called the *exchange energy*) is nonexistent, each of the two quantum states (up or down) has the same energy. This is therefore another case of the microcanonical formalism, since the total energy of the system is the sum of the individual energies of the spins and remains constant. We wish to enumerate all possible microstates of the system.

Consider a system consisting of eight sites on which magnetic spins will be placed. One microstate is that all atoms have their spins pointing up. There is only one such microstate state possible. Consider a microstate with one down spin. The down spin could be on any of the eight sites. Hence, there are eight such possible microstates with one down spin. Next, consider a microstate with two down spins. The first one could be on any of the eight atoms and the second could be on any of the remaining seven atoms. This would be 56 microstates, except that we have counted the states twice, since the order in which we placed the spins on the atoms could be switched without producing a new microstate. Hence, there are 28 microstates with two down spins. This can be calculated from the following formula:

$$6 \text{ up and } 2 \text{ down} = \frac{8!}{6!\cdot 2!} = 28$$

The case for three down spins can be calculated from

$$5 \text{ up and } 3 \text{ down} = \frac{8!}{5!\cdot 3!} = 56$$

The case for four up and four down can be determined as

$$4 \text{ up and } 4 \text{ down} = \frac{8!}{4!\cdot 4!} = 70$$

The other cases can easily be seen by symmetry to be

- 3 up and 5 down = 56
- 2 up and 6 down = 28
- 1 up and 7 down = 8
- 0 up and 8 down = 1

Thus, there are a total of $2^8 = 256$ possible microstates[*] of the spins, which can be divided into nine distinct groups (Figure 4.5).

---

[*] In the case under considerations here, the spin on an atom may be either up or down. In the case of the four white atoms and four gray atoms, the atoms could not change "color." This accounts for the different number of microstates in the eight-atom spin system (256) versus the number in the eight–colored atom system of Section 4.4.2, which was found to have 70 microstates.

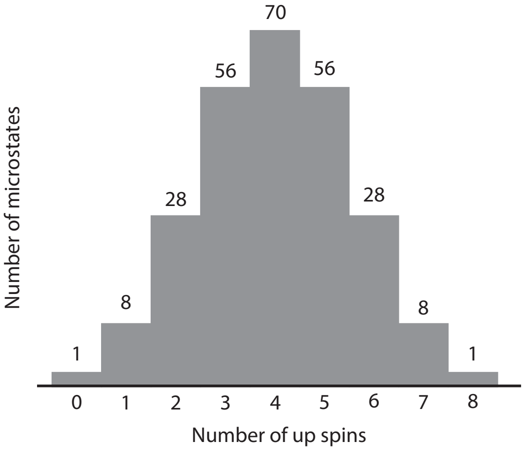

Figure 4.5 Plot of the number of microstates against the number of up spins in each microstate.

The magnetization of a material is defined as

$$M = \sum_i m_i \tag{4.4}$$

where:

M is the magnetization

$\sum_i m_i$ is the sum of the moments of the ± spins

It can be seen that *M* can be less than zero, equal to zero, or greater than zero, depending on the microstate. However, the most probable microstate has a total magnetization of zero, and this is considered to be the equilibrium state. It can also be seen that the average value of *M* over all microstates is also zero. A material in this state is called a *paramagnet*. If an external magnetic field is applied to the system, *M* would change to a nonzero value.

4.5 THE BOLTZMANN DISTRIBUTION

In this section, a general derivation of the *Boltzmann distribution* for a large number of particles among various energy levels is derived.

The number of arrangements within a given distribution, Ω, is calculated as follows: if n particles are distributed among the energy levels such that n_0 are on level ε_0, n_1 on level ε_1, n_2 on level ε_2,…, and n_r on ε_r, the highest level of occupancy, then the number of arrangements, Ω, is given by

$$\begin{aligned}\Omega &= \frac{n!}{n_0!n_1!n_2!\cdots n_i!} \\ &= \frac{n!}{\prod_{i=0}^{i=r} n_i!}\end{aligned} \tag{4.5}$$

For example, a consideration of the system discussed in Section 4.4.1 gives

$$\begin{aligned}\Omega(\text{distribution } a) &= \frac{3!}{3!0!0!} &= 1 \\ \Omega(\text{distribution } b) &= \frac{3!}{2!1!0!} &= 3 \\ \Omega(\text{distribution } c) &= \frac{3!}{1!1!1!} &= 6\end{aligned}$$

The most probable distribution is obtained by determining the set of numbers n_0, $n_1,\ldots, n_r$, which maximizes the value of Ω. When the values of n_i are large, Stirling's approximation can be used (i.e., $\ln X! = X \ln X - X$). Thus, taking the logarithms of the terms in Equation 4.5 gives

$$\ln\Omega = n\ln n - n - \sum_{i=0}^{i=r}(n_i \ln n_i - n_i) \tag{4.6}$$

Since the macrostate of the system is determined by the fixed values of U', V', and n, any distribution of the particles among the energy levels must conform to the conditions

$$\begin{aligned}U' &= \text{constant} = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots n_r\varepsilon_r \\ &= \sum_{i=0}^{i=r} n_i\varepsilon_i\end{aligned} \tag{4.7}$$

and

$$\begin{aligned}n &= \text{constant} = n_0 + n_1 + n_2 + \cdots n_r \\ &= \sum_{i=0}^{i=r} n_i\end{aligned} \tag{4.8}$$

From Equations 4.7 and 4.8, any interchange of particles among the energy levels must conform to the conditions

$$\delta U' = \sum_i \varepsilon_i \delta n_i = 0 \tag{4.9}$$

and

$$\delta n = \sum_i \delta n_i = 0 \tag{4.10}$$

Also, from Equation 4.6, any interchange of particles among the energy levels gives

$$\begin{aligned} \delta \ln \Omega \quad &= -\sum \left(\delta n_i \ln n_i + \frac{n_i \delta n_i}{n_i} - \delta n_i \right) \\ &= -\sum \left(\delta n_i \ln n_i \right) \end{aligned} \tag{4.11}$$

If Ω has the maximum possible value, then a small rearrangement of particles among the energy levels will not alter the value of Ω or the value of ln Ω. Thus, if the set of values of n_i is such that Ω has its maximum value, then

$$\delta \ln \Omega = -\Sigma \left(\delta n_i \ln n_i \right) = 0 \tag{4.12}$$

The condition that Ω has its maximum value for the given macrostate is thus that Equations 4.9, 4.10, and 4.12 are simultaneously satisfied. The set of values of n_i in the most probable distribution is obtained by the method of undetermined multipliers, in the following manner. Equation 4.9 is multiplied by the constant β, which has the units of reciprocal energy, to give

$$\Sigma \ \beta \varepsilon_i \delta n_i = 0 \tag{4.13}$$

Equation 4.10 is multiplied by the dimensionless constant *a* to give

$$\Sigma \ \alpha \delta n_i = 0 \tag{4.14}$$

and Equations 4.12, 4.13, and 4.14 are added to give

$$\sum_{i=0}^{i=r} \left(\ln n_i + \alpha + \beta \varepsilon_i \right) \delta n_i = 0 \tag{4.15}$$

that is,

$$\begin{gathered} (\ln n_0 + \alpha + \beta \varepsilon_0) \delta n_0 + \left(\ln n_1 + \alpha + \beta \varepsilon_1 \right) \delta n_1 \\ + \ (\ln n_2 + \alpha + \beta \varepsilon_2) \delta n2 + (\ln n_3 + \alpha + \beta \varepsilon_2) \delta n_3 \\ + (\ln n_r + \alpha + \beta \varepsilon_r) \delta n_r = 0 \end{gathered}$$

The solution of Equation 4.15 requires that each of the bracketed terms be individually equal to zero; that is,

$$\ln n_i + \alpha + \beta\varepsilon_i = 0$$

or

$$n_i = e^{-\alpha}e^{-\beta\varepsilon i} \tag{4.16}$$

Summing over all r energy levels gives

$$\sum_{i=0}^{i=r} n_i = n = e^{-\alpha}\sum_{i=0}^{i=r} e^{-\beta\varepsilon_i}$$

The summation

$$\sum e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \ldots + e^{-\beta\varepsilon_r}$$

which is determined by the magnitude of β and by the quantization of the energy, is called the *partition function*, $\mathcal{Z}$. Thus,

$$e^{-\alpha} = \frac{n}{\mathcal{Z}}$$

and thus,

$$n_i = \frac{ne^{-\beta\varepsilon_i}}{\mathcal{Z}} \tag{4.17}$$

The distribution of particles in the energy levels which maximizes Ω (i.e., the most probable distribution) is thus one in which the occupancy of the levels decreases exponentially with increasing energy, and the shape of this distribution is shown in Figure 4.6. The actual shape of the exponential curve in Figure 4.6 (for a given system) is determined by the value of β. β is inversely proportional to the absolute temperature, being given by

$$\beta = \frac{1}{k_B T} \tag{4.18}$$

in which k_B is Boltzmann's constant, an expression of the gas constant per atom or molecule; that is,

$$k_B = \frac{R}{N_O} = \frac{8.3144(6)}{6.0221 \times 10^{23}} = 1.38065 \times 10^{-23}\ \text{J/K}$$

where N_O is Avogadro's number. This brings us to a discussion of the role of temperature in a system.

4.6 THE INFLUENCE OF TEMPERATURE

The nature of the exponential distribution of particles in Figure 4.6 is determined by the temperature of the system. However, since the macrostate of the system is fixed by fixing the values of U', V', and n, then T, as a dependent variable, is also fixed. Equation 4.18 shows that T increases with decreasing β, and the shape of the exponential distribution changes as shown in Figure 4.7. An increase in temperature causes the upper energy levels to become relatively more populated, and this corresponds to an increase in the average energy of the particles; that is, to an increase in the value of U'/n, which, for fixed values of V and n, corresponds to an increase in U'.

As has been stated, when the number of particles in the system is very large, the number of arrangements within the most probable distribution, Ω_{max}, is the only term

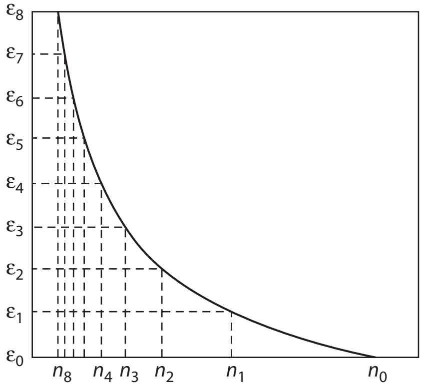

Figure 4.6 Schematic representation of the most probable distribution of particles among the quantized energy levels.

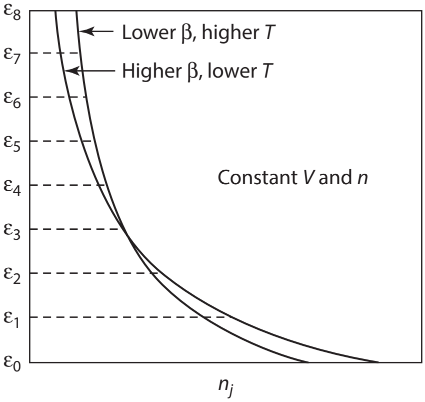

Figure 4.7 The influence of temperature on the most probable distribution of particles among energy levels in a closed system of constant volume.

which makes a significant contribution to the total number of arrangements, Ω_{total}, which the system may have; that is, Ω_{max} is significantly larger than the sum of all of the other arrangements. Thus, when the number of particles is large, Ω_{total} can be equated with Ω_{max}.

Substituting $\beta = 1/k_BT$, Equation 4.6 can be written as

$$\ln \Omega_{\text{total}} = \ln \Omega_{\text{max}} = n \ln n - \sum n_i \ln n_i$$

in which the values of n_i are given by Equation 4.17. Thus,

$$\begin{aligned}
\ln \Omega_{\text{total}} \quad &= n \ln n - \sum \frac{n}{\mathcal{Z}} e^{-\varepsilon_i/k_BT} \ln\left(\frac{n}{\mathcal{Z}} e^{-\varepsilon_i/k_BT}\right) \\
&= n \ln n - \frac{n}{\mathcal{Z}} \sum \left[e^{-\varepsilon_i/k_BT} \left(\ln n - \ln \mathcal{Z} - \frac{\varepsilon_i}{k_BT} \right)\right] \\
&= n \ln n - \frac{n}{\mathcal{Z}} (\ln n - \ln \mathcal{Z}) \sum e^{-\varepsilon_i/k_BT} + \frac{n}{\mathcal{Z}\, k_BT} \sum \varepsilon_i e^{-\varepsilon_i/k_BT}
\end{aligned}$$

But,

$$U' = \sum n_i \varepsilon_i = \sum \frac{n}{\mathcal{Z}} \varepsilon_i e^{-\varepsilon_i/k_BT} = \frac{n}{\mathcal{Z}} \sum \varepsilon_i e^{-\varepsilon_i/k_BT}$$

Therefore,

$$\sum \varepsilon_i e^{-\varepsilon_i/k_BT} = \frac{U'\mathcal{Z}}{n}$$

and thus,

$$\ln \Omega = n \ln \mathcal{Z} + \frac{U'}{k_BT}$$

or

$$k_BT \ln \Omega = nk_BT \ln \mathcal{Z} + U' \qquad (4.19)$$

In Chapter 5, a function called the *Helmholtz free energy* will be defined as

$$A' \equiv U' - TS'$$

It can be seen from Equation 4.19 that

$$A' = -nk_BT \ln \mathcal{Z} \qquad (4.20)$$

and that

$$S' = k_B \ln \Omega \qquad (4.21)$$

4.7 THERMAL EQUILIBRIUM AND THE BOLTZMANN EQUATION

Consider now a system of particles in thermal equilibrium with a constant-temperature *heat bath*. Let the state of the combined system (particles + heat bath) be fixed by fixing the values of U', V', and n, where:

$U' = U'_{\text{particles system}} + U'_{\text{heat bath}}$
$V' = V'_{\text{particles system}} + V'_{\text{heat bath}}$
n = the number of particles in the system + the heat bath of fixed size

Since the system of particles and the heat bath are in thermal equilibrium, small exchanges of energy can occur between them, and for such a small exchange at constant U', V', and n, Equation 4.19 for the system of particles gives

$$\delta \ln \Omega = \frac{\delta U'}{k_B T}$$

($\mathcal{Z}$ is dependent only on the values of ε_i and T). Since this exchange of energy is carried out at constant total volume, then

$$\delta U' = \delta q$$

that is, the energy exchange occurs as an exchange of heat. Thus,

$$\delta \ln \Omega = \frac{\delta q}{k_B T} \tag{4.22}$$

Since the exchange of heat occurs at constant temperature (i.e., occurs reversibly), then, from Chapter 3,

$$\frac{\delta q}{T} = \delta S'$$

and thus,

$$\delta S' = k_B \delta \ln \Omega$$

Since both S' and Ω are state functions, the preceding expression can be written as a differential equation, the integration of which gives

$$S' = k_B \ln \Omega \tag{4.23}$$

Equation 4.23, which is called the *Boltzmann equation*, is the required quantitative relationship between the entropy of a system and its degree of mixed-up-ness, in which the latter, given by Ω, is the number of ways in which the energy of the system can be distributed among the particles. The most probable state of the system is that in which Ω has a maximum value, consistent with the fixed values of U', V', and n, and hence, the equilibrium state of the system is that in which S is a maximum, consistent with the fixed values of U, V, and n. The Boltzmann equation thus provides a helpful qualitative understanding of entropy.

4.8 HEAT FLOW AND THE PRODUCTION OF ENTROPY

Classical thermodynamics shows that the transfer of thermal energy from a body at some temperature to a body at a lower temperature is an irreversible process which is accompanied by the production of entropy, and that the reverse process—that is, the flow of thermal energy up a temperature gradient—is an impossible spontaneous process. An examination of microstates shows that a microstate in which variations in temperature occur within a system is less probable than a microstate in which the temperature of the system is uniformly constant.

Consider two closed systems, A and B. Let the energy of A be U'_A and the number of complexions of A be Ω_A. Similarly, let the energy of B be U'_B and its number of complexions be Ω_B. When thermal contact is made between A and B, the product $\Omega_A\Omega_B$ will, generally, not have its maximum possible value, and thermal energy will be transferred either from A to B or from B to A. Thermal energy flows from A to B if, thereby, the increase in Ω_B, caused by the increase in U'_B, is greater than the decrease in Ω_A, caused by the decrease in U'_A. Thermal energy continues to flow from A to B as long as the product $\Omega_A\Omega_B$ continues to increase, and the flow of thermal energy ceases when $\Omega_A\Omega_B$ reaches its maximum value—that is, when the increase in Ω_B caused by the transfer of an increment of thermal energy from A is exactly compensated by the decrease in Ω_A. The condition for A to be in thermal equilibrium with B is thus that the transfer of a quantity of thermal energy from one body to the other does not cause a change in the value of $\Omega_A\Omega_B$. That is,

$$\delta \ln \Omega_A\Omega_B = 0$$

Consider a rearrangement of the particles in the quantized energy levels in B which causes U'_B to increase by a certain amount, and consider a simultaneous rearrangement of the particles in the energy levels of A which causes U'_A to decrease by the same amount; that is, $(U'_A + U'_B)$ remains constant. If the levels of A are populated in accordance with Equation 4.22 with $T = T_A$ and if the levels of B are populated in accordance with Equation 4.22 with $T = T_B$, then

$$\delta \ln \Omega_A = \frac{\delta q_A}{k_B T_A}$$

and

$$\delta \ln \Omega_B = \frac{\delta q_B}{k_B T_B}$$

When a quantity of thermal energy is transferred from A to B at total constant energy, then

$$\delta q_A = -\delta q_B$$

Thus,

$$\delta \ln \Omega_A \Omega_B = \delta \ln \Omega_A + \delta \ln \Omega_B = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \frac{\delta q}{k_B}$$

and hence, the condition that $\delta \ln \Omega_A \Omega_B$ be zero is that $T_A = T_B$. The reversible transfer of thermal energy from one body to another thus only occurs when the temperatures of the bodies are equal, since only in such a case does $\Omega_A \Omega_B$—and hence, the total entropy of the combined system ($S'_A + S'_B$)—remain constant. An irreversible transfer of thermal energy increases the value of the product $\Omega_A \Omega_B$, and hence, entropy is created. From the point of view of microstates, an irreversible process is one which takes the system from a less probable state to the most probable state. From the point of view of macrostates, an irreversible process takes the system from a nonequilibrium state to the equilibrium state. Thus, what is deemed in classical thermodynamics to be an impossible process is shown by the consideration of microstates to be a highly improbable process. As the size of the system increases, the probability of the "up-hill" flow of thermal energy approaches zero. For very small systems (clusters of atoms), these improbable processes must be considered.

The total entropy of a simple system consists of its thermal entropy, S'_{th}, which arises from the number of ways in which the energy of the system can be shared among the particles, and its configurational entropy, S'_{conf}, which arises from the number of distinguishable ways in which the particles can fill the space available to them. Thus,

$$\begin{aligned} S'_{\text{total}} &= S'_{\text{th}} + S'_{\text{conf}} \\ &= k_B \ln \Omega_{\text{th}} + k \ln \Omega_{\text{conf}} \\ &= k_B \ln \Omega_{\text{th}} \Omega_{\text{conf}} \end{aligned}$$

If two systems are placed together in thermal contact, the change in entropy is given as

$$\Delta S'_{\text{total}} = k_B \ln \frac{\Omega_{\text{th}(2)} \Omega_{\text{conf}(2)}}{\Omega_{\text{th}(1)} \Omega_{\text{conf}(1)}}$$

If, however, the two systems were closed systems, there can be no change in the configurational entropy: $\Omega_{\text{conf}(1)} = \Omega_{\text{conf}(2)}$. This is also true if the two systems were open systems which were chemically identical. Thus, in the case of thermal energy flow down a temperature gradient between two such systems, since only Ω_{th} changes, the increase in the entropy arising from the thermal energy transfer which takes the system from state 1 to state 2 is

$$\Delta S'_{\text{total}} = k_B \ln \frac{\Omega_{\text{th}(2)}\Omega_{\text{conf}(2)}}{\Omega_{\text{th}(1)}\Omega_{\text{conf}(1)}} = k \ln \frac{\Omega_{\text{th}(2)}}{\Omega_{\text{th}(1)}} = \Delta S'_{\text{th}}$$

Similarly, in the mixing of particles of A with particles of B, ΔS_{total} only equals $\Delta S'_{\text{conf}}$ if the mixing process does not cause a redistribution of the particles among the energy levels—that is, if $\Omega_{\text{th}(1)} = \Omega_{\text{th}(2)}$. This condition corresponds to the *ideal mixing* of the particles and requires that the quantization of energy be the same in crystals A and B. Ideal mixing is the exception rather than the rule, and, generally, when two or more components are mixed at constant U', V', and n, $\Omega_{\text{th}(2)}$ does not have the same value as $\Omega_{\text{th}(1)}$; thus, the completely random mixing of particles does not occur. In such cases, either the clustering of like particles (indicating difficulty in mixing) or ordering (indicating a tendency toward compound formation) occurs. In all cases, however, the equilibrium state of the system is that which, at constant U', V', and n, maximizes the product $\Omega_{\text{th}}\Omega_{\text{conf}}$. If, in addition to particles, the system is composed of magnetic spins, electric dipoles, and so on, their entropy must be included in the consideration of the total entropy of the system.

4.9 SUMMARY

1. A single macrostate of a system, which is determined when the independent variables of the system are fixed, contains a very large number of microstates, each of which is characterized by the manner in which
    - The thermal energy of the system is distributed among the particles
    - The particles are distributed in the configurations available to them
2. Although the occurrence of a system in any one of its microstates is equally probable (for the case of the closed system), greatly differing numbers of microstates occur in differing distributions. The distribution which contains the largest number of microstates is the most probable distribution.
3. In real systems (with a very large number of particles) the number of microstates in the most probable distribution is significantly larger than the sum of all of the other microstates occurring in all of the other distributions. This most probable distribution is the equilibrium thermodynamic state of the system.
4. The relationship between the number of microstates available to the system, Ω, and the entropy of the system is given by the Boltzmann equation:

$$S' = k_B \ln \Omega$$

in which k_B is Boltzmann's constant.

5. If a situation arises which allows an increase in the number of microstates available to the system (at constant energy), then spontaneous redistribution of the energy

among the particles (or particles over the available configurations) occurs until the newly available most probable distribution occurs. The Boltzmann equation shows that an increase in the number of microstates made available to the system causes an increase in the entropy of the system.

6. The total entropy of a system is the sum of each of the aspects of entropy:
   - Thermal entropy, S'_{th}
   - Configurational entropy, S'_{conf}
   - Any other aspect of entropy, such as spin entropy, electric dipole entropy, and so on
7. The thermal entropy arises from the number of ways in which the thermal energy available to the system can be shared among the constituent particles, Ω_{th}.
8. The configurational entropy arises from the number of ways in which the particles can be distributed over the configurations available to them, Ω_{conf}.
9. The spin entropy arises from the number of ways in which the spins can be distributed over the sites available to them, Ω_{spin}.
10. Since any of the thermal distributions can be combined with any of the configurational distributions, the total number of microstates available to the system is the product $\Omega_{\mathrm{th}}\Omega_{\mathrm{conf}}$ ($\Omega_{\mathrm{th}}\Omega_{\mathrm{conf}}\Omega_{\mathrm{spin}}$ if spins are present), and hence, from the logarithmic form of the Boltzmann equation, the total entropy of the system is the sum of the individual entropies of the system.

4.10 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 4

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Aspects of entropy
Boltzmann distribution
Boltzmann equation for entropy
Bond energy
Classical thermodynamics
Configurational entropy
Entropy as “mixed-up-ness”
Exchange field
External field
Macrostate
Microcanonical ensemble
Microstate
Most probable state
Paramagnet
Partition function
Phenomenological
Spin entropy
Spin system
Statistical thermodynamics
Thermal entropy

4.11 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

One mole of a FeX alloy of 50 at% X has its Fe and X atoms randomly arranged on a body centered cubic lattice (BBC). The spins on the Fe atoms are also randomly arranged. The X atoms do not have spins.

a. Calculate the configurational entropy of the alloy.
b. Calculate the spin entropy of the alloy.
c. Is the sum of the entropies for (a) and (b) the total entropy of the alloy? Explain.

Solution to Qualitative Problem 1

a. From Equation 4.3 we get

$$\Delta S_{\text{conf}} = k_B \ln \frac{(n_{\text{Fe}} + n_{\text{X}})!}{n_{\text{Fe}}! \ \cdot n_{\text{X}}!} =$$

$$\Delta S_{\text{conf}} = k_B \left[(n_{\text{Fe}} + n_{\text{X}}) \ln(n_{\text{Fe}} + n_{\text{X}}) - (n_{\text{Fe}} + n_{\text{X}}) - (n_{\text{Fe}} \ln n_{\text{Fe}} - n_{\text{Fe}} + n_{\text{X}} \ln n_{\text{X}} - n_{\text{X}}) \right]$$

$$\Delta S_{\text{conf}} = k_B (n_{\text{Fe}} + n_{\text{X}}) \left[\ln(n_{\text{Fe}} + n_{\text{X}}) - \frac{(n_{\text{Fe}} \ln n_{\text{Fe}} + n_{\text{X}} \ln n_{\text{X}})}{(n_{\text{Fe}} + n_{\text{X}})} \right]$$

$$\Delta S_{\text{conf}} = k_B (n_{\text{Fe}} + n_{\text{X}}) \left[\ln(n_{\text{Fe}} + n_{\text{X}}) - \text{X}_{\text{Fe}} \ln n_{\text{Fe}} + \text{X}_{\text{X}} \ln n_{\text{X}}) \right]$$

$$\Delta S_{\text{conf}} = -k_B (n_{\text{Fe}} + n_{\text{X}}) \frac{\left[\text{X}_{\text{Fe}} \ln n_{\text{Fe}} + \text{X}_{\text{X}} \ln n_{\text{X}}) \right]}{\ln(n_{\text{Fe}} + n_{\text{X}})} = -k_B (n_{\text{Fe}} + n_{\text{X}}) \left[\text{X}_{\text{Fe}} \ln \text{X}_{\text{Fe}} + \text{X}_{\text{X}} \ln \text{X}_{\text{X}}) \right]$$

If $n_{\text{Fe}} + n_X = 1$ mole:

$$\Delta S_{\text{conf}} - R(\text{X}_{\text{Fe}} \ln \text{X}_{\text{Fe}} + \text{X}_{\text{X}} \ln \text{X}_{\text{X}})$$

For a 50 atomic percent X alloy, we get:

$$\Delta S_{\text{conf}} = R \ln 2$$

b. The spin entropy is found by

$$\Delta S_{\text{spin}} = k_B \ln \left(\frac{1}{2} \right)^{n_{\text{Fe}}} = n_{\text{Fe}} k_B \ln 2$$

Since n_{Fe} is 0.5 moles,

$$\Delta S_{\text{spin}} = \frac{R}{2} \ln 2$$

c. No, there is also thermal entropy, which must be included.

Qualitative Problem 2

We saw in Section 4.6 that

$$A' = -nk_BT \ln \mathcal{Z}$$

In the next chapter, we will show that $\partial A'/\partial T = -S'$

Take the derivative of A' with respect to T and obtain expressions for S' and U' in terms of the partition function $\mathcal{Z}$.

Solution to Qualitative Problem 2

$$\frac{\partial A'}{\partial T} = -S' = -nk_B \ln \mathcal{Z} - nk_B \frac{\partial \ln \mathcal{Z}}{\partial T}$$

$$\therefore S' = nk_B \ln \mathcal{Z} + nk_B \frac{\partial \ln \mathcal{Z}}{\partial T}$$

$$A' = U' - TS'$$

$$-nk_BT \ln \mathcal{Z} = U' - T\left(nk_B \ln \mathcal{Z} + nk_B \frac{\partial \ln \mathcal{Z}}{\partial T} \right)$$

$$\therefore nk_BT^2 \frac{\partial \ln \mathcal{Z}}{\partial T} = U'$$

4.12 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Spectroscopic observation of molecular N_2 in an electrical discharge shows that the relative numbers of molecules in excited vibrational states with energies given by

$$\varepsilon_i = \left(i + \frac{1}{2} \right) h\nu \tag{4.24}$$

are

i	0	1	2	3
$\frac{n_i}{n}$	1.00	0.250	0.062	0.016

Show that the gas is in thermodynamic equilibrium with respect to the distribution of vibrational energy, and calculate the temperature of the gas. In Equation 4.24, i is an integer which has values in the range zero to infinity, h is Planck's constant of action (= 6.6252×10^{-34} J·s), and the vibration frequency, ν, is 7.00×10^{13} s^{-1}.

Solution to Quantitative Problem 1

From Equations 4.17, 4.18, and 4.24,

$$\frac{n_i}{n} = \frac{\exp\left[-\left(i+\frac{1}{2}\right)\frac{h\nu}{k_BT}\right]}{\mathcal{Z}}$$

Observation shows that

$$\frac{n_i}{n_0} = 0.250$$

Thus,

$$\frac{n_i}{n_0} = \frac{\exp\left(-\frac{3}{2}\frac{h\nu}{k_BT}\right)}{\exp\left(-\frac{1}{2}\frac{h\nu}{k_BT}\right)} = \exp\left(-\frac{h\nu}{k_BT}\right) = 0.250$$

which gives

$$\frac{h\nu}{k_BT} = 1.386$$

Then, from Equation 4.17,

$$\begin{aligned}
\mathcal{Z}\frac{n_0}{n} &= \exp\left(-\frac{1}{2}\frac{h\nu}{k_BT}\right) = 0.5 \\
\mathcal{Z}\frac{n_1}{n} &= \exp\left(-\frac{3}{2}\frac{h\nu}{k_BT}\right) = 0.125 \\
\mathcal{Z}\frac{n_2}{n} &= \exp\left(-\frac{5}{2}\frac{h\nu}{k_BT}\right) = 0.031
\end{aligned}$$

and

$$\mathcal{Z}\frac{n_3}{n} = \exp\left(-\frac{7}{2}\frac{h\nu}{k_BT}\right) = 0.008$$

Normalizing gives

$$\begin{aligned}
\frac{n_0}{n} &= 0.5/0.5 = 1.0 \\
\frac{n_1}{n} &= 0.125/0.5 = 0.25 \\
\frac{n_2}{n} &= 0.031/0.5 = 0.062 \\
\frac{n_3}{n} &= 0.008/0.5 = 0.016
\end{aligned}$$

which shows that the gas is in equilibrium with respect to the distribution of vibrational energy. The temperature of the gas is obtained as

$$T = \frac{h\nu}{1.386k_B} = \frac{(6.6262\times10^{-34})(7.00\times10^{13})}{1.386\times1.38065\times10^{-23}} = 2424\ \text{K}$$

Quantitative Problem 2

The isotopic composition of lead in atomic percent is as follows:

Atomic Weight	Atomic Percent
204	1.5
206	23.6
207	22.6
208	52.3

Calculate the molar configurational entropy of lead.

Solution to Quantitative Problem 2

The configurational entropy is obtained from the Boltzmann equation:

$$S = k_B \ln \Omega \tag{4.21}$$

where

$$\Omega = \frac{(N_O)!}{(0.015N_O)!(0.236N_O)!(0.226N_O)!(0.523N_O)!}$$

Stirling's theorem gives

$$\begin{aligned}\ln\Omega &= N_O \ln N_O - 0.015N_O \ln 0.015N_O - 0.236N_O \ln 0.236N_O \\ &\quad - 0.226N_O \ln 0.226N_O - 0.523N_O \ln 0.523N_O \\ &= 3.298\times10^{25} - 4.567\times10^{23} - 7.578\times10^{24} - 7.251\times10^{24} \\ &\quad - 1.704\times10^{25} \\ &= 6.498\times10^{23}\end{aligned}$$

Therefore, the molar configurational entropy is

$$S = k_B \ln\Omega = (1.38054\times10^{-23})\times(6.498\times10^{23}) = 8.97\ \text{J/K}$$

PROBLEMS

4.1 A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other contains 1 mole of ideal gas B at 1 atm. Calculate the increase in entropy which occurs when the partition between the two compartments is removed. If the first compartment had contained 2 moles of ideal gas A, what would have been the increase in entropy when the partition was removed? Calculate the corresponding increases in entropy in each of the preceding two situations if both compartments had contained ideal gas A.

4.2 Show that, when n atoms of A and n atoms of B form a randomly mixed solution, the fraction of the total number of distinguishable complexions which occur in the most probable distribution decreases with the increasing value of n.

4.3 Assuming that a silver–gold alloy is a random mixture of gold and silver atoms, calculate the increase in entropy when 10 g of gold are mixed with 20 g of silver to form a homogeneous alloy. The gram atomic weights of Au and Ag are, respectively, 198 and 107.9.

4.4 On the assumption that copper–nickel alloys are random mixtures of copper and nickel atoms, calculate the mass of copper which, when mixed with 100 g of nickel, causes an increase in entropy of 15 J/K. The gram atomic weights of Cu and Ni are, respectively, 63.55 and 58.69.

4.5* We saw in Section 4.6 (Equation 4.20) that $A' = -nk_BT \ln \mathcal{Z}$. We will see in the next chapter that $\partial A'/\partial T = -S'$. Perform the differentiation of A' with respect to temperature and obtain the relationship for the entropy of an isolated system in terms of its partition function $\mathcal{Z}$.

4.6* A weak magnetic field is applied to a system of up and down spins. The up spins have a slightly lower energy state than down spins. This is because the up spins are favored by the weak magnetic field. Thus,

$$\varepsilon^{\uparrow} < \varepsilon^{\downarrow}$$

a. Determine the partition function for this system under the influence of the weak magnetic field.
b. Determine the ratio of $n^{\uparrow}/n^{\downarrow}$ for very high temperatures and very low temperatures.

* New problem in this edition

CHAPTER 5

Fundamental Equations and Their Relationships

5.1 INTRODUCTION

The main power of the thermodynamic method stems from its provision of criteria for equilibrium in materials systems and for the determination of the effects that changes in the external influences acting on the system have on the equilibrium state. The practical usefulness of this power is, however, determined by the practicality of the equations of state for the system—that is, the relationships which can be established among the thermodynamic variables of the system.

Combining the First and Second Laws of Thermodynamics for one mole of a simple system leads to Equation 3.12:

$$dU = TdS - PdV$$

This fundamental equation gives the relationship between the dependent variable U (*molar internal energy*) and the independent molar variables S and V for a closed system, consisting of 1 mole of the material, which is undergoing a process involving a change of volume against the external pressure as the only form of work performed on, or by, the system. Combining the First and Second Laws also provides the following criteria for equilibrium:

- In a simple system of constant internal energy and constant volume, the molar entropy has its maximum value.
- In a simple system of constant entropy and constant volume, the molar internal energy has its minimum value.

The further development of thermodynamics beyond Equation 3.12 arises, in part, from the fact that, from a practical point of view, the choice of S and V as the independent variables is inconvenient. Although the volume of a system can be measured with relative ease and, in principle, can be controlled, entropy can be neither simply measured nor simply controlled. It is thus desirable to develop a simple expression, similar in form to Equation 3.12, which contains a more convenient choice of independent variables and which can accommodate changes in the composition of the system. From a practical point of view, a convenient pair of independent variables would be temperature and pressure, since these variables are easily measured and controlled. The derivation of an equation of state of the simple form of Equation 3.12, but using P and T as the independent variables, and of a criterion for equilibrium in a constant-pressure, constant-temperature system, are thus desirable. Alternatively, from the theoretician's point of view, a convenient choice of independent variables would be V and T, since constant-volume constant-temperature systems are easily examined by the methods of statistical mechanics. This arises because fixing the volume of a closed system fixes the quantization of its energy levels, and thus, the Boltzmann factor, $\exp(-\varepsilon_{i,j}/kT)$, and the partition function, both of which appear in Equation 4.17, have constant values in constant-volume constant-temperature systems. Thus, the derivation of an equation of state using V and T as the independent variables and the establishment of a criterion for equilibrium in a system of fixed volume and fixed temperature are also desirable. In Sections 5.3 and 5.4, fundamental equations using these independent variables will be developed.

Equation 3.12 cannot be applied to systems which undergo changes in composition caused by chemical reactions or to systems which perform work other than the work of expansion against an external pressure (so-called P-V work). Since systems which experience changes in composition are of prime importance to the materials scientist and engineer, composition variables must be included in any equation of state and in any criterion for equilibrium. Also, any equation of state must be capable of accommodating forms of work other than P-V work, such as the electrical work performed by a galvanic cell or magnetic work performed on the system by an applied external magnetic field.

Thus, although Equation 3.12 lays the foundation of thermodynamics, it is necessary to develop other thermodynamic potentials (which are sometimes called *auxiliary functions*) which, as dependent variables, are related in simple form to more convenient choices of independent variables. Also, with this increase in the number of thermodynamic functions, it is necessary to establish the relationships which exist among them. It is often found that some required thermodynamic expression which itself is not amenable to experimental measurement is related in a simple manner to some measurable quantity. Examples of this have been presented in Chapter 3, where it was found that

$$\left(\frac{\partial U'}{\partial S'}\right)_V = T, \quad -\left(\frac{\partial U'}{\partial V'}\right)_S = P, \quad \text{and} \quad \left(\frac{\partial S'}{\partial V'}\right)_U = \frac{P}{T}$$

In this chapter, the thermodynamic potentials (state functions) H (the enthalpy), A (the Helmholtz free energy), G (the Gibbs free energy), and μ_i (the chemical potential of the species i) are defined and their properties and interrelationships examined.

5.2 THE ENTHALPY, *H*

We have already been introduced to the state function enthalpy in Section 2.5. It is defined as

$$H' \equiv U' + PV'$$

Its full differential is seen to be

$$dH' = dU' + PdV' + V'dP$$

$$dH' = TdS' + V'dP \tag{5.1}$$

We see that the natural thermodynamic independent variables for enthalpy are S' and P; that is, $H' = H'(S',P)$. For a system undergoing a change of state at constant pressure and doing only P-V work, Equation 5.1 simplifies to

$$dH' = \delta q_P = TdS'$$

This equation shows that the change of state of a simple closed system at constant pressure, during which only P-V work is done, is the change in the enthalpy of the system and equals the thermal energy entering or leaving the system, q_P. For this reason, it was called the *heat function at constant pressure* by Gibbs (Josiah Willard Gibbs, 1839–1903), who introduced it in 1875.* More of the properties and applications of the enthalpy state variable will be examined in Chapter 6.

5.3 THE HELMHOLTZ FREE ENERGY, *A*

Changes in the internal energy, U, can be measured by processes involving heat and work. Changes in the enthalpy at constant pressure P quantify the changes in the thermal energy of the system. It may be asked, is there a thermodynamic potential that measures the maximum work that a change on the internal energy of a system can perform? There is, and it is called the *Helmholtz free energy* or work term A.

Consider a simple system that undergoes a spontaneous change of state at constant temperature T. Since the process is spontaneous, we can write

$$\Delta S'_{\text{tot}} = \Delta S'_{\text{system}} + \Delta S'_{\text{surroundings}} > 0$$

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* J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances", *Trans. Conn. Acad.* (1875), vol. 3, pp. 108–248.

If the process is done at constant volume, the change in the internal energy of the system is δq_V. This δq_V changes the entropy of the surroundings by the amount $\delta q_V / T$. Thus, we can write

$$\Delta S'_{\text{tot}} = \Delta S'_{\text{system}} - \frac{\Delta U'_{\text{system}}}{T}$$

or

$$-T\Delta S'_{\text{tot}} = \Delta U'_{\text{system}} - T\Delta S'_{\text{system}} \tag{5.2}$$

Since the process is spontaneous, $\Delta U'_{\text{system}} - T\Delta S'_{\text{system}} < 0$. This gives us a criterion for a spontaneous change in terms that only apply to the system. If $\Delta U'_{\text{system}} - T\Delta S'_{\text{system}} > 0$, no spontaneous change will occur, according to the Second Law of Thermodynamics.

Defining the Helmholtz free energy as

$$A' \equiv U' - TS'$$

we obtain, for a system undergoing a change of state from state 1 to state 2,

$$\left(A'_2 - A'_1\right) = \left(U'_2 - U'_1\right) - \left(T_2 S'_2 - T_1 S'_1\right)$$

and, if the system is closed,

$$\left(U'_2 - U'_1\right) = q - w$$

in which case

$$\left(A'_2 - A'_1\right) = q - w - \left(T_2 S'_2 - T_1 S'_1\right)$$

If the process is also isothermal—that is, $T_2 = T_1 = T$, which is the temperature of the heat reservoir which supplies or withdraws thermal energy during the process—then, from the Second Law, Equation 3.4a,

$$q \le T\left(S'_2 - S'_1\right)$$

and hence,

$$\left(A'_2 - A'_1\right) \le -w$$

A comparison with

$$\delta w \le T dS'_{\text{system}} - dU'_{\text{system}} \tag{3.11}$$

shows that the equality can be written as

$$\left(A'_2 - A'_1\right) + T\Delta S'_{\text{irr}} = -w \tag{5.3}$$

and thus, during a reversible isothermal process, for which $\Delta S'_{\text{irr}}$ is zero, the amount of work done by the system is a maximum and is equal to the decrease in the value of the Helmholtz free energy. For this reason, the Helmholtz free energy is sometimes called the *work function*. Furthermore, for an isothermal process conducted at constant volume, which, necessarily, does not perform P-V work, Equation 5.3 gives

$$(A'_2 - A'_1) + T\Delta S'_{\text{irr}} = 0 \tag{5.4}$$

or, for an increment of such a process,

$$dA' + TdS'_{\text{irr}} = 0$$

Since dS'_{irr} is always positive during a spontaneous process, it is seen that A' decreases during a spontaneous process, as shown.

Also, since $dS'_{\text{irr}} = 0$ is a criterion for a reversible process, equilibrium requires that

$$dA' = 0 \tag{5.5}$$

Thus, in a closed system held at constant T and V', the Helmholtz free energy can only decrease (for spontaneous processes) or remain constant. Equilibrium is attained in such a system when A' achieves its minimum value. The Helmholtz free energy thus provides a criterion for equilibrium in a system at constant temperature and constant volume—namely,

$$dA'_{T,V} = 0 \text{ and } d^2A'_{T,V} > 0$$

The natural independent thermodynamic variables for the Helmholtz free energy are seen to be T and V; that is, $A' = A'(T,V')$.

Consider a crystalline solid in equilibrium with its vapor, the system being at constant volume and its pressure below that of its triple point. As the temperature approaches 0 K, the internal energy of the two-phase system approaches its minimum value and the entropy of the two-phase system approaches zero, since the vapor phase vanishes and the entropy of the crystalline phase approaches zero (Figure 5.1a and Figure 5.2b). On the other hand, as the temperature of the system becomes very high, the solid phase disappears and all the atoms enter the vapor phase, which maximizes the entropy of the system (Figure 5.1c). At intermediate temperatures, there is an equilibrium between the vapor and solid phases. The number of atoms in the vapor phase in equilibrium with the solid can be determined from a plot of the Helmholtz energy versus n_v, since the Helmholtz energy is a minimum at equilibrium (Figure 5.3). This plot shows that the equilibrium is a trade-off between the system minimizing its internal energy, U', and maximizing its entropy. As the temperature

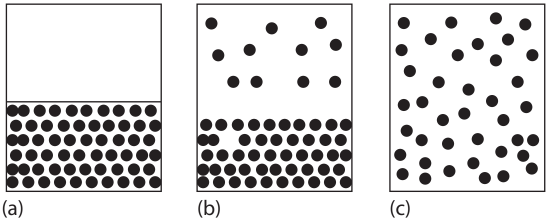

Figure 5.1 Schematic of a crystalline solid and its vapor at three different temperatures, where the pressure is below its triple point. (a) $T = 0$ K, (b) $0 < T$, (c) T very large. The volume of the system is fixed.

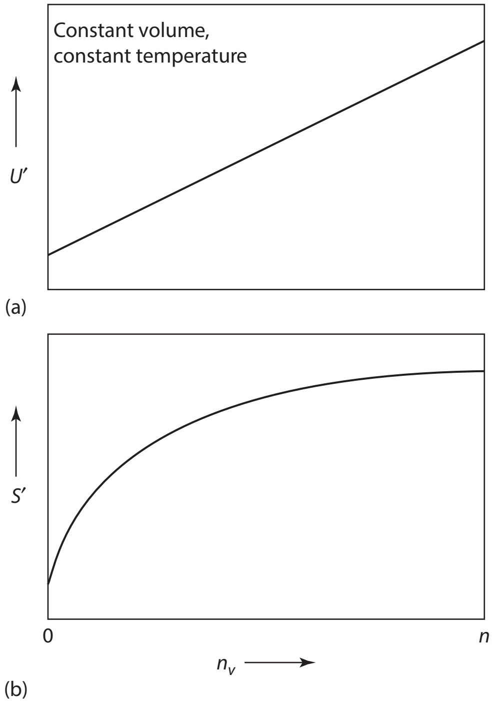

Figure 5.2 The variations of (a) internal energy, U', and (b) entropy, S', with the number of atoms in the vapor phase of a closed solid-vapor system at constant temperature and constant volume.

rises from T_1 to T_2 (Figure 5.4), the minimum in the Helmholtz energy moves to a larger number of atoms in the vapor—namely, $n_v(T_2) > n_v(T_1)$. Eventually, at the limit of very high temperature, all the atoms are in the vapor phase. It should also be noted that the schematic plot of the Helmholtz free energy shows that its slope at $n_v = 0$ is large and negative, meaning for all temperatures greater than 0 K, there will be a finite number of atoms in the vapor phase in equilibrium with the solid.

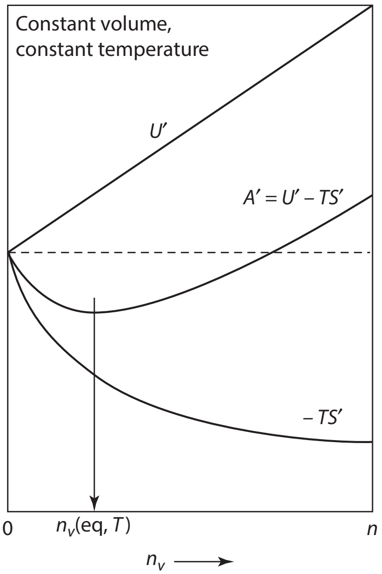

Figure 5.3 Illustration of the criterion for equilibrium in a closed solid-vapor system at constant temperature and constant volume.

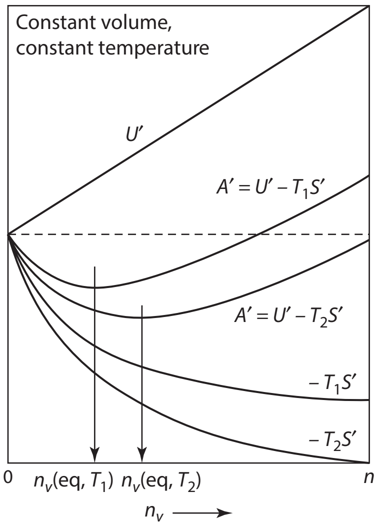

Figure 5.4 The influence of temperature on the equilibrium state of a closed solid-vapor system of constant volume.

5.4 THE GIBBS FREE ENERGY, *G*

The Gibbs free energy is defined as

$$G' \equiv H' - TS'$$

For a system of one mole, undergoing a change of state from 1 to 2, this yields

$$\begin{aligned}(G_2 - G_1) &= (H_2 - H_1) - (T_2S_2 - T_1S_1)\\ &= (U_2 - U_1) + (P_2V_2 - P_1V_1) - (T_2S_2 - T_1S_1)\end{aligned}$$

For a closed simple system, the First Law gives

$$(U_2 - U_1) = q - w$$

and thus,

$$\left(G_2 - G_1\right) = q - w + \left(P_2V_2 - P_1V_1\right) - \left(T_2S_2 - T_1S_1\right) \tag{5.6}$$

If the process is carried out such that $T_1 = T_2 = T$, which is the temperature of the heat reservoir which supplies or withdraws thermal energy from the system, and also, if $P_1 = P_2 = P$, which is the constant pressure at which the system undergoes a change in volume, then

$$(G_2 - G_1) = q - w + P\left(V_2 - V_1\right) - T\left(S_2 - S_1\right)$$

In the expression for the First Law, the work w is the *total* work done on or by the system during the process. Thus, if the system performs chemical, magnetic, or electrical work in addition to the work of expansion against the external pressure, then these work terms are included in w. Thus, w can be expressed as

$$w = w' + P\left(V_2 - V_1\right)$$

where:

$P(V_2 - V_1)$	is the *P-V* work done by the change in volume at the constant pressure P
w'	is the sum of all of the non–*P-V* forms of work done

Substituting into Equation 5.6 gives

$$(G_2 - G_1) = q - w' - T\left(S_2 - S_1\right)$$

and again, since

$$q \le T\left(S_2 - S_1\right)$$

then

$$w' \le -\left(G_2 - G_1\right) \tag{5.7}$$

The equality can be written as

$$-w' = \left(G_2 - G_1\right) + T\Delta S_{\text{irr}}$$

Thus, for an isothermal, isobaric process, during which no form of work other than P-V work is performed (i.e., $w' = 0$),

$$(G_2 - G_1) + T\Delta S_{\text{irr}} = 0 \tag{5.8}$$

Such a process can only occur spontaneously (with a consequent increase in entropy) if the Gibbs free energy decreases. Since $\Delta S_{\text{irr}} = 0$ is a criterion for thermodynamic equilibrium, then an increment of an isothermal isobaric process occurring at equilibrium requires that

$$dG = 0 \tag{5.9}$$

Thus, for a system undergoing a process at constant T and constant P, the Gibbs free energy can only decrease or remain constant, and the attainment of equilibrium in the system coincides with the system having the minimum value of G consistent with the values of P and T; that is,

$$dG_{T,P} = 0 \ \text{ and } \ d^2G_{T,P} > 0$$

This criterion of equilibrium, which is of considerable practical use, will be used extensively in the subsequent chapters.

5.5 THE FUNDAMENTAL EQUATIONS FOR A CLOSED SYSTEM

Using the aforementioned definitions for H, A, and G, we have the following four fundamental equations for one mole of a closed simple system:

$$dU = TdS - PdV \tag{5.10a}$$

$$dH = TdS + VdP \tag{5.10b}$$

$$dA = -SdT - PdV \tag{5.10c}$$

$$dG = -SdT + VdP \tag{5.10d}$$

As indicated earlier, work terms in addition to work against pressure may also be present. This adds terms to the fundamental equations. For example, if the system is also under the influence of an applied magnetic field, the work performed on the system is $V\mu_0\mathcal{H}dM$ (V is the molar volume) and must be added to the combined First and Second Laws expression (Equation 3.12) to obtain

$$dU' = TdS' - PdV' + V'\mu_0\mathcal{H}dM \tag{5.11a}$$

The other three forms of the fundamental equation become*

$$dH' = TdS' + V'dP - V'\mu_0 Md\mathcal{H} \tag{5.11b}$$

$$dA' = -S'dT - PdV' + V'\mu_0\mathcal{H}dM \tag{5.11c}$$

$$dG' = -S'dT + V'dP - V'\mu_0 Md\mathcal{H} \tag{5.11d}$$

Let us look at the fundamental equation which uses G' as the dependent variable and temperature, pressure, and magnetic field as the independent intensive variables.

$$dG' = -S'dT + V'dP - V'\mu_0 Md\mathcal{H}$$

The slope of the curve of the Gibbs free energy, G, versus temperature, T, at constant pressure and applied magnetic field can be seen to be

$$\left(\frac{\partial G'}{\partial T}\right)_{P,\mathcal{H}} = -S'$$

The curvature of G versus T at constant pressure is proportional to

$$\left(\frac{\partial^2 G'}{\partial T^2}\right)_{P,\mathcal{H}}$$

which is

$$\left(\frac{\partial^2 G'}{\partial T^2}\right)_{P,\mathcal{H}} = -\left(\frac{\partial S'}{\partial T}\right)_{P,\mathcal{H}} = -\left(\frac{C_{P,\mathcal{H}}}{T}\right) < 0$$

When there is no applied magnetic field, this reduces to the following equation:

$$\left(\frac{\partial^2 G'}{\partial T^2}\right)_{P} = -\left(\frac{\partial S'}{\partial T}\right)_{P} = -\left(\frac{C_P}{T}\right) < 0 \tag{5.12}$$

---

* The forms shown here are consistent with the modern texts of thermodynamics, using: $H = U + PV - V\mu_0 M\mathcal{H}$; $A = U - TS$, and $G = H - TS$. See R. C. O'Handley, *Modern Magnetic Materials: Principles and Applications*, John Wiley, New York, 2000; and J. M. D. Coey, *Magnetism and Magnetic Materials*, Cambridge University Press, Cambridge, UK, 2010.

5.6 THE VARIATION OF THE COMPOSITION WITHIN A CLOSED SYSTEM

So far, we have restricted our considerations to closed systems in which the phases were of fixed composition. In such cases, it was found that simple systems have two independent variables which, when fixed, uniquely determine the state of the system.

However, a closed system of a fixed amount of matter can still have changes of the composition of its phases. The number of moles of the various species present can change as the consequence of a chemical reaction occurring in the system. Also, new phases can be formed by chemical reaction. Thus, the minimization of G at constant P and T occurs when the system has a unique number or ratio of moles of each phase. For example, if the system contains the gaseous species CO, CO_2, H_2, and H_2O, then, at constant T and P, the minimization of G will occur when the reaction equilibrium $CO + H_2O = CO_2 + H_2$ is established (Figure 5.5).

5.7 THE CHEMICAL POTENTIAL

The Gibbs free energy of a simple closed system with no chemical reactions depends only on the temperature and the pressure. If the system is an open system, since the Gibbs free energy is an extensive property, its value is dependent on the amount of matter of the system. It is therefore necessary that the number of moles within the open system be specified. The Gibbs free energy is thus a function of T, P, and the numbers of moles of all of the species; that is,

$$G' = G'\left(T, P, n_i, n_j, n_k, \ \ldots\right) \tag{5.13}$$

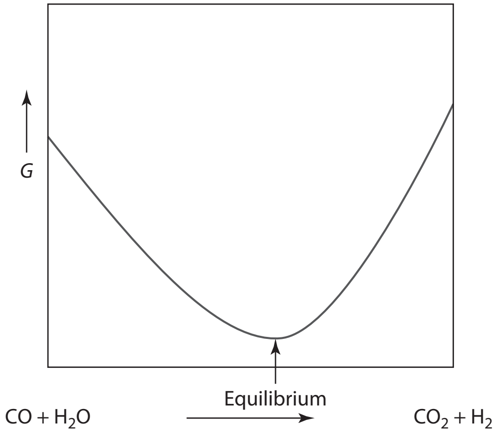

Figure 5.5 Schematic of the Gibbs free energy vs. degree of reaction completion for the $CO + H_2O \leftrightarrow CO_2 + H_2$ reaction.

in which G' is the total Gibbs free energy, and n_i, n_i, n_k, … are the numbers of moles of the species i, j, k, … present in the system, and the thermodynamic state of the system is only fixed when all of the independent variables are fixed. Differentiating Equation 5.13 gives

$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P,n_i,n_j,\cdots} dT + \left(\frac{\partial G'}{\partial P}\right)_{T,n_i,n_j,\cdots} dP + \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,n_k,\cdots} dn_i + \left(\frac{\partial G'}{\partial n_j}\right)_{T,P,n_i,n_k,\cdots} dn_j + \text{etc.} \tag{5.14}$$

$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P,n_i,n_j,\cdots} dT + \left(\frac{\partial G'}{\partial P}\right)_{T,n_i,n_j,\cdots} dP + \sum_{i=1}^{i=k}\left(\frac{\partial G'}{dn_i}\right)_{T,P,n_j,\cdots} dn_i \tag{5.15}$$

where

$$\sum_{i=1}^{i=k}\left(\frac{\partial G'}{dn_i}\right)_{T,P,n_j,\cdots} dn_i \tag{5.16}$$

is the sum of k terms (one for each of the k species), each of which is determined by the partial differentiation of G with respect to the number of moles of the ith species at constant T, P, and n_j, where n_j represents the numbers of moles of every species other than the ith species.

The term $(\partial G'/dn_i)_{T,P,n_j,\cdots}$ is called the *chemical potential* of species i, and is usually denoted as μ_i.

The chemical potential of the ith species in a homogeneous phase is thus the incremental change of the Gibbs free energy that accompanies an incremental increase of the species to the system at constant temperature, pressure, and numbers of moles of all of the other species. Alternatively, if the system is large enough that the addition of 1 mole of the ith species at constant temperature and pressure does not measurably change the composition of the system, then μ_i is the increase in the Gibbs free energy of the system caused by the addition.

Equation 5.15 can be written as

$$dG' = -S'dT + V'dP + \sum_{1}^{k} \mu_i dn_i \tag{5.17}$$

in which G' is expressed as a function of T, P, and the numbers of moles of each substance. Equation 5.15 can thus be applied to *open systems*, which exchange matter as well as thermal energy with their surroundings, and to *closed* systems, which undergo changes in composition caused by chemical reactions (Section 5.6).

Similarly, Equations 3.12, 5.10b, and 5.10c can be made applicable to open systems by including the terms describing the dependences on composition of, respectively, *U*, *H*, and *A*:

$$dU' = TdS' - PdV' + \sum_1^k \left(\frac{\partial U'}{\partial n_i}\right)_{S,V,n_j,\cdots} dn_i \tag{5.18}$$

$$dH' = TdS' - V'dP + \sum_1^k \left(\frac{\partial H'}{\partial n_i}\right)_{S,P,n_j,\cdots} dn_i \tag{5.19}$$

$$dA' = S'dT - PdV' + \sum_1^k \left(\frac{\partial A'}{\partial n_i}\right)_{S,V,n_j,\cdots} dn_i \tag{5.20}$$

Inspecting Equations 5.16 through 5.20 shows that

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial U'}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H'}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A'}{\partial n_i}\right)_{S,V,n_j} \tag{5.21}$$

Hence, the complete set of equations for open systems with only *P*-*V* work is as follows:

$$dU' = TdS' - PdV' + \Sigma\mu_i dn_i \tag{5.22}$$

$$dH' = TdS' + V'dP + \Sigma\mu_i dn_i \tag{5.23}$$

$$dA' = -S'dT - PdV' + \Sigma\mu_i dn_i \tag{5.24}$$

$$dG' = -S'dT + V'dP + \Sigma\mu_i dn_i \tag{5.25}$$

From Equations 5.22 through 5.25, we have the following:

- U' is the characteristic thermodynamic potential (state function) of the independent extensive variables S, V', and composition; that is, $U' = U'(S',V',n_i)$.
- H' is the characteristic thermodynamic potential (state function) of the independent variables S', P and composition; that is, $H' = H'(S',P,n_i)$.
- A' is the characteristic thermodynamic potential (state function) of the independent variables T, V', and composition; that is, $A' = A'(T,V',n_i)$.
- G' is the characteristic thermodynamic potential (state function) of the independent intensive variables T, P, and composition; that is, $G' = G'(T,P,n_i)$.

Although all four of the preceding equations are basic in nature, Equation 5.25 is sometimes called ***the*** *fundamental equation* because of its practical usefulness.

A comparison of the combined First and Second Laws of a simple system

$$dU' = \delta q - \delta w - \delta w'$$

with Equation 5.22, indicates that, for a closed system undergoing a process involving a reversible change in composition (e.g., a reversible chemical reaction),

$$\delta q = TdS'$$

and

$$\delta w = PdV' + \Sigma\mu_i dn_i$$

The term $\Sigma\mu_i dn_i$ is the *chemical work* done by the system, which was denoted as w' in Equation 5.7, and the total work w is the sum of the P-V work and the chemical work. Gibbs introduced this term to thermodynamics in 1875.*

5.8 THERMODYNAMIC RELATIONS

Including the chemical potential terms in Equations 5.11a through 5.11d yields an open system:

$$dU' = TdS' - PdV' + V'\mu_0\mathcal{H}\, dM + \Sigma\mu_i dn_i$$

$$dH' = TdS' + V'dP - V'\mu_0 Md\mathcal{H} + \Sigma\mu_i dn_i$$

$$dA' = -S'dT - PdV' + V'\mu_0\mathcal{H}\, dM + \Sigma\mu_i dn_i$$

$$dG' = -S'dT + V'dP - V'\mu_0 Md\mathcal{H} + \Sigma\mu_i dn_i$$

We see that the *intensive* thermodynamic state variables T, P, $\mathcal{H}$, and μ_i are equal to the derivatives of an energy potential with respect to their conjugate *extensive* variables, S, V, $\mathbf{M}$, and n_i, respectively:

$$T = \left(\frac{\partial U'}{\partial S'}\right)_{V,\boldsymbol{M},n_i} = \left(\frac{\partial H'}{\partial S'}\right)_{P,\mathcal{H},n_i} \tag{5.26}$$

$$P = -\left(\frac{\partial U'}{\partial V'}\right)_{S,\boldsymbol{M},n_i} = -\left(\frac{\partial A'}{\partial V'}\right)_{T,\boldsymbol{M},n_i} \tag{5.27}$$

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* J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances," *Trans. Conn. Acad.* (1875), vol. 3, pp. 108–248 (Equation 12).

$$\boldsymbol{\mathcal{H}} = \frac{1}{\mu_0 V'}\left(\frac{\partial U'}{\partial \boldsymbol{M}}\right)_{V,S,n_i} = \frac{1}{\mu_0 V'}\left(\frac{\partial A'}{\partial \boldsymbol{M}}\right)_{V,T,n_i} \tag{5.28}$$

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial U'}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H'}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A'}{\partial n_i}\right)_{S,V,n_j} \tag{5.21}$$

We also see that the *extensive* thermodynamic state functions are derivatives of a thermodynamic potential (energy) function with respect to their conjugate *intensive* state variables:

$$S' = -\left(\frac{\partial A'}{\partial T}\right)_{V,\boldsymbol{M},\mathrm{comp}} = -\left(\frac{\partial G'}{\partial T}\right)_{P,\boldsymbol{M},\mathrm{comp}} \tag{5.29}$$

$$V' = \left(\frac{\partial H'}{\partial P}\right)_{S,\boldsymbol{\mathcal{H}},\mathrm{comp}} = \left(\frac{\partial G'}{\partial P}\right)_{T,\boldsymbol{\mathcal{H}},\mathrm{comp}} \tag{5.30}$$

$$M = -\frac{1}{\mu_0 V'}\left(\frac{\partial H'}{\partial \boldsymbol{\mathcal{H}}}\right)_{P,S,\mathrm{comp}} = -\frac{1}{\mu_0 V'}\left(\frac{\partial G'}{\partial \boldsymbol{\mathcal{H}}}\right)_{P,T,\mathrm{comp}} \tag{5.31}$$

5.9 MAXWELL'S RELATIONS

If Z is a state function and x and y are chosen as the independent thermodynamic variables in a closed system of fixed composition, then we write

$$Z = Z(x, y)$$

differentiation of which gives

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$

If the partial derivative $(\partial Z/\partial x)_y$ is itself a function of x and y, being given by $(\partial Z/\partial x)_y = L(x, y)$, and similarly, the partial derivative $(\partial Z/\partial y)_x = M(x, y)$, then

$$dZ = Ldx + Mdy$$

Thus,

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial Z}{\partial x}\right)_y\right]_x = \left(\frac{\partial L}{\partial y}\right)_x$$

and

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial Z}{\partial y}\right)_x\right]_y = \left(\frac{\partial M}{\partial x}\right)_y$$

But, since Z is a state function, the change in Z is independent of the order of differentiation; that is,

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial Z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial Z}{\partial y}\right)_x\right]_y = \frac{\partial^2 Z}{\partial x \partial y}$$

and hence,

$$\left(\frac{\partial L}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y \tag{5.32}$$

Previously, we obtained the following equations of state for a one mole of closed simple system:

$$dU = TdS - PdV \tag{3.12}$$

$$dH = TdS + VdP \tag{5.10b}$$

$$dA = -SdT - PdV \tag{5.10c}$$

$$dG = -SdT + VdP \tag{5.10d}$$

These equations yield the following Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{5.32}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{5.33}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{5.34}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{5.35}$$

Additional Maxwell relations can be obtained by considering systems with variations in composition or with magnetic terms (see Problems 5.14* and 5.15*).

The value of the preceding Maxwell relations lies in the fact that they contain many experimentally measurable quantities that can be used to determine quantities that are not easy to measure directly. For example, Equation 5.35 shows that increasing the pressure on a material at constant temperature deceases the entropy of the material by an amount that is proportional to $\alpha V dP$.

5.10 EXAMPLES OF THE APPLICATION OF MAXWELL RELATIONS

5.10.1 The First *TdS* Equation

Consider the dependence of the entropy of 1 mole of a substance on the independent variables T and V.

$$S = S(T, V)$$

differentiation of which gives

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{i}$$

At constant volume, the First Law can be written as

$$TdS = \delta q_v = dU = c_v dT$$

The partial derivatives of Equation (i)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{c_v}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

are obtained from the Maxwell relation of equation 5.34.

Thus, Equation (i) can be written as

$$dS = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \tag{ii}$$

Multiplying the equation by T, the following is obtained.

$$TdS = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

This equation is called the first *TdS* equation by Zemansky.[*] The term $(\partial P/\partial T)_v$ can be shown to equal α/β_T. So, the equation can be written as

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[*] M. W. Zemansky, *Heat and Thermodynamics*, McGraw-Hill, New York, 1957.

$$TdS = c_v dT + \frac{T\alpha}{\beta_T} dV$$

We have the following cases:

- For an *isothermal expansion*:

$$\Delta S = \int \frac{\alpha}{\beta_T} dV > 0$$

- If the temperature is raised at constant volume:

$$\Delta S = \int \frac{c_v}{T} dT > 0$$

- For an *isentropic expansion*:

$$0 = c_v dT + \frac{T\alpha}{\beta_T} dV$$

$$\left(\frac{dT}{dV}\right)_S = -\frac{T\alpha}{c_v\beta_T} < 0$$

If the substance is 1 mole of an ideal gas, we can write

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad \text{(iii)}$$

and thus, Equation (ii) can be written as

$$dS = \frac{c_v}{T} dT + \frac{R}{V} dV \qquad \text{(iv)}$$

the integration of which (assuming constant c_v) between the states 1 and 2 gives, for an ideal gas,

$$S_2 - S_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) \qquad \text{(v)}$$

We have the following three special cases for 1 mole of an ideal gas:

- For an *isothermal expansion* of an ideal gas:

$$\Delta S_{\text{gas}} = R \ln\left(\frac{V_2}{V_1}\right)$$

- If the temperature of an ideal gas is raised at constant volume:

$$\Delta S_{\text{gas}} = c_v \ln\left(\frac{T_2}{T_1}\right)$$

- For an *isentropic expansion* of an ideal gas:

$$S_2 - S_1 = 0, \text{ and thus, } c_v \ln\left(\frac{T_2}{T_1}\right) = -R\ln\left(\frac{V_2}{V_1}\right)$$

and since $\gamma = c_P/c_V$ and $c_P - c_V = R$, for an ideal gas, we obtain (cf. Section 2.7)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

5.10.2 The Second *TdS* Equation

Consider the dependence of the entropy of 1 mole of a substance on the independent variables T and P:

$$S = S(T,P)$$

differentiation of which gives

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{vi}$$

At constant pressure, the First Law can be written as

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{c_P}{T} \text{ and, by Equation 5.35, } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Using these relations, we can write Equation (vi) in the form of the second *TdS* equation:

$$TdS = c_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = c_P dT - \alpha VTdP$$

We have the following cases:

- For an isothermal reversible change of pressure:

  $$dS = -\alpha VdP$$

  which shows that an increase in P at constant T decreases the entropy of the substance (cf. Equation 5.35).

- For an isobaric reversible change in temperature:

$$dS = c_P \frac{dT}{T}$$

$$\Delta S = \int c_P \frac{dT}{T} = c_P \ln\frac{T_2}{T_1} \quad \text{over a range where } c_P \text{ is constant}$$

Thus, increasing the temperature at constant pressure increases the entropy of the substance.

- For an isentropic process:

$$dS = 0 = \frac{c_P}{T}dT - \alpha V dP$$

$$\therefore \left(\frac{dT}{dP}\right)_S = \frac{\alpha V T}{c_P}$$

This shows that if the entropy is held constant, and the temperature is raised, the pressure is also raised if $\alpha > 0$.

These cases reduce to the following when we consider 1 mole of an ideal gas:

- For an isothermal reversible change of pressure of an ideal gas:

$$dS = -\alpha V dP = -\frac{V}{T}dP = -\frac{R}{P}dP$$

$$\Delta S_T = -R\ln\frac{P_2}{P_1} = R\ln\frac{P_1}{P_2} = R\ln\frac{V_2}{V_1}$$

- For an isobaric reversible change in temperature of an ideal gas:

$$\Delta S = c_P \ln\frac{T_2}{T_1} = \frac{5}{2}\mathrm{R}\ln\frac{T_2}{T_1} = \frac{5}{2}\mathrm{R}\ln\frac{V_2}{V_1}$$

- For an isentropic process of an ideal gas:

$$\frac{c_P}{T}dT - \alpha V dP$$

$$\left(\frac{dT}{dP}\right)_S = \frac{\alpha V T}{c_P} = \frac{V}{c_P}$$

Thus, if an ideal gas increases in temperature at constant entropy, the pressure must also increase. This can be rationalized as follows: increasing the temperature would increase the entropy of the gas, so the pressure must decrease to keep the entropy constant.

5.10.3 *S* and *V* as Dependent Variables and *T* and *P* as Independent Variables

We can write the entropy and the volume of a one mole of one-component simple system as a function of the intensive variables T and P (i.e., $S = S(T, P)$ and $V = V(T, P)$) and obtain the following:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

But we know that

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{c_P}{T},\ \left(\frac{\partial V}{\partial T}\right)_P = \alpha V,\ \text{and}\ \left(\frac{\partial V}{\partial P}\right)_T = -V\beta_T$$

and by a Maxwell relation (Equation 5.35):

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

Thus, we can write

$$dS = \frac{c_P}{T} dT - \alpha V dP$$

$$dV = \alpha V dT - V\beta_T dP$$

or, in matrix notation:

$$\begin{pmatrix} dS \\ dV \end{pmatrix} = \begin{pmatrix} \frac{c_P}{T} & -\alpha V \\ \alpha V & -V\beta_T \end{pmatrix} \begin{pmatrix} dT \\ dP \end{pmatrix}$$

This set of equations shows that the response of a material to a rise in temperature at constant pressure is twofold: the entropy changes by an amount proportional to the material's heat capacity and the volume changes by an amount proportional to the coefficient of expansion of the material. Furthermore, a change in the

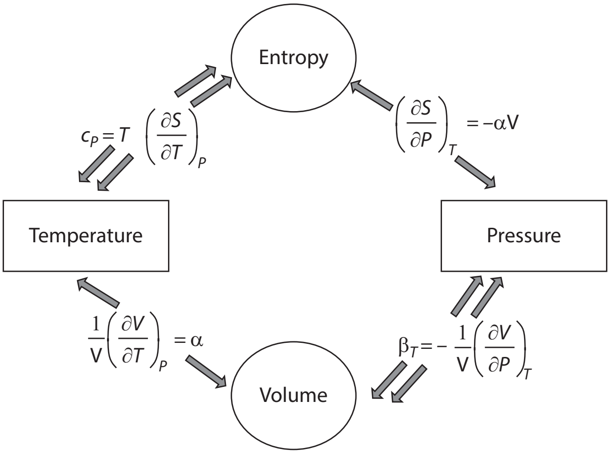

Figure 5.6 The intrinsic independent thermodynamic parameters *T* and *P* with their conjugate extrinsic thermodynamic parameters. Also shown are the properties which relate the various thermodynamic variables.

pressure of the system at constant temperature changes the material's volume by an amount which is proportional to the negative of its isothermal compressibility, while its entropy changes proportional to the negative of its coefficient of expansion. Figure 5.6 shows in diagrammatic form the relationship among the four thermodynamic variables under discussion.

5.10.4 An Energy Equation (Internal Energy)

Another example of the use of the Maxwell's relations is as follows. For one mole of a closed system of fixed composition, Equation 3.12 gives

$$dU = TdS - PdV$$

Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Using a Maxwell relation (Equation 5.34) allows this to be written as

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(vii)}$$

which is an equation of state relating the internal energy, *U*, of a closed system of fixed composition to the measurable quantities *T*, *V*, and *P*. If the system is 1 mole of ideal gas, substitution of Equation (iii) into (vii) gives $(\partial U/\partial V)_T = 0$, which shows that the internal energy of an ideal gas is independent of the volume of the gas.

5.10.5 Another Energy Equation (Enthalpy)

Similarly, for one mole of a closed system of fixed composition, Equation 5.10b gives $dH = TdS + VdP$, in which case

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Substituting a Maxwell relation (Equation 5.35) gives

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

which is an equation of state which gives the dependence of enthalpy on the measureable quantities T, P, and V. Again, if the system is 1 mole of an ideal gas, this equation of state shows that the enthalpy of an ideal gas is independent of its pressure.

5.10.6 A Magnetic Maxwell Relation

For another example, we obtain a Maxwell relation on the fundamental equation for a single-component material under the influence of an external magnetic field.

$$G' = G(T, P, \mathcal{H})$$

$$dG' = -S'dT + V'dP - V'\mu_0 \boldsymbol{M} d\mathcal{H}$$

$$\left(\frac{\partial S'}{\partial \mathcal{H}}\right)_{T,P} = V'\mu_0\left(\frac{\partial \boldsymbol{M}}{\partial T}\right)_{\mathcal{H},P}$$

Since increasing the applied field $\mathcal{H}$ decreases the spin entropy of a magnetic material, the plot of magnetization versus temperature must have negative slope. We will use this equation later to discuss the magnetocaloric effect. The applied magnetic field and the temperature oppose each other' s effects on the ordering or disordering of the magnetic spins.

In ferromagnetic materials, the magnetization is the order parameter of the system. Above the Curie temperature (T_C), where the material is paramagnetic, $\mathbf{M} = 0$. Below the Curie temperature, the material is ferromagnetic, and with decreasing temperature the magnetization increases continuously until it reaches its maximum value, $\mathbf{M}(0)$ at 0 K. Thus, increasing the temperature of a ferromagnet decreases its magnetization and increases its entropy. Figure 5.7 plots $\boldsymbol{M}(T)/\boldsymbol{M}(0)$ versus T/T_C (the reduced thermodynamic variables).

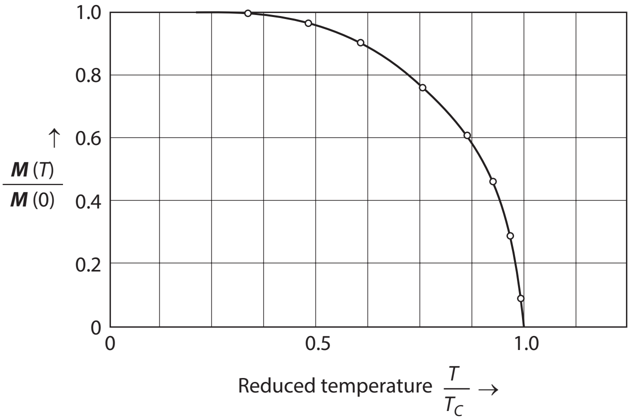

Figure 5.7 Reduced magnetization vs. reduced temperature for a magnetic material displaying a negative slope for $T > 0$.

5.10.7 *S*, *V*, and *M* with Independent Variables *T*, *P*, and $\mathcal{H}$

Writing the entropy, the volume, and the magnetization for one mole of a one-component system as a function of the intensive variables *T*, *P*, and $\boldsymbol{\mathcal{H}}$, we obtain the following:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,\mathcal{H}} dT + \left(\frac{\partial S}{\partial P}\right)_{T,\mathcal{H}} dP + \left(\frac{\partial S}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} d\boldsymbol{\mathcal{H}}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,\mathcal{H}} dT + \left(\frac{\partial V}{\partial P}\right)_{T,\mathcal{H}} dP + \left(\frac{\partial V}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} d\boldsymbol{\mathcal{H}}$$

$$d\boldsymbol{M} = \left(\frac{\partial \boldsymbol{M}}{\partial T}\right)_{P,\mathcal{H}} dT + \left(\frac{\partial \boldsymbol{M}}{\partial P}\right)_{T,\mathcal{H}} dP + \left(\frac{\partial \boldsymbol{M}}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} d\boldsymbol{\mathcal{H}}$$

These equations can be written in matrix form, as done previously for the two intensive variables case.

$$\begin{pmatrix} dS \\ dV \\ d\boldsymbol{M} \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial S}{\partial T}\right)_{P,\mathcal{H}} & \left(\frac{\partial S}{\partial P}\right)_{T,\mathcal{H}} & \left(\frac{\partial S}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} \\ \left(\frac{\partial V}{\partial T}\right)_{P,\mathcal{H}} & \left(\frac{\partial V}{\partial P}\right)_{T,\mathcal{H}} & \left(\frac{\partial V}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} \\ \left(\frac{\partial \boldsymbol{M}}{\partial T}\right)_{P,\mathcal{H}} & \left(\frac{\partial \boldsymbol{M}}{\partial P}\right)_{T,\mathcal{H}} & \left(\frac{\partial \boldsymbol{M}}{\partial \boldsymbol{\mathcal{H}}}\right)_{T,P} \end{pmatrix} \begin{pmatrix} dT \\ dP \\ d\boldsymbol{\mathcal{H}} \end{pmatrix}$$

Each of the terms in the 3 × 3 matrix represents a property of the substance in question. Also, it can be proved that the cross-diagonal terms are equal in absolute magnitude to each other.

5.11 ANOTHER IMPORTANT FORMULA

Given three state functions x, y, and z and a closed system of fixed composition, then

$$x = x(y, z)$$

or

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

For an incremental change of state at constant x,

$$\left(\frac{\partial x}{\partial y}\right)_z dy = -\left(\frac{\partial x}{\partial z}\right)_y dz$$

or

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

This can be written as

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{5.36}$$

Equation 5.36 can be used with any three state functions. It can be seen that each of the state functions appears once in the numerator, once in the denominator, and once outside the bracket.

5.12 THE GIBBS–HELMHOLTZ EQUATION

Starting with the definition of the Gibbs free energy for one mole of a substance,

$$G = H - TS$$

dividing by T and taking the derivative of both sides with respect to T at constant pressure, we obtain

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \frac{H}{T^2} - \left(\frac{\partial S}{\partial T}\right)_P$$

But,

$$\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_P}{T} \text{ and } \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Thus, we obtain

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = -\frac{H}{T^2} \tag{5.37}$$

which is a form of what is called the *Gibbs–Helmholtz equation*. It is applicable to a closed system of fixed composition undergoing processes at constant pressure.

For an isobaric change of state of a closed system of fixed composition, Equation 5.37 gives the relation of the change in G to the change in H as

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \tag{5.38}$$

This equation is of particular use in experimental thermodynamics, as it allows ΔG to be obtained from a measurement of ΔH *as well as* ΔH, the heat of a reaction, to be obtained from a measurement of the variation of ΔG, the free energy change for the reaction, with temperature. The usefulness of this equation will be developed and applied later in the text to the calculation of partial molar heats of solution as well as to the calculation of the temperature variation of the equilibrium constants of reactions in systems.

The corresponding relationship between the Helmholtz free energy and the internal energy is obtained as follows:

$$A = U - TS$$

Dividing by T and performing a similar procedure gives

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2} \tag{5.39}$$

This equation is applicable to closed systems of fixed composition undergoing processes at constant volume. As before, for a change of state under these conditions:

$$\left(\frac{\partial\left(\frac{\Delta A}{T}\right)}{\partial T}\right)_V = -\frac{\Delta U}{T^2} \tag{5.40}$$

5.13 SUMMARY

1. The Helmholtz free energy, A, is defined by $A \equiv U - TS$. In a closed system held at constant T and V, the Helmholtz free energy can only
   - Decrease, for a spontaneous process
   - Remain constant if the system is in equilibrium

   Equilibrium at constant T and V is attained when the Helmholtz free energy achieves its minimum value.
2. The Gibbs free energy, G, is defined by $G \equiv H - TS$. In a closed system at constant pressure and temperature, the Gibbs free energy is a minimum at equilibrium. During an isothermal, isobaric process during which no form of work other than P-V work is performed (i.e., $w' = 0$), G can only
   - Decrease for a spontaneous process
   - Remain constant if the system is in equilibrium

   Equilibrium is attained at constant T and P when the Gibbs free energy reaches its minimum value.
3. For a change of state at constant pressure, $\Delta H' = q_p$.
4. The chemical potential, μ_i, of the ith component can be expressed as

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial U'}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H'}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A'}{\partial n_i}\right)_{T,V,n_j}$$

5. The internal energy, U', varies with S', V', and composition as

$$dU' = TdS' - PdV' + \Sigma\mu_i dn_i$$

   The enthalpy, H', varies with S', P, and composition as

$$dH' = TdS' + V'dP + \Sigma\mu_i dn_i$$

   The Helmholtz free energy, A', varies with T, V', and composition as

$$dA' = -S'dT - PdV' + \Sigma\mu_i dn_i$$

   The Gibbs free energy, G', varies with T, P, and composition as

$$dG' = -S'dT + V'dP + \Sigma\mu_i dn_i$$

6. For one mole of a closed system with magnetic terms, the following holds.

$$dG = -SdT + VdP - V\mu_0 \boldsymbol{M} d\boldsymbol{\mathcal{H}}$$

7. The Maxwell relations for one mole of a closed simple system are

$$\left(\frac{\partial T}{dV}\right)_S = -\left(\frac{\partial P}{dS}\right)_V, \qquad \left(\frac{\partial T}{dP}\right)_S = \left(\frac{\partial V}{dS}\right)_P$$
$$\left(\frac{\partial S}{dV}\right)_T = \left(\frac{\partial P}{dT}\right)_V, \qquad \left(\frac{\partial S}{dP}\right)_T = -\left(\frac{\partial V}{dT}\right)_P$$

8. With x, y, and z as state functions, the following is valid.

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$$

9. The Gibbs–Helmholtz equations are

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P = -\frac{H}{T^2}$$

and

$$\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right]_V = -\frac{U}{T^2}$$

5.14 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 5

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Auxiliary functions
Chemical potential
Chemical reaction
Chemical work
Fundamental equations
Gibbs free energy
Gibbs–Helmholtz equation
Helmholtz free energy
Magnetic work
Magnetization as order parameter
Maximum entropy criterion
Maxwell relations
Minimum internal energy criterion
Work function

5.15 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Obtain the following expression:

$$c_p - c_v = \frac{VT\alpha^2}{\beta_T}$$

Solution to Qualitative Problem 1

Equation 2.8 gives the relationship between c_p and c_v as

$$c_p - c_v = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \tag{2.8}$$

Since we know that $\alpha = 1/V(\partial V/\partial T)_P$, we obtain $\alpha V = (\partial V/\partial T)_P$

Also, $P = -(\partial A/\partial V)_T$, so combining this with $\alpha V = (\partial V/\partial T)_P$, we obtain

$$c_p - c_v = \alpha V\left[-\left(\frac{\partial A}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$A = U - TS$$

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$$

Rearranging, we get

$$-\left(\frac{\partial A}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T$$

$$c_p - c_v = \alpha V\left[T\left(\frac{\partial S}{\partial V}\right)_T\right] = T\alpha V\left(\frac{\partial P}{\partial T}\right)_V$$

From Equation 5.36,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Finally,

$$c_p - c_v = (T\alpha V)\left(-\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right) = (T\alpha V)\cdot\left(\frac{1}{V\beta_T}\right)\cdot V\alpha = \frac{TV\alpha^2}{\beta_T}$$

Thus,

$$c_p - c_v = \frac{VT\alpha^2}{\beta_T} \tag{5.41}$$

and the right-hand side of this equation contains only experimentally measurable quantities. We see that $c_p - c_v > 0$ for all $T > 0$; $c_p = c_v = 0$ at $T = 0$.

Qualitative Problem 2

Derive the third *TdS* equation for one mole of a substance, namely, $TdS = c_V\left(\frac{\partial T}{\partial P}\right)_V dP + c_P\left(\frac{\partial T}{\partial V}\right)_P dV$.

Solution to Qualitative Problem 2

$$S = S(P,\ V)$$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$\text{but } \left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V = \frac{c_V}{T}\left(\frac{\partial T}{\partial P}\right)_V$$

$$\text{and } \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P = \frac{c_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$$

$$TdS = c_V\left(\frac{\partial T}{\partial P}\right)_V dP + c_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

5.16 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Determine the constant-volume heat capacity of aluminum given the following data:

At 20°C, aluminum has the following properties:

$$c_p = 24.36 \text{ J / mole} \cdot \text{K}$$

$$\alpha = 7.05 \times 10^{-5}\text{K}^{-1}$$

$$\beta_T = 1.20 \times 10^{-6}\text{atm}^{-1}$$

$$\text{density, } \rho = 2.70 \text{ g/cm}^3$$

Solution to Quantitative Problem 1

The atomic weight of aluminum is 26.98, and thus, at 20°C, the molar volume of aluminum, V, is

$$V = \frac{26.98}{2.70 \times 1000} = 0.010 \text{ liters/mole}$$

and thus, the difference between c_p and c_v is (see Qualitative Problem 1):

$$c_p - c_v = \frac{VT\alpha^2}{\beta_T}$$

$$\frac{0.010\times 293\times (7.05\times 10^{-5})^2}{1.20\times 10^{-6}} = 0.0121 \text{ liter}\cdot\text{atm/mole}\cdot\text{K}$$

$$0.0121\times\frac{8.3144}{0.08206} = 1.23 \text{ J/mole}\cdot\text{K}$$

The constant-volume molar heat capacity of aluminum at 20°C is thus

$$24.36 - 1.23 = 23.13 \text{ J/mole}\cdot\text{K}$$

Quantitative Problem 2

The following example was provided by Dr. Bill Fahrenholtz, University of Missouri–Rolla.

The adiabatic thermoelastic effect describes the change in temperature with pressure for a brittle solid when it is loaded rapidly (i.e., the rate of loading is much more rapid than the rate of heat transfer). This effect has been used to measure the stresses that develop around defects in composite materials using cyclic loading and a high-speed thermal imaging camera. Using Maxwell relations, derive an expression for the adiabatic thermoelastic effect. Estimate the change in temperature for one mole of alumina that is loaded to 500 MPa.

Data:

Initial temperature = 298 K

$\alpha = 2.2\times 10^{-5}$/K

$c_P = 80$ J/mole·K

Solution to Quantitative Problem 2

The problem requires calculation of the variation in temperature with pressure at constant entropy—that is, $(\partial T/\partial P)_s$.

Start with the second *TdS* equation:

$$dS = \frac{c_P dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP = \frac{c_P dT}{T} - \alpha dP$$

At constant entropy:

$$dS = 0 = \frac{c_P dT}{T} - \alpha V dP$$

$$\frac{c_P dT}{T} = \alpha V dP$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha V}{c_P}$$

It is reasonable to assume that Al_2O_3 is an incompressible solid and that its heat capacity does not vary significantly over small ranges of temperature and pressure. Thus, the variables can be separated for integration.

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{TV\alpha}{c_p}$$

$$\frac{dT}{T} = \frac{V\alpha dP}{c_p} \qquad \text{at constant } S \text{ (an adiabatic process)}$$

$$\ln\frac{T_2}{T_1} = \left(\frac{V\alpha}{c_p}\right)\Delta P$$

$$\begin{aligned}\ln\left(\frac{T_2}{298}\right) &= \left[\frac{\left(2.56\times10^{-5}\ \text{m}^3/\text{mole}\right)\left(2.2\times10^{-5}\ \text{K}^{-1}\right)}{80\ \ \text{J/mole}\cdot\text{K}}\right]\left(500\times10^{6}\ \text{N/m}^2\right)\\ &= 0.00352\end{aligned}$$

$$\therefore T_2 = 299\ \text{K and } \Delta T = 299 - 298\ \text{K} = 1.0\ \text{K}$$

PROBLEMS

5.1 Show that

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{c_p}{TV\alpha}$$

5.2 Show that

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{c_p\beta_T}{T\alpha} - V\alpha$$

5.3 Show that

$$\left(\frac{\partial A}{\partial P}\right)_V = -\frac{S\beta_T}{\alpha}$$

5.4 Show that

$$\left(\frac{\partial A}{\partial V}\right)_P = -\left(\frac{S}{V\alpha} + P\right)$$

5.5 Show that

$$\left(\frac{\partial H}{\partial S}\right)_V = T\left(1+\frac{V\alpha}{c_v\beta_T}\right)$$

5.6 Show that

$$\left(\frac{\partial H}{\partial V}\right)_S = -\frac{c_p}{c_v\beta_T}$$

5.7 Show that

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -TV\left(\alpha^2+\frac{d\alpha}{dT}\right)$$

5.8 Show that

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha V}{c_p}$$

5.9 Show that

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{c_p}{c_v V\beta_T}$$

5.10 Show that

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\frac{1}{\left(\frac{\partial^2 A}{\partial V^2}\right)_T}$$

5.11 Joule and Thomson showed experimentally that when a steady stream of nonideal gas is passed through a thermally insulated tube, in which is inserted a throttle valve, the temperature of the gas changes and the state of the gas is changed from P_1, T_1 to P_2, T_2. Show that this process is isenthalpic. The change in T is described in terms of the Joule–Thomson coefficient, μ_{J-T}, as follows:

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H$$

Show that

$$\mu_{J-T} = -\frac{V}{c_p}(1-\alpha T)$$

and show that the Joule–Thomson coefficient for an ideal gas is zero.

5.12 Determine the values of $\Delta U'$, $\Delta H'$, $\Delta S'$, $\Delta A'$, and $\Delta G'$ for the following processes (in (c), (d), and (e), show that an absolute value of the entropy is required):

a. The four processes in Problem 4.1
b. The expansion of 1 mole of an ideal gas at the pressure P and the temperature T into a vacuum to double its volume
c. The adiabatic expansion of 1 mole of an ideal gas from P_1, T_1 to P_2, T_2
d. The expansion of 1 mole of an ideal gas at constant pressure from V_1, T_1 to V_2, T_2
e. The expansion of 1 mole of an ideal gas at constant volume from P_1, T_1 to P_2, T_2

5.13* Show that the three *TdS* equations can be written as

$$1.\quad TdS = c_V dT + \frac{T\alpha}{\beta_T} dV$$

$$2.\quad TdS = c_P dT - TV\alpha dP$$

$$3.\quad TdS = c_V \frac{\beta_T}{\alpha} dP + \frac{c_P}{\alpha V} dV$$

5.14* Starting from the following equation valid for one mole of a closed system, obtain Maxwell relationships.

$$dH = TdS + VdP - \mu_0 V \boldsymbol{M} d\boldsymbol{\mathcal{H}}$$

5.15* Starting from the following equation valid for one mole of a closed system, obtain Maxwell relationships.

$$dA = -SdT - PdV + \mu_0 V \boldsymbol{\mathcal{H}} d\boldsymbol{M}$$

5.16* The cycle shown in Figure 5.8 consists of two isotherms (*AB* and *CD*) and two isobars (*BC* and *DA*). Use the *TdS* equations to draw the *T-S* diagram for this cycle.

5.17* Show that $\beta_T/\beta_S = c_P/c_V = \gamma$, where $\beta_T = 1/V(\partial V/\partial P)_T$ and $\beta_S = 1/V(\partial V/\partial P)_S$. *Hint*: use the *TdS* equations.

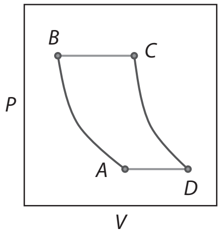

Figure 5.8 Pressure–volume diagram of two isothermals (*AB* and *CD*) and two isobaric changes (*BC* and *DA*) making up a cycle.

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* New problem in this edition

CHAPTER 6

Heat Capacity, Enthalpy, Entropy, and the Third Law of Thermodynamics

6.1 INTRODUCTION

We have defined two heat capacities—namely, the heat capacity at constant volume:

$$C_v = \left(\frac{\partial U'}{\partial T}\right)_V$$

and the heat capacity at constant pressure:

$$C_p = \left(\frac{\partial H'}{\partial T}\right)_P$$

Recall that in Chapter 5 we arrived at another equation for the constant-pressure heat capacity: namely,

$$\left(\frac{\partial^2 G'}{\partial T^2}\right)_P = -\left(\frac{\partial S'}{\partial T}\right)_P = -\left(\frac{C_P}{T}\right) \tag{5.12}$$

It can also be shown that the following holds for the constant-volume heat capacity:

$$\left(\frac{\partial^2 A'}{\partial T^2}\right)_V = -\left(\frac{\partial S'}{\partial T}\right)_V = -\left(\frac{C_V}{T}\right)$$

In Chapter 2, we also introduced the distinction between the heat capacity per mole of substance and the heat capacity of the entire substance as follows:

$$C_v dT = nc_v dT \qquad \text{or} \qquad dU = c_v dT \tag{2.6a}$$

$$C_p dT = nc_p dT \qquad \text{or} \qquad dH = c_p dT \tag{2.6b}$$

in which c_p and c_v are, respectively, the constant-pressure and constant-volume molar heat capacities and the internal energy and enthalpy are given for 1 mole of the substance. Integration of Equation 2.6b between the states (T_2,P) and (T_1,P) gives the difference between the molar enthalpies of the two states as

$$\Delta H = H(T_2,P) - H(T_1,P) = \int_{T_1}^{T_2} c_p dT \tag{6.1}$$

from which it is seen that knowledge of the variation of c_p with temperature is required for the determination of the temperature dependence of the enthalpy. Similarly, integration of Equation 2.6a between T_2 and T_1 at constant volume shows that knowledge of the variation of c_v with temperature is required for the determination of the temperature dependence of the internal energy. Later in this chapter, we will show that this is also the case for the determination of the temperature dependence of entropy. Thus, by knowing the temperature dependence at constant pressure (volume) of the heat capacity as a function of temperature, we will know the Gibbs (Helmholtz) free energy change with temperature, which will enable us to determine the equilibrium state of the system in question.

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

In 1819, as a result of experimental measurements, Dulong (Pierre Louis Dulong, 1785–1838) and Petit (Alexis Thérèse Petit, 1791–1820) introduced an empirical rule which states that the molar heat capacities (c_v) of all solid elements have the value $3R$ (= 24.9 J/K). In 1864, Kopp (Emile Kopp, 1817–1875) introduced a rule which states that, at ordinary temperatures, the molar heat capacity of a solid chemical compound is approximately equal to the sum of the molar heat capacities of its constituent chemical elements. Thus, for example, the molar heat capacity of an A_2B compound will be approximately $9R$ (i.e., $3 \times 3R$) at high temperatures. Although the molar heat capacities of most elements at room temperature have values which are close to $3R$, subsequent experimental measurement showed that the heat capacity usually increases slightly with increasing temperature and can have values significantly lower values than $3R$ at low temperatures. Figure 6.1 shows that, although lead and copper closely obey Dulong and Petit's rule at room temperature, the constant-volume heat capacities of silicon and diamond are significantly less than $3R$ at room temperature. Figure 6.1 also shows the significant decrease in the heat capacities at low temperatures.

Calculation of the heat capacity of a solid element, as a function of temperature, was one of the early successful applications of quantum theory to the solid state. The first such calculation was published in 1907 by Einstein (Albert Einstein, 1879–1955), who considered the properties of a solid containing n atoms, each of which behaves as a quantum harmonic oscillator vibrating independently in three orthogonal directions about its position. Furthermore, he assumed the behavior of

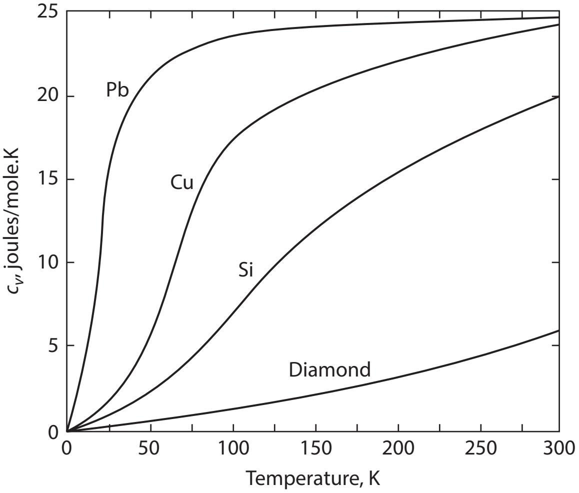


Figure 6.1 The constant-volume molar heat capacities of Pb, Cu, Si, and diamond as functions of temperature.

each of the $3n$ oscillators is not influenced by the behavior of its neighbors, and assigned a single frequency ν to each of the oscillators. Such a system of quantum oscillators is now called an *Einstein solid* (sometimes an *Einstein crystal*).

For a fixed frequency of vibration, the energy levels of a quantum harmonic oscillator take values of the ith energy level as

$$\varepsilon_i = \left(i + \frac{1}{2} \right) h\nu \tag{6.2}$$

In Equation 6.2, i is an integer which has values in the range zero to infinity, and h is Planck's constant (Max Karl Ernst Ludwig Planck, 1858–1947). Since each oscillator has three degrees of freedom (i.e., it can vibrate in the x, y, and z directions), the energy, U', of the Einstein solid (which can be considered to be a system of $3n$ linear independent [distinguishable] quantum harmonic oscillators) is given as

$$U' = 3\sum n_i \varepsilon_i \tag{6.3}$$

where, as before, n_i is the number of atoms in the ith energy level. In Chapter 4, we defined the partition function $\mathcal{Z}$ as

$$\mathcal{Z} \equiv \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T} \right)$$

and the number of particles (n_i) with a given energy ε_i was written as

$$n_i = \frac{n\exp\left(-\frac{\varepsilon_i}{k_BT}\right)}{\mathcal{Z}} \tag{6.4}$$

since the quantum oscillators are distinguishable. Substituting Equations 6.2 into 6.3 and simplifying, we obtain

$$U' = \sum_i 3n_i\varepsilon_i = \sum_i 3n_i\left(i+\frac{1}{2}\right)h\nu$$

Now, substituting Equation 6.4 into this equation, we obtain

$$U' = \sum_i 3\frac{n\exp\left(-\frac{\varepsilon_i}{k_BT}\right)}{\mathcal{Z}}\left(i+\frac{1}{2}\right)hu = 3nhu\sum_i\left(i+\frac{1}{2}\right)\left(\frac{\exp\left(-\frac{\varepsilon_i}{k_BT}\right)}{\sum_i\exp\left(-\frac{\varepsilon_i}{k_BT}\right)}\right)$$

This represents the total internal energy of an Einstein solid. This equation can be shown (see Appendix A to this chapter) to reduce to

$$U' = \frac{3}{2}nh\nu + \frac{3nh\nu}{\left(\exp\left(\frac{hu}{k_BT}\right)-1\right)} \tag{6.5}$$

U' is the total internal energy of a system composed of $3n$ quantum harmonic oscillators, which Einstein used to model the thermal properties of a solid with n atoms vibrating independently of each other. Equation 6.5 gives the variation of the energy of the system with temperature, and differentiation with respect to temperature at constant volume gives, by definition, the constant-volume heat capacity c_v. Maintaining a constant volume causes constant quantization of the energy levels. Thus,

$$\begin{aligned} C_v = \left(\frac{\partial U'}{\partial T}\right)_V &= 3nh\nu\left(\exp\left(\frac{h\nu}{k_BT}\right)-1\right)^{-2}\frac{h\nu}{kT^2}\exp\left(\frac{h\nu}{k_BT}\right) \\ &= 3nk\left(\frac{h\nu}{kT}\right)^2\frac{\exp\left(\frac{h\nu}{k_BT}\right)}{\left(\exp\left(\frac{h\nu}{k_BT}\right)-1\right)^2} \end{aligned}$$

Defining $hu/k_B = \theta_E$, where θ_E is the Einstein characteristic temperature, and taking n as equal to Avogadro's number, gives the constant-volume molar heat capacity of the crystal as

$$c_v = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{(e^{\frac{\theta_E}{T}} - 1)^2} \tag{6.6}$$

The variation of c_v with T/θ_E is shown in Figure 6.2a, which shows that as T/θ_E (and hence, T) increases, $c_v \rightarrow 3R$, in agreement with Dulong and Petit's law. We also see that as $T \rightarrow 0$, $c_v \rightarrow 0$, which is in agreement with experimental observations. The actual values of θ_E for any element and its vibration frequency, ν, are obtained by curve-fitting Equation 6.6 to experimentally measured heat capacity data. Such curve fitting, which is shown in Figure 6.2a, shows that although the Einstein equation adequately represents actual heat capacities at higher temperatures, the theoretical values of the Einstein model approach zero more rapidly than do the actual values. For example, as T/θ_E decreases from 0.02 to 0.01, the theoretical molar heat capacity decreases from 1.2×10^{-17} to 9.3×10^{-39} J/K. This discrepancy is caused by the fact that the quantum oscillators do not vibrate with a single frequency, as was assumed by Einstein, as well as the fact that the vibrations are correlated with each other (i.e., they do not vibrate independently of each other, as was also assumed).

The next step in the theory was made in 1912 by Debye (Peter Joseph William Debye, 1884–1966), who assumed that the range of frequencies of vibration (phonons) available to the oscillators is the same as that available to the elastic vibrations in a continuous solid. The lower limit of the wavelength of these vibrations is determined by the interatomic distances in the solid. Taking this minimum wavelength, $\lambda_{\min}$, to be in the order of 5×10^{-10} m, and the wave velocity, v, in the solid to be about 5×10^3 m/sec, gives the maximum frequency of vibration of an oscillator to be of the order of

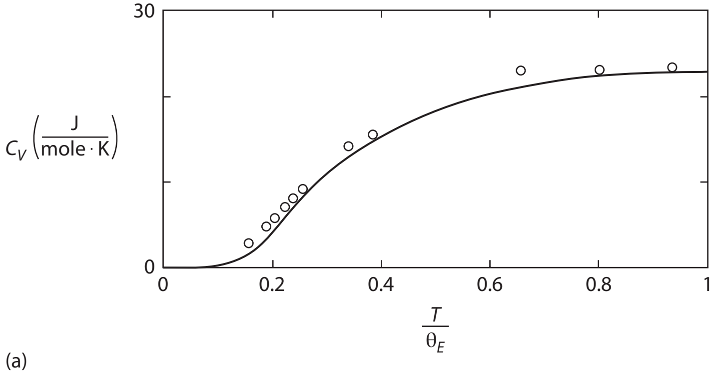


Figure 6.2a (a) The experimental constant-volume heat capacity for diamond, plotted with the best fit to the Einstein model of a solid, Θ_E = 1320 K (Adapted from DeHoff, *Thermodynamics in Materials Science*, CRC Press, Boca Raton, FL, 2006.)

$$v_{\max} = \frac{v}{\lambda_{\min}} = \frac{5\times 10^{3}\ \text{m/s}}{5\times 10^{-10}\ \text{m}} = 10^{13}\ \text{s}^{-1}$$

Debye assumed that the frequency distribution is one in which the number of vibrations per unit volume per unit frequency range increases parabolically with increasing frequency in the allowed range $0 \le v \le v_{\max}$, and, by integrating Einstein's equation over this range of frequencies, he obtained the heat capacity of the solid as

$$c_v = \frac{9nh^3}{k_B^2\theta_D^3}\int_0^{v_D} v^2\left(\frac{h\nu}{k_BT}\right)^2 \frac{\exp(\frac{h\nu}{kT})}{(1-\exp(\frac{h\nu}{kT}))^2}\,dv$$

which, with $x = h\nu/k_BT$, gives

$$c_v = 9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T} \frac{x^4e^{-x}}{(1-e^{-x})^2}\,dx \tag{6.7}$$

where:

v_D (the Debye frequency) = $v_{\max}$

$\theta_D = h\nu_D/k_B$ is the characteristic Debye temperature of the solid

Equation 6.7 is compared with Einstein's equation in Figure 6.2b. Debye's equation approaches the Dulong and Petit limit at high temperatures and shows an excellent fit to the experimental data at lower temperatures. Figure 6.3 shows the curve fitting of Debye's equation to the measured heat capacities of Pb, Ag, Al, and diamond. The curves are nearly identical, except for a horizontal displacement. The relative horizontal displacement is a measure of θ_D. When plotted as c_v versus $\log T/\theta_D$, the data in Figure 6.3 fall on a single curve. This is an example of a law of corresponding states. We will see another example of this when we study the van der Waals gas in Chapter 8.

The value of the integral in Equation 6.7 from zero to infinity is 25.98, and thus, for very low temperatures, Equation 6.7 becomes

$$c_v = 9R\times 25.98\left(\frac{T}{\theta_D}\right)^3 = 1944\left(\frac{T}{\theta_D}\right)^3$$

which is called the *Debye* T^3 *law* for low-temperature heat capacities.

Debye's theory does not consider the contribution made to the heat capacity by the uptake of energy by free electrons at the Fermi level in a metal at low temperatures.

For a metal at low temperatures, the heat capacity varies as

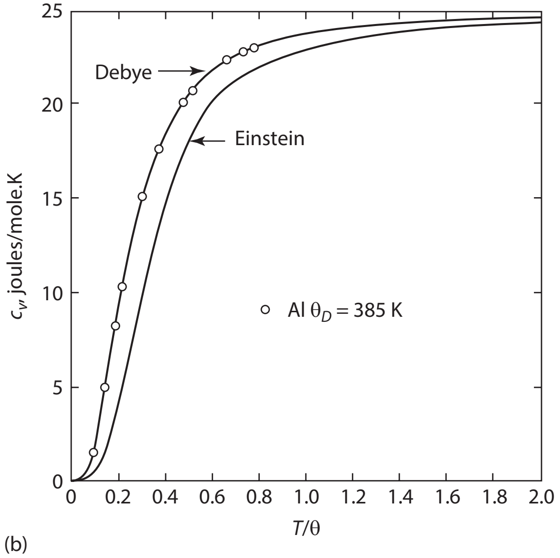


Figure 6.2b (b) Comparisons of the Debye heat capacity, the Einstein heat capacity, and the actual heat capacity of aluminum.

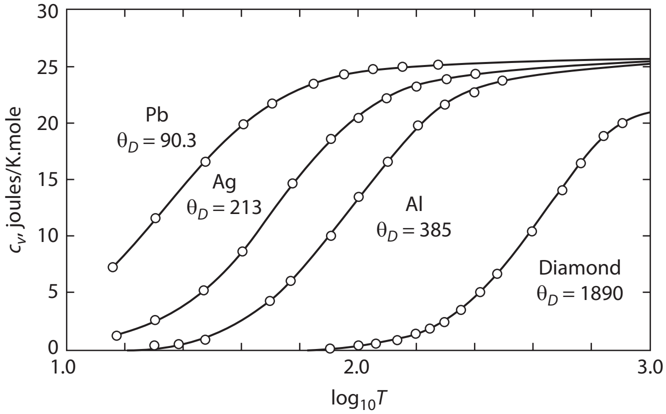


Figure 6.3 The constant-volume molar heat capacities of several solid elements. The curves are the Debye equation with the indicated values of θ_D.

$$c_v = \gamma T + 1943\left(\frac{T}{\theta_D}\right)^3$$

Thus, at temperatures approaching 0 K, c_v for a metal varies linearly with T.

Because of the various uncertainties in the theoretical calculation of heat capacities, it is normal practice to measure the variation of the constant-pressure molar heat capacity with temperature and express the relationship analytically.

6.3 THE EMPIRICAL REPRESENTATION OF HEAT CAPACITIES

The experimentally measured variation of the constant-pressure molar heat capacity of a material with temperature is normally fitted to an expression of the form

$$c_p = a + bT + \frac{c}{T^2}$$

It should be noted that the analytical expression is only applicable in the stated temperature range over which the values of the heat capacity were measured and fit to the equation. For example, ZrO_2 exists as monoclinic α-ZrO_2 from room temperature to 1478 K and as tetragonal β-ZrO_2 in the range of temperature 1478–2670 K, and each polymorph has its own equation giving the variation of its heat capacity with temperature.

$$\alpha - \mathrm{ZrO_2} c_p = 69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^5 T^{-2} \mathrm{J/K \cdot mole}$$

over the temperature range 298–1478 K, and

$$\beta - \mathrm{ZrO_2} c_p = 74.48 \text{ J/K} \cdot \text{mole}$$

from 1478 to 2670 K. At the transition temperature, the heat capacity drops by about 5.6 J/K·mole. In fitting the analytical expression to the measured heat capacities a, b, and c, each have nonzero values in the expression for α-ZrO_2, whereas the molar heat capacity of β-ZrO_2 is independent of temperature, in which case b and c are zero in the analytical expression. The variations, with temperature, of c_p for several elements and compounds which do not undergo phase transitions in the solid state are shown in Figure 6.4, and the variations for some elements which exhibit allotropy and compounds which exhibit polymorphism are shown in Figure 6.5. The data for α-ZrO_2 and β-ZrO_2 are included in Figure 6.5. Other values for the coefficients of the analytical expressions for selected elements and compounds are found in Table A-2 of Appendix A.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

For one mole of a closed system of fixed composition undergoing a change in temperature from T_1 to T_2 at the constant pressure P, integration of Equation 2.6b gives Equation 6.1:

$$\Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} c_p dT \tag{6.1}$$

ΔH is thus the area under a plot of c_p versus T between the limits T_1 and T_2. The change in enthalpy is thus $\Delta H = q_p$, which is simply the amount of thermal energy

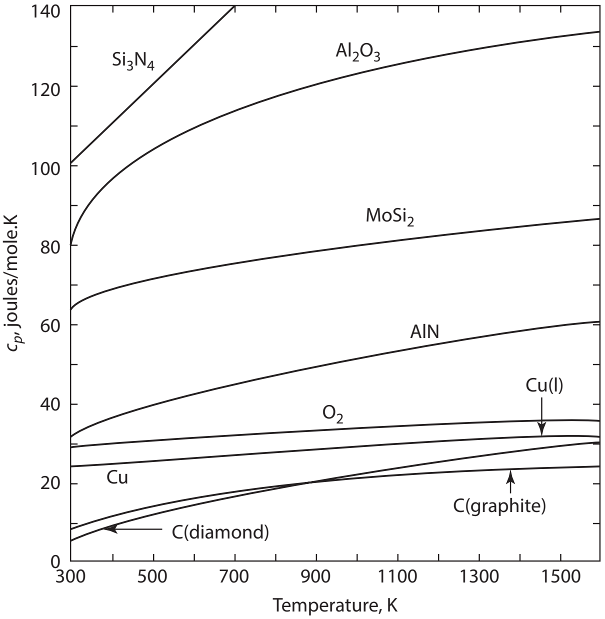


Figure 6.4 The variations, with temperature, of the constant-pressure heat capacities of several elements and compounds.

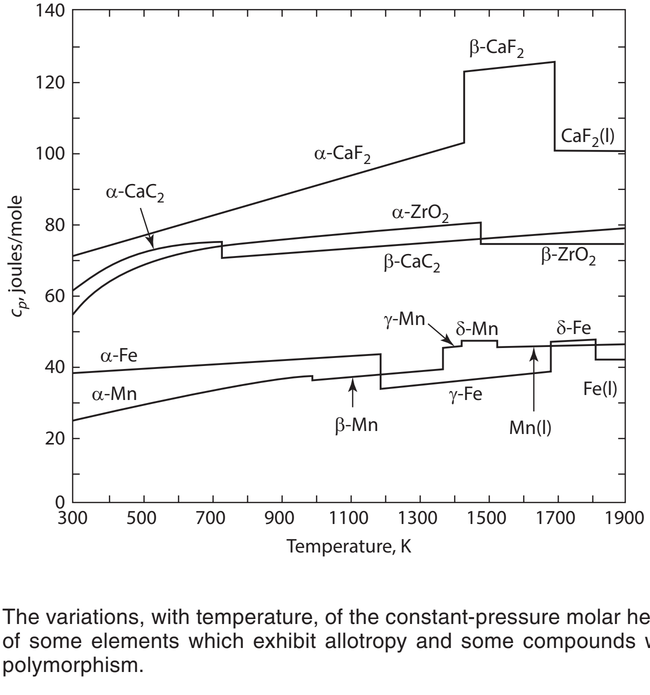


Figure 6.5 The variations, with temperature, of the constant-pressure molar heat capacities of some elements which exhibit allotropy and some compounds which exhibit polymorphism.

required to enter the system and to increase the temperature of 1 mole of the system from T_1 to T_2 at the constant pressure P.

When one mole of a system undergoes a chemical reaction or a phase transformation at constant temperature and pressure (e.g., the reaction $A + B = AB$), ΔH is the difference between the enthalpy of the products of the reaction (state 2) and the enthalpy of the reactants (state 1); that is,

$$\Delta H\left(T,P\right)=H_{AB}\left(T,P\right)-[H_A\left(T,P\right)+H_B\left(T,P\right)] \tag{6.8}$$

If ΔH is a positive quantity, the reaction causes the system to absorb thermal energy from its constant-temperature heat bath, and the reaction is called *endothermic*. Conversely, if ΔH is a negative quantity, the reaction occurs with an evolution of thermal energy and is called an *exothermic* process. This convention is the same as that used with the First Law for the sign of q, the thermal energy entering or leaving the system. The changes in enthalpy caused by changes in temperature and/or composition can be graphically represented on an enthalpy–temperature diagram (Figure 6.6). Consider the change of state

$$A_{(l)} \rightarrow A_{(s)}$$

That is, the solidification of liquid A, whose equilibrium solidification temperature (which is also the equilibrium melting temperature) is T_2. The segment cd is the change in enthalpy at the equilibrium liquid-to-solid transformation; that is, it is the heat of solidification and can be seen to be $H_S(T_2) - H_L(T_2) < 0$ (exothermic). A supercooled liquid can transform to a solid at T_1. The molar enthalpy of transformation at this temperature can be determined, since the enthalpy is a state function. Thus,

$$\Delta H\left(b\rightarrow a\right)=\Delta H\left(b\rightarrow c\right)+\Delta H\left(c\rightarrow d\right)+\Delta H\left(d\rightarrow a\right) \tag{i}$$

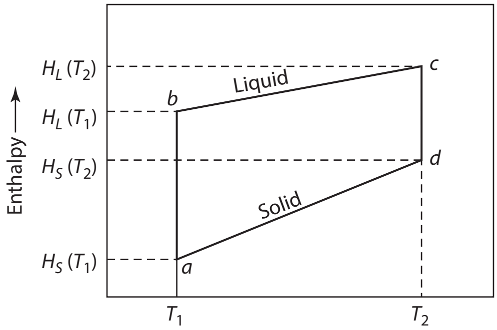


Figure 6.6 The variation, with temperature, of the molar enthalpies of the solid and liquid phases of a substance.

- $\Delta H(b \rightarrow a) = \Delta H(l \rightarrow s,T_1)$ is the molar enthalpy of transformation of the supercooled liquid to the solid at the temperature T_1.

  $$\Delta H(l \rightarrow s,T_1) = H(s,T_1) - H(l,T_2)$$

  This change in enthalpy is represented by *ba* in Figure 6.6 and is negative (exothermic).
- $\Delta H(b \rightarrow c)$ is the thermal energy which needs to be supplied to 1 mole of liquid to increase its temperature from T_1 to T_2.

  $$\int_{T_1}^{T_2} c_p(l)dT$$

  in which $c_p(l)$ is the molar heat capacity of liquid.
- $\Delta H(c \rightarrow d) = \Delta H(l \rightarrow s,T_2) = H(s,T_2) - H(l,T_2)$ is the molar enthalpy of transformation of the liquid at the equilibrium transition temperature T_2, which is represented in Figure 6.6 by *cd*.
- $\Delta H(d \rightarrow a)$ is the thermal energy required to leave the solid and decrease the temperature of 1 mole of solid from T_2 to T_1 at constant pressure.

  $$\Delta H\left(d \rightarrow a\right) = \int_{T_2}^{T_1} c_p(s)dT$$

  in which $c_p(s)$ is the molar heat capacity of solid. Substitution of the individual expressions into Equation (i) gives

  $$\Delta H(l \rightarrow s,T_1) = \int_{T_1}^{T_2} c_p(l)dT + \Delta H(l \rightarrow s,T_2) + \int_{T_2}^{T_1} c_p(s)dT$$

  $$\Delta H(l \rightarrow s,T_1) = \int_{T_1}^{T_2} \Delta c_p dT + \Delta H(l \rightarrow s,T_2) \qquad (6.9)$$

  Where $\Delta c_p = c_p(l) - c_p(s)$.
  The molar enthalpy of solidification (fusion) at T_1 is more negative than at T_2 for the material shown in Figure 6.6. Each of the terms on the right hand of Equation 6.9 are negative.

Thus, if the molar enthalpy of fusion is known at one temperature and the constant-pressure heat capacities of the products and the reactants are known (along with their dependencies on temperature), then the molar enthalpy of fusion at any other temperature can be calculated. It is to be noted that if $\Delta c_p = 0$, then $\Delta H_{T_2} = \Delta H_{T_1}$; that is, the thermal energy of the reaction, ΔH, is independent of the temperature. In Figure 6.6, the slope of the line *ad*, which is $\left(\partial H/\partial T\right)_P$, is the molar heat capacity of the solid, c_p. It is a straight line only if the heat capacity is independent of temperature.

Since H does not have an absolute value (only changes in H can be measured), it is convenient to introduce a convention which will allow the comparison of different enthalpy–temperature diagrams. This convention assigns the value of zero to the enthalpy of *elements in their stable states at 298 K* (25°C) and $P = 1$ atm. Thus, the enthalpy of a compound at 298 K and $P = 1$ atm is simply the enthalpy of formation of one mole of the compound from its elements at 298 K and $P = 1$ atm. For example, for the oxidation reaction

$$M_{(\text{solid})} + \frac{1}{2}O_{2(\text{gas})} = MO_{(\text{solid})} \text{ at 298 K and } P = 1 \text{ atm}$$

$$\Delta H_{298} = H_{\text{MO}(s)298} - H_{\text{M}(s)298} - \frac{1}{2}H_{\text{O}_2(g)298}$$

and, since $H_{\text{M},298}$ and $H_{\text{O}_2,298}$ are by convention set equal to zero, then

$$\Delta H_{298} = H_{\text{MO},298}$$

The variation of heats of chemical reaction (or heats of formation) with temperature at constant pressure can be represented on an enthalpy–temperature diagram, such as those in Figure 6.7a and b, which are drawn for the oxidation reaction

$$\text{Pb} + \frac{1}{2}\text{O}_2 = \text{PbO}$$

The pertinent thermochemical data for this system are listed in Table 6.1.

In Figure 6.7a:

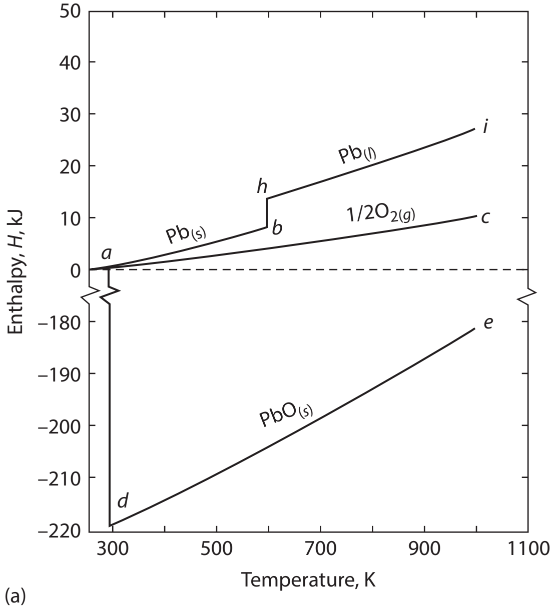
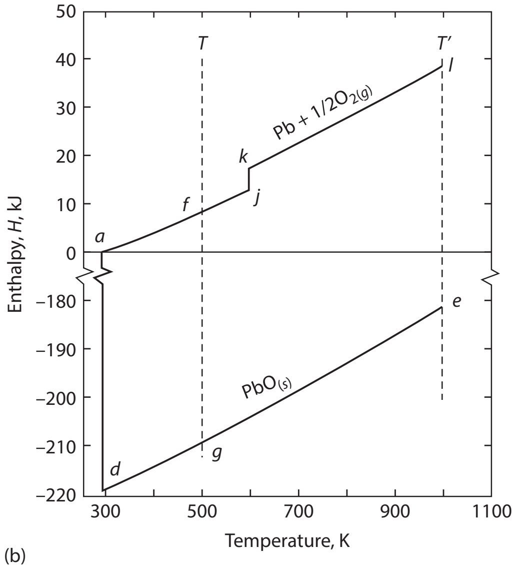


Figure 6.7a (a) The variation, with temperature, of the enthalpies of $\text{Pb}_{(s)}$, $\text{Pb}_{(l)}$, $1/2\text{O}_{2(g)}$, and $\text{PbO}_{(s)}$.



(b)

Figure 6.7b (b) The variation, with temperature, of the enthalpies of (Pb + $1/2O_2$) and PbO.

Table 6.1 Thermochemical Data for Pb, PbO, and O_2

$H_{Pbo(298)} = -219{,}000$ J/K
$c_{p,Pb(s)} = 23.6 + 9.75 \times 10^{-3}T$ J/K from 298 K to $T_{m,Pb}$
$c_{p,Pb(l)} = 32.4 - 3.1 \times 10^{-3}T$ J/K from $T_{m,Pb}$ to 1200 K
$c_{p,PbO(s)} = 37.9 + 26.8 \times 10^{-3}T$ J/K from 298 K to $T_{m,Pbo}$
$c_{p,O_2(g)} = 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{5}T^{-2}$ J/K from 298 K to 3000 K
$\Delta H_{m,Pb} = 4810$ J at $T_{m,Pb} = 600$ K
$T_{m,PbO} = 1159$ K

- *a* represents the enthalpy of 1/2 mole of oxygen gas and 1 mole of $Pb_{(s)}$ at 298 K (set = 0 by convention).
- *ab* represents the variation of $H_{Pb(s)}$ with temperature in the range $298 \le T \le 600$ K, where $H_{Pb(s)}, T$ is given by $\int_{298}^{T} c_{p,\,Pb(s)}\, dT$.
- *ac* represents the variation of $H_{\frac{1}{2}O_2(g)}$ with temperature in the range $298 < T < 3000$ K, where $H_{\frac{1}{2}O_2(g)}$ is given by $\frac{1}{2}\int_{298}^{T} c_{p,O_2(g)}\, dT$.
- *ad* is $\Delta H_{PbO(s),298\text{ K}} = -219{,}000$ J.
- *de* represents the variation of $H_{PbO(s)}$ with temperature in the range 298 K $\le T \le$ 1159 K, where $H_{PbO(s),T} = -219{,}000 + \int_{298}^{T} c_{p,PbO(s)} dT$ J.

In Figure 6.7b:

- *a* represents the enthalpy of 1/2 mole of $O_{2(g)}$ and 1 mole of $Pb_{(s)}$ at 298 K.
- *f* represents the enthalpy of 1/2 mole of $O_{2(g)}$ and 1 mole of $Pb_{(s)}$ at the temperature *T*.
- *g* represents the enthalpy of 1 mole of $PbO_{(s)}$ at the temperature *T*.

Thus,

$$\begin{aligned}\Delta H_{\text{PbO},298\text{ K}} &= \Delta H(a \to f) + \Delta H(f \to g) + \Delta H\ (g \to d)\\ &= \int_{298}^{T}\left(\frac{1}{2}c_{p,\text{O}_2(g)} + c_{p,\text{Pb}(s)}\right)dT + \Delta H_{\text{PbO},T} + \int_{T}^{298} c_{p,\text{PbO}(s)}dT\end{aligned}$$

and thus,

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta c_p dT$$

where:

$$\Delta c_p = c_{p,\text{PbO}(s)} - c_{p,\text{Pb}(s)} - \frac{1}{2}c_{p,\text{O}_2(g)}$$

From the data in Table 6.1,

$$\Delta c_p = -0.7 + 14.96\times 10^{-3}T + 0.85\times 10^{5}T^{-2}$$

and, thus, in the range of temperature from 298 to 600 K ($T_{m,\text{Pb}}$):

$$\begin{aligned}\Delta H_T &= -219{,}000 + \int_{298}^{T}(-0.7 + 14.96\times 10^{-3}T + 0.85\times 10^{5}T^{-2})dT\\ &= -219{,}000 - 0.7(T - 298) + 7.48\times 10^{-3}(T^2 - 298^2)\\ &\quad - 0.85\times 10^{5}\left(\frac{1}{T} - \frac{1}{298}\right)\end{aligned}$$

With T = 500 K, this gives $\Delta H_{500\text{ K}}$ = –217,800 J, as can be seen in Figures 6.7b and 6.8. If a phase change occurs in one or more of the reactants or products, between the two temperatures at which the reaction is being considered, then the enthalpies of transformation of the phase changes must be considered. In Figure 6.7a, *h* represents the enthalpy of 1 mole of $\text{Pb}_{(l)}$ at the melting temperature of 600 K, given as

$$H_{\text{Pb}(l),600\text{K}} = \int_{298}^{600} c_{p,\text{Pb}(s)}dT + \Delta H_{m,\text{Pb}}$$

hb is the enthalpy of melting of Pb at the melting temperature of 600 K (= 4810 J), and *hi* represents the variation of the enthalpy of 1 mole of $\text{Pb}_{(l)}$ with temperature in the range 600–1200 K.

$$H_{\text{Pb}(l),T} = \int_{298}^{600} c_{p,\text{Pb}(s)}dT + \Delta H_{m,\text{Pb}} + \int_{600}^{T} c_{p,\text{Pb}(l)}dT$$

In Figure 6.7b, *ajkl* represents the variation of the enthalpy of 1 mole of Pb and 1/2 moles of $\text{O}_{2(g)}$, and hence, $\Delta H_{T'}$ is calculated from the cycle

$$\Delta H_{298\,\mathrm{K}} = \Delta H(a \to d) = \Delta H(a \to j) + \Delta H(j \to k) + \Delta H(k \to l)$$
$$+ \Delta H(l \to e) + \Delta H(e \to g) + \Delta H(g \to d)$$

where:

$$\Delta H(a \to j) = \int_{298}^{T_{m,\mathrm{Pb}}} \left(c_{p,\mathrm{Pb}(s)} + \frac{1}{2} c_{p\mathrm{O}_2(g)} \right) dT$$

$\Delta H(j \to k) =$ the latent heat of melting of Pb at $T_{m,\mathrm{Pb}} = 4810$ J

$$\Delta H(k \to l) = \int_{T_{m,Pb}}^{T} \left(c_{p,\mathrm{Pb}(l)} + \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$

$$\Delta H(l \to e) = \Delta H_T$$

$$\Delta H(e \to g) = \int_{T}^{T_{m,\mathrm{Pb}}} c_{p,\mathrm{PbO}(s)} dT$$

$$\Delta H(g \to d) = \int_{T_{m,\mathrm{Pb}}}^{298} c_{p,\mathrm{PbO}(s)} dT$$

Thus,

$$\Delta H_T = \Delta H_{298K} + \int_{298}^{T_{m,\mathrm{Pb}}} \left(c_{p,\mathrm{PbO}(s)} - c_{p,\mathrm{Pb}(s)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$
$$- \Delta H_{m,\mathrm{Pb}} + \int_{T_{m,\mathrm{Pb}}}^{T} \left(c_{p,\mathrm{PbO}(s)} - c_{p,\mathrm{Pb}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$
$$= -219{,}000 + \int_{298}^{600} (-0.7 + 14.96 \times 10^{-3} T + 0.85 \times 10^{5} T^{-2}) dT$$
$$- 4810 + \int_{600}^{T} (-9.3 + 27.8 \times 10^{-3} T + 0.85 \times 10^{5} T^{-2}) dT$$

This gives $\Delta H_{1000} = -216{,}700$ J at $T' = 1000$ K, as is seen in Figures 6.7b and 6.8. Figure 6.8 shows the variation of $\Delta H_{\mathrm{PbO},T}$ with temperature in the range 298–1100 K. If the temperature of interest is higher than the melting temperatures of both the metal and its oxide, then both enthalpies of melting must be considered. For example, with reference to Figure 6.9, which is drawn for the general oxidation,

$$\mathrm{M} + \frac{1}{2}\mathrm{O}_2 = \mathrm{MO}$$

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T_{m,\mathrm{M}}} \left(c_{p,\mathrm{MO}(s)} - c_{p,\mathrm{M}(s)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$
$$- \Delta H_{m,\mathrm{M}} + \int_{T_{m,\mathrm{M}}}^{T_{m,\mathrm{MO}}} \left(c_{p,\mathrm{MO}(s)} - c_{p,\mathrm{M}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$
$$+ \Delta H_{m,\mathrm{MO}} + \int_{T_{m,\mathrm{MO}}}^{T} \left(c_{p,\mathrm{MO}(l)} - c_{p,\mathrm{M}(l)} - \frac{1}{2} c_{p,\mathrm{O}_2(g)} \right) dT$$

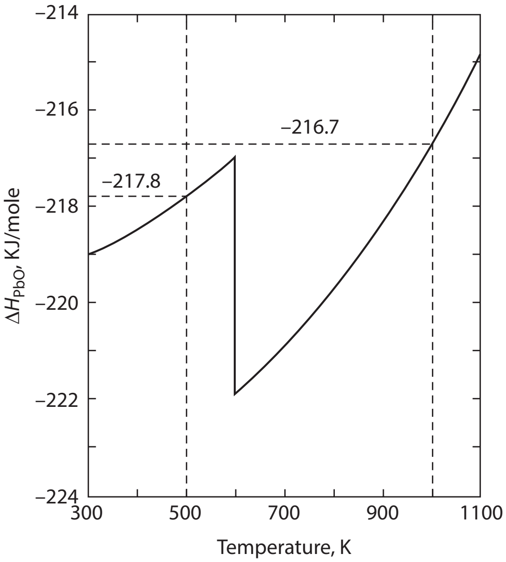


Figure 6.8 The variation, with temperature, of the enthalpy change for the reaction Pb + $1/2O_2$ = PbO.

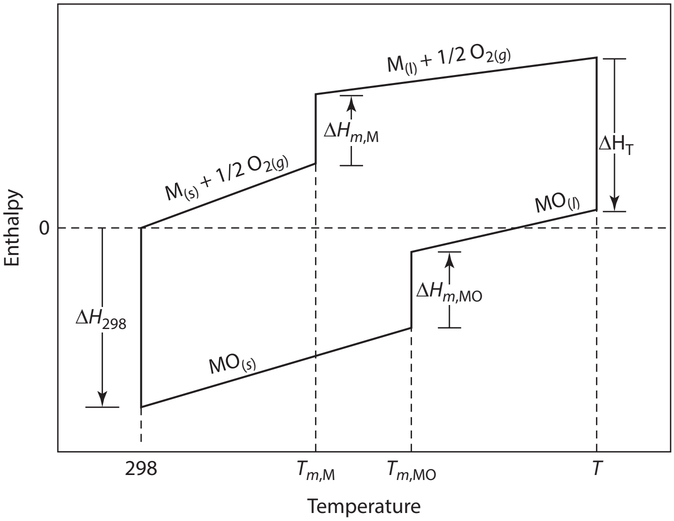


Figure 6.9 The effect of phase changes on ΔH for a chemical reaction.

When phase transformations of the reactants or products have to be considered, care must be taken with the signs of the changes in enthalpy. The signs can be obtained from a consideration of *Le Chatelier's principle* (Henry Louis Le Chatelier, 1850–1936), which can be stated as, "When a system, which is at equilibrium, is subjected to an external influence, the system moves in that direction which nullifies the effects of the external influence." Thus, if the system contains a low-temperature phase in equilibrium with a high-temperature phase at the equilibrium phase transition temperature, such as a solid coexisting with a liquid at the equilibrium melting temperature, then the introduction of heat to the system (the external influence) would be expected to increase the temperature of the system (the effect). However, the system undergoes an endothermic change, which absorbs the heat introduced at constant temperature and hence nullifies the effect of the external influence. The endothermic process is the melting of some of the solid. A phase change from a low- to a high-temperature phase is always endothermic, and hence, ΔH for the change is always a positive quantity. Thus, ΔH_m, the molar enthalpy of melting, which is the difference between the enthalpy of a mole of liquid and the enthalpy of a mole of solid, is always positive.

Consider a phase transition between two allotropes, α and β, the β being the high-temperature allotrope.

$$\text{For } \alpha\text{:} \quad \left(\frac{\partial H_\alpha}{\partial T}\right)_P = c_p^\alpha$$

$$\text{For } \beta\text{:} \quad \left(\frac{\partial H_\beta}{\partial T}\right)_P = c_p^\beta$$

Subtraction gives

$$\left(\frac{\partial H_\beta}{\partial T}\right)_P - \left(\frac{\partial H_\alpha}{\partial T}\right)_P = c_p^\beta - c_p^\alpha$$

$$\left(\frac{\partial (H_\beta - H_\alpha)}{\partial T}\right)_P = \Delta c_p$$

or

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta c_p \tag{6.10}$$

and integrating from state 1 to state 2 gives

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta c_p dT \tag{6.11}$$

Equations 6.10 and 6.11 are expressions of *Kirchhoff's law* (Gustav Robert Kirchhoff, 1824–1887).

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

6.5.1 Development of the Third Law of Thermodynamics

The molar change in Gibbs free energy for a reaction is given as

$$\Delta G = \Delta H - T\Delta S$$

If this expression can be determined as a function of temperature, the driving force for the reaction would be determined.
We have seen that ΔH for a reaction is given as

$$\Delta H(T_2) - \Delta H(T_1) = \int_{T_1}^{T_2} \Delta c_p dT$$

If the heat capacities of the reactants are known as a function of temperature, ΔH can be calculated at any temperature.

What about ΔS for a reaction at any temperature? For a closed system undergoing a reversible process, the Second Law gives

$$dS = \frac{\delta q_{\text{rev}}}{T} \tag{3.8}$$

If the process is conducted at constant pressure, then

$$dS = \left(\frac{\delta q_{\text{rev}}}{T}\right)_P = \left(\frac{dH}{T}\right)_P = \frac{c_p dT}{T}$$

and thus, if the temperature of a closed system of fixed composition is increased from T_1 to T_2 at constant pressure, the increase in the entropy per mole of the system, ΔS, is given by

$$\Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} \frac{c_p}{T} dT \tag{6.12}$$

This change of entropy is obtained as the area under a plot of c_p/T versus T between the limits T_2 and T_1, or, equivalently, as the area under a plot of c_p versus $\ln T$ between the limits $\ln T_2$ and $\ln T_1$. Generally, S_T, the molar entropy of the system at any temperature T, is given by

$$S_T = S_0 + \int_0^T \frac{c_p}{T} dT \tag{6.13}$$

where S_0 is the molar entropy of the system at 0 K. In turn, the Gibbs free energy can be written as

$$\Delta G = \int_0^T c_P dT - T\int_0^T \frac{c_P}{T} dT - TS_0$$

Clearly, if the entropy at 0 K is known, the thermodynamics of the reaction is completely known. This was proposed by Le Chatelier in 1888:

> It is highly probable that the constant of integration is a determinate function of certain physical properties of the substances in question. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium. It would permit us to determine a priori independently of any new experimental data, the full conditions of equilibrium corresponding to a chemical reaction.*

In other words, if the value of S_0 for a reaction could be determined, ΔG would be known as a function of temperature as well, and hence, the reaction thermodynamics would be known. Consideration of the value of S_0 in the late nineteenth and early twentieth century lead to the statement of the Third Law of Thermodynamics.

In 1902, Richards (Theodore William Richards, 1868–1928) collected data which showed, for many reactions, the values of ΔG and ΔH asymptotically approached each other at low temperatures with slopes that approached zero; that is,

$$\text{as T} \rightarrow 0 \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P \quad = \quad \left(\frac{\partial \Delta H}{\partial T}\right)_P = 0$$

In 1906, Nernst (Walther Hermann Nernst 1864–1941) postulated that this was true for all reactions involving liquids and solids, and this has become known as the *Nernst heat theorem*.

For any change in the state of a system (e.g., a chemical reaction at the constant temperature T):

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

and thus, ΔG for the reaction varies with temperature, as shown in Figure 6.10. Note that the values of ΔG, ΔH, and ΔS are for the transformation of the low-temperature state to that of the high-temperature state ($\alpha \rightarrow \beta$).

The slope of the line in Figure 6.10, at any temperature, is equal to $-\Delta S_T$, and the intercept, with the ΔG axis at $T = 0$, of the tangent to the line at any temperature is equal to ΔH_T, the change in the enthalpy at the temperature T. As the temperature approaches zero, the slope of both the ΔG and ΔH curves approaches zero. The consequences of this are that, as $T \rightarrow 0$, then $\Delta S \rightarrow 0$ and $\Delta c_p \rightarrow 0$. At constant p,

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* H. Le Chatelier, *Ann. Mines*, vol. 13, pp. 157ff., 1888. Translated by Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923, pp. 436ff.

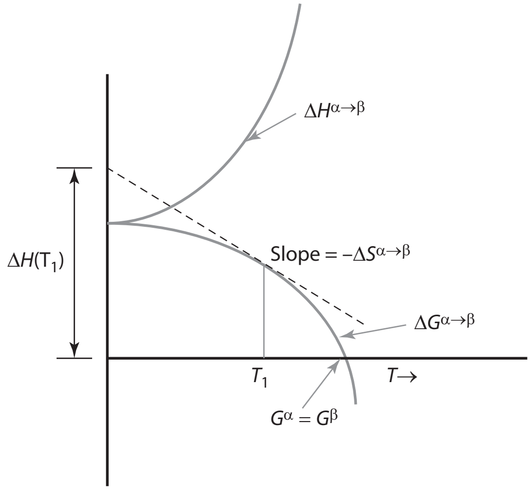

Figure 6.10 The variation of the change in the Gibbs free energy and the enthalpy for a reaction with temperature. As the temperature approaches absolute zero, their values approach each other and their slopes approach 0.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S$$

But,

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

and thus,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P = \Delta c_p$$

Since $\left(\partial \Delta G/\partial T\right)_P$ and $\left(\partial \Delta H/\partial T\right)_P$ approach zero as $T \to 0$, the values of ΔS and Δc_p approach zero as $T \to 0$ (provided that $\left(\partial \Delta S/\partial T\right)_P$ is not infinite at $T = 0$).

Thus, for the general reaction

$$A + B = AB$$

$\Delta S = S_{AB} - S_A - S_B = 0$ at $T = 0$, which shows that if the entropies of the pure substances A and B are equal to zero at 0 K, then the value of the entropy of the compound AB is also zero.

Planck (Max Karl Ernst Ludwig Planck, 1858–1947) extended the Nernst's heat theorem by positing to the effect that the entropy of any homogeneous substance which is in complete internal equilibrium is zero at 0 K. This has become known as the *Nernst–Planck–Simon statement* (Francis Simon, 1893–1956) of the Third Law. Thus, in the aforementioned reaction (the entropy of AB), the entropy of A and the entropy of B would all be zero at 0 K under the specifications of Planck. This statement summarizes the Third Law of Thermodynamics and has ramifications on the types of phases that are stable at the absolute zero. This will be utilized later in the text when equilibrium phase diagrams are discussed.

6.5.2 Apparent Contradictions to the Third Law of Thermodynamics

The requirement that the substance be in complete internal equilibrium is an important part of the statement of the Third Law of Thermodynamics. Counterexamples to the Third Law that are often brought against it fail in some way to have the system in complete equilibrium. Several examples of such purported failings of the Third Law follow.

1. Glasses are noncrystalline solids which form from supercooled liquids in which the disordered atomic arrangements occurring in the liquid state have been "frozen" into the solid state. Substances which form glasses often have complex atomic, ionic, or molecular structures in the liquid state, and the structures would require extensive atomic reorganization in order to assume a periodic structure characteristic of its equilibrium crystalline state. In the absence of the ability of the glass-forming substance to undergo the necessary atomic rearrangement at its freezing temperature, the supercooled liquid simply becomes more and more viscous and eventually loses its rotational degrees of freedom and forms a solid glass. If the solid glass were to crystallize, its enthalpy and entropy would decrease, and the decreases in the enthalpy and entropy would be, respectively, the enthalpy and entropy of crystallization at the temperature at which devitrification occurred. At temperatures below its equilibrium freezing temperature, the glassy state is not stable with respect to the crystalline state, and a glass, not being in internal equilibrium, has an entropy at 0 K which is greater than zero by an amount which is dependent on the cooling rate and the degree of atomic disorder in the glass.
2. Solutions are mixtures of atoms, ions, or molecules, and a contribution is made to their entropies by the fact that they are mixtures (see Equation 4.3). This contribution is called the *entropy of mixing* and is determined by the randomness with which the particles are mixed in the solution. The atomic randomness of a mixture determines its degree of order; for example, in a mixture containing 50 at% of A and 50 at% of B, complete ordering occurs when every atom of A is coordinated only by B atoms and vice versa, and complete randomness occurs when, on average, 50% of the neighbors of every atom are A atoms and 50% are B atoms.

   The degrees of order in these two extreme configurations are respectively unity and zero. The equilibrium degree of order is temperature dependent and increases with decreasing temperature. However, the maintenance of the equilibrium degree of order is dependent on the abilities of the particles to change their positions in the solution, and, with ever-decreasing temperature, as atomic mobility decreases exponentially with decreasing temperature, the maintenance of internal equilibrium becomes increasingly difficult. Consequently, a nonequilibrium degree of order can be frozen into the solid solution, in which case the entropy will not decrease to zero at 0 K.

3. Even chemically pure elements are mixtures of isotopes, and because of the chemical similarity between isotopes, it is to be expected that completely random mixing of the isotopes occurs. Thus, an entropy of mixing occurs, and consequently, the entropy does not decrease to zero at 0 K. For example, solid chlorine at 0 K is a solid solution of Cl^{35}–Cl^{35}, Cl^{35}–Cl^{37}, and Cl^{37}–Cl^{37} molecules. However, since this entropy of mixing is present in any other substance which contains the element, it is customary to ignore this aspect of the entropy.
4. At any finite temperature, a pure crystalline solid contains an equilibrium number of vacant lattice sites, which, because of their random positioning in the crystal, give rise to an entropy of mixing which is similar to the entropy of mixing in a chemical solution. Both the equilibrium number of vacancies and the diffusivity of the atoms in the crystal decrease exponentially with decreasing temperature, and since the vacancies “disappear” by diffusing to the free surface of the crystal, nonequilibrium concentrations of vacancies can be frozen into the crystal at low temperatures if diffusion is limited, causing a nonzero entropy at 0 K.
5. Random crystallographic orientation of molecules in the crystalline state can also give rise to a nonzero entropy at 0 K. Such is the case with solid CO, in which a structure such as the following can occur.

CO CO OC CO OC CO CO
OC CO CO OC CO OC OC
OC CO CO OC OC CO CO

The entropy would have its maximum value if equal numbers of molecules were oriented in opposite directions and random mixing of the two orientations occurred. From Equation 4.3, the molar configurational entropy of mixing would be

$$\Delta S_{\text{conf}} = k \ln \frac{(N_O)!}{\left(\frac{1}{2}N_O\right)!\left(\frac{1}{2}N_O\right)!}$$

where N_O is Avogadro’s Number, 6.0232×10^{23}. Thus, using Stirling’s approximation,

$$\begin{aligned}\Delta S_{\text{conf}} &= k\left[N_O \ln N_O - \frac{1}{2}N_O \ln\left(\frac{1}{2}N_O\right) - \frac{1}{2}N_O \ln\left(\frac{1}{2}N_O\right)\right] \\ &= k \times 4.175 \times 10^{23} \\ &= 1.38054 \times 10^{-23} \times 4.175 \times 10^{23} \\ &= 5.76\ \text{J/mole} \cdot \text{K}\end{aligned}$$

A comparison of this value with the measured value of 4.2 J/mole·K indicates that the actual molecular orientations in solid CO are not fully random.

In view of the these considerations, the statement of the Third Law of Thermodynamics requires the inclusion of the qualification that the system in question be in *complete internal equilibrium*.

In the next section, we discuss the experimental verification of the Third Law.

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

The Third Law can be verified by considering the phase transition of one mole of an element, such as

$$\alpha \to \beta$$

where α and β are allotropes of the element. In Figure 6.11, T_{trans} is the temperature, at atmospheric pressure, at which the α and β phases are in equilibrium with one another. For the cycle shown in Figure 6.11,

$$\Delta S_{\text{IV}} = \Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}}$$

For the Third Law to be obeyed, $\Delta S_{\text{IV}} = 0$, which requires that

$$\Delta S_{\text{II}} = -(\Delta S_{\text{I}} + \Delta S_{\text{III}})$$

where:

$$\Delta S_{\text{I}} = \int_0^{T_{\text{trans}}} \frac{c_{p(\alpha)}}{T} dT$$

$$\Delta S_{\text{II}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} = H(\beta, T_{\text{trans}}) - H(\alpha, T_{\text{trans}})$$

$$\Delta S_{\text{III}} = \int_{T_{\text{trans}}}^{0} \frac{c_{p(\beta)}}{T} dT$$

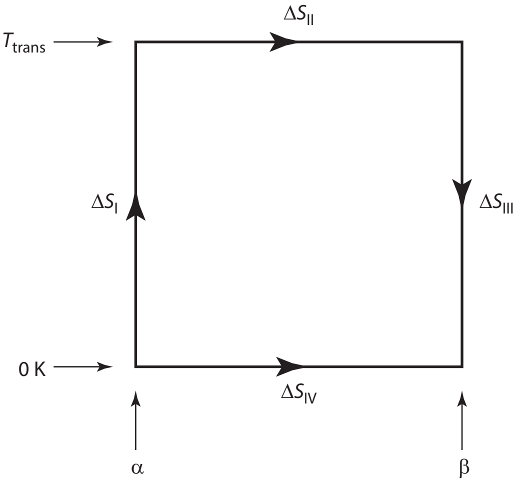

Figure 6.11 The cycle used for the experimental verification of the Third Law of Thermodynamics.

ΔS_{II} is called the *experimental entropy change*, and $-(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{III}})$ is called the *Third Law entropy change*. If the Third Law is valid, $\Delta S_{\mathrm{II}} = -(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{III}})$.

The cycle shown in Figure 6.11 has been examined for the case of sulfur, which has two allotropes: a monoclinic form which is stable above 368.5 K and an orthorhombic form which is stable below 368.5 K, with a molar enthalpy of transformation of 400 J/mole at the equilibrium transformation temperature of 368.5 K. Since monoclinic sulfur can be supercooled with relative ease, the variations, with temperature, of the heat capacities of both allotropes have been measured experimentally at temperatures below 368.5 K. The measured heat capacities give

$$\Delta S_{\mathrm{I}} = \int_0^{368.5} \frac{c_{p(\mathrm{rhombic})}}{T}\, dT = 36.86 \text{ J/K}$$

$$\Delta S_{\mathrm{II}} = \frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}} = \frac{400}{368.5} = 1.09 \text{ J/K}$$

and

$$\Delta S_{\mathrm{III}} \int_{368.5}^{0} \frac{c_{p(\mathrm{monoclinic})}}{T}\, dT = -37.8 \text{ J/K}$$

Thus,

$$\left(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{III}}\right) = -\left(36.86 - 37.8\right) = 0.94 \text{ J/K}$$

This is the value of the Third Law entropy change. The value of the experimental entropy change ΔS_{II} was shown to be 1.09 J/K. Since the difference between the experimental and the Third Law entropy changes (0.15 J/K) is less than the experimental error, the equality is taken as being an experimental verification of the Third Law. The same has been shown to be valid for many other allotropes.

Assigning a value of zero to S_0 allows the absolute value of the entropy of any material to be determined as

$$S_T = \int_0^T \frac{c_p}{T}\, dT \text{ J/K}$$

and molar entropies are normally tabulated at 298 K, where:

$$S_{298} = \int_0^{298} \frac{c_p}{T}\, dT \text{ J/K}$$

The variations, with temperature, of the molar entropies of several elements and compounds are shown in Figure 6.12. With the constant-pressure molar heat capacity of the solid expressed in the form

$$c_{p(s)} = a + bT + cT^{-2}$$

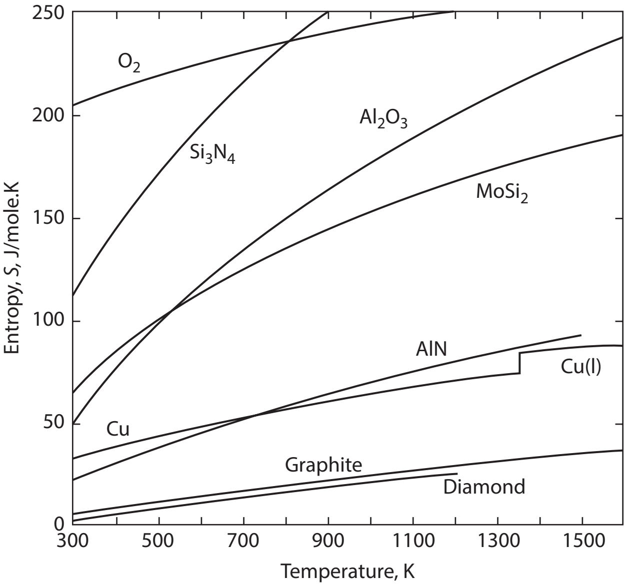

Figure 6.12 The variation, with temperature, of the molar entropies of several elements and compounds.

the molar entropy of the solid at the temperature T is obtained as

$$S_T = S_{298} + a\ln\left(\frac{T}{298}\right) + b(T-298) - \frac{1}{2}c\left(\frac{1}{T^2} - \frac{1}{298^2}\right)$$

At temperatures higher than the melting temperature, T_m, the molar entropy of the liquid is obtained as

$$S_T = S_{298} + \int_{298}^{T_m} \frac{c_{p(s)}}{T}\,dT + \Delta S_m + \int_{T_m}^{T} \frac{c_{p(l)}}{T}\,dT$$

where the molar entropy of the melting, ΔS_m, is obtained as $\Delta H_m / T_m$.

In 1897, Richards suggested that the enthalpies of fusion of metals should have the same value, which would require that a plot of ΔH_m versus T_m be a straight line. Figure 6.13 is a plot of the molar enthalpies of fusion versus the melting temperatures of 11 face-centered cubic (FCC) metals (open circles) and 27 body-centered cubic (BCC) metals (closed circles) which have melting temperatures below 3000 K. A least-squares analysis of the data for the face-centered cubic metals gives for the molar entropies of melting:

$$\Delta S_m^{\text{FCC}} = \frac{\Delta H_m^{\text{FCC}}}{T_m} = 9.6 \text{ J/K}$$

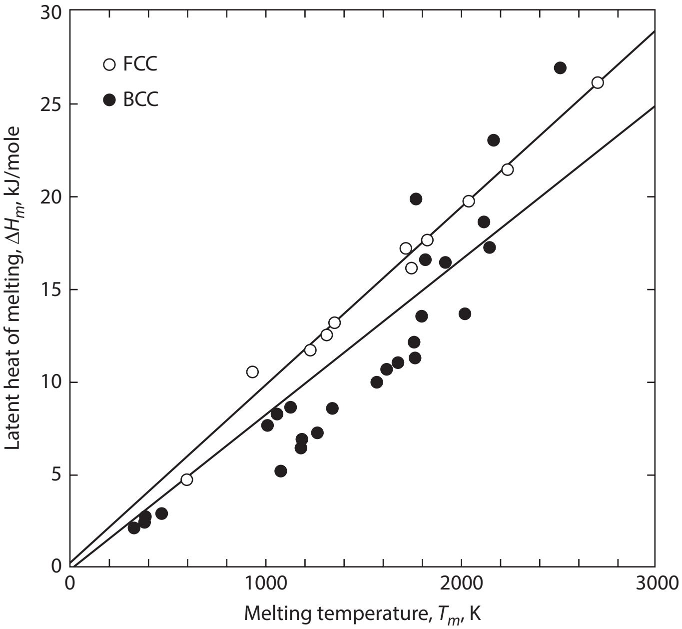

Figure 6.13 An illustration of Richard's rule.

and for body-centered cubic metals:

$$\Delta S_m^{\mathrm{BCC}} = \frac{\Delta H_m^{\mathrm{BCC}}}{T_m} = 8.25 \text{ J/K}$$

This observation, which is known as *Richards's rule*, indicates that the difference between the degree of disorder in the liquid structure (due to configurational and thermal entropy) and that in both the FCC and BCC crystal structures is approximately the same for FCC and BCC metals.

Trouton's rule (Frederick Thomas Trouton, 1863–1922) states that the molar entropy of boiling of a liquid metal is 88 J/K. Figure 6.14 shows a plot of ΔH_b versus the boiling temperature, T_b, for 29 liquid metals with boiling temperatures below 4000 K. A least-squares fit of the data, shown as the full line, gives

$$\Delta H_b = 121 T_B - 43 \text{ J/K}$$

However, a least-squares fit of the data for the 13 metals with boiling temperatures below 2100 K, shown as the broken line, gives

$$\Delta H_b = 87 T_b - 0.4 \text{ J/K}$$

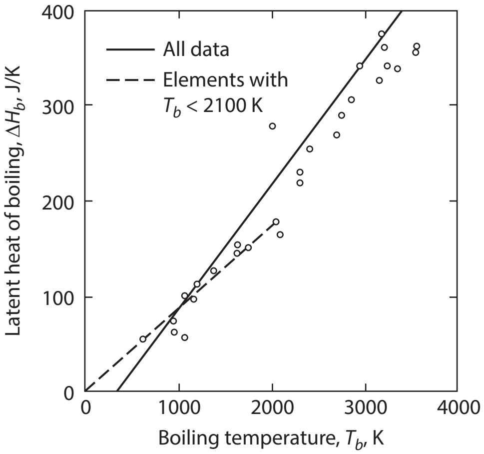

Figure 6.14 An illustration of Trouton's rule.

which indicates a common molar entropy of boiling of approximately 87 J/K for these metals.

Figure 6.15 is the entropy–temperature diagram for the reaction

$$\text{Pb} + \frac{1}{2}\text{O}_2 = \text{PbO}$$

corresponding to the enthalpy–temperature diagram shown in Figure 6.7. Because of the similar magnitudes of the molar entropies of the condensed phases Pb and PbO, it is seen that the entropy change for the reaction

$$\Delta S_T = S_{T,\text{PbO}} - S_{T,\text{Pb}} - \frac{1}{2}S_{T,\text{O}_2}$$

is very nearly equal to $-1/2\,S_{T,\text{O}_2}$. For example, at 298 K,

$$\begin{aligned}\Delta S_{298} &= S_{298,\text{PbO}} - S_{298,\text{Pb}} - \frac{1}{2}S_{298,\text{O2}}\\ &= 67.4 - 64.9 - \frac{1}{2}\times 205\\ &= -100\ \text{J/K}\end{aligned}$$

which is similar in magnitude to the decrease in entropy caused by the disappearance of 1/2 moles of oxygen gas. This approximation is generally valid; that is, in reactions in which a gas reacts with a condensed phase to produce another condensed phase, the change in the entropy is of similar magnitude to that caused by the disappearance of the gas.

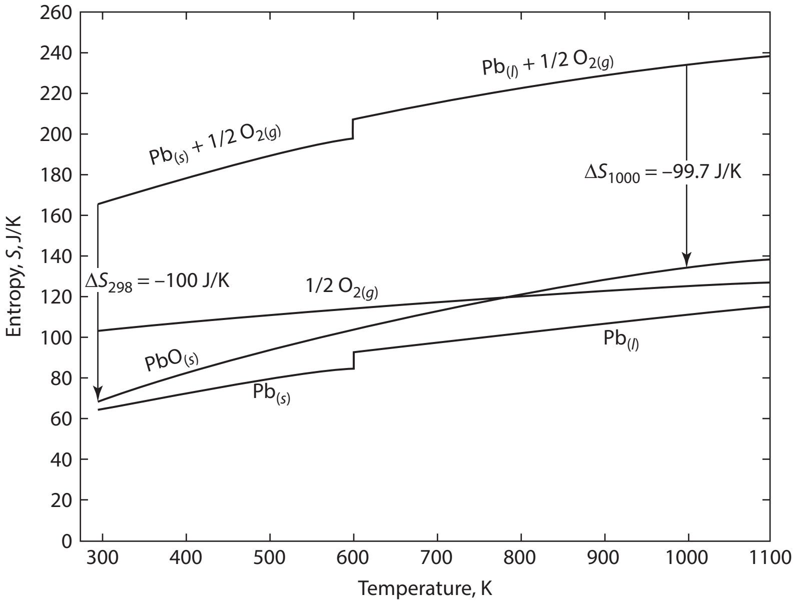

Figure 6.15 The variation, with temperature, of the entropies of $Pb_{(s)}$, $Pb_{(l)}$, $PbO_{(s)}$, and $1/2O_{2(g)}$, and the entropy change for the reaction $Pb + 1/2O_2 = PbO$.

6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

For one mole of a closed system of fixed composition undergoing a change of pressure at constant temperature,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP$$

Equation 5.10b gives $dH = TdS + VdP$, and thus,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

A Maxwell relation (Equation 5.35) gives

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

in which case

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

The isobaric coefficient of thermal expansion, α, is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and thus,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\alpha V + V = V(1-\alpha T)$$

The change in molar enthalpy caused by the change in state from (P_1,T) to (P_2,T) is thus

$$\Delta H = H(P_2,T) - H(P_1,T) = \int_{P_1}^{P_2} V(1-\alpha T)dP \tag{6.14}$$

For an ideal gas, $\alpha = 1/T$, and thus, Equation 6.14 shows once again that the enthalpy of an ideal gas is independent of pressure.

The molar volume and expansivity of Fe are, respectively, 7.1 cm^3 and 0.3×10^{-4} K^{-1}. Thus, an increase in the pressure exerted on Fe from 1 to 100 atm at 298 K causes the molar enthalpy to increase by

$$\begin{aligned} 7.1\times10^{-3}\times(1-0.3\times10^{-4}\times298)\times(100-1) &= 0.696 \text{ liter}\cdot\text{atm} \\ &= 0.696\times101.3 = 71 \text{ J} \end{aligned}$$

The same increase in molar enthalpy would be obtained by heating Fe from 298 to 301 K at 1 atm pressure, which demonstrates the relative insensitivity of the effect of pressure on the enthalpy of a solid.

For a closed system of fixed composition undergoing a change of pressure at constant temperature,

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP$$

Maxwell's relation (Equation 5.35) is

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

which, with the definition of α, gives

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

Thus, for the change of state (P_1,T) to (P_2,T),

$$\Delta S = S(P_2,T) - S(P_1,T) = -\int_{P_1}^{P_2} \alpha\, VdP \tag{6.15}$$

For an ideal gas, since $\alpha = 1/T$, Equation 6.15 simplifies to

$$\Delta S = -\int_{P_1}^{P_2} Rd\ln P = -R\ln\left(\frac{P_2}{P_1}\right) = R\ln\left(\frac{V_2}{V_1}\right)$$

as was obtained in Section 3.7.

An increase in the pressure exerted on Fe from 1 to 100 atm decreases the molar entropy by 0.0022 J/K, which is the same as is obtained by decreasing the temperature by 0.02 degrees from 298 K at 1 atm pressure. It is thus seen that the molar entropies of condensed phases are relatively insensitive to changes in pressure. In the majority of materials applications, in which the range of pressure is 0 to 1 atm, the influence of pressure on the enthalpies and entropies of condensed phases can be ignored.

For a closed system of fixed composition undergoing changes in both pressure and temperature, a combination of Equations 6.1 and 6.14 gives

$$\Delta H = H(P_2,T_2) - H(P_1,T_1) = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} V(1-\alpha T)dP \tag{6.16}$$

and the combination of Equations 6.12 and 6.15 gives

$$\Delta S = S(P_2,T_2) - S(P_1,T_1) = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \alpha\, VdP \tag{6.17}$$

The pressure dependence of V and α must be known for the integration of Equations 6.14 and 6.15. However, for condensed phases being considered over small ranges of pressure, these pressure dependencies can be ignored.

6.8 SUMMARY

1. Knowledge of the heat capacities and the entropies of substances and the heats of formation of compounds allows the enthalpy and entropy changes to be evaluated for any process—that is, for phase changes and chemical reactions.

2. The heat capacity of solids can be modeled by the statistical thermodynamic models of Einstein and Debye. The Debye model is best at low temperatures as it displays the experimentally observed T^3 dependence at low temperatures for non conductors.
3. Heat capacities can also be fit to experimental data via an equation of the form

$$c_P = a + bT + \frac{c}{T^2}$$

4. Since enthalpy does not have an absolute value, it is conventional to assign the value of zero to the enthalpy of all elements in their stable states of existence at 298 K and to consider changes in enthalpy with respect to this reference state.
5. The entropy of all substances which are in complete internal equilibrium is zero at 0 K. This is the Nernst–Planck–Simon statement of the Third Law of Thermodynamics.
6. Both the enthalpy and entropy are dependent on pressure and temperature; however, the pressure dependence of the enthalpy and entropy of condensed phases is normally small enough to be ignored, especially when the pressure of interest is in the range 0–1 atm.
7. The variation of enthalpies of transformation with temperature and pressure can be calculated by the application of the First Law of Thermodynamics to the changes in enthalpy with temperature and pressure, as well as the temperature dependence of the heat capacities and expansion coefficients.
8. The enthalpies and entropies of transformation at the melting point and boiling point of metals can be estimated by the rules of Richard and Trouton.
9. The determination of ΔH_T and ΔS_T for any change of state at any temperature and pressure allows the all-important change in the Gibbs free energy for the change of state to be calculated as

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

10. Since consideration of the Gibbs free energy in any isothermal, isobaric process provides the criterion for equilibrium, the equilibrium state of a system can be determined from knowledge of the thermochemical properties of the system.

6.9 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 6

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Allotropy
Corresponding states
Debye model of the heat capacity of a crystal
Einstein model of the heat capacity of a solid
Endothermic process
Exothermic process
Kirchhoff's law
Kopp rule of the heat capacity of compounds
Law of Dulong and Petit
Le Chatelier's principle

Nernst heat theorem
Phonon
Polymorphism
Third Law of Thermodynamics

6.10 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Estimate c_p, the molar heat capacity of the iron silicon spinel, Fe_2SiO_4, at very high temperatures (> 1400 K).

Solution to Qualitative Problem 1

Assume that this is in the range where the Dulong and Petit law is followed. There are seven atoms in the formula unit of the spinel. Thus, by Kopp's rule, we estimate c_v to be $7 \times 3R = 21R = 174.6$ J/mole·K; c_p would be larger than that number.

Actual c_p at 1400 K = 206 J/mole·K.

Qualitative Problem 2

Show that the following equation holds, relating the Helmholtz free energy to the constant-volume heat capacity of a material.

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{c_V}{T}\right)$$

Solution to Qualitative Problem 2

$$A = U - TS$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T\left(\frac{\partial S}{\partial T}\right)_V - S$$

$$\text{Thus, } \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = c_v$$

$$\text{We saw that } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_V = -\frac{\partial S}{\partial T} = -\frac{c_V}{T}$$

6.11 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

A mixture of Fe_2O_3 and Al, present in the molar ratio 1/2, is placed in an adiabatic container at 298 K, and the Thermit reaction

$$2\ \mathrm{Al} + \mathrm{Fe_2O_3} \rightarrow 2\mathrm{Fe} + \mathrm{Al_2O_3}$$

is allowed to proceed to completion. Calculate the state and the temperature of the reaction products.

Solution to Quantitative Problem 1

From the thermochemical data

$$H_{\mathrm{Al_2O_3},298} = -1{,}675{,}700\ \ \mathrm{J/mole}$$

and

$$H_{\mathrm{Fe_2O_3},298} = -823{,}400\ \ \mathrm{J/mole}$$

the heat released by the Thermit reaction at 298 K is calculated as

$$\Delta H_{298} = -1{,}675{,}700 + 823{,}400 = -852{,}300\ \mathrm{J}$$

and this heat raises the temperature of the reaction products. Assume, first, that the sensible heat raises the temperature of the products to the melting temperature of Fe, 1809 K, in which state the reactants occur as 2 moles of liquid Fe and 1 mole of solid Al_2O_3. The molar heat capacities and molar heats of transformation are

- $c_{p,\mathrm{Al_2O_3}(s)} = 117.49 + 10.38\times10^{-3}T - 37.11\times10^{5}T^{-2}$ in the range $298 - 2325$ K
- $c_{p,\mathrm{Fe}(\alpha)} = 37.12 + 6.17\times10^{-3}T - \ 56.92T^{-0.5}$J/K in the range $298 - 1187$ K
- $c_{p,\mathrm{Fe}(\gamma)} = 24.48 + 8.45\times10^{-3}T$ in the range $1187 - 1664$ K
- $c_{p,\mathrm{Fe}(\delta)} = 37.12 + 6.17\times10^{-3}T - 56.92T^{-0.5}$J/K in the range $1667 - 1809$ K
- For $\mathrm{Fe}_{(\alpha)} \rightarrow \mathrm{Fe}_{(\gamma)}$, $\Delta H_{\mathrm{trans}} = 670$ J at 1187 K
- For $\mathrm{Fe}_{(\gamma\,)} \rightarrow \mathrm{Fe}_{(\delta)}$, $\Delta H_{\mathrm{trans}} = 840$ J at 1664 K
- For $\mathrm{Fe}_{(\delta)} \rightarrow \mathrm{Fe}_{(l)}$, $\Delta H_m = 13{,}770$ J at 1809 K

The heat required to raise the temperature of 1 mole of Al_2O_3 from 298 to 1809 K is

$$\begin{aligned}\Delta H_1 &= \left[117.48\times(1809-298)\right]+\left[\frac{10.38}{2}\times10^{-3}(1809^2-298^2)\right]\\ &\quad +37.11\times10^5\left(\frac{1}{1809}-\frac{1}{298}\right)\\ &= 183{,}649\ \text{J}\end{aligned}$$

and the heat required to raise the temperature of 2 moles of Fe from 298 to 1809 K and melt the 2 moles at 1809 K is

$$\begin{aligned}\Delta H_2 &= \left[2\times37.12\times(1187-298)\right]+\left[\frac{2\times6.17}{2}\times10^{-3}(1187^2-298^2)\right]\\ &\quad +\left[\frac{2\times56.92}{0.5}(1187^{0.5}-298^{0.5})\right]+(2\times670)\\ &\quad +\left[2\times24.28\times(1664-1187)\right]+\left[\frac{2\times8.45}{2}\times10^{-3}(1664^2-1187^2)\right]\\ &\quad +(2\times840)+[2\times37.12\times(1809-1664)]\\ &\quad +\left[\frac{2\times6.17}{2}\times10^{-3}(1809^2-1664^2)\right]+\left[\frac{2\times56.92}{0.5}(1809^{0.5}-1664^{0.5})\right]\\ &\quad +(2\times13{,}770)\\ &= (78{,}058+1340+34{,}654+1680+14{,}268+27{,}540)\\ &= 157{,}541\ \text{J}\end{aligned}$$

The total heat required is thus

$$\Delta H_1+\Delta H_2 = 183{,}649+157{,}541 = 341{,}190\ \text{J}$$

The remaining available sensible heat is 852,300 – 341,190 = 511,110 J.

Consider that the remaining sensible heat raises the temperature of the system to the melting temperature of Al_2O_3, 2325 K, and melts the mole of Al_2O_3. The heat required to increase the temperature of the mole of Al_2O_3 is

$$\begin{aligned}\Delta H_3 &= [117.49\times(2325-1809)]+\left[\frac{10.38}{2}\times10^{-3}(2325^2-1809^2)\right]\\ &\quad +37.11\times10^5\left[\frac{1}{2325}-\frac{1}{1809}\right]\\ &= 71{,}240\ \text{J}\end{aligned}$$

and, with $c_{p,\text{Fe}(l)}$ = 41.84 J/K, the heat required to increase the temperature of the 2 moles of liquid Fe is

$$\Delta H_4 = 2\times 41.84\times(2325-1809) = 43{,}178 \text{ J}$$

The molar latent heat of melting of Al_2O_3 at its melting temperature of 2325 K is 107,000 J, and thus, the sensible heat consumed is

$$71{,}240 + 43{,}178 + 107{,}000 = 221{,}418 \text{ J}$$

which still leaves 511,110 – 221,418 = 289,692 J of sensible heat. Consider that this is sufficient to raise the temperature of the system to the boiling point of Fe, 3343 K. The constant-pressure molar heat capacity of liquid Al_2O_3 is 184.1 J/K, and thus, the heat required to increase the temperature of 1 mole of liquid Al_2O_3 and 2 moles of liquid Fe from 2325 to 3343 K is

$$(2\times 41.84 + 184.1)\times(3343-2325) = 272{,}600 \text{ J}$$

which leaves 289,692 – 272,600 = 17,092 J. The molar heat of boiling of Fe at its boiling temperature of 3343 K is 340,159 J, and thus, the remaining 17,092 J of sensible heat is used to convert

$$\frac{17{,}092}{340{,}159} = 0.05$$

moles of liquid iron to iron vapor. The final state of the system is thus 1 mole of liquid Al_2O_3, 1.95 moles of liquid Fe, and 0.05 moles of iron vapor at 3343 K.

Suppose, now, that it is required that the increase in the temperature of the products of the Thermit reaction be limited to 1809 K to produce liquid Fe at its melting temperature. This could be achieved by including Fe in the reactants in an amount sufficient to absorb the excess sensible heat. The sensible heat remaining after the temperature of the mole of Al_2O_3 and the 2 moles of Fe has been increased to 1809 K has been calculated as 511,110 J, and the heat required to raise the temperature of 2 moles of Fe from 298 to 1809 K and melt the Fe has been calculated as ΔH_2 = 157,541 J. The number of moles of Fe which must be added to the reacting mole of Fe_2O_3 and 2 moles of Al_2O_3 is thus

$$\frac{511{,}110}{0.5\times 157{,}541} = 6.49$$

The required final state is thus achieved by starting with Fe, Al, and Fe_2O_3 at 298 K, occurring in the ratio 6.49/2/1. The Thermit reaction is used to weld steel in locations which are not amenable to conventional welding equipment.

Quantitative Problem 2

A quantity of supercooled liquid tin is adiabatically contained at 495 K. Calculate the fraction of the tin which spontaneously freezes, given

$$\Delta H_{m,(\mathrm{Sn})} = 7070 \text{ J at } T_m = 505 \text{ K}$$
$$c_{p,\mathrm{Sn}(l)} = 34.7 - 9.2\times 10^{-2} T \text{ J/K}$$
$$c_{p,\mathrm{Sn}(s)} = 18.5 + 26\times 10^{-3} T \text{ J/K}$$

Solution to Quantitative Problem 2

The equilibrium state of the adiabatically contained system is that in which the solid, which has formed spontaneously, and the remaining liquid coexist at 505 K. Thus, the fraction of the liquid which freezes is that which releases just enough heat to increase the temperature of the system from 495 to 505 K.

Consider 1 mole of tin and let the molar fraction which freezes be x. In Figure 6.16, the process is represented by a change of state from a to c, and, as the process is adiabatic, the enthalpy of the system remains constant; that is,

$$\Delta H = H_c - H_a = 0$$

Either of two paths can be considered.

Path 1: $a \rightarrow b \rightarrow c$, during which the temperature of the 1 mole of liquid is increased from 495 to 505 K and then x moles freeze. In this case,

$$\Delta H_{(a\to b)} = -\Delta H_{(b\to c)}$$
$$\Delta H_{(a\to b)} = \int_{495}^{505} c_{p,\mathrm{Sn}(l)}dT = 34.7\times(505-495) - \frac{9.2}{2}\times 10^{-3}(505^2 - 495^2)$$
$$= 301 \text{ J}$$
$$\Delta H_{(b\to c)} = -7070x \text{ J}$$

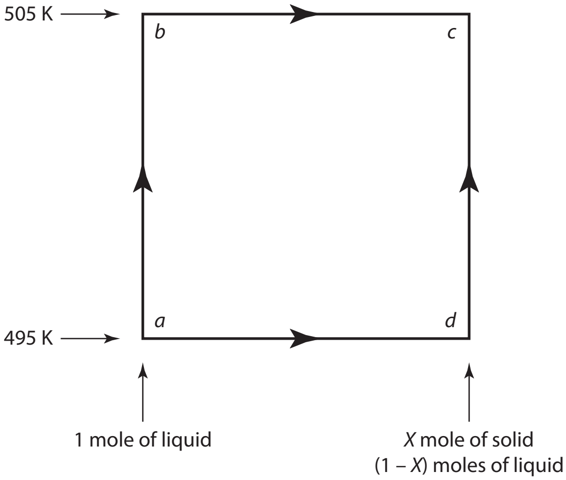

Figure 6.16 Changes in the state of Sn, considered in Quantitative Example 2.

and thus,

$$x = \frac{301}{7070} = 0.0426$$

That is, 4.26 mol% of the tin freezes.

Path 2: $a \rightarrow d \rightarrow c$; that is, the fraction x freezes at 495 K, and then, the temperature of the solid and the remaining liquid is increased from 495 to 505 K. In this case,

$$\begin{aligned} \Delta H_{(a\to d)} &= -\Delta H_{(d\to c)} \\ \Delta H_{(a\to d)} &= \text{the head of freezing } x \text{ moles of tin at 495 K} \\ &= -x\Delta H_m(495\text{ K}) \end{aligned}$$

But,

$$\begin{aligned} \Delta H_m(495K) &= \Delta H_m(505\text{ K}) + \int_{505}^{495} \Delta c_{p(s\to l)} dT \\ &= 7070 + 16.2(495-505) - \frac{35.2}{2}\times 10^{-3}(495^2 - 505^2) \\ &= 7084\text{ J} \end{aligned}$$

Thus,

$$\begin{aligned} \Delta H_{(a\to d)} &= -7084x\text{ J} \\ \Delta H_{(d\to c)} &= -x\int_{495}^{505} c_{p(s)} dT + (1-x)\int_{495}^{505} c_{p(l)} dT \\ &= x\left[18.5(505-495) + \frac{26}{2}\times 10^{-3}(505^2 - 495^2)\right] \\ &\quad + (1-x)\left[34.7(505-495) - \frac{9.2}{2}\times 10^{-3}(505^2 - 495^2)\right] \\ &= 301 + 14x \end{aligned}$$

Thus,

$$-7084x = -14x - 301$$

which gives

$$x = \frac{301}{7070} = 0.0426$$

The actual path the process follows is intermediate between paths 1 and 2; that is, the process of freezing and increase in temperature occur simultaneously.

The entropy produced by the spontaneous freezing is

$$\begin{aligned}\Delta S_{(a\to b)}+\Delta S_{(b\to c)} &= 34.7\times\ln\left(\frac{505}{495}\right)-[9.2\times10^{-3}(505-495)]\\ &\quad-\left(0.0426\times\frac{7070}{505}\right)\\ &= 0.602-0.596=0.006\ \text{J/K}\cdot\text{mole}\end{aligned}$$

Quantitative Problem 3

The adiabatic flame temperature is that temperature reached when all of the sensible heat released by the combustion of a fuel is used to raise the temperature of the gaseous products of combustion. Consider the adiabatic flame temperature reached when acetylene, C_2H_2, is combusted at 298 K with (1) the stoichiometric amount of oxygen and (2) the number of moles of air containing the stoichiometric number of moles of oxygen. Air is, by mole or volume percent, 21% O_2 and 79% N_2.

The combustion reaction with stoichiometric oxygen is

$$C_2H_2+2.5\ O_2=2\ CO_2+H_2O \tag{i}$$

For C_2H_2: $\Delta H_{298}=+226{,}700$ J
For CO_2: $\Delta H_{298}=-393{,}500$ J
For H_2O: $\Delta H_{298}=-241{,}800$ J

Solution to Quantitative Problem 3

Thus, for the reaction given by Equation (i):

$$\Delta H\left(\text{i}\right)_{298}=(-2\times393{,}500)-241{,}800-226{,}700=-1{,}255{,}500\ \text{J}$$

The constant-pressure molar heat capacities of the products of reaction are

For H_2O: $c_p,H_2O=30.00+10.71\times10^{-3}T+0.33\times10^{5}T^{2}$ J/K·mole
For CO_2: $c_p,CO_2=44.14+9.04\times10^{-3}T-8.54\times10^{5}T^{2}$ J/K·mole

The adiabatic flame temperature, T, is then obtained from the requirement

$$\Delta H(\text{i})_{298}+\int_{298}^{T}(2c_p,CO_2+c_p,H_2O)dT=0$$

or

$$\begin{aligned}&-1{,}255{,}500+118.28\times(T-298)+14.40\times10^{-3}\times(T^2-298^2)\\ &\quad+16.75\times10^{5}(1/T-1/298)=0\end{aligned}$$

which has the solution $T = 6{,}236$ K.

For combustion with the stoichiometric amount of air, the reaction is written as

$$C_2H_2 + 2.5\ O_2 + 2.5 \times (79/21)\ N_2 = 2CO_2 + H_2O + 9.41\ N_2$$

$$\text{For } N_2\text{:} \quad c_p,N_2 = 27.87 + 4.27 \times 10^{-3}T \text{ J/mole} \cdot \text{K}$$

and the adiabatic flame temperature, T, is obtained from

$$\Delta H(\mathrm{i})_{298} + \int_{298}^{T} (2c_p,CO_2 + c_p,H_2O + 9.41c_p,N_2)dT = 0$$

or

$$-1{,}255{,}500 + 380.1 \times (T - 298) + 40.16 \times 10^{-3} \times (T^2 - 298^2) \\ + 16.75 \times 10^5 (1/T - 1/298) = 0$$

as $T = 2{,}797$ K.

This high adiabatic flame temperature facilitates the use of acetylene for welding metals with high melting temperatures.

PROBLEMS*

6.1 Calculate ΔH_{1600} and ΔS_{1600} for the reaction $Zr(\beta) + O_2 = ZrO_2(\beta)$.

6.2 Which of the following two reactions is the more exothermic?

a. $C_{(\text{graphite})} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$ at 1000 K

b. $C_{(\text{diamond})} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$ at 1000 K

6.3 Calculate the change in enthalpy and the change in entropy at 1000 K for the reaction $CaO_{(s)} + TiO_{2(s)} \rightarrow CaTiO_{3(s)}$.

6.4 Copper exists in the state $T = 298$ K, $P = 1$ atm. Calculate the temperature to which the copper must be raised at 1 atm pressure to cause the same increase in molar enthalpy as is caused by increasing its pressure to 1000 atm at 298 K. The molar volume of Cu at 298 K is 7.09 cm^3, and the volumetric coefficient of thermal expansion is $0.501 \times 10^{-4}\ \text{K}^{-1}$. These values can be taken as being independent of pressure in the range 1–1000 atm.

6.5 Calculate ΔH_{298} and ΔS_{298} for the following reactions:

a. $2\ TiO + 1/2\ O_2 = Ti_2O_3$

b. $3\ Ti_2O_3 + 1/2\ O_2 = 2Ti_3O_5$

c. $Ti_3O_5 + 1/2\ O_2 = 3TiO_2$

6.6 An adiabatic vessel contains 1000 g of liquid aluminum at 700°C. Calculate the mass of Cr_2O_3 at room temperature, which, when added to the liquid aluminum (with which it reacts to form Cr and Al_3O_3), raises the temperature of the resulting mixture of Al_2O_3, Cr_2O_3, and Cr to 1600 K.

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* Thermodynamic data required for the solution of the end-of-chapter problems are tabulated in the appendices of the text.

6.7 Calculate the adiabatic flame temperature attained when methane, at 298 K, is combusted with (a) oxygen in the molar ratio $O_2/CH_4 = 2.0$, and (b) air in the molar ratio air/$CH_4 = 9.524$. Assume that CO_2 and H_2O are the products of combustion. The adiabatic flame temperature is that temperature reached if all of the heat of the oxidation reaction is used to increase the temperature of the products of the reaction. Air is 21 mol% O_2 and 79 mol% N_2.

6.8 Calculate the value of ΔG for the reaction

$$Si_3N_4 + 3\ O_2 = 3\ SiO_{2(\alpha-\text{quartz})} + 2\ N_2$$

at 800 K. What percentage error occurs if it is assumed that Δc_p for the reaction is zero?

6.9 Determine the stoichiometric coefficients for the reaction

$$(3\ CaO \cdot Al_2O_3 \cdot 3\ SiO_2) + a(CaO \cdot Al_2O_3 \cdot SiO_2) = b(CaO \cdot Al_2O_3 \cdot 2\ SiO_2) + c(2\ CaO \cdot Al_2O_3 \cdot SiO_2)$$

and calculate ΔH_{298}, ΔS_{298}, and ΔG_{298} for the reaction.

6.10 How much heat is required to increase the temperature of 1 kg of cordierite, $2\ MgO \cdot 2\ Al_2O_3 \cdot 5\ SiO_2$, from 298 K to its incongruent melting temperature of 1738 K?

6.11* A function $\Omega \equiv -A + \mu N$, has been defined, where A is the Helmholtz free energy, μ is the chemical potential and N is the number of particles in the system. Obtain an expression for $d\Omega$ and thus determine the independent variables for this function.

6.12* (a) Given that the Helmholtz energy can be written as

$$A = -N_{\text{system}} k_B T \ln \mathcal{Z}$$

Obtain simplified expressions for both A and S of an Einstein solid.

(b) Show that the entropy approaches 0 as the temperature approaches 0 in such a solid.

6.13* Obtain an expression for the internal energy of an Einstein solid as the temperature gets very large, differentiate it with respect to T, and show that the Dulong and Petit value for the heat capacity is attained.

APPENDIX 6A

In Section 6.2, we found that by substituting Equation 6.2 and 6.4 into 6.3 we obtain

$$U' = \sum_i 3 \frac{n \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\mathcal{Z}} \left(i + \frac{1}{2}\right) h\nu = 3nh\nu \sum_i \left(i + \frac{1}{2}\right) \left(\frac{\exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)} \right)$$

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* New problem in this edition

This represents the total internal energy of an Einstein solid. This equation can be expanded to obtain

$$U' = 3nh\nu\left(\frac{\sum_i i\exp\left(-\frac{\varepsilon_i}{k_BT}\right)}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_BT}\right)} + \frac{1}{2}\left(\frac{\sum_i \exp\left(-\frac{\varepsilon_i}{k_BT}\right)}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_BT}\right)}\right)\right)$$

$$U' = 3nh\nu\left(\frac{\sum_i i\exp\left(-\frac{i}{k_BT}\left(i+\frac{1}{2}\right)h\nu\right)}{\sum_i \exp\left(-\frac{1}{k_BT}\left(i+\frac{1}{2}\right)h\nu\right)} + \frac{1}{2}\right)$$

$$U' = 3nh\nu\left(\frac{\sum_i i\exp\left(-\frac{ih\nu}{k_BT}\right)}{\sum_i \exp\left(-\frac{ih\nu}{k_BT}\right)} + \frac{1}{2}\right)$$

Now we let

$$\sum_i i\exp\left(-\frac{ih\nu}{k_BT}\right) = \sum ix^i = x(1+2x+3x^2+\ldots) = \frac{x}{(1-x)^2}$$

and let

$$\sum_i \exp\left(-\frac{ih\nu}{k_BT}\right) = \sum x^i = 1+x+x^2+\ldots = \frac{1}{1-x}$$

where $x = \exp(-h\nu/k_BT)$.

Then, U' becomes

$$U' = \frac{3nh\nu}{2}\left(\frac{2\frac{x}{(1-x)^2}}{\frac{1}{1-x}} + 1\right) = \frac{3nh\nu}{2}\left(\frac{1+x}{1-x}\right)$$

$$U' = \frac{3nh\nu}{2}\left(\frac{1+\exp\left(-\frac{h\nu}{k_BT}\right)}{1-\exp\left(-\frac{h\nu}{k_BT}\right)}\right)$$

$$U' = \frac{3nh\nu}{2}\left(\frac{1+\exp\left(-\frac{h\nu}{k_B T}\right)}{1-\exp\left(-\frac{h\nu}{k_B T}\right)}\right) = \frac{3}{2}nh\nu + \frac{3nh\nu}{\left(\exp\left(\frac{h\nu}{k_B T}\right)-1\right)}$$

$$U' = \frac{3}{2}nh\nu + \frac{3nh\nu}{\left(\exp\left(\frac{h\nu}{k_B T}\right)-1\right)}$$

This gives us the total internal energy of a system composed of $3n$ quantum harmonic oscillators, which Einstein used to model the thermal properties of a solid with its n atoms vibrating independently of each other.

PART II

Phase Equilibria

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CHAPTER 7

Phase Equilibrium in a One-Component System

7.1 INTRODUCTION

The intensive thermodynamic variables which control the equilibrium of a system are the temperature, the pressure, and the chemical potentials of the various species that compose the system. If, within a system, a gradient exists in any one of these variables, there is a driving force for change in the system.

The *temperature* of a system is a measure of the intensity of the thermal energy (heat) in the system. If the system is able to exchange energy with its surroundings, and if the surroundings are of a different temperature than the system, the gradient in temperature is a measure of the tendency for thermal energy (heat) to leave or enter the system. If, within an isolated system, a gradient in temperature exists, it produces a driving force for the transport of thermal energy down the gradient from the part of the system at the higher temperature to the part of the system at the lower temperature. The spontaneous transfer of thermal energy (heat) occurs until the thermal energy gradient has been eliminated, in which state, the thermal energy is distributed at uniform intensity (temperature) throughout the system. Thus, in an isolated system, thermal equilibrium is established when the temperature is uniform throughout the system. We have seen that this means that the entropy of the system is maximized.

The *pressure* of a system is a measure of its potential for undergoing massive movement by expansion or contraction. If, in a system of fixed volume, the pressure exerted by one phase is greater than that exerted by another phase, then the tendency of the first phase to expand exceeds that of the second phase. The pressure gradient is the driving force for the expansion of the first phase, and this expansion decreases its pressure, hence its tendency for further expansion. The other phase contracts, which increases its pressure, hence its tendency to resist further contraction. Mechanical equilibrium is established when the massive movement of the two phases has occurred to the extent that the pressure gradient has been eliminated, in which state the pressure is uniform throughout the system.

The *chemical potential* of the species *i* in a phase is a measure of the tendency of the species *i* to leave the phase. It is thus a measure of the *chemical pressure* exerted by component i in the phase. If, at constant temperature and pressure, the chemical potential of i has different values in different phases of the system, then, as the escaping tendencies differ, the species i will tend to move from the phases in which it occurs at the higher chemical potential to the phases in which it occurs at the lower chemical potential. A gradient in chemical potential is the *driving force* for chemical diffusion, and equilibrium is attained when the species i is distributed throughout the various phases in the system, such that its chemical potential has the same value in all phases.

In a closed system of fixed composition (e.g., a one-component simple system), at the temperature T and the pressure, P, equilibrium occurs when the system exists in that state which has the *minimum* value of the total Gibbs free energy, G', of the *system*. The equilibrium state can thus be determined by means of an examination of the dependence of G' (or the molar Gibbs free energy G) on pressure and temperature. Throughout this chapter we deal with molar properties unless stated otherwise.

7.2 THE VARIATION OF GIBBS FREE ENERGY WITH TEMPERATURE AT CONSTANT PRESSURE

We have seen that the molar Gibbs free energy for a single-component closed system can be written as

$$dG = -SdT + VdP \tag{5.10d}$$

At constant pressure, this reduces to

$$dG = -SdT$$

Using this equation, we can sketch G versus T for a solid phase, α, as shown in Figure 7.1. We now examine the features of this plot.

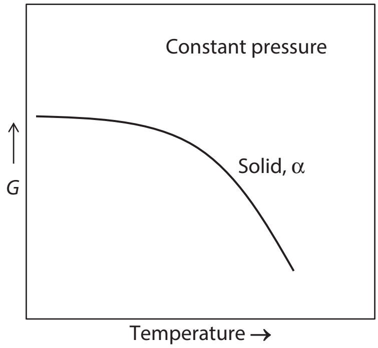

Figure 7.1 Schematic of the molar Gibbs free energy vs. temperature plot at constant pressure of a solid phase.

1. The slope of the curve is negative for $T > 0$, since the slope is equal to minus the entropy of the system and the entropy must be positive.
2. As T approaches zero, $S = -(\partial G/\partial T)_P$ approaches zero, as indicated by the Third Law of Thermodynamics (see Chapter 6).
3. The curvature of the plot is proportional to

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_P}{T} \tag{7.1}$$

   and since c_p and T are positive ($T > 0\text{K}$), the curvature is negative for $T > 0$ K.
4. As the temperature increases, the entropy of the system increases and the curvature of the plot decreases: $(\partial S/\partial T)_P = -(\partial^2 G/\partial T^2)_P$.

Now, consider the addition to the plot of the molar Gibbs free energy curve for the liquid phase of this one-component system (Figure 7.2). Once again, we examine the salient features of this plot.

1. We note that the Gibbs free energy of the liquid is greater than that of the solid at $T = 0$. This follows, since the solid phase is the stable phase below the system's melting point, T_m.
2. The slope of the Gibbs free energy curve for the liquid, $(\partial G^L/\partial T)_P$, is less than the slope for the solid, for $T > 0$ K, since the entropy of the liquid is greater than that of the solid at all temperatures greater than 0 K.
3. At the temperature denoted as T_m, the Gibbs free energy of the solid equals that of the liquid: $G^S = G^L$. This is the equilibrium melting temperature of the solid. It is also the equilibrium freezing temperature of the liquid.
4. At T_m, since the slope of the liquid Gibbs free energy is more negative than that of the solid (since $S^L > S^S$), the Gibbs free energy of the liquid begins to drop below that of the free energy of the solid, and hence, the liquid becomes the stable phase.

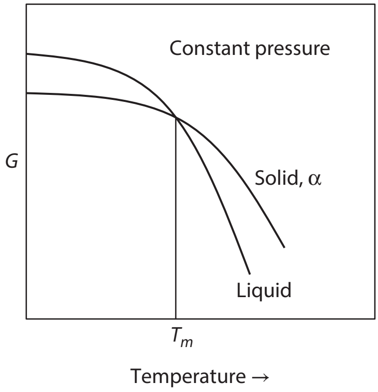

Figure 7.2 Schematic of the molar Gibbs free energy vs. temperature plot of the solid phase shown in Figure 7.1 along with the plot of its liquid phase. T_m is the melting point of the solid.

5. The curvature of the Gibbs free energy of the liquid is more negative than that of the solid, and hence, its heat capacity is greater than that of the solid.

$$-\frac{c_P^L}{T} = \left(\frac{\partial^2 G^L}{\partial T^2}\right)_P < \left(\frac{\partial^2 G^S}{\partial T^2}\right)_P = -\frac{c_P^S}{T} < 0$$

$$\frac{c_P^L}{T} > \frac{c_P^S}{T}$$

This is a general feature of competing phases in a simple system: the phase with the highest heat capacity is the stable phase at high temperatures. This was first stated by van’t Hoff (Jacobus Henricus van’t Hoff, 1852–1911) and is sometimes called the *van’t Hoff rule*.

These qualitative features of the molar Gibbs free energy plots of a solid phase and its liquid phase give insight into the underlying thermodynamic causes which bring about changes in the equilibrium of a system.

Let us now examine what happens to the solid phase when thermal energy (heat) is added to it at constant pressure and in a reversible manner, starting at $T = 0$. At constant pressure, the molar heat capacity, c_P^S, which equals $(\partial H^S / \partial T)_P$, increases as the temperature of the solid increases. The solid remains a solid until its equilibrium melting temperature T_m is reached. At this temperature (and pressure), the solid is able to exist in equilibrium with its liquid phase. If both phases are present at T_m and more thermal energy is added to the solid and liquid mixture, the temperature of the two-phase system will not increase. This is because the added thermal energy is utilized to melt the remaining solid until, eventually, only liquid at the melting temperature, T_m, remains. During the process of melting, the amount of thermal energy added to the system is written as ΔH_m and is called the *molar enthalpy of melting* (sometimes the *latent heat of melting*). During the melting process, thermal energy is added to the system, but there is no change in temperature. The two-phase mixture of the solid and liquid effectively has an infinite heat capacity at the melting point. After all of the solid has melted, the continued addition of thermal energy increases the temperature of the liquid. Since the transformation from solid to liquid occurs at constant temperature, we can calculate the entropy change of the melting process as follows:

$$\Delta S_{\text{melting}} = \frac{\Delta H_{\text{melting}}}{T_m} \tag{7.2}$$

This change in entropy is positive (thermal energy has entered the system), and therefore, as expected, the entropy of the liquid is greater than that of the solid from which it is formed.

It is of interest to plot the heat capacity of the system as a function of temperature. This is shown in Figure 7.3. This plot shows what was described in the previous paragraph during the process of heating the solid. The effective infinity in the heat capacity is denoted by the vertical arrow. The heat capacity of the liquid just above

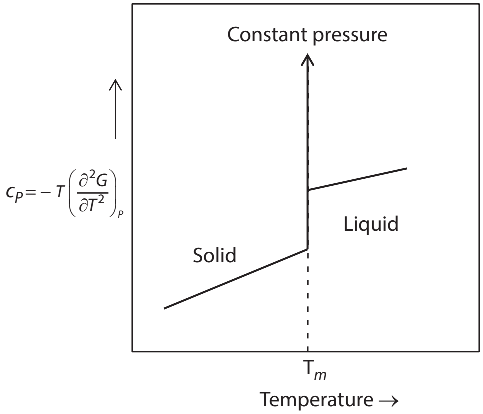

Figure 7.3 Schematic of the molar heat capacity vs. temperature plot at constant pressure of the system shown in Figures 7.1 and 7.2. At the equilibrium melting temperature, the heat capacity displays an effective infinity, indicating that there is a latent enthalpy of melting.

the melting temperature is shown to be larger than the heat capacity of the solid just before melting began, because the curvature of its molar Gibbs free energy plot is more negative than that of the solid (Figure 7.2).

Phase transformations such as the melting of a one-component solid were called *first-order phase changes* by Ehrenfest (Paul Ehrenfest, 1880–1933). This is based on the behavior of the derivative of the Gibbs free energy (or any other energy function of the system, such as U, H, or A) in the vicinity of the phase change. The order of a phase transition in this classification is defined as the lowest derivative of the Gibbs free energy with respect to temperature (or pressure), which is *discontinuous* at the transition temperature.

We have seen that the entropy, $S = -(\partial G/\partial T)_P$, is discontinuous at the melting temperature. Also, $(\partial G/\partial P)_T = V$ and $\left(\partial(G/T)/\partial(1/T)\right)_P = H$ are also discontinuous at the melting temperature. Each of these discontinuities in the derivatives shows that the variables derived (the molar entropy, S, the molar volume, V, and the molar enthalpy, H) have different values in the low-temperature phase and the high-temperature phase. The discontinuity in these thermodynamic state variables is a feature of first-order phase transitions. If they had the same values, the transitions would be called *higher-order* or *continuous transitions*.

We can also plot the change in the enthalpy and the Gibbs free energy for transformation between the solid and liquid phases as a function of temperature (Figure 7.4). It can be seen that ΔG and ΔH approach the same value as the temperature approaches 0 K. This follows from the definition of the Gibbs free energy; that is,

$$\Delta G = \Delta H - T\Delta S$$

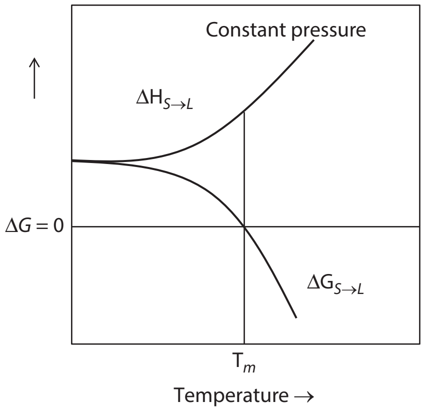

Figure 7.4 Schematic of the ΔH and ΔG plots of the solid to liquid transformation in the system depicted in Figures 7.1 and 7.2. At $T = 0$ K, $\Delta H = \Delta G$. At the equilibrium melting temperature, $\Delta G = 0$. Above T_m, $\Delta G_{S \to L} < 0$.

In addition their slopes, $\partial \Delta G / \partial T = -\Delta S$ and $\partial \Delta H / \partial T = \Delta C_P / T$ both approach zero as the temperature approaches 0 K. This was discussed in Chapter 6 when the Third Law of Thermodynamics was being considered.

As the temperature increases, the difference between ΔG and ΔH becomes larger. The difference is the value of $T \Delta S_{S \to L}$. Below T_m, $\Delta G_{S \to L} = G_L - G_S > 0$, indicating that the solid phase will not transform into the liquid phase, since it is the stable phase. At T_m, the value of $\Delta G_{S \to L}$ goes to zero since the solid and liquid are in equilibrium at that temperature. Above T_m, $\Delta G_{S \to L} < 0$, indicating that the solid phase will transform into the equilibrium liquid phase.

7.3 THE VARIATION OF GIBBS FREE ENERGY WITH PRESSURE AT CONSTANT TEMPERATURE

From Equation 5.10d, we see that the molar Gibbs free energy is a function of pressure as well as temperature. At constant temperature, we have

$$dG = VdP$$

A sketch of the molar Gibbs free energy versus pressure for the solid and liquid phases at a fixed temperature is shown in Figure 7.5. Since $(\partial G / \partial P)_T = V$, which is the molar volume of the phase, the slopes must be positive. The phase with the larger molar volume has the larger slope. Usually, this is the liquid phase, as shown in Figure 7.5. However, there are known examples to the contrary. The curvature of the plot of G versus P is proportional to $(\partial^2 G / \partial P^2)_T = \partial V / \partial P = -V\beta_T$, where β_T is the isothermal compressibility, which is inversely related to the elastic modulus in a

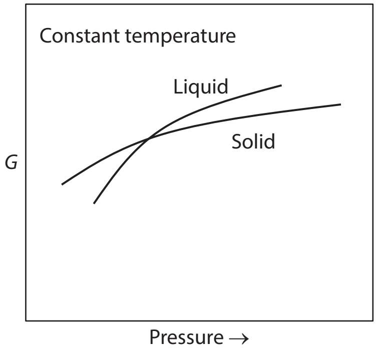

Figure 7.5 Schematic of the molar Gibbs free energy vs. pressure plot of the phases shown in Figures 7.1 and 7.2.

solid phase. The compressibility is positive as defined, so the curvatures of the plots of Figure 7.5 are negative, as shown.

If the constant temperature of the phase shown in Figure 7.5 is the melting temperature of the solid, the pressure where the Gibbs free energies of the solid and liquid are equal is 1 atm. At this temperature and pressure, the solid and liquid phases are in equilibrium, and, if the pressure is increased (holding the temperature constant), it is readily seen that the liquid phase becomes unstable with respect to the formation of the solid phase. The role of pressure on the equilibrium of a solid and a liquid can be considered from the point of view of the principle of Le Chatelier which states that, when subjected to an external influence, the state of a system at equilibrium shifts in that direction which tends to nullify the effect of the external influence. Thus, when the pressure exerted on a system is increased, the state of the system shifts in the direction which causes a decrease in its volume. The material system depicted by Figure 7.5 shows a larger molar volume for the liquid phase ($(\partial G_L/\partial P)_T > (\partial G_S/\partial P)_T$). If the liquid and solid phases are in equilibrium in this system, and if the external pressure is increased, the system divests itself of the higher molar volume liquid phase and becomes completely solid. This phase is the one with the lower isothermal compressibility. Water, at 0°C, has a smaller molar volume than has ice at 0°C, and therefore, the *melting* of ice is the change in state caused by an increase in pressure at its melting temperature.

7.4 THE GIBBS FREE ENERGY AS A FUNCTION OF TEMPERATURE AND PRESSURE

For a liquid and its solid phase to be in equilibrium, we know that their molar Gibbs free energies must be equal: $G^L = G^S$. Thus, for a single-component system, we know that $dG^L = dG^S$. Consider Equation 5.10d applied to both the solid and liquid phases:

$$dG^S = -S^S dT + V^S dP$$

$$dG^L = -S^L dT + V^L dP$$

For equilibrium to be maintained between the liquid and solid phases,

$$-S^S dT + V^S dP = -S^L dT + V^L dP$$

or

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{S^S - S^L}{V^S - V^L} = \frac{S^L - S^S}{V^L - V^S} = \frac{\Delta S}{\Delta V}$$

At equilibrium, $\Delta G = 0$, and hence, $\Delta H = T\Delta S$. When this is substituted into the preceding equation, we arrive at

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta H}{T\Delta V} \tag{7.3}$$

This is known as the *Clapeyron equation* (Benoît Paul Émile Clapeyron, 1799–1864) and it gives the relationship between the variation of temperature and pressure, which is required for the maintenance of equilibrium between the solid and the liquid phases.

Consider again the equilibrium between a solid and its liquid phase. When thermal energy is added to this two-phase equilibrium, it causes the solid to melt and $\Delta H_{(S\to L)} > 0$ (endothermic). The sign of $(dP/dT)_{\text{eq}}$ is thus determined by the sign of $\Delta V_{(S\to L)}$. The value of $\Delta V_{(S\to L)}$ for H_2O is negative. Thus, $(dP/dT)_{\text{eq}}$ for H_2O is negative; that is, an increase in pressure decreases the equilibrium melting temperature, as discussed in Section 7.3. Recall that for most materials, $\Delta V_{(S\to L)}$ is positive, which means that for most materials, an increase in pressure at the melting temperature causes the solid to be stable, and thereby, the melting temperature increases.

The thermodynamic states of the solid and liquid phases can be represented in a three-dimensional diagram with G, T, and P as coordinates. A schematic of such a diagram for H_2O is shown in Figure 7.6. In this figure, the solid and liquid states of existence are shown as a surface in G-T-P space. The curve along which the surfaces intersect represents the variation of P with T required for the maintenance of the equilibrium between the solid and liquid phases. At any state, which is determined by fixing the values of T and P, the equilibrium phase is that which has the lower value of G.

If the G-T-P surface for the states of existence of the vapor phase were included in Figure 7.6, the surface would intersect with the solid-state surface along another curve and would intersect with the liquid-state surface along yet another curve. Projection of these curves, together with the curve of the intersection of the solid- and liquid-state surfaces, onto the two-dimensional P-T basal plane of Figure 7.6 would produce a plot such as that shown in Figure 7.7. The three surfaces representing the

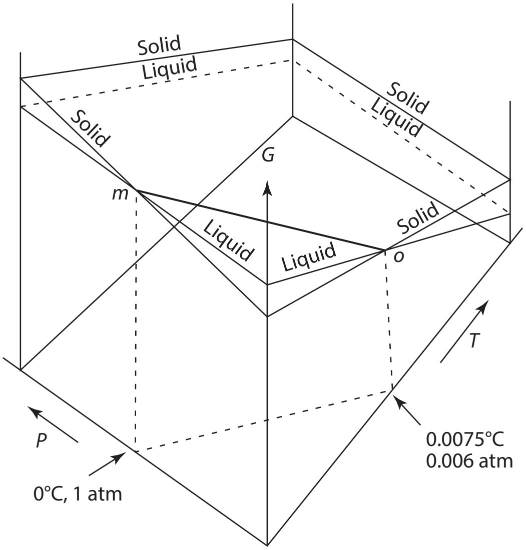

Figure 7.6 Schematic representation of the equilibrium surfaces of the solid and liquid phases of water in *G-T-P* space.

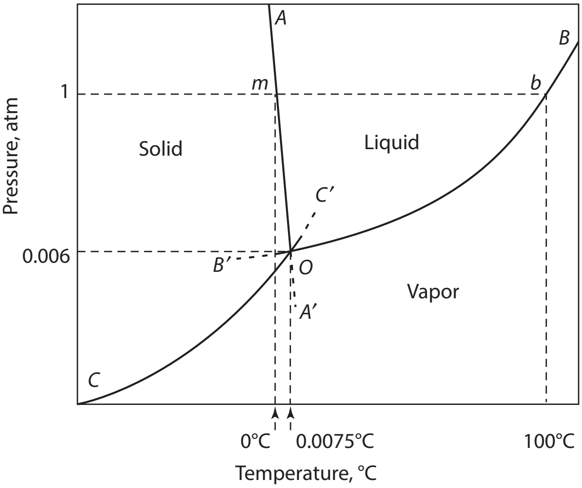

Figure 7.7 Schematic representation of part of the pressure–temperature phase diagram for H_2O, showing the metastable extensions of the two-phase equilibrium curves.

three phases, intersect at a point, the projection of which onto the *P-T* basal plane gives the invariant point *O*, known as the *triple point*. The dashed lines OA', OB', and OC' in Figure 7.7 represent, respectively, metastable solid–liquid, metastable vapor–liquid, and metastable vapor–solid equilibria. The equilibria are metastable because, in the case of the line OB', the intersection of the liquid- and vapor-state surfaces lies at higher values of G than does the solid-state surface for the same values of P and T. Similarly, the solid–liquid equilibrium OA' is metastable with respect to the vapor phase, and the solid–vapor equilibrium OC' is metastable with respect to the liquid phase.

Figure 7.8a shows the isobaric sections for the three phases of H_2O in the vicinity of the triple point for $P_1 > P_{\text{triple point}}$, $P_2 = P_{\text{triple point}}$, and $P_3 < P_{\text{triple point}}$. Figure 7.8b shows three isothermal sections at $T_1 < T_{\text{triple point}}$, $T_2 = T_{\text{triple point}}$, and $T_3 > T_{\text{triple point}}$. In Figure 7.8a, the slopes of the G versus T curves in any isobaric section increase negatively in the order solid, liquid, vapor, in accordance with the fact that

$$S^S < S^L < S^V$$

Similarly, in Figure 7.8b, the slopes of the G versus P curves in any isothermal section increase in the order liquid, solid, vapor in accordance with the fact that, for H_2O,

$$V^L < V^S < V^V$$

Notice that the relative positions of the metastable extensions of the stable curves can be determined from these plots.

The curves OA, OB, and OC divide Figure 7.7 into three areas, within each of which only one phase is stable. Within these areas, the pressure exerted on the phase and the temperature of the phase can be independently varied without changing the phase, which is in equilibrium. In this case, the equilibrium is said to have two *thermodynamic degrees of freedom*. The number of degrees of freedom that a system in equilibrium has is the maximum number of thermodynamic variables which may be independently varied without changing the phase(s) which is (are) in equilibrium. The single-phase areas meet at the lines OA, OB, and OC, along which two phases coexist in equilibrium, and for the continued maintenance of any of these two-phase equilibria, only one variable (either P or T) can be independently varied. Two-phase equilibria in a one-component system thus have only one thermodynamic degree of freedom. The three two-phase equilibria curves meet at the triple point, which is the invariant state at which solid, liquid, and vapor coexist in equilibrium. The three-phase equilibrium in a one-component system thus has no thermodynamic degrees of freedom. The maximum number of phases which can coexist at equilibrium in a one-component system is therefore three. The number of degrees of freedom, $\mathcal{F}$, that a system containing *one* component can have when ϕ phases are in equilibrium can be seen to be given by

$$\mathcal{F} = 3 - \phi \tag{7.4}$$

This expression is the *equilibrium Gibbs phase rule* for a single-component system. It will be extended in Section 13.4, to a system with C components present, to yield

$$\mathcal{F} = C + 2 - \phi$$

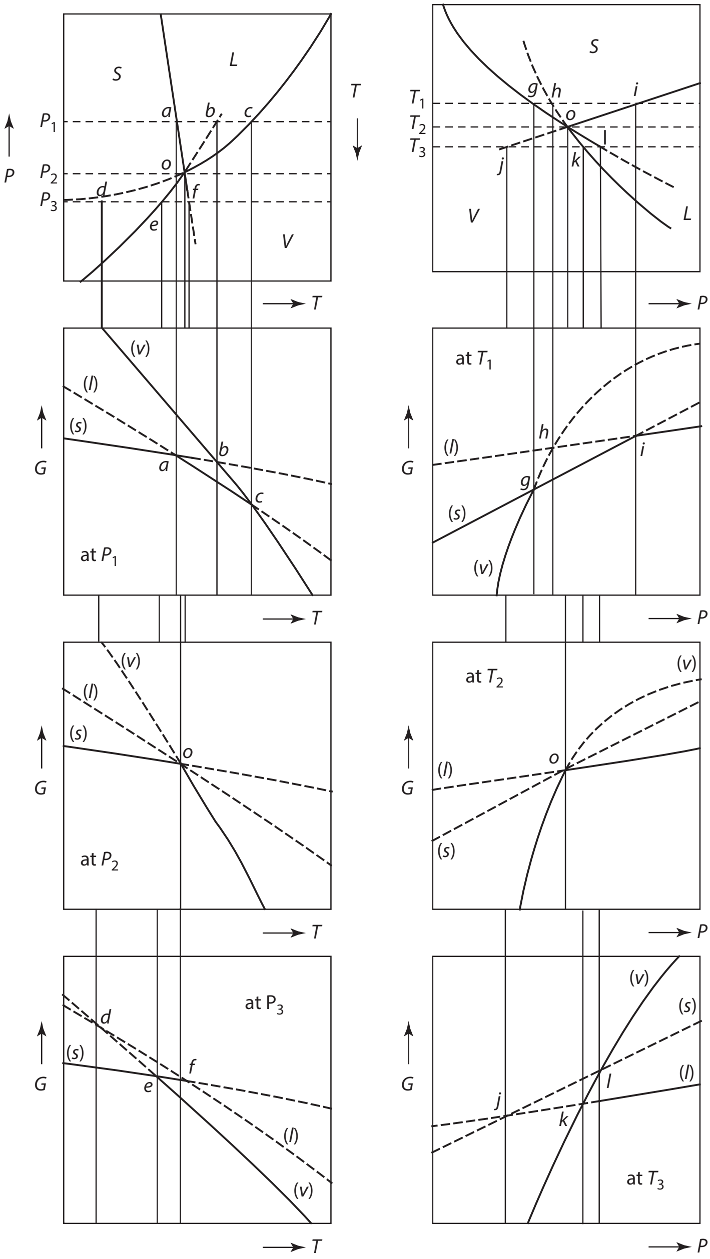

Figure 7.8a (a) Schematic of the constant-pressure variations of the molar Gibbs free energies of solid, liquid, and vapor H_2O at pressures above, at, and below the triple-point pressure; (b) Schematic of the constant-temperature variations of the molar Gibbs free energies of solid, liquid, and vapor H_2O at temperatures above, at, and below the triple-point temperature.

7.5 EQUILIBRIUM BETWEEN THE VAPOR PHASE AND A CONDENSED PHASE

If the Clapeyron equation is applied to the equilibrium between a vapor phase and a condensed phase, then ΔV is the change in the molar volume accompanying evaporation (liquid to vapor) or sublimation (solid to vapor), and ΔH is the corresponding change in the molar enthalpy—that is, the molar enthalpy of evaporation or of sublimation.

Now, $\Delta V = V^{\text{vapor}} - V^{\text{condensed phase}}$, and since the molar volume of the vapor, V^{vapor}, is much larger than the molar volume of the condensed phase, $V^{\text{condensed phase}}$, then, with the introduction of an insignificant error,

$$\Delta V = V^{\text{vapor}}$$

Thus, for condensed phase–vapor equilibria, the Clapeyron equation can be written as

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta H}{TV^{\text{vapor}}}$$

in which V^{vapor} is the molar volume of the vapor. If it is further assumed that the vapor in equilibrium with the condensed phase behaves ideally (i.e., $PV = RT$), then

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{P\Delta H}{RT^2}$$

rearrangement of which gives

$$\frac{dP}{P} = \frac{\Delta H}{RT^2}dT$$

or

$$d\ln P = \frac{\Delta H}{RT^2}dT \tag{7.6}$$

Equation 7.6 is known as the *Clausius–Clapeyron equation*.

If ΔH is independent of temperature—that is, if c_p(vapor) = c_p(condensed phase)—integration of Equation 7.6 gives

$$\ln P = -\frac{\Delta H}{RT} + \text{constant} \tag{7.6a}$$

where the initial pressure is assumed to be 1 atm. If we use the boiling point values of the pressure and temperature (P_0 and T_b), we can write

$$\ln\frac{P}{P_0} = -\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] \tag{7.7}$$

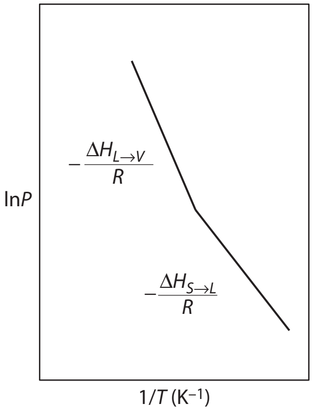

Figure 7.9 Schematic plot of ln*P* vs. 1/*T*. The slope of the plot is $-\Delta H/R$, and the slope changes at the melting point of the solid.

Since equilibrium is maintained between the vapor phase and the condensed phase, the value of P at any T in Equation 7.7 is the *saturated vapor pressure* exerted by the condensed phase at the temperature T. Equation 7.7 thus shows that the saturated vapor pressure exerted by a condensed phase increases exponentially with increasing temperature.

A plot of $\ln P$ versus $1/T$ is linear, in this approximation, with a slope of $-\Delta H/R$ (Figure 7.9). The change in slope in Figure 7.9 occurs at the melting point of the solid. The saturated vapor pressure versus temperature of several of the more common elements is depicted in Figure 7.10.

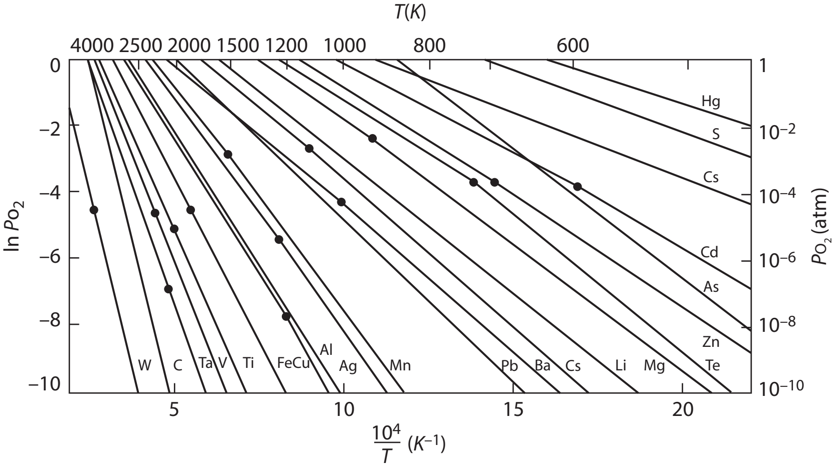

Figure 7.10 The vapor pressure vs. 1/*T* diagram of several elements as functions of temperature. The dots demark the melting points of the elements. (After R. Hultgren et al., *Selected Values of the Thermodynamic Properties of the Elements*, ASM, Metals Park, OH, 1973.)

7.6 GRAPHICAL REPRESENTATION OF VAPOR PHASE AND CONDENSED PHASE EQUILIBRIA

When a liquid and its vapor are in equilibrium, the normal boiling point of the liquid is defined as that temperature at which the saturated vapor pressure exerted by the liquid is 1 atm. Knowledge of the molar heat capacities of the liquid and vapor phases, the molar enthalpy of evaporation at any one temperature, $\Delta H_{\text{evap},T}$, and the normal boiling temperature allows the saturated vapor pressure–temperature to be determined for any material.

The phase diagram of a one-component system depicted in Figure 7.7 has T and P as the independent thermodynamic coordinates. The curve AOA' is a graphical representation of the integral of Equation 7.3, which is the variation of pressure with temperature required for phase equilibrium between the solid and liquid phases. If ΔH_m is independent of temperature, integration of Equation 7.3 gives an expression of the form

$$P = \frac{\Delta H}{\Delta V} \ln T + \text{constant} \tag{7.11}$$

By definition, the normal melting temperature of the material is the melting temperature at a pressure of 1 atm, and in Figure 7.7, the normal melting point is designated as the point m. The curve BOB' is the curve for equilibrium between the vapor and the liquid given by Equation 7.7, in which ΔH_T is $\Delta H_{\text{evap},T}$. In the case of water, the line BOB' represents the variation, with temperature, of the saturated vapor pressure of the liquid, or alternatively, the variation, with pressure, of the dew point of water vapor. The curve BOB' passes through the normal boiling point (represented by the point b in the figure) and intersects the line AOA' at the *triple point*, O. The triple point is the state represented by the invariant values of P and T at which the solid, liquid, and vapor phases are in equilibrium with each other. Knowledge of the triple point, together with the value of $\Delta H_{\text{sublim},T}$, allows the variation of the saturated vapor pressure of the solid with temperature to be determined. This equilibrium curve is drawn as COC' in Figure 7.7.

7.7 SOLID–SOLID EQUILIBRIA

Elements which can exist in more than one crystal form are said to exhibit *allotropy*, and chemical compounds or solid solutions which can exist in more than one solid form are said to exhibit *polymorphism*. The variation of pressure with temperature required to maintain equilibrium between two solids is given by Equation 7.3:

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta H}{T \Delta V}$$

in which ΔH and ΔV are the changes in the molar enthalpy and the molar volume for the change of state solid I → solid II.

Figure 7.11a is a schematic of the *P*-*T* diagram of an element exhibiting two allotropes. Figure 7.11b shows a schematic of the enthalpy of each of the phases as a function of temperature. Starting at low temperatures and atmospheric pressure, the stable phase is solid phase I. At $T_{\mathrm{I}\rightarrow\mathrm{II}}$, this phase transforms into the solid phase II. This transformation is shown to have an enthalpy of transformation, and is therefore a first-order transformation. Phase II melts at T_m, and the liquid boils at T_b. These transformations also display enthalpies of transformation and are thermodynamically first order.

The pressure–temperature phase diagram for iron at relatively low pressures is shown in Figure 7.12. Iron has the body-centered cubic crystal structures in the paramagnetic α and δ phases at, respectively, low and high temperatures and exhibits the

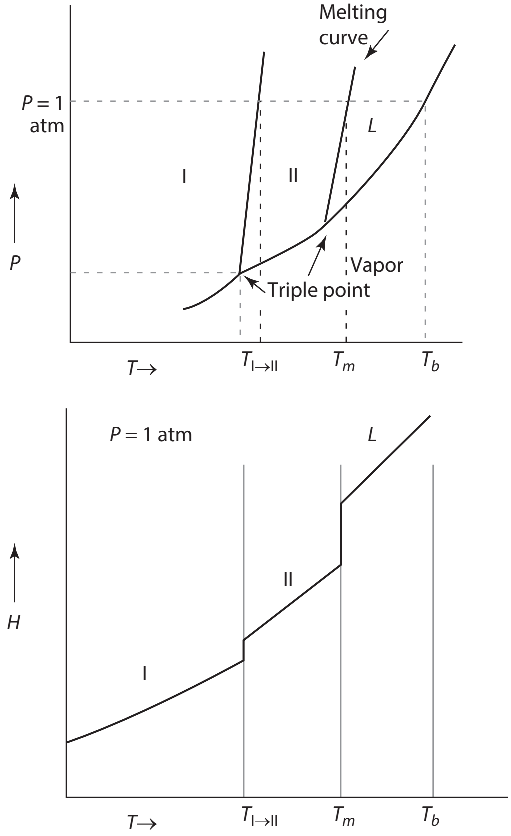

Figure 7.11 (a) Schematic pressure vs. temperature diagram of a system with two solid-state phases (I and II) and a liquid phase. (b) Schematic enthalpy vs. temperature diagram of the system in Figure 7.11a, showing the transformation temperature from I to II, the melting temperature, and the boiling temperature.

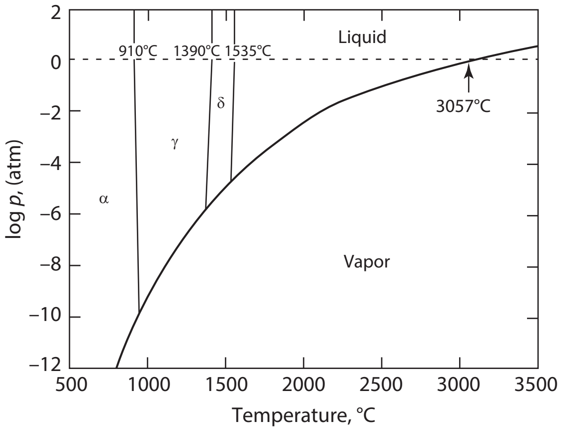

Figure 7.12 The pressure temperature phase diagram for iron.

face-centered cubic (FCC) crystal structure (γ phase) at intermediate temperatures. Figure 7.12 shows three triple points involving two condensed phases and the vapor phase.

It is of interest to consider the slope of the α–γ equilibrium curve. As was the case for the solid water–liquid water equilibrium curve, the slope is negative. For water, this was because of the anomalous density of liquid water, it being greater than that of solid water in the region of the equilibrium—that is $V_M(L) < V_M(S)$. This, combined with the greater entropy of liquid water, $S_M(L) > S_M(S)$, gives rise to a negative slope.

The negative slope of the P-T coexistence boundary for α and γ is also anomalous. The slope $dP/dT = \Delta S/\Delta V$ is usually positive in solids (considering only vibrational entropy), since the smaller molar volume phase usually has the smaller entropy. The volume change for Fe transforming from α to γ is negative. Since $\Delta V^{\alpha\to\gamma}$ is negative, $\Delta S^{\alpha\to\gamma}$ must be positive in order that the curve have a negative slope. This means that the entropy of the γ phase (FCC) is larger than that of α phase (body-centered cubic [BCC]), which is unusual.

To explain this, recall that there are various aspects of entropy, and in a magnetic solid, the spin entropy must be considered. Thus, the important aspects of entropy here are

- Vibrational entropy (thermal)
- The spin entropy of the moments on each Fe atom

The Clapeyron equation shows

$$S^{\gamma} > S^{\alpha}$$

Therefore,

$$S^{\gamma}_{\text{vibrational}} + S^{\gamma}_{\text{spin}} > S^{\alpha}_{\text{vibrational}} + S^{\alpha}_{\text{spin}}$$

The vibrational entropy for BCC metals is larger than that for FCC metals (see Chapter 6), so that it can be further concluded that

$$S^{\gamma}_{\text{spin}} > (S^{\alpha}_{\text{vibrational}} - S^{\gamma}_{\text{vibrational}}) + S^{\alpha}_{\text{spin}}$$

Since both terms on the right-hand side are positive, we conclude that

$$S^{\gamma}_{\text{spin}} > S^{\alpha}_{\text{spin}}$$

FCC γ iron must have larger spin entropy than BCC paramagnetic α iron does. The origin of the large c_p, and therefore, the entropy of the γ phase, is the disordering of the antiferromagnetic (AF) state of γ iron, which occurs at very low temperatures. It is this transition which gives the paramagnetic γ phase such a large spin entropy and stabilizes the γ phase at elevated temperatures. If γ iron were not antiferromagnetic at low temperatures, it would not have enough entropy to replace α iron at high temperatures. This would mean that martensite could not be formed in Fe-based alloys!

The curve for equilibrium between γ and δ has a positive slope. In this case, the high-temperature δ phase is BCC, so its vibrational entropy is greater than that of the FCC (γ) phase, and its molar volume is greater as well.

With increasing pressure, the slope of the γ–δ line becomes greater than that of the δ–liquid line, and the two lines meet at a triple point for the three-phase γ–δ–liquid equilibrium at $P = 14{,}420$ atm and $T = 1590°\text{C}$ (not shown in Figure 7.12). The vapor pressure of liquid iron, which is given by

$$\ln p\ (\text{atm}) = \frac{-19{,}710}{T} - 1.27 \ln T + 10.39$$

reaches 1 atm at 3330 K (3057°C), which is thus the normal boiling temperature of iron.

Figure 7.13 is a schematic representation of the variation of the molar Gibbs free energies with temperature (at constant pressure) of the BCC, FCC, liquid, and vapor phases of iron. In iron, the less close-packed phase BCC (α) is stable at 0 K because its internal energy is lowered due to its *ferromagnetism*. The curvature of the BCC (α) iron G versus T curve is more negative than that of the FCC (γ) curve, and hence, it intersects the FCC iron line twice, with the consequence that, at 1 atm pressure, BCC iron is stable relative to FCC iron at temperatures less than 910°C and at temperatures greater than 1390°C. Since the curvature of the Gibbs free energy of the BCC iron is always more negative than that of FCC iron, the heat capacity of FCC (γ) iron is less than that of BCC (α) iron near the temperatures of transformation (Figure 6.5).

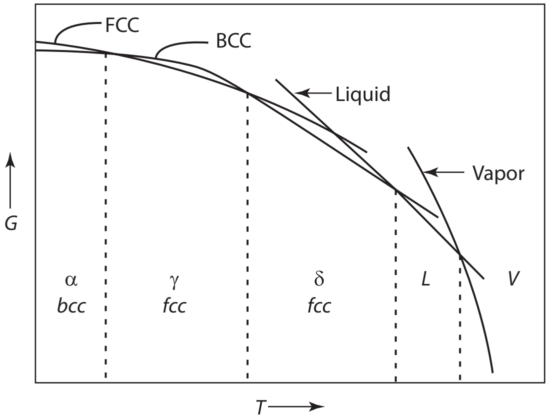

Figure 7.13 Schematic representation of the variation of the molar Gibbs free energies of the BCC, FCC, liquid, and vapor phases of iron with temperature at constant pressure.

A schematic phase diagram for zirconia, ZrO_2, is shown in Figure 7.14. Zirconia has monoclinic, tetragonal, and cubic polymorphs. Note that the point group symmetry of the stable polymorph increases as the temperature increases (monoclinic to tetragonal to cubic). Including the liquid and vapor phases, zirconium exhibits five stable phases, and hence, the phase diagram contains as many as 5!/3! = 20 triple points, five of which are shown in Figure 7.14. The states *a*, *b*, and *c* are stable triple points for, respectively, the three-phase equilibria monoclinic–tetragonal–vapor, tetragonal–cubic–vapor, and cubic–liquid–vapor, and the states *d* and *e* are metastable triple points. The state *d* is that at which the extrapolated vapor pressure lines

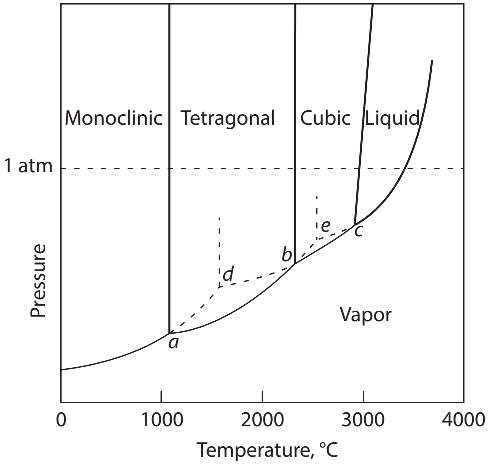

Figure 7.14 A schematic pressure temperature phase diagram for zirconia, ZrO_2.

of the monoclinic and the cubic lines meet in the phase field of stable tetragonal zirconia. The state *d* is thus the metastable triple point for the equilibrium between vapor, monoclinic, and cubic zirconia, which occurs at a higher value of molar Gibbs free energy than that of tetragonal zirconia at the same value of P and T. Similarly, the state *e*, which is that at which the extrapolated vapor pressures of tetragonal and liquid zirconia intersect in the phase field of stable cubic zirconia, is the metastable triple point for equilibrium between liquid, vapor, and tetragonal zirconia.

7.8 THE EFFECT OF AN APPLIED MAGNETIC FIELD ON THE *P-T* DIAGRAM

When a magnetic field is applied to a system in equilibrium, a change in the equilibrium state will occur. Consider the P-T diagram of Figure 7.15. The solid line represents equilibrium between the β and γ phases when $\mathcal{H} = 0$. If a magnetic field is now applied, there will be a change in the equilibrium state, indicated by the dotted line.

In Chapter 2, we saw that when a magnetic field is applied to a material, the field does work on the material.

$$\delta w' = -V\mu_0 \overrightarrow{\mathcal{H}} \cdot d\overrightarrow{\boldsymbol{M}}$$

In Qualitative Problem 2 of Chapter 2, we saw that $\mathcal{H} = M/\chi$ for the linear region of the $\mathcal{H}$–$\boldsymbol{M}$ plot, where χ is the magnetic susceptibility of the material. For equilibrium in a one-component system, we write the Gibbs free energy as

$$dG' = -S'dT + V'dP - V'\mu_0 \boldsymbol{M} d\mathcal{H}$$

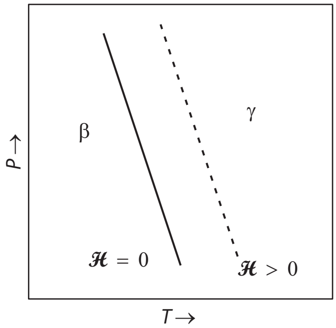

Figure 7.15 Schematic pressure vs. temperature diagram for two solid phases, β and γ. The β phase has the higher magnetic susceptibility. When a magnetic field is applied, the equilibrium curve shifts and expands the stability region of the phase with the higher magnetic susceptibility.

and substituting $\chi\mathcal{H}$ for M,

$$dG' = -S'dT + V'dP - V'\mu_0\chi\mathcal{H}\, d\mathcal{H}$$

It can be seen from the preceding equations that the Gibbs free energy is lowered more for the phase with the larger magnetic susceptibility when an external magnetic field $\mathcal{H}$ is applied. The applied magnetic field thus stabilizes the phase with the larger magnetic susceptibility. For the example in Figure 7.15, the β phase has a larger magnetic susceptibility than the γ phase; hence, the curve of β–γ equilibrium is shifted to higher temperatures. The applied magnetic field thus increases the *stability field* of the material with the higher magnetic susceptibility.

7.9 SUMMARY

1. Knowledge of the dependencies, on temperature and pressure, of the changes in molar enthalpy and molar entropy caused by phase changes in a system allows the determination of the corresponding change in the molar Gibbs free energy of the system.
2. Since a closed one-component system has only two independent variables, the dependence of G can be examined most simply by choosing the state variables T and P as the independent variables (these are the natural independent variables when G is the dependent variable). The phases in which the material can exist can thus be represented in a three-dimensional diagram using the state function G, the independent state variables P, and T as coordinates.
3. If sections of these three-dimensional diagrams are taken at constant P, one obtains G versus T plots for the phases. The phase that is in equilibrium at a given temperature is the one with the lowest G. Crossings of the curve represent temperatures at which two (or three) phases are in equilibrium. The slope of the G versus T plot is the negative of the entropy, and the curvature is related to the heat capacity of the phases delineated by the curves.
4. Sections of the three-dimensional diagrams may be taken at constant temperature. Such plots of P versus T show which phase is in equilibrium as a function of pressure. Their slopes are equal to the molar volume of the phases, and their curvatures are related to the isothermal compressibility of the phase being plotted.
5. In the three-dimensional diagrams, the various states in which the material can exist occur as surfaces. In any state, which is determined by the values of P and T, the stable phase is that which has the lowest Gibbs free energy. The surfaces in the diagram intersect with one another along curves, and these curves represent the variations of P with T required for equilibrium between the two phases.
6. The intersection of the surfaces for the solid and liquid phases gives the variation of the equilibrium melting temperature with pressure. The intersection of the surfaces for the liquid and vapor phases gives the variation of the boiling temperature with pressure. The normal melting and boiling points of the material occur on these intersections at $P = 1$ atm. Three surfaces intersect at a point in the diagram, and the values of P and T at which this intersection occurs are those of the invariant triple point at which an equilibrium occurs among three phases. In a one-component system, no more than three phases can coexist in equilibrium with one another.

7. The three-dimensional *G-T-P* diagram illustrates the differences between stable, metastable, and unstable states and, hence, shows the difference between reversible and irreversible process paths. At any value of *P* and *T*, the stable phase is that which has the lowest Gibbs free energy, and phases which have higher values of *G* at the same values of *P* and *T* are metastable with respect to the phase of lowest value of *G*. Phases with a value of *G* at any combination of *P* and *T* which do not lie on a surface in the diagram are unstable. A reversible process path involving a change in *P* and/or *T* lies on a phase surface, and the state of a phase is changed reversibly only when, during the change, the state of the system does not leave the surface of the phase. If the process path leaves the phase surface, then the change of state, which necessarily passes through nonequilibrium states, is irreversible.
8. Since the perspective representation, in two dimensions, of a three-dimensional diagram is difficult, it is normal practice to present the phase diagram for a one-component system as the basal plane of the *G-T-P* diagram (i.e., a *P-T* diagram), onto which are projected the lines along which two surfaces intersect (equilibrium between two phases) and the points at which three surfaces intersect (equilibrium among three phases). Such a diagram contains areas in which a single phase is stable, which are separated by curves along which two phases exist at equilibrium, and points at the intersection of three curves at which three phases coexist in equilibrium. The curves for equilibrium between a condensed phase and the vapor phase are called *vapor pressure curves*, and they are exponential in form. In view of the fact that saturated vapor pressures can vary over several orders of magnitude, pressure–temperature phase diagrams can often be presented in more useful form as plots of $\ln P$ versus $1/T$ than as plots of P versus T.
9. The development of phase diagrams for one-component systems demonstrates the use of the Gibbs free energy as a criterion for equilibrium when *T* and *P* are chosen as the independent state variables.
10. The equilibrium Gibbs phase rule for a one-component simple system is

$$\mathcal{F} = 3 - \phi$$

where $\mathcal{F}$ is the number of degrees of freedom and the ϕ number of phases allowed to be present in equilibrium.

11. Thermodynamic equilibrium is affected by the application of external fields, such as a magnetic or electrical field.

7.10 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 7

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Allotropy
Continuous transition
Curvature of Gibbs free energy versus temperature
Enthalpy of melting
Entropy of melting
First-order phase transition (transformation)

Gibbs equilibrium phase rule
Higher-order phase transition
Melting temperature
Polymorphism
Potential
Principle of Le Chatelier
Slope of Gibbs free energy versus temperature
Spin entropy
Thermodynamic degree of freedom
van't Hoff rule
Vibrational (thermal) entropy

7.11 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Three allotropes α,β, and γ of a certain element are in equilibrium at its triple point (Figure 7.16a). It is known that

$$V_m^\gamma < V_m^\alpha \text{ and } S_m^\gamma < S_m^\beta$$

Determine which regions of the diagram are α,β and γ. Explain your reasoning.

Solution to Qualitative Problem 1

If the pressure is increased, equilibrium of the system favors the lowest molar volume phase. Therefore, γ is in either region I or II of Figure 7.16a, since $V_m^\gamma < V_m^\alpha$. But, at the triple point, increasing the pressure moves equilibrium to the lowest molar volume phase. Thus, region I is the γ phase field.

If the temperature is increased, the equilibrium of the system favors the phase of the highest entropy. Therefore, the β phase is in either region II or III, since $S_m^\gamma < S_m^\beta$. But at the triple point, increasing the temperature moves equilibrium to the highest entropy phase; therefore, region III is the phase field for the β phase.

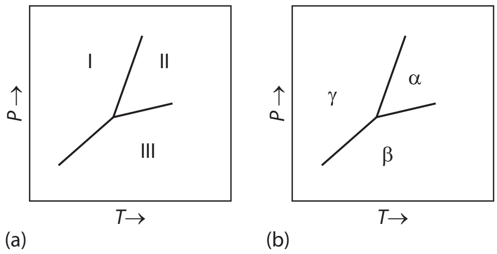

Figure 7.16 (a) Schematic pressure–temperature phase diagram for a one-component system in the vicinity of its triple point. All phases are solids. (b) Labeling of the phase fields using the properties $V_m^\gamma < V_m^\alpha$ and $S_m^\gamma < S_m^\beta$.

The phases are as they appear in Figure 7.16b.

Qualitative Problem 2

In Section 7.2, the order of a phase transformation was defined as the lowest derivative of the Gibbs free energy with respect to temperature (or pressure), which is *discontinuous* at the transition temperature. Sketch entropy versus temperature and heat capacity versus temperature plots for first- and *second*-order transformations.

Solution to Qualitative Problem 2

In a first-order transformation (Figure 7.17a), the first derivative of the Gibbs free energy is discontinuous; hence, the entropy versus temperature diagram shows a discontinuity. The second derivative which is related to the heat capacity by

$$c_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

displays an effective infinity at the transformation temperature, which is indicative of an enthalpy of transformation.

A second-order transformation (usually called a *continuous transformation*) has no discontinuity in the first derivative of its Gibbs free energy (the entropy), but the

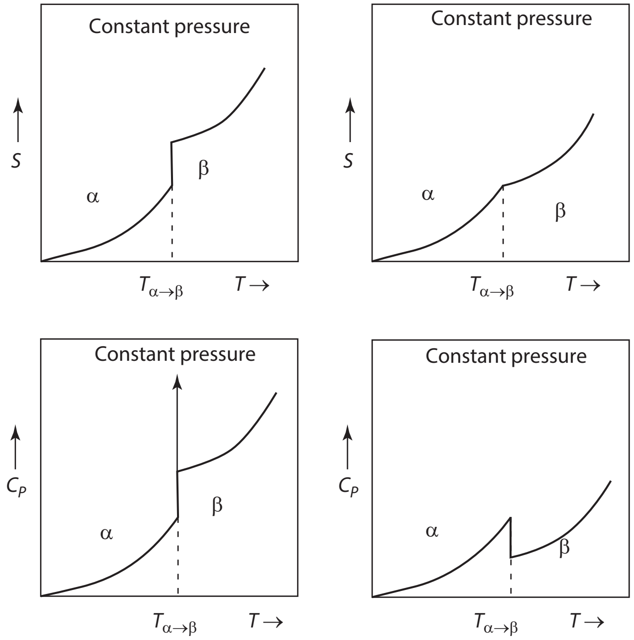

Figure 7.17 Schematic diagrams of entropy and heat capacity vs. temperature for (a) first-order transformations and (b) higher-order transformations.

second derivative is discontinuous. See the heat capacity versus temperature plot in Figure 7.17b.

It is very difficult to determine the order of higher-order transformations, and it is common to call all transformations greater than first order, continuous transformations.

7.12 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

The vapor pressure of solid NaF varies with temperature as

$$\ln p \text{ (atm)} = \frac{-34,450}{T} - 2.01 \ln T + 33.74$$

and the vapor pressure of liquid NaF varies with temperature as

$$\ln p \text{ (atm)} = \frac{-31,090}{T} - 2.52 \ln T + 34.66$$

Calculate

1. The normal boiling temperature of NaF
2. The temperature and pressure at the triple point
3. The molar enthalpy of evaporation of NaF at its normal boiling temperature
4. The molar enthalpy of melting of NaF at the triple point
5. The difference between the constant-pressure molar heat capacities of liquid and solid NaF

The phase diagram is shown schematically in Figure 7.18.

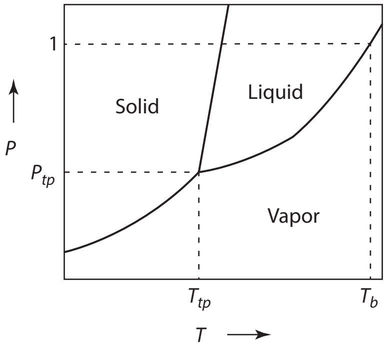

Figure 7.18 Schematic pressure–temperature phase diagram for a one-component system.

Solution to Quantitative Problem 1

1. The normal boiling temperature, T_b, is defined as that temperature at which the saturated vapor pressure of the liquid is 1 atm. Thus, from the equation for the vapor pressure of the liquid, T_b is

$$\ln(1) = 0 = -\frac{31{,}090}{T_b} - 2.52\ln T_b + 34.66$$

which has the solution

$$T_b = 2006 \text{ K}$$

2. The saturated vapor pressures for the solid and liquid phases intersect at the triple point. Thus, at the temperature, T_{tp}, of the triple point

$$-\frac{34{,}450}{T_{tp}} - 2.01\ln T_{tp} + 33.74 = -\frac{31{,}090}{T_{tp}} - 2.52\ln T_{tp} + 34.66$$

which has the solution

$$T_p = 1239 \text{ K}$$

The triple-point pressure is then calculated from the equation for the vapor pressure of the solid as

$$p = \exp\left(-\frac{34{,}450}{1239} - 2.01\ln 1239 + 33.74\right) = 2.29\times10^{-4} \text{ atm}$$

or from the equation for the vapor pressure for the liquid as

$$p = \exp\left(-\frac{31{,}090}{1239} - 2.52\ln 1239 + 34.66\right) = 2.29\times10^{-4} \text{ atm}$$

3. For vapor in equilibrium with the liquid:

$$\ln p \text{ (atm)} = -\frac{31{,}090}{T} - 2.52\ln T + 34.66$$

$$\frac{d\ln p}{dT} = \frac{\Delta H}{RT^2} = \frac{31{,}090}{T^2} - \frac{2.52}{T}$$

Thus,

$$\Delta H_{(l\rightarrow v)} = (31{,}090\times8.3144) - (2.52\times8.3144)T = 258{,}500 - 20.95\text{T}$$

and, at the normal boiling temperature of 2006 K,

$$\Delta H_{(l \to v)} = 258{,}500 - 20.95 \times 2006 = 216{,}500 \text{ J}$$

4. For vapor in equilibrium with the solid:

$$\ln p \text{ (atm)} = -\frac{34{,}450}{T} - 2.01 \ln T + 33.74$$

Thus,

$$\begin{aligned}\Delta H_{(s \to v)} &= (34{,}450 \times 8.3144) - (2.01 \times 8.3144)T \\ &= 286{,}400 - 16.71T \text{ J}\end{aligned}$$

Near the triple point,

$$\Delta H_{(s \to l)} + \Delta H_{(l \to v)} = \Delta H_{(s \to v)}$$

and thus,

$$\begin{aligned}\Delta H_{(s \to l)} &= 286{,}400 - 16.71T - 258{,}500 \times 20.95T \\ &= 27{,}900 + 4.24T\end{aligned}$$

At the triple point,

$$\Delta H_{(s \to l)} = 27{,}900 + \left(4.24 \times 1239\right) = 33{,}150 \text{ J}$$

5 $\Delta H_{(s \to l)}$ = 27,900 + 4.24T

$$\begin{aligned}\frac{d\Delta H}{dT} &= \Delta c_p = 4.24 \text{ J/K} \\ &= c_P^L - c_P^S > 0\end{aligned}$$

Quantitative Problem 2

Carbon has the following three allotropes: graphite, diamond, and a metallic form called solid III. Graphite is the stable form of 298 K and 1 atm pressure, and increasing the pressure on graphite at temperatures less than 1440 K causes the transformation of graphite to diamond and then the transformation of diamond to solid III. Calculate the pressure which, when applied to one mole graphite at 298 K, causes the transformation of graphite to diamond, given

- $H_{298\text{ K, (graphite)}} - H_{298\text{ K, (diamond)}} = -1900$ J.
- $S_{298\text{ K, (graphite)}} = 5.74$ J/K.
- $S_{298\text{ K, (diamond)}} = 2.37$ J/K.
- The density of graphite at 298 K is 2.22 g/cm^3.
- The density of diamond at 298 K is 3.515 g/cm^3.

Solution to Quantitative Problem 2

For the transformation graphite → diamond at 298 K:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S\\ &= 1900 - 298(2.37 - 5.74) = 2904 \text{ J}\end{aligned}$$

For the transformation of graphite to diamond at any temperature T:

$$\left(\frac{\partial \Delta G_{\text{graphite}\to\text{diamond}}}{\partial P}\right)_T = \Delta V_{\text{graphite}\to\text{diamond}}$$

$$V_{\text{graphite}} = \frac{12}{2.22} = 5.405 \text{ cm}^3/\text{mole}$$

and

$$V_{\text{diamond}} = \frac{12}{3.515} = 3.415 \text{ cm}^3/\text{mole}$$

Thus,

$$\Delta V = -1.99 \text{ cm}^3/\text{mole}$$

Equilibrium between graphite and diamond at 298 K requires that $\Delta G_{\text{graphite}\to\text{diamond}}$ be zero. Since

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$$

then

$$\Delta G(P, T = 298) = \Delta G(P = 1, T = 298) + \int_1^P \Delta V dP$$

If the difference between the isothermal compressibilities of the two phases is negligibly small (i.e., if the influence of pressure on ΔV can be ignored), then

$$\begin{aligned}1 \text{ cm}^3\cdot\text{atm} &= \frac{8.3144}{82.057} = 0.1013 \text{ J}\\ \Delta G(P, T = 298) &= 2904 + (-1.99 \times 0.1013)(P - 1)\end{aligned}$$

and thus,

$$(P - 1) = P = \frac{2904}{1.99 \times 0.1013} = 14{,}400 \text{ atm}$$

Transformation of graphite to diamond at 298 K requires the application of a pressure greater than 14,400 atm.

PROBLEMS

7.1 Using the vapor pressure–temperature relationships for $CaF_2(\alpha)$, $CaF_2(\beta)$, and liquid CaF_2, calculate

a. The temperatures and pressures of the triple points for the equilibria $CaF_2(\alpha)$ –$CaF_2(\beta)$–$CaF_2(v)$ and $CaF_2(\beta)$–$CaF_2(l)$–$CaF_2(v)$
b. The normal boiling temperature of CaF_2
c. The molar latent enthalpy of the transformation $CaF_2(\alpha) \rightarrow CaF_2(\beta)$
d. The molar latent enthalpy of melting of $CaF_2(\beta)$

7.2 Calculate the approximate pressure required to distill mercury at 100°C.

7.3 One mole of $SiCl_4$ vapor is contained at 1 atm pressure and 350 K in a rigid container of fixed volume. The temperature of the container and its contents is cooled to 280 K. At what temperature does condensation of the $SiCl_4$ vapor begin, and what fraction of the vapor has condensed when the temperature is 280 K?

7.4 The vapor pressures of zinc have been written as

$$\ln p\ (\text{atm}) = -\frac{15{,}780}{T} - 0.755 \ln\ T + 19.25 \qquad \text{(i)}$$

and

$$\ln p\ (\text{atm}) = -\frac{15{,}250}{T} - 1.255 \ln T + 21.79 \qquad \text{(ii)}$$

Which of the two equations is for solid zinc?

7.5 At the normal boiling temperature of iron, $T_b = 3330$ K, the rate of change of the vapor pressure of liquid iron with temperature is 3.72×10^{-3} atm/K. Calculate the molar latent enthalpy of boiling of iron at 3330 K.

7.6 Below the triple point (–56.2°C), the vapor pressure of solid CO_2 is given as

$$\ln p\ (\text{atm}) = -\frac{3116}{T} + 16.01$$

The molar latent enthalpy of melting of CO_2 is 8330 J. Calculate the vapor pressure exerted by liquid CO_2 at 25°C and explain why solid CO_2 is referred to as "dry ice."

7.7 The molar volumes of solid and liquid lead at the normal melting temperature of lead are, respectively, 18.92 and 19.47 cm^3. Calculate the pressure which must be applied to lead in order to increase its melting temperature by 20°C.

7.8 Nitrogen has a triple point at $P = 4650$ atm and $T = 44.5$ K, at which state the allotropes α, β, and γ coexist in equilibrium with one another. At the triple point, $V_\beta - V_\alpha = 0.043$ cm^3/mole and $V_\alpha - V_\gamma = 0.165$ cm^3/mole. Also at the triple point, $S_\beta - S_\alpha = 4.59$ J/K and $S_\alpha - S_\gamma = 1.25$ J/K. The state of $P = 1$ atm, $T = 36$ K lies on the boundary between the fields of stability of the α and β phases, and at this state, for the transformation of $\alpha \rightarrow \beta$, $\Delta S = 6.52$ J/K and $\Delta V = 0.22$ cm^3/mole. Sketch the phase diagram for nitrogen at low temperatures.

7.9 Measurements of the saturated vapor pressure of liquid $NdCl_5$ give 0.3045 atm at 478 K and 0.9310 atm at 520 K. Calculate the normal boiling temperature of $NdCl_5$.

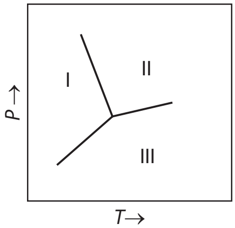

Figure 7.19 Schematic pressure–temperature phase diagram for a one-component system in the vicinity of its triple point. All phases are solids.

7.10* Three allotropes α,β, and γ of a certain element are in equilibrium at its triple point (Figure 7.19). It is known that

$$V_m^{\gamma} > V_m^{\alpha} \quad \text{and} \quad S_m^{\gamma} < S_m^{\beta}$$

Determine which regions of the diagram are αβ, and γ. Explain your reasoning.

7.11* Figure 7.11 shows a pressure versus temperature phase diagram for a system exhibiting two solid-state phases. Sketch the Gibbs free energy curves versus temperature for the two solid phases and the liquid phase. Comment on the slopes of the curves.

7.12* Figure 7.20 is the Gibbs free energy versus pressure plot for three phases, solid (*S*), liquid (*L*), and gas (*G*), near the triple point for the system. It is known that the molar volume of the solid is greater than that of the liquid.

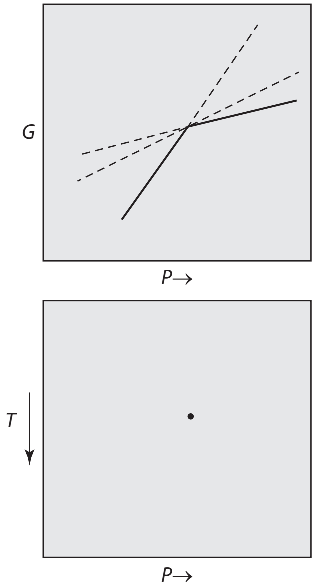

Figure 7.20 Schematic Gibbs free energy vs. temperature diagram for a one-component system and a template of the plot to be used in answering the problem.

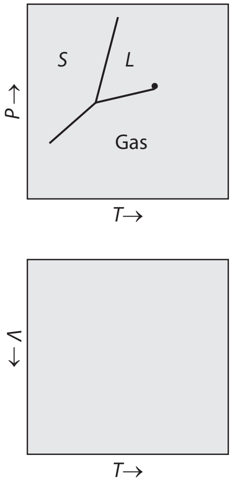

Figure 7.21 The pressure–temperature phase diagram of the system discussed in Problem 7.13 along with the volume vs. temperature template to be used in the answer.

a. Label the three plots of G versus P as S, L, or G.
b. Draw the T-P plot for the material as shown in Figure 7.19. Label the S, L, and G fields and any other points of interest. Note that the temperature is increasing in the downward direction.

7.13* The pressure–temperature phase diagram of a certain material is shown in Figure 7.21. Construct the volume–temperature diagram for this substance using the arrangement shown in the figure and label all phase fields.

7.14* It can be seen from Figure 7.7 that the metastable extensions of the two-phase equilibria go into single-phase fields. At the triple point, it can be seen that the stable and metastable equilibrium curves alternate as one goes around the triple point. Show that the metastable extensions must alternate with stable two-phase curves.

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* New problem in this edition

CHAPTER 8

The Behavior of Gases

8.1 INTRODUCTION

Up to this point, we have made frequent use of the *ideal gas* to illustrate the nature of changes in the thermodynamic state of a gaseous system. In this chapter, the behavior of *real gases* is compared with ideal behavior. The differences between the two are mainly related to the atomic or molecular interactions of real gases. Although knowledge of the physical properties of a real gas is not required in a thermodynamic examination of the gas, an appreciation of the origin of the physical properties provides a better understanding of the thermodynamic behavior.

8.2 THE *P-V-T* RELATIONSHIPS OF GASES

Experimental observation has shown that, for 1 mole of all real gases,

$$\text{limit } P \to 0 \ \frac{PV}{RT} \to 1 \tag{8.1}$$

where:

P is the pressure of the gas
V is the molar volume of the gas
R is the universal gas constant
T is the absolute temperature of the gas

Thus, as the pressure of the gas approaches zero, isotherms plotted on a P-V diagram approach the form of a rectangular hyperbola (Figure 1.3a), given by the equation

$$PV = RT \tag{8.2}$$

Equation 8.2 is the equation of state for 1 mole of an ideal gas and is called the *ideal gas law.* A gas which obeys this law over a range of states is said to behave ideally in this range of states, and a gas which obeys this law in *all states* is called a *perfect* *gas*. The perfect gas is a convenient model with which the behavior of real gases can be compared.

8.3 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

The variation of the molar Gibbs free energy with pressure of a closed system of fixed composition and at constant temperature is found from the *fundamental equation* (Equation 5.25) to be

$$dG = VdP \tag{8.3}$$

For 1 mole of an ideal gas, this can be written as

$$dG = \frac{RT}{P}dP = RTd\ln P \tag{8.4}$$

and thus, for an isothermal change of pressure from P_1 to P_2 at T,

$$G(P_2,T) - G(P_1,T) = RT\ln\frac{P_2}{P_1} \tag{8.5}$$

Since Gibbs free energies do not have absolute values (only changes in G can be measured), it is convenient to choose an arbitrary reference state from which the changes in Gibbs free energy can be measured. This reference state is called the *standard state* and is chosen as being the state of 1 mole of pure gas at 1 atm pressure and the temperature of interest. The Gibbs free energy of 1 mole of gas in the standard state $G(P = 1,T)$ is designated $G°(T)$, and thus, from Equation 8.5, the Gibbs free energy of 1 mole of gas at any other pressure P is given as

$$G(P,T) = G°(T) + RT\ln\frac{P}{P^0} \tag{8.6}$$

or simply,

$$G = G° + RT\ln P \tag{8.7}$$

since P^0 equals 1 atm. Notice that in Equation 8.7, the logarithm of a dimensionless ratio, $P/1$ *atm*, occurs in the right-hand term (P in atmospheres).

8.3.1 Mixtures of Ideal Gases

Before discussing the thermodynamic properties of mixtures of ideal gases, it is necessary to introduce the concepts of *mole fraction*, *partial pressure*, and *partial molar quantities*.

8.3.1.1 Mole Fraction

When a system contains more than one component (i.e., when the composition of the system is variable), it is necessary to devise a means of expressing the composition. In this text, we use the mole fraction, X_i, of the component i. The mole fraction is defined as the ratio of the number of moles of i in the system to the total number of moles of all of the components in the system. For example, if the system contains n_A moles of A, n_B moles of B, and n_C moles of C, then

$$X_A = \frac{n_A}{n_A + n_B + n_C} \tag{8.8}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C} \tag{8.9}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C} \tag{8.10}$$

The sum of the mole fractions of all of the components in a system is unity ($X_A + X_B + X_C = 1$). Thus, there are only two independent composition variables in a three-component system.

8.3.1.2 Dalton's Law of Partial Pressures

The pressure P exerted by a mixture of ideal gases is equal to the sum of the pressures exerted by each of the individual component gases. The contribution made to the total pressure, P, by each individual gas is called the *partial pressure* of that gas. The partial pressure exerted by a component gas, p_i, is thus the pressure that it would exert if it alone were present. In a mixture of the ideal gases A, B, and C,

$$P = p_A + p_B + p_C$$

Consider a fixed volume V' at the temperature T which contains n_A moles of an ideal gas A. The pressure exerted is thus

$$p_A = \frac{n_A RT}{V'} \tag{8.11}$$

If n_B moles of ideal gas B are added to this constant volume containing n_A moles of gas A, the pressure increases to

$$P = p_A + p_B = (n_A + n_B)\frac{RT}{V'} \tag{8.12}$$

Division of Equations 8.11 by 8.12 gives

$$\frac{p_A}{p_A + p_B} = \frac{n_A}{n_A + n_B}$$

which, for the gas A in the mixture, can be written as

$$\frac{p_A}{P} = X_A$$

or

$$p_A = X_A P \tag{8.13}$$

Thus, in a mixture of ideal gases, the partial pressure of a component gas is the product of its mole fraction and the total pressure of the gas mixture. Equation 8.13 is called *Dalton's law of partial pressures*.

8.3.1.3 Partial Molar Quantities

The partial molar value[*] of an extensive thermodynamic variable Q' is the rate of change of Q' with respect to the addition of n_i moles of component i at constant temperature, pressure, and composition. This can be written as

$$\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,p,n_j,n_k,\ldots} \tag{8.14}$$

where Q' is the value of the *extensive* thermodynamic variable for an arbitrary quantity of the mixture.

The definition of $\bar{Q}_i$ can also be made as follows. If 1 mole of i is added, at constant temperature and pressure, to a quantity of a solution which is sufficiently large that the addition causes virtually no change in the composition of the solution, the consequent increase in the value of Q' equals the value of $\bar{Q}_i$ in the solution. In the case of the extensive variable being the Gibbs free energy,

$$\bar{G}_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots}$$

and, from Equation 5.16 it is seen that

$$\bar{G}_i = \mu_i$$

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[*] Some texts call this the partial molal property, which emphasizes that the intensive variables of T and P are held constant for all the partial quantities.

That is, the partial molar Gibbs free energy of a component in a solution equals the chemical potential of the component in the solution.

The relationships among the various state variables developed in the preceding chapters are applicable to the partial molar properties of the components of a system. For example, the fundamental equation at constant T and composition gives

$$\left(\frac{\partial G'}{\partial P}\right)_{T,\text{comp}} = V'$$

where G' is the Gibbs free energy of the system and V' is the volume of the system. For a variation in n_i, the number of moles of component i in the system, at constant T, P, and n_j,

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial G'}{\partial P}\right)_{T,\text{comp}}\right]_{T,P,n_j} = \left(\frac{\partial V'}{\partial n_i}\right)_{T,P,n_j}$$

But, by definition,

$$\left(\frac{\partial V'}{\partial n_i}\right)_{T,P,n_j} = \bar{\mathrm{V}}_i$$

and since the Gibbs free energy is a thermodynamic *state variable*, in which case the order of partial differentiation has no influence on the result,

$$\begin{aligned}
\left[\frac{\partial}{\partial n_i}\left(\frac{\partial G'}{\partial P}\right)_{T,\text{comp}}\right]_{T,P,n_j} &= \left[\frac{\partial}{\partial P}\left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_j}\right]_{T,\text{comp}} \\
&= \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\text{comp}}
\end{aligned}$$

Hence,

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\text{comp}} = \bar{V}_i$$

which is simply the application of Equation 5.25 to the component i in the system. Thus, for the ideal gas A in a mixture of ideal gases,

$$d\bar{G}_A = \bar{V}_A dP$$

The partial molar volume, $\bar{V}_A$, in a gas mixture is

$$\bar{V}_A = \frac{V'}{\sum n_i} = \left(\frac{n_A}{\sum n_i}\right)\left(\frac{RT}{p_A}\right) = \frac{X_A RT}{p_A}$$

Taking the differential of Equation 8.13 at constant T and composition gives $dp_A = X_A dP$, and hence,

$$d\bar{G}_A = \bar{V}_A dP = \frac{X_A RT}{p_A}\frac{dp_A}{X_A} = RTd(\ln\, p_A)$$

Integration from $p_A = 1$ to $p_A = P$ gives

$$\begin{aligned} \bar{G}_A &= G_A^\circ + RT \ln P_A \\ &= G_A^\circ + RT\, \ln X_A + RT\, \ln P \end{aligned} \tag{8.15}$$

Equation 8.15 could also have been obtained by integrating Equation 8.4 from the standard state $p_A = P_A = 1$, $X_A = 1$, T to the state p_A, X_A, T.

8.3.2 The Enthalpy of Mixing of Ideal Gases

For each component gas in a mixture of ideal gases:

$$\bar{G}_i = G_i^\circ + RT \ln X_i + RT \ln P$$

where P is the total pressure of the gas mixture at the temperature T. Dividing by T and differentiating with respect to T at constant pressure and composition gives

$$\left(\frac{\partial(\frac{\bar{G}_i}{T})}{\partial T}\right)_{P,n_i} = \left(\frac{\partial(\frac{G_i^\circ}{T})}{\partial T}\right)_{P,n_i} \tag{8.16}$$

But, from Equation 5.37,

$$\left(\frac{\partial(\frac{G_i^\circ}{T})}{\partial T}\right)_{P,n_i} = -\frac{H_i^\circ}{T^2} \text{ and } \left(\frac{\partial(\frac{\bar{G}_i}{T})}{\partial T}\right)_{P,n_i} = -\frac{\bar{H}_i}{T^2} \tag{8.17}$$

and thus,

$$\bar{H}_i = H_i^\circ \tag{8.18}$$

That is, the partial molar enthalpy of ideal gas i in a mixture of ideal gases equals the molar enthalpy of pure i, and thus, the enthalpy of the gas mixture equals the sum of the enthalpies of the component gases before mixing; that is,

$$\Delta H'^{\text{mix}} = \sum_i n_i \bar{H}_i - \sum_i n_i H_i^\circ = 0 \tag{8.19}$$

where $\Delta H'^{\text{mix}}$ is the change in the enthalpy caused by the process of mixing. That is, the enthalpy change of mixing (the heat of mixing) of an ideal gas is zero. The zero heat of mixing of ideal gases is a consequence of the fact that the particles of an ideal gas do not interact with one another.

Since G_i° is, by definition, a function only of temperature, then, from Equations 8.16 and 8.17, it is seen that $\bar{H}_i$ is a function only of temperature. Thus, in addition to being independent of composition, the partial molar enthalpy of an ideal gas, $\bar{H}_i$, is independent of pressure.

8.3.3 The Gibbs Free Energy of Mixing of Ideal Gases

For each component gas i in a mixture of ideal gases,

$$\bar{G}_i = G_i^\circ + RT \ln p_i$$

and for each component gas before mixing,

$$G_i = G_i^\circ + RT \ln P_i$$

where:

p_i is the partial pressure of i in the gas mixture
P_i is the pressure of the pure gas i before mixing

The mixing process, being a change of state, can be written as

$$\text{unmixed components (state 1)} \rightarrow \text{mixed components (state 2)}$$

and

$$\begin{aligned} \Delta G(1 \rightarrow 2) &= G'(\text{mixture}) - G'(\text{unmixed components}) \\ &= \Delta G'^{\text{mix}} \\ &= \sum_i n_i \bar{G}_i - \sum_i n_i G_i \\ &= \sum_i n_i RT \ln\left(\frac{p_i}{P_i}\right) \end{aligned} \tag{8.20}$$

Thus, the value of $\Delta G'^{\text{mix}}$ depends on the value of p_i and P_i for each gas. If, before mixing, the gases are all at the same pressure (i.e., if $P_i = P_j = P_k = \ldots$) and mixing is carried out at total constant volume such that the total pressure of the mixture, P_{mix}, equals the initial pressures of the gases before mixing, then, since $p_i / P_i = X_i$,

$$\Delta G'^{\text{mix}} = \sum_i n_i RT \ln X_i \tag{8.21}$$

Since the values of X_i are less than unity, $\Delta G'^{\text{mix}}$ is a negative quantity, which corresponds with the fact that the mixing of ideal gases is a spontaneous process.

8.3.4 The Entropy of Mixing of Ideal Gases

Since $\Delta H'^{\text{mix}} = 0$ and

$$\Delta G'^{\text{mix}} = \Delta H'^{\text{mix}} - T\Delta S'^{\text{mix}}$$

then

$$\Delta S'^{\text{mix}} = -\sum_i n_i R \ln \left(\frac{p_i}{P_i} \right) \tag{8.22}$$

or, if $P_i = P_j = P_k = \ldots = P$, then

$$\Delta S'^{\text{mix}} = -R \sum_i n_i \ln X_i \tag{8.23}$$

which is seen to be positive, in accord with the fact that the mixing of ideal gases is a spontaneous process (i.e., the entropy increases). Any interaction among the particles of the gas would decrease the entropy of mixing.

8.4 DEVIATION FROM IDEALITY AND EQUATIONS OF STATE FOR REAL GASES

The variation of V with P at several temperatures for a typical real gas is shown in Figure 8.1. The figure shows that, as the temperature of the gas is decreased from the high temperature T_1, the shape of the P-V isotherms changes, and, eventually, a critical value of $T = T_{\text{cr}}$ is reached at which, at some fixed critical pressure, P_{cr}, and fixed molar volume, V_{cr}, a horizontal inflection occurs on the isotherm; that is,

$$\left(\frac{\partial P}{\partial V} \right)_{T_{\text{cr}}} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_{T_{\text{cr}}} = 0$$

At temperatures less than T_{cr}, two phases exist in equilibrium: a vapor phase and a liquid phase. For example, if 1 mole of vapor, initially in the state A (Figure 8.1),

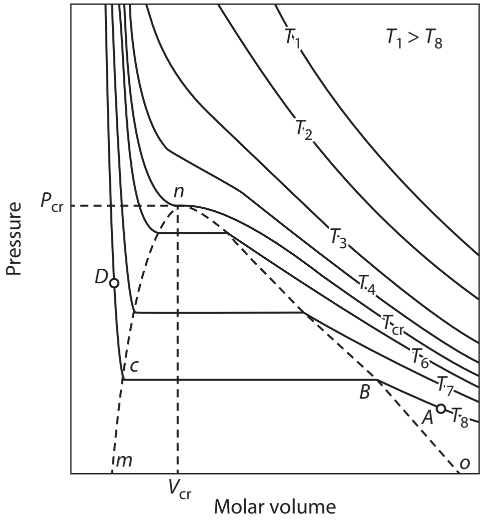

Figure 8.1 *P-V* isotherms for a typical real gas.

is isothermally compressed at T_8, the state of the vapor moves along the isotherm toward the state B. At B, the pressure of the vapor is the saturated vapor pressure of the liquid at T_8, and further compression of the system causes condensation of the vapor and the consequent appearance of the liquid phase. The liquid phase, which is in equilibrium with the vapor, first appears when the vapor reaches *B on the T8 isotherm*. V_C is the molar volume of the liquid at P_C and T_8. Further compression causes further condensation, during which the states of the liquid and vapor phases remain fixed at C and B, respectively, and the total volume of the system, which is determined by the relative proportions of the liquid and vapor phases, moves along the horizontal line from B to C. Eventually, condensation is complete, and the system exists as 100% liquid in the state C. Further increase in pressure moves the state of the system along the isotherm toward the state D. The large value of $-(\partial P/\partial V)_T$ in the range of liquid states and the smaller value of $-(\partial P/\partial V)_T$ in the range of vapor states indicate the low compressibility of the liquid phase and the high compressibility of the vapor phase. (recall that the isothermal compressibility equals).

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Figure 8.1 also shows that, as the temperature is increased from T_8 to T_{cr}, the molar volume of the liquid in equilibrium with the vapor (corresponding to the point C at T_8) progressively increases and the molar volume of the vapor in equilibrium with the liquid (corresponding to the point B at T_8) progressively decreases. Thus, as the temperature is increased toward T_{cr}, the vapor in equilibrium with liquid becomes more dense, and the liquid in equilibrium with the vapor becomes less dense. Eventually, when T_{cr} is reached, the molar volumes of the coexisting phases coincide at the state P_{cr}, T_{cr}. Thus, the critical point coincides with the equilibrium state in which the molar volume of the liquid equals the molar volume of the vapor.

At temperatures greater than T_{cr}, distinct two-phase equilibrium (involving two phases separated by a boundary, across which the properties of the system change abruptly) does not occur, and thus, the gaseous state cannot be liquefied by isothermal compression at temperatures greater than T_{cr}. Since the vapor can be condensed by isothermal compression at temperatures lower than T_{cr}, the critical isotherm provides a distinction between the gaseous and vapor states and defines the gaseous state phase field. The phase fields are shown in Figure 8.2. Note, however, that along the critical isotherm, there is no physical distinction between the vapor and gaseous phase.

Liquefaction of a gas requires that the gas be cooled. Consider the isobaric process path 1 → 2 in Figure 8.2. According to this path, which represents the cooling of the gas at constant pressure, the phase change gas → liquid occurs at the point *a*, at which the temperature falls below T_{cr}. In fact, at pressures greater than P_{cr}, the critical-temperature isotherm has no physical significance. In passing from the state 1 to the state 2, the molar volume of the system progressively decreases, and hence, the density of the system progressively increases. No phase separation occurs between the states 1 and 2, and the system in state 2 can equivalently be regarded as being a liquid of normal density or a gas of high density and in state 1 can be regarded as being a gas of normal density or a liquid of low density. Physically, no distinction can be made between the liquid and gaseous states at pressures greater than P_{cr}, and consequently, the system existing in these states is called a *supercritical fluid*. In the *P*-*T* phase diagram for the system shown in Figure 8.3, the critical point exists at the termination of the liquid–vapor coexistence equilibrium curve, where $P = P_{cr}$ and $T = T_{cr}$.

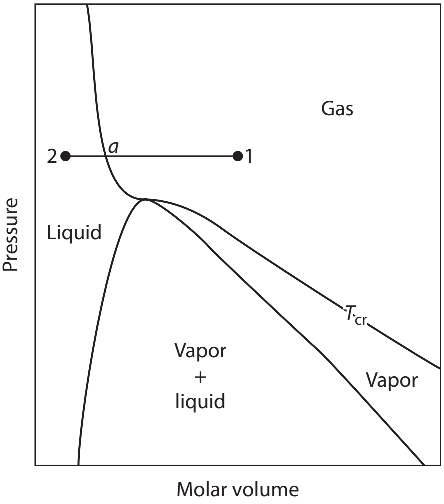

Figure 8.2 Schematic *P*-*V* diagram showing the fields of phase stability of a typical real gas.

The deviation of a real gas from ideal behavior can be measured as the deviation of the compressibility factor from unity. The compressibility factor, Z, is defined as

$$Z = \frac{PV}{RT} \tag{8.24}$$

which has the value of 1 for a perfect gas in all states of existence. Z itself is a function of state of the system and, thus, is dependent on any two chosen dependent variables; for example, $Z = Z(P,T)$. Figure 8.4 shows the variation of Z with P at constant temperature for several gases.

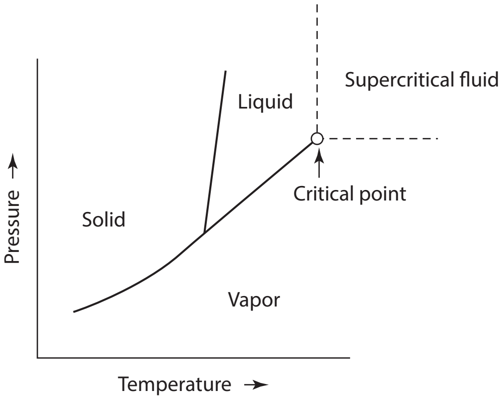

Figure 8.3 Schematic P-T diagram showing the critical point at the end of the liquid–vapor equilibrium curve.

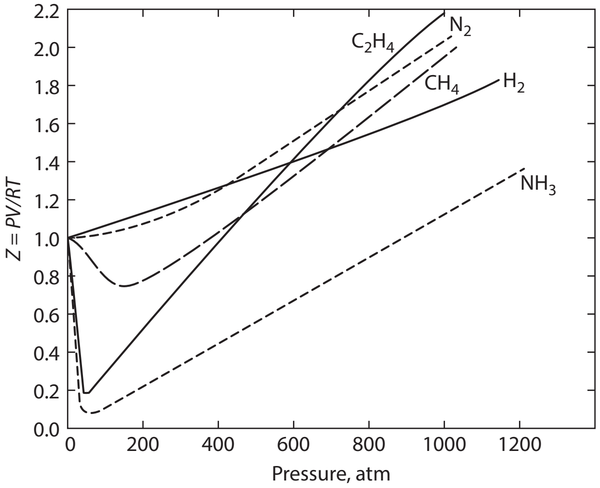

Figure 8.4 The variations, with pressure, of the compressibility factors of several gases at 0°C.

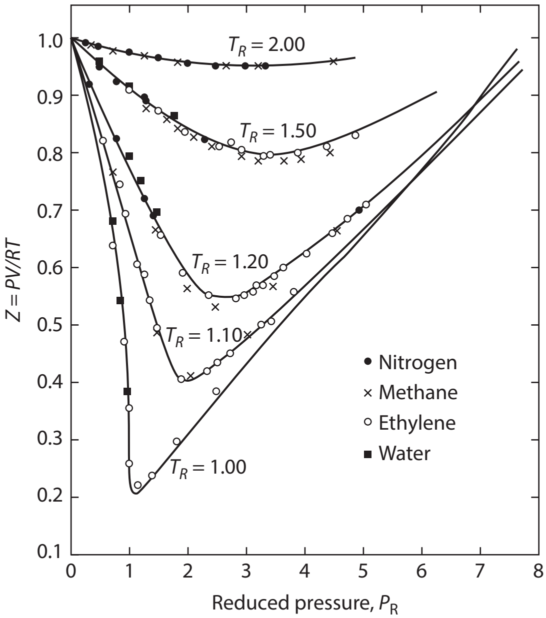

Figure 8.5 The variations of the compressibility factors of several gases with reduced pressure at several reduced temperatures, displaying the law of corresponding states.

If Figure 8.4 is replotted as Z versus the reduced pressure, P_R (where $P_R = P/P_{\text{cr}}$), for fixed values of the reduced temperature, T_R ($=T/T_{\text{cr}}$), it is found that all gases lie on a single curve. Figure 8.5 shows a series of such plots. The behavior shown in Figure 8.4 gives rise to the *law of corresponding states*, which states that all gases obey the same equation of state when expressed in terms of the reduced variables P_R, T_R, and V_R instead of P, T, and V. If the values of two reduced variables are identical for two gases, then the gases have approximately equal values of the third reduced variable and are then said to be in corresponding states. The compressibility factor is the same function of the reduced variables for all gases (see Problem 8.1).

8.5 THE VAN DER WAALS FLUID

Recall that an ideal gas obeys the ideal gas law and has an internal energy, U, which is a function only of temperature. An ideal gas is considered to consist of volumeless particles that do not interact with one another, the energy of which is entirely the translational energy of motion of the constituent particles. Attempts to derive equations of state for *real* gases have modified the ideal gas equation by taking into account two considerations:

- The particles of a real gas occupy a finite volume.
- The particles of a real gas interact with one another.

The magnitude of the importance of these two considerations depends on the state of the gas. For example, if the molar volume of the gas is large, then the volume fraction occupied by the particles themselves is small, and the magnitude of this effect on the behavior of the gas will be correspondingly small. Similarly, as the molar volume increases, the average distance between the particle increases, and thus, the effect of interactions between particles on the behavior of the gas decreases. For a fixed number of moles of gas, an increase in the molar volume corresponds to a decrease in the density, n/V'. These states of existence occur at low pressure and high temperature, as can be seen from the ideal gas equation; that is,

$$\frac{n}{V'} = \frac{P}{RT}$$

Thus, approach toward ideal behavior is to be expected as the pressure is decreased and the temperature is increased.

The most celebrated equation of state for nonideal gases, which was derived from considerations 1 and 2, is the van der Waals equation (Johannes Diderik van der Waals, 1837–1923), which, for 1 mole of gas, is written as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{8.25}$$

where:

P is the measured pressure of the gas

a/V^2 is a correction term for the interactions which occur among the particles of the gas

V is the measured volume of the gas

b is a correction term for the finite volume of the particles*

The term b is determined by considering a collision between two spherical particles. Two particles, of radius r, collide when the distance between their centers decreases to a value less than $2r$, and, as is shown in Figure 8.6a, at the point of collision, the particles exclude a volume of

$$\frac{4}{3}\pi(2r)^3$$

to all the other particles. The volume excluded per particle is thus

$$\begin{aligned} \frac{1}{2}\times\frac{4}{3}\pi(2r)^3 &= 4\times\frac{4}{3}\pi r^3 \\ &= 4\times \text{the volume of one particle} \end{aligned}$$

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* For n moles of a van der Waals fluid, the equation of state is $\left(P + \frac{n^2 a}{V'^2}\right)(V' - nb) = nRT$, where $V' = nV$.

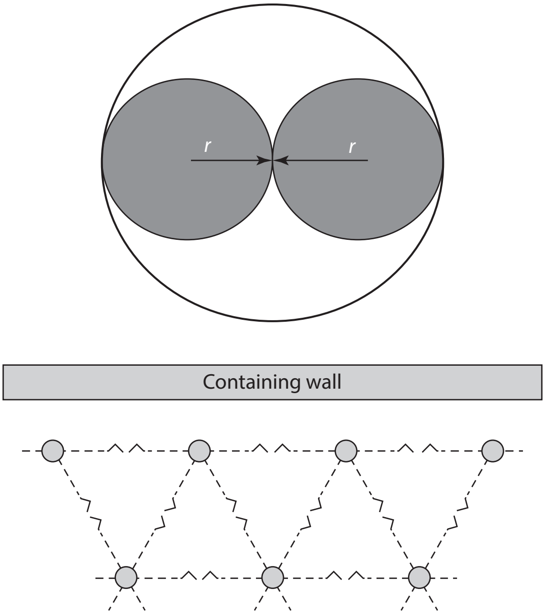

Figure 8.6 (a) Illustration of the volume excluded when two spherical atoms contact; (b) The interactions among atoms in a gas phase, showing that the interactions cause a lower pressure to be exerted on the walls of the container.

The volume excluded is thus four times the volume of all of the particles present and has the value b. Thus, in 1 mole of gas, the volume $(V - b)$ is that available for the motion of the particles of the gas and is the molar volume which the gas would have were the gas ideal—that is, if the particles were volumeless.

The long-range attractive forces operating between the gas particles decrease the pressure exerted on the containing wall to a value less than that which would be exerted in the absence of the forces. Van der Waals considered the following: the particles in the "layer" adjacent to the containing wall experience a net inward pull due to interaction with the particles in the next adjacent layer. These attractive forces give rise to the phenomenon of *internal pressure*, and the magnitude of the net inward pull (i.e., the decrease in the pressure exerted by the gas on the containing wall) is proportional to the number of particles in the "surface layer" and to the number of particles in the "next-to-the-surface layer." Both of these quantities are proportional to the density of the gas, n/V, and hence, the net inward pull is proportional to the square of the density of the gas, or, for 1 mole of gas, equal to a/V^2, where a is a constant. Thus, if P is the measured pressure of the gas, $P + a/V^2$ is the pressure which the gas would exert on the containing wall if the gas were ideal—that is, in the absence of interactions among the particles. The effect is illustrated in Figure 8.6b.

The van der Waals equation (Equation 8.25) can be written as

$$PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

Since this equation is cubic in V, there are three roots. Plotting V as a function of P for different values of T gives the family of isotherms shown in Figure 8.7. As the temperature is increased from T_1, the minimum and the maximum approach one another until, at a temperature designated as T_{cr}, they coincide and produce a horizontal inflection on the P-V curve. This is the critical point, $T = T_{\text{cr}}$, $P = P_{\text{cr}}$, and $V = V_{\text{cr}}$, and the van der Waals equation gives

$$\begin{aligned}
P_{\text{cr}} &= \frac{RT_{\text{cr}}}{(V_{\text{cr}} - b)} - \frac{a}{V_{\text{cr}}^2} \\
\left(\frac{\partial P}{\partial V}\right)_{T_{\text{cr}}} &= \frac{-RT_{\text{cr}}}{(V_{\text{cr}} - b)^2} + \frac{2a}{V_{\text{cr}}^3} = 0 \\
\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_{\text{cr}}} &= \frac{2RT_{\text{cr}}}{(V_{\text{cr}} - b)^3} - \frac{6a}{V_{\text{cr}}^4} = 0
\end{aligned}$$

Solving these equations gives

$$T_{\text{cr}} = \frac{8a}{27bR}, \qquad V_{\text{cr}} = 3b, \qquad P_{\text{cr}} = \frac{a}{27b^2} \tag{8.26}$$

Thus, the constants a and b for any gas can be evaluated from knowledge of the values of T_{cr} and P_{cr}. Alternatively, the values of a and b can be obtained by fitting the van der Waals equation to experimentally measured variations of V with T and P for real gases. The critical states, van der Waal constants, and values of Z at the critical point for several gases are listed in Table 8.1.

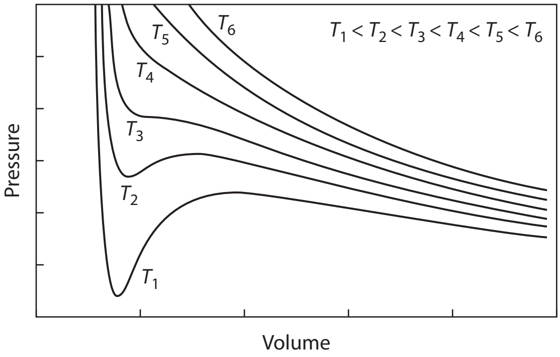

Figure 8.7 The isothermal variation of V with P for a van der Waals fluid at several temperatures.

Table 8.1 The Critical States, van der Waals Constants, and Values of Z at the Critical Points for Several Gases

Gas	T_{cr}, K	P_{cr}, atm	V_{cr}, cm³/mole	a, $\frac{l^2 \cdot atm}{mole^2}$	b, liters/mole	Z_{cr}
He	5.3	2.26	57.6	0.0341	0.0237	0.299
H_2	33.3	12.8	65.0	0.2461	0.0267	0.304
N_2	126.1	33.5	90.0	1.39	0.0391	0.292
CO	134.0	35.0	90.0	1.49	0.0399	0.295
O_2	153.4	49.7	74.4	1.36	0.0318	0.293
CO_2	304.2	73.0	95.7	3.59	0.0427	0.280
NH_3	405.6	111.5	72.4	4.17	0.0371	0.243
H_2O	647.2	217.7	45.0	5.46	0.0305	0.184

Consider the isothermal variation of V with P given by the van der Waals equation and shown in Figure 8.8. Any increase in the pressure exerted on a system must cause a decrease in the volume of the system, $\left(\partial P/\partial V\right)_T < 0$. This is a condition of *intrinsic stability*. In Figure 8.8, this condition is *violated* over the portion *JIHGF*, which means that this portion of the curve is a region of instability.

The equilibrium states of the system at this temperature can be obtained from a consideration of the variation of the Gibbs free energy with P along the isotherm. Equation 5.12 gives the variation of G with P at constant T as $dG = VdP$, and integration of this equation between the state (P,T) and (P_A,T) gives

$$G(P,T) - G(P_A,T) = \int_{P_A}^{P} VdP$$

or

$$G = G_A + \int_{P_A}^{P} VdP \tag{8.27}$$

If an arbitrary value is assigned to G_A, then graphical integration of the integral from Figure 8.8 allows the variation of G with P, to be plotted corresponding to the variation of V with P in Figure 8.8. The values of the integrals are listed in Table 8.2, and the variation of G with P is shown in Figure 8.9.

Figure 8.9 shows that, as the pressure is increased from P_1, the value of G increases. At pressures greater than P_2, three states of existence become available to the system. For example, at P_3, the three states are given by the points I, K, and C. The stable, or equilibrium, state is that with the lowest Gibbs free energy, and hence, over the range of pressure from P_2 to P_4, the stable states lie on the line BCD. As the pressure is increased above P_4, the state with the lowest Gibbs free energy no longer lies on the original line (the continuation of the curve BCD) but lies on the curve LMN. The change of stability at P_4 corresponds to a change of phase at this point; that is, at pressures less than P_4, one phase is stable (vapor), and at pressures greater

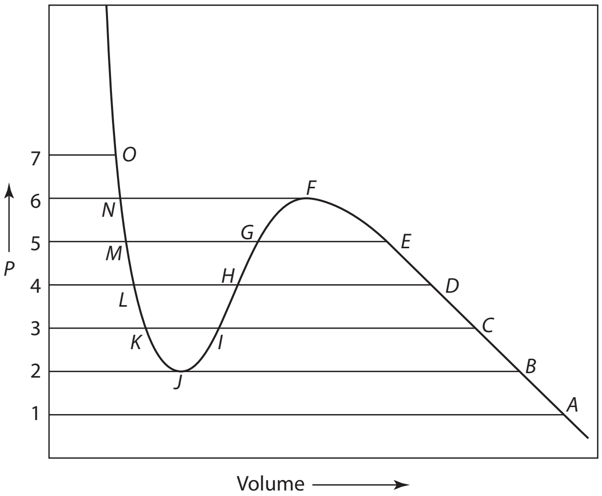

Figure 8.8 The isothermal variation, with pressure, of the volume of a van der Waals fluid at a temperature below the critical temperature.

Table 8.2 Graphical Integration of Figure 8.7

$G_B = G_A + \int_{P_A}^{P_B} VdP$	$= G_A$ + area 1*AB*2	
G_C	$= G_A$ + area 1*AC*3	
G_D	$= G_A$ + area 1*AD*4	
G_E	$= G_A$ + area 1*AE*5	
G_F	$= G_A$ + area 1*AF*6	
G_G	$= G_A$ + area 1*AE*5 + area *EFG*	
G_H	$= G_A$ + area 1*AD*4 + area *DFH*	
G_I	$= G_A$ + area 1*AC*3 + area *CFI*	
G_J	$= G_A$ + area 1*AB*2 + area *BFJ*	
G_K	$= G_A$ + area 1*AC*3 + area *CFI* – area *IJK*	
G_L	$= G_A$ + area 1*AD*4 + area *DFH* – area *HJL*	
G_M	$= G_A$ + area 1*AE*6 + area *EFG* – area *GJM*	
G_N	$= G_A$ + area 1*AF*6	– area *FJN*
G_O	$= G_A$ + area 1*AF*6	– area *FJN* + area 6*NO*7

than P_4, another phase is stable (liquid). At low pressures ($P < P_4$), the system exists as a vapor, and at high pressures ($P > P_4$), it exists as a liquid. At P_4, G_D, which is the molar Gibbs free energy of the vapor phase, equals G_L, which is the molar Gibbs free energy of the liquid phase, and thus, vapor and liquid coexist in equilibrium with one another at the state P_4,T. The transition from the vapor phase to the liquid phase is a first-order phase transition (see Chapter 7). In Figure 8.8, a tie-line connects the

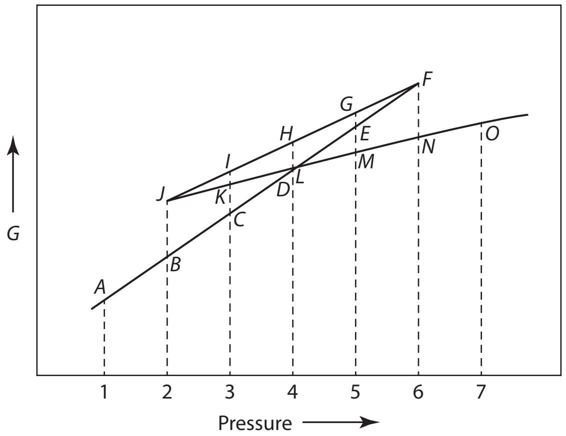

Figure 8.9 Schematic representation of the variation, with pressure, of the molar Gibbs free energy of a van der Waals fluid at a constant temperature lower than the critical temperature. Region *FGHIJ* is an instability region. *F* and *J* demark the limits of phase stability, sometimes called the *spinodals*.

points *D* and *L* across a two-phase region. In Figure 8.9, the line *DF* represents the metastable vapor phase and the line *LJ* represents the metastable liquid states. Thus, in the absence of the formation of the liquid phase from the vapor phase at the state *D*, a supersaturated vapor would exist along the curve *DEF*, and, in the absence of the formation of the vapor phase from the liquid phase at the state *L*, supersaturated liquid would exist along the line *LKJ*. In view of the violation of the criterion for intrinsic stability over the states path *JHF*, the states represented by this line in both Figure 8.8 and Figure 8.9 are unstable, and a transformation will occur spontaneously (i.e., without an energy barrier) to a two-phase equilibrium.

The points *F* and *J* represent the limits of metastability of the vapor and liquid phases, respectively. These were called *spina* by van der Waals in his *Lehrbuch der Thermodynamik* (1908).* The spina or *spinodes* occur where the value of $(\partial P/\partial V)_T = 0$, which, for an isotherm of the van der Waals fluid, yields two points. Between *JIHGF*, a single-phase absolute equilibrium does not exist. This region is a "gap" in the *P*-*V* diagram. Like all regions of instability, they are delineated by points where the second derivative of an energy state function with respect to an intensive variable (in this case, $(\partial^2 G/\partial V^2)_T$) equals zero. Figure 8.10 shows a typical *P*-*V* diagram of a van der Waal fluid in which the regions have been delineated: the region of stability, regions of metastability, and a region of absolute instability. We will encounter such gaps when we study equilibrium binary phase

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* "This singular point is located on the curve, the curve possesses a point (node) of return. From this form of its intersection which resembles a thorn (*spina*, in Latin) the curve obtains its name." Translated by A. H. Cahn, in J. W. Cahn, "Spinodal Decomposition," Appendix B, *Trans. Met. Soc. AIME* (1967), vol. 242, pp. 166–180.

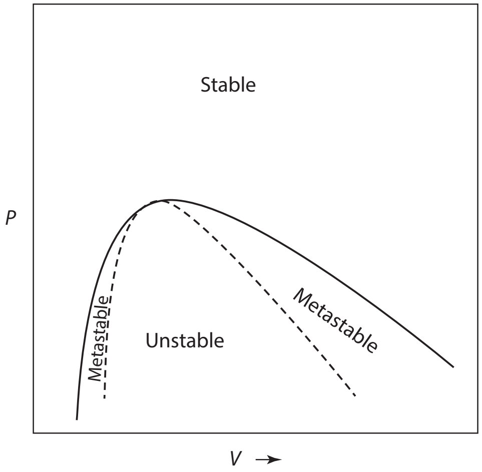

Figure 8.10 *P-V* diagram showing the locus of *spinodal* points and regions of metastability and instability.

diagrams in Chapter 9, where we call them *miscibility gaps*. Within the gap, the equilibrium state is a two-phase state.

It is thus seen that the van der Waals equation predicts the phase change which occurs in the system at temperatures less than T_{cr}. At any temperature below T_{cr}, the value of P for equilibrium between the vapor and liquid phases (e.g., P_4 in Figures 8.8 and 8.9) is that whereby the area *HFD* equals the area *LJH* in Figure 8.8. This is called the *Maxwell construction*.

The measured values of T_{cr} and P_{cr} for CO_2 are, respectively, 31°C and 72.9 atm. Thus, from Equation 8.26,

$$b = \frac{RT_{cr}}{8P_{cr}} = 0.0427 \text{ liters/mole}$$

and

$$a = 27b^2P_{cr} = 3.59 \text{ liters}^2 \cdot \text{atm/mole}^2$$

in which case the van der Waals equation for CO_2 is given as

$$\left(P + \frac{3.59}{V^2}\right)(V - 0.0427) = RT$$

The variation of P with V given by this equation is shown for several temperatures in Figure 8.11, in which it is seen that the 304 K isotherm exhibits a horizontal inflection at the critical point. At temperatures lower than 304 K, the isotherms show the expected maxima and minima. The variation, with temperature, of the saturated

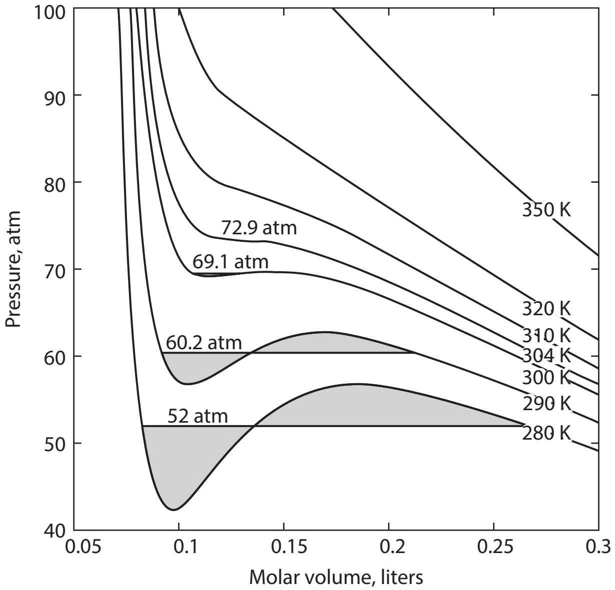

Figure 8.11 *P*-*V* isotherms for van der Waals CO_2.

vapor pressure of van der Waals liquid CO_2 can be determined by finding the tie-line on each isotherm which gives equal areas *DFH* and *LJH*, as explained with reference to Figure 8.8. Alternatively, the variation of the molar Gibbs free energy with pressure can be determined along each isotherm by graphical integration of the variation of *V* with *P*. These relationships are shown for several temperatures in Figure 8.12, which shows the variation of the saturated vapor pressure of liquid CO_2 (the points *P*) with temperature. Figure 8.12 also shows that, as the temperature increases toward the critical point, the range of unstable states (*J* to *F* in Figure 8.9) diminishes and finally disappears at T_{cr}. At temperatures greater than T_{cr}, the full line indicates that only one phase is stable over the entire range of pressure. Since G_A in Equation 8.27 is a function of temperature, the positions of the isotherms in Figure 8.12 with respect to one another are arbitrary; only the *P*-axis is quantitatively significant.

The variation of the saturated vapor pressure of liquid CO_2 with temperature, obtained from the van der Waals equation and plotted as the logarithm of *P* versus the reciprocal of the absolute temperature, is shown in Figure 8.13. Figure 8.13 also shows the variation of the measured saturated vapor pressure with temperature. Comparison shows that the van der Waals equation predicts values of vapor pressure which are higher than the measured values, although the difference between the two values decreases with increasing temperature. Consequently, the van der Waals equation predicts a value of the *molar latent*

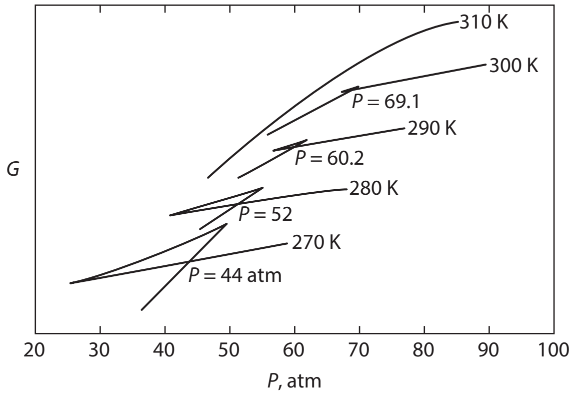

Figure 8.12 The variations of G with P for Van der Waals CO_2 at several temperatures.

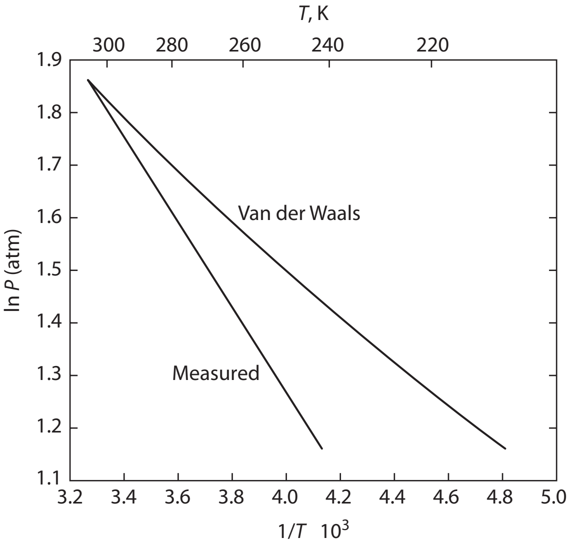

Figure 8.13 Comparison of the variation, with temperature, of the vapor pressure of van der Waals liquid CO_2 with the measured vapor pressures.

heat of evaporation of liquid CO_2 which is less than the measured value, with ΔH_{evap} being obtained as $-2.303\ R \times$ (the slope of the line) in Figure 8.13 (cf. Figures 7.9 and 7.10). The molar latent heat of evaporation of a liquefied van der Waals fluid can be calculated as follows:

$$\Delta H_{\text{evap}} = H_v - H_l = U_v - U_l + P\left(V_v - V_l\right)$$

where:

V_v and V_l are, respectively, the molar volumes of the coexisting vapor and liquid phases

P is the saturated vapor pressure at the temperature T

From Equations 3.12 and 5.34,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

which, applied to the van der Waals fluid, gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V-b}\right) - P = \frac{a}{V^2}$$

Integration gives

$$U = -\frac{a}{V} + \text{constant}$$

in which the integration constant is a function of temperature. Thus,

$$\Delta H_{\text{evap}} = -\frac{a}{V_v} + \frac{a}{V_l} + P(V_v - V_l) \tag{8.27}$$

$$= -a\left(\frac{1}{V_v} - \frac{1}{V_l}\right) + P(V_v - V_l) \tag{8.29}$$

Equation 8.29 thus correctly predicts that ΔH_{evap} for a van der Waals fluid rapidly falls to zero as the temperature approaches T_{cr}, in which state, $V_v = V_l$.

Although van der Waals developed his equation from a consideration of the physical factors causing nonideal behavior, the requirement that the pressure, volume, and temperature at the critical point be known for the calculation of a and b means that the equation is empirical. This, however, does not detract from the usefulness of the equation in representing the behavior of a gas which exhibits a relatively small departure from ideality. Importantly, the equation of state predicts a change of phase which is first order (when the vapor transforms in the liquid). It also predicts a continuous change of state when above the critical values of P and T.

8.6 OTHER EQUATIONS OF STATE FOR NONIDEAL GASES

Other examples of derived equations of state for nonideal gases include the *Dieterici equation* (Conrad Dieterici, 1858–1929):

$$P\left(V - b'\right)e^{a'/\text{RTV}} = RT$$

and the *Berthelot equation* (Pierre Eugène Marcellin Berthelot, 1827–1907):

$$\left(P+\frac{A}{TV^2}\right)(V-B)=RT$$

Neither of these equations has a fundamental basis.

Other general empirical equations include the *Beattie–Bridgeman equation* (James A. Beattie, 1895–1981; Oscar C. Bridgeman), which contains five constants in addition to R and fits the P-V-T relationships over wide ranges of temperature and pressure, and the *Kamerlingh Onnes* or *virial equation of state* (Heike Kamerlingh Onnes, 1853–1926). In the latter equation, it is assumed that PV/RT is a power series of either P or of $1/V$; that is,

$$\frac{PV}{RT}=1+BP+CP^2+\cdots$$

or

$$\frac{PV}{RT}=1+\frac{B'}{V}+\frac{C'}{V^2}+\cdots$$

The product PV is called the *virial*, B or B' is called the *first virial coefficient*, C or C' is called the *second virial coefficient*, and so on, and the virial coefficients are functions of temperature. In both equations, as pressure approaches zero and volume approaches infinity, $PV/RT \rightarrow 1$. The virial equation converges rapidly in the gas phase, and thus, the equation of state can be represented by the virial expansion over the entire range of densities and pressures. In practice, however, the virial equation is used only when the first few terms need to be retained. At low pressures or densities,

$$\frac{PV}{RT}=1+BP$$

or

$$\frac{PV}{RT}=1+\frac{B'}{V}$$

8.7 FURTHER THERMODYNAMIC TREATMENT OF NONIDEAL GASES

Equation 8.7 showed that, at any temperature, the molar Gibbs free energy of an ideal gas is a linear function of the logarithm of the pressure of the gas. This property arises from the ideal gas law, which was used in the derivation of this equation, and thus, if the gas is not ideal, then the relationship between the logarithm of the pressure of the gas and its molar Gibbs free energy is not linear. However, in view of the simple form of Equation 8.7, a function has been *defined* which, when used in place of pressure in Equation 8.7, gives a linear relationship between the molar Gibbs free energy of an nonideal gas and the logarithm of the function. This function is called the *fugacity*, f, and is partially defined by the equation

$$dG = RTd\ln f$$

The integration constant is chosen such that the fugacity approaches the pressure as the pressure approaches zero; that is,

$$\frac{f}{P} \to 1 \qquad \text{as} \qquad P \to 0$$

in which case

$$G = G^\circ + RT\ln f \tag{8.30}$$

where G° is the molar Gibbs free energy of the gas in its standard state, which is now defined as that state in which $f = 1$ at the temperature T; that is, $G^\circ = G(f = 1, T)$. The standard state for an ideal gas was defined as being $P = 1$, T.

Consider a gas which obeys the equation of state

$$V = \frac{RT}{P} - \alpha$$

where α is a function only of temperature and is a measure of the deviation of the gas from ideality. Equation 5.12 gives $dG = VdP$ at constant T, and Equation 8.30 gives $dG = RTd\ln f$ at constant T. Thus, at constant T,

$$VdP = RTd\ln f$$

and hence,

$$d\ln\left(\frac{f}{P}\right) = -\frac{\alpha}{RT}dP \tag{8.31}$$

Integration between the states $P = P$ and $P = 0$, at constant T gives

$$\ln\left(\frac{f}{P}\right)_{P=P} - \ln\left(\frac{f}{P}\right)_{P=0} = -\frac{\alpha P}{RT} \tag{8.32}$$

Since $(f/P) = 1$ when $P = 0$, then $\ln(f/P) = 0$ when $P = 0$, and hence,

$$\ln\left(\frac{f}{P}\right) = -\frac{\alpha P}{RT} \qquad \text{or} \qquad \frac{f}{P} = e^{-\alpha P/RT}$$

In order that α can be taken as being independent of pressure, the deviation of the gas from ideality must be small, in which case α is a small number. Thus,

$$e^{-\frac{\alpha P}{RT}} = 1 - \frac{\alpha P}{RT}$$

and hence,

$$\frac{f}{P} = 1 - \frac{\alpha P}{RT} = 1 - \left(\frac{RT}{P} - V \right) \frac{P}{RT} = \frac{PV}{RT}$$

If the gas behaved ideally, then the ideal pressure, P_{id}, would be given as RT/V. Thus,

$$\frac{f}{P} = \frac{P}{P_{\text{id}}} \tag{8.33}$$

which shows that the actual pressure of the gas is the *geometric mean* of its fugacity and the pressure which it would exert if it behaved ideally. It is also seen that the percentage error involved in assuming that the fugacity is equal to the pressure is the same as the percentage departure from the ideal gas law.

Alternatively, the fugacity can be considered in terms of the compressibility factor Z. From Equation 8.31,

$$d \ln \left(\frac{f}{P} \right) = -\frac{\alpha}{RT} dP = \left(\frac{V}{RT} - \frac{1}{P} \right) dP$$

But $Z = PV/RT$, and hence,

$$d \ln \left(\frac{f}{P} \right) = \frac{Z-1}{P} dP$$

and

$$\ln \left(\frac{f}{P} \right)_{P=P} = \int_{P=0}^{P=P} \frac{Z-1}{P} dP \tag{8.34}$$

This can be evaluated either by graphical integration of a plot of $(Z - 1)P$ versus P at constant T, or by direct integration if Z is known as a function of P—that is, if the virial equation of state of the gas is known.

For example, the variation of PV (cm^3·atm) with P in the range 0–200 atm for nitrogen gas at 0°C is represented by the equation

$$PV = 22{,}414.6 - 10.281P + 0.065189P^2 + 5.1955 \times 10^{-7} P^4$$
$$- 1.3156 \times 10^{-11} P^6 + 1.009 \times 10^{-16} P^8$$

Thus, dividing by $RT = 22{,}414.6$ at 0°C gives

$$\begin{aligned}\frac{PV}{RT} &= Z = 1 - 4.5867\times10^{-4}P + 2.9083\times10^{-6}P^2 + 2.3179\times10^{-11}P^4 \\ &\quad - 5.8694\times10^{-15}P^6 + 4.5015\times10^{-21}P^8\end{aligned}$$

This variation of Z with P is shown graphically in Figure 8.4. From integration of Equation 8.28, $\ln(f/P)$ is obtained as

$$\begin{aligned}\ln\left(\frac{f}{P}\right) &= -4.5867\times10^{-4}P + 1.4542\times10^{-6}P^2 + 5.794\times10^{-12}P^4 \\ &\quad - 0.9782\times10^{-16}P^6 + 5.627\times10^{-22}P^8\end{aligned}$$

This variation of f/P with P is shown in Figure 8.14. Note that as the pressure approaches one atmosphere, the fugacity approaches unity.

The change in the molar Gibbs free energy of an nonideal gas caused by an isothermal change in pressure can be calculated from either

$$dG = VdP$$

or

$$dG = RTd\ln f$$

The correspondence between these two approaches is illustrated as follows. The virial equation of state of the gas is

$$\frac{PV}{RT} = Z = 1 + BP + CP^2 + DP^3 + \cdots$$

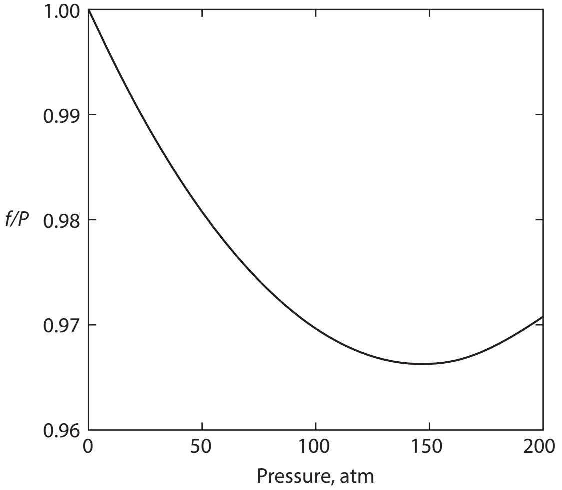

Figure 8.14 The variation of f/P with pressure for nitrogen gas at 0°C.

Then,

$$V = RT\left(\frac{1}{P} + B + CP + DP^2 + \cdots\right)$$

and so, for the change of state of 1 mole of gas from (P_1,T) to (P_2,T),

$$\begin{aligned}\Delta G = \int_{P_1}^{P_2} VdP \quad &= RT\int_{P_1}^{P_2}\left(\frac{1}{P} + B + CP + DP^2 + \cdots\right)dP \\ &= RT\left[\ln\frac{P_2}{P_1} + B(P_2 - P_1) + \frac{C}{2}(P_2^2 - P_1^2) + \frac{D}{3}(P_2^3 - P_1^3) + \cdots\right]\end{aligned}$$

If the gas had been ideal, then

$$\Delta G = RT\ln\left(\frac{P_2}{P_1}\right)$$

and so, the contribution to change in the molar Gibbs free energy arising from the nonideality of the gas is

$$RT\left[B(P_2 - P_1) + \frac{C}{2}(P_2^2 - P_1^2) + \frac{D}{3}(P_2^3 - P_1^3) + \cdots\right]$$

Alternatively, $dG = RT\, d\ln f$, where, from Equation 8.29,

$$\begin{aligned}\ln\left(\frac{f}{P}\right) \quad &= \int_0^P \frac{Z-1}{P}dP \\ &= \int_0^P (B + CB + DP^2 + \cdots)dP \\ &= BP + \frac{CP^2}{2} + \frac{DP^3}{3} + \cdots\end{aligned}$$

Now,

$$dG = RT\ d\ln f = RT\ d\ln\left(\frac{f}{P}\right) + RT\ d\ln P$$

and so,

$$\Delta G = RT\left[B(P_2 - P_1) + \frac{C}{2}\left(P_2^2 - P_1^2\right) + \frac{D}{3}(P_2^3 - P_1^3 + \cdots)\right] + RT\ln\left(\frac{P_2}{P_1}\right)$$

in agreement with the preceding equations.

Thus, for 1 mole of nitrogen at 0°C, the difference between the Gibbs free energy at $P = 150$ atm and that at $P = 1$ atm is

$$\Delta G = RT\left[\ln\left(\frac{f}{P}\right)_{150} - \ln\left(\frac{f}{P}\right)_{1}\right] + RT\ln 150$$

$$= 8.3144\times 273(-0.034117 + 0.000457) + 8.3144\times 273\times 5.011 \text{ J}$$

$$= -76 + 11{,}373$$

$$= 11{,}297 \text{ J}$$

The contribution due to the nonideality of nitrogen is thus seen to be only 76 J in almost 11,300 J.

The number of terms which must be retained in the virial equation depends on the magnitude of the range of pressure over which it must be applied. For example, in the virial equation for nitrogen at 0°C, only the first term is needed up to 6 atm and only the first two terms are needed up to 20 atm. When only the first term is needed, the expression is

$$\frac{PV}{RT} = 1 + BP$$

or

$$V = \frac{RT}{P} + BRT$$

and hence, $-BRT = a$ in Equation 8.31 and α is a function only of temperature.

Consider a nonideal gas which obeys the equation of state $PV = RT(1 + BP)$. The work done by this nonideal gas in a reversible, isothermal expansion from P_1 to P_2 is the same as that done when an ideal gas is reversibly and isothermally expanded from P_1 to P_2 at the same temperature. However, the work done by the nonideal gas in a reversible, isothermal expansion from V_1 to V_2 is greater than that done when an ideal gas is reversibly and isothermally expanded from V_1 to V_2 at the same temperature. Consider why this is so.

For the ideal gas $V = RT/P$, and for the nonideal gas $V = RT/P + BRT$. Thus, on a P-V diagram, any isotherm for the nonideal gas is displaced from the isotherm for the ideal gas by the constant increment in volume BRT, as shown in Figure 8.15. Because of the constant displacement, the area under the isotherm for the ideal gas between P_1 and P_2 (the area *abcd*) is the same as the area under the isotherm for the nonideal gas between the same pressures (the area *efgh*). Thus, the same amount of work is done by both gases in expanding isothermally from P_1 to P_2.

For the ideal gas,

$$w_{\text{ideal gas}} = \int_{V_1}^{V_2} PdV = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right)$$

and for the nonideal gas,

$$w_{\text{nonidealgas}} = \int_{V_1}^{V_2} PdV$$

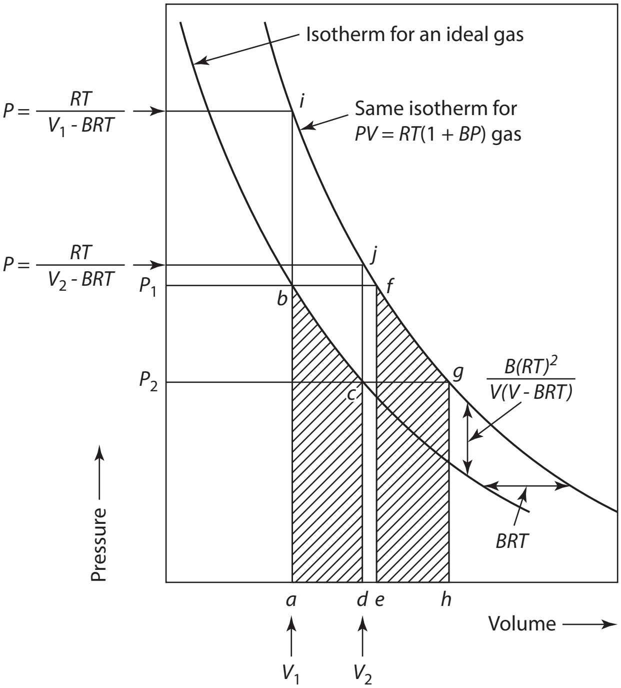

Figure 8.15 Isotherms for an ideal gas and a nonideal gas.

but, as $V = RT/P + BRT$, and hence, at constant T, $dV = -RT(dP/P^2)$, then

$$w_{\text{nonideal gas}} = -\int_{P_1}^{P_2} RT\left(\frac{dP}{P}\right) = RT\ln\left(\frac{P_1}{P_2}\right) = w_{\text{ideal gas}}$$

However, as any isotherm for the nonideal gas also lies above the isotherm for the ideal gas (for a positive value of B), the work done by the nonideal gas in expanding isothermally and reversibly from V_1 to V_2 (the area *aijd*) is greater than that done by the ideal gas in isothermally and reversibly expanding between V_1 and V_2 (the area *abcd*). The vertical separation between the two isotherms is

$$P_{\text{nonideal gas}} - P_{\text{ideal gas}} = \frac{RT}{V - BRT} - \frac{RT}{V} = \frac{B(RT)^2}{V(V - BRT)}$$

For the ideal gas, $w_{\text{ideal gas}} = RT \ln (V_2/V_1)$, and for the nonideal gas,

$$w = \int_{V_1}^{V_2} PdV$$

where

$$P = \frac{RT}{V - BRT}$$

such that

$$w_{\text{nonidealgas}} = RT\ln\left(\frac{V_2 - BRT}{V_1 - BRT}\right) > w_{\text{ideal gas}}$$

Consider the comparison of the behavior of hydrogen gas, for which $PV = RT(1 + 0.0064P)$, with that of an ideal gas in reversible isothermal expansions of 1 mole between $P_1 = 100$ atm and $P_2 = 50$ atm at 298 K:

$$V_{1(\text{ideal}, P_1=100\text{ atm}, T=298\text{ K})} = \frac{RT}{P_1} = \frac{0.08206 \times 298}{100} = 0.2445\text{ liters}$$

$$\begin{aligned} V_{1(H_2 P_1=100\text{ atm}, T=298\text{ K})} &= \frac{RT}{P_1} + RTB = 0.2445 + 0.08206\times 298\times 6.4\times 10^{-4} \\ &= 0.2445 + 0.0157 = 0.2602\text{ liters} \end{aligned}$$

$$V_2(\text{ideal}, P_2 = 50\text{ atm}, T = 298\text{ K}) = \frac{0.08206\times 298}{50} = 0.4890\text{ liters}$$

$$V_2(H_2 P_1 = 50\text{ atm}, T = 298\text{ K}) = 0.4890 + 0.0157 = 0.5047\text{ liters}$$

Thus, for the change of state

$$(V_1 = 0.2445, T = 298K) \rightarrow (V_2 = 0.4890, T = 298\text{ K})$$

$$\begin{aligned} w_{\text{ideal gas}} &= RT\ln\left(\frac{V_2}{V_1}\right) = 8.3144\times 298\times \ln\left(\frac{0.4890}{0.2445}\right) \\ &= 1717\text{ J} \end{aligned}$$

and

$$\begin{aligned} w_{\text{H}_2} &= RT\ln\left(\frac{V_2 - \text{RTB}}{V_1 - RTB}\right) = 8.3144 \times 298 \times \ln\left(\frac{0.4890 - 0.0157}{0.2445 - 0.0157}\right) \\ &= 1801\text{ J} \end{aligned}$$

At $V = 0.2445$ liters, $T = 298$ K, $P_{\text{ideal gas}} = 100$ atm, and

$$\begin{aligned} P_{\text{H}_2} &= \frac{RT}{V - RTB} = \frac{0.08206 \times 298}{0.2445 - 0.0157} \\ &= 106.4\text{ atm} \end{aligned}$$

and at $V = 0.489$ liters, $T = 298$ K, $P_{\text{ideal gas}} = 50$ atm, and

$$\begin{aligned} P_{H_2} &= \frac{0.08206 \times 298}{0.4890 - 0.0157} \\ &= 51.7\text{ atm} \end{aligned}$$

8.8 SUMMARY

1. An ideal gas is an assemblage of volumeless noninteracting particles which obeys the ideal gas law, $PV = RT$. The internal energy of an ideal gas arises solely from the translational motions of the gas particles and, hence, is a function only of temperature. The enthalpy of an ideal gas is also a function only of temperature.
2. A consequence of the ideal gas law is that, at constant temperature, the Gibbs free energy of an ideal gas is a linear function of the logarithm of the pressure of the gas.
3. Since Gibbs free energies do not have absolute magnitudes, it is convenient to measure changes in Gibbs free energy from some arbitrary state. This state is chosen as $P = 1$ atm at the temperature of interest and is called the standard state. Thus, the difference between the molar Gibbs free energy in the state (P,T) and that in the standard state $(P = 1 \text{ atm}, T)$ is $\Delta G = RT \ln P$.
4. The deviations of real gases from ideal behavior are caused by the atoms or molecules of real gases having finite volumes and by the interactions which occur among the atoms.
5. Various attempts have been made to correct the ideal gas law for these effects, and the best-known derived equation is the van der Waals equation of state, which can be applied to gases which show small deviations from ideality. This equation predicts the condensation of vapor caused by compression at temperatures below the critical temperature, but does not give the correct dependence on temperature of the saturated vapor pressure of the liquid phase. Generally, measured variations of the molar volumes of gases with P and T are fitted to power series equations, in P or $1/V$, of the function PV. Such equations are called virial equations.
6. The van der Waals equation predicts a phase change below the critical point.
7. The compressibility factor, $Z = PV/RT$, of all real gases at constant reduced temperature, $T_R = T/T_{cr}$, is the same function of the reduced pressure, $P_R = P/P_{cr}$. This gives rise to the law of corresponding states, which states that when two gases have identical values of two reduced variables, they have almost identical values of the third reduced variable.
8. Consideration of the thermodynamic behavior of nonideal gases is facilitated by the introduction of the fugacity, f, which is defined by the equation $dG = RT\, d \ln f$ and by the condition $f/P \to 1$ as $P \to 0$. Thus, the standard state for a nonideal gas is that in which the fugacity is unity at the temperature of interest. For small deviations from ideality, the pressure of the gas is the geometric mean of its fugacity and P_{id}, the pressure which the gas would exert if it were ideal.
9. The composition of a mixture of gases is most conveniently expressed in terms of the mole fractions of its component gases, and if the mixture is ideal, the partial pressures exerted by the component gases are related to the total pressure P and the mole fraction X_i by $p_i = X_i P$. This equation is called Dalton's law of partial pressures. In a mixture of ideal gases, the partial molar Gibbs free energy of a component gas is a linear function of the logarithm of its partial pressure, and in a mixture of nonideal gases it is a linear function of the logarithm of its fugacity.
10. Since the atoms in an ideal gas do not interact with one another, no change in enthalpy occurs when different ideal gases are mixed; that is, the enthalpy change of mixing of ideal gases, $\Delta H'^{\text{mix}}$, is zero. The entropy change occurring when ideal gases are mixed arises solely from complete randomization of the different types of atoms in the available volume, and thus, as $\Delta H^{\text{mix}} = 0$, $\Delta G^{\text{mix}} = -T\Delta S^{\text{mix}}$.

8.9 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 8

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Compressibility factor, Z
Critical point
Dalton's law of partial pressure
Enthalpy of mixing
Entropy of mixing
Fugacity
Gibbs free energy of mixing
Ideal/perfect gas
Law of corresponding states
Liquid/vapor equilibrium
Maxwell construction
Mixture
Mole fraction
Partial molar quantity
Stable/unstable/metastable
Standard state
Supercritical fluid
Van der Waals fluid
Virial equation

8.10 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Obtain a simplified expression for the total derivative of the pressure for one mole of an ideal gas.

Solution to Qualitative Problem 1

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

For an ideal gas,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

and

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} = -\frac{P}{V}$$

Thus,

$$dP = \frac{R}{V}dT - \frac{P}{V}dV$$

Qualitative Problem 2

One mole of an ideal gas doubles its volume at constant temperature. Calculate the change in the Gibbs free energy of the gas for this process. Also calculate the change in entropy of the gas.

Solution to Qualitative Problem 2

$$dG = -SdT + VdP$$

At constant T,

$$dG = VdP = \frac{RT}{P}dP$$

but,

$$dP = -\frac{RT}{V^2}dV$$

$$\frac{dP}{P} = -\frac{RT}{PV^2}dV = -\frac{dV}{V}$$

Thus,

$$\Delta G = -RT\ln\frac{V_2}{V_1} = -RT\ln 2$$

Since the gas is ideal, $\Delta H = 0$ and $\Delta S = R \ln 2 > 0$.

8.11 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Assuming that nitrogen behaves as a van der Waals gas with $a = 1.391$ (liters)^2·atm/mole^2 and $b = 39.1$ cm^3/mole, calculate the change in the Gibbs free energy and the change in entropy when the volume of 1 mole of nitrogen is increased from 1 to 2 liters at 400 K.

Solution to Quantitative Problem 1

For a van der Waals fluid,

$$P = \frac{RT}{V-b} - \frac{a^2}{V^2}$$

and thus,

$$dP = -\frac{RTdV}{(V-b)^2} + \frac{RdT}{(V-b)} + \frac{2a^2dV}{V^3}$$

$$= \frac{RdT}{V-b} + \left[\frac{2a^2}{V^3} - \frac{RT}{(V-b)^2}\right]dV \tag{i}$$

$$= \frac{RdT}{V-b} + \left[\frac{2a^2(V-b)^2 - RTV^3}{V^3(V-b)}\right]dV \tag{ii}$$

At constant temperature,

$$dG = VdP$$

which, from Equation (i), gives

$$dG = \left[\frac{2a^2}{V^2} - \frac{RTV}{(V-b)}\right]dV$$

Integrating between V_2 and V_1 gives

$$\Delta G = \int_{V_1}^{V_2} \left[\frac{2a^2}{V^2} - \frac{RTV}{(V-b)^2}\right]dV$$

$$= \left[-\frac{2a^2}{V} + \frac{RTb}{V-b} - RT\ \ln\,(V-b)\right]_{V_1}^{V_2}$$

$$= RTb\left(\frac{1}{V_2-b} - \frac{1}{V_1-b}\right) - RT\ln\frac{V_2-b}{V_1-b} - 2a^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= 0.08207 \times 400 \times 0.0391\left(\frac{1}{2 - 0.0391} - \frac{1}{1 - 0.0391}\right)$$

$$= -0.082057 \times 400\ln\frac{2 - 0.0391}{1 - 0.0394} - 2 \times 1.39^2\left(\frac{1}{2} - \frac{1}{1}\right)$$

$$= -0.68 - 23.41 - 1.93$$

$$= -26.021 \cdot \text{atm}$$

$$= -\frac{26.02 \times 8.3144}{0.082057}\,\text{J}$$

$$= -2636\ \text{J}$$

From Equation 6.17, at constant temperature:

$$dS = -\alpha V dP$$

where:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

From Equation (ii), at constant pressure:

$$\frac{dV}{dT} = \frac{R}{(V-b)} \frac{V^3(V-b)^2}{\left[2a^2(V-b)^2 - RTV^3\right]}$$

and thus, for a van der Waals fluid:

$$\alpha = \frac{RV^2(V-b)}{2\alpha^2(V-b)^2 - RTV^3}$$

and

$$\begin{aligned} dS &= -\left[\frac{RV^2(V-b)}{2a^2(V-b)^2 - RTV^3}\right] V \left[\frac{2a^2(V-b)^2 - RTV}{V^3(V-b)}\right] dV \\ &= -\frac{RdV}{V-b} \end{aligned}$$

Therefore,

$$\begin{aligned} \Delta S &= R \ln \frac{V_2 - b}{V_1 - b} \\ &= 8.3144 \ln \frac{2 - 0.0391}{1 - 0.0391} \\ &= 5.93 \text{ J/K} \end{aligned}$$

If the nitrogen had behaved as an ideal gas, the changes in Gibbs free energy and entropy would have been

$$\begin{aligned} \Delta G &= RT \ln \frac{V_1}{V_2} \\ &= 8.3144 \times 400 \times \ln \frac{1}{2} \\ &= -2305 \text{ J} \end{aligned}$$

and

$$\begin{aligned}\Delta S &= R\ln\frac{V_2}{V_1}\\ &= 8.3144\times\ln 2\\ &= 5.76\text{ J/K}\end{aligned}$$

Quantitative Problem 2

The virial equation of state for *n*-butane at 460 K is $Z = 1 + A/V + B/V^2$, in which $A = -265$ cm^3/g·mole and $B = 30{,}250$ cm^6/g·mole^2. Calculate the change in the Gibbs free energy when the volume of 1 mole of *n*-butane is decreased from 400 to 200 cm^3 at 460 K.

Solution to Quantitative Problem 2

The equation of state is

$$\begin{aligned}PV &= RT\left(1-\frac{265}{V}+\frac{30{,}250}{V^2}\right)\\ \therefore P &= RT\left(\frac{1}{V}-\frac{265}{V^2}+\frac{30{,}250}{V^3}\right)\end{aligned}$$

and, at constant temperature,

$$dP = RT\left(-\frac{1}{V^2}+\frac{2\times 265}{V^3}-\frac{3\times 30{,}250}{V^4}\right)dV$$

Thus,

$$dG = VdP = RT\left(-\frac{1}{V}+\frac{530}{V^2}-\frac{90{,}750}{V^3}\right)dV$$

and

$$\begin{aligned}\Delta G &= RT\left[-\ln\frac{V_2}{V_1}-530\left(\frac{1}{V_2}-\frac{1}{V_1}\right)+\frac{90{,}750}{2}\left(\frac{1}{V_2^2}-\frac{1}{V_1^2}\right)\right]\\ &= 8.3144\times 460\left[-\ln\frac{1}{2}-530\left(\frac{1}{200}-\frac{1}{400}\right)+43{,}375\left(\frac{1}{200^2}-\frac{1}{400^2}\right)\right]\\ &= 8.3144\times 460(0.693-1.325+0.851)\\ &= 838\text{ J}\end{aligned}$$

PROBLEMS

8.1 Demonstrate the law of corresponding states by writing the van der Waals equation in terms of the reduced variables. Calculate the compressibility factor for a van der Waals fluid at its critical point and compare the result with the values obtained for real gases at their critical points listed in Table 8.1. Calculate the value of $(\partial U/\partial V)_T$ for a van der Waals fluid.

8.2 n moles of an ideal gas A and $(1 - n)$ moles of an ideal gas B, each at 1 atm pressure, are mixed at total constant pressure. What ratio of A to B in the mixture maximizes the decrease in the Gibbs free energy of the system? If the decrease in the Gibbs free energy is ΔG^M, to what value must the pressure be increased in order to increase the Gibbs free energy of the gas mixture by $1/2\Delta G^M$?

8.3 You are responsible for the purchase of oxygen gas which, before use, will be stored at a pressure of 200 atm at 300 K in a cylindrical vessel of diameter 0.2 m and height 2 m. Would you prefer that the gas behaved ideally or as a van der Waals fluid? The van der Waals constants for oxygen are $a = 1.36$ liters^2·atm·mole^{-2} and $b = 0.0318$ liters/mole.

8.4 The virial equation of state for n-butane at 460 K is $Z = 1 + A/V + B/V^2$, in which $A = -265$ cm^3/g·mole and $B = 30{,}250$ cm^6/g·mole^2. Calculate the work required to reversibly compress 1 mole of n-butane from 50 to 100 atm at 460 K.

8.5 For sulfur dioxide, $T_{\mathrm{cr}} = 430.7$ K and $P_{\mathrm{cr}} = 77.8$ atm. Calculate

a. The critical van der Waals constants for the gas
b. The critical volume of van der Waals SO_2
c. The pressure exerted by 1 mole of SO_2 occupying a volume of 500 cm^3 at 500 K. Compare this with the pressure which would be exerted by an ideal gas occupying the same molar volume at the same temperature.

8.6 One hundred moles of hydrogen gas at 298 K are reversibly and isothermally compressed from 30 to 10 liters. The van der Waals constants for hydrogen are $a = 0.2461$ liters^2·atm·mole^{-2} and $b = 0.02668$ liters/mole, and in the range of pressure 0–1500 atm, the virial equation for hydrogen is $PV = RT\,(1 + 6.4 \times 10^{-4}\,P)$. Calculate the work that must be done on the system to effect the required change in volume and compare this with the values that would be calculated assuming that (a) hydrogen behaves as a van der Waals fluid and (b) hydrogen behaves as an ideal gas.

8.7 Using the virial equation of state for hydrogen at 298 K given in Problem 8.6, calculate

a. The fugacity of hydrogen at 500 atm and 298 K
b. The pressure at which the fugacity is twice the pressure
c. The change in the Gibbs free energy caused by a compression of 1 mole of hydrogen at 298 K from 1 to 500 atm

What is the magnitude of the contribution to (c) caused by the nonideality of hydrogen?

8.8* Show that the truncated Kamerlingh Onnes virial equation

$$\frac{PV}{RT} = 1 + \frac{B'(T)}{V}$$

reduces to $P(V - b') = RT$, and find the expression for b'.

8.9* Figure 8.8 shows an isothermal variation, with pressure, of the volume of a van der Waals fluid at a temperature below its critical temperature. Redraw this figure and below it sketch the Helmholtz free energy versus volume plot. Be sure to indicate important points on the A versus V plot.

8.10* Obtain a simplified expression for the total derivative of the pressure for a van der Waals gas.

8.11* Show that the truncated Kamerlingh Onnes virial equation

$$\frac{PV}{RT} = 1 + \frac{B'(T)}{V}$$

reduces to $P(V - b') = RT$, and find the expression for b'.

8.12* Derive an expression for Z_{cr} of a van der Waals fluid.

$$Z_{\text{cr}} = \frac{P_{\text{cr}}V_{\text{cr}}}{RT_{\text{cr}}}$$

8.13* The ideal entropy of mixing of a binary solution is given as

$$\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$$

a. Sketch the entropy of mixing versus X_B.
b. Calculate (using the expression for the ideal entropy of mixing) the ideal entropy of mixing at $B = 0.25$.
c. Calculate the slope of this curve at $X_B = 0.25$.
d. Calculate the partial molar entropy of component B for the composition $X_B = 0.25$.
e. Calculate the partial molar entropy of component A for the composition $X_B = 0.25$.
f. Show that your answers in (d) and (e) are consistent with your answer in (c).

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* New problem in this edition

CHAPTER 9

The Behavior of Solutions

9.1 INTRODUCTION

We have seen in previous chapters that gases may be considered to be ideal when there is no interaction among their constituent atoms or molecules. This lack of interaction allows the gas to exist in a state in which its configurational entropy has its highest possible value. Gases which can be considered to be ideal all have the same thermodynamic mixing properties. Any interaction, such as is present in a van der Waals gas, lowers the entropy of the gas, and with decreasing temperature, the interactions eventually lead to the gas condensing to a liquid or a solid, depending on its pressure.

Condensed phases do have interactions existing among their constituent atoms, molecules, or ions. The nature and magnitudes of these interactions have a significant influence on the thermodynamic behavior of the solution. The interactions are determined by such factors as atomic size, electronegativity, and electron-to-atom ratio, and these determine the extent to which a component is soluble in a solution and whether or not two or more components will react chemically to form a new species. Solution thermodynamics is concerned with the vapor pressure–temperature–composition relationships of the components of a solution. An examination of solution thermodynamics is made in this chapter.

9.2 RAOULT'S LAW AND HENRY'S LAW

If a quantity of pure liquid A is placed in a closed, initially evacuated vessel at the temperature T, some of the liquid will spontaneously evaporate until the pressure in the vessel reaches the saturated vapor pressure of liquid A, p_A°, at the temperature T. In this state, a dynamic equilibrium is established in which the rate of evaporation of liquid A equals the rate of condensation of the vapor A. The rate of evaporation, $r_{e(A)}$, is determined by the magnitude of the energy of the bonds between the atoms of A at the surface of the liquid. The forces exerted between the atoms are such that each surface atom is located near the bottom of a potential energy well, and for an atom to leave the surface of the liquid and enter the vapor phase, it must acquire an activation energy, E^*. The intrinsic rate of evaporation, $r_{e(A)}$, is determined by the depth of the potential energy well—that is, by the magnitude of E^*—and by the temperature T. On the other hand, the rate of condensation, $r_{c(A)}$, is proportional to the number of A atoms in the vapor phase which strike the surface of the liquid in a unit time. For a given temperature, this is proportional to the pressure of the vapor. Thus, $r_{c(A)} = k^A p_A^\circ$, and at equilibrium, $r_{e(A)} = r_{c(A)}$, and thus,

$$r_{e(A)} = k^A p_A^\circ \tag{9.1}$$

The energies of the atoms at the surface are quantized, and the distribution of the surface atoms among the available quantized energy levels is given by Equation 4.17 as

$$n_i = \frac{n \exp(-\frac{E_i}{k_B T})}{\mathcal{Z}}$$

where n_i/n is the fraction of the atoms in the E_ith energy level, and $\mathcal{Z}$, the partition function, is given by

$$\mathcal{Z} = \sum_0^\infty \exp\left(-\frac{E_i}{k_B T}\right)$$

If the quantized energy levels are spaced closely enough that the summation can be replaced by an integral, then

$$\mathcal{Z} = \int_0^\infty \exp\left(-\frac{E_i}{k_B T}\right) dE = kT$$

which is the average energy per atom. Thus, the fraction of surface atoms which have energies greater than the activation energy for evaporation, E^*, is

$$\frac{n_i^*}{n} = \frac{1}{k_B T}\int_{E^*}^\infty \exp\left(-\frac{E_i}{k_B T}\right) dE = \exp\left(-\frac{E^*}{k_B T}\right)$$

The evaporation rate, $r_{e(A)}$, is proportional to n_i^*/n, and thus, it increases exponentially with increasing temperature and decreases exponentially with the increasing value of E^*. Equation 9.1 illustrates why the saturated vapor pressures of liquids are exponential functions of temperature. Similarly, when pure liquid B is placed in an initially evacuated vessel at the temperature T, equilibrium between the liquid and its vapor phases occurs when

$$r_{e(B)} = k^B p_B^\circ \tag{9.2}$$

Consider the effect of the addition of a small quantity of liquid B to liquid A. If the mole fraction of A in the solution is X_A and the atomic diameters of A and B are similar, then, assuming that the composition of the surface of the liquid is the same as that of the bulk liquid, the fraction of the surface sites occupied by A atoms is X_A. Since A can only evaporate from surface sites occupied by A atoms, the rate of evaporation of A is decreased by the factor X_A, and since the rates of evaporation and condensation are equal to one another at equilibrium, the equilibrium vapor pressure of A exerted by the A–B solution is decreased from p_A° to p_A, where

$$r_{e(A)}X_A = k^A p_A \tag{9.3}$$

Similarly, for liquid B containing a small amount of A,

$$r_{e(B)}X_B = k^B p_B \tag{9.4}$$

Combination of Equations 9.1 and 9.3 gives

$$p_A = X_A p_A^\circ \tag{9.5}$$

and combination of Equations 9.2 and 9.4 gives

$$p_B = X_B p_B^\circ \tag{9.6}$$

Equations 9.5 and 9.6 are expressions of *Raoult's law*, which states that the vapor pressure exerted by a component i in a solution is equal to the product of the mole fraction of i in the solution and the saturated vapor pressure of pure liquid i at the temperature of the solution. Raoult's law is shown in Figure 9.1; the components of a solution which obey Raoult's law are said to exhibit *Raoultian* behavior.

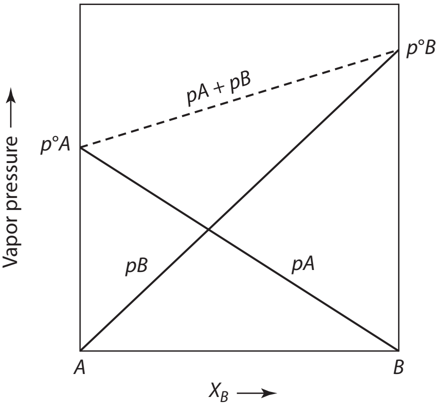

Figure 9.1 The vapor pressures exerted by the components of a binary solution as a function of composition. Both components of this solution obey Raoult's law at all compositions.

The derivations of Equations 9.3 and 9.4 require the assumption that the intrinsic rates of evaporation of A and B are independent of the composition of the solution. This requires that the magnitudes of the A–A, B–B, and A–B bond energies in the solution be identical, in which case the depth of the potential energy well of an atom at the surface is independent of the types of atoms which it has as its nearest neighbors. When this happens, the arrangement of the atoms does not depend on the bond energies, and hence, they will take a configuration which maximizes the configurational entropy of the solution.

Consider the case in which the A–B bond energy is considerably more negative than the A–A and B–B bond energies, and consider a solution of B in A which is sufficiently dilute that every B atom on the surface of the liquid is surrounded only by A atoms. In this case, the B atoms at the surface are each located in a deeper potential energy well than are the B atoms at the surface of pure B. Thus, in order to leave the surface and enter the vapor phase, the B atoms have to overcome larger energy barriers, and, consequently, the intrinsic rate of evaporation of B is decreased from $r_{e(B)}$ to $r'_{e(B)}$. Equilibrium between the condensed solution and the vapor phase occurs when

$$r'_{e(B)}X_B = k^B p_B \tag{9.7}$$

Combination of Equation 9.1 and 9.7 then gives

$$p_B = \frac{r'_{e(B)}}{r_{e(B)}} X_B p_B^{\circ} \tag{9.8}$$

and since $r'_{e(B)} < r_{e(B)}$, p_B in Equation 9.8 is a smaller quantity than p_B in Equation 9.5. Equation 9.8 can be written as

$$p_B = k^B X_B \tag{9.9}$$

where $k^B < 1$.

As the mole fraction of B in the A–B solution is increased, the probability that all of the B atoms on the surface of the liquid are surrounded only by A atoms decreases. The occurrence of a pair of neighboring B atoms on the surface decreases the depth of the potential wells in which they are located and, hence, increases the value of $r'_{e(B)}$. Beyond some critical mole fraction of A, $r'_{e(B)}$ varies with composition, and hence, Equation 9.9 is no longer obeyed by B in solution. Consequently, Equation 9.9 is obeyed only over an initial range of concentration of B in A, the extent of which is dependent on the temperature of the solution and on the relative magnitudes of the A–A, B–B, and A–B bond energies. A similar consideration of dilute solutions of A in B gives

$$p_A = k^A X_A \tag{9.10}$$

which is obeyed over an initial range of concentration. Equations 9.9 and 9.10 are known as *Henry's law*, and, in the ranges of composition in which Henry's

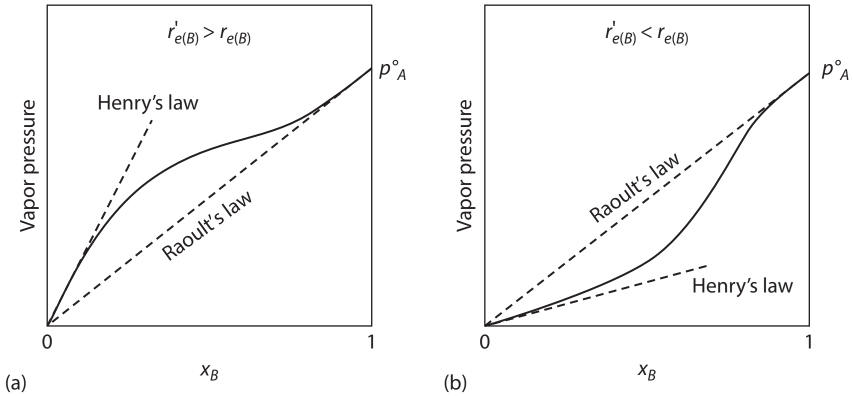

Figure 9.2 (a) The vapor pressure of a solute of a binary solution which exhibits positive deviation from Raoultian behavior. (b) The vapor pressure of a solute of a binary solution which exhibits negative deviation from Raoultian behavior.

law is obeyed, the solutes are said to exhibit *Henrian* behavior. If the *A*–*B* bond energy is less negative than the *A*–*A* and *B*–*B* bond energies, then, since $r'_{e(B)} > r_{e(B)}$, the Henry's law line lies above the Raoult's law line (Figure 9.2a). The solutes in such solutions are said to exhibit *positive deviations* from *Raoultian behavior*. Conversely, if the *A*–*B* bond energy is more negative than the *A*–*B* and *B*–*B* bond energies, the solute atom, surrounded only by solvent atoms, is located in a deeper potential energy well than that which occurs in the pure solute. In this case, $r'_{e(B)} < r_{e(B)}$, and hence, the Henry's law line for the solute lies below the Raoult's law line (Figure 9.2b). The solute in these solutions is said to exhibit *negative deviations* from Raoultian behavior, and $k^B < 1$. This is the case described previously and summarized in Equation 9.9.

9.3 THE THERMODYNAMIC ACTIVITY OF A COMPONENT IN SOLUTION

The thermodynamic activity of a component in any state at the temperature *T* is formally defined as being the ratio of the fugacity (see Section 8.7) of the substance in that state to its fugacity in its standard state. For the species or substance *i*,

$$\text{activity of } i \equiv a_i \equiv \frac{f_i}{f_i^\circ} \tag{9.11}$$

In a condensed solution, f_i is the fugacity of the component *i* in the solution at the temperature *T*, and f_i° is the fugacity of pure *i* (the standard state) at the temperature *T*. If the vapor in equilibrium with the condensed solution is ideal, then $f_i = p_i$, in which case

$$a_i = \frac{p_i}{p_i^\circ} \tag{9.12}$$

That is, the activity of i in a solution, with respect to pure i, is the ratio of the partial pressure of i exerted by the solution to the saturated vapor pressure of pure i at the same temperature. If the component i exhibits Raoultian behavior, then Equations 9.5 and 9.12 give

$$a_i = X_i \tag{9.13}$$

which is an alternative expression of Raoult's law (cf. Equations 9.5 and 9.6). Figure 9.3 shows Raoultian behavior over all compositions in a liquid binary solution of Fe and Cr, in terms of the activities of the two components. The definition of activity normalizes the vapor pressure–composition relationship with respect to the saturated vapor pressure exerted in the standard state. In an equilibrium state, the activity can never exceed unity.

Over the composition range in which Henry's law is obeyed by the solute i, Equations 9.9 and 9.12 give

$$a_i = \frac{k^i X_i}{p_i^\circ} = k_{(i)} X_i \tag{9.14}$$

which is an alternative expression of Henry's law (cf. Equations 9.9 and 9.10). Henrian behavior, in terms of the activity of a component of a binary solution, is

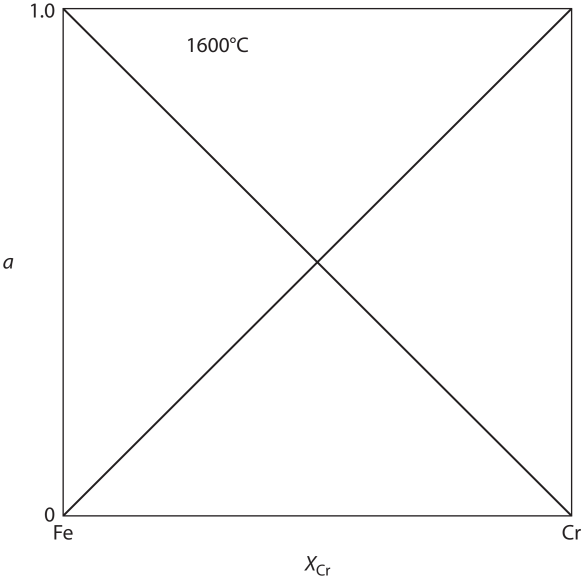

Figure 9.3 Activities in the liquid binary system iron–chromium at 1600°C.

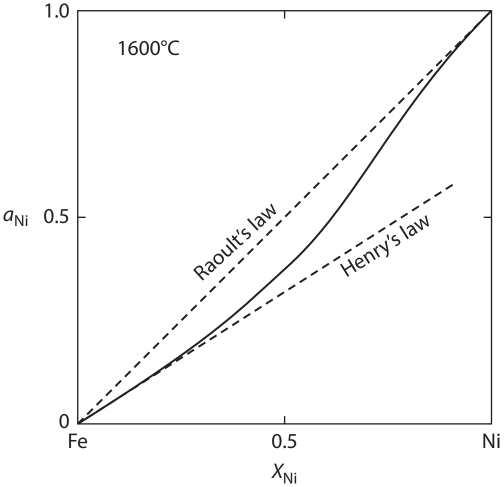

Figure 9.4 The activity of nickel in the liquid iron–nickel system at 1600°C displaying negative deviation from Raoultian behavior.

shown in Figure 9.4. It can be seen that at $X_{Ni} = 0.5$, the Ni atoms in a liquid solution of Fe–Ni are less "active" than they would be if such a solution were a Raoultian one. This implies that the Ni atoms are bonded more tightly to Fe atoms than they are to other Ni atoms; that is, $E_{Ni-Fe} < E_{Ni-Ni}$. The liquid Fe–Ni system exhibits negative deviation from ideality. It is of interest to note that in the solid state, the Fe–Ni system has an atomically ordered phase which has opposite (i.e., Fe–Ni) near neighbors (e.g., $FeNi_3$, $L1_2$, $Pm\bar{3}m$, $cP4$).

9.4 THE GIBBS–DUHEM EQUATION

It is frequently found that the extensive thermodynamic variables of only one component of a binary (or multicomponent) solution are amenable to experimental measurement. In such cases, the corresponding extensive variables of the other component can be obtained from a general relationship between the values of the properties of both components. This relationship, which is known as the Gibbs–Duhem relationship, is introduced in this section, and some of its applications are discussed in Section 9.8.

The value of an extensive thermodynamic variable (state function) of a solution is a function of the temperature, the pressure, and the numbers of moles of the components of the solution; that is, if Q is an extensive molar property then

$$Q' = Q'\ (T, P, n_i, n_j, n_k, \ldots)$$

At constant T and P, the variation of Q' with the composition of the solution is given as

$$dQ' = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} dn_i + \left(\frac{\partial Q'}{\partial n_j}\right)_{T,P,n_i,n_k,\ldots} dn_j + \left(\frac{\partial Q'}{\partial n_k}\right)_{T,P,n_i,n_j,\ldots} dn_k + \cdots \tag{9.15}$$

In Chapter 8, the partial molar value of an extensive property of a component was defined as

$$\overline{Q}_i = \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots}$$

In which case Equation 9.15 can be written as

$$dQ' = \overline{Q}_i dn_i + \overline{Q}_j dn_j + \overline{Q}_k dn_k + \cdots \tag{9.16}$$

Also in Chapter 8, it was seen that $\overline{Q}_i$ is the increase in the value of Q' for the mixture or solution when 1 mole of i is added to a large quantity of the solution at constant T and P. (The stipulation that the quantity of solution be large is necessitated by the requirement that the addition of 1 mole of i to the solution should not cause a measurable change in its composition.) Thus, if $\overline{Q}_i$ is the value of Q per mole of i in the solution, then the value of Q' for the solution itself is

$$Q' = n_i \overline{Q}_i + n_j \overline{Q}_j + n_k \overline{Q}_k + \cdots \tag{9.17}$$

differentiation of which gives

$$dQ' = n_i \overline{Q}_i + n_j \overline{Q}_j + n_k \overline{Q}_k + \cdots + \overline{Q}_i dn_i + \overline{Q}_j dn_j + \overline{Q}_k dn_k + \cdots \tag{9.18}$$

Comparison of Equations 9.16 and 9.18 shows that, at constant T and P,

$$n_i \overline{Q}_i + n_j \overline{Q}_j + n_k \overline{Q}_k + \cdots = 0$$

or, generally,

$$\sum_i n_i d\overline{Q}_i = 0 \tag{9.19a}$$

Division of Equation 9.19 by n, the total number of moles of all the components of the solution, gives

$$\sum_i X_i d\overline{Q}_i = 0 \tag{9.19b}$$

Equations 9.19a and b are equivalent expressions of the generalized *Gibbs–Duhem equation*.

For example, at constant temperature and pressure, the partial molar Gibbs free energies (chemical potentials) in a binary system are related as

$$X_A d\overline{G}_A + X_B d\overline{G}_B = 0 \tag{9.20}$$

9.5 THE GIBBS FREE ENERGY OF FORMATION OF A SOLUTION

9.5.1 The Molar Gibbs Free Energy of a Solution and the Partial Molar Gibbs Free Energies of the Components of the Solution

Applying Equation 9.17 to a binary solution, the Gibbs free energy (an extensive thermodynamic state function) at fixed temperature and pressure is

$$G' = n_A \overline{G}_A + n_B \overline{G}_B \tag{9.21}$$

where:

$\overline{G}_A$ and $\overline{G}_B$	are, respectively, the partial molar Gibbs free energies of A and B in the solution
G'	is the total Gibbs free energy of the solution

Dividing both sides of Equation 9.21 by $n_A + n_B$ gives the molar Gibbs free energy of the solution as

$$G = X_A \overline{G}_A + X_B \overline{G}_B \tag{9.22}$$

This relation can also be seen graphically in Figure 9.5a, as follows:

$$G(X_B) = \overline{G}_A + X_B \frac{dG(X_B)}{dX_B} \tag{9.23}$$

But,

$$\frac{dG(X_B)}{dX_B} = \overline{G}_B - \overline{G}_A \tag{9.24}$$

Thus,

$$\mathrm{G}(X_B) = \overline{G}_A + X_B(\overline{G}_B - \overline{G}_A) \tag{9.25}$$

$$G(X_B) = X_A \overline{G}_A + X_B \overline{G}_B \tag{9.26}$$

Inserting Equations 9.24 into 9.25 and rearranging yields

$$\overline{G}_A = G - X_B \frac{dG}{dX_B} \tag{9.27a}$$

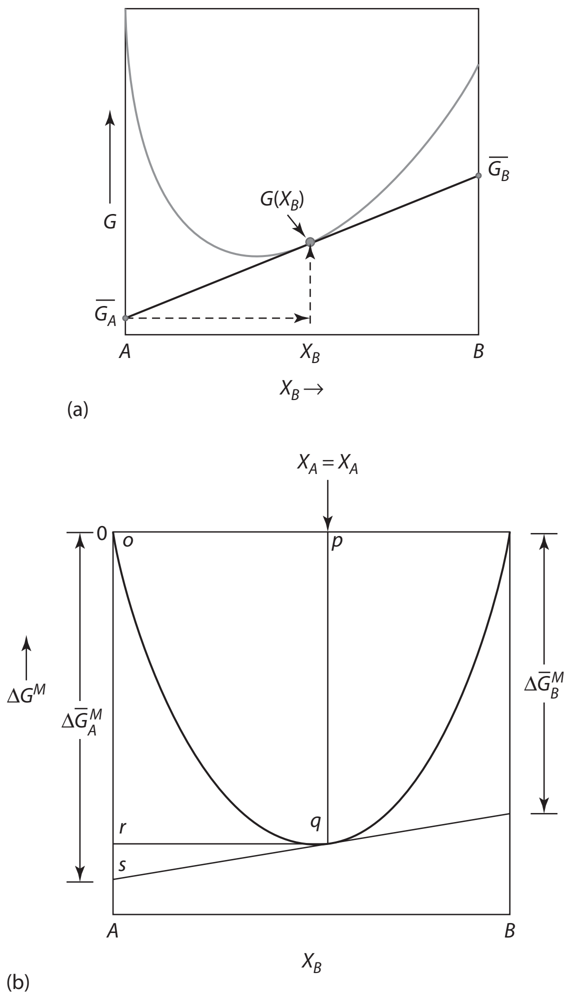

Figure 9.5a (a) The variation of the molar Gibbs free energy with composition, showing the partial molar Gibbs free energies of components *A* and *B* for the solution; (b) The variation, with composition, of the molar Gibbs free energy of formation (mixing) of a binary solution at a temperature, *T*. The partial molar values for the alloy $X_B = q$ are shown by the tangent intercepts with ordinate axes. At this temperature, there is complete solubility of *A* in *B* and *B* in *A*.

Replacing X_B in Equation 9.25 with $(1 - X_A)$ and rearranging the resulting equation gives

$$\overline{G}_B = G + X_A \frac{dG}{dX_B} \tag{9.27b}$$

These expressions relate the dependence on composition of the partial molar Gibbs free energies of the components of a binary and the molar Gibbs free energy of the solution.

9.5.2 The Change in Gibbs Free Energy due to the Formation of a Solution

Recall from our discussion in Section 9.2 that the pure component i, occurring in a condensed state at the temperature T, exerts an equilibrium vapor pressure, p_i°, and when occurring in a condensed solution at the temperature T, it exerts a lower equilibrium pressure, p_i. Consider the following isothermal three-step process:

1. The evaporation of 1 mole of pure condensed i to vapor i at the pressure p_i°
2. A decrease in the pressure of 1 mole of vapor i from p_i° to p_i
3. The condensation of 1 mole of vapor i from the pressure p_i to the condensed solution

The difference between the molar Gibbs free energy of i in the solution and the molar Gibbs free energy of pure i is given by the sum $\Delta G_{(a)} + \Delta G_{(b)} + \Delta G_{(c)}$. However, since steps (a) and (c) are processes conducted at equilibrium, $\Delta G_{(a)}$ and $\Delta G_{(c)}$ are both equal to zero. The overall change in Gibbs free energy which accompanies the isothermal three-step process is thus $\Delta G_{(b)}$, which, from Equation 8.5, is given as

$$\Delta G_{(b)} = RT \ln\left(\frac{p_i}{p_i^\circ}\right)$$

and, from Equation 9.12, this can be written as

$$\Delta G_{(b)} = G_i\left(\text{in solution}\right) - G_i\left(\text{pure}\right) = RT \ln a_i$$

But G_i (in solution) is simply the partial molar Gibbs free energy of i in the solution, and G_i (pure) is the molar Gibbs free energy of pure i. The difference between the two is the change in the Gibbs free energy accompanying the addition of 1 mole of i into the solution. This quantity is designated $\Delta\overline{G}_i^M$ and is the partial molar Gibbs free energy of mixing of the solution of i. Thus,

$$\Delta\overline{G}_i^M = \overline{G}_i - G_i^\circ = RT \ln a_i \tag{9.28}$$

If n_A moles of A and n_B moles of B are mixed to form a solution at constant temperature and pressure,

$$\text{the Gibbs free energy before mixing} = n_A G_A^\circ + n_B G_B^\circ$$

and

$$\text{the Gibbs free energy after mixing} = n_A \overline{G}_A + n_B \overline{G}_B$$

The change in the *total* Gibbs free energy caused by the mixing process, $\Delta G'^M$, sometimes referred to as the *integral* Gibbs free energy of mixing (total Gibbs free energy of mixing), is the difference between these quantities; that is,

$$\begin{aligned}\Delta G'^M &= \left(n_A\overline{G}_A + n_B\overline{G}_B\right) - \left(n_A G_A^\circ + n_B G_B^\circ\right)\\ &= n_A\left(\overline{G}_A - G_A^\circ\right) + n_B(\overline{G}_B - G_B^\circ)\end{aligned}$$

Substitution from Equation 9.28 gives

$$\Delta G'^M = n_A\Delta\overline{G}_A^M + n_B\Delta\overline{G}_B^M \tag{9.29}$$

or

$$\Delta G'^M = RT(n_A \ln a_A + n_B \ln a_B) \tag{9.30}$$

For 1 mole of solution, Equations 9.29 and 9.30, respectively, become

$$\Delta G^M = X_A\Delta\overline{G}_A^M + X_B\Delta\overline{G}_B^M \tag{9.31}$$

and

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B) \tag{9.32}$$

The variation of ΔG^M with composition, given by Equation 9.32, is shown in Figure 9.5b. $\Delta G^M(X_B = q)$ is given by the segment $\overline{pq}$ and the segment $\overline{or}$.

9.5.3 The Method of Tangential Intercepts

From Figure 9.5b and Equation 9.27a and b, it can be seen that

$$\Delta\overline{G}_A^M = \Delta G^M - X_B\frac{d\Delta G^M}{dX_B} \tag{9.33a}$$

and

$$\Delta\overline{G}_B^M = \Delta G^M + X_A\frac{d\Delta G^M}{dX_B} \tag{9.33b}$$

Here, the partial molar Gibbs free energy of mixing of the components *A* and *B* can be read directly from the tangential intercepts at $X_B = 0$ and $X_B = 1$, respectively, just as the partial molar Gibbs free energies of X_B and X_A (their chemical potentials) can be read directly from Figure 9.5a.

9.6 THE PROPERTIES OF IDEAL SOLUTIONS

The components of a Raoultian solution obey the relation $a_i = X_i$. An ideal solution is a solution which obeys Raoult's law at all temperatures, pressures, and compositions. Thus, for an ideal binary *A*–*B* solution, the Gibbs free energy of mixing from Equation 9.32 becomes

$$\Delta G^{M,\mathrm{id}} = RT(X_A \ln X_A + X_B \ln X_B) \tag{9.34}$$

with the partial Gibbs free energy of mixing of the components *A* and *B* given as

$$\Delta \overline{G}_A^{M,\mathrm{id}} = RT \ln X_A \qquad \text{and} \qquad \Delta \overline{G}_B^{M,\mathrm{id}} = RT \ln X_B$$

As discussed in Chapter 8, the general thermodynamic relationships between the state properties of a system are applicable to the partial molar properties of the components of a system. Thus, for the species *i* occurring in a solution,

$$\left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,\mathrm{comp}} = \overline{V}_i \tag{9.35}$$

and, for pure *i*,

$$\left(\frac{\partial G_i^\circ}{\partial P}\right)_{T,\mathrm{comp}} = V_i^\circ \tag{9.36}$$

9.6.1 The Change in Volume Accompanying the Formation of an Ideal Solution

Subtraction of Equations 9.36 from 9.35 gives

$$\left[\frac{\partial\left(\overline{G}_i - G_i^\circ\right)}{\partial P}\right]_{T,\mathrm{comp}} = \left(\overline{V}_i - V_i^\circ\right)$$

or

$$\left(\frac{\partial \Delta \overline{G}_i^M}{\partial P}\right)_{T.\mathrm{comp}} = \Delta \overline{V}_i^M \tag{9.37}$$

The change in volume due to mixing, $\Delta V'^M$, is the difference between the volumes of the components in the solution and the volumes of the pure components; that is, for a binary *A*–*B* solution containing n_A moles of *A* and n_B moles of *B*,

$$\begin{aligned}\Delta V'^{M} &= \left(n_A \overline{V}_A + n_B \overline{V}_B\right) - \left(n_A V_A^\circ + n_B V_B^\circ\right)\\ &= n_A\left(\overline{V}_A - V_A^\circ\right) + n_B\left(\overline{V}_B - V_B^\circ\right)\\ &= n_A \Delta \overline{V}_A^{M} + n_B \Delta \overline{V}_B^{M}\end{aligned}$$

In an ideal solution, $\Delta \overline{G}_i^{M,\mathrm{id}} = RT \ln X_i$, and since this term is not a function of pressure, $\Delta \overline{V}_i^{M,\mathrm{id}} = 0$. Thus, it is seen that the change in volume accompanying an ideal solution is zero; that is,

$$\Delta V'^{M,\mathrm{id}} = 0 \tag{9.38}$$

The volume of an ideal solution is thus equal to the sum of the volumes of the pure components. The variation, with composition, of the molar volume of an ideal binary solution is shown in Figure 9.6. At any composition, the values of the partial molar volumes $\overline{V}_A^{M}$ and $\overline{V}_B^{M}$ are obtained as the intercepts of the tangents to the volume–composition line with the respective axes. Since the molar volume of an ideal solution is a linear function of composition (i.e., it follows the rule of mixtures), the tangent at any point coincides with the straight line, such that

$$\overline{V}_A = V_A^\circ \quad \text{and} \quad \overline{V}_B = V_B^\circ$$

For crystalline solids, this plot is similar to the case where the lattice parameter versus composition is linear (called *Vegard's law*, after Lars Vegard, 1880–1963).

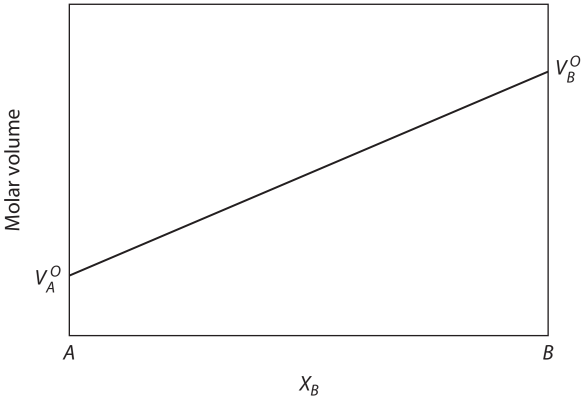

Figure 9.6 The variation, with composition, of the molar volume of a binary ideal solution.

9.6.2 The Enthalpy of Formation of an Ideal Solution

For a component in a solution, the Gibbs–Helmholtz equation (Equation 5.37), can be used to obtain

$$\left[\frac{\partial \frac{\overline{G}_i}{T}}{\partial T}\right]_{P,\text{comp}} = -\frac{\overline{H}_i}{T^2} \tag{9.39}$$

and, for the pure component,

$$\left[\frac{\partial \frac{G_i^\circ}{T}}{\partial T}\right]_{P,\text{comp}} = -\frac{H_i^\circ}{T^2} \tag{9.40}$$

where $\overline{H}_i$ and H_i° are, respectively, the partial molar enthalpy of i in the solution and the standard molar enthalpy of i. Subtraction of Equation 9.40 from Equation 9.39 gives

$$\left[\frac{\partial\left(\frac{\overline{G}_i - G_i^\circ}{T}\right)}{\partial T}\right]_{P,\text{comp}} = -\frac{\left(\overline{H}_i - H_i^\circ\right)}{T^2}$$

or

$$\left[\frac{\partial\left(\frac{\Delta\overline{G}_i^M}{T}\right)}{\partial T}\right]_{P,\text{comp}} = -\frac{\Delta\overline{H}_i^M}{T^2} \tag{9.41}$$

where $\Delta\overline{H}_i^M$ is the partial molar enthalpy of mixing of solution of i.

In an ideal solution, $\Delta\overline{G}_i^{M,\text{id}} = RT\ln X_i$, substitution of which into Equation 9.41 gives

$$\frac{d\left(R\ln X_i\right)}{dT} = -\frac{\Delta\overline{H}_i^M}{T^2}$$

and, since the first term is not a function of temperature, it is seen that, for a component of an ideal solution,

$$\Delta\overline{H}_i^{M,\text{id}} = \overline{H}_i - H_i^\circ = 0$$

or

$$\overline{H}_i = H_i^\circ \tag{9.42}$$

The enthalpy of formation of a solution (or the enthalpy of mixing of the components) is the difference between the enthalpies of the components in solution and the enthalpies of the pure components before mixing. Thus, for a mixture of n_A moles of A and n_B moles of B,

$$\begin{aligned}\Delta H'^M &= \left(n_A\overline{H}_A + n_B\overline{H}_B\right) - \left(n_A H_A^\circ + n_B H_B^\circ\right)\\ &= n_A(\overline{H}_A - H_A^\circ) + n_B(\overline{H}_B - H_B^\circ)\\ &= n_A\Delta\overline{H}_A^M + n_B\Delta\overline{H}_B^M\end{aligned}$$

and

$$\Delta H^M = X_A\Delta\overline{H}_A^M + X_B\Delta\overline{H}_B^M$$

For an ideal solution, $\Delta\overline{H}_i^M = 0$, and thus, it is seen that the enthalpy of formation (or the enthalpy of mixing) of an ideal solution is zero; that is,

$$\Delta H^{M,\text{id}} = 0 \tag{9.43}$$

9.6.3 The Entropy of Formation of an Ideal Solution

The fundamental equation (Equation 5.25), gives

$$\left(\frac{\partial G}{\partial T}\right)_{P,\text{comp}} = -S$$

Thus, for the formation of one mole of a solution,

$$\left(\frac{\partial \Delta G^M}{\partial T}\right)_{P,\text{comp}} = -\Delta S^M$$

For an ideal solution, Equation 9.34 showed that

$$\Delta G^{M,\text{id}} = RT(X_A\ln X_A + X_B\ln X_B)$$

and hence,

$$\begin{aligned}\Delta S^{M,\mathrm{id}} &= -\left(\frac{\partial \Delta G^{M,\mathrm{id}}}{\partial T}\right)_{P,\mathrm{comp}} \\ &= -R(X_A \ln X_A + X_B \ln X_B)\end{aligned} \tag{9.44}$$

Equation 9.44 shows that the entropy of formation of an ideal binary solution is independent of temperature and is positive.

Equation 4.3 for total change in configurational entropy gives, for the mixing of N_A particles of A with N_B particles of B,

$$\begin{aligned}\Delta S'^{M} &= k_B \ln \frac{(N_A + N_B)!}{N_A!N_B!} \\ &= k_B[\ln(N_A + N_B)! \; - \ln N_A! \; - \ln N_B!]\end{aligned}$$

Application of *Stirling's theorem*[*] (after James Sterling, 1692–1770) gives

$$\begin{aligned}\Delta S'^{M} &= k_B[(N_A + N_B)\ln(N_A + N_B) \\ &\quad -(N_A + N_B) - N_A \ln N_A + N_A - N_B \ln N_B + N_B] \\ &= -k_B\left[N_A \ln\left(\frac{N_A}{N_A + N_B}\right) + N_B\left(\frac{N_B}{N_A + N_B}\right)\right]\end{aligned}$$

Now,

$$\frac{N_A}{N_A + N_B} = \frac{n_A}{n_A + n_B} = X_A$$

and, similarly,

$$\frac{N_B}{N_A + N_B} = X_B$$

Also,

$$N_A \text{ particles of } A = \frac{N_A}{N_\mathrm{O}} \text{ moles of } A = n_A \text{ moles of } A$$

and

$$N_B \text{ particles of } B = \frac{N_B}{N_\mathrm{O}} \text{ moles of } B = n_B \text{ moles of } B$$

---

[*] Stirling's theorem is $m! = \sqrt{2\pi m}\; m^m e^m$, and thus, ln $m!$ = ln (2 πm) + m ln m – m, which, for large values of m, can be written as ln $m!$ = m ln m – m.

where N_O is Avogadro's number. Thus,

$$\Delta S'^M = -k_B N_O (n_A \ln X_A + n_B \ln X_B)$$

But, since Boltzmann's constant, k_B, times Avogadro's number, N_O, equals the gas constant, R,

$$\Delta S'^M = -R(n_A \ln X_A + n_B \ln X_B)$$

Division by the total number of moles, $n_A + n_B$, gives

$$\Delta S^M = -R\left(X_A \ln X_A + X_B \ln X_B\right) \tag{9.45}$$

which is identical to Equation 9.44. The increase in entropy accompanying the formation of 1 mole of an ideal solution is a measure of the increase in the number of *spatial configurations* which become available to the system as a result of the mixing process. This is dependent only on the numbers of moles of the components in the solution and is independent of temperature. The variation of $\Delta S^{M,\text{id}}$ with composition in a binary A–B solution is shown in Figure 9.7. Note that this is symmetric about $X_B = 0.5$ and has a maximum value of $R \ln 2$. The function has infinite slopes at $X_B = 0$ and $X_B = 1$.

Since

$$\Delta S^M = X_A \Delta \overline{S}_A^M + X_B \Delta \overline{S}_B^M$$

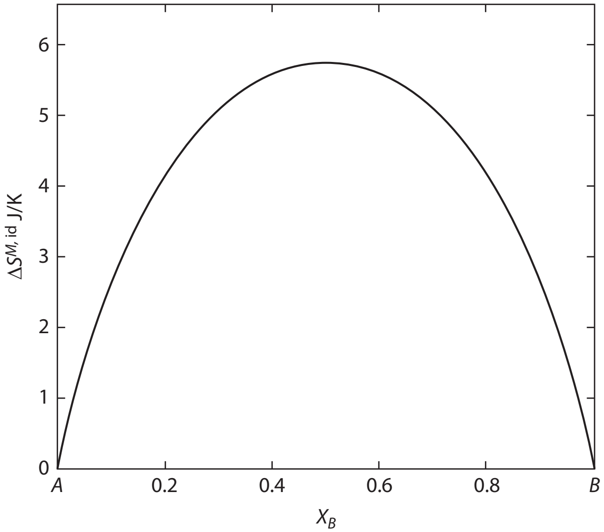

Figure 9.7 The variation, with composition, of the molar entropy of formation of a binary ideal solution. The maximum value is R ln 2.

it is seen that, in an ideal solution,

$$\Delta\overline{S}_A^{M,\mathrm{id}} = -R\ln X_A \qquad \text{and} \qquad \Delta\overline{S}_B^{M,\mathrm{id}} = -R\ln X_B$$

For any solution,

$$\Delta G^M = \Delta H^M - T\Delta S^M$$

and, for an ideal solution, since $\Delta H^{M,\mathrm{id}} = 0$, then

$$\Delta G^{M,\mathrm{id}} = -T\Delta S^{M,\mathrm{id}} < 0$$

9.7 NONIDEAL SOLUTIONS

A nonideal solution is one in which the activities of the components are not equal to their mole fractions at all compositions or temperatures. However, in view of the convenience of the concept of activity and the simplicity of Raoult's law, it is convenient to define an additional thermodynamic function called the *activity coefficient*, γ. The activity coefficient of a component of a solution is defined as the ratio of the activity of the component to its mole fraction; that is, for the component *i*,

$$\gamma_i = \frac{a_i}{X_i} \tag{9.46}$$

The value of γ_i can be greater or less than unity ($\gamma_i = 1$ gives Raoultian behavior).

If $\gamma_i > 1$, then the component *i* is said to exhibit a *positive deviation* from Raoultian behavior, and, if $\gamma_i < 1$, then the component *i* is said to exhibit a *negative deviation* from Raoult's law. Figure 9.8 shows the variation of a_i with X_i for a component *i* which exhibits negative deviations. Figure 9.9 shows a system which exhibits positive deviations.

If γ_i varies with temperature, then $\Delta\overline{H}_i^M$ has a nonzero value; that is, from Equation 9.41,

$$\frac{\partial\left(\dfrac{\Delta\overline{G}_i^M}{T}\right)}{\partial T} = -\frac{\Delta\overline{H}_i^M}{T^2}$$

and

$$\Delta\overline{G}_i^M = RT\ln a_i = RT\ln\gamma_i + RT\ln X_i$$

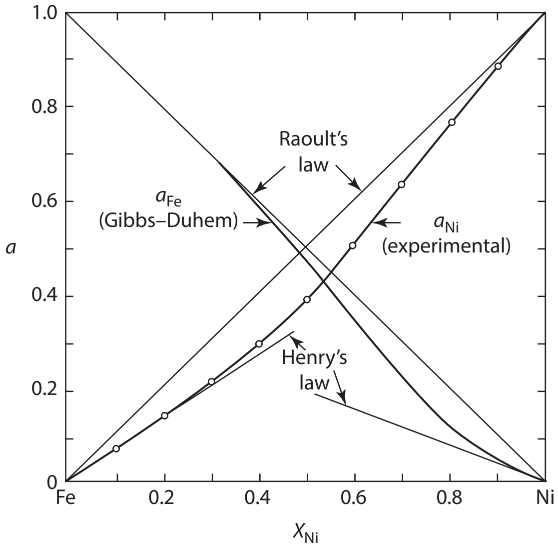

Figure 9.8 Activities in the liquid system iron–nickel at 1600°C which display negative deviation from ideality. (From G. R. Zellars, S. L. Payne, J. P. Morris, and R. L. Kipp, "The Activities of Iron and Nickel in Liquid Fe–Ni Alloys," *Trans. AIME* (1959), vol. 215, p. 181.)

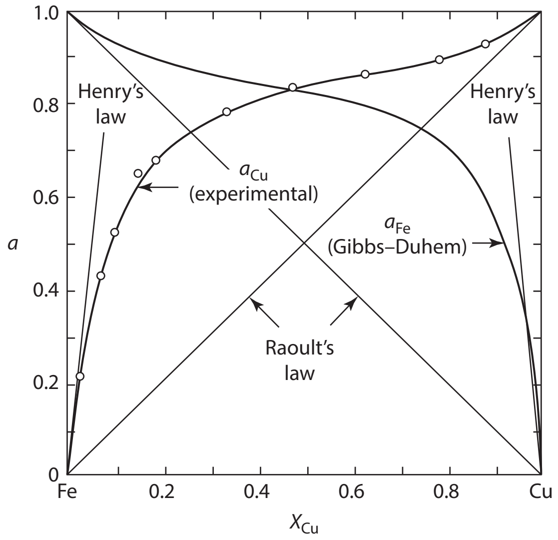

Figure 9.9 Activities in the liquid system iron–copper at 1550°C which display positive deviation from ideality. (From J. P. Morris and G. R. Zellars, "Vapor Pressure of Liquid Copper and Activities in Liquid Fe–Cu Alloys," *Trans. AIME* (1956), vol. 206, p. 1086.)

Thus,

$$\frac{\partial\left(\dfrac{\Delta\overline{G}_i^M}{T}\right)}{\partial T}=\frac{\partial\left(R\ln\gamma_i\right)}{\partial T}=-\frac{\Delta\overline{H}_i^M}{T^2}$$

and since

$$d\left(\frac{1}{T}\right)=-\frac{dT}{T^2}$$

then

$$\frac{\partial(R\ln\gamma_i)}{\partial\left(\dfrac{1}{T}\right)}=\Delta\overline{H}_i^M \tag{9.47}$$

In general, increasing the temperature of a nonideal solution causes a decrease in the extent to which its components deviate from ideal behavior; that is, if $\gamma_i > 1$, then an increase in temperature causes γ_i to decrease toward unity, and if $\gamma_i < 1$, an increase in temperature causes γ_i to increase toward unity. Thus, in a solution, the components of which exhibit positive deviations from ideality, the values of the activity coefficients decrease with increasing temperature, and since

$$\frac{\partial(R\ln\gamma_i)}{\partial\left(\dfrac{1}{T}\right)}=\Delta\overline{H}_i^M$$

the partial molar enthalpies of formation of the components are *positive* quantities. This means that the molar enthalpy of formation (mixing) of the solution, ΔH^M, is a positive quantity, which indicates that the mixing process is endothermic. ΔH^M is the quantity of thermal energy absorbed from the thermal reservoir surrounding the solution per mole of solution formed at the temperature T. Conversely, in a solution, the components of which exhibit negative deviations from ideality, the activity coefficients increase with increasing temperature, and hence, the partial molar enthalpies of mixing and the molar enthalpy of mixing are negative. Such a solution forms *exothermically*, and ΔH^M is the enthalpy absorbed by the constant-temperature thermal reservoir, per mole of solution formed, at the temperature T. These trends can be understood by assuming that the interactions among particles decrease as the temperature rises, because the particles have greater movement with increasing temperature and therefore less chance of interacting with each other.

Exothermic mixing in an A–B binary condensed system occurs when the A–B bond energy is more negative than both the A–A and B–B bond energies, and this causes a tendency toward atomic *ordering* in the solution, in which the A atoms (B atoms) attempt to have as many B atoms (A atoms) as the nearest neighbors as is possible for the overall composition of the solution. Exothermic mixing thus indicates a tendency toward the formation of an atomically ordered phase or compound between the two components (e.g., the Fe–Ni system). Conversely, endothermic mixing occurs when the A–B bond energy is less negative than both the A–A and B–B bond energies, and this causes a tendency toward phase separation or *clustering* in the solution (e.g., the Fe–Cu system). The A atoms attempt to be coordinated only by A atoms, and the B atoms attempt to be coordinated only by B atoms.

In both of these cases (exothermic and endothermic), the equilibrium configuration of the solution is reached as a compromise between the enthalpy and entropy factors. The enthalpy, being determined by the relative magnitudes of the bond energies, attempts to either completely order (negative deviation from ideality) or completely unmix (positive deviation from ideality) the solution. The entropy factor attempts to maximize the randomness of mixing of the atoms in the solution. For the clustering case, as the temperature approaches 0 K, the equilibrium state approaches that of pure A and pure B, and hence, as the temperature approaches 0 K, the configurational entropy of a solid solution approaches zero. For the ordering case, the situation is more complex and will be discussed later in Chapter 10. However, it too predicts zero configurational entropy for the crystalline alloy as the temperature approaches 0 K. These are Third Law constraints on the ground state (0 K) equilibrium entropy of alloys.

9.8 APPLICATION OF THE GIBBS–DUHEM RELATION TO THE DETERMINATION OF ACTIVITY

Applied to a binary A–B solution and using the partial molar Gibbs free energy of mixing (Equation 9.28) as the extensive property, Equation 9.19b becomes

$$X_A d\Delta\overline{G}_A^M + X_B d\Delta\overline{G}_B^M = 0 \tag{9.48}$$

and, since $\Delta\overline{G}_i^M = RT \ln a_i$, then

$$X_A d\ln a_A + X_B d\ln a_B = 0 \tag{9.49a}$$

$$X_A d\log a_A + X_B d\log a_B = 0 \tag{9.49b}$$

or

$$d\ln a_A = -\frac{X_B}{X_A} d\ln a_B \tag{9.50a}$$

$$d\log a_A = -\frac{X_B}{X_A} d\log a_B \tag{9.50b}$$

If the variation of a_B with composition is known, then the integration of Equation 9.50b from $X_A = 1$ to X_A gives the value of log a_A at X_A as

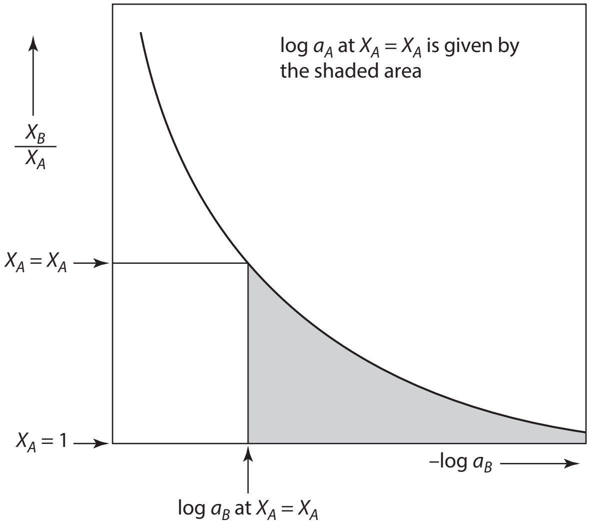

Figure 9.10 A schematic representation of the variation of log a_B with X_B/X_A in a binary solution, illustrating the application of the Gibbs–Duhem equation to the calculation of the activity of component A.

$$\log a_A \text{ at } X_A = -\int_{\log a_B \text{ at } X_A=1}^{\log a_B \text{ at } X_A=X_A} \left(\frac{X_B}{X_A}\right) d\log a_B \tag{9.51}$$

Since an analytical expression for the variation of the activity of B is not usually computed, Equation 9.51 is solved by graphical integration.

Figure 9.10 shows a typical variation of log a_B with composition, and the value of log a_A at $X_A = X_A$ is equal to the shaded area under the curve. Two points are to be noticed in Figure 9.10.

1. $X_B \to 1$, $a_B \to 1$, $\log a_B \to 0$, and $X_B/X_A \to \infty$. Thus, the curve exhibits a tail to infinity as $X_B \to 1$.
2. $X_B \to 0$, $a_B \to 0$, and $\log a_B \to -\infty$. Thus, the curve exhibits a tail to minus infinity as $X_B \to 0$.

These points have been addressed by Darken and Gurry,* and methods of integrating with better accuracy are presented in their text.

9.8.1 The Relationship between Henry's and Raoult's Laws

Henry's law for the solute B in a binary A–B solution (Equation 9.14) can be written as

$$a_B = \gamma_B X_B$$

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* L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953, pp. 258–266.

or, in terms of logarithms,

$$\ln a_B = \ln \gamma_B + \ln X_B$$

differentiation of which gives

$$d \ln a_B = d \ln X_B$$

Inserting this into the Gibbs–Duhem equation gives

$$\begin{aligned} d \ln a_A &= -\frac{X_B}{X_B} d \ln X_B = -\frac{X_B}{X_A}\frac{dX_B}{X_B} = -\frac{dX_B}{X_A} \\ &= \frac{dX_A}{X_A} = d \ln X_A \end{aligned}$$

Integration gives

$$\ln a_A = \ln X_A + \ln\text{ (constant)}$$

or

$$a_A = \text{constant} \times X_A$$

But, by definition, $a_i = 1$ when $X_i = 1$, and thus, the integration constant equals unity. Consequently, in the range of composition over which the solute B obeys Henry's law, the solvent A obeys Raoult's law. As an example of this, see Figure 9.8, where Henry's law holds for the solute Ni up to about $X_{\text{Ni}} = 0.3$ and Raoult's law holds for the solvent Fe for $X_{\text{Ni}} < 0.3$.

9.8.3 Direct Calculation of the Total Molar Gibbs Free Energy of Mixing

Equation 9.33b gave

$$\Delta \overline{G}_A^M = \Delta G^M + X_B \frac{d\Delta G^M}{dX_A}$$

Rearranging and dividing by X_B^2 gives

$$\frac{\Delta \overline{G}_A^M dX_A}{X_B^2} = \frac{X_B d\Delta G^M - \Delta G^M dX_B}{X_B^2} = d\left(\frac{\Delta G^M}{X_B}\right)$$

or

$$d\left(\frac{\Delta G^M}{X_B}\right) = \frac{\Delta \overline{G}_A^M}{X_B^2} dX_A$$

Integrating between $X_A = X_A$ and $X_A = 0$ gives

$$\Delta G^M = X_B \int_0^{X_A} \frac{\Delta \overline{G}_A^M}{X_B^2} dX_A \tag{9.52}$$

Since $\Delta \overline{G}_A^M = RT \ln a_A$, the integral molar Gibbs free energy of mixing of A and B can be obtained directly from the variation of a_A with composition as

$$\Delta G^M = RTX_B \int_0^{X_A} \frac{\ln a_A}{X_B^2} dX_A \tag{9.53}$$

The measured activities of Ni in Fe and Cu in Fe shown in Figures 9.8 and 9.9 can be used to obtain

$$\Delta G^M (\text{in the system Fe} - \text{Ni}) = RTX_{\text{Fe}} \int_0^{X_{\text{Ni}}} \frac{\ln a_{\text{Ni}}}{X_{\text{Fe}}^2} dX_{\text{Ni}}$$

and

$$\Delta G^M (\text{in the system Cu} - \text{Fe}) = RTX_{\text{Fe}} \int_0^{X_{\text{Cu}}} \frac{\ln a_{\text{Cu}}}{X_{\text{Fe}}^2} dX_{\text{Cu}}$$

The graphical integrations of these equations are shown in Figure 9.11, in which curve (a) is $(\ln a_{\text{Cu}})/X_{\text{Fe}}^2$ versus X_{Cu} and curve (c) is $(\ln a_{\text{Ni}})/X_{\text{Fe}}^2$ versus X_{Ni}. Curve (b) shows the variation of $(\ln X_i)/(1 - X_i)^2$ with X_i, which is the variation of the function for a component i which exhibits Raoultian behavior. As is seen, some uncertainty is introduced into the integration by virtue of the fact that the function $(\ln a_i)/(1 - X_i)^2 \rightarrow -\infty$, as $X_i \rightarrow 0$. In Figure 9.11, the shaded area (which is the value of the integral between $X_{\text{Cu}} = 0.5$ and $X_{\text{Cu}} = 0$) multiplied by the factor (2.303 × 8.3144 × 1823 × 0.5) gives the value of ΔG^M at $X_{\text{Fe}} = 0.5$.

The variations of ΔG^M obtained from graphical integrations are shown in Figure 9.12. Here, the α function $\alpha_i = \ln \gamma_i / (1 - X_i)^2$ introduced by Darken and Gurry* is applied to a solution which exhibits ideal ($\gamma_i = 1$) behavior (curve b); integration gives

$$\begin{aligned}
\Delta G^M \quad &= RT(1 - X_B) \int_0^{X_B} \frac{\ln X_B}{(1 - X_B)^2} dX_B \\
&= RT(1 - X_B) \left[\frac{X_B \ln X_B}{1 - X_B} + \ln(1 - X_B) \right] \\
&= RT \left[X_B \ln X_B + (1 - X_B) \ln(1 - X_B) \right] \\
&= RT \left[X_B \ln X_B + X_A \ln X_A \right]
\end{aligned}$$

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* L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953, pp. 258–266.

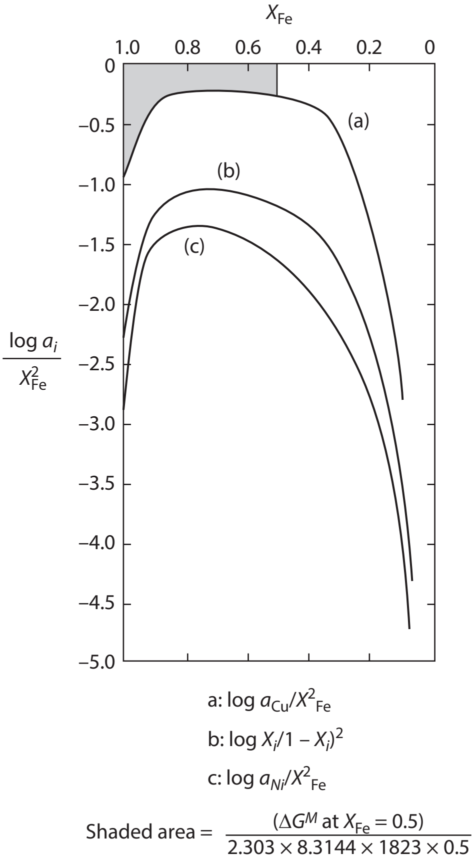

Figure 9.11 Illustration of the direct calculation of the molar Gibbs free energies of mixing in the liquid systems iron–copper at 1550°C and iron–nickel at 1600°C.

which is in agreement with Equation 9.34.

9.9 REGULAR SOLUTIONS

Up to this point, two classes of solutions have been identified. The first is the ideal solution, in which

$$a_i = X_i$$

$$\Delta \overline{H}_i^M = 0$$

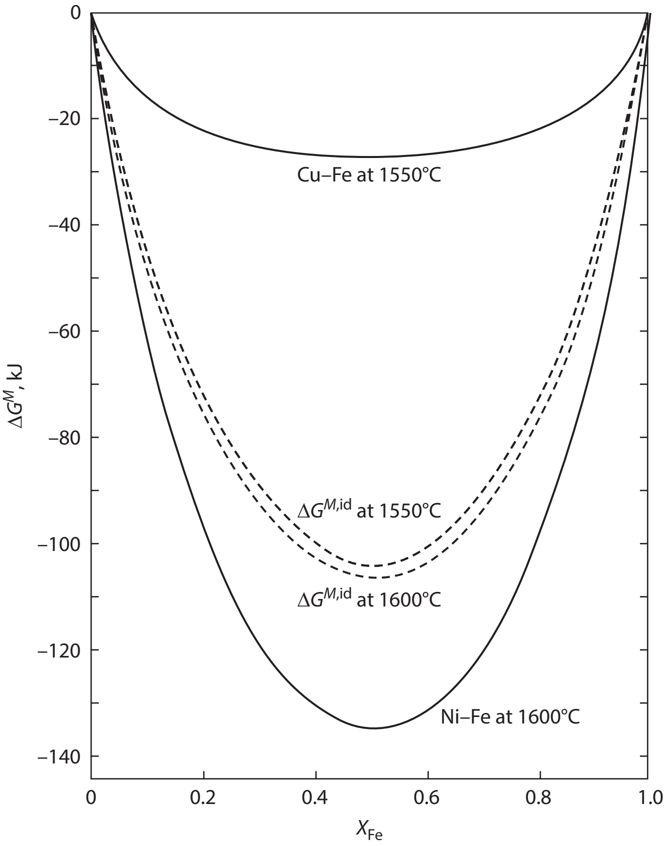

Figure 9.12 The molar Gibbs free energies of mixing in the liquid systems iron–copper at 1550°C and iron–nickel at 1600°C. Iron nickel displays negative deviations from ideality and iron copper displays positive deviations from ideality.

$$\Delta \overline{V}_i^M = 0$$

$$\Delta \overline{S}_i^M = -R \ln X_i$$

for all X_i, all temperatures and all pressures. All other solutions can be classified as nonideal solutions in which the relationships $a_i = X_i$ and $\Delta \overline{H}_i^M = 0$ are not valid.

Attempts to classify nonideal solutions have involved the development of equations that describe the behavior of hypothetical solutions, and the simplest of these mathematical formalisms is that which generates what is known as *regular solution behavior*.

A regular solution is one in which

$$\Delta H^M = \alpha X_A X_B \tag{9.54}$$

and

$$\Delta S^M = \Delta S^{M,\text{ideal}} \tag{9.55}$$

where α is a constant.

Thus, for a regular solution:

$$\Delta G^M = \alpha X_A X_B - T\Delta S^{M,\text{ideal}} \tag{9.56}$$

It is common to define excess functions as the value of the state function minus that of the ideal value of the state function.

$$G^{\text{XS}} = G - G^{\text{id}} \tag{9.57}$$

Thus, for a regular solution, the excess molar Gibbs free energy of mixing is

$$G^{\text{XS}} = \Delta G^M - \Delta G^{M,\text{ideal}} = \Delta H^M = \alpha X_A X_B \tag{9.58}$$

Also, for a regular solution,

$$\frac{\partial G^{\text{XS}}}{\partial T} = -S^{\text{XS}} = 0$$

We see that, at any composition,

$$\overline{G}_A^{\text{XS}} = RT \ln \gamma_A$$

is independent of temperature. Thus,

$$\overline{G}_A^{\text{XS}} = RT_1 \ln \gamma_A(T_1) = RT_2 \ln \gamma_A(T_2)$$

from which we see that

$$\frac{\ln \gamma_A(T_2)}{\ln \gamma_A(T_1)} = \frac{T_1}{T_2} \tag{9.59}$$

Equation 9.59 is of considerable practical use in converting activity data for a regular solution at one temperature to activity data at another temperature. We also see that as T_2 becomes very large, $\gamma_A(T_2)$ approaches unity (see also the discussion in Section 9.7 concerning Equation 9.47).

We can write

$$\Delta\overline{H}_B = \Delta H^M + (1 - X_B)\frac{d\Delta H^M}{dX_B}$$

and since $\Delta H^M = \alpha X_A X_B$, this yields

$$\Delta \overline{H}_B = \alpha X_A^2 \tag{9.61}$$

Since all the state functions of a regular solution are symmetric with respect to the interchanging of X_A and X_B, we can also write

$$\Delta \overline{H}_A = \alpha X_B^2 \tag{9.62}$$

Now,

$$\Delta \overline{G}_A^M = RT \ln a_A = \Delta \overline{H}_A^M - T\Delta \overline{S}_A^M$$

$$RT \ln a_A + T\Delta \overline{S}_A^M = \Delta \overline{H}_A^M$$

$$RT \ln \gamma_A + RT \ln X_A - RT \ln X_A = \Delta \overline{H}_A^M$$

$$\therefore\ RT \ln \gamma_A = \Delta \overline{H}_A^M = \alpha X_B^2 \tag{9.63}$$

Finally, this gives us

$$\gamma_A = \exp\left(\frac{\alpha X_B^2}{RT}\right) \tag{9.64}$$

$$\gamma_B = \exp\left(\frac{\alpha X_A^2}{RT}\right) \tag{9.65}$$

The following relationships are valid for a regular solution.

As $X_A \to 1$, $\gamma_A = \exp\left(\frac{\alpha \cdot 0}{RT}\right) \to 1$, A is a Raultian solution.

As $X_A \to 0$, $\gamma_A = \exp\left(\frac{\alpha \cdot 1}{RT}\right) \to$ a constant, A is a Henrian solution.

As $X_B \to 1$, $\gamma_B = \exp\left(\frac{\alpha \cdot 0}{RT}\right) \to 1$, B is a Raultian solution.

As $X_B \to 0$, $\gamma_B = \exp\left(\frac{\alpha \cdot 1}{RT}\right) \to$ a constant, B is a Henrian solution.

Figures 9.13 and 9.14, respectively, show the symmetrical variation, with composition, of the activities and activity coefficients in the liquid system tin–thallium measured by Hildebrand

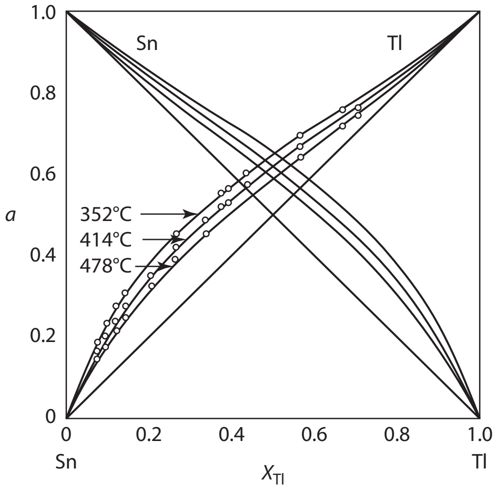

Figure 9.13 Activities in the liquid system tin–thallium. (From J. H. Hildebrand and J. N. Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.)

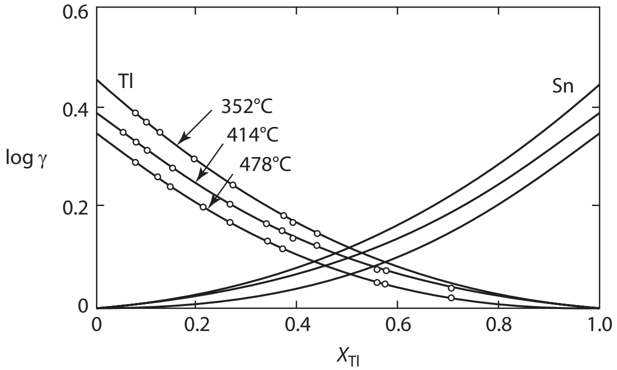

Figure 9.14 Activity coefficients in the liquid system tin–thallium. (From J. H. Hildebrand and J. N. Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am Chem Soc.* (1929), vol. 51, p. 462.)

and Sharma* at three temperatures. Figure 9.15 shows the linear variations of log γ_{Tl} with X_{Sn}^2, the slopes of which equal α at the given temperatures.

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* J. H. Hildebrand and J. N. Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.

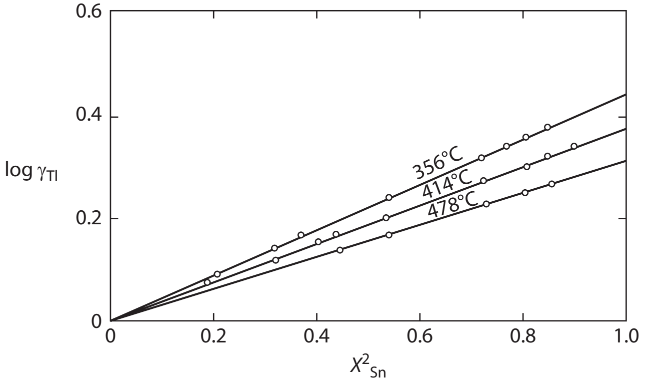

Figure 9.15 Log γ_{T1} vs. X^2_{Sn} in the system tin–thallium. (From J. H. Hildebrand and J. N. Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.)

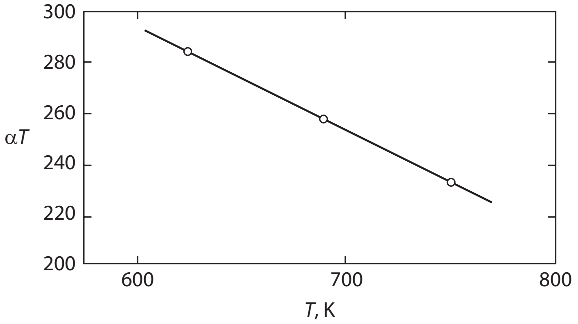

Figure 9.16 The variation of the product αT with T in the system Sn–Tl, showing that the system does not conform to a regular solution, since αT depends on T.

The variation of γ_i with X_i is that of a regular solution, but Figure 9.16 shows that αT, which for strict adherence to regular behavior should be independent of T, decreases slowly with increasing temperature. Figure 9.17 shows the variations, with composition, of ΔG^M, ΔH^M, and $-T\Delta S^M$ for the liquid system Sn–Tl at 414°C. It is to be noted that a parabolic form for ΔH^M or G^{XS} should not be taken as being a demonstration that the solution is regular, as it is frequently found that ΔH^M or G^{XS} can be adequately expressed by means of the relations

$$\Delta H^M = bX_AX_B \quad \text{or} \quad G^{XS} = b'X_AX_B$$

where b and b' are unequal, in which case

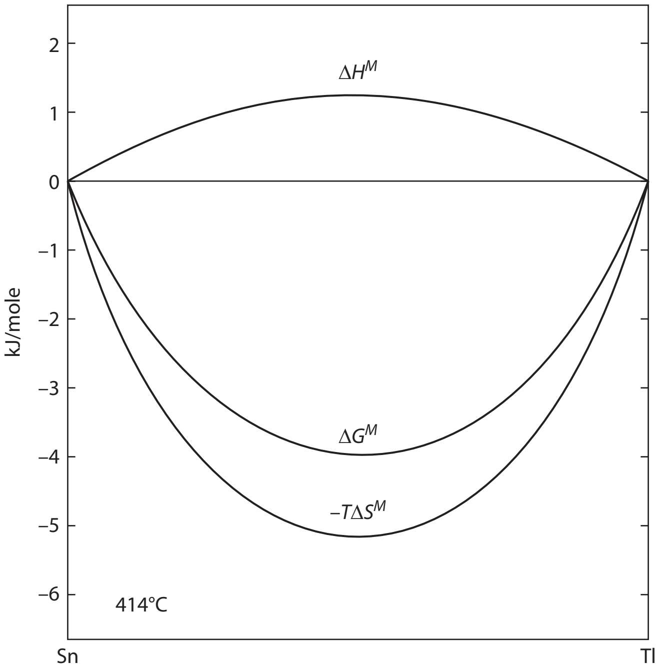

Figure 9.17 The molar enthalpy, entropy, and Gibbs free energy of mixing of liquid tin and thallium at 414°C. The system exhibits positive deviations from ideality.

$$\Delta S^M \neq \Delta S^{M,\text{id}}$$

If only configurational entropy is considered, then $\Delta S^M < \Delta S^{M,\text{id}}$. If, however, other aspects of entropy exist in the alloy (e.g., magnetic spins, defects, volume effects), ΔS^M may be greater than $\Delta S^{M,\text{id}}$.

9.10 A STATISTICAL MODEL OF SOLUTIONS

Regular solution behavior can be understood by the application of the statistical mixing model, introduced in Chapter 4, to two components which have equal molar volumes and which do not exhibit a change in molar volume when mixed; that is, $\Delta \overline{V}_i^M = 0$. In both the pure state and in solution, the interatomic forces are assumed to exist only between neighboring atoms (near-neighbor model), in which case the energy of the solution is the sum of the interatomic near-neighbor bond energies.

Consider 1 mole of a mixed crystal containing N_A atoms of A and N_B atoms of B, such that

$$X_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{N_O} \quad \text{and} \quad X_B = \frac{N_B}{N_O}$$

where N_O is Avogadro's number. The mixed crystal, or solid solution, contains three types of atomic bonds:

1. A–A bonds with energy E_{AA}
2. B–B bonds with energy E_{BB}
3. A–B bonds with energy E_{AB}

By considering the relative zero of energy to be that when the atoms are infinitely far apart, the bond energies E_{AA}, E_{BB}, and E_{AB} are *negative quantities*. Let the coordination number of an atom in the crystal be z; that is, each atom has z nearest neighbors. If, in the solution, there are P_{AA} A–A bonds, P_{BB} B–B bonds, and P_{AB} A–B bonds, the energy of the solution, E, is obtained as the linear combination

$$E = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB} \tag{9.66}$$

and the problem of calculating E becomes one of calculating the values of P_{AA}, P_{BB}, and P_{AB}.

$$\text{the number of } A \text{ atoms} \times \text{the number of bonds per atom}$$

$$= \text{the number of } A - B \text{ bonds} + 2 \times \text{the number of } A - A \text{ bonds}$$

(The factor 2 arises because each A–A bond involves two A atoms). Thus,

$$zN_A = P_{AB} + 2P_{AA}$$

or

$$P_{AA} = \frac{zN_A}{2} - \frac{P_{AB}}{2} \tag{9.67}$$

Similarly, for B, $zN_B = P_{AB} + 2P_{BB}$, or

$$P_{BB} = \frac{zN_B}{2} - \frac{P_{AB}}{2} \tag{9.68}$$

The substitution of Equations 9.67 and 9.68 into Equation 9.66 gives

$$\begin{aligned} E &= \left(\frac{zN_A}{2} - \frac{P_{AB}}{2} \right) E_{AA} + \left(\frac{zN_B}{2} - \frac{P_{AB}}{2} \right) E_{BB} + P_{AB}E_{AB} \\ &= \frac{1}{2} zN_A E_{AA} + \frac{1}{2} zN_B E_{BB} + P_{AB}\left[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})\right] \end{aligned} \tag{9.69}$$

Consider now the energies of the pure components before mixing. With N_A atoms in pure A,

$$2 \times \text{the number of } A-A \text{ bonds}$$

$$= \text{the number of atoms} \times \text{the number of bonds per atom}$$

That is,

$$P_{AA} = \frac{1}{2} z N_A$$

and similarly, for N_B atoms in pure B,

$$P_{BB} = \frac{1}{2} z N_B$$

Thus,

$$\begin{aligned} \Delta E^M &= (\text{the energy of the solution}) - (\text{the energy of the unimixed components}) \\ &= P_{AB}\left[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})\right] \end{aligned}$$

For the mixing process, from Equation 5.10b,

$$\Delta H^M = \Delta E^M - P\Delta V^M$$

and, since it has been stipulated that $\Delta V^M = 0$, then

$$\Delta H^M = \Delta E^M = P_{AB}\left[E_{AB} - \frac{1}{2}\left(E_{AA} + E_{BB}\right)\right] \tag{9.70}$$

Equation 9.70 shows that, for given values of E_{AA}, E_{BB}, and E_{AB}, ΔH^M depends on P_{AB}, and further that, for the solution to be ideal (i.e., for $\Delta H^M = 0$),

$$E_{AB} = \frac{\left(E_{AA} + E_{BB}\right)}{2} \tag{9.71}$$

Thus, contrary to the preliminary discussion in Section 9.2 which suggested that ideal mixing required the condition $E_{AB} = E_{AA} = E_{BB}$, it is seen that a sufficient condition is that E_{AB} be the average of E_{AA} and E_{BB}.

If $|E_{AB}| > |½(E_{AA} + E_{BB})|$, then, from Equation 9.70, ΔH^M is a negative quantity, corresponding to negative deviations from Raoultian ideal behavior, and, if $|E_{AB}| < |½(E_{AA} + E_{BB})|$, then ΔH^M is a positive quantity, corresponding to positive deviations from Raoultian ideality.

If $\Delta H^M = 0$, then the mixing of the N_A atoms with the N_B atoms of B is random, in which case Equation 9.45 gives

$$\Delta S^M = \Delta S^{M,\text{id}} = -R(X_A \ln X_A + X_B \ln X_B)$$

In solutions which exhibit relatively small deviations from ideal behavior (i.e., $|\Delta H^M| \leq RT$), it can be assumed that the mixing of the atoms is also approximately random, in which case P_{AB} can be calculated as follows. Consider two neighboring lattice sites in the crystal labeled 1 and 2. The probability that site 1 is occupied by an A atom is

$$\frac{\text{the number of } A \text{ atoms in the crystal}}{\text{the number of lattice sites in the crystal}} = \frac{N_A}{N_\text{O}} = X_A$$

and similarly, the probability that site 2 is occupied by a B atom is X_B. The probability that site 1 is occupied by an A atom and site 2 is simultaneously occupied by a B atom is thus $X_A X_B$. But the probability that site 1 is occupied by a B atom and site 2 is simultaneously occupied by an A atom is also $X_A X_B$. Thus, the probability that a neighboring pair of sites contains an A–B pair is $2X_A X_B$. By a similar argument, the probability that the neighboring sites contain an A–A pair is X_A^2 and that the neighboring sites contain a B–B pair is X_B^2. The probability that the neighboring sites contain an A–B pair or an A–A pair or a B–B pair is

$$\begin{aligned} &X_A^2 + 2X_A X_B + X_B^2 \\ &= (X_A + X_B)^2 \\ &= 1 \end{aligned}$$

Since a mole of crystal contains ½ zN_O pairs of lattice sites, then

$$\text{the number of } A - B \text{ pairs}$$

$$= \text{the number of pairs of sites} \times \text{the probability of an } A - B \text{ pair}$$

That is,

$$P_{AB} = \text{y}zN_\text{O} \times 2X_A X_B = zN_\text{O} X_A X_B \tag{9.72}$$

Similarly,

$$P_{AA} = \frac{1}{2} zN_\text{O} \times X_A^2 = \frac{1}{2} zN_\text{O} X_A^2$$

and

$$P_{BB} = \frac{1}{2} zN_\text{O} X_B^2$$

Substituting Equation 9.72 into 9.70 gives

$$\Delta H^M = zN_O X_A X_B \left[E_{AB} - \frac{1}{2}\left(E_{AA} + E_{BB}\right) \right]$$

and if we set W_1 as

$$W_1 = \left[E_{AB} - \frac{1}{2}\left(E_{AA} + E_{BB}\right) \right]$$

then

$$\Delta \mathrm{H}^M = zN_0 W_1 X_A X_B \tag{9.73}$$

which shows that ΔH^M is a parabolic function of composition. Since random mixing is assumed, the statistical model corresponds to the regular solution model; that is,

$$\Delta \mathrm{H}^M = G^{XS} = zN_0 W_1 X_A X_B \tag{9.74}$$

Thus, $zN_O\ W_1 = \alpha$ in Equation 9.54.

> The applicability of the statistical model to real solutions decreases as the magnitude of W_1 increases; that is, if the magnitude of E_{AB} is significantly greater or less than the average of E_{AA} and E_{BB}, then random mixing of the A and B atoms cannot be assumed. The equilibrium configuration of a solution at constant T and P is that which minimizes the Gibbs free energy, G, where $G = H - TS$ is measured relative to the unmixed components. As has been seen, the minimization of G occurs as a compromise between the minimization of H and the maximization of S. If $|\mathrm{E}_{\mathrm{AB}}| > |½(E_{AA} + E_{BB})|$, then the minimization of H corresponds to the maximization of the number of A–B pairs (complete ordering of the solution). On the other hand, the maximization of S corresponds to completely random mixing. The minimization of G thus occurs as a compromise between the maximization of P_{AB} (the tendency toward which increases with increasingly negative values of W_1) and random mixing (the tendency toward which increases with increasing temperature). The critical parameters are thus W_1 and T, and, if W_1 is appreciably negative and the temperature is not too high, then the value of P_{AB} will be greater than that for random mixing, in which case the assumption of random mixing is not valid.
>
> Similarly, if $|\mathrm{E}_{\mathrm{AB}}| < |\ ½\ (E_{AA} + E_{BB})|$, then the minimization of H corresponds to the minimization of the number of A–B pairs (complete clustering in the solution), and the minimization of G occurs as a compromise between the minimization of P_{AB} (the tendency toward which increases with increasingly positive values of W_1) and random mixing. Thus, if W_1 is appreciably positive and the temperature is not too high, then the value of P_{AB} will be less than that for random mixing, in which case the assumption of random mixing is again invalid.
>
> In order for the statistical model—and hence, the regular solution model—to be applicable, it is necessary that the aforementioned compromise be such that the equilibrium solution configuration be not too distant from random mixing. Since the entropy contribution to the Gibbs free energy is dependent on temperature, then

1. For any value of W_1, more nearly random mixing occurs as the temperature is increased.
2. For any given temperature, more nearly random mixing occurs with smaller values of W_1.

9.10.1 Extensions of the Regular Solution Model: The Atomic Order Parameter

As mentioned previously, a major flaw in the regular solution model is that, in counting neighbors to obtain the enthalpy of mixing as well as the entropy of mixing, it is assumed that the atoms are randomly placed on the lattice. But if the expression

$$E_{AB} - \frac{1}{2}\left(E_{AA} + E_{BB}\right)$$

is not zero, the atoms will not be random! For atomic ordering transformations, this can be improved by including a thermodynamic variable which accounts for the nonrandom configuration of the atoms. This factor is the *long-range order parameter* (LRO), η.

Consider the ordering transformation of a random A–B solution phase (fully disordered) with a BCC (A2) structure to the fully ordered phase with the CsCl (B2) structure (Figure 9.18).

The LRO parameter η is defined to be

$$\eta = \frac{r_\alpha - X_A}{Y_\beta} = \frac{r_\beta - X_B}{Y_\alpha}$$

where r_α (r_β) is the fraction of α (β) sites that are “rightly” occupied, X_i is the fraction of the ith component, and Y_α (Y_β) is the fraction of α (β) sites in the lattice. For the BCC → B2 transformation, Y_α and Y_β are ½. Thus, for an equiatomic alloy ($X_A = X_B = ½$), we have

$$\eta = 2r_\alpha - 1 = 2r_\beta - 1$$

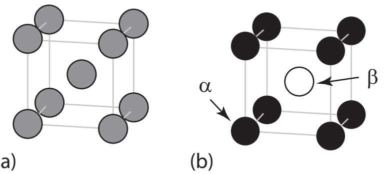

Figure 9.18 (a) BCC (A2) and (b) CsCl (B2) structures. The white and black atoms are randomly arranged in the BCC structure, but in the CsCl structure, the black atoms (A atoms) sit on the α sites and the white atoms (B atoms) are on the β sites.

If all the α sites are occupied by A atoms, $r_\alpha = 1$ and $\eta = 1$.
If all the α sites are occupied by B atoms, $r_\alpha = 1$ and $\eta = -1$.
If the α sites are randomly occupied, $r_\alpha = ½$ and $\eta = 0$.

(The case for $\eta = -1$ corresponds to a translational domain of the B2-ordered system.)

The expression for the enthalpy of formation of a system from the pure A and pure B components was given previously as

$$\Delta H^M = zN_O X_A X_B W_1$$

where $W_1 = E_{AB} - ½(E_{AA} + E_{BB})$. For $W_1 < 0$, atomic ordering is favored. For $W_1 = 0$, the alloy is random, and for $W_1 > 0$, clustering is favored.

If we include the effect of atomic ordering on the occupation of the sites, we obtain

$$\Delta H^M = zN_O W_1\left(X_A X_B + \frac{\eta^2}{4}\right)$$

For a full order of an equiatomic alloy, this yields $\Delta H^M = zN_O W_1/2$. This can be seen to be twice as negative as the expression which does not include the order parameter.

The effect of ordering also can be included in the entropy of mixing as follows:

$$\Delta S^M(\eta) = -\frac{Nk_B}{2}\left\{\left(X_A + \frac{\eta}{2}\right)\ln\left(X_A + \frac{\eta}{2}\right) + \left(X_B - \frac{\eta}{2}\right)\ln\left(X_B - \frac{\eta}{2}\right) + \left(X_A - \frac{\eta}{2}\right)\ln\left(X_A - \frac{\eta}{2}\right) + \left(X_B + \frac{\eta}{2}\right)\ln\left(X_B + \frac{\eta}{2}\right)\right\}$$

For full order of an equiatomic alloy this yields $\Delta S_{\text{conf}} = 0$, since the pure elements have zero configurational entropy and the fully ordered B2 phase has zero configurational entropy.

Combining the expressions for enthalpy of mixing and the entropy of mixing we obtain:

$$\Delta G^M(\eta, T) = zN_O W_1\left(X_A X_B + \frac{\eta^2}{4}\right) + \frac{Nk_B T}{2}\left\{\left(X_A + \frac{\eta}{2}\right)\ln\left(X_A + \frac{\eta}{2}\right) + \left(X_B - \frac{\eta}{2}\right)\ln\left(X_B - \frac{\eta}{2}\right) + \left(X_A - \frac{\eta}{2}\right)\ln\left(X_A - \frac{\eta}{2}\right) + \left(X_B + \frac{\eta}{2}\right)\ln\left(X_B + \frac{\eta}{2}\right)\right\}$$

Since ΔG^M is a function of the order parameter, we take its derivative with respect to it and set it equal to zero:

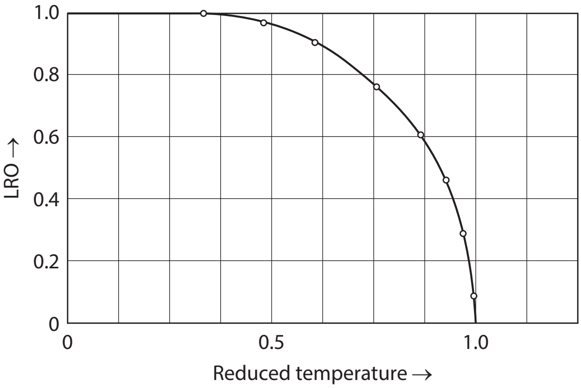

Figure 9.19 The atomic LRO parameter η vs. temperature plot for a Bragg–Williams model. Note the infinite slope as T approaches T_C and the zero slope as T approaches 0 K.

$$\frac{\partial \Delta G^M}{\partial \eta} = \frac{zN_0W_1\eta}{2} + \frac{N_0k_BT}{2}\ln\left(\frac{1+\eta}{1-\eta}\right) = 0$$

As η approaches zero, the temperature approaches the transition temperature. For small η,

$$\ln\left(\frac{1+\eta}{1-\eta}\right) = 2[\eta + \frac{\eta^3}{3} + ...] \approx 2\eta$$

Thus,

$$\frac{zN_0W_1\eta}{2} + \frac{2N_0k_BT\eta}{2} = 0$$

which yields

$$T_C = -\frac{4W_1}{k_B}$$

A plot of η versus T is shown in Figure 9.19. Thus, this model produces an atomic ordering phase transition at T_C. Above this temperature, the equilibrium phase is disordered BCC. Below this temperature, the equilibrium phase is ordered CsCl with an LRO parameter η that increases continuously with decreasing temperature and which approaches unity as T approaches 0 K.

The Gibbs free energy of mixing, ΔG^M, versus the order parameter, η is plotted in Figure 9.20 for several temperatures. At temperatures above T_C, the minimum in ΔG^M occurs at $\eta = 0$; that is, the disordered phase is the stable one. Below T_C, two minima appear at $\pm\ \eta_{eq}$. A maximum appears at $\eta = 0$, showing that the disordered phase is unstable below T_C. As the temperature is lowered, η_{eq} increases

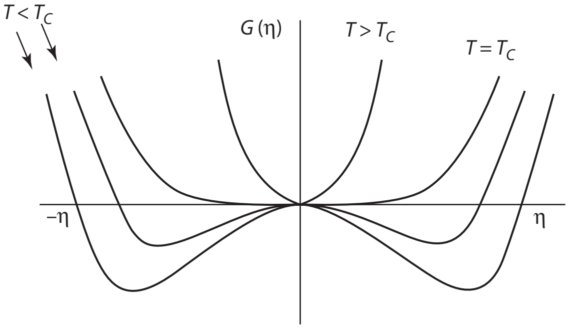

Figure 9.20 Gibbs free energy of mixing, ΔG^M, vs. order parameter at various temperatures relative to the critical temperature.

until, at $T = 0$ K, $\eta_{eq} = 1$. Plots such as this will be discussed in Chapter 15 under the discussion of the Landau theory of transitions. For now, we notice that ΔG^M versus η can be written in a Taylor series form as follows:

$$\Delta G^M = a + b\eta^2 + c\eta^4$$

Where a is a constant of integration, b is a function of T, and c can be considered a positive constant (see Problem 9.13).

9.10.2 Including Second-Neighbor Interactions

Another extension of this solution model can be made by adding second-neighbor interactions. Previously, we defined first-neighbor interactions as

$$W_1 = E_{AB}^{(1)} - \frac{1}{2}(E_{AA}^{(1)} + E_{BB}^{(1)})$$

Second-neighbor interaction energies can be written as

$$W_2 = E_{AB}^{(2)} - \frac{1}{2}(E_{AA}^{(2)} + E_{BB}^{(2)})$$

This expression can be added to the one for the heat of transformation used previously to obtain

$$\Delta H^M = N_O X_A X_B [z_1 W_1 + z_2 W_2] + \frac{N_O \eta^2}{2}[z_1 W_1 - z_2 W_2]$$

It can be seen from Figure 9.18 that for the B2-ordered structure, although $W_1 < 0$ (favoring opposite first neighbors), $W_2 > 0$ (favoring the same second neighbors). The details and further work on these expressions can be found in Soffa and Laughlin and Soffa, Laughlin, and Singh,* where the authors analyze the transformations FCC → $L1_2$ and FCC → $L1_0$.

9.11 SUBREGULAR SOLUTIONS

In the regular solution model, the constant value of α, which, via Equation 9.73, gives a parabolic variation of ΔH^M, and the ideal entropy of mixing lead to variations of G^{XS} and ΔG^M which are symmetrical about the composition $X_A = 0.5$. The model can be made more flexible by arbitrarily allowing α to vary with composition such as

$$\alpha = a + bX_B + cX_B^2 + dX_B^3 + \cdots \tag{9.75}$$

The so-called subregular solution model is one in which the values of all of the constants in Equation 9.75, other than a and b, are zero. Thus, the subregular solution model gives the molar excess Gibbs free energy of formation of a binary A–B solution as

$$G^{XS} = (a + bX_B)X_A X_B \tag{9.76}$$

Equation 9.76 is an empirical equation; that is, the constants a and b have no physical significance and are simply parameters, the values of which can be adjusted in an attempt to fit the equation to experimentally measured data. The application of Equations 9.27a and 9.27b to Equation 9.76 gives the partial molar excess Gibbs free energies of the components A and B as

$$\overline{G}_A^{XS} = aX_B^2 + bX_B^2(X_B - X_A) \tag{9.77}$$

and

$$\overline{G}_B^{XS} = aX_A^2 + 2bX_A^2 X_B \tag{9.78}$$

The maxima and/or minima in the curves occur at

$$\frac{dG^{XS}}{dX_B} = 0$$

which, from Equation 9.76, written as

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* W. Soffa, D. E. Laughlin, and N. Singh, "Interplay of Ordering and Spinodal Decomposition in the Formation of Ordered Precipitates in Binary Fee Alloys: Role of Second Nearest-Neighbor Interactions," *Philos. Mag.* (2010), vol. 90(1–4), pp. 287–304.
W. A. Soffa, D. E. Laughlin, N. Singh, "Re-examination of A1 → L10 Ordering: Generalized Bragg–Williams Model with Elastic Relaxation," in *Solid–Solid Phase Transformations in Inorganic Materials*, Trans Tech, Enfield, NH, 2011.

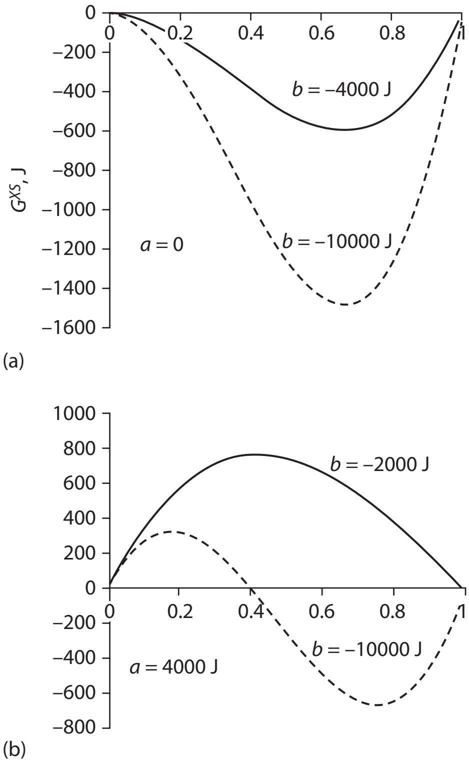

Figure 9.21 Excess molar Gibbs free energy curves generated by the subregular solution model for various values of *a* and *b*.

$$G^{\mathrm{XS}} = aX_B + (b-a)X_B^2 - bX_B^3$$

gives

$$\frac{dG^{\mathrm{XS}}}{dX_B} = a + 2(b-a)X_B - 3bX_B^2 = 0$$

or

$$X_B = \frac{2(b-a) \pm 2\sqrt{b^2 + ab + a^2}}{6b}$$

Thus, as shown in Figure 9.21a, with $a = 0$ and $b \neq 0$, the minimum in the curve occurs at $X_B = ⅔$, if $b \neq 0$. In Figure 9.21b, with $a = 4000$ J and $b = -10{,}000$ J, a maximum occurs in the curve at $X_B = 0.17$ and a minimum occurs at $X_B = 0.76$. If, however, $b = -2{,}000$ J, no minimum occurs, only a maximum.

The influence of temperature on the behavior of subregular solutions is accommodated by introducing a third constant, τ, to give the molar excess Gibbs free energy of mixing as

$$G^{\mathrm{XS}} = (a_0 + b_0 X_B) X_A X_B \left(1 - \frac{T}{\tau}\right) \tag{9.79}$$

The molar excess entropy of mixing is thus

$$\begin{aligned} S^{\mathrm{XS}} &= -\frac{\partial G^{\mathrm{XS}}}{\partial T} \\ &= \frac{(a_0 + b_0) X_A X_B}{\tau} \end{aligned} \tag{9.80}$$

and the molar enthalpy of mixing (which is also the molar excess enthalpy of mixing) is given by

$$\begin{aligned} \Delta H^M &= G^{\mathrm{XS}} + T S^{\mathrm{XS}} \\ &= (a_0 + b_0 X_B) X_A X_B \left(2 - \frac{T}{\tau}\right) \end{aligned} \tag{9.81}$$

9.12 MODIFIED REGULAR SOLUTION MODEL FOR APPLICATION TO POLYMERS

9.12.1 The Flory–Huggins Model*

In 1942, Flory and Huggins independently modified the regular solution model to account for some of the differences that polymers present to the modeling of the thermodynamics of the mixing of polymers.

The main difference lies in the entropy of mixing term, which in modern notation is written as

$$\Delta S^{\mathrm{mix}} = -R\left(\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B\right)$$

where ϕ_i is the volume fraction of the ith monomers which make up the polymer and N_i is the average number of *monomers* in the length of the molecule (the degree of polymerization). For polymers, the entity which is randomly located in the solution is not a single atom or molecule but rather a long chain consisting of the many *-mers*

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* M. L. Huggins, "Solutions of Long Chain Compounds," *J. Chem. Phys.* (1942), vol. 9(5), p. 440; P. J. Flory, "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.* (1942), vol. 9(8), p. 660.

of the polymer. This lowers the number of ways that the polymer can be arranged in a given volume, and it is accounted for by the N_i terms in the expression for the entropy of mixing. This greatly lowers the role of entropic mixing in large polymers.

The enthalpy of mixing term was written as

$$\Delta H^{\text{mix}} = \phi_A \phi_A \chi$$

where χ accounts for the increase (decrease) in the enthalpy of the solution due to interactions between the polymers.

This term, combined with the entropy of mixing term, gave rise to the Gibbs free energy of mixing term:*

$$\Delta G^{\text{mix}} = RT\left(\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \phi_A\phi_A\chi\right)$$

It can be seen for polymers of long length (N_i large), the entropy of mixing term is not as large as that for solutions of single atoms or small molecules. Since most polymers have positive enthalpies of mixing, this accounts for the limited miscibility of many polymers.

The expression shows that if one of the polymers is not very long, it can act as the solvent and the long-chained polymer as the solute (a polymer blend). This enables much more miscibility for the polymer solutions, as the entropy term becomes more significant to the polymer thermodynamics.

9.13 SUMMARY

1. Raoult's law is $p_i = X_i p_i^\circ$, and a component of a solution that conforms with this law is said to exhibit Raoultian behavior. In all solutions, the behavior of the component i approaches Raoult's law as $X_i \to 1$.
2. Henry's law is $p_i = k'X_i$, and a component of a solution which conforms with this equation is said to exhibit Henrian behavior. In all solutions, the behavior of the component i approaches Henry's law as $X_i \to 0$. In a binary solution, Henry's law is obeyed by the solute in that composition range over which Raoult's law is obeyed by the solvent.
3. The activity of the component i in a solution, with respect to a given standard state, is the ratio of the vapor pressure (strictly, the fugacity) of i exerted by the solution to the vapor pressure (the fugacity) of i in the given standard state. If the standard state is chosen as being pure i, then $a_i = p_i/p_i^\circ$. An activity is thus a ratio, and its introduction effects a normalization of the vapor pressure exerted by the component i in the solution. In terms of activity, Raoult's law is $a_i = X_i$, and Henry's law is $a_i = k^B X_i$.
4. The difference between the value of an extensive thermodynamic property per mole of i in a solution and the value of the property per mole of i in its standard

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* The regular solution "constant" in the Flory–Huggins model is thus $RT\chi$.

state is called the partial molar property change of i for the solution process; that is, if Q is any extensive thermodynamic property, the change in the property due to the solution of 1 mole of i is $\Delta\overline{Q}_i^M = \overline{Q}_i - Q_i^\circ$. In the case of the Gibbs free energy, $\Delta\overline{G}_i^M = \overline{G}_i - G_i^\circ$. This difference in the molar Gibbs free energy is related to the activity of i in solution, with respect to the standard state, as $\Delta\overline{G}_i^M = RT \ln a_i$, and $\Delta\overline{G}_i^M$ is called the partial molar Gibbs free energy of solution of i.

The change in the Gibbs free energy accompanying the formation of 1 mole of solution from the pure components i (called the integral Gibbs free energy change) is $\Delta G^M = \sum_i X_i \Delta\overline{G}_i^M$, so that, for the binary A–B, $\Delta G^M = X_A \Delta\overline{G}_A^M + X_B \Delta\overline{G}_B^M$. Since $\Delta\overline{G}_A^M = RT \ln a_A$, then

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$$

In a Raoultian solution, since $a_i = X_i$, then

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B)$$

For any general extensive thermodynamic property,

$$Q, \ \ \Delta Q^M = \sum\nolimits_i X_i \Delta\overline{Q}_i^M$$

5. An ideal solution has the following properties:
   - $a_i = X_i$
   - $\overline{V}_i = V_i^\circ$ (i.e., there is no change in volume when the components are mixed)
   - $\overline{H}_i^M = H_i^\circ$ (i.e., there is zero heat of mixing)
   - $\Delta G^{M,\text{id}} = RT(X_A + X_B \ln X_B)$

   Since $\Delta S^{M,\text{id}} = -(\partial \Delta G^{M,\text{Bid}}/\partial T)$, $\partial S^{M,\text{id}} = -R \ln \sum_i X_i$, in an ideal solution, $\Delta\overline{S}_i^M = -R \ln X_i$. $\Delta S^{M,\text{id}}$ is thus independent of temperature and is simply an expression for the maximum number of spatial configurations available to the system.
6. The thermodynamic behavior of non-Raoultian solutions is dealt with by introducing the activity coefficient, γ, which for the component i is defined as $\gamma_i = a_i / X_i$. The coefficient γ_i, which can have values of greater or less than unity, thus quantifies the deviation of i from Raoultian behavior. Since $\ln a_i = \ln X_i + \ln \gamma_i$,

   $$\frac{d \ln a_i}{d\left(\frac{1}{T}\right)} = \frac{\Delta\overline{H}_i^M}{R} = \frac{d \ln \gamma_i}{d\left(\frac{1}{T}\right)}$$

   Thus, if $d\gamma_i / dT$ is positive, $\Delta\overline{H}_i^M$ is negative, and if $d\gamma_i / dT$ is negative, $\Delta\overline{H}_i^M$ is positive. The magnitude of the heat of formation of a nonideal solution is determined by the magnitudes of the deviations of the components of the solution from ideal behavior. Nonideal components approach Raoultian behavior with increasing temperature. Thus, if $\gamma_i < 1$, then $d\gamma_i / dT$ is positive, and if $\gamma_i > 1$, $d\gamma_i / dT$ is negative. Solutions, the components of which exhibit negative deviations from Raoult's law, form exothermically; that is, $\Delta H^M < 0$, and those that exhibit positive deviations form endothermically.

7. The Gibbs–Duhem relationship is $\sum_i X_i d\overline{Q}_i = 0$ at constant temperature and pressure, where $\overline{Q}_i$ is the partial molar value of the extensive thermodynamic function Q of the solution component i. The excess value of an extensive thermodynamic property of a solution is the difference between the actual value and the value that the property would have if the components obeyed Raoult's law. Thus, for the general function Q, $Q^{XS} = Q - Q^{id}$, or for the Gibbs free energy, $G^{XS} = G - G^{id}$, or $G^{XS} = \Delta G^M - \Delta G^{M,id}$. Since $\gamma_i = a_i/X_i$, then

$$G^{XS} = RT \sum X_i \ln \gamma_i$$

8. A regular solution is one which has an ideal entropy of formation and a nonzero heat of formation from its pure components. The activity coefficients of the components of a regular binary solution are given by the expression

$$RT\ln\gamma_i = \alpha\left(1 - X_i\right)^2$$

where α is a temperature-independent constant, the value of which is characteristic of the particular solution. Thus, $\ln \gamma_i$ varies inversely with temperature, and, since $\overline{G}_i^{XS} = RT \ln \gamma_i$, then $\overline{G}_i^{XS} = \Delta \overline{H}_i^M$ is independent of temperature. Furthermore, the heat of formation of a regular solution, being equal to G^{XS}, is a parabolic function of composition, given by

$$\Delta H^M = G^{XS} = \alpha X_A X_B$$

9. Regular solution behavior is predicted by a statistical solution model in which it is assumed that the atoms mix randomly and that the energy of the solution is the sum of the individual interatomic bond energies in the solution. Random mixing can be assumed only if, in the system A–B, the A–B bond energy is not significantly different from the average of the A–A and B–B bond energies in the pure components. For any such deviation, the validity of the assumption of random mixing increases with increasing temperature. The statistical model predicts tendency toward Raoultian behavior and Henrian behavior as, respectively, $X_i \rightarrow 1$ and $X_i \rightarrow 0$.
10. The statistical solution model can be improved by adding the effect of second-nearest neighbors. In the case of solutions with ordering tendency (negative deviations from Raoultian behavior), the model for both the molar enthalpy and molar entropy of formation can be improved by adding an LRO parameter to the molar enthalpy and molar entropy terms.
11. The subregular solution model is one in which the value of α is assumed to be a linear function of composition, being given by $\alpha = a + bX_B$. The variation of the molar excess Gibbs free energy of mixing is thus given by $G^{XS} = (a + bX_B)X_A X_B$. This can give rise to asymmetric dependence of the molar properties of formation. The constants a and b are curve-fitting parameters and have no physical significance.

9.14 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 9

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Activation energy
Activity
Bond energy
Condensation/sublimation
Condensed phases
Deviations from ideality
Dynamic equilibrium
Endothermic
Evaporation
Exothermic
Flory–Huggins model
Gibbs free energy of mixing (solution)
Henry's law
Interactions among particles
Order parameter
Raoult's law
Regular solution
Subregular solution

9.15 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

The activities of liquid iron nickel solutions at 1600°C as a function of composition are shown in Figure 9.8. Sketch the activity coefficients as a function of composition at this temperature.

Solution to Qualitative Problem 1

Figure 9.22 shows the actual plot of the activity coefficients γ_{Fe} and γ_{Ni} as a function of composition. Your plot should show the following:

1. γ_{Fe} starts at $\gamma_{Fe} = 1$ and drops off after Henrys' law no longer holds ($\sim X_{Fe} = 0.7$).
2. γ_{Ni} starts at less than one and begins to rise and approach one after $\sim X_{Ni} = 0.3$).
3. $\gamma_{Fe} = 1$ at pure Fe and γ_{Ni} = one at pure Ni.

Qualitative Problem 2

The LRO parameter, η, versus temperature plot of an ordered phase is shown in Figure 9.19.

1. Explain why the LRO parameter goes to unity at $T = 0$ K.
2. The slope of the LRO versus T plot goes to 0 as T approaches 0. Show why this is true.

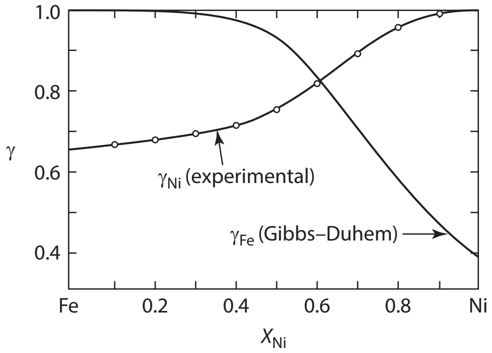

Figure 9.22 Activity coefficients in the liquid system iron–nickel at 1600°C (also see Figure 9.8).

Hint: Start by writing $G = G(\eta,T$ and take the full differential dG. By the time you finish, you will have to use a form of L'Hôpital's rule:

$$\lim \text{ of } \frac{f(x)}{g(x)} \text{ as x} \to 0 = \frac{f'(x)}{g'(x)}$$

Solution to Qualitative Problem 2

1. From the Third Law of Thermodynamics, we expect that the configurational entropy of a system in equilibrium goes to zero as the temperature goes to zero.
2. First we write $G = G(T, \eta)$,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{\eta} dT + \left(\frac{\partial G}{\partial \eta}\right)_{T} d\eta = 0$$

$$\frac{d\eta}{dT} = -\frac{\left(\frac{\partial G}{\partial T}\right)_{\eta}}{\left(\frac{\partial G}{\partial \eta}\right)_{T}} = \frac{S}{\left(\frac{\partial G}{\partial \eta}\right)_{T}}$$

Since both terms go to zero in the quotient (at equilibrium), we need to apply L'Hôpital's rule:

$$\lim \text{ of } \left(\frac{d\eta}{dT}\right) \text{ as T} \to 0 = \frac{\left(\frac{\partial S}{\partial \eta}\right)}{\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{T}} = \frac{0}{+} = 0$$

9.16 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Copper and gold form the complete range of solid solution at temperatures between 410°C and 889°C, and, at 600°C, the excess molar Gibbs free energy of formation of the solid solutions is given by

$$G^{XS} = -28{,}280 X_{Au} X_{Cu} \text{ J}$$

Calculate the partial pressures of Au and Cu exerted by the solid solution of $X_{Cu} = 0.6$ at 600°C.

The saturated vapor pressure of solid copper is given by

$$\ln p^{\circ}_{Cu}(\text{atm}) = -\frac{40{,}920}{T} - 0.86 \ln T + 21.67$$

and the saturated vapor pressure of solid gold is given by

$$\ln p^{\circ}_{Au}(\text{atm}) = -\frac{45{,}650}{T} - 0.306 \ln T + 10.81$$

Solution to Quantitative Problem 1

The solid solutions are regular with $\alpha = -28{,}280$ J. Therefore, from Equation 9.64,

$$\ln \gamma_{Cu} = \frac{\alpha}{RT} X_{Au}^2 = -\frac{28{,}280 \times 0.4^2}{8.3144 \times 873} = -0.624$$

Thus,

$$\gamma_{Cu} = 0.536 \text{ and } a_{Cu} = \gamma_{Cu} X_{Cu} = 0.536 \times 0.6 = 0.322$$

Similarly,

$$\ln \gamma_{Au} = \frac{28{,}280 \times 0.6^2}{8.3144 \times 873} = -1.403$$

Thus,

$$\gamma_{Au} = 0.246 \text{ and } a_{Au} = 0.246 \times 0.4 = 0.098$$

Therefore, at 873 K,

$$p^{\circ}_{Cu} = 3.35 \times 10^{-14} \text{atm}$$

and

$$p^{\circ}_{\text{Au}} = 1.52 \times 10^{-16}\,\text{atm}$$

From Equation 9.12, $a_i = p_i/p_i^0$, and thus, the partial pressures exerted by the alloy are

$$p_{\text{Cu}} = 0.322 \times 3.35 \times 10^{-14} = 1.08 \times 10^{-14}\,\text{atm}$$

and

$$p_{\text{Au}} = 0.098 \times 1.52 \times 10^{-16} = 1.50 \times 10^{-16}\,\text{atm}$$

Quantitative Problem 2

At 700 K, the activity of Ga in a liquid Ga–Cd solution of composition $X_{\text{Ga}} = 0.5$ has the value 0.79. On the assumption that liquid solutions of Ga and Cd exhibit regular solution behavior, estimate the energy of the Ga–Cd bond in the solution. The molar enthalpies of evaporation of liquid Ga and liquid Cd at their melting temperatures are, respectively, 270,000 and 100,000 J.

At their melting temperatures, the coordination numbers of liquid Cd and liquid Ga are, respectively, 8 and 11. It will thus be assumed that the coordination number in the 50:50 solution is the average of 8 and 11—namely, 9.5.

Solution to Quantitative Problem 2

With $a_{\text{Ga}} = 0.79$ at $X_{\text{Ga}} = 0.5$,

$$\gamma_{\text{Ga}} = \frac{a_{\text{Ga}}}{X_{\text{Ga}}} = \frac{0.79}{0.5} = 1.59$$

Therefore, from Equation 9.64,

$$\ln 1.59 = \frac{\alpha \times 0.5^2}{8.3144 \times 700}$$

which gives

$$\alpha = \frac{0.464 \times 8.3144 \times 700}{0.5^2} = 10{,}795\ \text{J}$$

The bond energy, $E_{\text{Ga-Ga}}$, is obtained from the molar enthalpy of evaporation, ΔH_{evap}, according to

$$\Delta H_{\text{evap,Ga-Ga}} = -\frac{1}{2} z N_{\text{O}} E_{\text{Ga-Ga}}$$

The negative sign is required to conform with the convention that bond energies are negative quantities. Thus,

$$E_{\text{Ga-Ga}} = -\frac{270{,}000 \times 2}{11 \times 6.023 \times 10^{23}} = -8.15 \times 10^{-20}\ \text{J}$$

and similarly,

$$E_{\text{Cd-Cd}} = -\frac{100{,}000 \times 2}{8 \times 6.023 \times 10^{23}} = -4.15 \times 10^{-20}\ \text{J}$$

The bond energy, $E_{\text{Cd-Ga}}$, is obtained from

$$\alpha = zN_O\left[E_{\text{Cd-Ga}} - \frac{1}{2}\left(E_{\text{Cd-Cd}} + E_{\text{Ga-Ga}}\right)\right]$$

That is,

$$10{,}795 = 9.5 \times 6.023 \times 10^{23}\left[E_{\text{Cd-Ga}} - \frac{1}{2}\left(-4.15 \times 10^{-20} - 8.15 \times 10^{-20}\right)\right]$$

Thus, $E_{\text{Cd-Ga}} = -5.96 \times 10^{-20}$ J.

PROBLEMS

For some of these problems, the tables in the Appendix may be needed.

9.1 One mole of solid Cr_2O_3 at 2500 K is dissolved in a large volume of a liquid Raoultian solution of Al_2O_3 and Cr_2O_3, in which $X_{Cr_2O_3} = 0.2$ and which is also at 2500 K. Calculate the changes in enthalpy and entropy caused by the addition. The normal melting temperature of Cr_2O_3 is 2538 K, and it can be assumed that $\Delta S_{m,Al_2O_3} = \Delta S_{m,Cr_2O_3}$.

9.2 When 1 mole of argon gas is bubbled through a large volume of an Fe–Mn melt of $X_{Mn} = 0.5$ at 1863 K, the evaporation of Mn into the Ar causes the mass of the melt to decrease by 1.5 g. The gas leaves the melt at a pressure of 1 atm. Calculate the activity coefficient of Mn in the liquid alloy.

9.3 The variation, with composition, of G^{XS} for liquid Fe–Mn alloys at 1863 K is as follows:

X_{Mn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
G_{XS} **J**	395	703	925	1054	1100	1054	925	703	395

a. Does the system exhibit regular solution behavior?
b. Calculate $\overline{G}^{XS}_{Fe}$ and $\overline{G}^{XS}_{Mn}$ at $X_{Mn} = 0.6$.
c. Calculate AG^M at $X_{Mn} = 0.4$.
d. Calculate the partial pressures of Mn and Fe exerted by the alloy of $X_{Mn} = 0.2$.

9.4 Calculate the heat required to form a liquid solution at 1356 K, starting with 1 mole of Cu and 1 mole of Ag at 298 K. At 1356 K, the molar heat of mixing of liquid Cu and liquid Ag is given by $\Delta H^M = -20{,}590 X_{\text{Cu}} X_{\text{Ag}}$.

9.5 Melts in the system Pb–Sn exhibit regular solution behavior. At 473°C, $a_{\text{Pb}} = 0.055$ in a liquid solution of $X_{\text{Pb}} = 0.1$. Calculate the value of α for the system and calculate the activity of Sn in the liquid solution of $X_{\text{Sn}} = 0.5$ at 500°C.

9.6* a. Calculate the values of $\Delta\overline{G}_B$ and a_B for an alloy of $X_B = 0.5$ at 1000 K, assuming the solution is ideal.

b. Calculate the values of $\Delta\overline{G}_B$ and a_B for an alloy of $X_B = 0.5$ at 1000 K that is a regular solution with $\Delta H_{\text{mixing}} = 16{,}628 * X_A * X_B$.

9.7* A regular solution exhibits a miscibility gap. Sketch the activity of X_B versus X_A at a temperature within the miscibility gap.

Denote regions where Henry's law is obeyed and where Raoult's law is obeyed, if applicable.

9.8 Tin obeys Henry's law in dilute liquid solutions of Sn and Cd, and the Henrian activity coefficient of Sn, γ°_{Sn}, varies with temperature as

$$\ln \gamma^\circ_{\text{Sn}} = -\frac{840}{T} + 1.58$$

Calculate the change in temperature when 1 mole of liquid Sn and 99 moles of liquid Cd are mixed in an adiabatic enclosure. The molar constant-pressure heat capacity of the alloy formed is 29.5 J/K.

9.9 Use the Gibbs–Duhem equation to show that, if the activity coefficients of the components of a binary solution can be expressed as

$$\ln \gamma_A = \alpha_1 X_B + \frac{1}{2}\alpha_2 X_B^2 + \frac{1}{3}\alpha_3 X_B^3 + \cdots$$

and

$$\ln \gamma_B = \beta_1 X_A + \frac{1}{2}\beta_2 X_A^2 + \frac{1}{3}\beta_3 X_A^3 + \cdots$$

over the entire range of composition, then $\alpha_1 = \beta_1 = 0$, and that, if the variation can be represented by the quadratic terms alone, then $\alpha_2 = \beta_2$.

9.10 The activity coefficient of Zn in liquid Zn–Cd alloys at 435°C can be represented as

$$\ln \gamma_{\text{Zn}} = 0.875 X_{\text{Cd}}^2 - 0.30 X_{\text{Cd}}^3$$

Derive the corresponding expression for the dependence of ln γ_{Cd} on composition and calculate the activity of cadmium in the alloy of $X_{\text{Cd}} = 0.5$ at 435°C.

9.11 The molar excess Gibbs free energy of formation of solid solutions in the system Au–Ni can be represented by

$$G^{\text{XS}} = X_{\text{Ni}} X_{\text{Au}}(24{,}140 X_{\text{Au}} + 38{,}280 X_{\text{Ni}} - 14{,}230 X_{\text{Au}} X_{\text{Ni}})\left(1 - \frac{T}{2660}\right)\text{J}$$

Calculate the activities of Au and Ni in the alloy of $X_{\text{Au}} = 0.5$ at 1100 K.

9.12* The activities of liquid iron–copper solutions at 1550°C as a function of composition are shown in Figure 9.9. Sketch the activity coefficients as a function of composition at this temperature.

9.13* Use the equation $\Delta G^{\mathrm{XS}} = b(T - T_C)\eta^2 + c\eta^4$ to derive the following equation:

$$\text{for } \eta = \eta(T): \ \eta_{\mathrm{eq}} = \left(1 - \frac{T}{T_C}\right)^{1/2}, \text{ where } b > 0$$

Hint: Use the Third Law of Thermodynamics to set $\eta = 1$ at $T = 0$.

9.14* It has been found that in a certain solution, the activity $a_A = X_A$ over a certain range of composition. Determine the relationship between a_B and X_B over the same range of composition.

9.15* All regular solutions with positive heats of mixing have the same value of the activity of its components (A or B) at the critical point of the miscibility gap.

a. Calculate this activity.

b. Plot temperature versus a_B for a regular solution miscibility gap.

9.16* At a certain temperature, T, the A–B system exhibits regular solution behavior. The activity coefficient of A is given by

$$\ln(\gamma_A) = -b(1 - X_A)^2$$

where b is a constant at the given T.

Compute the corresponding equation for the variation of γ_B with composition at the same temperature. Be sure to state the justification for the steps of your solution.

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* New problem in this edition

CHAPTER 10

Gibbs Free Energy Composition and Phase Diagrams of Binary Systems

10.1 INTRODUCTION

We have seen in Chapter 7 that when temperature and pressure are the independent variables of a one-component system, the phase(s) with the lowest Gibbs free energy is (are) the stable phase(s). Likewise, in a two-component (binary) system at constant temperature and pressure, the stable state of existence at each composition of a system is that which has the lowest possible value of Gibbs free energy. Thus, phase stability, in a system presented on an isobaric temperature versus composition binary phase diagram, can be determined from knowledge of the variations of the Gibbs free energies of the various possible phases with composition and temperature.

When a liquid solution is cooled, a liquidus temperature is eventually reached, at which point a solid phase begins to separate from the liquid solution. This solid phase could be a virtually pure component, a solid solution of the same or different composition from the liquid, or a chemical compound formed by reaction between two or more of the components. In each of these cases, the composition of the solid phase which is in equilibrium with the liquid solution is that which minimizes the Gibbs free energy of the system. If liquid solutions are stable over the entire range of composition, then the Gibbs free energies of the liquid states are lower than those of any possible solid-state phase. Conversely, if the temperature of the system is lower than the lowest solidus temperature, then the Gibbs free energies of the solid states are everywhere lower than those of liquid-state phases. At intermediate temperatures, the variation of Gibbs free energy with composition will consist of ranges of composition over which liquid states are stable, ranges over which solid states are stable, and intermediate ranges in which solid and liquid phases coexist in equilibrium with one another. Thus, there must exist a quantitative correspondence between Gibbs free energy–composition diagrams and the equilibrium phase diagrams by virtue of the following facts:

1. The state of lowest Gibbs free energy is the stable state.
2. When phases coexist in equilibrium, the partial molar Gibbs free energy of component i, $\bar{G}_i$, has the same value in all of the coexisting phases.

This correspondence is examined in this chapter, in which it will be seen that temperature–composition phase diagrams are generated by, and are representations of, Gibbs free energy–composition–temperature diagrams.

10.2 GIBBS FREE ENERGY AND THERMODYNAMIC ACTIVITY

The Gibbs free energy of mixing of the components A and B to form a mole of solution is given by

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$$

where ΔG^M is the difference between the Gibbs free energy of a mole of the homogeneous solution and the Gibbs free energy of the corresponding numbers of moles of the unmixed components. Since only changes in Gibbs free energy can be measured, the Gibbs free energies of the pure unmixed components are assigned the value of zero. If the solution is ideal (i.e., if $a_i = X_i$), then the molar ideal Gibbs free energy of mixing is given by

$$\Delta G^{M,\text{id}} = RT(X_A \ln X_A + X_B \ln X_B)$$

and has the characteristic shape shown, at the temperature T, as curve I in Figure 10.1. Since $\Delta H^{M,\text{id}} = 0$, then $\Delta G^{M,\text{id}} = -T\Delta S^{M,\text{id}}$. The curve I in Figure 10.1 is obtained by inverting the ideal entropy of mixing curve (Figure 9.7) and multiplying it by the temperature in question. It is thus seen that the shape of the variation of $\Delta G^{M,\text{id}}$ with composition depends only on the temperature of the solution.

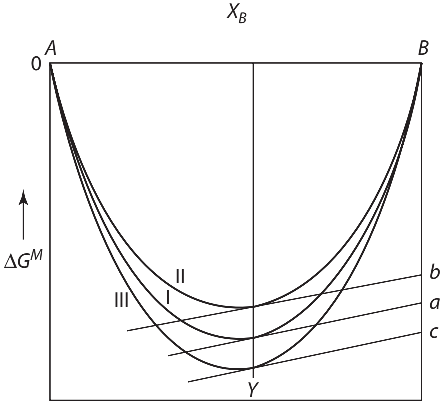

Figure 10.1 The molar Gibbs free energies of mixing in binary systems exhibiting ideal behavior (I), positive deviation from ideal behavior (II), and negative deviation from ideal behavior (III).

If the solution exhibits a small positive deviation from ideal mixing (i.e., if $\gamma_i > 1$ and $a_i > X_i$), then, at the temperature T, the Gibbs free energy of mixing curve is typically as shown by curve II in Figure 10.1. If the solution shows a slight negative deviation from ideal mixing (i.e., if $\gamma_i < 1$ and $a_i < X_i$), the Gibbs free energy of mixing curve is typically as shown by curve III in Figure 10.1. We know from the discussion of Equation 9.33a and b that the tangent drawn to the ΔG^M curve at any composition intersects the $X_A = 1$ and $X_B = 1$ axes at $\Delta \bar{G}_A^M$ and $\Delta \bar{G}_B^M$, respectively. Also, since $\Delta \bar{G}_i^M = RT \ln a_i$, there is a relationship between the ΔG^M–composition and the activity–composition plots.

In Figure 10.1, at the composition Y, tangents drawn to curves I, II, and III intersect the $X_B = 1$ axis at a, b, and c, respectively. Thus,

$$\left|Bb = \Delta \bar{G}_B^M = RT \ln a_B (\text{in system II})\right| < \left|Ba = \Delta \bar{G}_B^M = RT \ln X_B\right|$$
$$< \left|Bc = \Delta \bar{G}_B^M = RT \ln a_B (\text{in system III})\right|$$

from which it is seen that

$$\gamma_B \text{ in system II} > 1 > \gamma_B \text{ in system III}$$

The variation, with composition, of the tangential intercepts generates the variations of activity with composition shown in Figure 10.2. It can be seen from Figure 10.2 that the solutions II and III follow Henry's law for $X_B \to 0$ and Raoult's law for $X_B \to 1$.

As $X_i \to 0$, $a_i \to 0$, the tangential intercept $\Delta \bar{G}_i^M = RT \ln a_i \to -\infty$ (see Figure 10.1), which indicates that all Gibbs free energy of mixing curves have vertical tangents at their extremities. These vertical tangents indicate that the first atom of B

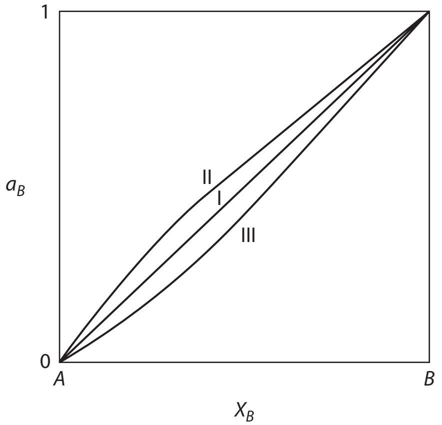

Figure 10.2 The activities of component B obtained from lines I, II, and III in Figure 10.1. Solution II exhibits positive deviation from ideality, and solution III exhibits negative deviation from ideality.

added to pure *A* decreases the Gibbs free energy! This also can be seen from the ideal entropy of mixing curve in Figure 9.7, which by virtue of being logarithmic, has vertical tangents at its extremities. This thermodynamic principle thus implies that pure elemental components are highly unlikely.

10.3 QUALITATIVE OVERVIEW OF COMMON BINARY EQUILIBRIUM PHASE DIAGRAMS

In this section, we will examine the qualitative features of common binary equilibrium phase diagrams. We will examine the phase diagrams and discuss some of their important features. We also will look at several of the isobaric molar Gibbs free energy versus composition curves that are thermodynamically consistent with the phase diagrams. A more quantitative approach will be given in subsequent sections of this chapter.

10.3.1 The Lens Diagram: Regular Solution Model

Figure 10.3 shows a simple way that a liquid and solid in a binary isobaric system can be in equilibrium. The end points of the diagram represent the melting points of A, $T_{m(A)}$ and of B, $T_{m(B)}$. At temperatures in between the melting temperatures, there are three equilibrium states across the composition range:

1. A liquid solution of B in A, $A(B)$
2. A two-phase mixture of liquid $A(B)$ and solid $B(A)$
3. A solid solution of A in B, $B(A)$

The lever rule determines the amount of the phases in the two-phase region. See Section 1.7.

If we model the Gibbs free energies of the solid and liquid as regular solutions, and if the enthalpies of mixing are approximately the same, the Gibbs free energy terms take the form shown in Figure 10.3b. It can be seen that for compositions $B < e$, the liquid phase has the lowest Gibbs energy. For compositions of $B > f$, the solid phase has the lowest Gibbs energy. In between these values, the lowest Gibbs energy is obtained by a two-phase equilibrium between a liquid of composition e and a solid of composition f. The common tangent demonstrates that the partial molar Gibbs free energies of the two phases of each of the components are equal in the two-phase region; that is,

$$\Delta\overline{G}_A^{\mathrm{L}} = \Delta\overline{G}_A^{\mathrm{S}}$$

$$\Delta\overline{G}_B^{\mathrm{L}} = \Delta\overline{G}_B^{\mathrm{S}}$$

where S stands for solid solution and L stands for liquid solution. These values are found where the common tangent intersects the molar Gibbs free energy of mixing ordinates $X_B = 0$ and $X_B = 1$, respectively.

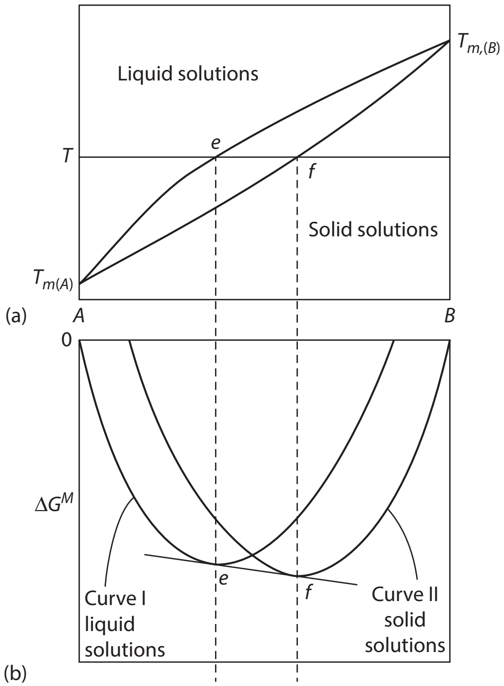

Figure 10.3 (a) The equilibrium phase diagram for a system *A*–*B* exhibiting a lens diagram for the liquid–solid region. (b) The Gibbs free energies of mixing in the system *A*–*B* at the temperature *T*, showing the equilibrium compositions of the phases.

With a change in the temperature, the Gibbs energy curves shift relative to one another, since their temperature derivatives are proportional to the entropy of the phases. As the temperature decreases, the intersections e and f shift to lower values of X_B until, at $T_{m(A)}$, the Gibbs energy curve of the solid is completely below the liquid free energy curve. From that temperature and lower, only a single solid-solution phase is present.

10.3.2 Unequal Enthalpies of Mixing

If we model the Gibbs free energies of the solid and liquid as regular solutions, and if the enthalpy of mixing of the liquid is negative and the enthalpy of mixing of the solid is positive, the Gibbs energy curves of the phases will look as shown in Figure 10.4b and the phase diagram as shown in Figure 10.4a. The lower value of the enthalpy of mixing stabilizes the liquid solution and results in an enlarged region of stability for it. At a temperature above the congruent temperature (where the liquidus and solidus curves are tangent to each other), there are two solid–liquid equilibrium-phase fields and a single liquid-phase field in between. If the opposite relationship between the enthalpies of mixing were to hold (negative enthalpy of mixing of the solid and zero or positive enthalpy of mixing for the liquid), the enlarged single

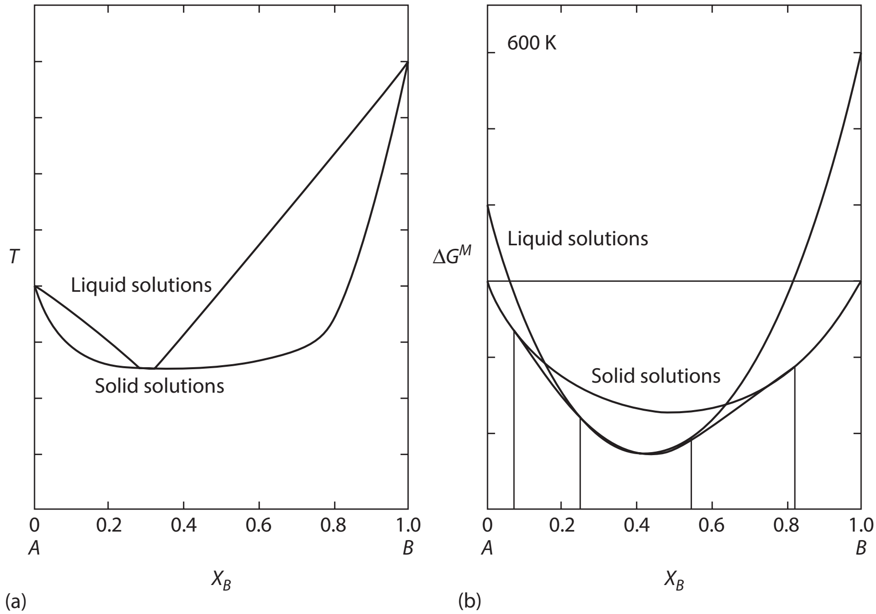

Figure 10.4 (a) The equilibrium phase diagram of a binary system with negative enthalpy of mixing of the liquid solution and positive enthalpy of mixing of the solid solution. (b) Schematic representations of the Gibbs free energy of mixing for the solutions at the temperature *T*.

solid-phase field would produce a congruent point at a maximum, enlarging the field of stability of the solid solution.

Congruent points are interesting from the point of view of the liquid-to-solid transformation in that the composition of the new phase (solid on cooling, liquid on heating) is the same as that phase from which it forms. The slopes of the solidus and liquidus curves must be zero at the congruent points and must be tangential to one another, according to the Gibbs–Konovalov rule* (Dmitry Petrovich Konovalov, 1856–1929).

10.3.3 The Low-Temperature Regions in Phase Diagrams

In Figures 10.3 and 10.4, once the temperature is below the regions of liquid stability, a single solid solution is seen to be present. This solid solution may exist down to room temperature and even to lower temperatures, but cannot continue as a single-phase solid solution region to very low temperatures because of atomic interactions (see Section 6.5 on the Third Law of Thermodynamics). Since the enthalpy of mixing of the solid was said to be positive for the system shown in Figure 10.4, the solution will exhibit a low-temperature miscibility gap, as shown in Figure 10.5. This

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* D. Goodman, J. Cahn, and L. Bennett, “The Centennial of the Gibbs Konovalov Rule for Congruent Points,” *Bulletin of Alloy Phase Diagrams* (1981), vol. 2(1), pp. 29–34.

is consistent with the Third Law, in that at 0 K, the two phases in equilibrium would be pure *A* and *B*, and therefore have zero configurational entropy. The free energy curves that develop such miscibility gaps for the solid solution will be discussed in Section 10.5.

10.3.4 The Eutectic and Eutectoid Phase Diagrams

Another frequently encountered binary phase diagram type is shown in Figure 10.6, denoted as the *eutectic* phase diagram (from the Greek for "easy melting"). In this isobaric phase diagram, there are three equilibrium phases: two solid phases (α and β) and a liquid phase. Above the invariant temperature (the horizontal line, known as the *eutectic temperature*), the diagram is divided into regions similar to those displayed in Figure 10.4a—that is, two single-phase solid regions (one of α and the other of β), two two-phase regions (α/L and β/L), and a single-phase liquid region.

At the unique eutectic composition, this phase diagram displays the solidification reaction

$$L \rightarrow \alpha + \beta$$

which is commonly called a *eutectic reaction*. Two solid-phase solutions form from the liquid solution concomitantly, often giving rise to striking microstructures. Use of the Gibbs equilibrium phase rule shows that in a binary isobaric system, the three

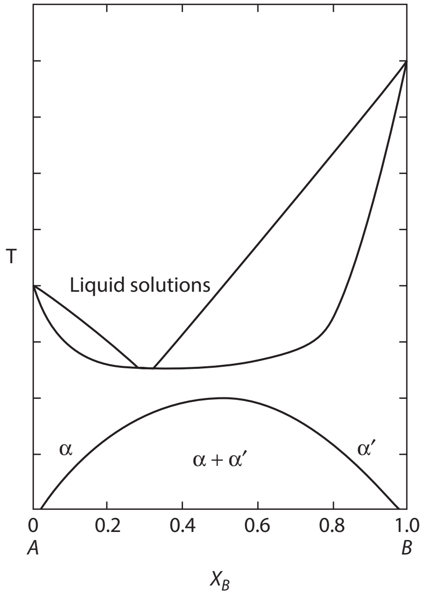

Figure 10.5 Low-temperature region of the phase diagram shown in Figure 10.4a, showing a solid-state miscibility gap.

phases α, L, and β can be in equilibrium with each other only at a fixed temperature (i.e., the equilibrium has zero degrees of freedom). Therefore, the three-phase equilibrium must exist on a horizontal line (fixed temperature) in isobaric binary phase diagrams.

In this diagram, there are two other temperature-invariant reactions that may occur involving three phases: namely, the hypoeutectic reaction

$$\alpha + \mathrm{L} \rightarrow \alpha + \beta$$

and the hypereutectic reaction

$$\beta + \mathrm{L} \rightarrow \alpha + \beta$$

The free energy of mixing curves at three temperatures for this phase diagram are shown in Figure 10.6 b,c, and d. Figure 10.6b shows the relative positions of the three free energy of mixing curves at a temperature above the eutectic temperature

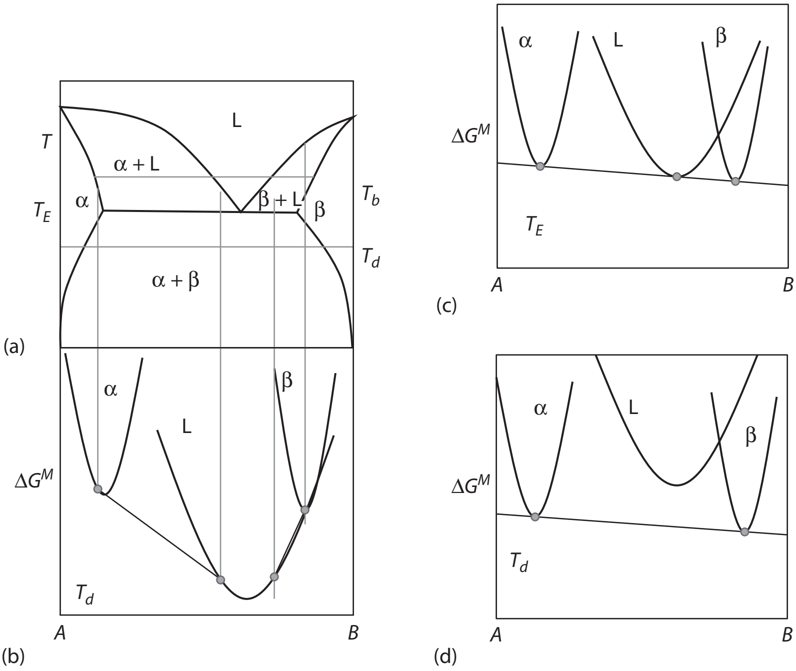

Figure 10.6 (a) An isobaric eutectic binary phase diagram displaying two solid phases (α and β) and one liquid phase. (b) Gibbs free energy of mixing curves of the three phases at a temperature above the eutectic temperature. (c) Gibbs free energy curves of the three phases at the eutectic temperature T_E. (d) Gibbs free energy curves of the three phases at the temperature T_d.

T_E. Note that the liquid free energy curve lies between those of the two solids. Also, it can be seen that above the eutectic temperature, T_E, the free energy of mixing of the liquid lies below those of the two solids. As the temperature decreases, the free energy of mixing curve of the liquid rises faster than those of the solids. This occurs because the temperature dependence of the free energy, $\left((\partial G/\partial T)_P = -S\right)$, is the negative of the entropy of the phase, and since the liquid has the larger entropy, it will be displaced to higher values of free energy of mixing at a greater rate than the two solid curves. At the eutectic temperature, T_E, the three free energy of mixing curves of the phase lie on a common tangent (Figure 10.6c). Thus, all three phases have equal partial molar Gibbs free energies; that is,

$$\Delta\overline{G}_A^{\mathrm{L}} = \Delta\overline{G}_A^{\alpha} = \Delta\overline{G}_A^{\beta}$$

$$\Delta\overline{G}_B^{\mathrm{L}} = \Delta\overline{G}_B^{\alpha} = \Delta\overline{G}_B^{\beta}$$

Below T_E, only the two solid phases are present in equilibrium and their compositions continuously shift to that of the pure components A and B.

If the high-temperature phase in these diagrams is replaced by a solid phase, the diagram is called a *eutectoid* (eutectic-like) phase diagram. The alloy system Fe–C has the important constant-temperature eutectoid transformation $\gamma \rightarrow \alpha + \mathrm{Fe_3C}$, producing the well-known constituent pearlite (a two-phase lamellar mixture of $\alpha + \mathrm{Fe_3C}$).

10.3.5 The Peritectic and Peritectoid Phase Diagrams

In the eutectic phase diagrams, the high-temperature liquid phase has a composition between that of the two low-temperature phases at the invariant temperature. It is possible for the liquid phase to be the richest in solute (or solvent) at the invariant temperature, as shown in Figure 10.7. For these diagrams, commonly called *peritectic* diagrams, on cooling, an alloy of the peritectic composition passing through the invariant temperature undergoes a transformation of the form

$$\alpha + \mathrm{L} \rightarrow \beta$$

This is followed by the reaction

$$\beta \rightarrow \alpha + \beta$$

There are two other invariant reactions that may occur involving three phases in the peritectic system: namely, the hypo-peritectic reaction

$$\alpha + \mathrm{L} \rightarrow \alpha + \beta$$

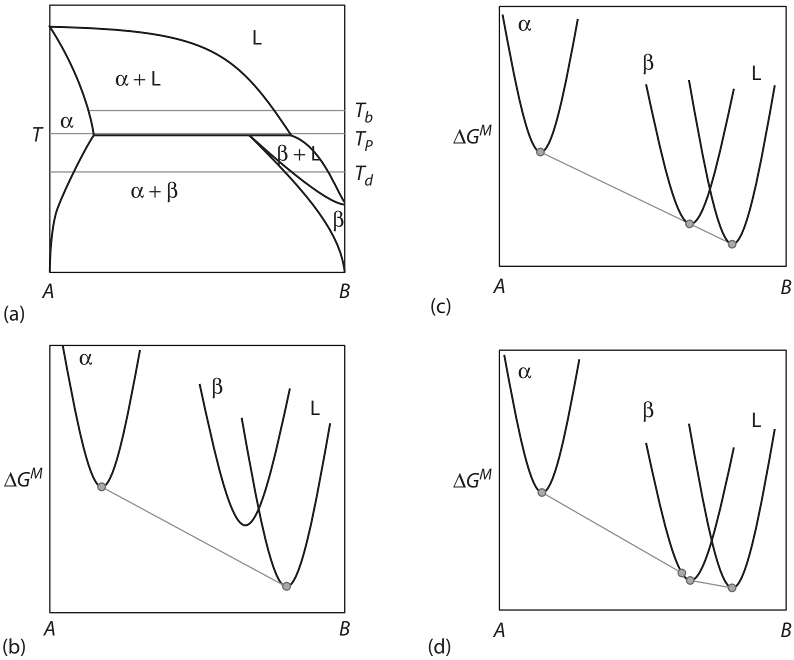

Figure 10.7 (a) A peritectic binary phase diagram displaying two solid phases (a and b) and one liquid phase. (b) Gibbs free energy of mixing curves of the three phases at a temperature above the peritectic invariant temperature. Note that the free energy curve of the liquid phase is to the *B*-rich side of both free energy curves of the solid phases. (c) Gibbs free energy of mixing curves of the three phases at the peritectic temperature T_P. (d) Gibbs free energy of mixing curves of the three phases at the temperature T_d.

And the hyper-peritectic reaction

$$\alpha + \mathrm{L} \rightarrow \beta + \mathrm{L}$$

The arrangements of the Gibbs free energy of mixing curves necessary to obtain such a phase diagram are shown in Figure 10.7b and c. It can be seen that the free energy of mixing curve of the liquid lies to the solute-rich side of both the solid phases in the diagram.

If the liquid phase is replaced by a third solid phase, α, the diagram will look similar but without the liquid phase. Such a diagram is called a *peritectoid* diagram. In this case, for an alloy of the peritectoid composition cooling from the α + γ region, the invariant reaction is

$$\alpha + \gamma \rightarrow \beta$$

There are other invariant types of binary equilibrium phase diagrams. For example, Figures 10.23 and 10.26 display monotectic phase diagrams in which the invariant reaction is

$$\mathrm{L}_1 \rightarrow \alpha + \mathrm{L}_2$$

Also, a *metatectic* (or *catatectic*) diagram displays the invariant reaction on cooling

$$\beta \rightarrow \alpha + \mathrm{L}$$

(See Problem 10.8.)

10.4 LIQUID AND SOLID STANDARD STATES

The choice of the standard state of a component of a condensed system is often that of the pure component in its stable state at the particular temperature and pressure of interest. At 1 atm pressure (the pressure normally considered), the stable state is determined by whether or not the temperature of interest is above or below the normal melting temperature of the component. It is often assumed that the temperature of interest is either above or below the melting temperatures of both components. An activity versus composition curve could be drawn for liquid immiscibility, in which case the standard states are the two pure liquids, or it could be drawn for solid immiscibility, in which case the standard states are the two pure solids. Since the standard state of a component is simply a reference state with which the component in any other state is compared, it follows that any state can be chosen as the standard state, and the choice is normally made purely on the basis of convenience.

Consider the binary system A–B at the temperature T, which is below the melting temperature of B, $T_{m(B)}$, and above the melting temperature of A, $T_{m(A)}$. Consider, further, that this system forms Raoultian *ideal liquid* solutions and Raoultian *ideal solid* solutions. The phase diagram for the system is shown in Figure 10.8a. Figure 10.8 b shows the two Gibbs free energy of mixing curves at the temperature of interest. Curve I is drawn for liquid solutions and curve II is drawn for solid solutions. At the temperature T, the stable states of pure A and B are located at $\Delta G^M = 0$, with pure liquid A located at $X_A = 1$ (the point a) and pure solid B located at $X_B = 1$ (the point b). The point c represents the molar Gibbs free energy of solid A relative to that of liquid A at the temperature T, and $T > T_{m(A)}$. Thus, $G^\circ_{A(s)} - G^\circ_{A(l)}$ is a positive quantity which is equal to the negative of the molar Gibbs free energy of melting of A at the temperature T. That is,

$$G^\circ_{A(s)} - G^\circ_{A(l)} = -\Delta G^\circ_{m(A)} = -(\Delta H^\circ_{m(A)} - T\Delta S^\circ_{m(A)})$$

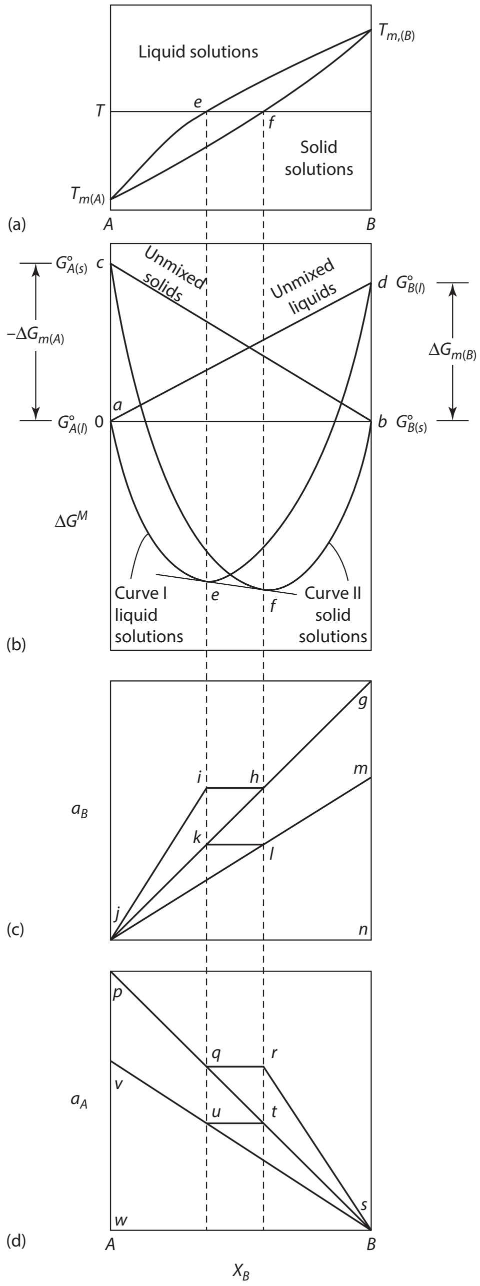

Figure 10.8 (a) The phase diagram for the system A–B. (b) The Gibbs free energies of mixing in the system A–B at the temperature T. (c) The activities of B at the temperature T and comparison of the solid and liquid standard states. (d) The activities of A at the temperature T and comparison of the solid and liquid standard states.

and if $c_{p,A(s)} = c_{p,A(l)}$ (i.e., if $\Delta H^\circ_{m(A)}$ and $\Delta S^\circ_{m(A)}$ are independent of temperature), then

$$\Delta G^\circ_{m(A)} = \Delta H^\circ_{m(A)} \left(\frac{T_{m(A)} - T}{T_{m(A)}} \right) \tag{10.1}$$

As the temperature decreases and approaches the melting point of A, $\Delta G^\circ_{m(A)}(T)$ approaches zero.

Similarly, the point *d* represents the molar Gibbs free energy of liquid *B* relative to that of solid *B* at the temperature *T*, and, since $T < T_{m(B)}$, then $G^\circ_{B(l)} - G^\circ_{B(s)}$ is a positive quantity equal to $\Delta G^\circ_{m(B)}$.

The line in Figure 10.8a joining *a* and *d* represents the Gibbs free energy of unmixed liquid *A* and liquid *B* relative to that of the standard state of unmixed liquid *A* and solid *B*, and the line joining *c* and *b* represents the Gibbs free energy of unmixed solid *A* and solid *B* relative to that of the standard state. The line *cb* can be represented by the equation

$$\Delta G = -X_A \Delta G^\circ_{m(A)}$$

and the equation for the line *ad* is

$$\Delta G = X_B \Delta G^\circ_{m(B)}$$

At any composition, the formation of a homogeneous liquid solution from pure liquid *A* and pure solid *B* can be considered as being a two-step process involving

1. The melting of X_B moles of *B*, which involves the change in Gibbs free energy

$$\Delta G = X_B \Delta G^\circ_{m(B)}$$

2. The mixing of X_B moles of liquid *B* and X_A moles of liquid *A* to form an ideal liquid solution, which involves the change in Gibbs free energy

$$\Delta G = \Delta G^{M,\text{id}} = RT(X_A \ln X_A + X_B \ln X_B)$$

Thus, the molar Gibbs free energy of mixing (which can also be called the *molar Gibbs free energy of formation*) of an ideal liquid solution, $\Delta G^M_{(l)}$, from liquid *A* and solid *B* is given by

$$\Delta G^M_{(l)} = RT(X_A \ln X_A + X_B \ln X_B) + X_B \Delta G^\circ_{m(B)} \tag{10.2}$$

which is the equation of curve I in Figure 10.8b.

Similarly, at any composition, the formation of an ideal solid solution from liquid *A* and solid *B* involves a change in Gibbs free energy of

$$\Delta G_{(s)}^{M} = RT(X_A \ln X_A + X_B \ln X_B) - X_A \Delta G_{m(A)}^{\circ} \tag{10.3}$$

which is the equation of curve II in Figure 10.8b.

At the composition *e*, the tangent to the free energy of mixing curve for the liquid solution is also the tangent to the free energy of mixing curve of the solid solution at the composition *f*. Thus, at the temperature *T*, the liquid of composition *e* is in equilibrium with the solid of composition *f*; that is, *e* is the liquidus composition and *f* is the solidus composition, as seen in Figure 10.8a. As the temperature is lowered, the magnitude of *ca* decreases until, at the melting point of *A*, the length of *ca* equals zero. With decreasing temperature, the magnitude of *db* increases. The consequent movement of the positions of curves I and II relative to one another is such that the positions *e* and *f* of the double tangent to the curves shift to the left. Correspondingly, if the temperature is increased, the relative movement of the Gibbs free energy curves is such that *e* and *f* shift to the right. The loci of *e* and *f* with change in temperature trace out the liquidus and solidus curves, respectively.

The equations for the solidus and liquidus curves of this system are derived in Appendix 10A of this chapter. There, the equations are found to be

$$X_{A(s)} = \frac{1 - \exp\left(-\dfrac{\Delta G_{m(B)}^{\circ}}{RT}\right)}{\exp\left(-\dfrac{\Delta G_{m(A)}^{\circ}}{RT}\right) - \exp\left(-\dfrac{\Delta G_{m(B)}^{\circ}}{RT}\right)} \tag{10.4}$$

and

$$X_{A(l)} = \frac{\left[1 - \exp\left(-\dfrac{\Delta G_{m(B)}^{\circ}}{RT}\right)\right]\exp\left(-\dfrac{\Delta G_{m(A)}^{\circ}}{RT}\right)}{\exp\left(-\dfrac{\Delta G_{m(A)}^{\circ}}{RT}\right) - \exp\left(-\dfrac{\Delta G_{m(B)}^{\circ}}{RT}\right)} \tag{10.5}$$

If $c_{p,i(s)} = c_{p,i(l)}$, we obtain from Equation 10.1, for $i = A$ and B,

$$\Delta G_{m(i)}^{\circ} = \Delta H_{m(i)}^{\circ}\left[\frac{T_{m(i)} - T}{T_{m(i)}}\right]$$

Thus, the phase diagram for a system which forms ideal solid and liquid solutions is determined only by the melting temperatures and the molar heats of melting of the components.

Figure 10.9 shows the Gibbs free energy of mixing curves for a binary system *A*–*B* which forms ideal solid solutions and ideal liquid solutions, drawn at a temperature of 500 K, which is lower than $T_{m,(B)}$ and higher than $T_{m,(A)}$. At 500 K, $\Delta G_{m,A}^{\circ} = -1500$ J and $\Delta G_{m,B}^{\circ} = 1000$ J. Figure 10.9a shows the curves when liquid *A* and solid *B* are chosen as the standard states, located at $\Delta G^M = 0$. Figure 10.9b shows the curves when liquid *A* and liquid *B* are chosen as the standard states, and

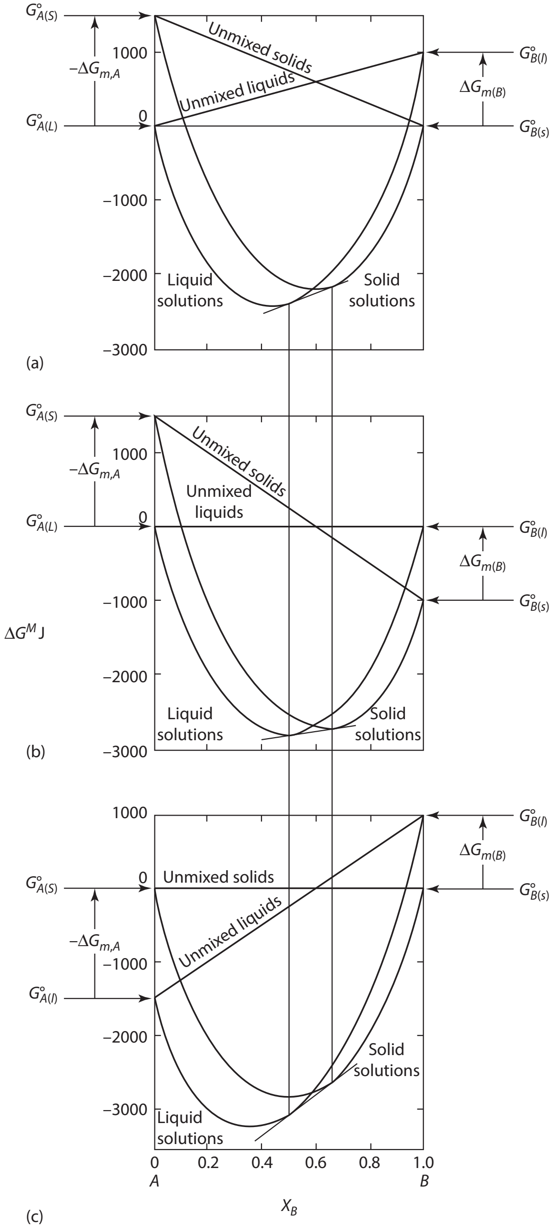

Figure 10.9 The Gibbs free energy of mixing curves for a binary system A–B which forms ideal solid solutions and ideal liquid solutions, at a temperature which is higher than $T_{m(A)}$ and lower than $T_{M(B)}$. (a) Liquid A and solid B chosen as standard states located at $\Delta G^M = 0$. (b) Liquid A and liquid B chosen as standard states located at $\Delta G^M = 0$. (c) Solid A and solid B chosen as standard states located at $\Delta G^M = 0$. The positions of the points of double tangency are not influenced by the choice of standard state.

Figure 10.9c shows the curves when solid *A* and solid *B* are chosen as the standard states. Comparison among the three shows that, because of the logarithmic nature of the Gibbs free energy curves, the positions of the points of common tangency are not influenced by the choice of standard state; they are determined *only* by the temperature *T* and by the magnitude of the difference between $G^\circ_{(l)}$ and $G^\circ_{(s)}$ for both components at the temperature *T*.

The activity–composition relationships for component *B* are shown in Figure 10.8c. There are two possible standard states (Figure 10.8b). The point *b* for solid *B* and the point *d* for liquid *B* could be chosen as standard states. The lengths of the tangential intercepts with the $X_B = 1$ axis can be measured from *b*, in which case the activities of *B* are obtained with respect to solid *B* as the standard state, or the lengths can be measured from *d*, which gives the activities with respect to liquid *B* as the standard state.

If pure solid *B* is chosen as the standard state and is located at the point *g* in Figure 10.8c, then the length *gn* is, by definition, unity, and this defines the solid standard-state activity scale. The line *ghij* then represents a_B in the solutions, with respect to solid *B* having unit activity at *g*. The line is obtained from the variation of the tangential intercepts from the curve *aefb* to the $X_B = 1$ axis, measured from the point *b*. On this activity scale, Raoult's law is given by *jg*, and the points *i* and *h* represent, respectively, the activity of *B* in the coexisting liquid solution *e* and solid solution *f*.

The point *m* represents the activity of pure liquid *B* measured on the solid standard-state activity scale of *B*. This activity is less than unity, being given by the ratio mn/gn. For *B* in any state along the *aefb* Gibbs free energy of mixing curve, in which state the partial molar Gibbs free energy of *B* is $\bar{G}_B$, the following relations hold.

$$\bar{G}_B = G^\circ_{B(l)} + RT \ln \ (a_B \text{ with respect to liquid } B)$$

and

$$\bar{G}_B = G^\circ_{B(s)} + RT \ln \ (a_B \text{ with respect to solid } B)$$

Thus,

$$G^\circ_{B(l)} - G^\circ_{B(s)} = \Delta G^\circ_{m(B)} = RT \ln\left(\frac{a_B \text{ with respect to solid } B}{a_B \text{ with respect to liquid } B}\right) \tag{10.6}$$

Since $T < T_{m(B)}$, $\Delta G^\circ_{m(B)}$ is a positive quantity, the activity of *B* in any solution with respect to solid *B* as the standard state is less than the activity of *B* with respect to liquid *B* as the standard state, where both activities are measured on the same (solid or liquid) activity scale. For pure *B*, $a_{B(s)} > a_{B(l)}$ (i.e., $gn > mn$ in Figure 10.3c), and, if $gn = 1$, then $mn = \exp(-\Delta G^\circ_{m(B)}/RT)$. Equation 10.6 simply states that the length of the tangential intercept from any point on the curve *aefb*, measured from *b* added to the length *bd* equals the length of the tangential intercept from the same point on the curve measured from *d*, which is a restatement of Equation 10.6.

If pure liquid *B* is chosen as the standard state and is located at the point *m*, then the length *mn* is, by definition, unity, and this defines the liquid standard-state activity scale. Raoult's law on this scale is given by the line *jm*, and the activities of *B* in solution, with respect to pure liquid *B* having unit activity, are represented by the line *mlkj*. The activity of solid *B*, located at *g*, is greater than unity on the liquid standard-state activity scale, being equal to $\exp\left(\Delta G^\circ_{m(B)}/RT\right)$. When measured on one or the other of the two activity scales, the lines *jihg* and *jklm* vary in the constant ratio $\exp\left(\Delta G^\circ_{m(B)}/RT\right)$, but *jihg* measured on the solid standard-state activity scale is identical with *jklm* measured on the liquid standard-state activity scale.

The variation of a_A with composition is shown in Figure 10.8d. In this case, since $T > T_{m(A)}$, $\Delta G^\circ_{m(A)}$ is a negative quantity, and hence,

$$a_A \text{ (with respect to liquid } A) > a_A \text{ (with respect to solid } A)$$

when measured on the same activity scale. If pure liquid *A* is chosen as the standard state and is located at the point *p*, then the length of *pw* is, by definition, unity, and the line *pqrs* represents the activity of *A* in the solution with respect to the liquid standard state. On the liquid standard-state activity scale, the activity of pure solid *A*, located at the point *v*, has the value $\exp\left(\Delta G^\circ_{m(A)}/RT\right)$. If, on the other hand, pure solid *A* is chosen as the standard state, then the length of *vw* is, by definition, unity, and Raoult's law is given by versus. The line *vuts* represents the activities of *A* in the solutions with respect to pure solid *A*. On the solid standard-state activity scale, liquid *A*, located at the point *p*, has the value $\exp\left(-\Delta G^\circ_{m(A)}/RT\right)$. Again, the two lines, measured on one or the other of the two activity scales, vary in the constant ratio $\exp\left(\Delta G^\circ_{m(A)}/RT\right)$, and when measured on their respective scales, they are identical.

If the temperature of the system is decreased to a value less than *T* indicated in Figure 10.8a, then the length of *ac*, being equal to $\left|\Delta G^\circ_{m(A)}\right|$ at the temperature of interest, decreases; correspondingly, the magnitude of $\left|\Delta G^\circ_{m(B)}\right|$, and hence the length of *bd*, increases. The consequent change in the positions of the Gibbs free energy of mixing curves I and II in Figure 10.8b causes the double tangent points *e* and *f* to shift to the left toward *A*. The effect on the activities is as follows. In the case of both components,

$$\frac{a_i \text{ with respect to solid } i}{a_i \text{ with respect to liquid } i} = \exp\left(\frac{\Delta G^\circ_{m(i)}}{RT}\right)$$

which, from Equation 10.1,

$$= \exp\left[\Delta H^\circ_{m(i)}\left(\frac{T_{m(i)} - T}{RTT_{m(i)}}\right)\right] \tag{10.7}$$

With respect to component B, if the temperature, which is less than $T_{m(B)}$, is decreased, the ratio $a_{B(\text{solid})}/a_{B(\text{liquid})}$, which is greater than unity, increases. Thus, in Figure 10.8c, the ratio gn/mn increases. With respect to the component A, if the temperature, which is higher than $T_{m(A)}$, is decreased, then the ratio $a_{A(\text{solid})}/a_{A(\text{liquid})}$, which is less than unity, increases. Thus, the ratio vw/pw in Figure 10.8d increases. At the temperature $T_{m(B)}$, solid and liquid B coexist in equilibrium, $\Delta G^{\circ}_{m(A)} = 0$, and the points p and v coincide. Similarly, at the temperature $T^{\circ}_{m(B)}$, the points m and g coincide.

10.5 THE GIBBS FREE ENERGY OF FORMATION OF REGULAR SOLUTIONS

Since curves II and III in Figure 10.1 are drawn for regular solutions, then the deviation of ΔG^M from $\Delta G^{M,\text{id}}$ is due only to the nonzero molar enthalpy of mixing and the difference between the two curves:

$$\Delta G^M - \Delta G^{M,\text{id}} \equiv G^{XS} = \Delta H^M = \text{a}X_A X_B$$

For curve II, $|\Delta G^M| < |\Delta G^{M,\text{id}}|$, and thus, ΔH^M and α are positive quantities (see Section 9.9). It is of interest to consider the effect of increasingly positive values of α on the shape of the Gibbs free energy of mixing curve for a regular solution. In Figure 10.10, curve I is drawn as $-\Delta S^{M,\text{id}}/R = X_A \ln X_A + X_B \ln X_B$. This curve represents $\Delta G^{M,\text{id}}/RT$. Curves for $\Delta H^M/RT = \alpha X_A X_B/RT$ are drawn for $\alpha/RT = 0, +1.0, +2.0$, and $+3.0$, and the corresponding $\Delta G^M/RT$ curves are drawn as the sum of the particular $\Delta H^M/RT$ and $-(\Delta S^{M,\text{id}}/R)$ curves. As the magnitude of α/RT is increased, it is seen that the shape of the $\Delta G^M/RT$ curve continuously changes from a shape typified by $\alpha = 0$ to a form typified by $\alpha/RT = 3$.

Before discussing the consequences of this change of shape on the behavior of the solutions, it is pertinent to examine the significance of the shape of the curve. Curve I from Figure 10.1 is reproduced in Figure 10.11a. This curve has positive curvature at all compositions. Thus, the homogeneous solution formed from any mixture of A and B is the stable state at the temperature in question, since this state has the lowest possible Gibbs free energy. Consider, further, two separate solutions—say, a and b in Figure 10.11a. Before the mixing of these two solutions, the Gibbs free energy of the two-solution system, with respect to pure A and pure B, lies on the straight line joining a and b, with the exact position being determined, via the lever rule, by the relative proportions of the separate solutions. If the solutions a and b are present in equal amounts, then the Gibbs free energy of the system is given by the point c. When mixed, the two solutions form a new homogeneous solution, since the Gibbs free energy of the system is thereby decreased from c to d, the minimum Gibbs free energy of mixing it can have. Consider now Figure 10.11b, in which the $\Delta G^M/RT$ curve for $\alpha/RT > 2$ is shown. This curve has positive curvature between A and n and between p and B, and it has negative curvature between n and p. The Gibbs free

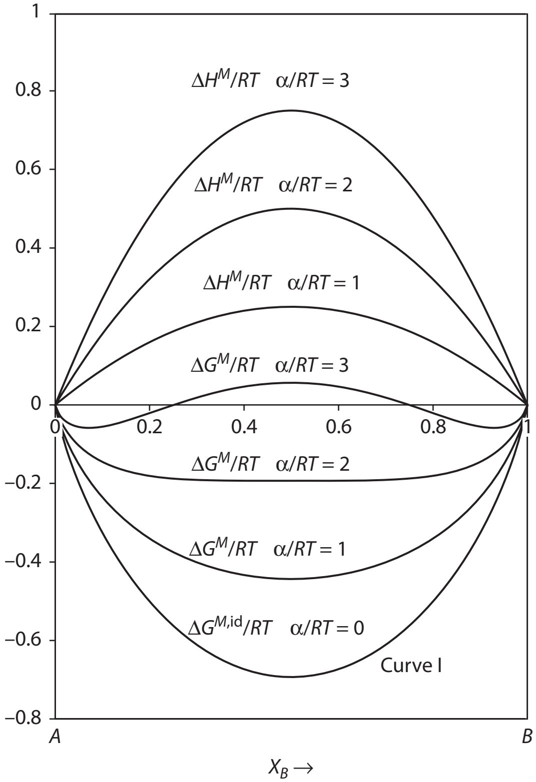

Figure 10.10 The effect of the magnitude of α / RT on the reduced enthalpies and integral molar Gibbs free energies of formation of a binary regular solution.

energy of mixing of a system of composition between m and q is minimized when the system occurs as two solutions, one of composition m and the other of composition q; for example, if the homogeneous solution of composition r separates into the two coexisting solutions m and q, the Gibbs free energy of mixing of the system is decreased from r to s. The equilibrium coexistence of two separate solutions at the temperature T and pressure P requires that

$$\bar{G}_A(\text{in solution } m) = \bar{G}_A(\text{in solution } q) \tag{i}$$

and

$$\bar{G}_B(\text{in solution } m) = \bar{G}_B(\text{in solution } q) \tag{ii}$$

Subtracting G_A° from both sides of Equation (i) gives

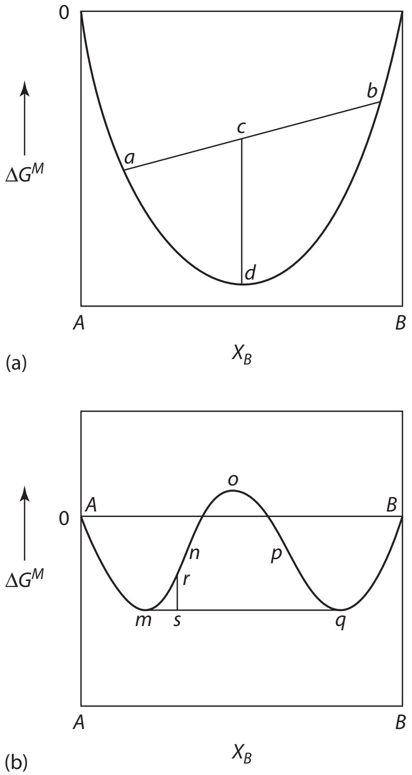

Figure 10.11 (a) The molar Gibbs free energies of mixing of binary components at a temperature which forms a complete range of solutions. (b) The molar Gibbs free energies of mixing of binary components at a temperature in a system which exhibits a miscibility gap (two-phase region).

$$RT \ln a_{A\ (\text{in solution } m)} = RT \ln a_{A\ (\text{in solution } q)}$$

or

$$a_{A\ (\text{in solution } m)} = a_{A\ (\text{in solution } q)} \tag{iii}$$

Similarly,

$$a_{B\ (\text{in solution } m)} = a_{B\ (\text{in solution } q)} \tag{iv}$$

Equations (iii) and (iv) are the criteria for equilibrium coexistence of two solutions (or phases) at constant T and P. Since

$\Delta \bar{G}_A^M$ (in solution m) = $\Delta \bar{G}_A^M$ (in solution q), and
$\Delta \bar{G}_B^M$ (in solution m) = $\Delta \bar{G}_B^M$ (in solution q),

it is seen that the tangent to the curve at the point *m* is also the tangent to the curve at the point *q*. The positioning of this common tangent defines the positions of the points *m* and *q* on the Gibbs free energy of mixing curve.

The *A*–*B* system, as represented in Figure 10.11b, is one in which, at the temperature *T*, the value of α/RT is sufficiently positive that the consequent tendency toward clustering of like atoms is great enough to cause phase separation. A homogeneous solution (phase I) is formed when *B* is initially added to *A* and the saturation of phase I with *B* occurs at the composition *m*. Further addition of *B* causes the appearance of a second solution (phase II) of composition *q* (which is phase II saturated with *A*), and continued addition of *B* causes an increase in the ratio of phase II to phase I occurring, until the overall composition of the two-phase system reaches *q*, at which point phase I disappears. A homogeneous solution (phase II) occurs between the compositions *q* and *B*. The curve *mn* represents the Gibbs free energy of mixing of phase I supersaturated with *B*, and the curve *qp* represents the Gibbs free energy of mixing of phase II supersaturated with *B*. Since the line *AmqB* represents the equilibrium states of the system, then this line alone has physical significance, and the line is the isobaric, isothermal section of the system as it occurs in *G*-*T*-*P*–composition space.

10.6 CRITERIA FOR PHASE STABILITY IN REGULAR SOLUTIONS

If we consider Figure 10.10, for a given temperature, it is obvious that a critical value of α/RT occurs, below which a homogeneous solution is stable over the entire range of composition and above which phase separation occurs. The criteria used to determine this critical value are illustrated in Figure 10.12. Figure 10.12a, b, and c shows how ΔG^M, $\partial\Delta G^M/\partial X_B$, $\partial^2\Delta G^M/\partial X_B^2$, and $\partial^3\Delta G^M/\partial X_B^3$ vary with composition for $\alpha/RT < \alpha_{\text{critical}}/RT$, $\alpha/RT = \alpha_{\text{critical}}/RT$, and $\alpha/RT > \alpha_{\text{critical}}/RT$, respectively. The critical value of α/RT is seen to be that which makes $\partial^2\Delta G^M/\partial X_B^2$ and $\partial^3\Delta G^M/\partial X_B^3$ simultaneously equal to zero at that composition at which immiscibility becomes imminent. For a regular solution,

$$\begin{aligned}
\Delta G^M &= RT(X_A \ln X_A + X_B \ln X_B) + \alpha X_A X_B \\
\frac{\partial \Delta G^M}{\partial X_B} &= RT\left[\ln \frac{X_B}{X_A}\right] + \alpha(1 - 2X_B) \\
\frac{\partial^2 \Delta G^M}{\partial X_B^2} &= RT\left(\frac{1}{X_A} + \frac{1}{X_B}\right) - 2\alpha
\end{aligned}$$

and

$$\frac{\partial^3 \Delta G^M}{\partial X_B^3} = RT\left(\frac{1}{X_A^2} - \frac{1}{X_B^2}\right)$$

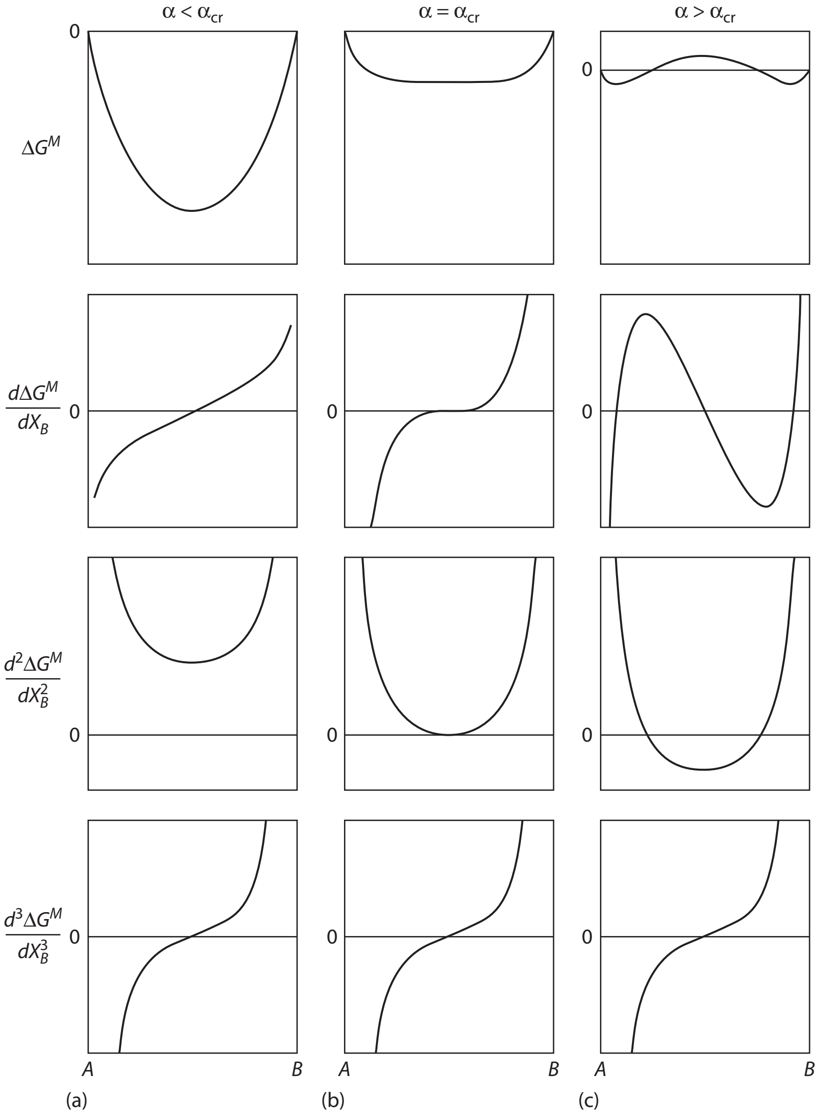

Figure 10.12 The effect of the magnitude of α on the first, second, and third derivatives of the integral Gibbs free energy of mixing with respect to composition.

The third derivative, $\partial^3 \Delta G^M / \partial X_B^3 = 0$ at $X_A = X_B = 0.5$, and thus, the second derivative, $\partial^2 \Delta G^M / \partial X_B^2 = 0$ at $X_A = 0.5$, when $\alpha/RT = 2$, which is thus the *critical value* of α/RT above which phase separation occurs (Figure 10.10).

Thus, if $\alpha/RT > 0$, the critical temperature of the miscibility gap is

$$T_{\text{cr}} = \frac{\alpha}{2R} \tag{10.8}$$

Figure 10.13a shows the variation, with temperature, of the Gibbs free energy of mixing curve for a regular solution which has a positive molar heat of mixing (α = 16,630 J) and a critical temperature of $T_{\text{cr}} = 16630/2R = 1000$ K. The Gibbs free energy of mixing expression contains a negative logarithmic term, the magnitude of which is proportional to temperature, and a positive parabolic term which is independent of temperature. At high enough temperature, the logarithmic contribution predominates and the Gibbs free energy of mixing has positive curvature at all compositions. However, with decreasing temperature, the contribution of the logarithmic term decreases, and eventually, the positive parabolic term predominates and produces a range of composition centered on $X_B = 0.5$, over which the Gibbs free energy curve has negative curvature. The logarithmic term still requires that the tangents to the curve at $X_A = 1$ and $X_B = 1$ be vertical. Figure 10.13b shows the phase diagram for the system, in which the miscibility curve bounding the two-phase region is simply the locus of the common tangent compositions in Figure 10.13a. The influence of temperature on the variations of the activity of component B with composition is shown in Figure 10.13c. The activities are obtained from the intercepts, with the $X_B = 1$ axis, of tangents drawn to the free energy curves as $\Delta \bar{G}_B^M = RT \ln aB$. At T_{cr}, the activity exhibits a horizontal inflection at $X_B = 0.5$, as is seen from the following. From Equation (9.33b),

$$\Delta \bar{G}_B^M = \Delta G^M + X_A \left(\frac{\partial \Delta G^M}{\partial X_B} \right) = RT \ln a_B$$

Thus,

$$\frac{\partial \Delta \bar{G}_B^M}{\partial X_B} = X_A \frac{\partial^2 \Delta G^M}{\partial X_B^2} = \frac{RT}{a_B} \frac{\partial a_B}{\partial X_B} \tag{10.9}$$

and

$$\frac{\partial^2 \Delta \bar{G}_B^M}{\partial X_B^2} = X_A \left(\frac{\partial^3 \Delta G^M}{\partial X_B^3} \right) - \left(\frac{\partial^2 \Delta G^M}{\partial X_B^2} \right) = \frac{RT}{a_B} \frac{\partial^2 a_B}{\partial X_B^2} - \frac{RT}{a_B^2} \left(\frac{\partial a_B}{\partial X_B} \right)^2 \tag{10.10}$$

At T_{cr} and $X_B = 0.5$, both the second and third derivatives of ΔG^M with respect to X_B are zero, and thus, from Equations 10.9 and 10.10, the first and second derivatives of a_B with respect to X_B are zero, which produces a horizontal inflection point on the activity curve at $X_B = 0.5$ and T_{cr}. For $T < T_{\text{cr}}$, the activity curve has a maximum and a minimum, which occur at the spinodal compositions (where $\partial^2 \Delta G^M / \partial X_B^2$ and hence $\partial a_B / \partial X_B$ are zero)—for example, the points n and p in Figure 10.11b and the points b and c on the activity curve at 800 K shown in Figure 10.14. The portion of

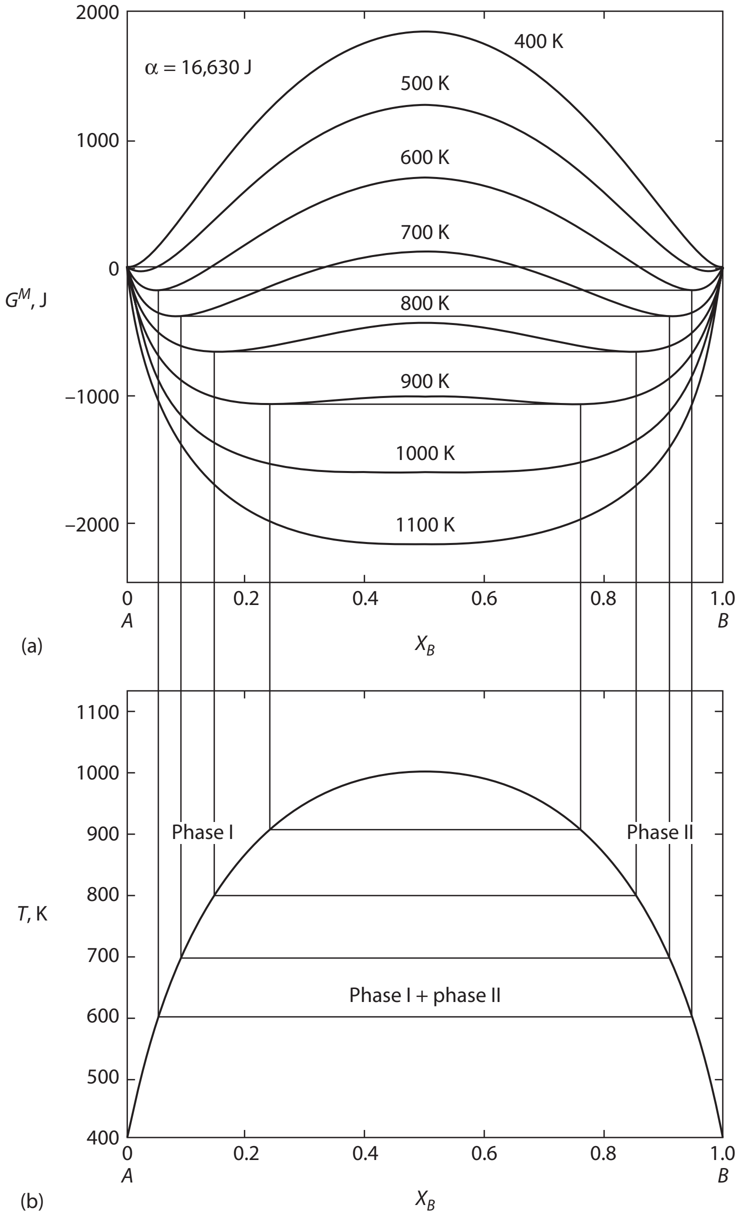

Figure 10.13a (a) The effect of temperature on the molar Gibbs free energy of mixing a binary regular solution for which α = 16,630 J. (b) The loci of the common tangent points in (a), which generate the phase diagram for the system.

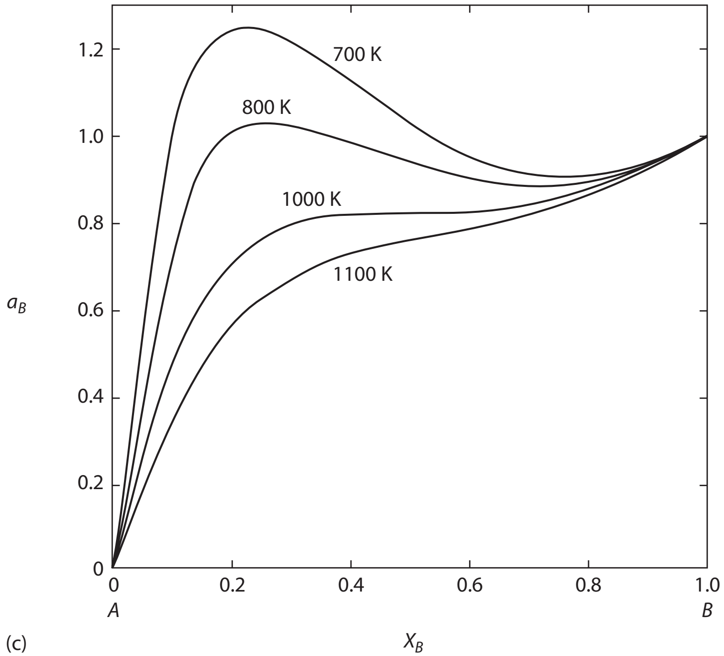

Figure 10.13b (Continued) (c) The activities of component *B* derived from (a).

the curve given by *ab* in Figure 10.14 represents the activity of *B* in phase I which is supersaturated with *B*, and the portion of the activity curve given by *cd* represents the activity of *B* in phase II which is supersaturated with *A*. The value of $\partial a_B/\partial X_B$ is negative between *b* and *c*, and this violates an intrinsic criterion for stability, which requires that $\partial a_i/\partial X_i$ always be positive [cf. $\left(\partial P/\partial V\right)_T > 0$ over the portion *JHF* in, Figure 8.8]. Thus, the derived activity curve between *b* and *c*, and, consequently, the Gibbs free energy of mixing curve between the spinodal compositions, are regions of *absolute instability*. The horizontal line drawn between *a* and *d* in Figure 10.14 represents the actual constant activity of *B* in the equilibrium two-phase region, and the compositions *a* and *d* are those of the double tangents to the Gibbs free energy of mixing curve.

Thus, the regular solution under discussion has the following different regions of stability at 800 K (see Figure 10.14):

- $X_B = 0$ to $X_B = a$, the single-phase solution I is *stable*.
- $X_B =$ a to $X_B = d$, the stable state is a two-phase mixture of solution I and II.
- $X_B = a$ to $X_B = b$, the single-phase solution of I is *metastable* (it will decompose into solution I of composition *a* and solution II of composition *d*).
- $X_B = b$ to $X_B = c$, the homogeneous solution is absolutely *unstable*.
- $X_B = c$ to $X_B = d$, the single-phase solution of I is *metastable*.
- $X_B = d$ to $X_B = 1$, the solid solution II is the *i* phase.

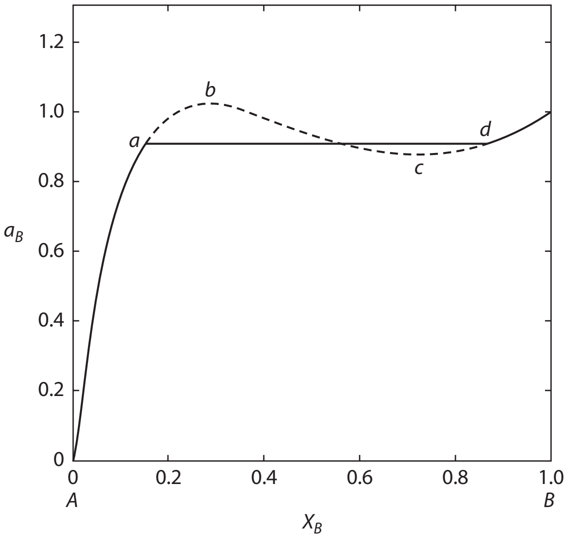

Figure 10.14 The activity of *B* at 800 K derived from Figure 10.13a.

10.7 PHASE DIAGRAMS, GIBBS FREE ENERGY, AND THERMODYNAMIC ACTIVITY

Complete mutual solid solubility of the components *A* and *B* requires that *A* and *B* have the same crystal structures, that they be of comparable atomic size, and that they have similar electronegativities and valencies. If any one of these conditions is not met, then one or more two-phase regions will occur in the solid state. Consider the eutectic *A*–*B* binary system, the phase diagram of which is shown in Figure 10.15a, in which *A* and *B* have different crystal structures. Two terminal solid solutions, α and β, occur. The molar Gibbs free energy of mixing curves, at the temperature T_1, are shown in Figure 10.15b. In this figure, *a* and *c*, located at $\Delta G^M = 0$, represent, respectively, the molar Gibbs free energies of pure solid *A* and pure liquid *B*. The points *b* and *d* represent, respectively, the molar Gibbs free energies of pure liquid *A* and pure solid *B*. The curve *aeg* (curve I) is the Gibbs free energy of mixing of solid *A* and solid *B* to form homogeneous α solid solutions, which have the same crystal structure as has *A*. This curve intersects the $X_B = 1$ axis at the molar Gibbs free energy which solid *B* would have if it had the same crystal structure as has *A*. Similarly, the curve *dh* (curve II) represents the Gibbs free energy of mixing of solid *B* and solid *A* to form homogeneous β solid solutions which have the same crystal structure as has *B*. This curve intersects the $X_A = 1$ axis at the molar Gibbs free energy which *A* would have if it had the same crystal structure as *B*. The curve *bfc* (curve III) represents the molar Gibbs free energy of mixing of liquid *A* and liquid *B* to form a homogeneous liquid solution. Since curve II lies everywhere above curve III, solid β solutions are not stable at the temperature T_1. The common tangent

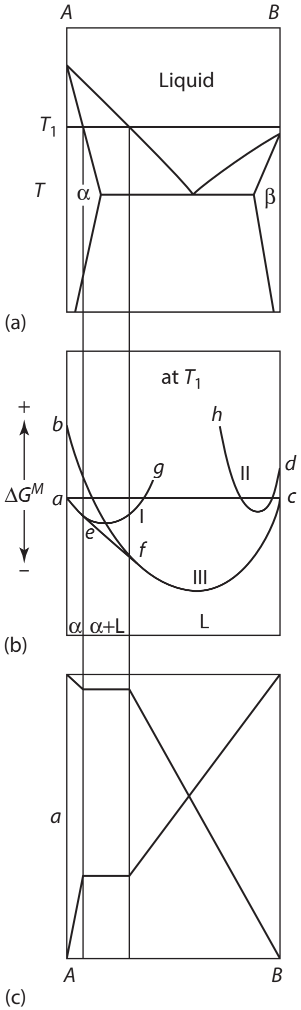

Figure 10.15 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system A–B.

to the curves I and III identifies the α solidus composition at the temperature T_1 as *e* and the liquidus composition as *f*. Figure 10.15c shows the activity–composition relationships of the components at the temperature T_1, drawn with respect to solid as the standard state for A and liquid as the standard state for B. These relationships are drawn in accordance with the assumption that the liquid solutions exhibit Raoultian ideality and the solid solutions show positive deviations from Raoult's law.

As the temperature decreases below T_1, the length of *ab* increases and the length of *cd* decreases until, at $T = T_{m(B)}$, the points *c* and *d* coincide at $\Delta G^{\mathrm{M}} = 0$. At $T_2 < T_{m(B)}$ the point *c* (liquid B) lies above *d* in Figure 10.16b, and since curve II

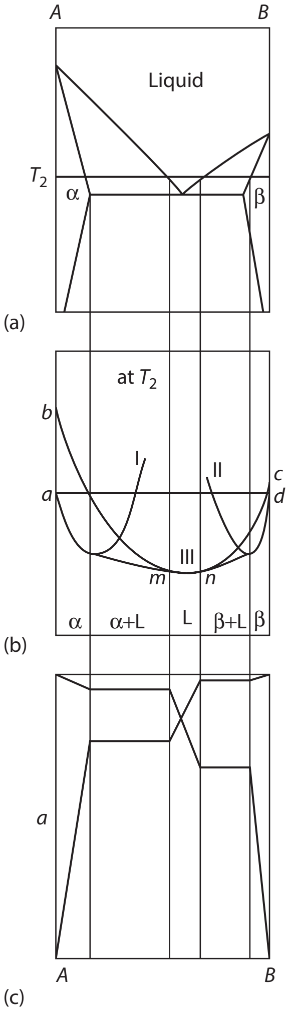

Figure 10.16 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system *A*–*B*.

lies partially below curve III, two common tangents can be drawn: one to the curves I and III, which defines the compositions of the solidus α and its conjugate liquidus, and one to the curves II and III, which defines the compositions of the solidus β and its conjugate liquidus. The activity-composition curves at T_2 are shown in Figure 10.16c, in which the solid is the standard state for both components.

With the further decrease in temperature, the two liquidus compositions *m* and *n* in Figure 10.17b approach one another and, at the unique temperature T_E (the eutectic temperature), they coincide, which means that the two common tangents merge to form the "triple" common tangent to the three curves shown in Figure 10.17b. At

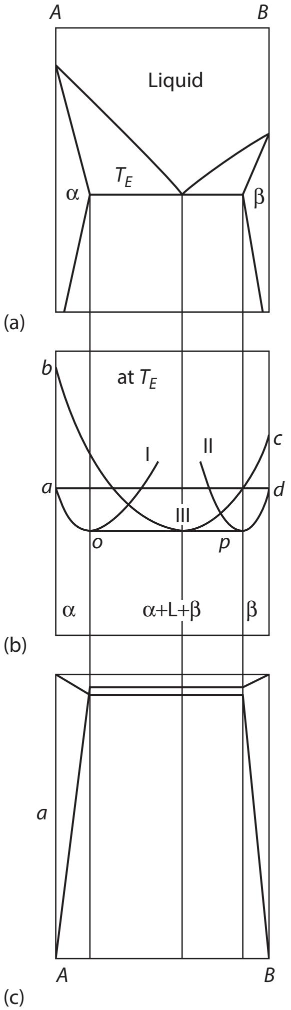

Figure 10.17 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system *A*–*B*.

compositions between *o* and *p* in Figure 10.17b, a doubly saturated eutectic liquid coexists in equilibrium with α and β solid solutions. From the Gibbs phase rule discussed in Section 7.4, this three-phase equilibrium has one degree of freedom, which is used to specify the pressure of the system. Thus, at the specified pressure, the three-phase equilibrium is invariant (the compositions of the three phases are fixed and the temperature is fixed). Figure 10.17c shows the activities of *A* and *B* at T_E. At $T_3 < T_E$, curve III lies above the common tangent to curves I and II, and thus, the liquid phase is not stable. This behavior and the corresponding activity–composition relationships are shown, respectively, in Figure 10.18b and c.

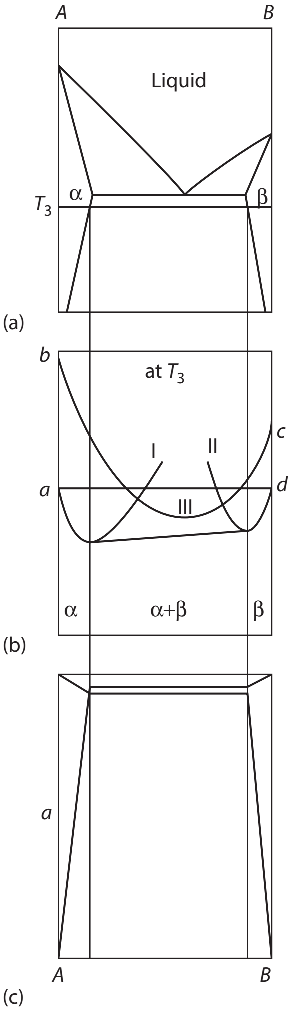

Figure 10.18 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system *A*–*B*.

If the ranges of solid solubility in the α and β phases are immeasurably small, then, as a reasonable approximation, it can be said that *A* and *B* are insoluble in one another in the solid state. The phase diagram for such a system is shown in Figure 10.19a. Since the range of solid solubility in Figure 10.19a is so small that it may be neglected on the scale of Figure 10.19a, then the molar Gibbs free energy of mixing curves for the formation of α and β (curves I and II in Figures 10.15 through 10.18) are also compressed toward the $X_A = 1$ and $X_B = 1$ axes, respectively. On the scale of Figures 10.15 through 10.18, they coincide with the vertical axes. The sequence in Figure 10.20 shows how, as the solubility of *B* in α decreases, the

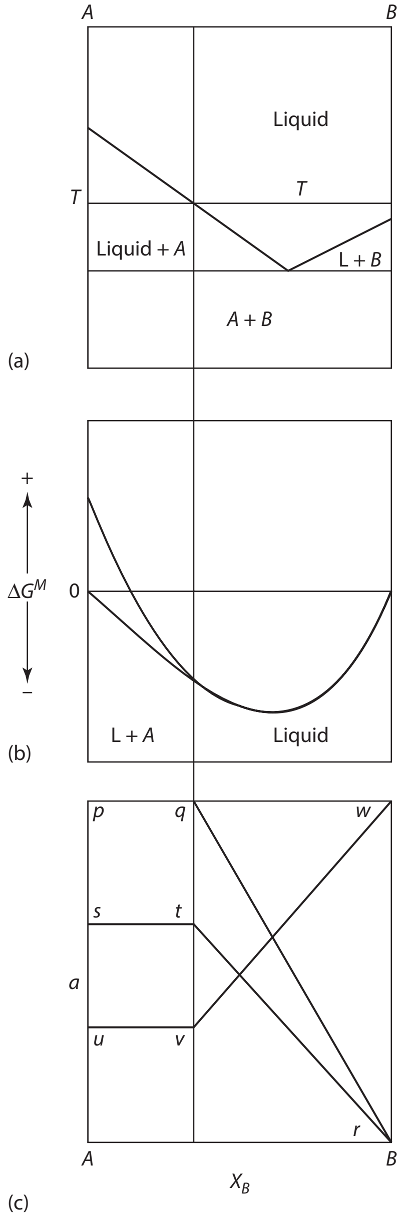

Figure 10.19 The molar Gibbs free energy of mixing and the activities in a binary eutectic system that exhibits complete liquid miscibility and virtually complete solid immiscibility.

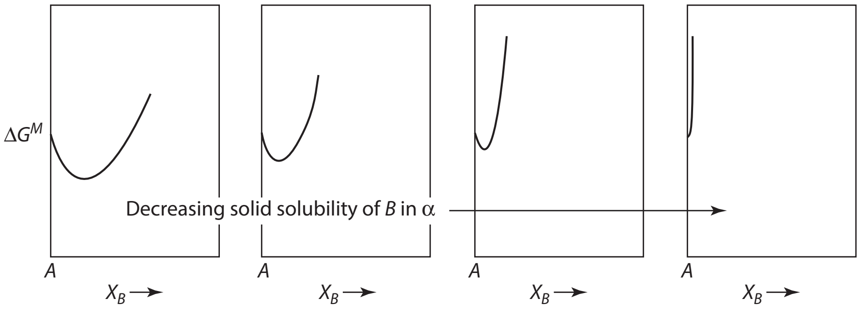

Figure 10.20 The effect of decreasing solid solubility on the molar Gibbs free energy of mixing curve.

Gibbs free energy curve for α is compressed against the $X_A = 1$ axis. The Gibbs free energy of formation of the liquid solutions in the system A–B at the temperature T is shown in Figure 10.19b. The common tangent to the α solid solution and liquid solution curves is reduced to a tangent drawn from the point on the $X_A = 1$ axis which represents pure solid A to the liquid solutions curve. The corresponding activity–composition relations are shown in Figure 10.19c. Again, these are drawn in accordance with the supposition that the liquid solutions are ideal. In Figure 10.19c, *pqr* is the activity of A with respect to pure solid A at p, s is the activity of pure liquid A with respect to solid A at p, *str* is the activity of A with respect to liquid A having unit activity at s, and *Auvw* is the activity of B with respect to liquid B having unit activity at w.

In a binary system which exhibits complete miscibility in the liquid state and virtually complete immiscibility in the solid state (e.g., Figure 10.19a), the variations of the activities of the components of the liquid solutions can be obtained from consideration of the liquidus curves. At any temperature T (Figure 10.19a), the system with a composition between pure A and the liquidus composition exists as virtually pure solid A in equilibrium with a liquid solution of the liquidus composition. Thus, at T,

$$\begin{aligned} G^\circ_{A(s)} &= \bar{G}^A_{(l)} \\ &= G^\circ_{A(l)} + RT\ln a_A \end{aligned}$$

in which a_A is with respect to liquid A as the standard state. Thus,

$$\Delta G^\circ_{m(A)} = -RT\ln a_A \tag{10.11}$$

or, if the liquid solutions are Raoultian,

$$\Delta G^\circ_{m(A)} = -RT\ln X_A \tag{10.12}$$

Figure 10.21 shows the binary phase diagram for the Bi–Cd system. This system shows the limited solubility of Bi in Cd and virtually zero solubility of Cd in Bi.

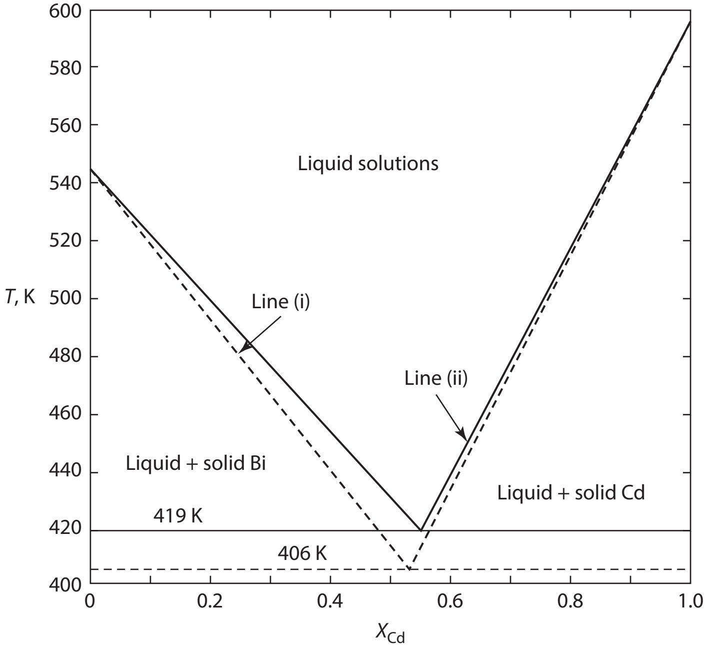

Figure 10.21 The phase diagram for the system Bi–Cd. The full lines are the measured liquidus lines, and the broken lines are calculated assuming no solid solution and ideal mixing in the liquid solutions.

In Appendix 10B to this chapter, the liquidus lines are calculated using Equation 10.24 and ancillary information.

It is of interest to examine what happens to the liquidus line as the magnitude of the positive deviation from Raoultian behavior in the liquids increases—that is, as G^{XS} becomes increasingly positive. Assuming regular solution behavior, Equation 10.11, written in the form

$$-\Delta G^{\circ}_{m(A)} = RT \ln X_A + RT \ln \gamma_A$$

becomes

$$-\Delta G^{\circ}_{m(A)} = RT \ln X_A + \alpha(1 - X_A)^2 \tag{10.13}$$

Consider a hypothetical system A–B in which $\Delta H^{\circ}_{m(A)} = 10$ kJ at $T_{m,A}$ = 2000 K. Thus, for this system,

$$-10{,}000 + 5T = RT \ln X_A + \alpha(1 - X_A)^2$$

where X_A is the composition of the A liquidus at the temperature T. The A liquidus lines, drawn for $\alpha = 0.0, 10.0, 20.0, 25.3, 30.0, 40.0$, and 50.0 kJ, are shown in Figure 10.22. As α exceeds some critical value (which is 25.3 kJ in this case), the form of the liquidus line changes from a monotonic decrease in liquidus temperature with decreasing X_A to a form which contains a maximum and a minimum (e.g., the liquidus for $\alpha = 30$ kJ). At the critical value of α, the maximum and minimum coincide at $X_A = 0.5$ to produce a horizontal inflection in the liquidus curve. It is apparent that, when α exceeds the critical value, isothermal tie-lines cannot be drawn between pure solid A and all points on the liquidus lines, which, necessarily, means that the calculated liquidus lines are impossible.

From Equation 10.6:

$$\ln a_A = \frac{-\Delta H^\circ_{m(A)}}{RT} + \frac{\Delta H^\circ_{m(A)}}{RT_{m(A)}}$$

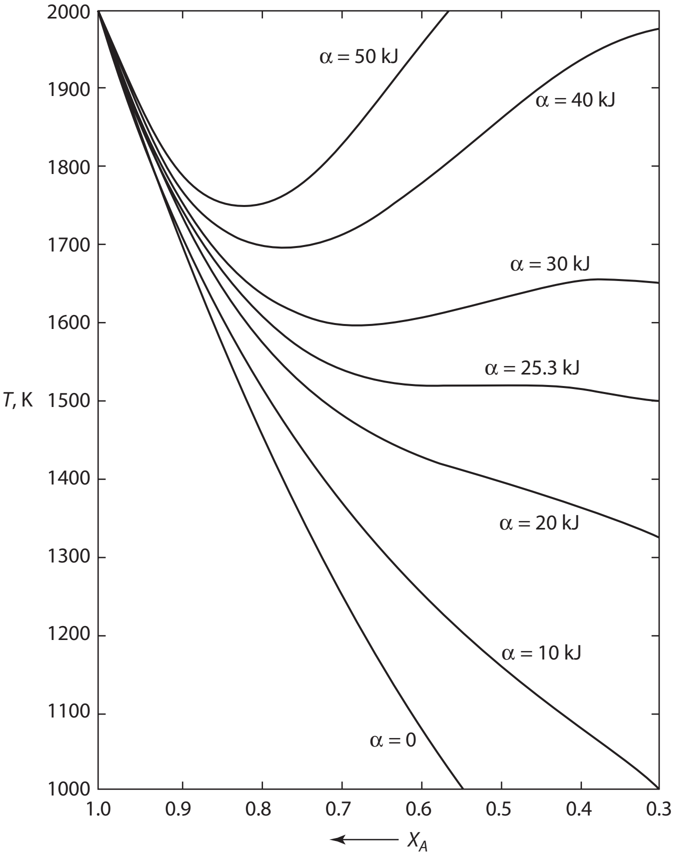

Figure 10.22 Calculated liquidus lines assuming regular solution behavior in the liquid solutions and no solid solubility.

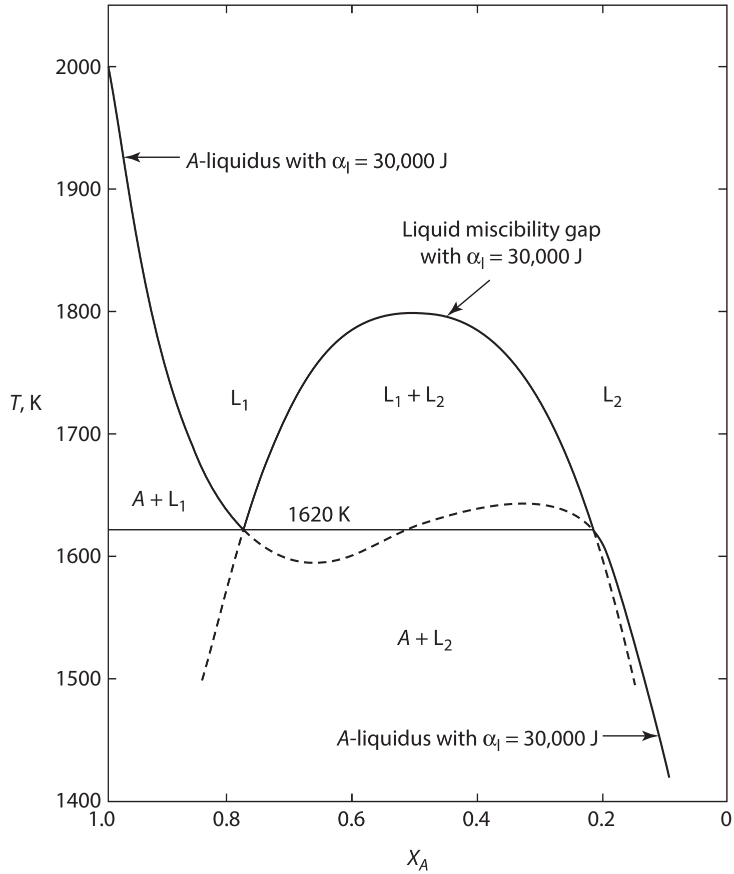

Figure 10.23 The monotectic equilibrium in a binary system in which the liquid solutions exhibit regular solution behavior with α_l = 30,000 J.

Thus,

$$d\ln a_A = \frac{da_A}{a_A} = \frac{\Delta H^\circ_{m(A)}}{RT^2}dT$$

or

$$\frac{dT}{dX_A} = \frac{RT^2}{\Delta H^\circ_{m(A)}a_A}\frac{da_A}{dX_A} \tag{10.14}$$

and also,

$$\frac{d^2T}{dX_A^2} = \frac{2RT}{\Delta H^\circ_{m(A)}a_A}\frac{da_A}{dX_A}\frac{dT}{dX_A} - \frac{RT^2}{\Delta H^\circ_{m(A)}a_A^2}\left(\frac{da_A}{dX_A}\right)^2 + \frac{RT^2}{\Delta H^\circ_{m(A)}a_A}\frac{d^2a_A}{dX_A^2} \tag{10.15}$$

In Equations 10.9 and 10.10, it was seen that $da_A/dX_A = d^2a_A/dX_A^2 = 0$ at the state of imminent immiscibility. Thus, in Equations 10.14 and 10.15, $dT/dX_A = d^2T/dX_A^2 = 0$ at the state of imminent immiscibility. In Figure 10.22, $\alpha_{\text{cr,r}}$ = 25.3 kJ, and the horizontal inflection in the critical liquidus curve occurs at X_A = 0.5, T = 1413 K. Thus,

$$\frac{\alpha_{\text{cr}}}{RT_{\text{cr}}} = \frac{25{,}390}{8.3144 \times 1413} = 2$$

which is in accord with Equation 10.8. The phase equilibria generated when $\alpha_{\text{cr}} > \alpha_{\text{cr,r}}$ are shown in Figure 10.23 which shows the immiscibility in regular liquid solutions with α_{cr} = 30,000 J and the A-liquidus for α = 30,000 J shown in Figure 10.22. The liquid immiscibility curve and the A-liquidus curve intersect at 1620 K to produce a three-phase monotectic equilibrium between A and liquidus L_1 and L_2. The liquid immiscibility curve is metastable at temperatures less than 1620 K, and the calculated A-liquidus is physically impossible between the compositions of L_1 and L_2 at 1620 K.

10.8 THE PHASE DIAGRAMS OF BINARY SYSTEMS THAT EXHIBIT REGULAR SOLUTION BEHAVIOR IN THE LIQUID AND SOLID STATES

Consider the binary system A–B which forms regular liquid solutions and regular solid solutions. The melting temperatures of A and B are, respectively, 800 and 1200 K, and the molar Gibbs free energies of melting in J are

$$\begin{aligned} \Delta G_{m,(A)} &= 8000 - 10T \\ \Delta G_{m,(B)} &= 12{,}000 - 10T \end{aligned}$$

Consider the system in which α_l = –20,000 J in the liquid solutions and α_s = 0 in the solid solutions. The Gibbs free energy of mixing curves at 1000 K are shown in Figure 10.24a. Since $T_{m,(A)} <$ 1000 K $< T_{m,(B)}$, the liquid is chosen as the standard state for A, and the solid is chosen as the standard state for B. With reference to these standard states, the Gibbs free energies of mixing are

$$\Delta G_l^M = X_B \Delta G^\circ_{m,(B)} + RT(X_A \ln X_A + X_B \ln X_B) + \alpha_l X_A X_B$$

for the liquid solutions and

$$\Delta G_s^M = -X_A \Delta G^\circ_{m,(A)} + RT(X_A \ln X_A + X_B \ln X_B) + \alpha_s X_A X_B$$

for the solid solutions. Inserting the numerical data gives

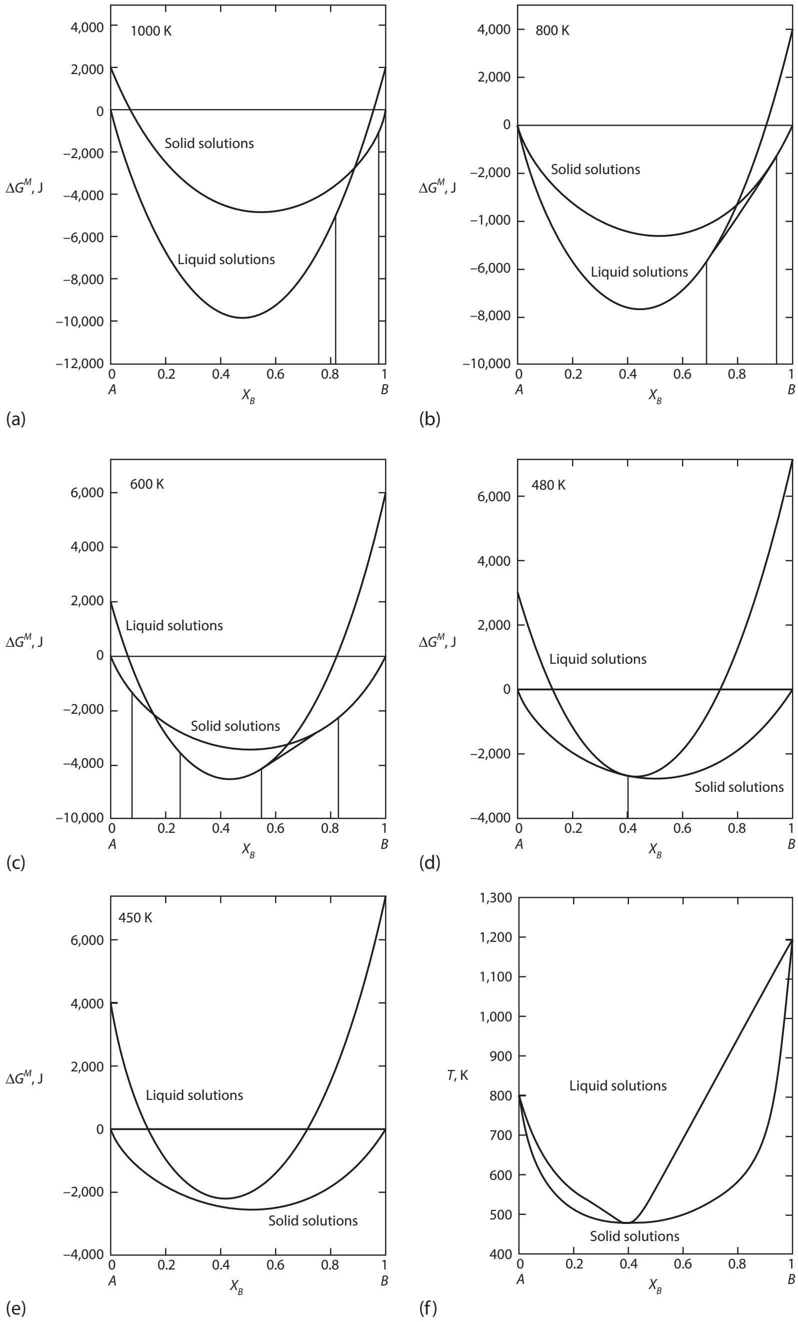

Figure 10.24 The molar Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which $\alpha_s = 0$ and regular liquid solutions in which $\alpha_l = -20{,}000$ J.

$$\Delta G_l^M = (12{,}000 - 10T)X_A + 8.3144T(X_A \ln X_A + X_B \ln X_B) - 20{,}000X_AX_B$$

and

$$\Delta G_s^M = -(8000 - 10T)X_A + 8.3144T(X_A \ln X_A + X_B \ln X_B)$$

The common tangent to the curves in Figure 10.24a gives the liquidus composition of $X_B = 0.82$ and the solidus composition of $X_B = 0.97$. Decreasing the temperature causes the Gibbs free energies of the liquids to increase relative to those of the solids. As shown in Figure 10.24b, the Gibbs free energies of pure solid A and pure liquid B are equal at the melting temperature of A, and the common tangent gives liquidus and solidus compositions of $X_B = 0.69$ and $X_B = 0.94$, respectively. At temperatures lower than $T_{m,(A)}$ and $T_{m,(B)}$, solid is chosen as the standard state for both components and the Gibbs free energies of mixing are written as

$$\begin{aligned}\Delta G_l^M = {} & (12{,}000 - 10T)X_B + (8000 - 10T)X_A \\ & + 8.3144T(X_A \ln X_A + X_B \ln X_B) - 20{,}000X_AX_B\end{aligned}$$

and

$$\Delta G_s^M = RT(X_A \ln X_A + X_B \ln X_B)$$

The curves at 600 K, shown in Figure 10.24c, contain two common tangents, and as the temperature is further decreased, the curve for the liquids is raised relative to the curve for the solids until, at 480 K, the two double tangents collapse to a single point of contact between the curves at $X_B = 0.41$. At temperatures less than 480 K, the curve for the liquids lies above that for the solids, and thus, solid solutions are stable over the entire range of composition. The variations, with temperature, of the compositions of the double tangents give the phase diagram shown in Figure 10.24f.

The behavior of the system in which $a_l = -2000$ J and $\alpha_s = 10{,}000$ J is shown in Figure 10.25. As seen in Figures 10.25a–c, the behavior is similar to that shown in Figure 10.24. However, with a positive value of α_s, a critical temperature exists below which immiscibility occurs in the solid state, as discussed in Section 10.2. With $\alpha_s = 10{,}000$ J, the critical temperature is $10{,}000/2R = 601$ K, and the mixing curves at 601 K are shown in Figure 10.25d. The phase diagram is shown in Figure 10.25f. With increasingly negative values of α_l and increasingly positive values of α_s, the temperature of the point of contact of the liquidus curve with the solidus curve decreases and the critical temperature in the solid-state increases, which eventually produces a eutectic system.

The behavior of a system in which $\alpha_l = 20{,}000$ J and $\alpha_s = 30{,}000$ J is shown in Figure 10.26. The critical temperatures for the liquid and solid solutions are, respectively, 1203 and 1804 K, and the Gibbs free energy of mixing curves at 1203 K are shown in Figure 10.26a. At $T \geq 1203$ K, homogeneous liquids are the stable state, and at temperatures lower than 1203 K, immiscibility occurs in the liquid

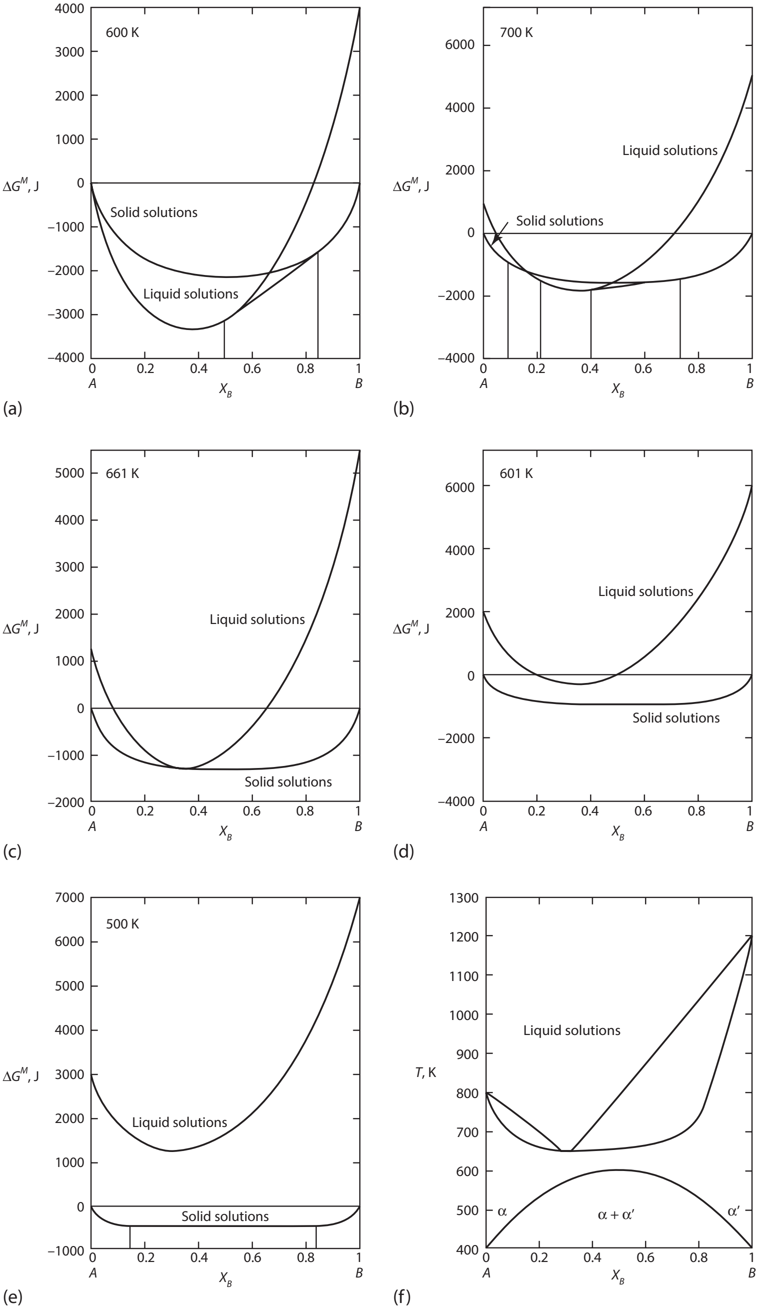

Figure 10.25 The molar Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which α_s = 10,000 J and regular liquid solutions in which α_l = –2000 J.

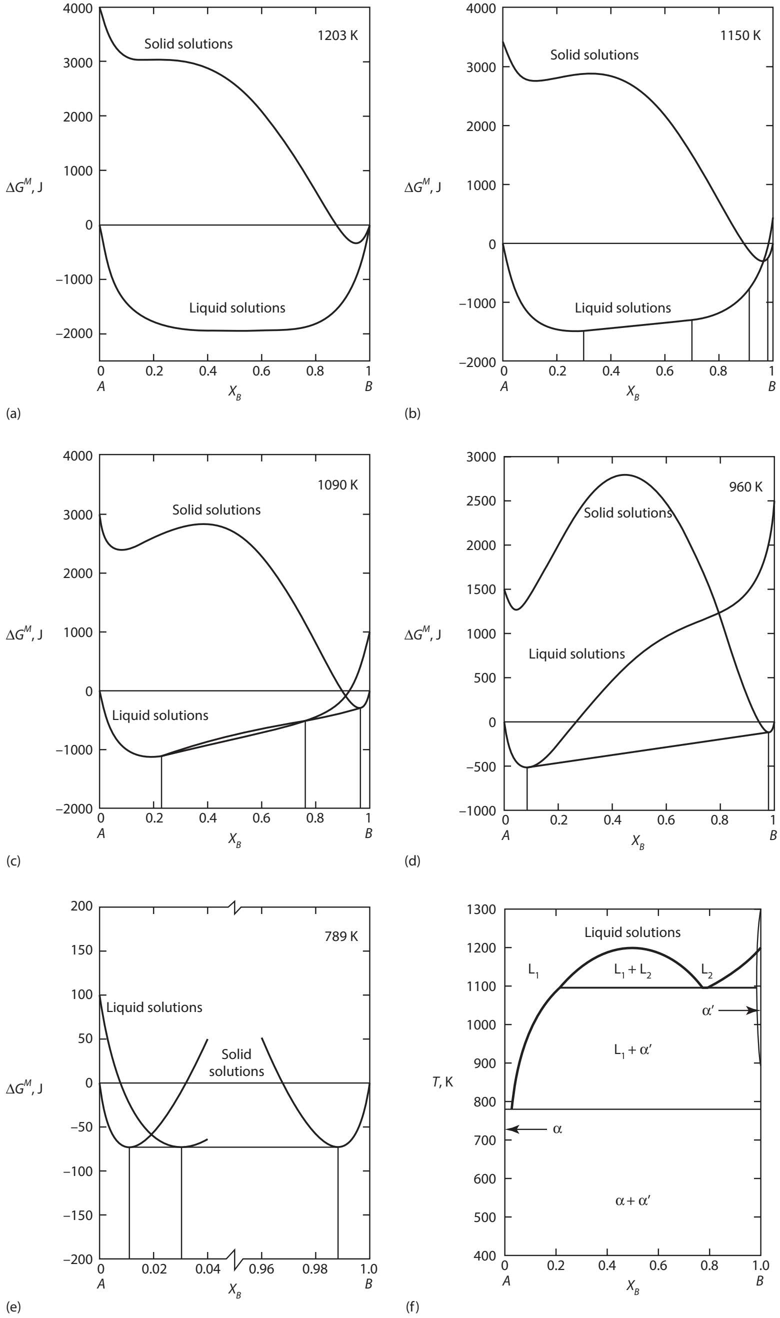

Figure 10.26 The molar Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which α_s = 30,000 J and regular liquid solutions in which α_l = 20,000 J.

state. The curves shown in Figure 10.26b at 1150 K contain two common tangents, one joining the conjugate liquid solutions L_1 and L_2 and one connecting the liquidus L_2 with the solidus α'. With decreasing temperature, the compositions of the conjugate liquid L_2 and the liquidus L_2 approach one another until, at 1090 K, the two common tangents merge to form a triple tangent to liquid compositions at $X_B = 0.23$ and 0.77 and α' at $X_B = 0.98$. This is a monotectic equilibrium (see also Figure 10.23). Further cooling produces a common tangent between L_1 and α', as shown in Figure 10.26*c*, and at 789 K another "triple" common tangent occurs between α at $X_B = 0.01$, L_1 at $X_B = 0.03$, and $\alpha' = 0.99$. At temperatures lower than the eutectic temperature of 789 K, the liquid phase is not stable, and, depending on its composition, the system exists as α, $\alpha + \alpha'$, or α'. The monotectic and eutectic equilibria are shown in the phase diagram in Figure 10.26f.

The influence of systematic changes in the values of α_l and α_s on the phase relationships which occur in the binary system A–B which forms regular solid and liquid solutions is shown in Figure 10.27.*

- In moving from the bottom of any column to the top, the value of α_s becomes more positive at constant α_l, and in moving from left to right along any row, the value of α_l becomes more positive at constant α_s.
- In the sequence Figure 10.27a–e, the liquid solutions become increasing less stable relative to the solid phases, with the consequence that the eutectic temperature is increased.
- In the transition Figure 10.27d–e, the A-liquidus becomes unstable and a monotectic equilibrium occurs.
- In the sequence Figure 10.27h–i, the temperature at which the three-phase equilibrium occurs is increased from 633 to 799 K, with the consequence that the eutectic equilibrium in Figure 10.23h becomes a peritectic equilibrium in Figure 10.27i.
- In Figure 10.27j, the immiscibility in the solid state disappears at a temperature below that at which a peritectic equilibrium could occur.
- With $\alpha_l = 20$ kJ in Figure 10.27j, liquid immiscibility occurs at temperatures lower than $20{,}000 / (2 \times 8.3144) = 1202$ K, and hence, a monotectic equilibrium occurs at 1190 K.
- In Figure 10.27k, the three-phase L_1–L_2–α equilibrium occurs at 1360 K, which, being higher than $T_{m,(B)}$, produces a syntectic equilibrium in which the composition of the α phase lies between the compositions of the two liquids.
- In the sequence p → l → f in Figure 10.27, the solid phase becomes increasingly less stable than the liquid phase, which deepens the depression of the liquidus and solidus curves and eventually forms a eutectic.
- Figures 10.24 and 10.26, respectively, show the Gibbs free energy relations in Figure 10.27l and e.
- Figure 10.25 shows the phase equilibria occurring between those in Figure 10.27l and those in Figure 10.27f.

Thus, even though the calculations are performed using a simple solution model, the trends of changing the regular solution constants α_l and α_s do shed light on the

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* A. D. Pelton and W. T. Thompson, *Prog. Solid State Chem.* (1975), vol. 10(3), p. 119.

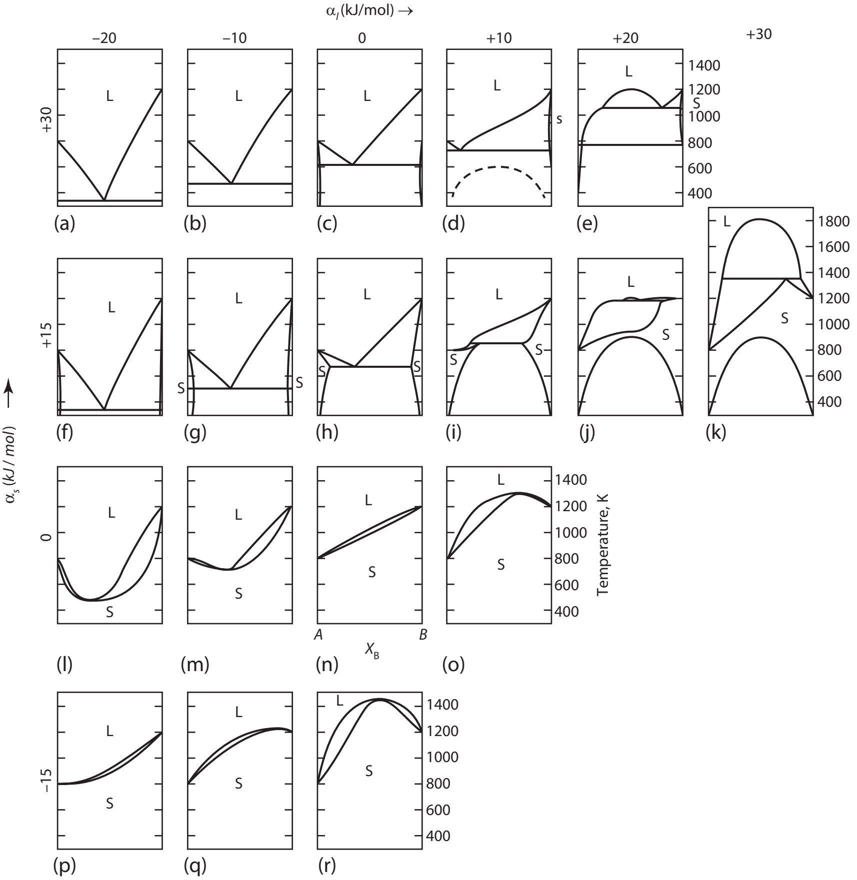

Figure 10.27 Topological changes in the phase diagram for a system *A*–*B* with regular solid and liquid solutions, brought about by systematic changes in the values of α_s and α_l. The melting temperatures of *A* and *B* are, respectively, 800 and 1200 K, and the molar entropies of melting of both components are 10 J/K. (From A. D. Pelton and W. T. Thompson, *Prog. Solid State Chem.* (1975), vol. 10, part 3, p. 119.)

way in which various experimentally determined diagrams vary with respect to each other.

10.9 SUMMARY

1. The molar Gibbs free energy of formation of binary solution *A*–*B* is given by

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$$

2. For a regular solution,

$$\Delta G^{M} - \Delta G^{M,\text{id}} = \text{G}^{\text{xs}} = \alpha X_A X_B = \Delta H^{M}$$

3. The criteria for equilibrium between the phases α and β in the binary system A–B are

$$a_A(\text{in } \alpha) = a_A(\text{in } \beta)$$

and

$$a_B(\text{in } \alpha) = a_B(\text{in } \beta)$$

4. Common binary phase diagrams displaying invariant reactions include eutectic, eutectoid, peritectic, peritectoid, monotectic, monotectoid, and metatectic.
5. Immiscibility becomes imminent in a regular solution at the critical value of $\alpha = 2$. The critical temperature, below which immiscibility occurs in a regular system, is given by $T_{\text{cr}} = \alpha / 2R$.
6. In a binary system A–B which forms ideal liquid solutions and ideal solid solutions, the solidus is given by

$$X_{A(s)} = \frac{1 - \exp\left(-\Delta G^{\circ}_{m(B)} \big/ RT\right)}{\exp\left(-\Delta G^{\circ}_{m(A)} \big/ RT\right) - \exp\left(-\Delta G^{\circ}_{m(B)} \big/ RT\right)}$$

and the liquidus line is given by

$$X_{A(l)} = \frac{\left[1 - \exp\left(-\Delta G^{\circ}_{m(B)} \big/ RT\right]\exp\left(-\Delta G^{\circ}_{m(A)} \big/ RT\right)}{\exp\left(-\Delta G^{\circ}_{m(A)} \big/ RT\right) - \exp\left(-\Delta G^{\circ}_{m(B)} \big/ RT\right)}$$

7. In a binary system A–B which contains a eutectic equilibrium and in which the extent of solid solution is negligibly small, the liquidus lines are determined by the conditions

$$\Delta G^{\circ}_{m(A)} = -RT \ln a_A (\text{in the } A\text{-liquidus melt})$$

and

$$\Delta G^{\circ}_{m(B)} = -RT \ln a_B (\text{in the } B\text{-liquidus melt})$$

8. Thus, if the liquid solutions are ideal, the A-liquidus compositions are given by

$$-\Delta G^{\circ}_{m(A)} = RT \ln X_A$$

and if the liquid solutions are regular, the A-liquidus compositions are given by

$$-\Delta G^{\circ}_{m(A)} = RT \ln X_A + \alpha(1 - X_A)^2$$

10.10 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 10

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Common tangent
Congruent temperature
Constituent
Eutectic phase diagram
Eutectoid phase diagram
Gibbs free energy versus composition curves
Gibbs–Konovalov rule
Horizontal inflection point
Hypereutectic
Hypoeutectic
Lens phase diagram
Liquidus curve
Metatectic phase diagram
Molar free energy of melting
Monotectic
Monotectoid
Peritectic phase diagram
Peritectoid phase diagram
Solidus curve
Syntectic phase diagram
Temperature versus composition phase diagram

10.11 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Part of binary phase diagram is shown in Figure 10.28a. When a magnetic field is applied, the solubility of the β phase decreases, as shown by the dotted line. Using Gibbs free energy plots of the α and β phases, determine which phase has the larger magnetic susceptibility.

Solution to Qualitative Problem 1

The Gibbs free energy plots for the α and β phases are shown in Figure 10.28b. Since the solubility of β has decreased, its free energy curve must have decreased more than that of the α phase in order for the common tangent to move to the left. Hence, the β phase must have the larger magnetic susceptibility. As in the case discussed in Section 7.8, applying a magnetic field enlarges the region of stability of the phase with the higher magnetic susceptibility.

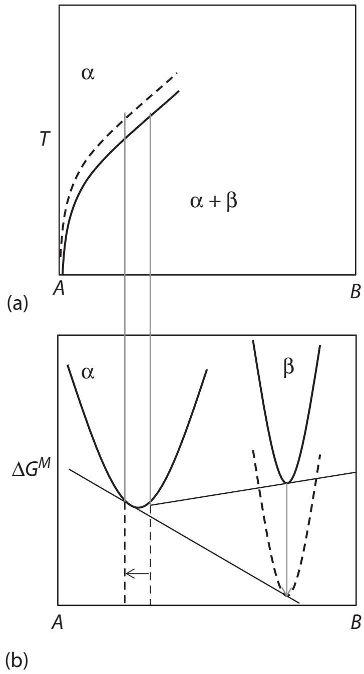

Figure 10.28 The *A*-rich section of a binary phase diagram showing the shift in the β solvus when an external magnetic field is applied. In this case $\chi_\beta > \chi_\alpha$.

Qualitative Problem 2

All regular solutions with positive enthalpies of mixing have the same value of the activity of its components (*A* or *B*) at the critical point of the miscibility gap. Calculate the activity a_A and a_B at T_C for a regular solution with regular solution constant α.

Solution to Qualitative Problem 2

At the critical temperature,

$$RT_c \ln a_B = \bar{G}_B(0.5) = \Delta G^M(0.5) = \Delta H^M(0.5) - T_c\Delta S^M(0.5)$$

$$RT_c \ln a_B(0.5) = \Delta H^M(0.5) - T_c\Delta S^M(0.5)$$

$$R\left(\frac{\alpha}{2R}\right)\ln a(0.5) = \frac{\alpha}{4} - \left(\frac{\alpha}{2R}\right)R \ln 2$$

$$a_B(0.5) = 0.824$$

10.12 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

The phase diagram for the system Cs–Rb is shown in Figure 10.29. Examine the extent to which the phase diagram can be reproduced, assuming that the liquid solutions are ideal and that the solid solutions are regular.

For Cs:

$$\Delta G^{\circ}_{m,Cs} = 2100 - 6.95T \text{ J}$$

and for Rb:

$$\Delta G^{\circ}_{m,\mathrm{Rb}} = 2200 - 7.05T$$

Solution to Quantitative Problem 1

Initially, draw the Gibbs free energy of mixing curves for the solid and liquid solutions at 9.7°C (282.7 K) and determine if some value of α gives Gibbs free energy of mixing curves similar to those shown in Figure 10.25c; that is, the curve for the liquid solutions lies above the curve for the solid solutions, except at a single composition where the two curves touch one another.

Relative to the pure solids as standard states at the temperature T,

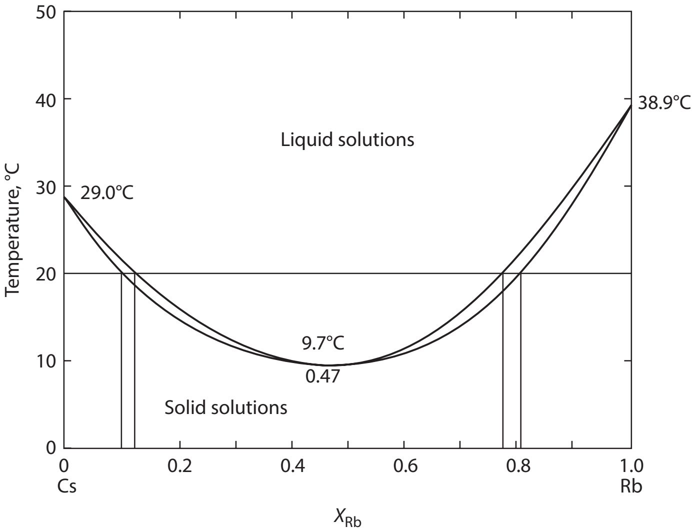

Figure 10.29 The phase diagram for the system Cs–Rb.

$$\Delta G^M(\text{liquid solutions}) = X_{\text{Rb}}\Delta G^\circ_{m,\text{Rb}} + X_{\text{Cs}}\Delta G^\circ_{m,\text{Cs}} + RT(X_{\text{Rb}}\ln X_{\text{Rb}} + X_{\text{Cs}}\ln X_{\text{Cs}}) \quad \text{(i)}$$

which, at 282.7 K, becomes

$$\Delta G^M(\text{liquid solutions}) = 205X_{\text{Rb}} + 133(1 - X_{\text{Rb}}) + 8.3144\times 282.7 \times [X_{\text{Rb}}\ln X_{\text{Rb}} + (1 - X_{\text{Rb}})\ln(1 - X_{\text{Rb}})]$$

Also,

$$\Delta G^M(\text{solid solutions}) = RT(X_{\text{Rb}}\ln X_{\text{Rb}} + X_{\text{Cs}}\ln X_{\text{Cs}}) + \alpha X_{\text{Rb}}X_{\text{Cs}} \quad \text{(ii)}$$

Which at 282.7 K becomes

$$\Delta G^M\left(\text{solid solutions}\right) = 8.3144\times 282.7\times(X_{\text{Rb}}\ln X_{\text{Rb}} + X_{\text{Cs}}\ln X_{\text{Cs}}) + \alpha X_{\text{Rb}}X_{\text{Cs}}$$

The Gibbs free energy of mixing curves, drawn with $\alpha = 668$ J, are shown in Figure 10.30, which shows that the curves touch one another at $X_{\text{Rb}} = 0.47$, in exact agreement with Figure 10.29.

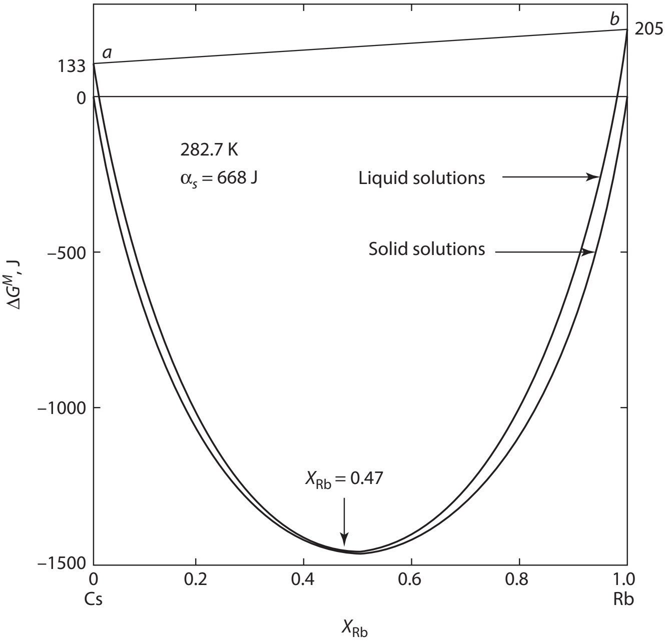

Figure 10.30 The molar Gibbs free energy of mixing curves for ideal liquid solutions and regular solid solutions (with $\alpha_S = 668$ J) at 282.7 K, drawn using the Gibbs free energies of melting of Cs and Rb.

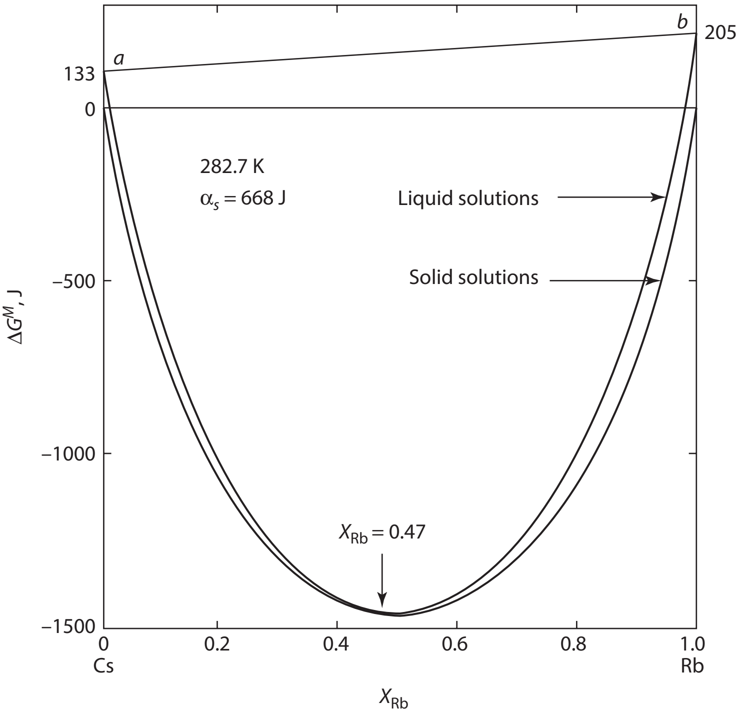

Figure 10.31 The molar Gibbs free energy of mixing curves for ideal liquid solutions and regular solid solutions (with α_S = 668 J) at 293 K, drawn using the Gibbs free energies of melting of Cs and Rb.

The Gibbs free energies of mixing, given by Equations (i) and (ii), with = 668 J and T = 292 K, are shown in Figure 10.31. The common tangent at the Cs-rich side of the diagram gives the solidus composition as $X_{Rb} = 0.10$ and the liquidus composition as $X_{Rb} = 0.13$, which is in excellent agreement with the phase diagram. At the Rb-rich side of the diagram, the double tangent gives the solidus and liquidus compositions as, respectively, $X_{Rb} = 0.81$, and $X_{Rb} = 0.75$, which are in good agreement with the phase diagram values of 0.80 and 0.77.

It is thus seen that the phase diagram is reproduced by assuming that the liquid solutions are ideal and the solid solutions are regular with α = 668 J.

Quantitative Problem 2

The Ge–Si System

The system Ge–Si exhibits the complete ranges of liquid and solid solutions.

a. Calculate the phase diagram for the system assuming that the solid and liquid solutions are Raoultian in their behavior.
b. Calculate the temperature at which the liquidus (and hence the solidus) composition exerts its maximum vapor pressure.

Given:

Silicon melts at 1685 K, and its standard Gibbs free energy change on melting is

$$\Delta G^{\circ}_{m,\mathrm{Si}} = 50,200 - 29.8T \text{ J}$$

The saturated vapor pressure of solid Si is

$$\log p^{\circ}_{\mathrm{Si}(s)}(\mathrm{atm}) = -\frac{23,550}{T} - 0.565 \log T + 9.47$$

Germanium melts at 1213 K and its standard Gibbs free energy change on melting is

$$\Delta G^{\circ}_{m,\mathrm{Ge}} = 36,800 - 30.3T \text{ J}$$

The saturated vapor pressure of liquid Ge is

$$\log\ p^{\circ}_{\mathrm{Ge}(l)}(\mathrm{atm}) = -\frac{18,700}{T} - 0.565\ \log\ T + 9.99$$

Solution to Quantitative Problem 2a

The equation of the liquidus curve is obtained from Equation 10.5 as

$$X_{\mathrm{Ge,(liquidus)},T} = \frac{\exp\left(\frac{-\Delta G^{\circ}_{m,\mathrm{Ge}}}{RT}\right)\left[1 - \exp\left(\frac{-\Delta G^{\circ}_{m,\mathrm{Si}}}{RT}\right)\right]}{\exp\left(\frac{-\Delta G^{\circ}_{m,\mathrm{Ge}}}{RT}\right) - \exp\left(\frac{-\Delta G^{\circ}_{m,\mathrm{Si}}}{RT}\right)}$$

and the equation of the solidus curve is obtained from Equation 10.4 as

$$X_{\mathrm{Ge,(solidus)},T} = \frac{1 - \exp\left(\frac{-\Delta G^{\circ}_{m,Si}}{RT}\right)}{\exp\left(\frac{-\Delta G^{\circ}_{m,Ge}}{RT}\right) - \exp\left(\frac{-\Delta G^{\circ}_{m,Si}}{RT}\right)}$$

The calculated liquidus and solidus curves are shown in comparison with the measured lines in Figure 10.32a.

Solution to Quantitative Problem 2b

The partial pressure of Si exerted by the solidus composition (and hence by the corresponding liquidus melt) at the temperature T is

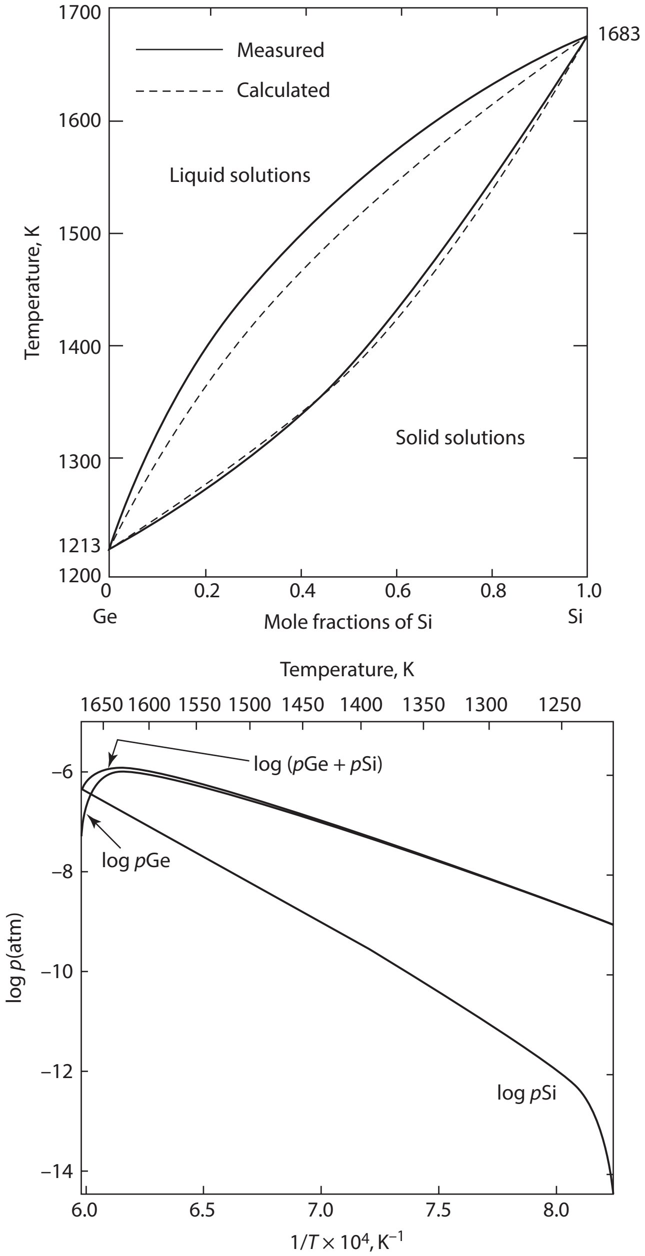

Figure 10.32 (a) The calculated phase diagram for the system Ge–Si assuming Raoultian behavior of the solid and liquid solutions. (b) The variations, with temperature, of the partial pressures of Ge and Si (and their sum) with composition along the liquidus line.

$$p_{\text{Si},T} = X_{\text{Si,(solidus)},T} \times p^{\circ}_{\text{Si},(s),T} \tag{i}$$

and the partial pressure of Ge exerted by the liquidus melt composition (and hence by the corresponding solidus) is

$$p_{\text{Ge},T} = X_{\text{Ge,(liquidus)},T} \times p^{\circ}_{\text{Ge},(l),T} \tag{ii}$$

Equations (i) and (ii), together with the sum of the partial pressures, are shown in Figure 10.32b. In Equation (i) the values of both $X_{\text{Si,(solidus)},T}$ and $p^{\circ}_{\text{Si},(s),T}$ increase with increasing liquidus temperature, and thus, the partial pressure of Si exerted by the liquidus composition increases from zero at 1213 K to the saturated vapor pressure of pure solid Si $\left(\log p^{\circ}_{Si,(s),1683\text{ K}} = -6.33\right)$ at 1685 K. In contrast, in Equation (ii), increasing the liquidus temperature causes an increase in $p^{\circ}_{\text{Ge},(l),T}$ and a decrease in $X_{\text{Ge,(liquidus)},T}$, and Figure 10.32b shows that, at lower liquidus temperatures, the influence of $p^{\circ}_{\text{Ge},(l),T}$ on the partial pressure of Ge predominates and the partial pressure initially increases with increasing liquidus temperature. However, with the continued increase in temperature along the liquidus line, the relative influence of the dilution of Ge increases, and the partial pressure of Ge passes through a maximum at the liquidus state $X_{\text{Ge}} = 0.193$, $T = 1621$ K before decreasing rapidly to zero at 1685 K. The maximum in the partial pressure of Ge causes a maximum in the total vapor pressure to occur at the liquidus state $X_{\text{Ge}} = 0.165$, $T = 1630$ K.

PROBLEMS

10.1 CaF_2 and MgF_2 are mutually insoluble in the solid state and form a simple binary eutectic system. Calculate the composition and temperature of the eutectic melt assuming that the liquid solutions are Raoultian. The actual eutectic occurs at $X_{\text{CaF}_2} = 0.45$ and $T = 1243$ K.

10.2 Gold and silicon are mutually insoluble in the solid state and form a eutectic system with a eutectic temperature of 636 K and a eutectic composition of $X_{\text{Si}} = 0.186$. Calculate the Gibbs free energy of the eutectic melt relative to (a) unmixed liquid Au and liquid Si, and (b) unmixed solid Au and solid Si.

$$\text{At 636 K } \Delta G^{\circ}_{m,Au} = 12{,}600\left[\frac{1338-636}{1338}\right] = 6{,}611\text{ J}$$

$$\text{and } \Delta G^{\circ}_{m,\text{Si}} = 50{,}200\left[\frac{1685-636}{1685}\right] = 30{,}943\text{ J}$$

a. $\Delta G^{\text{M}} = ab = -(0.186 \times 30{,}943 + 0.814 \times 6{,}611)\text{ J} = -11{,}140\text{ J}$
b. $\Delta G^{\text{M}} = 0$

10.3 Al_2O_3, which melts at 2324 K, and Cr_2O_3, which melts at 2538 K, form complete ranges of solid and liquid solutions. Assuming that $\Delta S^{\circ}_{m,\text{Cr}_2\text{O}_3} = \Delta S^{\circ}_{m,\text{Al}_2\text{O}_3}$ and that the solid and liquid solutions in the system Al_2O_3–Cr_2O_3 behave ideally, calculate

a. The temperature at which equilibrium melting begins when an alloy of $X_{Al_2O_3} = 0.5$ is heated
b. The composition of the melt which first forms
c. The temperature at which equilibrium melting is complete
d. The composition of the last-formed solid

10.4 $Na_2O{\cdot}B_2O_3$ and $K_2O{\cdot}B_2O_3$ form complete ranges of solid and liquid solutions and the solidus and liquidus show a common minimum at the equimolar composition and $T = 1123$ K. Calculate the molar Gibbs free energy of formation of the equimolar solid solution from solid $Na_2O{\cdot}B_2O_3$ at 1123 K, assuming that the liquid solutions are ideal.

10.5 SiO_2, which melts at 1723°C, and TiO_2, which melts at 1842°C, are immiscible in the solid state, and the SiO_2–TiO_2 binary system contains a monotectic equilibrium at 1794°C, at which temperature virtually pure TiO_2 is in equilibrium with two liquids containing mole fractions of SiO_2 of 0.04 and 0.76. If, for the purpose of simple calculation, it is assumed that the compositions of the two liquids are $X_{SiO_2} = 0.24$ and $X_{SiO_2} = 0.76$ and that the liquid solutions are regular in their behavior, what is the value of α_l and at what temperature does the liquid immiscibility gap disappear?

10.6 The binary system Ge–Si contains complete solid and liquid solutions. The melting temperatures are $T_{m,\text{Si}} = 1685$ K and $T_{m,\text{Ge}} = 1210$ K, and $\Delta H^\circ_{m,\text{Si}} = 50{,}200$ J. At 1200°C, the liquidus and solidus compositions are, respectively, $X_{\text{Si}} = 0.32$ and $X_{\text{Si}} = 0.665$. Calculate the value of $\Delta H^\circ_{m,\text{Ge}}$, assuming that

a. The liquid solutions are ideal.
b. The solid solutions are ideal.

Which assumption gives the better estimate? The actual value of $\Delta H^\circ_{m,\text{Ge}}$ at $T_{m,\text{Ge}}$ is 36,900 J.

10.7 CaO and MgO form a simple eutectic system with limited ranges of solid solubility. The eutectic temperature is 2370°C. Assuming that the solutes in the two solid solutions obey Henry's law with $\gamma^\circ_{\text{CaO}}$ in MgO = 12.88 and $\gamma^\circ_{\text{MgO}}$ in CaO = 6.23 at 2300°C, calculate the solubility of CaO in MgO and the solubility of MgO in CaO at 2300°C.

10.8* A metatectic binary phase diagram displays the following invariant transformation on cooling:

$$\beta \rightarrow \alpha + \text{L}$$

Sketch such a phase diagram and then draw free energy curves of mixing just below, at, and just above the invariant temperature.

10.9* The free energy of mixing of a regular solution is given by

$$\Delta G_{\text{mix}} = \alpha X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

$$\text{and } \alpha = 24{,}943 \text{ J/mole}$$

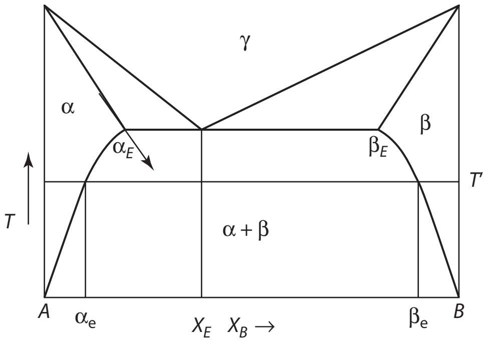

Figure 10.33 A eutectoid phase diagram showing the extension of the α/γ equilibrium curve into the α/β solvus.

a. Plot ΔG_{mix} versus X_B at 1400, 1500, and 1600 K.
b. Plot $\partial \Delta G_{\text{mix}} / \partial X_B$ versus X_B at the same temperatures as (a).
c. Determine the critical temperature for this alloy. Show your work.

10.10* A certain solid solution of A and B has a $\Delta G_{\text{mix}}^{\text{xs}}$ as follows:

$$\Delta G_{\text{mix}}^{\text{xs}} = \Delta G_{\text{mix}} - \Delta G_{\text{mix}}^{\text{id}} = X_B X_A [a_1 X_A + a_2 X_B] + RT[X_A \ln X_A + X_B \ln X_B]$$

Where:
a_1 = 12,500 J/mole
a_2 = 5,500 J/mole

a. Plot $\Delta G_{\text{mix}}^{\text{xs}}$ at $T = 500$ and 700 K.
b. Sketch the T versus X_B phase diagram of this alloy.
c. Determine the critical temperature and composition of this alloy.

10.11* The phase diagram of an alloy that has a eutectoid transformation is shown in Figure 10.33.

a. Sketch the Gibbs free energy curves for this alloy at $T = T'$.
b. Show that the α/γ solvus must enter the α/β two-phase field (as shown by the arrow).

10.12* A eutectoid phase diagram is shown in Figure 10.33. Draw the phase diagram that would result if for some reason it were impossible to form the α phase.

APPENDIX 10A

Here we derive equations for the phase diagram of a system which consists of ideal solid and ideal liquid solutions.

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* New problem in this edition

For equilibrium between the solid and liquid phases,

$$\Delta\bar{G}_A^M\left(\text{in the solid solution}\right) = \Delta\bar{G}_A^M\left(\text{in the liquid solution}\right) \qquad (10A.1)$$

and

$$\Delta\bar{G}_B^M\left(\text{in the liquid solution}\right) = \Delta\bar{G}_B^M\left(\text{in the solid solution}\right) \qquad (10A.2)$$

At any temperature T, these two conditions fix the solidus and liquidus compositions —that is, the position of the points of common tangency. From Equation 10.2:

$$\frac{\partial \Delta G_{(l)}^M}{\partial X_{A(l)}} = RT(\ln X_{A(l)} - \ln X_{B(l)}) - \Delta G_{m(B)}^{\circ}$$

Thus,

$$X_{B(l)}\frac{\partial \Delta G_{(l)}^M}{\partial X_{A(l)}} = RT(X_{B(l)}\ln X_{A(l)} - X_{B(l)}\ln X_{B(l)}) - X_{B(l)}\Delta G_{m(B)}^{\circ} \qquad (10A.3)$$

From Equation 9.33a:

$$\Delta\bar{G}_A^M(\text{in liquid solutions}) = \Delta G_{(l)}^M + X_{B(l)}\frac{\partial \Delta G_{(l)}^M}{\partial X_{A(l)}}$$

Thus, adding Equation 10.2 and 10A.3 gives

$$\Delta\bar{G}_A^M(\text{in liquid solutions}) = RT\ln X_{A(l)} \qquad (10A.4)$$

From Equation 10.3:

$$\frac{\partial \Delta G_{(s)}^M}{\partial X_{A(s)}} = RT(\ln X_{A(s)} - \ln X_{B(s)}) - \Delta G_{m(A)}^{\circ}$$

Thus,

$$X_{B(s)}\frac{\partial \Delta G_{(s)}^M}{\partial X_{A(s)}} = RT(X_{B(s)}\ln X_{A(s)} - X_{B(s)}\ln X_{B(s)}) - X_{B(s)}\Delta G_{m(A)}^{\circ} \qquad (10A.5)$$

Adding Equations 10.3 and 10A.5 gives

$$\Delta\bar{G}_A^M(\text{in solid solutions}) = \Delta G_{(s)}^M + X_{B(s)}\frac{\partial \Delta G_{(s)}^M}{\partial X_{A(s)}} = RT\ln X_{A(s)} - \Delta G_{m(A)}^{\circ} \qquad (10A.6)$$

Thus, from Equations 10A.1, 10A.4 and 10A.6:

$$RT\ln X_{A(l)} = RT\ln X_{A(s)} - \Delta G^{\circ}_{m(A)} \tag{10A.7}$$

Similarly, from Equations 10.2 and 9.33b:

$$\Delta\bar{G}^M_B\,(\text{in liquid solutions}) = \Delta G^M_{(l)} + X_{A(l)}\frac{\partial \Delta G^M_{(l)}}{\partial X_{B(l)}} = RT\ln X_{B(l)} + \Delta G^{\circ}_{m(B)} \tag{10A.8}$$

and from Equations 10.3 and 9.33b:

$$\Delta\bar{G}^M_B\,(\text{in solid solutions}) = \Delta G^M_{(s)} + X_{A(s)}\frac{\partial \Delta G_{(s)}}{\partial X_{B(s)}} = RT\ln X_{B(s)} \tag{10A.9}$$

Thus, from Equations 10A.2, 10A.8, and 10A.9:

$$RT\ln X_{B(l)} + \Delta G^{\circ}_{m(B)} = RT\ln X_{B(s)} \tag{10A.10}$$

The solidus and liquidus compositions are thus determined by Equations 10A.7 and 10A.10 as follows. Equation 10A.7 can be written as

$$X_{A(l)} = X_{A(s)}\exp\left(\frac{-\Delta G^{\circ}_{m(A)}}{RT}\right) \tag{10A.11}$$

and, noting that $X_B = 1 - X_A$, Equation 10A.10 can be written as

$$\left(1 - X_{A(l)}\right) = \left(1 - X_{A(s)}\right)\exp\left(\frac{-\Delta G^{\circ}_{m(B)}}{RT}\right) \tag{10A.12}$$

Combination of Equations 10A.11 and 10A.12 gives

$$X_{A(s)} = \frac{1 - \exp(-\frac{\Delta G^{\circ}_{m(B)}}{RT})}{\exp(-\frac{\Delta G^{\circ}_{m(A)}}{RT}) - \exp(-\frac{\Delta G^{\circ}_{m(B)}}{RT})} \tag{10A.13}$$

and

$$X_{A(l)} = \frac{\left[1 - \exp(-\frac{\Delta G^{\circ}_{m(B)}}{RT})\right]\exp(-\frac{\Delta G^{\circ}_{m(A)}}{RT})}{\exp(-\frac{\Delta G^{\circ}_{m(A)}}{RT}) - \exp(-\frac{\Delta G^{\circ}_{m(B)}}{RT})} \tag{10A.14}$$

If $c_{p,i(s)} = c_{p,i(l)}$, we get from Equation 10.1, for $i = A$ and B,

$$\Delta G^{\circ}_{m(i)} = \Delta H^{\circ}_{m(i)}\left[\frac{T_{m(i)} - T}{T_{m(i)}}\right]$$

Thus, the phase diagram for a system which forms ideal solid and liquid solutions is determined only by the melting temperatures and the molar heats of melting of the components.

APPENDIX 10B

Consider the application of Equation 10.12 to the calculation of the liquidus lines in a binary eutectic system. In the system Cd–Bi, the phase diagram for which is shown in Figure 10.21, cadmium is virtually insoluble in solid bismuth, and the maximum solubility of bismuth in solid cadmium is 2.75 mole percent at the eutectic temperature of 419 K. If the liquidus solutions are ideal, the Bi liquidus is obtained from Equation 10.12 as

$$\Delta G^{\circ}_{m(Bi)} = -RT \ln X_{\mathrm{Bi(liquidus)}}$$

$\Delta H^{\circ}_{m(\mathrm{Bi})} = 10{,}900$ J at $T_{m(\mathrm{Bi})} = 544$ K, and thus,

$$\Delta S^{\circ}_{m(\mathrm{Bi})} = \frac{10{,}900}{544} = 20.0 \text{ J/K at } 544 \text{ K}$$

The molar constant pressure heat capacities of solid and liquid bismuth vary with temperature as

$$c_{p,\mathrm{Bi}(s)} = 18.8 + 22.6\times10^{-3}T \text{ J/K}$$
$$c_{p,\mathrm{Bi}(l)} = 20 + 6.15\times10^{-3}T + 21.1\times10^{5}T^{-2} \text{ J/K}$$

Thus,

$$c_{p},_{\mathrm{Bi}(l)} - c_{p},_{\mathrm{Bi}(s)} = \Delta c_{p},_{\mathrm{Bi}} = 1.2 - 16.45\times10^{-3}T + 21.1\times10^{5}T^{-2}\mathrm{J/K}$$

and

$$\begin{aligned}\Delta G^{\circ}_{m(\mathrm{Bi})} &= \Delta H^{\circ}_{m(\mathrm{Bi}),544} + \int_{544}^{T} \Delta c_{p,\mathrm{Bi}} dT - T\left(\Delta S^{\circ}_{m(\mathrm{Bi}),544} + \int_{544}^{T} \frac{\Delta c_{p,\mathrm{Bi}}}{T} dT\right)\\ &= 16{,}560 - 23.79T - 1.2\ln T + 8.225\times10^{-3}T^{2} - 10.22\times10^{5}T^{-1_{544}} \qquad (10\mathrm{B}.1)\\ &= -RT\ln X_{\mathrm{Bi(liquidus)}}\end{aligned}$$

or

$$\ln X_{\mathrm{Bi(liquidus)}} = -\frac{1992}{T} + 2.861 + 0.144\ln T - 9.892\times10^{-4}T + 1.269\times\frac{10^{5}}{T^{2}}$$

This equation is drawn as the broken line (i) in Figure 10.21.

Similarly, if the small solid solubility of Bi in Cd is ignored,

$$\Delta G^{\circ}_{m(\mathrm{Cd})} = -RT \ln X_{\mathrm{Cd(liquidus)}}$$

$\Delta H^{\circ}_{m(\mathrm{Cd})} = 6400$ J at $T_{m,\mathrm{Cd}}$ = 594 K, and thus, $\Delta S^{\circ}_{m(\mathrm{Cd})} = 6400/594 = 10.77$ J/K at 594 K. The constant-pressure molar heat capacities are

$$c_{p,\mathrm{Cd}(l)} = 22.2 + 12.3 \times 10^{-3} T \text{ J/K}$$

and

$$c_{p,\mathrm{Cd}(l)} = 29.7 \text{ J / K}$$

Thus,

$$c_{p,\mathrm{Cd}(l)} - c_{p,\mathrm{Cd}(s)} = \Delta c_{p,\mathrm{Cd}} = 7.5 - 12.3 \times 10^{-3} T \text{ J/K}$$

$$\begin{aligned} \Delta G^{\circ}_{m(\mathrm{Cd})} &= \Delta H^{\circ}_{m(\mathrm{Cd}),594} + \int_{594}^{T} \Delta c_{p,\mathrm{Cd}} dT - T\left(\Delta S^{\circ}_{m(\mathrm{Cd}),594} + \int_{594}^{T} \frac{\Delta c_{p,\mathrm{Cd}}}{T} dT \right) \\ &= 4155 + 37.32T - 7.5T \ln T + 6.15 \times 10^{-3} T^2 \text{ J} \qquad (10\mathrm{B}.2) \\ &= -RT \ln X_{\mathrm{Cd(liquidus)}} \end{aligned}$$

or

$$\ln X_{\mathrm{Cd(liquidus)}} = -\frac{495}{T} - 4.489 + 0.90 \ln T - 7.397 \times 10^{-4} T$$

which is drawn as the broken line (ii) in Figure 10.21. Lines (i) and (ii) intersect at the composition of the Raoultian liquid which is simultaneously saturated with Cd and Bi and at 406 K, which would be the eutectic temperature if the liquids were ideal. The actual liquidus lines lie above those calculated, and the actual eutectic temperature is 419 K. From Equation 10B.1, $\Delta G^{\circ}_{m(\mathrm{Bi}),419\text{ K}} = 2482$ J, and from Equation 10B.2, $\Delta G^{\circ}_{m(\mathrm{Cd}),419\text{ K}} = 1898$ J. Thus, from Equation 10.11, in the actual eutectic melt,

$$a_{\mathrm{Bi}} = \exp\left(-\frac{2482}{8.3144 \times 419} \right) = 0.49$$

and

$$a_{\mathrm{Cd}} = \exp\left(-\frac{1898}{8.3144 \times 419} \right) = 0.58$$

The actual eutectic composition is $X_{Cd} = 0.55$, $X_{Bi} = 0.45$, and thus, the activity coefficients are

$$\gamma_{Bi} = \frac{0.49}{0.45} = 1.09$$

and

$$\gamma_{Cd} = \frac{0.58}{0.55} = 1.05$$

Thus, positive deviations from Raoultian ideality cause an increase in the liquidus temperatures.

PART III

Reactions and Transformations of Phases

CHAPTER 11

Reactions Involving Gases

11.1 INTRODUCTION

In Chapter 8, it was seen that the absence of interatomic forces between the atoms of ideal gases causes the enthalpy of mixing of ideal gases to be zero. This situation represents one extreme of a range of possible situations. Toward the other extreme of this range is the situation in which gases are mixed which exhibit marked chemical affinity for one another. For example, considerable heat is released when gaseous hydrogen and oxygen are mixed in the presence of a catalyst. The thermodynamics of such a system can be treated in either of two ways:

1. The mixture can be considered to be a highly nonideal mixture of H_2 and O_2, the thermodynamic equilibrium state of which, at a given temperature and pressure, can be defined in terms of the fugacities of the components H_2 and O_2.
2. It can be considered that the H_2 and O_2 have reacted with one another to some extent to produce the product species H_2O.

In the latter case, if the pressure of the system is low enough, the equilibrium state at the given temperature can be defined in terms of the partial pressures exerted by the three species, H_2, O_2, and H_2O, occurring in the system. Although both treatments are thermodynamically equivalent, the latter is the more convenient and practical.

As with any constant-pressure, constant-temperature system, the equilibrium state is that in which the Gibbs free energy of the system has its minimum possible value. If the gases which are present initially in the system react to form distinct product species, the total change in the Gibbs free energy of the system comprises a contribution arising from

- The change in Gibbs free energy due to the chemical reaction
- The mixing of the appearing product gases with the remaining reactant gases

Knowledge of the variation of this total change in the Gibbs free energy with composition (which ranges from the pure unmixed reactant gases to the pure unmixed product gases) allows for the determination of the equilibrium state in any system of reactive gases. This determination is facilitated by the introduction of the equilibrium constant for the reaction, and it will be seen that the relation between this constant and the standard Gibbs free energy change for the reaction is one of the more important relationships in reaction equilibrium thermodynamics.

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

Consider the reaction

$$A_{(g)} + B_{(g)} = 2C_{(g)}$$

occurring at constant temperature T and constant pressure P. At any instant during the reaction, the total Gibbs free energy of the system is

$$G' = n_A\bar{G}_A + n_B\bar{G}_B + n_C\bar{G}_C \tag{11.1}$$

where n_A, n_B, and n_C are, respectively, the numbers of moles of A, B, and C present in the reaction system at that instant, and $\bar{G}_A$, $\bar{G}_B$, and $\bar{G}_C$ are, respectively, the partial molar Gibbs free energies of A, B, and C in the gas mixture which occurs at that instant. It is of interest to determine the values of n_A, n_B, and n_C which minimize the value of G' in Equation 11.1, since this state of minimum Gibbs free energy is the equilibrium state of the system at the given temperature and pressure. That is, once the chemical reaction between A and B has proceeded to the extent that the Gibbs free energy of the system has been minimized, the reaction at the macroscopic level appears to stop. On the microscopic level, however, reaction equilibrium occurs when the rate of the chemical reaction proceeding from right to left equals that of the reaction proceeding from left to right. This is a *dynamic equilibrium*: that is, reactions still occur when the system is at equilibrium.

The stoichiometry of the reaction allows the numbers of moles of all the species present at any instant to be expressed in terms of the number of moles of any one of the species. Starting with 1 mole of A and 1 mole of B (i.e., 2 moles of gas), as 1 atom of A reacts with 1 atom of B to produce 2 molecules of C, then, at any time during the reaction,

$$n_A = n_B$$

and

$$n_C = 2 - n_A - n_B = 2(1 - n_A)$$

Equation 11.1 can thus be written as

$$G' = n_A\bar{G}_A + n_A\bar{G}_B + 2(1 - n_A)\bar{G}_C$$

From Equation 8.15:

$$\bar{G}_i = G_i^\circ + RT \ln P + RT \ln X_i$$

and

$$X_A = \frac{n_A}{2}, \qquad X_B = \frac{n_A}{2}, \qquad X_C = \frac{2(1-n_A)}{2} = (1-n_A)$$

substitution of which gives

$$\begin{aligned} G' = {} & n_A(G_A^\circ + G_C^\circ + 2G_C^\circ) + 2G_C^\circ + 2RT \ln P \\ & + 2RT\left[n_A \ln \left(\frac{n_A}{2}\right) + (1-n_A) \ln (1-n_\mathrm{A}) \right] \end{aligned}$$

or

$$\begin{aligned} G' - 2G_C^\circ \quad & = n_A(-\Delta G^\circ) + 2\ RT \ln P \\ & + \ 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1-n_A)\ln(1-n_\mathrm{A}) \right] \end{aligned} \tag{11.2}$$

The term $\Delta G^\circ = 2G_C^\circ - G_A^\circ - G_B^\circ$ is the *standard Gibbs free energy change* for the chemical reaction at the temperature T.

The standard Gibbs free energy change for any reaction is the difference between the sum of the Gibbs free energies of the reaction products in their standard states and the sum of the Gibbs free energies of the reactants in their standard states. In the present case, ΔG° is the difference between the Gibbs free energy of 2 moles of C at 1 atm pressure and the temperature T, and 1 mole of A and 1 mole of B, each at 1 atm pressure and the temperature T. If the total pressure of the system is 1 atm, then Equation 11.2 simplifies to

$$G' - 2G_C^\circ = n_A(-\Delta G^\circ) + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1-n_A)\ln(1-n_A) \right] \tag{11.3}$$

The left-hand side of Equation 11.3 is the difference between the Gibbs free energy of the 2-mole system when $n_A = n_B$ and the Gibbs free energy of the system when it consists of 2 moles of C. This difference is determined by two factors:

1. The *change* in the Gibbs free energy due to the chemical reaction—that is, due to the disappearance of the reactants and the appearance of the products, given by the first term on the right-hand side of Equation 11.3
2. The *decrease* in the Gibbs free energy caused by mixing of the gases, given by the second term on the right-hand side of Equation 11.3

Figure 11.1 is drawn for the reaction.

$$A_{(g)} + B_{(g)} = 2C_{(g)}$$

at 500 K and 1 atm pressure. ΔG°_{500} for the reaction is taken as –5000 J. If the reference for the Gibbs free energy is arbitrarily chosen as $(G^\circ_A + G^\circ_B) = 0$, then $2G^\circ_C = -5000$ J. In Figure 11.1, the ordinate $\Delta G'$ is plotted as the difference between the Gibbs free energy of the system containing n_A moles of A and the Gibbs free energy of the system comprising 1 mole of A and 1 mole of B before the mixing of A and B occurs. Thus, the point L ($n_A = 1$, $n_B = 1$ before mixing) is located at $\Delta G' = 0$, and the point Q ($n_C = 2$) is located at $\Delta G' = -5000$ J.

The point M represents the decrease in the Gibbs free energy due to mixing of 1 mole of A and 1 mole of B before any chemical reaction between the two occurs; that is, from Equation 8.20:

$$\begin{aligned} \Delta G'(L \to M) &= \sum_i n_i RT \ln\left(\frac{p_i}{P_i}\right) \\ &= RT\left[n_A \ln\left(\frac{p_A}{P_A}\right) + n_B \ln\left(\frac{p_B}{P_B}\right)\right] \end{aligned}$$

But $n_A = n_B = 1$, and

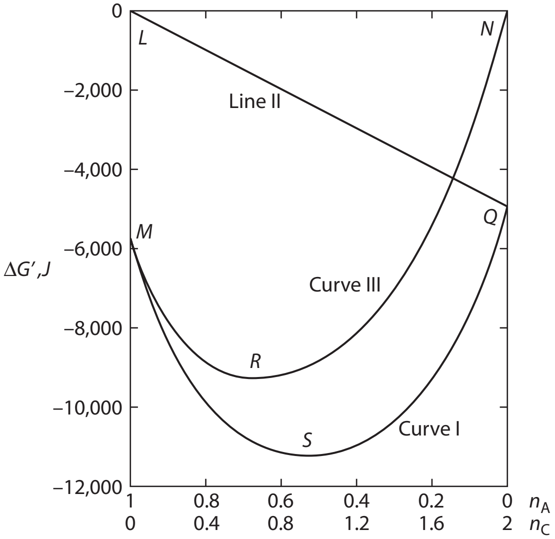

Figure 11.1 The variations of the contributions to the decrease in the Gibbs free energy due to chemical reaction (line II), the contribution to the decrease in the Gibbs free energy due to gas mixing (curve III), with the extent of the reaction $A_{(g)} + B_{(g)} = 2C_{(g)}$, for which $\Delta G^\circ = -5000$ J at 500 K. Curve I is the sum of curves II and III.

$$p_A = p_B = P_{\text{mixture}} = 1$$

in which case

$$p_A = p_B = \frac{1}{2}$$

Thus,

$$\begin{aligned} \Delta G = (L \to M) &= 8.3144 \times 500 \times 2 \times \ln 0.5 \\ &= -5763 \text{ J} \end{aligned}$$

Substituting this into Equation 11.3 we obtain

$$G' + 5000 = \left(1 \times 5000\right) - 5763 \text{ J}$$

and hence,

$$G' = -5763 \text{ J}$$

Thus, at M,

$$\Delta G' = G' - (G_A^\circ + G_B^\circ) = -5763 \text{ J}$$

Curve I represents the variation of $\Delta G'$ with n_A. It is obtained as the sum of line II (given by the first term on the right-hand side of Equation 11.3, the decrease in Gibbs free energy due to chemical reaction) and curve III (given by the second term on the right-hand side of Equation 11.3, the decrease in Gibbs free energy due to gas mixing). It can be seen that the magnitude of the chemical reaction contribution to the decrease in the Gibbs free energy of the system increases linearly with increasing n_C, but the magnitude of the *contribution to the change* in the total Gibbs free energy due to gas mixing is greatest at the composition R. R occurs at that composition of the gas mixture which permits maximum randomization of the system. Further chemical reaction, which takes the composition of the system beyond R, decreases the magnitude of the gas-mixing contribution, since further increase in n_C, at the expense of n_A and n_B, decreases the randomness of the system. Eventually, the composition S is reached, in which state the sum of the two contributions to the *decrease* in the Gibbs free energy is a *maximum*. If chemical reaction continued beyond S, then, since the decrease in line II is smaller than the increase in curve III, the total Gibbs free energy of the system would increase. The composition S is thus that at which the Gibbs free energy of the system has its minimum value and is hence the equilibrium state.

The position of the minimum in curve I is fixed by the criterion that, at the minimum,

$$\left(\frac{\partial G'}{\partial n_A}\right)_{T,P} = 0$$

and since

$$G' = n_A\bar{G}_A + n_A\bar{G}_B + 2(1-n_A)\bar{G}_C$$

and including the use of the Gibbs–Duhem equation,*

$$\left(\frac{\partial G'}{\partial n_A}\right) = \bar{G}_A + \bar{G}_B - 2\bar{G}_C = 0$$

That is, the criterion for reaction equilibrium is

$$\bar{G}_A + \bar{G}_B = 2\bar{G}_C \tag{11.4}$$

Equation 11.4 can be written as

$$G_A^\circ + RT\ln p_A + G_B^\circ + RT\ln p_B = 2G_C^\circ + 2RT\ln p_C \tag{11.5}$$

where p_A, p_B, and p_C are, respectively, the partial pressures of A, B, and C *which occur at reaction equilibrium*. Rearrangement of Equation 11.5 gives

$$2G_C^\circ - G_A^\circ - G_B^\circ = -RT\ln\frac{p_C^2}{p_A p_B}$$

or

$$\Delta G^\circ = -RT\ln\left(\frac{p_C^2}{p_A p_B}\right) \tag{11.6}$$

The quotient of the equilibrium partial pressure of the reactants and products occurring as the logarithmic term in Equation 11.6 is termed the *equilibrium constant for the reaction*, Kp; that is,

$$\left(\frac{p_C^2}{p_A p_B}\right)_{\text{eq}} = K_p \tag{11.7}$$

and hence,

$$\Delta G^\circ = -RT\ln K_p \tag{11.8}$$

---

[*] Equation 9.19a: $n_A d\bar{G}_A + n_B d\bar{G}_B + n_C d\bar{G}_C = 0$.

Since ΔG° is a function only of temperature, it follows from Equation 11.8 that K_p is a function only of temperature.

For the example used in Figure 11.1,

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = \frac{5000}{8.3144 \times 500} = 1.203$$

Therefore,

$$K_p = 3.329$$

Now,

$$K_p = \frac{p_C^2}{p_A p_B} = \frac{X_C^2 P^2}{X_A P X_B P} = \frac{X_C^2}{X_A X_B}$$

and since $X_A = X_B = n_A/2$ and $X_C = (1 - n_A)$,

$$= \frac{(1-n_A)^2}{\left(\frac{n_A^2}{4}\right)} = 3.329$$

Thus,

$$n_A = 0.523 \ \left(\text{the other solution}, n_A = 11.4, \text{ is nonphysical}\right)$$

The minimum in curve I in Figure 11.1 occurs at $n_A = n_B = 0.523$ and

$$n_C = 2 - 2x(0.523) = 0.954$$

The chemical reaction $A + B = 2C$ has proceeded to 47.7% completion.

If the temperature T was such that ΔG° for the reaction was zero, there would be no chemical reaction contribution to $\Delta G'$, and the variation of $\Delta G'$ with n_A would be given by curve III in Figure 11.1; that is, the criterion for reaction equilibrium would be the maximization of the configurational entropy of the system, which occurs at the composition R. From Equation 11.8, if $\Delta G^\circ = 0$, then $K_P = 1$, and thus,

$$1 = \frac{4(1-n_A)^2}{n_A^2} \quad \text{and} \quad n_A = \frac{2}{3}$$

The minimum in curve III occurs at $n_A = n_B = n_C = 2/3$, and thus, maximum entropy in the system occurs when all three species are present in equal amounts.

It is important to note that the minimum in curve I in Figure 11.1, in representing the equilibrium state of the system at $P = 1$ atm and 500 K, is the only point on curve I which has any significance within the scope of classical equilibrium thermodynamics. The point S is the only state on the curve I which lies on the equilibrium surface in P-T–composition space for the fixed values of $P = 1$ atm and $T = 500$ K. Any change in P and/or T changes the curves II and III, which in turn produces a "new" curve I. This new curve I has a different minimum and hence represents a new equilibrium state. This is discussed further in the following section.

11.3 THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

The position of the minimum in curve I in Figure 11.1 is determined by the difference between the lengths of LM and NQ. The length LM is the decrease in the Gibbs free energy caused by mixing of the gases *before the reaction begins*, and the length NQ is the standard Gibbs free energy change, ΔG°, for the reaction. The lengths of both of these lines are dependent on temperature.

$$LM = 2RT \ln 0.5$$

$$NQ = \Delta G^\circ = f\left(T\right)$$

The effect of temperature on the composition at which the minimum occurs in curve I (and hence on the value of K_p) thus depends on the relative effects of temperature on the lengths of LM and NQ. For given reactants, the length of LM increases linearly with temperature, and the variation of the length NQ with temperature is determined by the sign and magnitude of the standard entropy change for the reaction according to

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\Delta S^\circ$$

Increasing the temperature increases the length of LM, and if ΔS° is negative, increasing T must decrease ΔG°, hence decreasing the length of NQ. Thus, the position of the minimum in the curve I shifts to the left, which indicates that K_p decreases with increasing temperature.

The exact variation of Kp with temperature is obtained from consideration of the Gibbs–Helmholtz equation (Equation 5.38):

$$\left[\frac{\partial(\Delta G^\circ / T}{\partial T}\right]_P = -\frac{\Delta H^\circ}{T^2}$$

From Equation 11.8, $\Delta G^\circ = -RT \ln K_p$, *and since* ΔG° *is only a function of* T,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{11.9}$$

or

$$\frac{d \ln K_p}{d\,(1/T)} = -\frac{\Delta H^\circ}{R} \tag{11.10}$$

Equation 11.10 is known as the *van't Hoff equation* (Jacobus Henricus van't Hoff, 1852–1911). The equation shows that the effect of temperature on K_p is determined by the *sign* and *magnitude* of ΔH° for the reaction.

- If ΔH° is positive, the reaction is endothermic and K_p increases with increasing temperature.
- If ΔH° is negative, the reaction is exothermic and K_p decreases with increasing temperature.

Integration of Equation 11.10 requires knowledge of the temperature dependence of ΔH°, which, as was seen in Chapter 6, depends on the value of Δc_p for the reaction.

The van't Hoff equation enables the determination of ΔH° from a plot of ln K_P versus the inverse of absolute temperature. The slope of the plot is $-(\Delta H^\circ/R)$ (Figure 11.2).

The direction of the variation of K_p with temperature can be obtained from the application of Le Chatelier's principle (Henry Louis Le Chatelier, 1850–1936). If thermal energy is added to a system at reaction equilibrium, then the equilibrium is displaced in that direction which involves the absorption of heat. Consider the simple gaseous reaction

$$Cl_2 = 2Cl$$

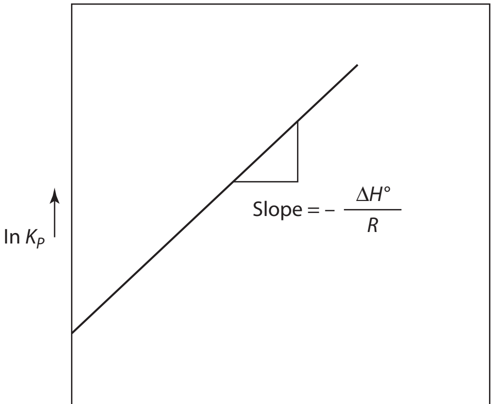

Figure 11.2 The variation of the ln (K_P) versus 1/T of an exothermic reaction (a van't Hoff plot).

This reaction is endothermic and hence has a positive value of ΔH°. Thus, the equilibrium constant, $K_p = p_{\text{Cl}}^2/p_{\text{Cl}_2}$, increases with increasing temperature; that is, the equilibrium shifts in that direction which involves the absorption of thermal energy. Conversely, if the reaction were written as

$$2\text{Cl} = \text{Cl}_2$$

then, since the reaction has a negative value of ΔH°, $K_P = p_{\text{Cl}_2}/p_{\text{Cl}}^2$ decreases with increasing temperature; that is, the equilibrium shifts in that direction which involves the absorption of thermal energy. In both cases, an increase in temperature increases p_{Cl} and decreases p_{Cl_2}.

11.4 THE EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT

The equilibrium constant, K_p, as defined by Equation 11.7, is independent of pressure. This is a consequence of the fact that ΔG° is the difference between the Gibbs free energies of the pure products (each at unit pressure) and the Gibbs free energies of the pure reactants (each at unit pressure), which is, by definition, independent of pressure. However, if reaction equilibrium is expressed in terms of the number of moles of species present rather than in terms of the partial pressures of the species present, the constant is dependent on the total pressure if the chemical reaction involves a change in the total number of moles present.

Consider again the reaction $\text{Cl}_2 = 2\text{Cl}$. Completion of this reaction causes a doubling of the number of moles present, and the effect of a change in pressure can again be obtained by the application of Le Chatelier's principle. If the pressure exerted on a system at reaction equilibrium is increased, then the equilibrium shifts in that direction which tends to decrease the pressure exerted by the system; that is, it shifts in that direction which decreases the number of moles present. Thus, if the pressure exerted on the Cl–Cl_2 system is increased, the equilibrium will shift toward the Cl_2 side, as, thereby, the total number of moles present will be decreased to accommodate the increased pressure. Specifically, the effect of pressure on the reaction equilibrium expressed in terms of the number of moles present (or in terms of mole fractions) can be seen as follows:

$$\begin{aligned} K_p &= \frac{p_{\text{Cl}}^2}{p_{\text{Cl}_2}}, \text{ which is independent of pressure} \\ &= \frac{X_{\text{Cl}}^2 P^2}{X_{\text{Cl}_2} P} = \frac{X_{\text{Cl}}^2 P}{X_{\text{Cl}_2}} = K_x P \end{aligned}$$

where K_x is the equilibrium constant expressed in terms of the mole fractions. Thus, if the pressure is increased, then K_x decreases in order to maintain K_p constant, and the decrease in K_x is achieved by the reaction equilibrium shifting toward the Cl_2 side such that X_{Cl} decreases and X_{Cl_2} increases.

In the case of the reaction $A + B = 2C$, the system at all times contains 2 moles of gas, and thus, the reaction equilibrium, expressed in terms of the mole fractions, is independent of pressure; that is,

$$K_p = \frac{p_C^2}{p_A p_B} = \frac{X_C^2 P^2}{(X_A P)(X_B P)} = \frac{X_C^2}{X_A X_B} = K_x$$

This can also be seen from Equation 11.2, since, if $P \neq 1$, then the effect of the nonzero term $2RT \ln P$ is the raising or lowering of curve I in Figure 11.1 without affecting the position of the minimum with respect to the composition axis.

The magnitude of the effect of a change in pressure on the value of K_x depends on the magnitude of the change in the number of moles present in the system, occurring as a result of the chemical reaction. For the general reaction

$$aA + bB = cC + \mathrm{d}D$$

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{X_C^c X_D^d}{X_A^a X_B^b} \frac{P^c P^d}{P^a P^b} = K_x P^{(c+d-a-b)}$$

which shows that K_x is independent of the total pressure only if $c + d = a + b$.

11.5 REACTION EQUILIBRIUM AS A COMPROMISE BETWEEN ENTHALPY AND ENTROPY

Since the Gibbs free energy of a system is defined as

$$G' = H' - TS'$$

low values of G are obtained with low values of H and large values of S. It was seen in the discussion of one-component systems in Chapter 7 that equilibrium occurs as the result of a compromise between enthalpy and entropy considerations. A similar discussion is now made concerning chemical reaction equilibria.

Consider again the reaction $Cl_2 = 2Cl$. This reaction has a positive value of ΔH° (ΔH° is the thermal energy required to break Avogadro's number of Cl–Cl bonds) and has a positive value of ΔS° (2 moles of chlorine atoms are produced from 1 mole of chlorine molecules). Thus,

- The system occurring as Cl atoms has a high value of H and a high value of S.
- The system occurring as Cl_2 molecules has a low value of H and a low value of S.

The minimum value of G thus occurs somewhere between the two extreme states. This compromise between the enthalpy and the entropy is analogous to the compromise between the contributions of the chemical reaction and the mixing of gases to the decrease in Gibbs free energy shown in Figure 11.1.

For the reaction $A + B = 2C$, Equation 11.3 can be written as

$$
\begin{aligned}
G' - 2G_C^\circ &= n_A(-\Delta H^0) + n_A(T\Delta S^\circ) + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1-n_A)\ln(1-n_A)\right] \\
&= \left[n_A(-\Delta H^\circ)\right] + T\left\{n_A \Delta S^\circ + 2R\left[n_A \ln\left(\frac{n_A}{2}\right) + (1-n_A)\ln(1-n_A)\right]\right\}
\end{aligned}
\tag{11.11}
$$

The term in the first brackets is the enthalpy contribution to the change in the Gibbs free energy. The second term on the right-hand side of the equation is the entropy contribution, with $n_A \Delta S^\circ$ being the entropy change caused by the chemical reaction and $2R[n_A \ln (n_A/2) + (1 - n_A) \ln (1 - n_A)]$ being the entropy change caused by gas mixing. In the example in Section 11.2, ΔG° equaled –5000 J at 500 K. Let it be that $\Delta H^\circ = -2500$ J and $\Delta S^\circ = 5$ J/K, in which case Figure 11.3 can be drawn from Figure 11.1. In Figure 11.3, the $\Delta H'$ line is the first term on the right-hand side of Equation 11.11 and the $T\Delta S'$ curve is the second term. The sum of these two gives $G' - 2G_C^\circ$, the scale of which is given on the left-hand ordinate of Figure 11.3. The scale on the right-hand ordinate of the figure is $\Delta G'$, where, as before, the reference zero of Gibbs free energy is chosen as $G_A^\circ + G_B^\circ = 0$, such that $\Delta G' = G'$ (i.e., the scale is displaced by $2G_C^\circ = -5000$ J). On this scale, the $\Delta G'$ curve in Figure 11.3 is identical with curve I in Figure 11.1. It can be seen that the minimum in the $\Delta G'$ curve is determined as a compromise between the minimum value of H' at $n_A = 0$

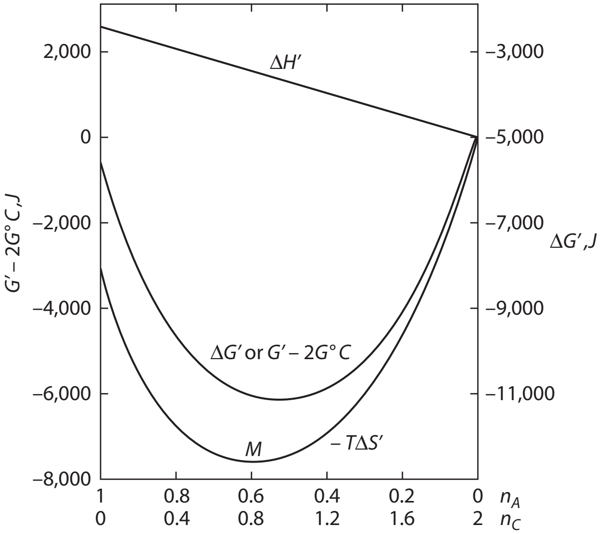

Figure 11.3 The variations at 500 K of $\Delta H'$, $-T\Delta S'$, and $\Delta G'$ with the extent of reaction $A_{(g)} + B_{(g)} = 2C_{(g)}$, for which $\Delta G^\circ = -2500 - 5T$.

and the maximum value of $T\Delta S'$ at $n_A = 0.597$ (the point M in Figure 11.2). If the temperature is increased, then the $T\Delta S'$ term becomes relatively more important, and hence the equilibrium value of n_A increases (the minimum in the $\Delta G'$ curve shifts to the left). Thus, K_p decreases with increasing temperature in accordance with Equation 11.9 for negative ΔH°.

The effect of temperature on the $\Delta G'$ curve is illustrated in Figure 11.4, in which curves are drawn for the reaction $A + B = 2C$ at 500, 1000, and 1500 K. It is assumed that Δc_p for the reaction is zero, in which case ΔH° and ΔS° are independent of temperature. Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$,

$$\Delta G^\circ_{500} = -2{,}500 - (500 \times 5) = -5{,}000 \text{ J} \quad K_{p,500} = 3.329$$

$$\Delta G^\circ_{1000} = -2{,}500 - (1{,}000 \times 5) = -7{,}500 \text{ J} \quad K_{p,1000} = 2.465$$

$$\Delta G^\circ_{1500} = -2{,}500 - (1{,}500 \times 5) = -10{,}000 \text{ J} \quad K_{p,1500} = 2.229$$

The equilibrium values of n_A at 500, 1000, and 1500 K are thus, respectively, 0.523, 0.560, and 0.572. Thus, increasing the temperature shifts the minimum to the left, thereby increasing the amount of A and B in equilibrium.

Although K_p is constant at constant temperature, note that an infinite set of partial pressures of reactants and products correspond to the fixed value of K_p. If the reaction involves three species, then an arbitrary choice of the partial pressures of

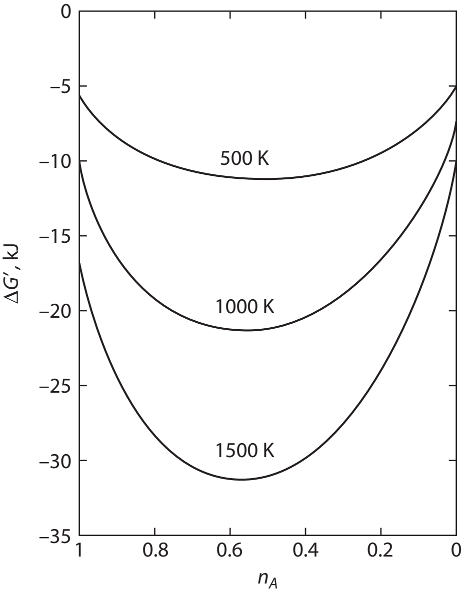

Figure 11.4 The effect of temperature on the equilibrium state of the reaction $A_{(g)} + B_{(g)} = 2C_{(g)}$, for which $\Delta G^\circ = -2500 - 5T$ J.

two of the species uniquely fixes the equilibrium partial pressure of the third. This can also be shown by the Gibbs' equilibrium phase rule (see Qualitative Problem 2 in Section 11.10).

11.6 REACTION EQUILIBRIUM IN THE SYSTEM $SO_{2(g)}$–$SO_{3(g)}$–$O_{2(g)}$

Consider the equilibrium reaction of the oxidation of sulfur dioxide to sulfur trioxide:

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} = SO_3(g) \tag{11.12}$$

The standard Gibbs free energy change for this reaction is

$$\Delta G^\circ = -94{,}600 + 89.37T \text{ J}$$

Thus, at 1000 K,

$$\Delta G^\circ_{1000} = -5230 \text{ J}$$

$$\ln K_p = \frac{5230}{8.3144 \times 1000} = 0.629$$

and

$$K_p = 1.876 = \frac{p_{SO_3}}{p_{SO_2} p_{O_2}^{1/2}}$$

Consider the reaction between 1 mole of SO_2 gas at 1 atm pressure and ½ mole of O_2 gas at 1 atm pressure to form an equilibrium mixture of SO_2, SO_3, and O_2 at 1 atm pressure and 1000 K. From the stoichiometry of the chemical reaction given by Equation 11.12, x moles of SO_3 are formed from the reaction of x moles of SO_2 and ½x moles of O_2. Thus, any reacting mixture contains x moles of SO_3, (1 – x) moles of SO_2, and ½(1 – x) moles of O_2; that is,

	SO_2	+	$\frac{1}{2}O_2$	→	SO_3
initially,	1		$\frac{1}{2}$		0
upon reaction,	$1-x$		$\frac{1}{2}-\frac{1}{2}x$		x

The total number of moles in the system, n_T, is

$$n_T = 1 - x + \frac{1}{2} - \frac{1}{2}x + x = \frac{1}{2}(3 - x)$$

and, since

$$p_i = \frac{n_i}{n_T} P$$

then

$$p_{SO_2} = \frac{2(1-x)P}{(3-x)}, \quad p_{O_2} = \frac{(1-x)P}{(3-x)}, \quad p_{SO_3} = \frac{2xP}{(3-x)}$$

Thus,

$$K_p^2 = \frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2}} = \frac{(3-x)x^2}{(1-x)^3 P}$$

or

$$(1-PK_p^2)x^3 + (3PK_p^2 - 3)x^2 - 3PK_p^2 x + PK_p^2 = 0 \tag{11.13}$$

which, with $P = 1$ and $K_p = 1.876$, gives $x = 0.463$. Thus, at equilibrium, there are 0.537 moles of SO_2, 0.269 moles of O_2, and 0.463 moles of SO_3, such that

$$p_{SO_2} = \frac{2(1-0.463)}{(3-0.463)} = 0.423 \text{ atm}$$

$$p_{O_2} = \frac{(1-0.463)}{(3-0.463)} = 0.212 \text{ atm}$$

and

$$p_{SO_3} = \frac{2 \times 0.463}{(3-0.463)} = 0.365 \text{ atm}$$

As a check,

$$K_p = \frac{0.365}{0.423 \times 0.212^{1/2}} = 1.874$$

The composition of the equilibrium gas is thus 42.3% SO_2, 21.2% O_2, and 36.5% SO_3.

11.6.1 The Effect of Temperature

Since ΔH° for the reaction given by Equation 11.12 is negative (–94,600 J), and Le Chatelier's principle predicts that a decrease in temperature at constant pressure shifts the equilibrium in that direction which involves an evolution of heat, decreasing the temperature at constant pressure causes the equilibrium to shift toward the SO_3 side. At 900 K,

$$\Delta G^{\circ}_{900} = -14{,}167 \text{ J}$$

$$\ln K_p = \frac{14{,}167}{8.3144 \times 900} = 1.893$$

and thus,

$$K_p = 6.64$$

Substituting K_p = 6.64 and P = 1 atm into Equation 11.13 gives x = 0.704, and thus,

$$p_{SO_2} = 0.258 \text{ atm}, p_{O_2} = 0.129 \text{ atm}, p_{SO_3} = 0.613 \text{ atm}$$

As a check,

$$K_p = \frac{0.613}{0.258 \times 0.129^{1/2}} = 6.64$$

Thus, of the total number of moles present,

- SO_2 constitutes 25.8%, which is a decrease from 42.3% at 1000 K.
- O_2 constitutes 12.9%, which is a decrease from 21.2% at 1000 K.
- SO_3 constitutes 61.3%, which is an increase from 36.5% at 1000 K.

It is seen that a decrease in temperature has shifted the equilibrium toward the SO_3 side.

11.6.2 The Effect of Pressure

Although K_p is independent of pressure, Le Chatelier's principle predicts that an increase in total pressure at constant temperature shifts the equilibrium in that direction which involves a decrease in the number of moles in the system—that is, toward the SO_3 side. Consider the equilibrium mixture at P = 10 atm and T = 1000 K. Substituting P = 10 and K_p = 1.876 into Equation 11.13 gives x = 0.686, in which case $n_{SO_2} = 0.314, n_{O_2} = 0.157, n_{SO_3} = 0.686$. Thus,

$$p_{SO_2} = \frac{2(1-0.686)\times 10}{(3-0.686)} = 2.714 \text{ atm}$$

$$p_{O_2} = \frac{(1-0.686)\times 10}{(3-0.686)} = 1.357 \text{ atm}$$

and

$$p_{SO_3} = \frac{2\times 0.686 \times 10}{(3-0.686)} = 5.929 \text{ atm}$$

As a check,

$$K_p = \frac{5.929}{2.714 \times 1.357^{1/2}} = 1.875$$

Of the total number of moles present

- SO_2 constitutes 27.1%, which is a decrease from 42.3% at $P = 1$ atm.
- O_2 constitutes 13.75%, which is a decrease from 21.2% at $P = 1$ atm.
- SO_3 constitutes 59.29%, which is an increase from 36.5% at $P = 1$ atm.

Thus, it is seen that an increase in pressure has shifted the equilibrium toward the SO_3 side.

11.6.3 The Effect of Changes in Temperature and Pressure

In order to simultaneously vary the temperature and the pressure in such a manner that the numbers of moles of the three gaseous species present remain constant, Equation 11.13 indicates that the variation must be such that the term PK_p^2 remains constant, where

$$K_p = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(\frac{94{,}600}{8.3144 \cdot T}\right) \cdot \exp\left(\frac{-89.37}{8.3144}\right)$$

It is apparent that, by mixing SO_2 gas and SO_3 gas, an equilibrium mixture with a known partial pressure of O_2 can be produced. For example, consider that it was required to have an SO_3–SO_2–O_2 mixture at 1 atm total pressure in which $p_{O_2} = 0.1$ atm. To obtain this gas mixture, SO_3 and SO_2, both at 1 atm pressure, would be mixed in the molar ratio $SO_2/SO_3 = a$ and allowed to equilibrate. If a moles of SO_2 and 1 mole of SO_3 are mixed, then from the stoichiometry of Equation 11.12, x moles of SO_3 would decompose to form x moles of SO_2 and ½x moles of O_2, such that, at equilibrium, the number of moles present would be

$$\begin{array}{lccccc} & SO_2 & + & \frac{1}{2}O_2 & \rightarrow & SO_3 \\ \text{initially,} & a & & 0 & & 1 \\ \text{upon reaction,} & a + x & & \frac{1}{2}x & & 1 - x \end{array}$$

with

$$n_T = a + x + \frac{1}{2}x + 1 - x = \frac{1}{2}(2a + 2 + x)$$

In this gas mixture,

$$p_{O_2} = \frac{n_{O_2}}{n_T} = \frac{x}{2a + 2 + x} P$$

which, for $P = 1$ and $p_{SO_2} = 0.1$, gives $a = 4.5x - 1$. Also,

$$K_p^2 = \frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2}} = \frac{(1-x)^2(2a+2+x)}{(a+x)^2 xP}$$

At 1000 K, $K_p = 1.876$. Thus, substituting for a in terms of x and taking $K_p^2 = 3.519$ gives

$$96.45x^3 - 18.709x^2 - 6.481x = 0$$

or, since $x \neq 0$,

$$96.45x^2 - 18.709x - 6.481 = 0$$

which has the solution $x = 0.374$. Thus,

$$a = (4.5 \times 0.374) - 1 = 0.683$$

$$p_{O_2} = \frac{xP}{2a+2+x} = \frac{0.374}{(2\times 0.683)+2+0.374} = 0.1 \text{ atm}$$

$$p_{SO_3} = \frac{2(1-x)}{2a+2+x} = \frac{2(1-0.374)}{(2\times 0.683)+2+0.374} = 0.335 \text{ atm}$$

and

$$p_{SO_2} = \frac{2(a+x)}{2a+2+x} = \frac{2(0.683+0.374)}{(2\times 0.683)+2+0.374} = 0.565 \text{ atm}$$

In the equilibrium mixture, $p_{SO_2}/p_{SO_3} = 1.7$, compared with $p_{SO_2}/p_{SO_3} = a = 0.683$ in the initial mixture. As a check,

$$K_p = \frac{0.355}{0.565 \times 0.1^{1/2}} = 1.875$$

If it had been required to have $p_{O_2} = 0.212$ atm (the equilibrium value of p_{O_2} in an equilibrated gas at 1 atm pressure of initial composition 1 mole of SO_2 + ½ mole of O_2), then the solution of the stoichiometric condition would have given $a = 0$, which indicates that pure SO_3 at 1000 K and 1 atm pressure decomposes to the same equilibrium gas mixture as that formed from an initial mixture of 1 mole of SO_2 + ½ mole of O_2 at 1 atm. Thus, 0.212 atm is the maximum value of p_{O_2} which can be produced in an SO_2–SO_3 mixture at 1000 K and 1 atm total pressure.

11.7 EQUILIBRIUM IN H_2O–H_2 AND CO_2–CO MIXTURES

H_2O–H_2 and CO_2–CO gas mixtures are used when it is required that the partial pressure of oxygen in a gas phase be fixed at a very low value. For example, if it were required to have a gaseous atmosphere containing a partial pressure of oxygen of 10^{-10} atm, then such an oxygen potential can be obtained with relative ease by establishing the equilibrium

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} = \mathrm{H_2O}$$

for which

$$\Delta G^{\circ} = -247{,}500 + 55.85T \text{ J}$$

From Equation 11.8,

$$\ln K_p = \frac{247{,}500}{8{,}3144 \cdot T} - \frac{55.85}{8.3144}$$

If it is required to have an atmosphere containing $p_{O_2} = 10^{-10}$ atm at T = 2000 K, then, at this temperature,

$$\begin{aligned} \ln K_p &= \frac{247{,}500}{8.3144 \cdot 2000} - \frac{55.85}{8.3144} \\ &= 8.167 \end{aligned}$$

Therefore,

$$K_p = 3.521 \times 10^3 = \frac{p_{\mathrm{H_2O}}}{p_{H_2} p_{\mathrm{O_2}}^{1/2}}$$

and with $p_{O_2} = 10^{-10}$ atm,

$$\frac{p_{H_2O}}{p_{H_2}} = 3.521 \times 10^3 \times 10^{-5} = 3.521 \times 10^{-2}$$

Thus, in the H_2–H_2O gas mixture, if $p_{H_2} = 1$ atm, then p_{H_2O} must be 0.0352 atm.

The saturated vapor pressure of liquid water at 27.0°C is found from

$$\log p \text{ (atm)} = -\frac{2900}{T} - 4.65 \cdot \log T + 19.732$$

to be 0.0352. Thus, the required gas mixture can be produced by bubbling hydrogen gas at 1 atm pressure through pure liquid water at 27.0°C to saturate it with water vapor. The establishment of reaction equilibrium at 2000 K gives $p_{O_2} = 10^{-10}$ atm in the gas.

Similarly, the partial pressure of oxygen in a gaseous atmosphere can be determined by establishing the reaction

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} = \mathrm{CO_2}$$

The standard Gibbs free energy change for the reaction

$$\mathrm{CO}_{(g)} = \tfrac{1}{2}\mathrm{O}_{2(g)} + C_{(s)}$$

is

$$\Delta G^\circ = 111{,}700 + 87.65T \text{ J}$$

and that for the reaction

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} = \mathrm{CO}_{2(g)}$$

is

$$\Delta G^\circ = -394{,}100 - 0.84T \text{ J}$$

Summation of the standard Gibbs free energy changes gives

$$\Delta G^\circ = -282{,}400 + 86.81T \text{ J}$$

for the reaction

$$\mathrm{CO}_{(g)} + \tfrac{1}{2}\mathrm{O}_{2(g)} = \mathrm{CO}_{2(g)}$$

Thus,

$$\ln K_p = \frac{282{,}400}{8.3144 \cdot T} - \frac{86.81}{8.3144}$$

If it were required to have $p_{O_2} = 10^{-20}$ atm at 1000 K, then

$$\ln K_p = \frac{282{,}400}{8.3144 \cdot 1000} - \frac{86.81}{8.3144} = 23.52$$

Therefore,

$$K_p = 1.646 \times 10^{10} = \frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}} p_{\mathrm{O_2}}^{1/2}} = \frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}} \cdot 10^{-10}}$$

and so

$$\frac{p_{CO_2}}{p_{CO}} = 1.646$$

If the total pressure P = 1 atm, then, since $p_{CO_2} + p_{CO} = 1$, the partial pressure, $p_{CO_2} = 1.646(1 - p_{CO_2}) = 0.622$ atm and p_{CO} = 0.378. The required mixture is produced by mixing CO_2 and CO in the volume ratio 1.561/1—that is, 62.2 volume percent CO_2 and 37.8 volume percent CO.

In both of the preceding equilibria, the oxygen pressure in the equilibrated gas is so small that the p_{H_2}/p_{H_2O} and p_{CO_2}/p_{CO} ratios in the equilibrated gases are negligibly different from the corresponding ratios in the initial mixtures. The equality of the ratio of the volume percentages with the ratio of the partial pressures in a gas mixture can be demonstrated as follows. Consider a cm^3 of gas A at 1 atm pressure and b cm^3 of gas B at 1 atm pressure being mixed at constant pressure (and hence at constant total volume, $a + b$). The number of moles of $A = n_A = (1 + a)/RT = a/RT$, and the number of moles of $B = n_B = (1 \times b)/RT = b/RT$. Therefore, in the mixture,

$$p_A = \frac{n_A RT}{V'} = \frac{n_A RT}{(a+b)}$$

and

$$p_B = \frac{n_B RT}{(a+b)}$$

Thus,

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{a}{b} = \frac{\text{volume percentage of } A}{\text{volume percentage of } B}$$

11.8 SUMMARY

1. The equilibrium state of the reaction $aA + bB = cC + dD$ is that in which $a\overline{G}_A + b\overline{G}_B = c\overline{G}_C + d\overline{G}_D$. The equilibrium state of the reaction is thus determined by the value of ΔG° for the reaction and is quantified by the equilibrium constant K_p, where $K_p = (p_C^c p_D^d / p_A^a p_B^b)_{eq}$ and the standard state for each reactant and product gas is the pure gas at 1 atm pressure.
2. ΔG° and K_p are related by $\Delta G^\circ = -RT \ln K_p$. This relation is one of the more powerful equations in chemical thermodynamics and will be used extensively in subsequent chapters. For increasingly negative values of ΔG°, K_p becomes increasingly greater than unity, and, conversely, for increasingly positive values of ΔG°, K_p becomes increasingly less than unity.
3. Since ΔG° is a function only of temperature, K_p is a function only of temperature, and the dependence of K_p on temperature is determined by the value of ΔH° for the reaction; that is,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_p$$

and hence,

$$\ln K_p = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

or

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

or

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

Thus, for an exothermic reaction, K_p decreases with increasing temperature, and for an endothermic reaction, K_p increases with increasing temperature.

4. Since $p_i = X_i P$ in an ideal gas mixture, the equilibrium constant can be written in terms of the mole fractions; that is,

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{X_C^c X_D^d}{X_A^a X_B^b} P^{(c+d-a-b)} = K_x P^{(c+d-a-b)}$$

Although K_p is, by definition, independent of pressure, K_x is independent of pressure only if $(c + d - a - \mathrm{b}) = 0$—that is, if the gas mixture contains a constant number of moles in all states along the reaction coordinate. If the forward progression of the reaction decreases the number of moles present (i.e., if $[c + d - a - b] < 0$), then an increase in pressure increases the value of K_x; conversely, if $(c + d - a - b) > 0$, an increase in pressure decreases the value of K_x. The dependence of K_x on pressure and the dependence of K_p on temperature are examples of Le Chatelier's principle.

5. If ΔH° and ΔS° are known for the reaction, the following can be stated.
   - If $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, the reaction will occur spontaneously at high temperatures.
   - If $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, the reaction will occur spontaneously at low temperatures.
   - If $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the reaction will not occur spontaneously.
   - If $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, the reaction will occur spontaneously at all temperatures.

11.9 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 11

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Catalyst
Chemical affinity
Dynamic equilibrium
Equilibrium constant K_P
Equilibrium constant K_X
Gaseous reaction
Gibbs free energy change due to chemical reaction
Le Chatelier's principle
Reactants and products
Standard Gibbs free energy change
Stoichiometry

11.10 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

In Figure 11.2, the natural log of K_P was plotted against $1/T$. Its slope was found to be $-\Delta H^0/R$. What is the value of its intercept with the ordinate axis?

Solution to Qualitative Problem 1

Earlier we wrote $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K_p$.

Hence, $\ln K_p = -(\Delta H^\circ/RT) + (\Delta S^\circ/R)$. In a plot of $\ln K_P$ versus $1/T$, the intercept is $\Delta S^\circ/R$.

This value may be positive or negative depending on the magnitude of the $\ln K_P$ intercept.

If the intercept of $\ln K_P > 1$, the standard entropy change is positive, and if the intercept of $\ln K_P < 1$, the standard entropy change of the reaction is < 0.

Qualitative Problem 2

Use the Gibbs equilibrium phase rule to show that the gaseous reaction

$$A + B = 2C$$

has only 2 degrees of freedom at a fixed temperature.

Solution to Qualitative Problem 2

The Gibbs equilibrium phase rule is written as

$$\Phi + \mathcal{F} = C + 2$$

For $\Phi = 1$ and fixed temperature, we get

$$\mathcal{F} = C$$

In this case, the number of independent components is reduced by one since there is one reaction that exists among the components. Thus, $\mathscr{F} = 2$. Only 2 partial pressure can be chosen arbitrarily.

11.11 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Consider the partial decomposition of gaseous P_4 according to

$$P_{4(g)} = 2P_{2(g)}$$

Calculate

a. The temperature at which $X_{P_4} = X_{P_2} = 0.5$ at a total pressure of 1 atm
b. The total pressure at which $X_{P_4} = X_{P_2} = 0.5$ at 2000 K

given that, for the reaction $P_{4(g)} = 2P_{2(g)}$,

$$\Delta G^{\circ} = 225{,}400 + 7.90T\ln T - 209.4T \text{ J}$$

Solution to Quantitative Problem 1

a. Since $\Delta G^{\circ} = 225{,}400 + 7.90T \ln T - 209.4T$ J,

$$\ln K_p = \frac{-27{,}109}{T} - 0.95\ln T + 25.18 \tag{i}$$

Partial decomposition of 1 mole of P_4 produces $(1 - x)$ moles of P_4 and $2x$ moles of P_2. Thus, for $X_{P_4} = (1-x)/(1+x) = 0.5, x = 1/3$, we can write

$$p_{P_4} = \left(\frac{1-\frac{1}{3}}{1+\frac{1}{3}}\right)P = 0.5P$$

and

$$p_{P_2} = \left(\frac{2\times\frac{1}{3}}{1+\frac{1}{3}}\right)P = 0.5P$$

Thus, with $X_{P_4} = X_{P_2} = 0.5$ and the pressure P,

$$K_p = \frac{p_{P_2}^2}{p_{P_4}} = 0.5P \tag{ii}$$

With P = 1 atm, Equation (i) gives

$$\ln K_p = \ln(0.5) = \frac{-27{,}109}{T} - 0.95\ln T + 25.18$$

which has the solution T = 1429 K. Thus, at P = 1 atm and T = 1429 K, $X_{P_2} = X_{P_4} = 0.5$ in a P_4–P_2 mixture.

b. From Equations (i) and (ii):

$$K_{p,2000\text{ K}} = 81.83 = 0.5P$$

which gives P = 163.6 atm. Thus, at P = 163.6 atm and T = 2000 K, $X_{P_4} = X_{P_2} = 0.5$ in the mixture.

The variations of X_{P_4} and X_{P_2} with temperature in an equilibrated P_4–P_2 mixture at P = 1 atm and at P = 163.3 atm are shown in Figure 11.5. Since the dissociation of P_4 is endothermic, increasing the temperature at constant pressure shifts the equilibrium toward P_2, and since the dissociation increases the number of moles present, increasing the pressure at constant temperature shifts the equilibrium toward P_4.

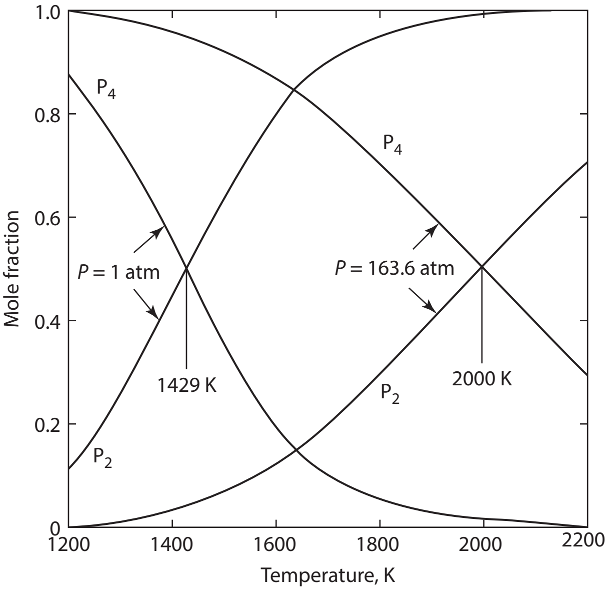

Figure 11.5 The variations of the mole fractions of P_2 and P_4 with temperature in an equilibrated P_2–P_4 mixture at P = 1 atm and at P = 163.6 atm.

Quantitative Problem 2

Consider the cracking of gaseous ammonia according to the reaction

$$2NH_{3(g)} = N_{2(g)} + 3H_{2(g)} \qquad \text{(i)}$$

under the following conditions:

a. Constant total pressure
b. Constant volume at 400°C

Solution to Quantitative Problem 2

a. The standard Gibbs free energy change for the reaction given by Equation (i) is

$$\Delta G^\circ = 87{,}030 - 25.8T\ln T - 31.7T \text{ J}$$

Therefore,

$$\Delta G^\circ_{673\text{ K}} = -47{,}370 \text{ J and } K_{p,673\text{ K}} = 4748$$

From the stoichiometry of the reaction, partial decomposition of 1 mole of NH_3 produces $3x$ moles of H_2, x moles of N_2, and $(1 - 2x)$ moles of NH_3. Thus, for

	$2NH_3$	$\rightarrow$	N_2	+	$3H_2$
initially,	1		0		0
upon decomposition,	$1-2x$		x		$3x$

and $n_T = 1 - 2x + x + 3x = 1 + 2x$ moles. Thus,

$$p_{H_2} = \frac{3x}{1+2x}P, \quad p_{N_2} = \frac{x}{1+2x}P, \quad \text{and} \quad p_{NH_3} = \frac{1-x}{1+2x}P$$

such that

$$K_{p,673\text{ K}} = \frac{p^3_{H_2}p_{N_2}}{p^2_{NH_3}} = \frac{27x^4P^2}{(1+2x)^2(1-2x)^2} \tag{ii}$$

Using the identity $(1 - y)(1 + y) = 1 - y^2$, Equation (ii) can be written as

$$K_p = \frac{27x^4P^2}{[1-(2x)^2]^2}$$

or

$$K_p^{1/2} = \frac{5.196x^2P}{(1-4x^2)}$$

Thus, for a constant total pressure of 1 atm,

$$\left(4748\right)^{1/2}\left(1-4x^2\right) = 5.196x^2$$

which has the solution $x = 0.4954$. Thus, at equilibrium,

$$p_{H_2} = \frac{3x}{1+2x} = 0.7465 \text{ atm}$$
$$p_{N_2} = \frac{x}{1+2x} = 0.2488 \text{ atm}$$

and

$$p_{NH_3} = \frac{1-2x}{1+2x} = 0.0047 \text{ atm}$$

in which state, 99.08% of the NH_3 has decomposed.

An alternative approach to the problem is as follows. From the stoichiometry of the reaction, at all times

$$p_{H_2} = 3p_{N_2} \tag{iii}$$

and

$$P = p_{NH_3} + p_{N_2} + p_{H_2} \tag{iv}$$

Eliminating p_{NH_3} and p_{H_2} from Equations (iii) and (iv) and substituting into Equation (ii) gives

$$K_p = \frac{27p_{N_2}^4}{(P-4p_{N_2})^2}$$

or

$$K_p^{1/2} = \frac{(27)^{1/2}p_{N_2}^2}{(P-4p_{N_2})}$$

with $P = 1$ atm,

$$(4784)^{1/2}(1-4p_{N_2}) = (27)^{1/2}p_{N_2}^2$$

which gives

$$p_{N_2} = 0.2488 \text{ atm}$$
$$p_{H_2} = 3p_{N_2} = 0.7464 \text{ atm}$$

and

$$p_{NH_3} = 1 - p_{H_2} - p_{N_2} = 0.0048 \text{ atm}$$

b. Now consider that the decomposition occurs at constant volume. As the decomposition reaction increases the number of moles of gas from 1 to (1 + 2*x*), the reaction at constant *P* increases the volume of the gas by the factor (1 + 2*x*). From Le Chatelier's principle, an increase in pressure shifts the equilibrium in that direction which decreases the number of moles of gas present—that is, in the direction $3H_2 + N_2 \rightarrow 2NH_3$. Thus, the extent of equilibrium decomposition of ammonia at constant volume will be less than that occurring at constant pressure and will cause an increase in pressure.

As before,

$$p_{H_2} = \frac{3x}{1+2x}P'$$

$$p_{N_2} = \frac{x}{1+2x}P'$$

and

$$p_{NH_3} = \frac{1-2x}{1+2x}P' \tag{v}$$

where P' is the pressure of the reacting mixture. Before decomposition begins, the 1 mole of NH_3 obeys the relation $PV = RT$. The decomposition reaction, at constant V and T, increases the number of moles of gas to $(1 + 2x)$ and hence increases the total pressure of the gas to P', where

$$P'V = (1 + 2x)RT$$

Therefore,

$$V = \text{constant} = \frac{RT}{P} = \frac{(1+2x)RT}{P'}$$

such that, in Equation (v), the original pressure of NH_3 at volume V before decomposition started is equal to $P'/(1 + 2x)$. Thus, for an original pressure of $P = 1$ atm, at equilibrium,

$$p_{H_2} = 3x$$

$$p_{N_2} = x$$

and

$$p_{NH_3} = 1 - 2x$$

Hence,

$$K_p = \frac{27x^4}{(1-2x)^2}$$

or

$$K_p^{1/2} = (4784)^{1/2} = \frac{(27)^{1/2}x^2}{(1-2x)}$$

which has the solution $x = 0.4909$. Thus,

$$\begin{aligned} p_{H_2} &= 3x = 1.4727 \text{ atm} \\ p_{N_2} &= x = 0.4909 \text{ atm} \\ p_{NH_3} &= 1 - 2x = 0.0182 \text{ atm} \\ P &= \sum_i p_i = 1.9819 = 1 + 2x \end{aligned}$$

in which state, 98.18% of the NH_3 has decomposed.

It can be shown that the yield of NH_3 formed by reaction between H_2 and N_2 is maximized when the reactants H_2 and N_2 are mixed in the molar ratio 3/1. In the mixture, $P = p_{H_2} + p_{N_2} + p_{NH_3}$, and, at reaction equilibrium, let it be that

$$p_{H_2} = ap_{N_2}$$

Thus,

$$p_{NH_3} = P - (a+1)p_{N_2}$$

or

$$p_{N_2} = \frac{P - p_{NH_3}}{a+1} \quad \text{and} \quad p_{H_2} = \frac{a(P - p_{NH_3})}{(a+1)}$$

and hence,

$$\begin{aligned} K_p = \frac{p^2_{NH_3}}{p^3_{H_2}p_{N_2}} &= \frac{p^2_{NH_3}}{[a(P - p_{NH_3})/(a+1)]^3[(P - p_{NH_3})/(a+1)]} \\ &= \frac{p^2_{NH_3}(a+1)^4}{a^3(P - p_{NH_3})^4} \end{aligned}$$

It now must be shown that p_{NH_3} has its maximum value when $a = 3$; that is,

$$\frac{dp_{NH_3}}{da} = 0 \quad \text{when} \quad a = 3$$

The derivative is most easily obtained by taking the logarithms of Equation (vi):

$$\ln K_p + 3\ln a + 4\ln a(P - p_{NH_3}) = 2\ln p_{NH_3} + 4\ln(a+1)$$

and differentiating to obtain

$$\left[\frac{3}{a} - \frac{4}{(1+a)}\right]da = \left[\frac{2}{p_{NH_3}} + \frac{4}{(P - p_{NH_3})}\right]dp_{NH_3}$$

Thus, $dp_{NH_3}/da = 0$ requires that $3/a = 4/(1+a)$, or $a = 3$.

The stoichiometry of the reaction shows that, for the ratio p_{H_2}/p_{N_2} to have the value 3 in the equilibrium mixture, the reactants H_2 and N_2 must be mixed in the ratio 3/1.

PROBLEMS

11.1 A gas mixture of 50% CO, 25% CO_2, and 25% H_2 (by volume) is fed to a furnace at 900°C. Determine the composition of the equilibrium $CO–CO_2–H_2–H_2O$ gas if the total pressure of the gas in the furnace is 1 atm.

11.2 How much heat is evolved when 1 mole of SO_2 and ½ mole of O_2, each at 1 atm pressure, react to form the equilibrium $SO_3–SO_2–O_2$ mixture at 1000 K and 1 atm pressure?

11.3 A $CO_2–CO–H_2O–H_2$ gas mixture at a total pressure of 1 atm exerts a partial pressure of oxygen of 10^{-7} atm at 1600°C. In what ratio were the CO_2 and H_2 mixed to produce the gas with this oxygen pressure?

11.4 Lithium bromide vapor dissociates according to $LiBr_{(g)} \rightarrow Li_{(g)} + ½Br_{2,(g)}$. At what temperature does the partial pressure of Li reach the value of 10^{-5} atm when the gas is heated at a constant total pressure of 1 atm?

11.5 When SO_3 is decomposed at the constant pressure P and $T = 1000$ K, the partial pressure of O_2 in the equilibrium gas is 0.05 atm. What is the pressure *P?* If the pressure of this equilibrated gas is increased to 1 atm, to what value must the temperature be decreased to produce a gas mixture in which $p_{O_2} = 0.05$ atm?

11.6 For the dissociation of nitrogen according to

$$N_2 = 2N$$

$$\Delta G^\circ = 945{,}000 - 114.9T\text{J}$$

calculate

a. The equilibrium partial pressure of N in nitrogen gas at 3000 K and a total pressure of 1 atm

b. The total pressure of the gas, at 3000 K, at which the partial pressure of N_2 is 90% of the total pressure

11.7 Ammonia gas is heated to 300°C. At what total pressure is the mole fraction of N_2 in the equilibrium gas mixture equal to 0.2? Calculate the standard enthalpy change and the standard entropy change for the reaction

$$\frac{3}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} = NH_{3(g)}$$

at 300°C.

11.8 By establishing the equilibrium

$$PCl_{5(g)} = PCl_{3(g)} + Cl_{2(g)}$$

at 500 K in a mixture of PCl_5 and PCl_3, a gas is obtained at 1 atm total pressure in which the partial pressure of Cl_2 is 0.1 atm. In what ratio were PCl_5 and PCl_3 mixed to obtain this equilibrium gas?

11.9 Air and hydrogen are mixed in the ratio 1/4 and are heated to 1200 K. Calculate the partial pressures of H_2 and O_2 in the equilibrium gas at 1 atm pressure and at 10 atm pressure. Air contains 21 volume percent O_2.

11.10 One mole of each of hydrogen, iodine vapor, and HI gas are allowed to react at 1500 K and $P = 1$ atm. Calculate the mole fractions of H_2, I_2, and HI in the equilibrium mixture. The temperature is then changed to that value at which p_{HI} in the equilibrated gas is five times p_{H_2}. What is this temperature?

11.11* Consider the reduction of magnetite by CO to form pure iron:

$$Fe_3O_4(s) + 4CO(g) = 3Fe(s) + 4CO_2(g)$$

Calculate the partial pressure of CO and CO_2 in terms of the equilibrium constant K_P for the reaction.

11.12* It is known that at 300 K, the value of K_P for a certain reaction is 10^{12}. For the reaction, ΔH° is 100 kJ/mole.

a. Determine if this reaction is favorable at 800 K and estimate K_P (800K). Explain.
b. The actual value of K_P (800) is 35. Explain any discrepancy from your estimate.

11.13* Sketch the natural log of K_P versus $1/T$ for the following cases:

a. $\Delta H^\circ < 0$ $\Delta S^\circ < 0$
b. $\Delta H^\circ < 0$ $\Delta S^\circ > 0$
c. $\Delta H^\circ > 0$ $\Delta S^\circ > 0$
d. $\Delta H^\circ > 0$ $\Delta S^\circ < 0$

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* New problem in this edition

CHAPTER 12

Reactions Involving Pure Condensed Phases and a Gaseous Phase

12.1 INTRODUCTION

The criterion for equilibrium in a gaseous reaction system was discussed in Chapter 11. The question now is, how is the situation changed if one or more of the reactants or products of the reaction occurs as a condensed phase? In this chapter, we consider condensed phases that are of pure species—that is, are of fixed composition. Many practical systems occur in this category: for example, the reaction of pure metals with gaseous elements to form pure metal oxides, sulfides, halides, and so on. Questions of interest include

1. What is the maximum oxygen pressure which can be tolerated in a gaseous atmosphere without oxidation of a given metal occurring at a given temperature?
2. To what temperature must a given carbonate be heated in a gaseous atmosphere of given partial pressure of carbon dioxide to cause the decomposition of the carbonate?

The first question is of interest in any of the many annealing processes that are performed in the laboratory or industrial plants. The second is of interest in, for example, the production of lime from limestone.

In such systems, complete equilibrium entails the establishment of

- Phase equilibrium among the individual condensed phases and the gas phase
- Reaction equilibrium among the various species present in the gas phase

Since phase equilibrium is established when the pure condensed phases exert their saturated vapor pressures, which are uniquely fixed when the temperature of the system is fixed, then the only pressures which can be varied at constant temperature are those of the species which exist only in the gas phase. The unique variations, with temperature, of the saturated vapor pressures of pure condensed-phase species and the relative insensitivity of the Gibbs free energies of condensed phases to changes in pressure considerably simplify the thermodynamic treatment of reaction equilibria in systems containing both gaseous and pure condensed phases.

12.2 REACTION EQUILIBRIUM IN A SYSTEM CONTAINING PURE CONDENSED PHASES AND A GAS PHASE

Consider the reaction equilibrium between a pure solid metal M, its pure oxide* MO, and oxygen gas at the temperature T and the pressure P:

$$M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$$

Here we assume that the oxygen is insoluble in the solid metal and that MO is stoichiometric.

Both the metal M and the oxide MO are in equilibrium with their vapor species in the gas phase, as is required by the criterion for phase equilibrium; that is,

$$\bar{G}_{M}(\text{in the gas phase}) = G_{M}(\text{in the solid metal phase})$$

and

$$\bar{G}_{MO}(\text{in the gas phase}) = G_{MO}(\text{in the solid oxide phase})$$

Thus, the reaction equilibrium

$$M_{(g)} + \frac{1}{2}O_{2(g)} = MO_{(g)}$$

is established in the gas phase. From Equation 11.6, the criterion for this reaction equilibrium to occur at the temperature T is

$$G^{\circ}_{MO(g)} - \frac{1}{2}G^{\circ}_{O_2(g)} - G^{\circ}_{M(g)} = -RT\ln\frac{p_{MO}}{p_M p_{O_2}^{1/2}} \tag{12.1}$$

or

$$\Delta G^{\circ} = -RT\ln\frac{p_{MO}}{p_M p_{O_2}^{1/2}}$$

where ΔG° is the difference between the Gibbs free energy of 1 mole of *gaseous* MO *at 1 atm pressure* and the sum of the Gibbs free energies of ½ mole of oxygen gas at 1 atm pressure and 1 mole of *gaseous* M *at 1 atm pressure*, all at the temperature T. Since M and MO are present in the system as pure solids, phase equilibrium requires that p_{MO} in Equation 12.1 be the saturated vapor pressure of solid MO at the temperature T, and that p_M be the saturated vapor pressure of solid M at the temperature T. Thus, the values of p_{MO} and p_M in the gas phase are uniquely fixed by the temperature T, and so the value of p_{O_2} in Equation 12.1, at which reaction equilibrium

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* By *pure oxide*, it is meant that there is no third element dissolved in it. It acts as a single component.

is established, is fixed at the temperature *T*. As stated previously, phase equilibrium in the system requires that

$$\bar{G}_{\mathrm{M}}(\text{in the gas}) = G_{\mathrm{M}}(\text{in the solid metal phase}) \tag{12.2}$$

and

$$\bar{G}_{\mathrm{MO}}(\text{in the gas phase}) = G_{\mathrm{MO}}(\text{in the solid oxide phase}) \tag{12.3}$$

Equation 12.2 can be written as

$$G^{\circ}_{\mathrm{M}(g)} + RT\ln p_{\mathrm{M}(g)} = G^{\circ}_{\mathrm{M}(s)} + \int_{P=1}^{P=p_{\mathrm{M}(g)}} V_{\mathrm{M}(s)}dP \tag{12.4}$$

and Equation 12.3 can be written as

$$G^{\circ}_{\mathrm{MO}(g)} + RT\ln p_{\mathrm{MO}(g)} = G^{\circ}_{\mathrm{MO}(s)} + \int_{P=1}^{P=p_{\mathrm{MO}(g)}} V_{\mathrm{MO}}dP \tag{12.5}$$

Consider Equation 12.4.

- $G^{\circ}_{\mathrm{M}(s)}$ is the molar Gibbs free energy of solid M under a pressure of 1 atm at the temperature *T*.
- The integral $\int_{P=1}^{P=p_{\mathrm{M}(g)}} V_{\mathrm{M}(s)}dP$ is the effect of a change in pressure from $P = 1$ atm to $P = P$ on the value of the molar Gibbs free energy of solid M at the temperature *T* (where $V_{\mathrm{M}(s)}$ is the molar volume of the solid metal at the pressure *P* and temperature *T*).

In the following, it is shown that the value of the integral is negligible compared with the other values in Equation 12.4, and hence Equation 12.4 can be written as

$$G^{\circ}_{\mathrm{M}(g)} + RT\ln p_{\mathrm{M}(g)} = G^{\circ}_{\mathrm{M}(s)} \tag{12.4a}$$

As an example to show this is the case, consider iron as a typical metal at a temperature of 1000°C. The saturated vapor pressure of solid iron at 1000°C is 6×10^{-10} atm, and thus, the term $RT \ln p_{M(g)}$ has the value $8.3144 \times 1273 \times \ln(6 \times 10^{-10}) = -224{,}750$ J. The molar volume of solid iron at 1000°C is 7.34 cm^3, which in the range 0–1 atm is independent of pressure. The value of the integral for $P = 6 \times 10^{-10}$ atm is -7.34×1 cm^3·atm $= -0.74$ J. It is thus seen that $G^{\circ}_{\mathrm{Fe}(g)}$ at 1000°C is much larger in value than $G^{\circ}_{\mathrm{Fe}(s)}$ at 1000°C, which is to be expected in view of the large metastability of the iron vapor at 1 atm pressure and a temperature of 1000°C with respect to the solid. Since the value of the integral (–0.74 J), is small compared with –224,750 J, Equation 12.4 can be written as Equation 12.4a.

As a consequence of the negligible effect of pressure on the Gibbs free energy of a condensed phase (when the pressure is in the range 0–1 atm), the standard state of a species occurring as a condensed phase can be defined as being the *pure species at* *the temperature* T; the specification that the pressure be 1 atm is no longer required. $G^\circ_{M(s)}$ is now simply the molar Gibbs free energy of pure solid M at the temperature T.

Similarly, Equation 12.5 can be written as

$$G^\circ_{MO(g)} + RT\ln p_{MO(g)} = G^\circ_{MO(s)} \tag{12.5a}$$

and thus, Equation 12.1 can be written as

$$G^\circ_{MO(s)} - \frac{1}{2}G^\circ_{O_2(g)} - G^\circ_{M(s)} = -RT\ln\left(\frac{1}{p^{1/2}_{O_2}}\right)$$

or

$$\Delta G^\circ = -RT\ln K \tag{12.6}$$

Where $K = 1/p^{1/2}_{O_2}$, and ΔG° is the *standard Gibbs free energy change for the reaction*

$$M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$$

Thus, in the case of a reaction equilibrium involving only pure condensed phases and a gas phase, the equilibrium constant K can be written solely in terms of those species which occur only in the gas phase. Again, since ΔG° is a function only of temperature, then K is a function only of temperature. Thus, at any fixed temperature, the establishment of reaction equilibrium occurs at a unique value of $p_{O_2} = p_{O_2(\text{eq}.T)}$. The equilibrium has one thermodynamic degree of freedom, as can be seen from application of the Gibbs equilibrium phase rule:

$$\Phi = 3 \ (\text{two pure solids and a gas phase})$$

$$C = 2 \ (\text{metal M} + \text{oxygen})$$

Thus,

$$\mathcal{F} = C + 2 - \Phi = 2 + 2 - 3 = 1$$

If, at any temperature T, the actual partial pressure of oxygen in a closed metal–metal oxide–oxygen system is greater than $p_{O_2(\text{eq}.T)}$, spontaneous oxidation of the metal will occur, consuming oxygen and decreasing the oxygen pressure in the gas phase. When the actual oxygen pressure has thus been decreased to $p_{O_2(\text{eq}.T)}$, then, provided that both solid phases are still present, the oxidation ceases and reaction equilibrium is reestablished. Similarly, if the oxygen pressure in the closed vessel was originally less than $p_{O_2(\text{eq}.T)}$, spontaneous reduction of the oxide would occur until $p_{O_2(\text{eq}.T)}$ was reached.

Extraction metallurgical processes involving the reduction of oxide ores depend on the achievement and maintenance of an oxygen pressure less than $p_{O_2(\text{eq}.T)}$ in the reaction vessel. For example, the standard Gibbs free energy change for the reaction

$$4Cu_{(s)} + O_{2(g)} = 2Cu_2O_{(s)}$$

is

$$\Delta G^\circ = -324,400 + 138.5T\,\text{J}$$

in the temperature range 298–1200 K. Thus,

$$-\ln K = \ln p_{O_2(\text{eq}.T)} = \frac{\Delta G^\circ}{RT}$$

or

$$\begin{aligned}\log p_{O_2(\text{eq}.T)} &= -\frac{324,400}{2.303\times 8.3144T} + \frac{138.5}{2.303\times 8.3144}\\ &= -\frac{16,940}{T} + 7.23\end{aligned}$$

This variation of log $p_{O_2(\text{eq}.T)}$ with $1/T$ is drawn as the line *ab* in Figure 12.1a, and all points on the line represent the unique oxygen pressure, $p_{O_2(\text{eq}.T)}$, required for equilibrium between solid Cu, solid Cu_2O, and oxygen gas at the particular temperature *T*. Thus, the line *ab* divides the diagram into two regions. Above the line *ab* (where $p_{O_2} > p_{O_2(\text{eq}.T)}$), the metal phase is not stable, and thus, the system exists as $Cu_2O_{(s)}$ + $O_{2(g)}$; below the line *ab* (where $p_{O_2} < p_{O_2(\text{eq}.T)}$), the oxide is not stable, and hence the system exists as $Cu_{(s)}$ + $O_{2(g)}$.

Other equilibria among two condensed pure phases and a gas phase include the formation of hydroxides and carbonates.

For example, at the temperature *T*, the equilibrium

$$MO_{(s)} + H_2O_{(g)} = M(OH)_{2(s)}$$

occurs when

$$G^\circ_{MO(s)} + G^\circ_{H_2O(g)} + RT\ln p_{H_2O} = G^\circ_{M(OH)_{2(s)}}$$

that is, when

$$\Delta G^\circ = -RT\ln K = RT\ln p_{H_2O(\text{eq}.T)}$$

Similarly, the equilibrium

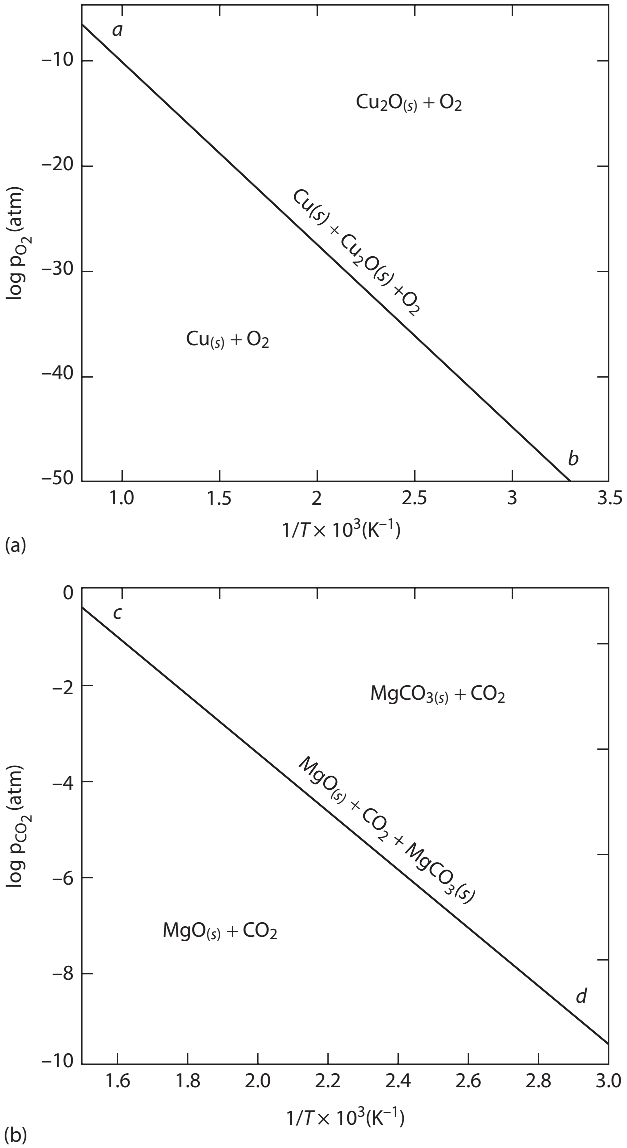

Figure 12.1 (a) The variation, with temperature, of the oxygen pressure required for maintenance of the equilibrium $4Cu_{(s)} + O_2 = 2Cu_2O$. (b) The variation, with temperature, of the carbon dioxide pressure required for maintenance of the equilibrium $MgO_{(s)} + CO_2 = MgCO_{3(s)}$.

$$\mathrm{MO}_{(s)} + \mathrm{CO}_{2(g)} = \mathrm{MCO}_{3(s)}$$

occurs when

$$G^{\circ}_{\mathrm{MO}(s)} + G^{\circ}_{\mathrm{CO}_2\,(g)} + RT\ln p_{\mathrm{CO}_2\,(\mathrm{eq}.T)} = G^{\circ}_{\mathrm{MCO}_3\,(s)}$$

that is, when

$$\Delta G^{\circ} = -RT\ln K = RT\ln p_{\mathrm{CO}_2\,(\mathrm{eq}.T)}$$

For the reaction

$$\begin{gathered}\mathrm{MgO}_{(s)} + \mathrm{CO}_{2(g)} = \mathrm{MgCO}_{3(s)} \\ \Delta G^{\circ} = -117{,}600 + 170T \text{ J}\end{gathered}$$

in the temperature range 298 to 1000 K, and thus,

$$\begin{aligned}\log p_{\mathrm{CO}_2\,(\mathrm{eq}.T)} &= -\frac{117{,}600}{2.303\times 8.3144T} + \frac{170}{2.303\times 8.3133} \\ &= -\frac{6141}{T} + 8.88\end{aligned}$$

This variation is shown in Figure 12.1b as the line *cd*, which again divides the diagram into two regions: one in which $\mathrm{MgO}_{(s)}$ + $\mathrm{CO}_{2(g)}$ are stable, and one in which $\mathrm{MgCO}_{3(s)}$ + $\mathrm{CO}_{2(\mathrm{g})}$ are stable.

12.3 THE VARIATION OF THE STANDARD GIBBS FREE ENERGY CHANGE WITH TEMPERATURE

For any chemical reaction, combination of Equations 6.11 and 6.12 gives ΔG° for the reaction as a function of temperature:

$$\begin{aligned}\Delta G^{\circ}_T &= \Delta H^{\circ}_T - T\Delta S^{\circ}_T \\ &= \Delta H^{\circ}_{298} + \int_{298}^{T}\Delta c_p dT - T\Delta S^{\circ}_{298} - T\int_{298}^{T}\frac{\Delta c_p}{T}dT\end{aligned} \tag{12.7}$$

from which it is seen that the deviation from linearity between ΔG° and T depends on the sign and the magnitude of Δc_p for the reaction. Generally, however, the variation of ΔG° with T is considered as follows. For each of the individual reactants and products of the reaction, the molar heat capacity, c_p, is expressed, over a stated range of temperature, in the form

$$c_p = a + bT + cT^{-2}$$

Hence, for the reaction, again within the stated range of temperature,

$$\Delta c_p = \Delta a + \Delta bT + \Delta cT^{-2}$$

From Kirchhoff's law:

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = \Delta c_p = \Delta a + \Delta bT + \Delta cT^{-2}$$

where ΔH° is the standard enthalpy change for the reaction. Integration gives

$$\Delta H_T^\circ = \Delta H_0 + \Delta aT + \frac{\Delta bT^2}{2} - \frac{\Delta c}{T} \tag{12.8}$$

where $\Delta \mathrm{H}_0$ is an integration constant which would be equal to the standard enthalpy of the reaction at 0 K only if the analytical expression for Δc_p as a function of T was valid down to 0 K. ΔH_0 is normally evaluated by substituting a known value of ΔH_T° into Equation 12.8.

The Gibbs–Helmholtz equation for the reaction is

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} = -\frac{\Delta H^\circ}{T^2} = -\frac{\Delta H_0}{T^2} - \frac{\Delta a}{T} - \frac{\Delta b}{2} + \frac{\Delta c}{T^3}$$

integration of which gives

$$\frac{\Delta G^\circ}{T} = I + \frac{\Delta H_0}{T} - \Delta a \ln T - \frac{\Delta bT}{2} - \frac{\Delta c}{2T^2}$$

or

$$\Delta G^\circ = IT + \Delta H_0 - \Delta aT \ln T - \frac{\Delta bT^2}{2} - \frac{\Delta c}{2T} \tag{12.9}$$

where I is an integration constant.

Since $\Delta G^\circ = -RT \ln K$, then Equation 12.9 gives

$$\ln K = -\frac{\Delta H_0}{RT} - \frac{I}{R} + \frac{\Delta a \ln T}{R} + \frac{\Delta bT}{2R} + \frac{\Delta c}{2RT^2} \tag{12.10}$$

In Appendix 12A, the value of the constant I is found to be 171.7 J/K.

The variation of ΔG_T°, as calculated from the experimentally measured variation of $p_{O_2(\mathrm{eq}.T)}$ with temperature, can be fitted to an equation of the form

$$\Delta G^\circ = A + BT \ln T + CT$$

For the oxidation of $4\mathrm{Cu}_{(s)}$ to $2\mathrm{Cu}_2\mathrm{O}_{(s)}$, this gives

$$\Delta G^\circ = -338{,}900 - 14.2T \ln T + 247T \text{ J} \tag{ii}$$

which can be approximated in linear form by

$$\Delta G^\circ = -333{,}000 + 141.3T \text{ J} \tag{iii}$$

Equations 12A(i), (ii), and (iii) give, respectively, –282.8, –289.1, and –290.6 kJ, and, at 1200 K, give –169.7, –163.3, and –163.4 kJ.

It can be noticed that Equation 12.10 is similar to the vapor pressure equation (Equation 7.8). The relationship between the two can be seen as follows. Consider the evaporation of A:

$$A_{(l)} = A_{(v)}$$

Equilibrium occurs at the temperature T when

$$G^\circ_{A(l)} = G^\circ_{A(v)} + RT \ln p_A$$

that is, when

$$\Delta G^\circ = -RT \ln p_A = -RT \ln K$$

If the liquid and the vapor have the same molar heat capacity, then

$$\ln p_A = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

This is to be compared with Equation 7.6a (Chapter 7), which gave

$$\ln p_A = -\frac{\Delta H_{\text{evap}}}{RT} + \text{constant}$$

If the vapor behaves ideally, then, at constant temperature, $H_{(v)}$ is independent of pressure, and thus,

$$\Delta H^\circ = H^\circ_{(v)} - H^\circ_{(l)} = H_{(v)} - H_{(l)} = \Delta H_{\text{evap}}$$

However, from Equation 6.15, for the vapor

$$S(T, p_A) = S^\circ_T - R \ln p_A$$

and thus,

$$\begin{aligned}\Delta S^\circ_{(l\to v)} &= S^\circ_{(v)} - S^\circ_{(l)}\\ &= S_{(v)} - S^\circ_{(l)} + R\ln p_A\\ &= \Delta S_{\text{evap}} + R\ln p_A\end{aligned}$$

The constant in Equation 7.6a thus has the value $\Delta S_{\text{evap}}/R + \ln p_A$, and Equation 7.6a becomes

$$\ln p_A = -\frac{\Delta H_{\text{evap}}}{RT} + \frac{\Delta S_{\text{evap}}}{R} + \ln p_A$$

indicating that when the vapor is in equilibrium with the liquid at the temperature T,

$$\Delta S_{\text{evap}} = \frac{\Delta H_{\text{evap}}}{T}$$

or, as is required,

$$\Delta G_{\text{evap}} = 0$$

12.4 ELLINGHAM DIAGRAMS

Ellingham* (Harold Johann Thomas Ellingham, 1897–1975) plotted the experimentally determined variations of ΔG° with T for the oxidation and sulfidation of a series of metals and found that, in spite of the terms involving $\ln T$, T^2, and T^{-1} in Equation 12.9, the relationship approximated to straight lines over ranges of temperature in which no change of state occurred. The relations could thus be expressed by means of the simple equation

$$\Delta G^\circ = A + BT \tag{12.11}$$

in which the constant A is identified with the temperature-independent standard enthalpy change for the reaction, ΔH°, and the constant B is identified with the negative of the temperature-independent standard entropy change for the reaction, $-\Delta S^\circ$.

The variation of ΔG° with T for the oxidation reaction

$$4\text{Ag}_{(s)} + \text{O}_{2(g)} = 2\text{Ag}_2\text{O}_{(s)}$$

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* H. J. T. Ellingham, "Reducibility of Oxides and Sulfides in Metallurgical Processes," *J. Soc. Chem. Ind.* (1944), vol. 63, p. 125.

is shown in Figure 12.2, which is known as an *Ellingham diagram*. From Equation 12.11, the length of the intercept of the line with the $T = 0$ K axis gives $\Delta H°$, and $\Delta S°$ is given by the negative of the slope of the line. Since $\Delta S°$ is a negative quantity (the reaction involves the disappearance of a mole of gas), the line has a positive slope. $\Delta G° = 0$ at $T = 462$ K, and thus, at this temperature, pure solid silver and oxygen gas at 1 atm pressure are in equilibrium with pure solid silver oxide. From Equation 12.6, $\Delta G° = -RT \ln K = RT \ln p_{O_2(\text{eq}.T)} = 0$ at 462 K, and, therefore, $p_{O_2(\text{eq}.462\text{ K})} = 1$. If the temperature of the system (pure Ag_2O, pure $Ag_{(s)}$, and oxygen gas at 1 atm pressure) is decreased to T_1, then, since $\Delta G°$ for the oxidation reaction becomes negative, the metal phase becomes unstable relative to silver oxide and oxygen gas at 1 atm pressure and is hence spontaneously oxidized. The value of $p_{O_2(\text{eq}.T_1)}$ is calculated from $\Delta G^\circ_{T_1} = RT_1 \ln p_{O_2(\text{eq}.T_1)}$, and, as $\Delta G^\circ_{T_1}$ is a negative quantity, $p_{O_2(\text{eq}.T_1)} < 1$ atm.

Similarly, if the temperature of the system is increased from 462 K to T_2, then, since $\Delta G°$ for the oxidation becomes positive, the oxide phase becomes unstable relative to silver metal and oxygen gas at 1 atm and spontaneously dissociates. Since ΔG_{T_2} is a positive quantity, $p_{O_2(\text{eq}.T_2)}$ is greater than 1 atm. The value of $\Delta G°$ for oxidation is thus a measure of the chemical affinity of the metal for oxygen, and the more negative the value of $\Delta G°$ at any temperature, the more stable is the oxide.

For the oxidation reaction $A_{(s)} + O_{2(g)} = AO_{2(s)}$,

$$\Delta S^\circ = S^\circ_{AO_2(s)} - S^\circ_{O_2(g)} - S^\circ_{A(s)}$$

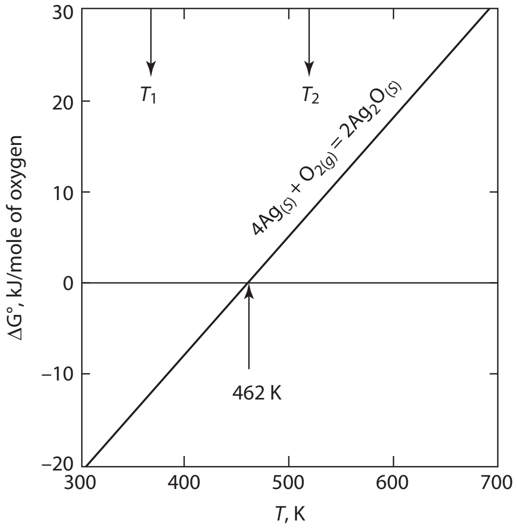

Figure 12.2 The Ellingham line for the oxidation of silver.

and since, generally, in the temperature range in which A and AO_2 are solid, $S^\circ_{O_2}$ is considerably greater than both S°_A and $S^\circ_{AO_2}$ (see, for example, Figure 6.15), then

$$\Delta S^\circ \sim S^\circ_{O_2}$$

Thus, the standard entropy changes for oxidation reactions involving solid phases have nearly the same values, which correspond to the disappearance of 1 mole of oxygen gas initially at 1 atm pressure. Since the slopes of the lines in an Ellingham diagram are equal to $-\Delta S^\circ$, the lines are more or less parallel to one another, as will be seen in the Ellingham diagram presented in Section 12.6.

ΔG° at any temperature is the sum of the enthalpy contribution ΔH° (which is independent of T if $\Delta c_p = 0$) and the entropy contribution $-T\Delta S$ (which, if $\Delta c_p = 0$, is a linear function of temperature). The two contributions are illustrated in Figure 12.3 for the oxidation reaction of cobalt:

$$2\mathrm{Co}_{(s)} + \mathrm{O}_{2(g)} = 2\mathrm{CoO}_{(s)}$$

for which

$$\Delta G^\circ = -467{,}800 + 143.7T \text{ J}$$

in the temperature range 298–1763 K, and for the oxidation reaction of manganese,

$$2\mathrm{Mn}_{(s)} + \mathrm{O}_{2(g)} = 2\mathrm{MnO}_{(s)}$$

for which

$$\Delta G^\circ = -769{,}400 + 145.6T \text{ J}$$

in the temperature range 298–1500 K.

Since the values of ΔS° for these two reactions are virtually equal to one another, Figure 12.3 shows that the relative stabilities of the oxides CoO and MnO are determined by their values of ΔH°, in that the more negative the value of ΔH°, the more negative the value of ΔG°, and hence the more stable the oxide. Since

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = \ln\left(\frac{1}{p_{O_2(\mathrm{eq}.T)}}\right)$$

then

$$p_{O_2(\mathrm{eq}.T)} = \exp\frac{\Delta H^\circ}{RT}\exp\frac{-\Delta S^\circ}{R} = \mathrm{constant} \times \exp\frac{\Delta H^\circ}{RT}$$

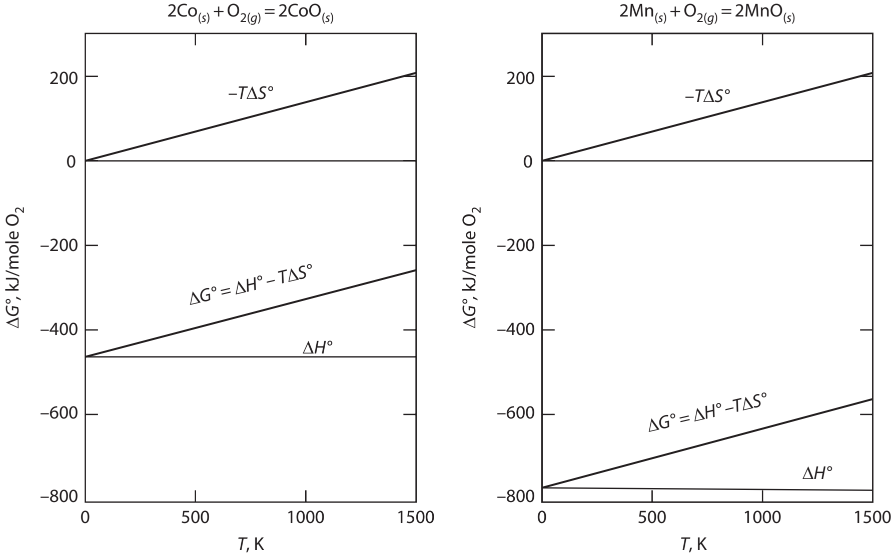

Figure 12.3 Illustration of the effect of the magnitude of ΔH° on the $\Delta G^\circ - T$ relationships for reactions of the type $2M_{(s)} + O_{2(g)} = 2MO_{(s)}$.

Since ΔH° is a negative quantity, $p_{O_2(\text{eq}.T)}$ increases exponentially with increasing temperature and, at any temperature, $p_{O_2(\text{eq}.T)}$ decreases as ΔH° becomes more negative.

Consider two oxidation reactions, the Ellingham lines of which intersect each other; for example,

$$2A + O_2 = 2AO \tag{i}$$

and

$$B + O_2 = BO_2 \tag{ii}$$

which are shown in Figure 12.4. From Figure 12.4 it is seen that $\Delta H^\circ_{(ii)}$ is more negative than $\Delta H^\circ_{(i)}$ and that $\Delta S^\circ_{(ii)}$ is more negative than $\Delta S^\circ_{(i)}$. The subtraction of reaction (i) from reaction (ii) gives

$$B + 2AO = 2A + BO_2 \tag{iii}$$

for which the variation of ΔG° with T is as shown in Figure 12.5. At temperatures less than T_E, A and BO_2 are stable with respect to B and AO, and at temperatures higher than T_E, the reverse is the case. At T_E, A, B, AO, and BO_2, occurring in their standard states, are in equilibrium with one another. The equilibrium at T_E (as with

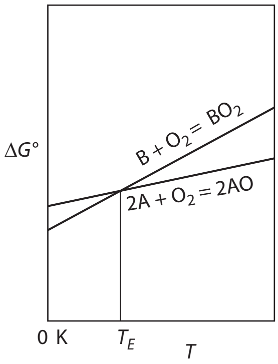

Figure 12.4 Intersecting Ellingham lines for two hypothetical oxidation reactions.

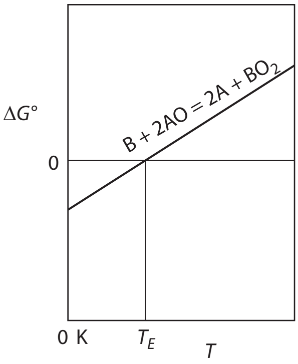

Figure 12.5 The variation of $\Delta G°$ with T for $B + 2AO = 2A + BO_2$ from Figure 12.4.

any equilibrium) occurs as the result of a compromise between enthalpy and entropy considerations. Since $\Delta H^\circ_{\text{(iii)}} = \Delta H^\circ_{\text{(ii)}} - \Delta H^\circ_{\text{(i)}} < 0$ and $\Delta S^\circ_{\text{(iii)}} = \Delta S^\circ_{\text{(ii)}} - \Delta S^\circ_{\text{(i)}} < 0$, the system $A + B + O_2$ has

- A minimum enthalpy when the system occurs as $A + BO_2$
- A maximum entropy when the system occurs as $B + AO$

At T_E, $\Delta H^\circ_{\text{(iii)}}$ equals $-T_E \Delta S^\circ_{\text{(iii)}}$, and thus, $\Delta G^\circ_{\text{(ii)}} = 0$. At temperatures less than T_E, the enthalpy contribution to $\Delta G^\circ_{\text{(iii)}}$ outweighs the entropy contribution, and thus, $\Delta G^\circ_{\text{(iii)}}$ is negative and $A + BO_2$ is the stable state. At temperatures greater than T_E, the reverse is the case: $\Delta G^\circ_{\text{(iii)}}$ is positive and $B + AO$ is the stable state.

Figure 12.5 thus shows that if pure A were to be used as a reducing agent to reduce pure BO_2, to form pure B and pure AO, then the reduction would have to be conducted at temperatures greater than T_E. The foregoing discussion also illustrates that, in order to compare the stabilities of different oxides, the Ellingham diagrams must be drawn for oxidation reactions involving the consumption of the same number of moles of oxygen. Thus, the unit of ΔG° for the oxidation reaction must be one of energy (e.g., joules) per mole of oxygen.

In order to avoid having to calculate the value of $p_{O_2(\text{eq}.T)}$ for any oxidation reaction, Richardson* added a nomographic scale to the Ellingham diagram. This scale is constructed as follows. At any temperature T, the standard Gibbs free energy change for an oxidation reaction, ΔG_T°, is given by Equation 12.6 as $RT \ln p_{O_2(\text{eq}.T)}$. However, from Equation 8.7,

$$G = G^\circ + RT \ln P$$

ΔG_T° is seen to be numerically equal to the decrease in the Gibbs free energy of 1 mole of oxygen gas when its pressure is decreased from 1 atm to $p_{O_2(\text{eq}.T)}$ atm at the temperature T. Consider the variation of ΔG with T in Equation 8.7. For a decrease in the pressure of 1 mole of ideal gas from 1 atm to P atm, ΔG versus T is a straight line with a slope of $R \ln P$, and, since $P < 1$, the line has a negative slope. Similarly, for an increase in the pressure of 1 mole of ideal gas from 1 to P atm, the variation of ΔG with T is linear with a positive slope of $R \ln P$. Thus, a series of lines can be drawn for given pressure changes (from 1 to P atm) as a function of temperature. These lines radiate from the point $\Delta G = 0$, $T = 0$, as shown in Figure 12.6. The superimposition of Figure 12.6 with a typical Ellingham diagram is shown in Figure 12.7. In Figure 12.7,

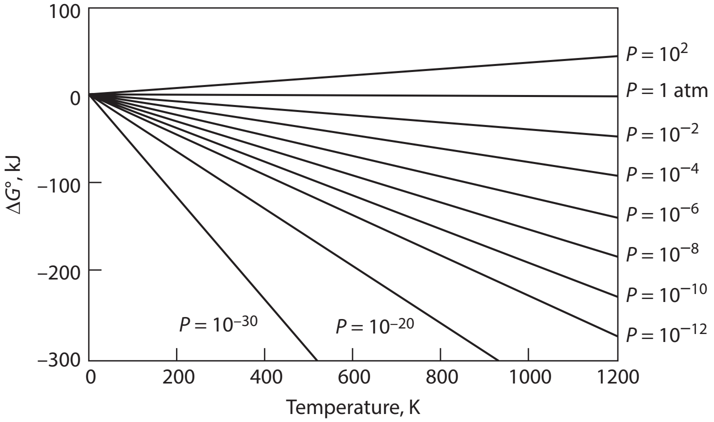

Figure 12.6 The variation, with temperature, of the difference between the Gibbs free energy of 1 mole of ideal gas in the state ($P = P$ atm, T) and the Gibbs free energy of 1 mole of ideal gas in the state ($P = 1$ atm, T).

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* F. D. Richardson and J. H. E. Jeffes, "The Thermodynamics of Substances of Interest in Iron and Steel Making from 0°C to 2400°C: I—Oxides," *J. Iron and Steel Inst.* (1948), vol. 160, p. 261.

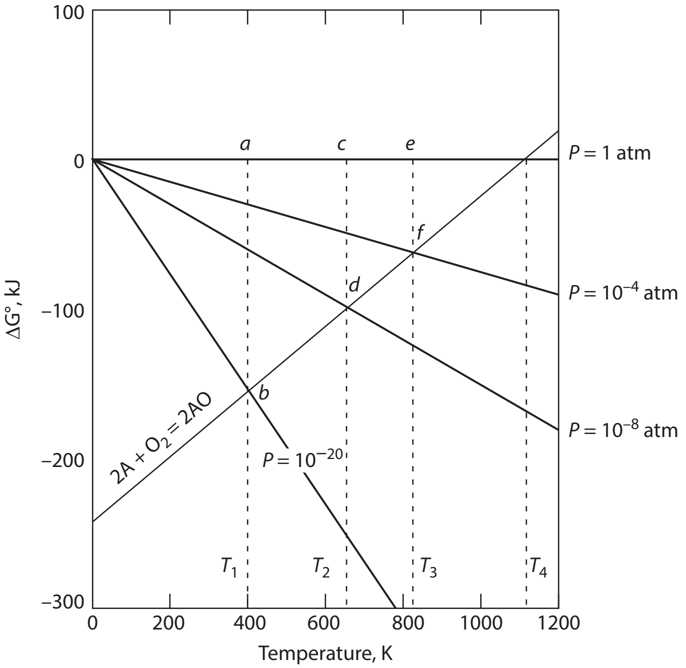

Figure 12.7 The superimposition of an Ellingham line onto Figure 12.6.

- At T_1, $\Delta G^\circ_{T_1} = ab$ = the decrease in Gibbs free energy when p_{O_2} is decreased from 1 atm to 10^{-20} atm at T_1.
- At T_2, $\Delta G^\circ_{T_2} = cd$ = the decrease in Gibbs free energy when p_{O_2} is decreased from 1 atm to 10^{-8} atm at T_2.
- At T_3, $\Delta G^\circ_{T_3} = ef$ = the decrease in Gibbs free energy when p_{O_2} is decreased from 1 atm to 10^{-4} atm at T_3.
- At T_4, $\Delta G = 0$, which corresponds to no change of p_{O_2} from 1 atm. Thus, $p_{O_2(\text{eq}.T_4)}$ = 1 atm.

The $p_{O_2(\text{eq}.T)}$ nomographic scale is thus added to the Ellingham diagram along the right-hand edge and along the bottom edge. The value of $p_{O_2(\text{eq}.T)}$ for any metal–metal oxide equilibrium is read off the graph as that value on the scale which is collinear with the points $\Delta G^\circ = 0$, $T = 0$, and ΔG°_T, $T = T$.

The reactions (i) and (ii) shown in Figure 12.4 can be reexamined using the $p_{O_2(\text{eq}.T)}$ nomographic scale. Figure 12.4 is reproduced with a nomographic oxygen pressure scale in Figure 12.8. At any temperature lower than T_E (say, T_1), it is seen that

$$p_{O_2}\ (\text{equation for reaction (ii) at } T_1) < p_{O_2}\ (\text{equation for reaction (i) at } T_1)$$

Thus, if metal A and metal B are placed in a closed system in an atmosphere of oxygen at $P = 1$ atm, both metals spontaneously oxidize. As a consequence of the consumption of oxygen to form the oxides, the pressure of oxygen decreases. Oxidation of both metals continues until the oxygen pressure is decreased to the value p_{O_2} (equation for reaction (i) at T_1), at which point the oxidation of A ceases. However, since B + O_2 at p_{O_2} (equation for reaction (i) at T_1) is still unstable with respect to BO_2, the oxidation of B continues until the oxygen pressure has been decreased to p_{O_2} (equation for reaction (ii) at T_1). Since the oxygen pressure is decreased below p_{O_2} (equation from reaction (i) at T_1), then AO becomes unstable with respect to A and O_2 at the prevailing pressure, and hence AO decomposes. When complete equilibrium is attained, the state of the system is A + BO_2 + O_2 at p_{O_2} (equation for reaction (ii) at T_1).

At any temperature higher than T_E (say, T_2),

$$p_{O_2}\left(\text{equation for reaction (i) at } T_2\right) < p_{O_2}\left(\text{equation for reaction (ii) at } T_2\right)$$

and an argument similar to this shows that the equilibrium state of the closed system containing, initially, A + B + O_2 at 1 atm pressure, is B + AO + O_2 at p_{O_2} [equation for reaction (i) at T_2]. It is thus obvious that A, B, AO, BO_2, and an oxygen atmosphere are in equilibrium only at that temperature T at which

$$p_{O_2(\text{eq.[i]}T)} = p_{O_2(\text{eq.[ii]}T)}$$

Figure 12.8 shows that this unique temperature is T_E, the temperature at which the Ellingham lines intersect one another. The system has no degrees of freedom.

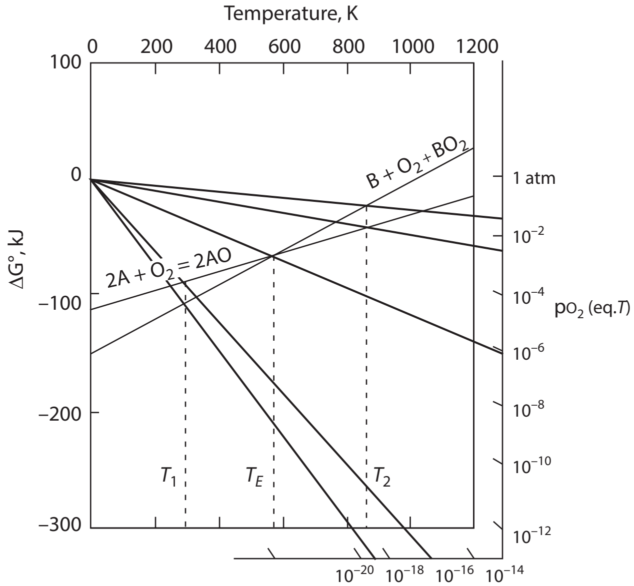

Figure 12.8 Illustration of the addition of the Richardson oxygen pressure nomographic scale to an Ellingham diagram.

12.5 THE EFFECT OF PHASE TRANSFORMATIONS

In the previous section, it was stated that the variation of ΔG° with temperature can be approximated by a straight line only over ranges of temperature in which no change of phase of a reactant or product occurs. However, the enthalpy of a high-temperature phase (e.g., the liquid phase) exceeds that of a low-temperature phase (e.g., the solid phase) by the latent enthalpy of the phase change. Similarly, the entropy of the higher-temperature phase exceeds that of the lower-temperature phase. Thus, a change in the slope of the ΔG° line (an *elbow*) occurs on an Ellingham line at the temperature of a phase change in either a reactant phase or product phase of the reaction.

Consider the reaction

$$A_{(s)} + O_{2(g)} = AO_{2(s)}$$

for which ΔH° is the standard enthalpy change and ΔS° is the standard entropy change. At $T_{m,A}$, the melting temperature of A, the change of phase

$$A_{(s)} \rightarrow A_{(l)}$$

occurs, for which the standard enthalpy change (the enthalpy of melting) is $\Delta H^\circ_{m,A}$ and the corresponding change in entropy is $\Delta S^\circ_{m,A}$. Thus, for the reaction

$$A_{(l)} + O_{2(g)} = AO_{2(s)}$$

the standard enthalpy change is $\Delta H^\circ - \Delta H^\circ_{m,A}$ and the standard entropy change is $\Delta S^\circ - \Delta S^\circ_{m,A}$. Since $\Delta H^\circ_{m,A}$ and $\Delta S^\circ_{m,A}$ are positive quantities (melting is an endothermic process), then $\Delta H^\circ - \Delta H^\circ_{m,A}$ is a larger negative quantity than is ΔH° and $\Delta S^\circ - \Delta S^\circ_{m,A}$ is a larger negative quantity than is ΔS°. Consequently, the Ellingham line for the oxidation of liquid A to form solid AO_2 has a greater slope than the corresponding line for the oxidation of solid A, and the line contains an *elbow upward* at $T_{m,A}$. This is shown in Figure 12.9a. The line does not contain a discontinuity, since, at $T_{m,A}$, $G^\circ_{A(s)} = G^\circ_{A(l)}$.

If the melting temperature of the oxide, T_{m,AO_2}, is lower than the melting temperature of the metal, then, at T_{m,AO_2}, the change of phase

$$AO_{2(s)} \rightarrow AO_{2(l)}$$

occurs, for which the standard enthalpy and entropy changes are, respectively, $\Delta H^\circ_{m,AO_2}$ and $\Delta S^\circ_{m,AO_2}$. Thus, for the reaction

$$A_{(s)} + O_{2(g)} = AO_{2(l)}$$

the standard enthalpy change is $\Delta H^\circ + \Delta H^\circ_{m,AO_2}$ and the standard entropy change is $\Delta S^\circ + \Delta S^\circ_{m,AO_2}$, both of which are less than the corresponding quantities ΔH° and

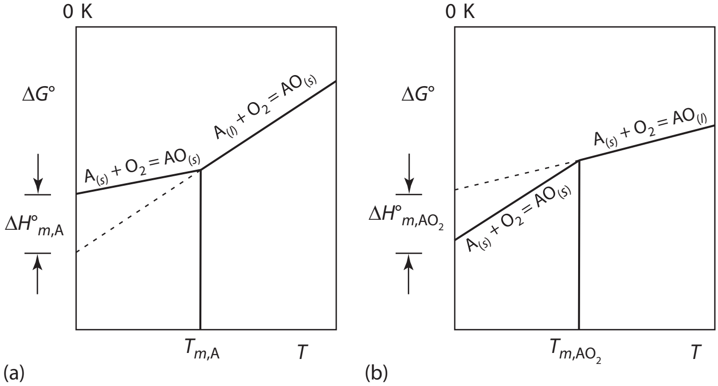

Figure 12.9 (a) The effect of melting of the metal on the Ellingham line for the oxidation of the metal. (b) The effect of melting of the metal oxide on the Ellingham line for the oxidation of the metal.

$\Delta S°$. In this case, the Ellingham line for oxidation of the solid metal to produce the liquid oxide has a lower slope than the line for oxidation of the solid metal to the solid oxide, and thus, as shown in Figure 12.9b, the Ellingham line has an *elbow downward* at T_{m,AO_2}. In brief, if $T_{m,\text{A}} < T_{m,\text{AO}_2}$, the Ellingham line is as shown in Figure 12.10a, and, if $T_{m,\text{A}} > T_{m,\text{AO}_2}$, the line is as shown in Figure 12.10b.

12.5.1 Example of the Oxidation of Copper

Copper is a metal which melts at a lower temperature than its lowest oxide Cu_2O. The standard Gibbs free energy change for the oxidation of solid copper to form solid cuprous oxide in the range of temperature 298 K to $T_{m,\text{Cu}}$ is

$$\Delta G° = -338{,}900 - 14.2T \ln T + 247T \tag{i}$$

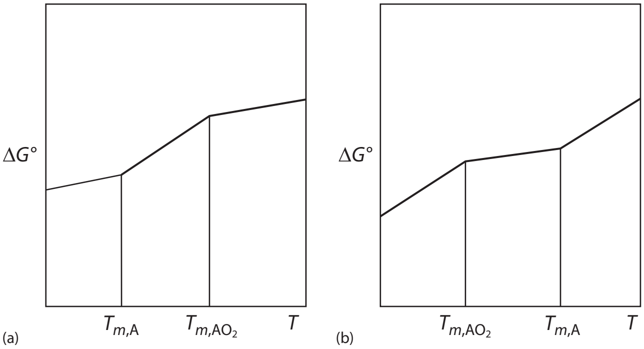

Figure 12.10 Illustration of the effects of phase changes of the reactants and products of a reaction on the Ellingham line for the reaction.

and for the oxidation of liquid copper to form solid cuprous oxide in the range of temperature $T_{m,\mathrm{Cu}}$ to 1503 K,

$$\Delta G^\circ = -\,390{,}800 - 14.2T \ln T + 285.3T \text{ J} \tag{ii}$$

These two lines, which are drawn in Figure 12.11, intersect at 1356 K, which is the melting temperature of copper. $\Delta G^\circ_{(\mathrm{I})} - \Delta G^\circ_{(\mathrm{ii})}$ gives

$$\Delta G = 51{,}900 - 38.3T \text{ J}$$

for the phase change

$$4\mathrm{Cu}_{(s)} = 4\mathrm{Cu}_{(l)}$$

or, for the melting of 1 mole of Cu,

$$\Delta G^\circ_{m,\mathrm{Cu}} = 12{,}970 - 9.58T \text{ J}$$

from which

$$\Delta H^\circ_{m,\mathrm{Cu}} = 12{,}970 \text{ J}$$

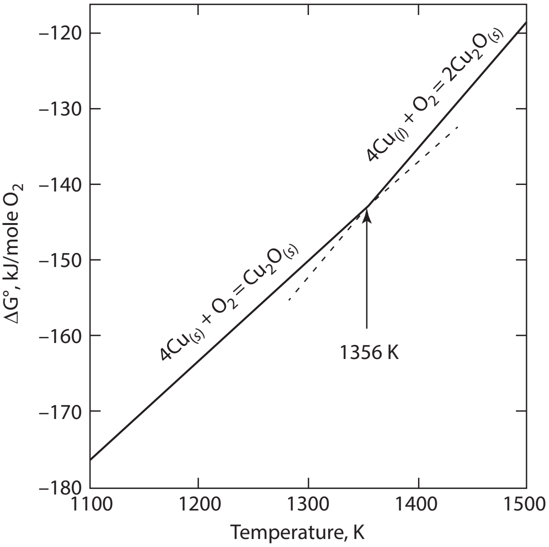

Figure 12.11 The Ellingham line for the oxidation of copper.

and

$$\Delta S^{\circ}_{m,\mathrm{Cu}} = 9.58 \text{ J/K}$$

Thus, at $T_{m,\mathrm{Cu}}$, the slope of the Ellingham line for the oxidation of Cu increases by 9.58 J/K.

12.5.2 EXAMPLE OF THE CHLORINATION OF IRON

Since $FeCl_2$ boils at a lower temperature than the melting temperature of Fe, the Ellingham diagram for the chlorination of Fe shows elbows downward at the melting temperature of $FeCl_2$ and at the boiling temperature of $FeCl_2$. For

$$\mathrm{Fe}_{(s)} + \mathrm{Cl}_{2(g)} = \mathrm{FeCl}_{2(s)}$$

$$\Delta G^{\circ} = -346{,}300 - 12.68T \ln T + 212.9T \text{ J} \tag{iii}$$

in the range 298 K to $T_{m,\mathrm{FeCl_2}}$. For

$$\mathrm{Fe}_{(s)} + \mathrm{C1}_{2(g)} = \mathrm{FeC1}_{2(l)}$$

$$\Delta G^{\circ} = -\ 286{,}400 + 63.68T \text{ J} \tag{iv}$$

in the range $T_{m,\mathrm{FeCl_2}}$ to $T_{b,\mathrm{FeCl_2}}$. For

$$\mathrm{Fe}_{(s)} + \mathrm{Cl}_{2(g)} = \mathrm{FeCl}_{2(g)}$$

$$\Delta G^{\circ} = -105{,}600 + 41.87 \ln T - 375.1T \text{ J} \tag{v}$$

in the range $T_{b,\mathrm{Cl_2}}$ to $T_{m,\mathrm{Fe}}$. Lines (iii), (iv), and (v) are shown in Figure 12.12, which shows that

$$T_{m,\mathrm{FeCl_2}} = 969 \text{ K} \quad \text{and} \quad T_{b,\mathrm{FeCl_2}} = 1298 \text{ K}$$

For $\mathrm{FeCl}_{2(s)} \rightarrow \mathrm{FeCl}_{2(l)}$, $\Delta G^{\circ}_{(\mathrm{iv})} - \Delta G^{\circ}_{(\mathrm{iii})}$ gives

$$\Delta G^{\circ}_{m,\mathrm{FeCl_2}} = 59{,}900 + 12.68T \ln T - 149.0T \text{ J}$$

Thus,

$$\Delta H^{\circ}_{m,\mathrm{FeCl_2}} = -T^2 \left[\frac{\partial \left(\Delta G^{\circ}_{m,\mathrm{FeCl_2}} / T \right)}{\partial T} \right] = 59{,}900 - 12.68T \text{ J}$$

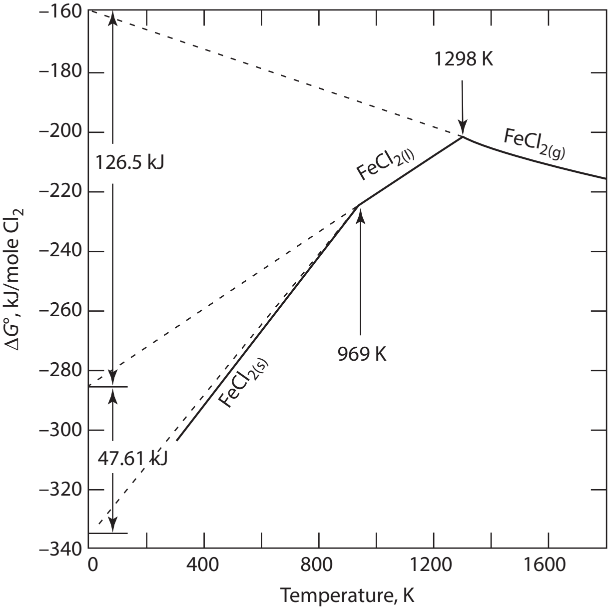

Figure 12.12 The Ellingham diagram for the chlorination of iron.

which, at 969 K, gives $\Delta H^\circ_{m,\mathrm{FeCl_2}} = 47{,}610$ J.

$$\begin{aligned}\Delta S^\circ_{m,\mathrm{FeCl_2}} &= \frac{\partial \Delta G^\circ_{m,\mathrm{FeCl_2}}}{\partial T}\\ &= -12.68\ \ln\ T - 12.68 + 149.0\ \mathrm{J/K}\\ &= 49.13\ \mathrm{J/K\ at\ 969\ K}\end{aligned}$$

or, alternatively,

$$\Delta S^\circ_{m,\mathrm{FeCl_2}} = \frac{\Delta H^\circ_{m,\mathrm{FeCl_2}}}{T_{m,\mathrm{FeCl_2}}} = \frac{47{,}610}{969} = 49.13\ \mathrm{J/K}$$

Thus, the difference in slope between lines (iii) and (iv) at 969 K is 49.13 J/K, and the difference between the tangential intercepts of the slopes of the two lines at 969 K, with the $T = 0$ axis, is 47,610 J.

Similarly, $\Delta G^\circ_{(\mathrm{v})} - \Delta G^\circ_{(\mathrm{iv})}$ gives

$$\Delta G^\circ_{b,\mathrm{FeCl_2}} = 180{,}800 + 41.8T\ln T - 438.8T\ \mathrm{J}$$

Thus,

$$\begin{aligned}\Delta H^\circ_{b,\mathrm{FeCl_2}} &= -T^2\left[\frac{\partial\left(\Delta G^\circ_{b,\mathrm{FeCl_2}}/T\right)}{\partial T}\right]\\ &= 180{,}800 - 41.8T \text{ J}\\ &= 126{,}500 \text{ J at 1298 K}\end{aligned}$$

and

$$\Delta S^\circ_{b,\mathrm{FeCl_2}} = \frac{126{,}500}{1298} = 97.46 \text{ J/K at 1298 K}$$

Thus, the change in slope between lines (iv) and (v) at 1298 K is 97.46 J/K, and the difference between the tangential intercepts is 126,500 J.

12.6 THE OXIDES OF CARBON

Carbon forms two gaseous oxides, CO and CO_2, according to

$$C_{(gr)} + O_{2(g)} = CO_{2(g)} \tag{i}$$

for which $\Delta G^\circ_{(i)} = -394{,}100 - 0.84T$ J, and

$$2C_{(gr)} + O_{2(g)} = 2CO_{(g)} \tag{ii}$$

for which $\Delta G^\circ_{(ii)} = -223{,}400 - 175.3T$ J.

Combination of reactions (i) and (ii) gives

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)} \tag{iii}$$

for which $\Delta G^\circ_{(iii)} = 2\Delta G^\circ_{(i)} - \Delta G^\circ_{(ii)} = -564{,}800 + 173.62T$ J.

The Ellingham lines for reactions (i), (ii), and (iii) are included in Figure 12.13, in which it is seen that

- The line for reaction (iii) has a positive slope (2 moles of gas produced from 3 moles of gas, $\Delta S^\circ_{(iii)} = -173.62$ J/K).
- The line for reaction (i) has virtually zero slope (1 mole of gas produced from 1 mole of gas, $\Delta S^\circ_{(i)} = 0.84$ J/K).
- The line for reaction (ii) has a negative slope (2 moles of gas produced from 1 mole of gas, $\Delta S^\circ_{(ii)} = 175.3$ J/K).

Consider the equilibrium

$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)} \tag{iv}$$

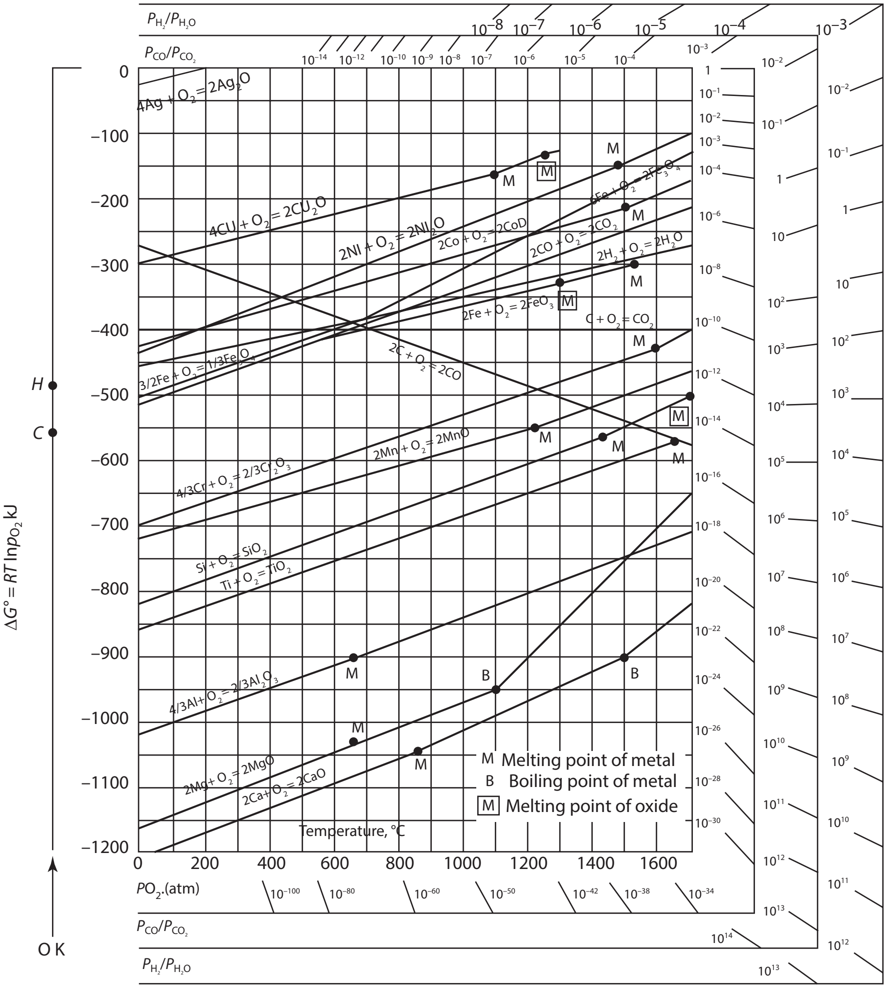

Figure 12.13 The Ellingham diagram for selected oxides.

for which $\Delta G^\circ_{(iv)} = \Delta G^\circ_{(ii)} - \Delta G^\circ_{(i)} = 170{,}700 - 174.5T$. Reaction (iv) is known as the *Boudouard reaction* (Octave Leopold Boudouard, 1872–1923) and is important in the reduction of the oxides of iron in the blast furnace.

The value of $\Delta G^\circ_{(iv)} = 0$ at $T = 978$ K (705°C), the temperature at which the Ellingham lines for reactions (i) and (ii) intersect one another. At this temperature, CO and CO_2, in their standard states (i.e., both at 1 atm pressure), are in equilibrium with solid graphite, and the total pressure of the system is 2 atm. Since reaction equilibria are normally considered for systems under a total pressure of 1 atm, it is instructive to calculate the temperature at which CO and CO_2, each at a pressure of

0.5 atm, are in equilibrium with solid C. Consideration of Le Chatelier's principle indicates whether this temperature is higher or lower than 978 K. For reaction (iv), $\Delta G^{\circ}_{978\ \mathrm{K}} = 0 = -RT \ln K_p = -RT \ln \left(p^2_{\mathrm{CO}}/p_{\mathrm{CO_2}}\right)$; that is, at 978 K, $K_p = 1$, and hence $p_{\mathrm{CO_2}} = p_{\mathrm{CO}} = 1$ and $P_{\mathrm{total}} = 2$ atm. If the pressure of the system is decreased to 1 atm, then, as K_p is independent of pressure (remaining equal to unity) p_{CO} becomes greater than $p_{\mathrm{CO_2}}$; that is, the equilibrium shifts toward the CO side, as is predicted by Le Chatelier's principle. Since $\Delta H^{\circ}_{(\mathrm{iv})} = +170{,}700$ J, reaction (iv) is endothermic, and thus, from Le Chatelier's principle, as a decrease in temperature shifts the equilibrium in that direction which involves an evolution of heat, a decrease in temperature shifts the equilibrium toward the C + CO_2 side. Thus, if it is required to decrease the pressure of the system from 2 to 1 atm and, at the same time, maintain $p_{\mathrm{CO}} = p_{\mathrm{CO_2}}$, the temperature of the system must be decreased.

The temperature required for $p_{\mathrm{CO}} = p_{\mathrm{CO_2}}$ is calculated as follows. For reaction (i):

$$\mathrm{C} + \mathrm{O_2} = \mathrm{CO}, \quad \Delta G^{\circ}_{(\mathrm{i})} = -394{,}100 - 0.84T \text{ J}$$

If the pressure of the CO_2, which is produced at 1 atm, is decreased to 0.5 atm, then, for the change of state

$$\mathrm{CO_2}\left(T, P = 1 \text{ atm}\right) \rightarrow \mathrm{CO_2}(T, P = 0.5 \text{ atm}) \tag{v}$$

the decrease in Gibbs free energy is $\Delta G_{(\mathrm{v})} = RT \ln 0.5$, and hence, for the reaction

$$\mathrm{C}_{(gr)} + \mathrm{O}_{2(g, P\,=\,1\text{ atm})} = \mathrm{CO}_{2(\mathrm{g}, P\,=\,0.5\text{ atm})}$$

$$\begin{aligned} \Delta G_{(\mathrm{iv})} &= \Delta G^{\circ}_{(\mathrm{i})} + \Delta G_{(\mathrm{v})} \\ &= -394{,}100 - 0.84T + RT \ln 0.5 \text{ J} \end{aligned} \tag{vi}$$

This line is obtained on the Ellingham diagram by rotating the line for reaction (i) clockwise about its point of intersection with the $T = 0$ axis until, at the temperature T, the vertical separation between line (i) and line (vi) is $RT \ln 0.5$. This is illustrated in Figure 12.14.

Similarly, the Ellingham line for the reaction

$$2\mathrm{C}_{(gr)} + \mathrm{O}_{2(g,P=1\text{ atm})} = 2\mathrm{CO}_{(g,P=0.5\text{ atm})} \tag{vii}$$

is obtained as the sum of $\Delta G^{\circ}_{(\mathrm{ii})}$ and ΔG for the change of state

$$2\mathrm{CO}(T, P = 1 \text{ atm}) \;\rightarrow\; 2\mathrm{CO}(T, P = 0.5 \text{ atm})$$

That is,

$$\Delta G_{(\mathrm{vii})} = -\ 223{,}400 - 175.3T + 2RT\ln 0.5 \text{ J}$$

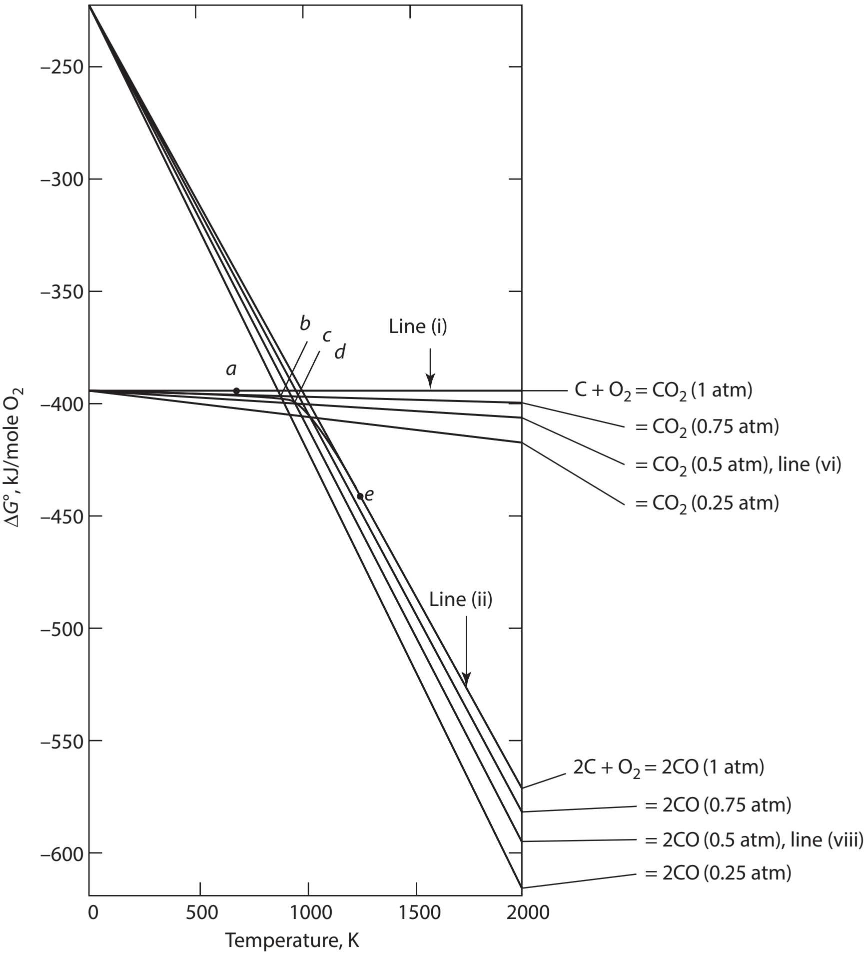

Figure 12.14 The effect of varying the pressures of the product gases of the reactions $C_{(gr)} + O_{2(g,p=1\text{ atm})} = CO_{2(g)}$ and $2C_{(gr)} + O_{2(g,p=1\text{ atm})} = 2CO_{(g)}$ on the variations of ΔG with T for the two reactions.

This line is obtained by rotating the line for reaction (ii) clockwise about its point of intersection with the $T = 0$ axis until, at any temperature T, the vertical separation between line (ii) and line (i) is $2RT \ln 0.5$.

Combination of reactions (vi) and (vii) gives

$$C_{(gr)} + CO_{2(g,0.5\text{ atm})} = 2CO_{(g,0.5\text{ atm})} \tag{viii}$$

for which

$$\Delta G_{(\text{viii})} = \Delta G^{\circ}_{(\text{iv})} + RT \ln 0.5$$

Thus, CO_2 and CO, each at 0.5 atm pressure, are in equilibrium with solid C at that temperature at which $\Delta G_{(viii)} = 0$, the temperature of intersection of the lines (vi) and (vii) in Figure 12.14 (point *c*).

The temperature at which CO (at 0.25 atm) and CO_2 (at 0.75 atm) are in equilibrium with solid C is obtained in a similar manner as the intersection of line (i) rotated clockwise until, at T, it has been displaced a vertical distance $RT \ln 0.75$ and line (ii) rotated clockwise until, at T, it has been displaced a vertical distance $2RT$ (ln 0.25). This is the point *b* in Figure 12.14. Similarly, the point *d* in Figure 12.14 is the temperature at which CO at 0.75 atm pressure and CO_2 at 0.25 atm pressure are in equilibrium with solid C. For a mixture of CO and CO_2 at 1 atm pressure in equilibrium with solid C, the variation of percent CO by volume in the gas with temperature is shown in Figure 12.15. Figure 12.15 includes the points *a*, *b*, *c*, *d*, and *e* drawn in Figure 12.14.

Figure 12.15 shows that, at temperatures less than 600 K, the equilibrium gas is virtually CO_2 at 1 atm pressure and, at temperatures greater than 1400 K, the equilibrium gas is virtually CO at 1 atm pressure. These points are, respectively, the points *a* and *e* in Figure 12.14. Thus, in Figure 12.14, the variation, with temperature, of the Gibbs free energy change for oxidation of solid C to produce a CO–CO_2 mixture at 1 atm pressure which is in equilibrium with solid C is given by line (i) up to the point *a*, then by the line *abcde*, and then by the line (ii) beyond the point *e*.

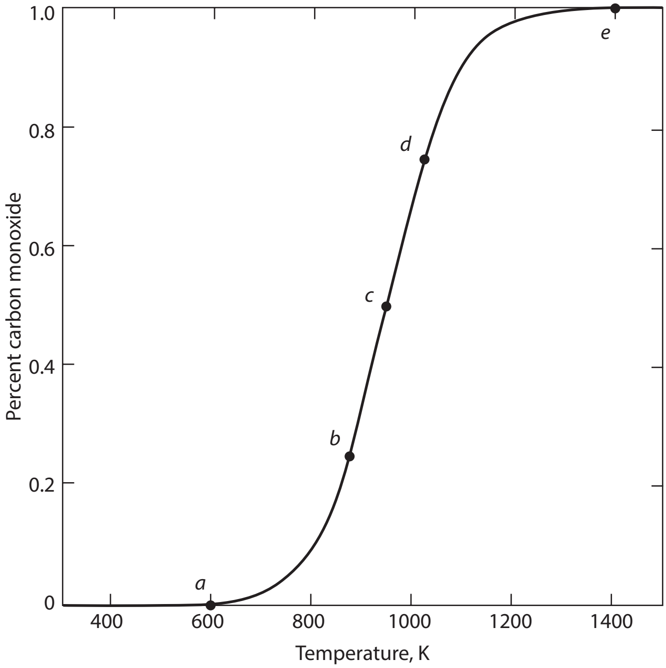

Figure 12.15 The variation, with temperature, of the composition of the CO–CO_2 gas mixture in equilibrium with solid graphite at $P_{total} = 1$ atm.

At any temperature T, the CO–CO_2 mixture in equilibrium with C exerts an equilibrium oxygen pressure via the equilibrium

$$2CO + O_2 = 2CO_2$$

for which

$$\begin{aligned}\Delta G^\circ_{(iii)} &= -564{,}800 + 173.62T \text{ J} = -\text{RT} \ln\left(\frac{p^2_{CO_2}}{p^2_{CO}p_{O_2}}\right) \\ &= 2\,RT\ \ln\left(\frac{p_{CO}}{p_{CO_2}}\right)_{\text{eq. with C}} + RT \ln\, p_{O_2(\text{eq.})}\end{aligned}$$

Thus,

$$\ln p_{O_2(\text{eq.}T)} = -\frac{564{,}800}{8.3144T} + \frac{173.62}{8.3144} + 2\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq. with C}} \tag{12.12}$$

If it is required that solid carbon be used as a reducing agent to reduce a metal oxide MO_2 at the temperature T, then $p_{O_2(\text{eq.}T)}$ in Equation 12.12 must be lower than $p_{O_2(\text{eq.}T)}$ for the equilibrium M + O_2 = MO_2 (see Section 12.7).

12.6.1 The Equilibrium 2CO + O_2 = 2CO_2

The Ellingham line for the reaction 2CO + O_2 = 2CO_2 is shown in Figure 12.16 as the line *cs*. Since it is the variation, with temperature, of the standard Gibbs free energy of formation, ΔG°, this line is for the reaction which produces CO_2 at 1 atm pressure from CO at 1 atm pressure and O_2 at 1 atm pressure. The effect of producing the CO_2 at any pressure, P, other than 1 atm (from CO and O_2 each at 1 atm) is the rotation of the Ellingham line *cs* about the point *c*, clockwise if $P < 1$ atm and anticlockwise if $P > 1$ atm. For the given value of P the rotation is such that, as before, at the temperature T, the vertical displacement of *cs* is $2RT \ln P$. A series of lines, radiating from the point *c*, can thus be drawn for different pressures of CO_2 produced from CO and O_2, each at 1 atm. Figure 12.16 shows four of these lines:

- Line *cq* for CO_2 produced at 10^2 atm
- Line *cr* for CO_2 produced at 10 atm
- Line *cu* for CO_2 produced at 0.1 atm
- Line *cv* for CO_2 produced at 10^{-2} atm

The significance of this series of lines, with respect to the possibility of using CO–CO_2 gas mixtures as reducing agents for the metal oxide MO_2, is illustrated as follows. The Ellingham line for the reaction M + O_2 = MO_2 is drawn in Figure 12.16.

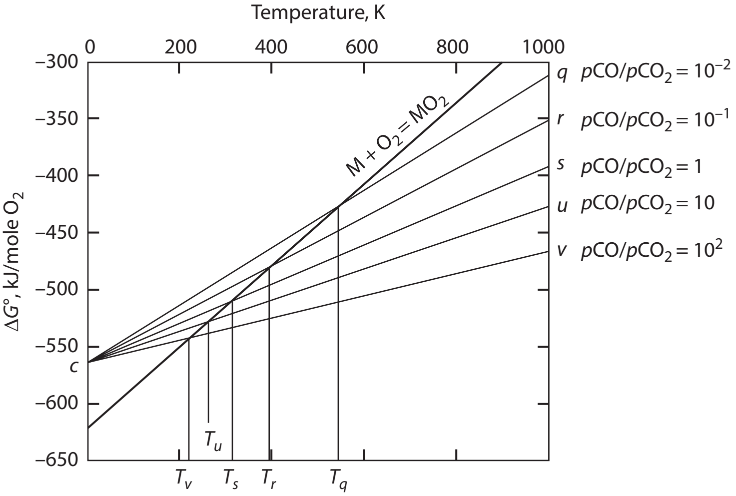

Figure 12.16 Illustration of the effect of the ratio p_{CO_2}/p_{CO} in a CO_2-CO gas mixture on the temperature at which the equilibrium M + CO_2 = MO + CO is established.

This intersects the line *cs* at the temperature T_s, which is thus the temperature at which the standard Gibbs free energy change for reaction

$$MO_2 + 2CO = M + 2CO_2 \tag{ix}$$

is zero; that is,

$$\Delta G^\circ_{(ix)} \text{ at } T_s = 0 = -RT \ \ln\left(\frac{p_{CO_2}}{p_{CO}}\right)^2$$

and thus,

$$\frac{p_{CO_2}}{p_{CO}} = 1$$

At temperatures higher than T_s, a CO–CO_2 mixture of $p_{CO}/p_{CO_2} = 1$ is reducing with respect to MO_2, and at temperatures lower than T_s, it is oxidizing with respect to the metal M. Compare this with the previous discussion of Figure 12.2.

If it is required that a CO–CO_2 mixture be made to be reducing with respect to MO_2 at temperatures lower than T_s, then the ratio p_{CO}/p_{CO_2} must be *increased* to a value greater than unity. The Ellingham line for the reaction M + O_2 = MO_2 intersects the line *cu* at the temperature T_u, and T_u is thus the temperature at which the reaction

$$MO_2 + 2CO(1\text{ atm}) = M + 2CO_2(0.1\text{ atm}) \tag{x}$$

is at equilibrium; that is,

$$\Delta G_{(x)} \text{ at } T_u = \Delta G^\circ_{(ix)} + 2RT\ln 0.1$$

But, by definition,

$$\Delta G^\circ_{(ix)} = -RT\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)^2_{eq}$$

and thus,

$$\Delta G_{(x)} = 0 = -2RT\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)_{eq} + 2RT\ln 0.1$$

Thus, $(p_{CO}/p_{CO_2})_{eq} = 10$ at T_u, and hence, by decreasing the temperature from T_s to T_u, the CO/CO_2 ratio must be increased from 1 to 10 in order to maintain reaction equilibrium.

Similarly, at T_v the equilibrium CO/CO_2 ratio is 100, at T_r the equilibrium CO/CO_2 ratio is 0.1, and at T_q the equilibrium ratio is 0.01. Thus, a CO/CO_2 nomographic scale can be added to the Ellingham diagram, and for any reaction

$$MO_2 + 2CO = M + 2CO_2$$

the equilibrium CO/CO_2 ratio at any temperature T is read off the nomographic scale as that point which is collinear with the point C and the point ΔG°_T, $T = T$, for the reaction $M + O_2 = MO_2$. This scale is included in Figure 12.13.

Figure 12.15 is generated by reading off the equilibrium CO/CO_2 ratios for the reaction $C + O_2 = CO_2$ up to the point a in Figure 12.14, then the CO/CO_2 ratios along the line $abcde$, and finally the CO/CO_2 ratios for the reaction $2C + O_2 = 2CO$ beyond the point e.

In exactly the same manner, the H_2/H_2O nomographic scale is added to Figure 12.13 by considering the effect of the variation of the pressure of H_2O on the reaction equilibrium

$$2H_2 + O_2 = 2H_2O$$

The equilibrium H_2/H_2O ratio at the temperature T for the reaction

$$MO_2 + 2H_2 = M + 2H_2O$$

is read off the H_2/H_2O scale as the point which is collinear with the points H and ΔG°_T, $T = T$ for the reaction $M + O_2 = MO_2$.

12.7 GRAPHICAL REPRESENTATION OF EQUILIBRIA IN THE SYSTEM METAL–CARBON–OXYGEN

The main criteria for graphical representation of equilibria in a system are

- The amount of information provided
- Clarity

and both of these considerations are dependent on the coordinates chosen for use in the graphical representation. Since the nomographic scale for the ratio CO/CO_2 in Figure 12.13 shows that the range of interest of values of p_{CO}/p_{CO_2} is 10^{-14} to 10^{14}, it is convenient to present this ratio on a logarithmic scale. Figure 12.17, which uses the coordinates $\log\left(p_{CO_2}/p_{CO}\right)$, and T represents a convenient method of clearly presenting the reaction equilibrium in the carbon–oxygen and carbon–oxygen–metal systems.

From Equation (iii), for

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$$

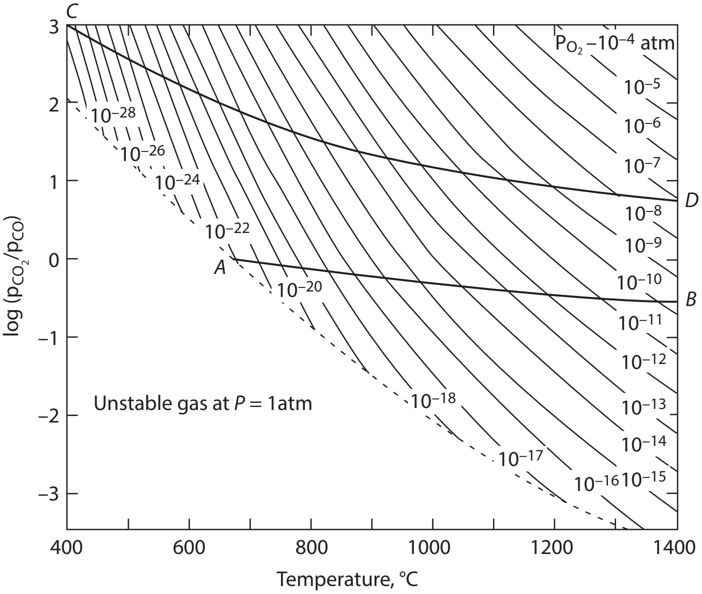

Figure 12.17 The relationship between the partial pressure of oxygen in a CO_2–CO gas mixture and temperature. The broken line is the variation, with temperature, of the composition of the gas which is in equilibrium with graphite at 1 atm pressure. The lines *AB* and *CD* represent, respectively, the equilibria Fe + CO_2 = FeO + CO and Co + CO_2 = CoO + CO.

$$\begin{aligned}\Delta G^\circ_{(\mathrm{iii})} &= -546{,}800 + 173.62T \text{ J}\\ &= -RT \ln\left(\frac{p^2_{CO_2}}{p^2_{CO}p_{O_2}}\right)\end{aligned}$$

and thus,

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right) = \frac{1}{2}\log p_{O_2} + \frac{564{,}800}{2\times 2.303\times 8.3144T} - \frac{173.62}{2\times 2.303\times 8.3144} \tag{xi}$$

For any given value of p_{O_2}, this gives the variation of the given oxygen isobar with $\log(p_{CO_2}/p_{CO})$ and temperature. The oxygen isobars in the range 10^{-29} to 10^{-4} atm are drawn as a function of $\log(p_{CO_2}/p_{CO})$ and T in Figure 12.17.

The equilibrium

$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)} \tag{iv}$$

sets a lower limit on the CO_2/CO ratio which can be obtained at any temperature:

$$\Delta G^\circ_{(\mathrm{iv})} = 170{,}700 - 174.5T \text{ J} = -RT\ln\left(\frac{p^2_{CO}}{p_{CO_2}}\right)$$

and thus, at a total pressure of 1 atm (i.e., when $p_{CO_2} = 1 - p_{CO}$),

$$\frac{p^2_{CO}}{1-p_{CO}} = \exp\left(\frac{-170{,}700}{8.3144T}\right)\exp\left(\frac{174.5}{8.3144}\right) = x$$

or

$$p^2_{CO} + p_{CO}x - x = 0$$

solution of which gives

$$p_{CO} = \frac{-x+\sqrt{x^2+4x}}{2}$$

$$p_{CO_2} = \frac{2+x-\sqrt{x^2+4x}}{2}$$

and

$$\frac{p_{CO_2}}{p_{CO}} = \frac{2+x-\sqrt{x^2+4x}}{\sqrt{x^2+4x}-x} \tag{xii}$$

The value of p_{CO_2}/p_{CO} given by Equation (xii) is the minimum obtainable value at the temperature T. If an attempt is made to mix CO and CO_2 (at $P_{\text{total}} = 1$ atm) in a ratio p_{CO_2}/p_{CO} lower than that given by Equation (xii), carbon will precipitate until, thereby, the ratio is increased to the unique value required for equilibrium with carbon at the temperature T. The variation of $\log(p_{CO_2}/p_{CO})_{\text{eq.C/CO/CO}_2}$ with temperature is shown as the broken line in Figure 12.17. The variation of the corresponding minimum values of p_{O_2} with temperature in Figure 12.17 is given by the intersections of the oxygen isobars with the carbon deposition line.

Equilibria such as

$$\text{MO} + \text{CO} = \text{M} + \text{CO}_2$$

can readily be presented on plots such as that in Figure 12.17. For example, for

$$\text{FeO}_{(s)} + \text{CO}_{(g)} = \text{Fe}_{(s)} + \text{CO}_{2(g)}$$

$$\Delta G^{\circ} = -22{,}800 + 24.26T \text{ J}$$

and thus, the variation of the equilibrium ratio CO_2/CO with temperature is given by

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq.FeO/Fe}} = \frac{22{,}800}{2.303\times 8.3144T} - \frac{24.26}{2.303\times 8.3144}$$

This variation is drawn as the line AB in Figure 12.17, and thus, any gas, the state of which lies above the line AB, is oxidizing with respect to Fe, and states below AB are reducing with respect to FeO. The variation of $\log p_{O_2(\text{eq.T,Fe/FeO})}$ with temperature is given by the intersections of the oxygen isobars with the line AB. The temperature at which AB intersects the carbon deposition line is the minimum temperature at which solid FeO can be reduced to solid Fe by graphite, and this is the temperature at which $\text{Fe}_{(s)}$, $\text{FeO}_{(s)}$, $\text{C}_{(s)}$, and the CO–CO_2 atmosphere at 1 atm pressure coexist in equilibrium; that is, it is the temperature at which

$$p_{CO_2(\text{eq.C/CO/CO}_2)} = p_{O_2(\text{eq.Fe/FeO})}$$

The line CD in Figure 12.17 represents the variation of $\log(p_{CO_2}/p_{CO})$ with T for the equilibrium

$$\text{CoO}_{(s)} + \text{CO}_{(g)} = \text{Co}_{(s)} + \text{CO}_{2(g)}$$

for which

$$\Delta G^{\circ} = -48{,}500 + 14.9T \text{ J}$$

and

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq.Co/CoO}} = \frac{48{,}500}{2.303\times 8.3144T} - \frac{14.9}{2.303\times 8.3144}$$

Since the equilibrium constant K for the reaction

$$\mathrm{MO + CO = M + CO_2}$$

is given by $p_{\mathrm{CO_2}}/p_{\mathrm{CO(eq.}T\mathrm{,M/MO)}}$, a plot of $\log p_{\mathrm{CO_2}}/p_{\mathrm{CO(eq.}T\mathrm{,M/MO)}}$ versus $1/T$ is a plot of $\log K$ versus $1/T$. Figure 12.18 shows the information given in Figure 12.17 as such a plot. With respect to the amount of information which can be obtained from a graphical representation of equilibria in a system, Figure 12.18 is a better representation than is Figure 12.17.

Since

$$\left[\frac{d\ln K}{d\left(\dfrac{1}{T}\right)}\right] = -\frac{\Delta H^\circ}{R}$$

the slope of a tangent to an equilibrium line at the temperature T gives the value of $-\Delta H^\circ/R$. If $\Delta c_p = 0$, $\log K$ is a linear function of $1/T$. Thus, the slope of the line AB in Figure 12.18 equals $-\Delta H^\circ/R$ for the reaction $\mathrm{FeO + CO = Fe + CO_2}$, and the slope of the line CD equals $-\Delta H^\circ/R$ for the reaction $\mathrm{CoO + CO = Co + CO_2}$. Also,

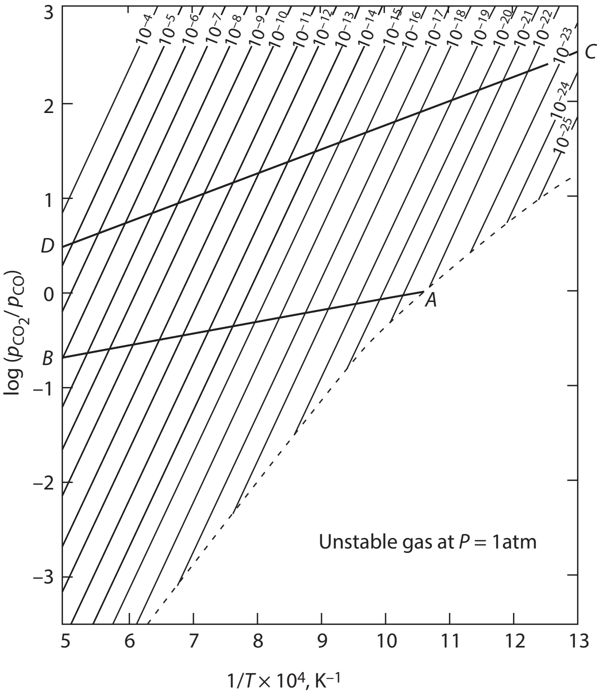

Figure 12.18 Figure 12.17 reproduced as $\log(p_{\mathrm{CO_2}}/p_{\mathrm{CO}})$ vs. $1/T$.

if they are linear, the intercepts of the lines themselves with the $1/T = 0$ axis give the corresponding values of $\Delta S^\circ/R$ for the reactions. From Equation (xi), the slope of any oxygen isobar equals $-\Delta H^\circ/2R$ for the reaction $2CO + O_2 = 2CO_2$, and thus, the oxygen isobars in Figure 12.18 are parallel lines.

12.8 SUMMARY

1. The following two facts facilitate a convenient definition of the standard state of species occurring as condensed phases.
    - A pure species occurring as a condensed phase exerts a unique saturated vapor pressure at the temperature T.
    - The dependence of the Gibbs free energy of a condensed phase on pressure (at low pressure) is negligibly small.

   This standard state is simply the pure species in its stable condensed state at the temperature T.
2. Using this standard state, the equilibrium constant for a reaction involving pure condensed phases and a gas phase can be written in terms of the partial pressures of those species which occur only in the gas phase. For example, for the oxidation of a pure metal to its pure stoichiometric oxide, the equilibrium constant is given by $1/p_{O_2(\text{eq}.T)}$, where $p_{O_2(\text{eq}.T)}$ is the unique partial pressure of oxygen required for equilibrium between the metal, its oxide, and the gas phase at the temperature T. This pressure is such that

$$G^\circ_M + G^\circ_{O_2} + RT\ln p_{O_2(\text{eq}.T)} = G^\circ_{MO_2}$$

   or

$$\Delta G^\circ_T = -RT\ln K = -RT\ln\left(\frac{1}{p_{O_2(\text{eq}.T)}}\right)$$

3. Determination of the equilibrium state of a chemical reaction system requires knowledge of the variation, with temperature, of the standard Gibbs free energy change for the reaction. This relationship can be obtained from thermochemical data—that is, from knowledge of the standard enthalpy and entropy changes at a single temperature (usually ΔH°_{298} and ΔS°_{298}) and the variations, with temperature, of the constant-pressure molar heat capacities of the reactants and products, or it can be determined from knowledge of the variation, with temperature, of the equilibrium constant for the reaction.
4. For the oxidation of a pure metal to its pure oxide, experimental measurement of the variation of $p_{O_2(\text{eq}.T)}$ with temperature gives the variation of ΔG° with temperature as

$$\ln\left(\frac{1}{p_{O_2(\text{eq}.T)}}\right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta G^\circ}{RT}$$

If ΔH° and ΔS° are independent of temperature (i.e., if $\Delta c_p = 0$), ln K is a linear function of $1/T$.

5. The fitting of the variation of ΔG° with T to a line produces the so-called Ellingham line for the reaction, and a plot of ΔG° versus T is known as an Ellingham diagram. Ellingham lines plotted on a single diagram for a series of similar reactions (e.g., for the formation of oxides, sulfides, etc.) provide a convenient representation of the relative stabilities of the compounds.
6. The addition of $p_{O_2}, p_{CO}/p_{CO_2}$ and p_{H_2}/p_{H_2O} nomographic scales to these diagrams facilitates the geometric determination of $p_{O_2(\text{eq.}T)}, p_{CO}/p_{CO_2(\text{eq.}T)}$, and $p_{H_2}/p_{H_2O(\text{eq.}T)}$ for, respectively, the equilibria $2M + O_2 = 2MO$, $M + CO_2 = MO + CO$, and $M + H_2O = MO + H_2$.

12.9 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 12

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Blast furnace
Boudouard reaction
Carbon–oxygen reactions
Chemical affinity
Chlorination of a metal
Condensed-phase reactions with gases
Decomposition of a solid phase
Ellingham diagrams
Gibbs equilibrium phase rule
Log pressure versus $1/T$ phase diagram
Metal–carbon–oxygen equilibria
Oxidation of pure solid phase
Phase transformations and the Ellingham diagram
Pure species
Reduction of an oxide
Richardson nomographic scale
Temperature dependence of the standard free energy change

12.10 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Problem 1

Apply the Gibbs equilibrium phase rule to the oxidation of Cu to form cuprous oxide (Figure 12.1).

Solution to Qualitative Problem 1

$$4\text{Cu}_{(s)} + \text{O}_{2(g)} = 2\text{Cu}_2\text{O}_{(s)}$$

We use the equation

$$\Phi + \mathscr{F} = \left(C - r\right) + 2$$

where:

Φ is the number of phases in equilibrium
$\mathscr{F}$ is the thermodynamic degrees of freedom
C is the number of components
r is the number of chemical reactions needed to specify equilibrium
2 accounts for the intensive variables pressure and temperature

For this case:

$r = 1$
$\Phi = 3$ (2 solids and one gaseous)
$3 + \mathscr{F} = (3 - 1) + 2$ or $\mathscr{F} = 1$

We can see from Figure 12.1 that when the temperature is specified, there is only one possible partial pressure of oxygen gas that allows for the equilibrium of the given reaction. Or, if a specific partial pressure is desired, it can be found at but one temperature.

Qualitative Problem 2

Apply the Gibbs equilibrium phase rule to the reduction of cupric oxide by ammonia and determine the number of degrees of freedom that exist for the reaction.

Solution to Qualitative Problem 2

$$3\text{CuO}_{(s)} + 2\text{NH}_{3(g)} = 3\text{Cu}_{(s)} + 3\text{H}_2\text{O}_{(g)} + \text{N}_{2(g)}$$

We use the equation

$$\Phi + \mathscr{F} = \left(C - r\right) + 2$$

Where:

Φ is the number of phases in equilibrium
$\mathscr{F}$ is the thermodynamic degrees of freedom
C is the number of components
r is the number of chemical reactions needed to specify equilibrium
2 accounts for the intensive variables pressure and temperature

For this case:

$r = 1$
$\Phi = 3$ (2 solids and one gaseous)
$3 + \mathscr{F} = (5 - 1) + 2$ or $\mathscr{F} = 3$

12.11 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Compare the relative efficiencies of H_2 and CO as reducing agents for metal oxides. For $CO + ½O_2 = CO_2$,

$$\Delta G^\circ_{\text{(i)}} = -282{,}400 + 86.81T \text{ J} \tag{i}$$

and for $H_2 + ½O_2 = H_2O$,

$$\Delta G^\circ_{\text{(ii)}} = -247{,}500 + 55.85T \text{ J} \tag{ii}$$

Solution to Quantitative Problem 1

The values of ΔH° and ΔS° for these two reactions cause their Ellingham lines to intersect at 1127 K, as shown in Figure 12.13, with $\Delta G^\circ_{\text{(ii)}}$ being more negative than $\Delta G^\circ_{\text{(i)}}$ at temperatures higher than 1125 K and $\Delta G^\circ_{\text{(i)}}$ being more negative than $\Delta G^\circ_{\text{(ii)}}$ at temperatures lower than 1125 K. This indicates that H_2 is the more efficient reducing agent at higher temperatures and that CO is the more efficient reducing agent at lower temperatures.

Consider the reduction of CoO by each of H_2 and CO at 1673 K and at 873 K.

For $CoO(s) = Co_{(s)} + ½O_{2(g)}$:

$$\Delta G^\circ_{\text{(iii)}} = +233{,}900 - 71.85T \text{ J} \tag{iii}$$

Combination of $\Delta G^\circ_{\text{(i)}}$ and $\Delta G^\circ_{\text{(iii)}}$ gives

$$\Delta G^\circ_{\text{(iv)}} = -48{,}500 + 14.96 \text{ T} \tag{iv}$$

for $CoO + CO = Co + CO_2$, and combination of $\Delta G^\circ_{\text{(iii)}}$ and $\Delta G^\circ_{\text{(ii)}}$ gives

$$\Delta G^\circ_{\text{(v)}} = -12{,}500 - 17.05T \text{ J} \tag{v}$$

for $CoO + H_2 = Co + H_2O$. The positive value of $\Delta S^\circ_{\text{(v)}}$ causes $\Delta G^\circ_{\text{(v)}}$ to become more negative with increasing temperature and the negative value of $\Delta S^\circ_{\text{(iv)}}$ causes $\Delta G^\circ_{\text{(iv)}}$ to become less negative with increasing temperature. At 1673 K $\Delta G^\circ_{\text{(v)}} = -41{,}024$ J, and thus,

$$K_{\text{(v)},1673\text{ K}} = \exp\left(\frac{41{,}024}{8.3144 \times 1673}\right) = 19.1 = \left(\frac{p_{H_2O}}{p_{H_2}}\right)_{\text{eq.}}$$

Thus, if H_2 at 1673 K is passed through a column of CoO, which is long enough that reaction equilibrium is achieved before the gas leaves the column, the fraction of H_2 which is consumed before equilibrium is reached is 19.1/20.1 = 0.95, and thus, 1 mole of H_2 is required to reduce 0.95 moles of CoO.

At 1673 K, $\Delta G^\circ_{(\text{iv})} = -23{,}470$ J, and thus,

$$K_{(\text{iv}),1673} = 5.40 = \left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq.}}$$

and thus, the fraction of CO which is consumed by the reduction reaction at 1673 K before equilibrium is reached is 5.40/6.40 = 0.844. Thus, 1 mole of CO is required to reduce 0.844 moles of CoO.

At 873 K, $\Delta G^\circ_{(\text{iv})} = -27{,}384$ J, which gives

$$K_{(\text{v}),873} = 43.5 = \left(\frac{p_{H_2O}}{p_{H_2}}\right)_{\text{eq.}}$$

and thus, the fraction of H_2 consumed is 43.5/44.5 = 0.978 and 1 mole of H_2 reduces 0.978 moles of CoO.

At 873, $\Delta G^\circ_{(\text{iv})} = -35{,}440$ J, which gives

$$K_{(\text{iv}),873} = 132 = \left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq.}}$$

Thus, the fraction of CO consumed is 132/133 = 0.992, and 1 mole of CO reduces 0.992 moles of CoO. Thus, H_2 is the more efficient reducing agent at higher temperatures and CO is the more efficient at lower temperatures, and decreasing the temperature at which the reduction reaction is conducted increases the efficiencies of both reductants.

Quantitative Problem 2

Consider the reduction of solid ZnO by CO to form Zn vapor and CO_2 according to

$$ZnO_{(s)} + CO_{(g)} = Zn_{(v)} + CO_2(g) \tag{i}$$

For $ZnO_{(s)} = Zn_{(v)} + \frac{1}{2}O_{2(g)}$:

$$\Delta G^\circ_{(\text{ii})} = 460{,}200 - 198T \text{ J} \tag{ii}$$

For $CO_{(g)} + \frac{1}{2}\ O_{2(g)} = CO_{2(g)}$:

$$\Delta G^\circ_{(\text{iii})} = \quad 282{,}400 + 86.81T \text{ J} \tag{iii}$$

Summing $\Delta G^\circ_{(\text{ii})}$ and $\Delta G^\circ_{(\text{iii})}$ gives

$$\Delta G^\circ_{(\text{i})} - 177{,}800 - 111.2T \text{ J}$$

The equilibrium involves three components (Zn, O, and C) and two phases (a solid and a gas), and thus, from the phase rule, has

$$\mathcal{F} = C + 2 - \Phi = 3 + 2 - 2 = 3 \text{ degrees of freedom}$$

However, the stoichiometric requirement that $p_{\text{Zn}} = p_{\text{CO}_2}$ uses one of the degrees of freedom, and thus, the equilibrium is fixed when the temperature and total pressure are fixed.

a. Calculate the composition of the gas phase at 950°C and $P = 1$ atm.
b. To what value must the total pressure of the gas mixture be increased in order to cause condensation of the zinc vapor at 1223 K?
c. Calculate the composition of the gas phase if the total pressure is increased to 150 atm at 1223 K.

Solution to Quantitative Problem 2

a. At 1223 K,

$$\Delta G^\circ_{(\text{i})} = 177{,}800 - (111.2 \times 1223) = 41{,}800 \text{ J}$$

and thus,

$$K_{(\text{iii})\ 1223\ \text{K}} = \exp\left(\frac{-41{,}800}{8.3144 \times 1223}\right) = 0.0164 = \frac{p_{\text{Zn}}p_{\text{CO}_2}}{p_{\text{CO}}}$$

From the stoichiometry, $p_{\text{Zn}} = p_{\text{CO}_2}$ and the total pressure P is

$$P = p_{\text{CO}} + p_{\text{Zn}} + p_{\text{CO}_2} \tag{iv}$$

Thus, with $P = 1$ atm, $p_{\text{CO}} = 1 - 2p_{\text{Zn}}$ and

$$0.0164 = \frac{p^2_{\text{Zn}}}{1 - 2p_{\text{Zn}}} \tag{v}$$

which has the solution $p_{\text{Zn}} = 0.113$ atm. Therefore, $p_{\text{CO}_2} = 0.113$ atm and $p_{\text{CO}} = 1 - (2 \times 0.113) = 0.775$ atm. At $P = 1$ atm, the mole fractions of the species in the gas phase are equal to their partial pressures.

b. Condensation occurs when the partial pressure of Zn reaches the value of the saturated vapor pressure of liquid zinc at 1223 K. The saturated vapor pressure of liquid zinc is given by

$$\ln p^\circ_{\text{Zn},(l)}(\text{atm}) = \frac{-15{,}250}{T} - 1.255 \ln T + 21.79$$

which gives $p^\circ_{\mathrm{Zn},(l)} = 1.49$ atm at 1223 K. Therefore,

$$K_{\mathrm{(iii)\ 1223\ K}} = 0.0164 = \frac{1.49^2}{P-(2\times 1.49)}$$

which has the solution P = 138 atm. Thus, p_{Zn} = p_{CO} = 1.49 atm and $p_{\mathrm{CO_2}} = 138-(2\times 1.49) = 135$ atm. At the point of condensation of zinc, the mole fractions of the species in the gas phase are X_{Zn} = $X_{\mathrm{CO_2}}$ = 1.49/138 = 0.011 and X_{CO} = 135/138 = 0.978.

c. The system now contains three phases and the equilibrium thus has two degrees of freedom. Condensation of the zinc eliminates the stoichiometric requirement that $p_{\mathrm{Zn}} = p_{\mathrm{CO_2}}$, but phase equilibrium between liquid zinc and zinc vapor at 1223 K requires that the partial pressure of zinc be the saturated value of 1.49 atm. Thus,

$$K_{\mathrm{1223\ K}} = 0.0164 = \frac{1.49\times p_{\mathrm{CO_2}}}{p_{\mathrm{CO}}} \tag{vi}$$

and

$$P = 150 = 1.49 + p_{\mathrm{CO}} + p_{\mathrm{CO_2}} \tag{vii}$$

Simultaneous solution of Equation (vi) and (vii) gives p_{CO} = 146.9 atm and $p_{\mathrm{CO_2}} = 1.61$ atm. The mole fractions of the species in the gas phase are thus X_{Zn} = 1.49/150 = 0.01, $X_{\mathrm{CO_2}} = 1.61/150 = 0.011$, and X_{CO} = 146.9/150 = 0.98.

Further considerations:

i. Consider, now, the reduction of ZnO by graphite to form zinc vapor, CO, and CO_2 according to

$$\mathrm{ZnO}_{(s)} + \mathrm{C}_{(gr)} = \mathrm{Zn}_{(v)} + \mathrm{CO}_{(g)} \tag{viii}$$

and

$$2\mathrm{ZnO}_{(s)} + \mathrm{C}_{(gr)} = 2\mathrm{Zn}_{(v)} + \mathrm{CO}_{2(g)} \tag{ix}$$

For $2C + O_2 = 2CO$:

$$\Delta G^\circ_{\mathrm{(x)}} = -223{,}400 - 175.3T \text{ J} \tag{x}$$

For $C + O_2 = CO_2$:

$$\Delta G^\circ_{\mathrm{(xi)}} = -394{,}100 - 0.84T \text{ J} \tag{xi}$$

Combination of $\Delta G^\circ_{\mathrm{(ii)}}$ and $\Delta G^\circ_{\mathrm{(x)}}/2$ gives

$$\Delta G^\circ_{\mathrm{(viii)}} = 348{,}500 - 285.7T \text{ J}$$

for ZnO + C = Zn + CO, and combination of $2\Delta G^\circ_{(ii)}$ and $\Delta G^\circ_{(xi)}$ gives

$$\Delta G^\circ_{(ix)} = 526{,}300 - 396.8T \text{ J}$$

for 2ZnO + C = 2Zn + CO_2.

ii. The equilibrium involves three components and three phases (ZnO, graphite, and a gas phase) and thus, according to the phase rule, has two degrees of freedom. However, as stoichiometric ZnO is the only source of oxygen and zinc in the gas phase, one of the degrees of freedom is used by the requirement that equal numbers of moles of Zn and O occur in the gas phase. Alternatively, as ZnO has a fixed composition, the system can be considered to be the quasi-binary ZnO–C, in which case the phase rule gives one degree of freedom to the equilibrium. Thus, fixing either (1) the temperature, (2) the total pressure, (3) p_{Zn}, (4) p_{CO}, or (5) p_{CO_2} fixes the equilibrium. Determine the equilibrium state at 1223 K.

At 1223 K, $\Delta G^\circ_{(viii)1223\text{ K}} = -850 \text{ J}$ and thus,

$$K_{(viii)1223\text{K}} = \exp\left(\frac{850}{8.3144 \times 1223}\right) = 1.087 = p_{Zn}p_{CO} \tag{xii}$$

and $\Delta G^\circ_{(ix)1223\text{ K}} = 40{,}960 \text{ J}$, in which case

$$K_{(ix)1223\text{ K}} = \exp\left(\frac{-40{,}960}{8.3144 \times 1223}\right) = 0.018 = p^2_{Zn}p_{CO_2} \tag{xiii}$$

The requirement that $n_{Zn}/n_O = 1$ in the gas phase leads to

$$\frac{n_{Zn}}{n_O} = 1 = \frac{n_{Zn}}{n_{CO} + 2n_{CO_2}} = \frac{p_{Zn}}{p_{CO} + 2p_{CO_2}}$$

Thus,

$$p_{Zn} = p_{CO} + 2p_{CO_2} \tag{xiv}$$

Substitution of Equations (xiv) into (xii) gives

$$\left(p_{CO} + 2p_{CO_2}\right)p_{CO} = 1.08 \tag{xv}$$

and substitution of Equations (xiv) into (xiii) gives

$$\left(p_{CO} + 2p_{CO_2}\right)^2 p_{CO_2} = 0.018 \tag{xvi}$$

Simultaneous solution of Equations (xv) and (xvi) gives p_{CO} = 1.023 atm and $p_{CO_2} = 0.016$ atm, and Equation xiv gives p_{Zn} = 1.023 + (2 × 0.016) = 1.055 atm. The total pressure at which the equilibrium exists at 1223 K is thus 1.055 + 1.023 + 0.016 = 2.094 atm.

iii. Consider now the temperature at which the total pressure is 1 atm. Rewriting Equations (xii) and (xiii) to include temperature as a variable gives

$$K_{(\mathrm{viii}),\,T} = \exp\left(\frac{-\Delta G^\circ_{(\mathrm{viii})}}{RT}\right) = p_{\mathrm{Zn}} p_{\mathrm{CO}}$$

or, substituting for $\Delta G^\circ_{(\mathrm{viii})}$ and p_{Zn},

$$\exp\left(\frac{-348{,}500}{8.3144T}\right)\exp\left(\frac{285.7}{8.3144}\right) = (p_{\mathrm{CO}} + 2p_{\mathrm{CO_2}})p_{\mathrm{CO}} \tag{xvii}$$

and

$$K_{(\mathrm{ix}),\,T} = \exp\left(\frac{-\Delta G^\circ_{(\mathrm{ix})}}{RT}\right) = \mathrm{p}^2_{\mathrm{Zn}} p_{\mathrm{CO_2}}$$

or, substituting for $\Delta G^\circ_{(\mathrm{ix})}$ and p_{Zn},

$$K_{(\mathrm{ix}),T} = \exp\left(\frac{-526{,}300}{8.3144T}\right)\exp\left(\frac{396.8}{8.3144}\right) = (p_{\mathrm{CO}} + 2p_{\mathrm{CO_2}})^2 p_{\mathrm{CO_2}} \tag{xviii}$$

The third equation is

$$P = 1 = p_{\mathrm{Zn}} + p_{\mathrm{CO}} + p_{\mathrm{CO_2}}$$

or

$$1 = (p_{\mathrm{CO}} + 2p_{\mathrm{CO_2}}) + p_{\mathrm{CO}} + p_{\mathrm{CO_2}} \tag{xix}$$

Simultaneous solution of Equations (xvii), (xviii), and (xix) gives

$$T = 1172 \text{ K}$$

$$p_{\mathrm{CO}} = 0.489 \text{ atm}$$

and

$$p_{\mathrm{CO_2}} = 0.007 \text{ atm}$$

Thus, $p_{\mathrm{Zn}} = 0.489 + (2 \times 0.007) = 0.503$ atm, and the total pressure is $0.489 + 0.503 + 0.007 = 1$ atm.

Quantitative Problem 3

During the chlorination of NiO in a reactor at 900 K, it is required that 90% conversion of the chlorine gas be achieved during a single pass through the reactor. Calculate the required total gas pressure.

The reaction is

$$\mathrm{NiO}_{(s)} + \mathrm{Cl}_{2(g)} = \mathrm{NiCl}_{2(s)} + \frac{1}{2}\mathrm{O}_{2(g)}$$

for which $\Delta G^{\circ}_{900\ \mathrm{K}} = -15{,}490$ J. Thus,

$$K_{900\ \mathrm{K}} = \exp\left(\frac{15{,}490}{8.3144 \times 900}\right) = 7.925$$

From the stoichiometry of the reaction,

$$\mathrm{NiO}_{(s)} + \mathrm{Cl}_{2(g)} = \mathrm{NiCl}_{2(s)} + \frac{1}{2}\mathrm{O}_{2(g)}$$

For 90% conversion of the Cl_2, $x = 0.9$, and thus, $n_{\mathrm{Cl}_2} = 0.1$, $n_{\mathrm{O}_2} = 0.45$, and $n_{\mathrm{T}} = 0.55$. In a Cl_2–O_2 mixture at the pressure P, the partial pressures of chlorine and oxygen are thus

$$p_{\mathrm{Cl}_2} = \frac{0.1}{0.55}P = 0.182P \quad \text{and} \quad p_{\mathrm{O}_2} = \frac{0.45}{0.55}P = 0.818P$$

Thus,

$$K_{900\ \mathrm{K}} = 7.925 = \frac{p_{\mathrm{O}_2}^{1/2}}{p_{\mathrm{Cl}_2}} = \frac{(0.818P)^{1/2}}{0.182P} = \frac{4.969}{P^{1/2}}$$

which has the solution $P = 0.393$ atm.

For another Quantitative Problem, see Appendix 12.B.

PROBLEMS

12.1 To what temperature must $MgCO_3$ be heated in an atmosphere containing a partial pressure of CO_2 of 10^{-2} atm to cause the decomposition of the carbonate?

12.2 Using the standard Gibbs free energies of formation of NiO from solid Ni and liquid Ni, calculate the melting temperature, molar heat of melting, and the molar entropy of melting of nickel.

12.3 Calculate the temperature at which pure Ag_2O decomposes to Ag metal and O_2 gas when heated in (a) pure oxygen at 1 atm pressure, and (b) air.

12.4 Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic?

12.5 A mixture of argon gas and hydrogen gas at 1 atm total pressure is passed through a reaction vessel containing a mixture of liquid Sn and liquid $SnCl_2$ at

900 K. The composition of the gas leaving the vessel is 50% H_2, 7% HCl, and 43% Ar. Has equilibrium been attained between the gas phase and the liquid phases in the vessel?

12.6 Fe and FeO are in equilibrium with a gas mixture of composition 71.8% CO–28.2% CO_2 at 1273 K. Which of the two solid phases disappears if the composition of the gas is held constant and the temperature of the system is decreased?

12.7 Calculate the vapor pressure of Mg exerted at 1400°C by the system in which the following reaction equilibrium is established.

$$MgO_{(s)} + Si_{(s)} = 2Mg_{(g)} + Mg_2SiO_{4(s)}$$

12.8 One gram of $CaCO_3$ is placed in an evacuated rigid vessel of volume 1 liter at room temperature, and the system is heated. Calculate (a) the highest temperature at which the $CaCO_3$ phase is present, (b) the pressure in the vessel at 1000 K, and (c) the pressure in the vessel at 1500 K. The molecular weight of $CaCO_3$ is 100.

12.9 Calculate the total pressure $\left(p_{SO_3} + p_{SO_2} + p_{O_2}\right)$ exerted by equilibrated CoO and $CoSO_4$ at 1223 K.

12.10 A gas mixture initially containing 90% CO, 0.4% COS, and 9.6% inert constituents (by volume) is passed over sponge iron at 1000 K to remove sulfur by the following reaction:

$$COS_{(g)} + Fe_{(s)} = CO_{(g)} + FeS_{(s)}$$

a. Assuming that the effluent gas is in equilibrium with Fe and FeS, calculate the percentage of sulfur removed from the gas by reaction with the sponge iron.
b. Calculate the partial pressure of S_2 in the effluent gas.

12.11 An Ar–H_2O gas mixture of $p_{H_2O} = 0.9$ atm ($P_{total} = 1$ atm) is passed over solid CaF_2, as a result of which CaO forms according to

$$CaF_{2(s)} + H_2O_{(g)} = CaO_{(s)} + 2HF_{(g)}$$

The reaction proceeds to equilibrium and solid CaO and solid CaF_2 are mutually immiscible. When the gas flow rate (measured at 298 K and 1 atm pressure) over the sample is 1 liter per minute, the measured rates of weight loss of the sample are 2.69×10^{-4} and 8.30×10^{-3} grams per hour at 900 and 1100 K, respectively. Use these data to calculate the variation of ΔG° for the preceding reaction with temperature. The atomic weights are

$$O = 16,\ F = 19,\ \text{and}\ Ca = 40.08$$

12.12 Magnetite (Fe_3O_4) is reduced to sponge iron (Fe) in a continuous reactor operating at 800 K using methane gas (CH_4) as the reducing agent. The gaseous reaction product leaving the reactor at a total pressure of 1 atm is a mixture of CO, CO_2, H_2, and H_2O with a negligible methane content. The gas is at equilibrium with the Fe–Fe_3O_4 mixture in the reactor. Calculate the consumption of methane as moles of methane used per mole of sponge iron produced.

12.13 Three equations for the oxidation of Mg according to Mg + ½$O_{2(g)}$ = $MgO_{(s)}$ are

$$\Delta G^\circ = -604{,}000 - 5.36T \ln T + 142.0T \text{ J} \tag{i}$$

$$\Delta G^\circ = -759{,}800 - 13.4T \ln T + 317T \text{ J} \tag{ii}$$

$$\Delta G^\circ = -608{,}100 - 0.44T \ln T + 112.8T \text{ J} \tag{iii}$$

One of these expressions is for the oxidation of solid Mg, one is for the oxidation of liquid Mg, and one is for the oxidation of gaseous Mg. Determine which equation is for which oxidation and calculate the melting and normal boiling temperature of Mg.

12.14 Two hundred grams of liquid zinc are placed in a crucible at 1030 K. Two moles of air are bubbled through the liquid zinc, and the gas comes to equilibrium with the liquid before leaving the system. If the total pressure of the gas remains constant at 0.8 atm throughout the process, how many grams of *metallic* zinc are left in the crucible? The atomic weights of Zn and O are, respectively, 65.38 and 16.

12.15 Methane gas is burned with twice the amount of stoichiometric air (i.e., the initial ratio of CH_4 and O_2 in the mixture is 0.25), and the combustion gas produced, in which the concentration of methane is negligible, is used to calcine $CaCO_3$ in an isothermal furnace. The gas and the solids are at 1080 K and the pressure of the gas is maintained constant at 1 atm. How many moles of $CaCO_3$ are decomposed per mole of CH_4 burned?

12.16 Mercuric oxide (HgO) is placed in a vessel which is then evacuated, filled with nitrogen, and heated to 600 K, at which temperature it is observed that the total pressure in the vessel is 2 atm. Calculate the mole fractions of O_2 and Hg vapor in the gas phase.

12.17 In Figure 12.17 the line *AB*, which represents the equilibrium

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$$

intersects the carbon deposition line at the point *A* ($T = 972$ K, $p_{CO(s)} = 0.595$ atm, $p_{CO_2} = 0.405$ atm, $P = 1.000$ atm). At what total pressure does the point of intersection of the lines occur at 1000 K, and what are the values of the partial pressures of CO and CO_2 in this state?

APPENDIX 12A

The value of *I* can be determined if *K* is known at any temperature *T*. For the reaction

$$4Cu_{(s)} + O_{2(g)} + 2Cu_2O_{(s)}$$

gives I = 171.8 J/K. Hence

$$\Delta H^\circ_{298} = -324{,}400 \text{ J}$$
$$\Delta S^\circ_{298} = -138.5 \text{ J/K}$$

and thus,

$$\Delta G^\circ_{298} = -324{,}400 + (298 \times 138.5) = -283{,}100 \text{ J}$$

which is K = K(T) with no unknown constants.

In the range 298–1356 K,

$$c_{p,\mathrm{Cu}(s)} = 22.6 + 6.3 \times 10^{-3}T \text{ J/K}$$

In the range 298–1200 K,

$$c_{p,\mathrm{Cu_2O}(s)} = 62.34 + 24 \times 10^{-3}T \text{ J/K}$$

and in the range 298–3000 K,

$$c_{p,\mathrm{O_2}(g)} = 30 + 4.2 \times 10^{-3}T - 1.7 \times 10^{5}T^{-2} \text{ J/K}$$

such that in the temperature range 298–1200 K,

$$\begin{aligned}\Delta c_p &= 2c_{p,\mathrm{Cu_2O}(s)} - 4c_{p,\mathrm{Cu}(s)} - c_{p,\mathrm{O_2}(g)} \\ &= 4.28 + 18.6 \times 10^{-3}T + 1.7 \times 10^{5}T^{-2} \text{ J/K}\end{aligned}$$

Thus,

$$\Delta H_T^\circ = \Delta H_0 + 4.28T + 9.3 \times 10^{-3}T^2 - 1.7 \times 10^5 T^{-1} \text{ J}$$

Substitution of $\Delta H_{298}^\circ = -324{,}400$ J gives $\Delta H_0 = -325{,}900$ J. Dividing by $-T^2$, integrating with respect to T, and multiplying through by T gives

$$\Delta G_T^\circ = -325{,}900 - 4.28\ \ln T - 9.3 \times 10^{-3}T^2 - 0.85 \times 10^5 T^{-1} + IT$$

Substitution of $\Delta G_{298}^\circ = -283{,}100$ J gives $I = 171.7$, and hence,

$$\Delta G_T^\circ = -325{,}900 - 4.28 \ln T - 9.3 \times 10^{-3}T^2 - 0.85 \times 10^5 T^{-1} + 171.7 \text{ J} \tag{i}$$

and

$$\begin{aligned}-\ln K = \frac{\Delta G_T^\circ}{RT} &= \ln\ p_{\mathrm{O_2}(\mathrm{eq}.T)} \\ &= -\frac{39{,}200}{T} - 0.515 \ln T - 1.1 \times 10^{-3}T - \frac{1.0 \times 10^4}{T^2} + 20.65\end{aligned}$$

APPENDIX 12B

Quantitative Problem 4

What is the equilibrium state of a CO–CO_2–H_2–H_2O gas mixture produced by mixing CO_2 and H_2 in the molar ratio 1/1 at 1000 K and a total pressure of 1 atm?

The reaction which occurs is

$$CO_2 + H_2 = CO + H_2O \tag{i}$$

As the molar ratio of CO_2 to H_2 in the initial mixture is 1/1 and $P = 1$ atm, then, before reaction begins, $p_{CO_2} = p_{H_2} = 0.5$ atm. From the stoichiometry of the reaction, at any time during the reaction, $p_{CO_2} = p_{H_2}$ and $p_{CO} = p_{H_2O}$. At equilibrium,

$$K_{p,(i)} = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} \tag{ii}$$

The total pressure is

$$P = p_{CO_2} + p_{CO} + p_{H_2O} + p_{H_2} = 1$$

but, as

$$p_{CO_2} = p_{H_2} \quad \text{and} \quad p_{CO} = p_{H_2O}$$

then

$$P = 1 = 2p_{H_2O} + 2p_{H_2}$$

Thus,

$$p_{H_2O} = 0.5 - p_{H_2} \quad \text{and} \quad p_{CO_2} = p_{H_2}$$

substitution of which into Equation (ii) gives

$$K_{p,(i)} = \frac{(0.5 - p_{H_2})^2}{p_{H_2}^2}$$

The standard Gibbs free energy change for the reaction given by Equation (i) is $\Delta G^\circ_{(i)} = 36{,}000 - 32T$ J, and thus, $\Delta G^\circ_{(i)1000\text{ K}} = 4000$ J and

$$K_{p,(i),1000\text{ K}} = \exp\left(\frac{-4000}{8.3144 \times 1000}\right) = 0.618 = \frac{(0.5 - p_{H_2})^2}{p_{H_2}^2}$$

which has the solution $p_{H_2} = 0.28$ atm. Thus, at reaction equilibrium,

$$p_{H_2} = p_{CO_2} = 0.28 \text{ atm}$$

and

$$p_{H_2O} = p_{CO} = 0.22 \text{ atm}$$

Consider that this equilibrated gas is contained at 1 atm pressure and 1000 K in a rigid vessel of constant volume. What happens if some CaO is placed in the vessel? The reactions

$$\mathrm{CaO}_{(s)} + 5\mathrm{CO}_{(g)} = \mathrm{CaC}_{2(s)} + 3\mathrm{CO}_{2(g)} \tag{iii}$$

$$\mathrm{CaO}_{(s)} + \mathrm{H_2O}_{(g)} = \mathrm{Ca}\left(\mathrm{OH}\right)_{2(s)} \tag{iv}$$

and

$$\mathrm{CaO}_{(s)} + \mathrm{CO}_{2(g)} = \mathrm{CaCO}_{3(s)} \tag{v}$$

are possible.

Consider the possible formation of $\mathrm{CaC_2}$ according to (iii). Summing

$$\Delta G^\circ = -48{,}620 - 36.1T \text{ J} \quad \text{for} \quad \mathrm{Ca} + 2\mathrm{C} = \mathrm{CaC_2}$$

$$\Delta G^\circ = -1{,}182{,}000 - 2.4T \text{ J} \quad \text{for} \quad 3\mathrm{C} + \mathrm{O_2} = 3\mathrm{CO_2}$$

$$\Delta G^\circ = 633{,}140 - 99T \text{ J} \quad \text{for} \quad \mathrm{CaO} = \mathrm{Ca} + \frac{1}{2}\mathrm{O_2}$$

and

$$\Delta G^\circ = 560{,}000 + 438.3T \text{ J} \quad \text{for} \quad 5\mathrm{CO} = 5\mathrm{C} + \frac{5}{2}\mathrm{O_2}$$

gives

$$\Delta G^\circ_{\text{(iii)}} = -37{,}480 + 300.7T \text{ J}$$

Thus, $\Delta G^\circ_{\text{(iii)},1000\text{ K}} = 263{,}200$ J and

$$K_{p,\text{(iii)},1000\text{ K}} = 1.78\times10^{-14} = \left(\frac{p^3_{\mathrm{CO_2}}}{p^5_{\mathrm{CO}}}\right)_{(\text{eq})}$$

Thus, if the CaO were to react with the CO in the gas mixture (which exists at $p_{\mathrm{CO}} =$ 0.22 atm) to form $\mathrm{CaC_2}$ and $\mathrm{CO_2}$, the pressure of $\mathrm{CO_2}$ in the gas mixture would have to be less than

$$(1.78\times10^{\ 14}\times0.22^5)^{1/3}$$

that is, less than 2.09×10^{-6} atm. As the partial pressure of $\mathrm{CO_2}$ in the gas is 0.28 atm, reaction (iii) does not occur.

Consider the possible formation of $\mathrm{Ca(OH)_2}$ according to reaction (iv), $\Delta G^\circ_{\text{(iv)}} = -117{,}600 + 145T$ J, and thus, $\Delta G^\circ_{\text{(iv)}.1000\text{ K}} = 27{,}400$ J and

$$K_{p,(\text{iv}),1000\text{ K}} = 0.037 = \frac{1}{p_{H_2O(\text{eq})}}$$

Thus, the pressure of water vapor required for equilibrium between CaO, $Ca(OH)_2$, and water vapor at 1000 K is 1/0.037 = 20 atm. As the actual pressure of water vapor in the vessel is 0.22 atm, reaction (iv) does not occur.

Consider the possible formation of $CaCO_3$ according to reaction (v):

$$\Delta G^\circ_{(\text{v})} = -168{,}400 + 144T \text{ J}$$

Thus, $\Delta G^\circ_{(\text{v}),1000\text{ K}} = -24{,}400$ J, and hence,

$$K_{\text{p},(\text{v}),1000\text{ K}} = 18.82 = \frac{1}{p_{CO_2(\text{eq})}}$$

or, for equilibrium between CaO, $CaCO_3$, and CO_2 at 1000 K, p_{CO_2} must be 1/18.82 = 0.053 atm. The actual partial pressure of CO_2 in the vessel is greater than 0.053, and thus, the CO_2 reacts with the CaO to form $CaCO_3$. Consider that an excess of CaO is added to the vessel so that some CaO remains after the formation of $CaCO_3$ has decreased the partial pressure of CO_2 in the vessel to 0.053 atm. Now calculate the new equilibrium state of the gas.

The removal of CO_2 from the gas has two effects: (1) the pressure exerted by the gas in the constant volume is decreased, and (2) the equilibrium of reaction (i) is shifted to the left. However, as all of the hydrogen in the vessel, occurring as H_2 or as H_2O, remains in the constant-volume gas phase, the sum $p_{H_2} + p_{H_2O}$ is not changed by the shift in the equilibrium. Also, from the stoichiometry of reaction (i), $p_{CO} = p_{H_2O}$ during the shift. Thus, at the new equilibrium state,

$$\begin{aligned} p_{H_2} + p_{H_2O} &= 0.5 \text{ atm} \\ p_{CO} &= p_{H_2O} \\ p_{CO_2} &= 0.053 \text{ atm} \end{aligned}$$

and

This has the solution p_{H_2O} = 0.113 atm, and thus, the new equilibrium state is

$$\begin{aligned} p_{H_2O} &= p_{CO} = 0.113 \text{ atm} \\ p_{H_2} &= 0.387 \text{ atm} \\ p_{CO_2} &= 0.053 \text{ atm} \\ P &= 0.666 \text{ atm} \end{aligned}$$

What happens now if graphite is introduced to the system? If excess graphite is added, the equilibrium

$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)} \tag{vi}$$

must be established:

$$\Delta G^{\circ}_{(\text{vi})} = 170{,}700 - 174.5T \text{ J}$$

Thus, $\Delta G^{\circ}_{(\text{vi}),1000\text{ K}} = -3800$ J and

$$K_{p,(\text{vi}),1000\text{ K}} = 1.579 = \left(\frac{p^2_{CO}}{p_{CO_2}} \right)_{(\text{e.q})}$$

Thus, as $p_{CO_2} = 0.053$ atm is required for the CaO–CaCO$_3$–CO$_2$ equilibrium, the value of p_{CO} in the gas mixture must change from 0.113 atm to

$$(1.579 \times 0.053)^{1/2} = 0.289 \text{ atm}$$

to establish the C–CO–CO$_2$ equilibrium. Again, as all of the hydrogen remains in the gas phase, $p_{H_2} + p_{H_2O} = 0.5$ atm, and so,

$$K_{p,(\text{i}),1000\text{ K}} = 0.618 = \frac{0.289 \times (0.5 - p_{H_2})}{0.053 p_{H_2}}$$

which has the solution $p_{H_2} = 0.449$ atm. Thus, the newly equilibrated gas mixture, which is now in equilibrium with CaO, CaCO$_3$, and graphite, is

$$\begin{aligned} p_{H_2} &= 0.449 \text{ atm} \\ p_{H_2O} &= 0.051 \text{ atm} \\ p_{CO} &= 0.289 \text{ atm} \\ p_{CO_2} &= 0.053 \text{ atm} \\ P &= 0.842 \text{ atm} \end{aligned}$$

Consider now that the graphite is added *before* the CaO; that is, that graphite is added to the original gas mixture in which $p_{CO} = p_{H_2O} = 0.022$ atm and $p_{H_2} = p_{CO_2} = 0.28$ atm, contained in the rigid vessel at 1000 K. The equilibrium (vi) is established, which requires that the values of p_{CO} and p_{CO_2} in the mixture must change to conform with

$$K_{p,(\text{vi}),1000\text{ K}} = 1.579 = \frac{p^2_{CO}}{p_{CO_2}}$$

Before any reaction, the partial pressure of CO in the gas mixture is 0.22 atm, which, for the C–CO–CO_2 equilibrium, would require $p_{CO_2} = (0.22)^2/1.579 = 0.031$ atm (which is lower than the value occurring in the gas mixture), or, for the existing p_{CO_2} of 0.28, establishment of the C–CO–CO_2 equilibrium would require $p_{CO} = (1.579 \times 0.28)^{1/2} = 0.665$ atm (which is higher than the value occurring in the gas mixture). Thus, reaction (vi) must proceed from left to right and the gas-phase equilibrium (i) must shift from right to left until, simultaneously,

$$\frac{p_{CO}^2}{p_{CO_2}} = 1.59 \quad \text{and} \quad \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = 0.618$$

As before, $p_{H_2} + p_{H_2O} = 0.5$ atm, and the fourth condition (required for determination of the values of the four partial pressures) is obtained from consideration of the oxygen and hydrogen mole balances. The reaction of graphite with CO_2 to form CO does not change the number of moles of oxygen in the gas phase. In the original mixture, $CO_2/H_2 = 1$, and thus, equal numbers of moles of oxygen and hydrogen occur in the gas phase. The number of moles of oxygen in the gas is

$$2n_{CO_2} + n_{CO} + n_{H_2O}$$

and the number of moles of hydrogen is

$$2n_{H_2} + 2n_{H_2O}$$

Thus, in the gas mixture,

$$2n_{CO_2} + n_{CO} + n_{H_2O} = 2n_{H_2O} + 2n_{H_2}$$

or

$$n_{CO_2} + \frac{1}{2}n_{CO} = n_{H_2} + \frac{1}{2}n_{H_2O}$$

Under conditions of constant volume and temperature, $p_i \propto n_i$, and thus,

$$p_{CO_2} + \frac{1}{2}p_{CO} = p_{H_2} + \frac{1}{2}p_{H_2O}$$

which, in combination with

$$p_{H_2O} + p_{H_2} = 0.5$$

gives

$$p_{H_2O} = 1 - 2p_{CO_2} - p_{CO}$$

Thus,

$$
\begin{aligned}
p_{CO_2} &= \frac{p_{CO}^2}{1.579} = 0.633 p_{CO}^2 \\
p_{H_2O} &= 1 - 2p_{CO_2} - p_{CO} = 1 - 1.266 p_{CO}^2 - p_{CO} \\
p_{H_2} &= 0.5 - p_{H_2O} = 1.266 p_{CO}^2 + p_{CO} - 0.5
\end{aligned}
$$

substitution of which into Equation (ii) gives

$$K_{p,(\text{i}),1000\text{ K}} = 0.618 = \frac{(1 - 1.266 p_{CO}^2 - p_{CO}) p_{CO}}{(1.266 p_{CO}^2 + p_{CO} - 0.5) \times 0.633 p_{CO}^2}$$

Or

$$p_{CO}^3 + 3.346 p_{CO}^2 + 1.624 p_{CO} - 2.019 = 0 \qquad \text{(vii)}$$

which has the solution $p_{CO} = 0.541$ atm, and thus, the new equilibrium state is

$$
\begin{aligned}
p_{CO} &= 0.541 \text{ atm} \\
p_{CO_2} &= 0.185 \text{ atm} \\
p_{H_2} &= 0.412 \text{ atm} \\
p_{H_2O} &= 0.088 \text{ atm} \\
p &= 1.226 \text{ atm}
\end{aligned}
$$

Now add excess CaO to the system. The partial pressure of CO_2 in the gas (p_{CO_2} = 0.185 atm) is greater than the value of 0.053 atm required for equilibrium between CaO, $CaCO_3$, and CO_2 at 1000 K. Thus, the CO_2 reacts with the CaO to form $CaCO_3$ until, thereby, the partial pressure of CO_2 has been decreased to the equilibrium value of 0.053 atm, and the gas-phase equilibrium shifts in order to maintain the C–CO–CO_2 equilibrium. Thus, at the new equilibrium,

$$p_{CO_2} = 0.053 \text{ atm} \qquad \text{and} \qquad p_{CO} = (1.579 \times 0.053)^{1/2} = 0.289 \text{ atm}$$

Also,

$$K_{p,(\text{i}),1000\text{ K}} = 0.618 = \frac{0.289 p_{H_2O}}{0.053 p_{H_2}}$$

which gives

$$\frac{p_{H_2O}}{p_{H_2}} = 0.133$$

which, with $p_{H_2} + p_{H_2O} = 0.5$ atm, gives $p_{H_2} = 0.499$ atm and $p_{H_2O} = 0.051$ atm. Thus, the new equilibrium gas is

$$\begin{aligned} p_{H_2} &= 0.499 \text{ atm} \\ p_{H_2O} &= 0.051 \text{ atm} \\ p_{CO} &= 0.289 \text{ atm} \\ p_{CO_2} &= 0.053 \text{ atm} \\ P &= 0.842 \text{ atm} \end{aligned}$$

which, necessarily, is the same state as that produced by introducing the CaO before the graphite.

CHAPTER 13

Reaction Equilibria in Systems Containing Components in Condensed Solution

13.1 INTRODUCTION

Dissolving the pure component i in a condensed solution which is in contact with a vapor phase causes a decrease in the vapor pressure exerted by i from the value p_i° (exerted by pure i) to p_i (exerted by i when it occurs in solution). This decrease in the equilibrium vapor pressure corresponds, via Equation 8.5, to a decrease of $RT \ln (p_i/p_i^\circ)$ in the value of the partial molar Gibbs free energy of i in the vapor phase. Since phase equilibrium is maintained between the vapor phase and the condensed solution, the partial molar Gibbs free energy of i in the solution is $RT \ln (p_i/p_i^\circ)$ lower than the molar Gibbs free energy of pure condensed i at the temperature T. Since the activity, a_i, of i in the solution with respect to pure i is defined by (p_i/p_i°), the partial molal Gibbs free energy of i in the condensed solution is lower than the molar Gibbs free energy of pure i by the amount $RT \ln a_i$. The value of p_i, and hence a_i, depends on the composition and the nature of the components of the solution and on temperature, and inasmuch as the solution of i affects the value of $\overline{G}_i$, it necessarily affects the equilibrium state of any chemical reaction system in which the component i is involved.

As an example, consider the equilibrium between silica, silicon, and oxygen gas:

$$\mathrm{SiO}_{2(s)} = \mathrm{Si}_{(s)} + \mathrm{O}_{2(g)}$$

From Equation 11.4, the equality

$$\overline{G}_{\mathrm{SiO}_2} = \overline{G}_{\mathrm{Si}} + \overline{G}_{\mathrm{O}_2}$$

is the criterion for reaction equilibrium at any temperature and total pressure. If the SiO_2 and the Si present in the system are both pure, and the pure solids are chosen as the standard states, then

$$G^\circ_{\mathrm{SiO}_2} = G^\circ_{\mathrm{Si}} + \overline{G}_{\mathrm{O}_2}$$

or

$$G^{\circ}_{SiO_2} = G^{\circ}_{Si} + G^{\circ}_{O_2} + RT\ln p_{O_2(eq.T)}$$

It has been seen in Chapter 11 that, since the values of G°_i are dependent only on temperature, then at the temperature T there exists a unique partial pressure of oxygen, $p_{O_2(eq.T)}$, at which equilibrium occurs in the system. This unique oxygen pressure is calculated as

$$p_{O_2(eq.T)} = \exp\left[\frac{1}{RT}\left(G^{\circ}_{SiO_2} - G^{\circ}_{Si} - G^{\circ}_{O_2}\right)\right]$$

and, if it is required to reduce pure silica at the temperature T, the oxygen pressure in the system must be lower than $p_{O_2(eq.T)}$. Suppose now that the silica occurs at the activity a_{SiO_2} in an Al_2O_3–SiO_2 solution. The criterion for equilibrium among SiO_2, Si, and O_2 is still

$$\bar{G}_{SiO_2} = \bar{G}_{Si} + \bar{G}_{O_2}$$

but now

$$\bar{G}_{SiO_2} = G^{\circ}_{SiO_2} + RT\ln a_{SiO_2}$$

and thus, in terms of standard Gibbs free energies,

$$G^{\circ}_{SiO_2} + RT\ln a_{SiO_2} = G^{\circ}_{Si} + G^{\circ}_{O_2} + RT\ln p'_{O_2(eq.T)}$$

Thus, for a given value of a_{SiO_2}, there now exists a new unique equilibrium oxygen pressure, $p'_{O_2(eq.T)}$, which is given by

$$p'_{O_2(eq.T)} = p_{O_2(eq.T)}a_{SiO_2}$$

and so, if it is required to reduce SiO_2 from an Al_2O_3 solution to form pure Si, the oxygen pressure in the system must be lower than $p'_{O_2(eq.T)}$. It is thus seen that the possibility of reducing SiO_2 from an Al_2O_3–SiO_2 solution to produce pure Si with a gas of given partial pressure of oxygen at a given temperature is determined by *the solution thermodynamics* of the system Al_2O_3–SiO_2. Generally, the calculation of the equilibrium state of any reaction involving components in condensed solution requires knowledge of the thermodynamic properties of the various solutions present in the system. The influence of solution thermodynamics on reaction equilibria is examined in this chapter.

13.2 THE CRITERIA FOR REACTION EQUILIBRIUM IN SYSTEMS CONTAINING COMPONENTS IN CONDENSED SOLUTION

Consider the general reaction

$$aA + bB = cC + dD$$

occurring at the temperature T and the pressure P. If none of the reactants or products of the reaction occurs in its standard state, the change in the Gibbs free energy for the reaction is

$$\Delta G' = c\overline{G}_C + d\overline{G}_D - a\overline{G}_A - b\overline{G}_B \tag{13.1}$$

If, however, all of the reaction and products occur in their standard states, the change in the Gibbs free energy is the standard Gibbs free energy change, ΔG°, given by

$$\Delta G^\circ = cG_C^\circ + dG_D^\circ + aG_A^\circ - bG_B^\circ \tag{13.2}$$

Subtraction of Equation 13.2 from Equation 13.1 gives

$$\Delta G - \Delta G^\circ = c(\overline{G}_C - G_C^\circ) + d(\overline{G}_D - G_D^\circ) - a(\overline{G}_A - G_A^\circ) - b(\overline{G}_B - G_B^\circ) \tag{13.3}$$

For a component i occurring in some state other than its standard state, Equation 9.28 gives

$$\overline{G}_i = G_i^\circ + RT \ln a_i$$

where a_i is the activity of i with respect to the standard state, and thus, Equation 13.3 can be written as

$$\begin{aligned} \Delta G' - \Delta G^\circ &= c(RT \ln a_C) + d(RT \ln a_D) - a(RT \ln a_A) - b(RT \ln a_B) \\ &= RT \ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right) = RT \ln Q \end{aligned} \tag{13.4}$$

where $Q = a_C^c\, a_D^d / a_A^a a_B^b$ is called the *activity quotient*. Reaction equilibrium is established when the reaction has proceeded to such an extent that

$$a\overline{G}_A + b\overline{G}_B = c\overline{G}_C + d\overline{G}_D$$

that is, that the Gibbs free energy of the system at the fixed temperature and pressure has been minimized, or that ΔG for the reaction is zero. Thus, at equilibrium,

$$\Delta G^\circ = -RT\ \ln Q^{\text{eq}} \tag{13.5}$$

where Q^{eq} is the value of the activity quotient at equilibrium. From Equation 11.8,

$$\Delta G^{\circ} = -RT \ln K$$

and thus,

$$Q^{\text{eq}} = K$$

That is, at reaction equilibrium, the activity quotient is numerically equal to the equilibrium constant K. Consider the oxidation of the pure solid metal M by gaseous oxygen to form the pure solid metal oxide MO_2:

$$M_{(s)} + O_{2(g)} = MO_{2(s)} \tag{i}$$

at the temperature T and the pressure P. For this reaction,

$$Q = \frac{a_{MO_2}}{a_M a_{O_2}}$$

Since M and MO_2 are pure (i.e., occur in their standard states), then $a_M = a_{MO_2} = 1$, and, from the formal definition of activity, the activity of oxygen gas is given as

$$a_{O_2} = \frac{\text{the pressure of oxygen in the gas phase}}{\text{the pressure of oxygen in its standard state}}$$

Since the standard state for gaseous species has been chosen as being the gas at 1 atm pressure and the temperature of interest, then the activity of oxygen in the gas phase is equal to its partial pressure (assuming ideal behavior of the gas). Thus,

$$Q = \frac{1}{p_{O_2}} \quad \text{and} \quad Q^{\text{eq}} = \frac{1}{p_{O_2(\text{eq}.T)}} = K$$

Now consider that the metal in equilibrium with its pure oxide and oxygen in a gaseous atmosphere occurs at the activity a_M in a solution. In this case,

$$Q^{\text{eq}} = \frac{1}{a_M p_{O_2(\text{eq}.T)}} = K$$

and, since K is dependent only on temperature and $a_M < 1$, it is seen that the oxygen pressure required to maintain equilibrium between M in solution and pure MO_2 is larger than that required for equilibrium between pure M and pure MO_2 at the same temperature. Similarly, if the pure metal M is in equilibrium with MO_2 occurring at the activity a_{MO_2} in solution and oxygen in a gas phase, then

$$Q^{\text{eq}} = \frac{a_{MO_2}}{p_{O_2(\text{eq}.T)}} = K$$

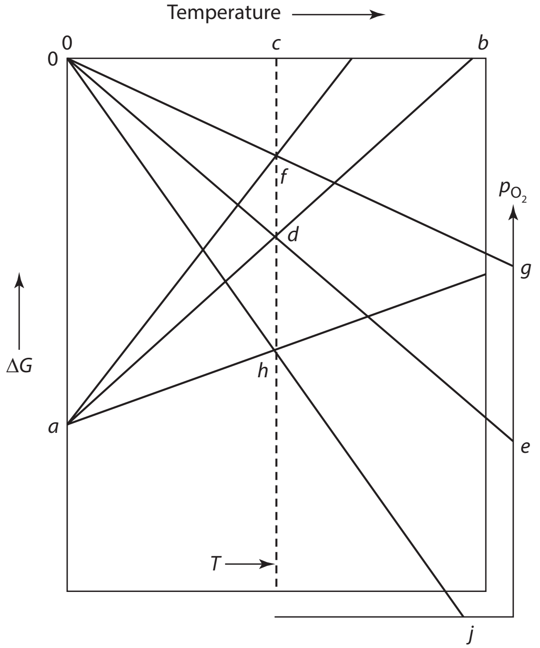

Figure 13.1 The influence of nonunit activities of the reactants and products of a reaction on the Δ*G*–*T* relationship for the reaction.

in which case the oxygen pressure required for the equilibrium between pure M and its oxide in solution is lower than that for the equilibrium between pure M and pure MO_2. In Figure 13.1, the line *ab* is drawn as the variation of the standard Gibbs free energy change, with temperature for the oxidation

$$M_{(s)} + O_{2(g,1\text{ atm})} = MO_{2(s)} \tag{i}$$

At the temperature *T*, $\Delta G^\circ = cd$, and the oxygen pressure for equilibrium between pure solid M and pure solid MO_2 is drawn as the point *e* on the oxygen pressure nomographic scale. Now consider the reaction

$$M_{(\text{in solid solution at } a_M)} + O_{2(g,1\text{ atm})} = MO_{2(s)} \tag{ii}$$

for which, at the temperature *T*, the Gibbs free energy change is $\Delta G_{(\text{ii})}$. Reaction (ii) can be written as the sum of

$$M_{(\text{in solid solution at } a_M)} \rightarrow M_{(s,\text{pure})} \tag{iii}$$

for which

$$\Delta G_{(\text{iii})} = G^\circ_M - \overline{G}_M = -RT \ln a_M$$

and

$$M_{(s)} + O_{2(g,1\ \text{atm})} = MO_{2(s)} \tag{i}$$

for which

$$\Delta G_{(\text{i})} = \Delta G^\circ \text{at the temperature } T$$

Thus,

$$\begin{aligned}\Delta G_{(\text{ii})} &= \Delta G_{(\text{i})} + \Delta G_{(\text{iii})}\\ &= \Delta G^\circ - RT\ln a_{\text{M}}\end{aligned}$$

At the temperature T, ΔG° is a negative quantity, and, since $a_{\text{M}} < 1$, then $\Delta G_{(\text{ii})}$ is a smaller negative quantity, drawn in Figure 13.1 as *cf*. The effect of the solution of M on its oxidation is thus an anticlockwise rotation of the standard Gibbs free energy line about the point *a* (ΔG° at $T = 0$), with the extent of this rotation being such that, at the temperature T, the vertical separation from the standard line equals $RT \ln a_{\text{M}}$. The extent of the rotation is determined by the value of a_{M}. The oxygen pressure required for equilibrium between M in solution and pure MO_2 is increased from *e* to *g* in accordance with

$$\begin{aligned}K_T &= \frac{1}{p_{O_2(T,\text{eq }M_{2(s)})}}\\ &= \frac{1}{a_{\text{M}}\,p_{O_2(T,\text{eq }M_{(\text{at } a_{\text{M}})}/MO_{2(s)})}}\end{aligned}$$

Consider the reaction

$$M_{(s,\text{pure})} + O_{2(g,1\ \text{atm})} = MO_{2(\text{in solid solution at } a_{MO_2})} \tag{iv}$$

for which, at the temperature T, the Gibbs free energy change is $\Delta G_{(\text{iv})}$. Reaction (iv) can be written as the sum of

$$MO_{2(s,\text{pure})} \rightarrow MO_{2(\text{in solution at } a_{MO_2})} \tag{v}$$

and reaction (i); that is,

$$\Delta G_{(\text{iv})} = \Delta G^\circ + RT\ln a_{MO_2}$$

At the temperature T, ΔG° is a negative quantity, and, since $a_{MO_2} < 1$, then $\Delta G_{(\text{iv})}$ is a larger negative quantity, drawn in Figure 13.1 as *ch*. The effect of the solution of MO_2 on the oxidation of M is thus seen to be a clockwise rotation of the Gibbs free energy line about the point *a* with the extent of the rotation being such that, at the temperature T, the vertical separation from the standard Gibbs free energy line equals $RT \ln a_{MO_2}$. The extent of the rotation is determined by the value of a_{MO_2}, and the oxygen pressure required for equilibrium between pure M and MO_2 in solution is decreased from *e* to *j* in accordance with

$$\begin{aligned} K_T &= \frac{1}{p_{O_2(T,\text{eq } M_{(s)}/MO_{2(s)})}} \\ &= \frac{a_{MO_2}}{p_{O_2[T,\text{eq } M_{(s)}/MO_2(\text{at } a_{MO_2})]}} \end{aligned}$$

In the general case,

$$M_{(\text{in solution at } a_M)} + O_{2(g,\text{at } p_{O_2})} = MO_{2(\text{in solution at } a_{MO_2})} \tag{vi}$$

for which, at the temperature *T*, the free energy change is $\Delta G_{(vi)}$:

$$\begin{aligned} \Delta G_{(vi)} &= \Delta G^\circ - RT \ln a_M - RT \ln p_{O_2} + RT \ln a_{MO_2} \\ &= \Delta G^\circ + RT \ln \frac{a_{MO_2}}{a_M p_{O_2}} \\ &= \Delta G^\circ + RT \ln Q \end{aligned}$$

At equilibrium, the values of a_M, a_{MO_2}, and p_{O_2} are such that $\Delta G_{(vi)} = 0$, and thus,

$$\Delta G^\circ = -RT \ln Q^{eq} = -RT \ln K$$

as in Equation 13.5.

Example

Examine the conditions under which a liquid Fe–Mn alloy can be in equilibrium with an FeO–MnO liquid solution in an atmosphere containing oxygen at 1800°C. For

$$Mn_{(l)} + \frac{1}{2}O_{2(g)} = MnO_{(l)} \tag{i}$$

$$\Delta G^\circ_{(i)} = -344{,}800 + 55.90T \text{ J}$$

and for

$$Fe_{(l)} + \frac{1}{2}O_{2(g)} = FeO_{(l)} \tag{ii}$$

$$\Delta G^\circ_{(ii)} = -232{,}700 + 45.13T \text{ J}$$

Solution

The pertinent equilibrium is

$$FeO_{(l)} + Mn_{(l)} = MnO_{(l)} + Fe_{(l)} \tag{iii}$$

for which

$$\begin{aligned}\Delta G^{\circ}_{(\text{iii}),2073\text{ K}} &= \Delta G^{\circ}_{(\text{i}),2073\text{ K}} - \Delta G^{\circ}_{(\text{ii}),2073\text{ K}}\\ &= -228{,}900 + 138{,}800 = -90{,}100\text{ J}\\ &= -8.3144 \times 2073 \ln K_{(\text{iii}),2073\text{ K}}\text{ J}\end{aligned}$$

Therefore,

$$K_{(\text{iii}),2073\text{ K}} = 186 = \frac{(a_{\text{MnO}})[a_{\text{Fe}}]}{(a_{\text{FeO}})[a_{\text{Mn}}]}$$

where:

(a_{MnO}) = the activity of MnO in the liquid oxide phase with respect to pure MnO

v(a_{FeO}) = the activity of FeO in the liquid oxide phase with respect to iron-saturated liquid iron oxide

$[a_{\text{Mn}}]$ = the activity of Mn in the liquid metal phase with respect to pure liquid Mn

$[a_{\text{Fe}}]$ = the activity of Fe in the liquid metal phase with respect to pure liquid Fe.

Since both the liquid metal solution and the liquid oxide solution exhibit Raoultian behavior, the condition for phase equilibrium between the two is

$$\frac{(X_{\text{MnO}})[X_{\text{Fe}}]}{(X_{\text{FeO}})[X_{\text{Mn}}]} = 186 \tag{iv}$$

or

$$\frac{[X_{\text{Fe}}]}{[X_{\text{Mn}}]} = 186\frac{(X_{\text{FeO}})}{(X_{\text{MnO}})}$$

A series of tie-lines joining the compositions of equilibrated metal and oxide solutions is shown in Figure 13.2. Consider the metallic alloy of composition $X_{\text{Fe}} = 0.5$. Equation (iv) gives

$$1 = 186\frac{(X_{\text{FeO}})}{1-(X_{\text{FeO}})}$$

or

$$\left(X_{\text{FeO}}\right) = 0.00535$$

and thus, when a metallic alloy of composition $X_{\text{Fe}} = 0.5$ is equilibrated with an oxide solution, the composition of the latter is $X_{\text{FeO}} = 0.00535$. Consider now the influence of the partial pressure of oxygen in the gaseous atmosphere:

$$\Delta G^{\circ}_{(\text{i})} = -RT\ln K_{(\text{i})} = -RT\ln\frac{(a_{\text{MnO}})}{[a_{\text{Mn}}]p_{O_2}^{1/2}}$$

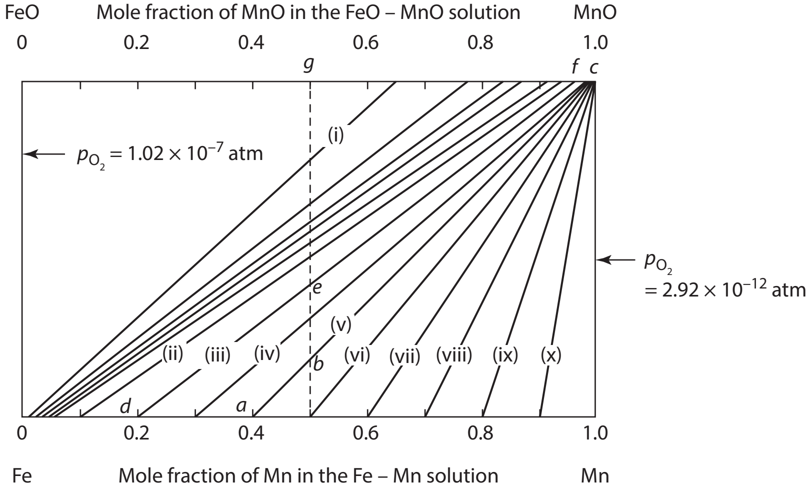

Figure 13.2 Tie-lines between the compositions of equilibrated metallic and oxide alloys in the system Fe–Mn–O. The tie-lines are also oxygen isobars with oxygen pressures as follows: (i) 1.24 × 10^{-8} atm, (ii) 2.65 × 10^{-10} atm, (iii) 7.0 × 10^{-11} atm, (iv) 3.14 × 10^{-11} atm, (v) 1.79 × 10^{-11} atm, (vi) 1.15 × 10^{-11} atm, (vii) 8.04 × 10^{-12} atm, (viii) 5.92 × 10^{-12} atm, (ix) 4.46 × 10^{-12} atm, and (x) 3.58 × 10^{-12} atm.

Thus, since

$$\Delta G^\circ_{\text{(i)},2073\text{ K}} = -228{,}900\text{ J}$$

$$K_{\text{(i)},2073\text{ K}} = 5.856\times 10^5 = \frac{(a_{\text{MnO}})}{[a_{\text{Mn}}]p_{O_2}^{1/2}}$$

or, since the metallic and oxide solutions are ideal,

$$\frac{(X_{\text{MnO}})}{[X_{\text{Mn}}]} = 5.856\times 10^5 p_{O_2}^{1/2} \qquad \text{(v)}$$

Similarly,

$$\Delta G^\circ_{\text{(ii)}} = -RT\ln\frac{(a_{\text{FeO}})}{[a_{\text{Fe}}]p_{O_2}^{1/2}}$$

and since

$$\Delta G^\circ_{\text{(ii)},2073\text{ K}} = -138{,}800\text{ J}$$

then

$$K_{\text{(ii)},2073\text{ K}} = 3143 = \frac{(a_{\text{FeO}})}{[a_{\text{Fe}}]p_{O_2}^{1/2}}$$

or

$$\frac{(a_{\text{FeO}})}{[a_{\text{Fe}}]} = 3143\, p_{O_2}^{1/2}$$

The ideal Raoultian behavior of the two solutions allows Equation (vi) to be written as

$$\frac{(X_{\text{FeO}})}{[X_{\text{Fe}}]} = 3143\, p_{O_2}^{1/2}$$

Consider the equilibrium between the metallic alloy of $X_{\text{Fe}} = 0.5$ and the oxide solution of $X_{\text{FeO}} = 0.00535$. From Equation (v),

$$p_{O_2} = \left(\frac{0.99465}{0.5} \times \frac{1}{5.856 \times 10^5} \right)^2 = 1.15 \times 10^{-11} \text{ atm}$$

and from Equation (vi)

$$p_{O_2} = \left(\frac{0.00535}{0.5} \times \frac{1}{3143} \right)^2 = 1.15 \times 10^{-11} \text{ atm}$$

Thus, the tie-line connecting the compositions of the equilibrated metallic and oxide alloy is also the oxygen isobar in Figure 13.2. Thus, at any fixed oxygen pressure, the individual ratios

$$\frac{(a_{\text{FeO}})}{[a_{\text{Fe}}]} \left(= \frac{(X_{\text{FeO}})}{[X_{\text{Fe}}]} \right) \quad \text{and} \quad \frac{(a_{\text{MnO}})}{[a_{\text{Mn}}]} \left(= \frac{(X_{\text{MnO}})}{[X_{\text{Mn}}]} \right)$$

are fixed by Equations (v) and (vi), combination of which gives

$$\frac{(X_{\text{MnO}})[X_{\text{Fe}}]}{(X_{\text{FeO}})[X_{\text{Mn}}]} = \frac{5.856 \times 10^5}{3143} = 186$$

in accordance with Equation (iv). Consider the oxidation of a finite quantity of a liquid metallic alloy of composition $X_{\text{Fe}} = 0.5$ by an infinite oxygen-containing gaseous atmosphere in which the partial pressure of oxygen is slowly increased. From Figure 13.2, the metal phase is stable when the partial pressure of oxygen is less than 1.15×10^{-11} atm. At $p_{O_2} = 1.15 \times 10^{-11}$ atm, the metallic alloy is in equilibrium with an oxide solution of $X_{\text{FeO}} = 0.00535$. Increasing the partial pressure of oxygen to 1.79×10^{-11} atm moves the state of the system to the state *b* on the (v) isobar in Figure 13.2. In this state, a metallic alloy of $X_{\text{Fe}} = 0.6$ (at *a*) is in equilibrium with an oxide solution of $X_{\text{FeO}} = 0.0053$ (at *c*), and the relative quantities of the two phases are given by application of the lever rule to the tie-line (v); that is, the fraction of the system occurring as the metallic alloy in state *a* is *bc*/*ac*, and the fraction occurring as the oxide solution in state *c* is *ab*/*ac*. Increasing the oxygen pressure to 7.0×10^{-11} atm moves the system to the state *e* on the (iii) isobar, where a metallic alloy of $X_{\text{Fe}} = 0.8$ (at *d*) is in equilibrium with an oxide solution of $X_{\text{FeO}} = 0.021$ (at *f*). The ratio of metallic alloy to oxide solution occurring is *ef*/*de*. Continued increase in the partial pressure of oxygen moves the state of the system upward along the broken line in Figure 13.2, during which the ratio of oxide-to-metal phase increases and the mole fraction of Fe in the metal phase and the mole fraction of FeO in the oxide phase increase. When the composition of the oxide reaches $X_{\text{FeO}} = 0.5$ (at *g*), the infinitesimal amount of equilibrium metal phase has the composition $X_{\text{Mn}} = 0.00535$ and the oxygen pressure is 2.55×10^{-8} atm. The oxidation of Fe–Mn alloys at 2073 K occurs between the limits of oxygen pressure 2.92×10^{-12} atm for the equilibrium between pure Mn and pure MnO, and 1.02×10^{-7} atm for the equilibrium between pure Fe and pure FeO. The establishment of equilibrium (iii) requires that the ΔG–T lines for the oxidation of Fe and Mn intersect at 2073 K—that is, that $\Delta G_{\text{(iii)},2073\text{ K}} = 0$. For any oxidation $2\text{M} + \text{O}_2 = 2\text{MO}$, clockwise rotation of the ΔG–T line (e.g., the line *ab* in Figure 13.1) about its point of intersection with the $T = 0$ axis occurs when the ratio $a_{\text{MO}}/a_{\text{M}}$ is decreased to a value less than unity, and, conversely, anticlockwise rotation of the line occurs when the ratio $a_{\text{MO}}/a_{\text{M}}$ is increased to a value greater than unity. Also, since the equilibrium constant K is a function only of temperature, then, at any oxygen pressure p_{O_2} in the system M–MO$_2$–O$_2$ at the temperature T, the equilibrium ratio $a_{\text{MO}}/a_{\text{M}}$ must be

$$\frac{a_{\text{MO}}}{a_{\text{M}}} = \frac{p_{\text{O}_2}^{1/2}}{p_{\text{O}_2(\text{eq } T \text{ pure M/pure MO})}^{1/2}}$$

where $p_{\text{O}_2(\text{eq}T \text{ pure M/pure MO})}$ is that unique oxygen pressure at the temperature T required for equilibrium between pure M and pure MO. Thus, for any oxygen pressure within the allowed limits, equilibrium (iii) occurs when Equations (v) and (vi) are satisfied, and, under these conditions, the ΔG–T lines for the oxidation of Fe and Mn intersect at 1800°C. Thus, as a consequence of the ability to vary a_{M} and a_{MO}, equilibrium (iii) can be established at any T and any p_{O_2} (within the aforementioned limits). This is in contrast to the situation illustrated in Figures 12.4 and 12.5, in which, if both metals and both oxides are present in their pure states, then an equilibrium such as (iii) can only be achieved at the single unique state (unique T and unique p_{O_2}) at which the Ellingham lines for the two oxidation reactions intersect with one another. The restrictions on general multicomponent multiphase equilibria are discussed in Section 13.4.

13.3 ALTERNATIVE STANDARD STATES

Up to this point, the standard state of a component of a system has been chosen as being the pure component in its stable state of existence at the temperature of interest. This is called the *Raoultian standard state*; in Figure 13.3, the Raoultian standard state for the component B is located at point *r*.

In situations in which the pure component exists in a physical state which differs from that of the solution, the Henrian standard state may be more convenient than the Raoultian standard state. Such situations include the solution of a gas in a solid

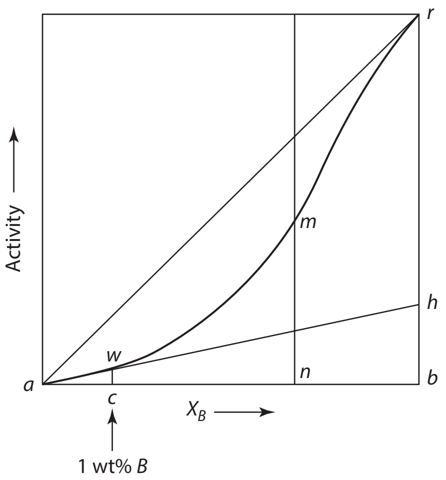

Figure 13.3 Illustration of the Raoultian, Henrian, and 1 wt% standard states for component *B* in a binary *A*–*B* system.

or liquid solvent and the solution of a solid in a liquid solvent. The Henrian standard state is obtained from consideration of Henry's law, which, strictly being a limiting law obeyed by the solute *B* at infinite dilution, is expressed as

$$\frac{a_B}{X_B} \to k_B \qquad \text{as} \qquad X_B \to 0$$

where:

a_B	is the activity of *B* in the solution with respect to the Raoultian standard state
k_B	is the Henry's law constant at the temperature *T*

Alternatively, Henry's law can be written as

$$\frac{a_B}{X_B} \to \gamma_B^{\circ} \qquad \text{as} \qquad X_B \to 0 \tag{13.6}$$

where $\gamma_B^{\circ}(=k_B)$ is the constant activity coefficient which quantifies the difference between the Raoultian solution behavior of *B* and the Henrian solution behavior of *B*. If the solute obeys Henry's law over a finite range of composition, then, over this range,

$$a_B = \gamma_B^{\circ} X_B$$

The Henrian standard state is obtained by extrapolating the Henry's law line to $X_B = 1$. This state (the point *h* in Figure 13.3) represents pure *B* in the hypothetical nonphysical state in which it would exist as a pure component, if it behaved as it does in dilute solution. The activity of B in the Henrian standard state with respect to the Raoultian standard state having unit activity is given by Equation 13.6 as

$$a_B = \gamma_B^\circ$$

Thus, in Figure 13.3, if the length rb is unity, then $hb = \gamma_B^\circ$.

Having thus defined the Henrian standard state, the activity of B in a solution, with respect to the Henrian standard state having unit activity, is given by

$$h_B = f_B X_B \tag{13.7}$$

where h_B is the Henrian activity and f_B is the Henrian activity coefficient. In the range of composition in which the solute B obeys Henry's law, $f_\mathrm{B} = 1$, and the solute exhibits Henrian ideality.

The mole fraction of B in an A–B solution is related to the weight percentage of B by

$$X_B = \frac{\dfrac{\mathrm{wt\%}B}{MW_B}}{\dfrac{\mathrm{wt\%}B}{MW_B} + \dfrac{(100 - wt\%B)}{MW_A}}$$

where MW_A and MW_B are, respectively, the molecular weights of A and B. Thus, in dilute solution, as the mole fraction of B is virtually proportional to the weight percentage of B; that is,

$$X_B \sim \frac{\mathrm{wt\%}B \times MW_A}{100 \times MW_B}$$

a third standard state can be introduced. This is the 1 wt% standard state, which is defined as

$$\frac{h_{B(1\ \mathrm{wt\%})}}{\mathrm{wt\%}B} \to 1 \text{ as } \mathrm{wt\%}B \to 0$$

and is located at the point on the Henry's law line which corresponds to a concentration of 1 wt% B (the point w in Figure 13.3). With respect to the 1 wt% standard state having unit activity, the activity of B, $h_{B(1\ \mathrm{wt\%})}$, is given by

$$h_{B(1\ \mathrm{wt\%})} = f_{B(1\ \mathrm{wt\%})}\mathrm{wt\%}B \tag{13.8}$$

where $f_{B(1\ \mathrm{wt\%})}$ is the 1 wt% activity coefficient, and in the range of composition in which the solute B obeys Henry's law, $f_{B(1\ \mathrm{wt\%})} = 1$, and hence,

$$h_{B(1\ \mathrm{wt\%})} = \mathrm{wt\%}B$$

which is of considerable practical convenience.

From consideration of the similar triangles *awc* and *ahb* in Figure 13.3, the activity of B in the 1 wt% standard state with respect to the Henrian standard state having unity activity is

$$\frac{wc}{hb} = \frac{ac}{ab} = \frac{MW_A}{100MW_B}$$

and, with respect to the Raoultian standard state having unit activity, is

$$\frac{\overset{\circ}{\gamma}_B MW_A}{100MW_B}$$

The value of the equilibrium constant for any reaction, being equal to the quotient of the activities of the reactants and products at reaction equilibrium, necessarily depends on the choice of standard states for the components. Similarly, the magnitude of ΔG° for the reaction depends on the choice of standard states and thus, in order to convert from the use of one standard state to another, it is necessary that the differences between the Gibbs free energies of the standard states be known.

For the change of standard state

$$B_{(\text{in the Raoultian standard state})} \rightarrow B_{(\text{in the Henrian standard state})}$$

$$G_B^\circ(R \rightarrow H) = G_{B(H)}^\circ - G_{B(R)}^\circ = RT \ln \frac{a_{B(\text{in the Henrian standard state})}}{a_{B(\text{in the Raoultian standard state})}}$$

where both activities are measured on the same activity scale. On either the Raoultian or Henrian scales,

$$\frac{a_{B(\text{in the Henrian standard state})}}{a_{B(\text{in the Raoultian standard state})}} = \frac{hb}{rb} = \overset{\circ}{\gamma}_B$$

and thus,

$$\Delta G_{B(R \rightarrow H)}^\circ = RT \ln \overset{\circ}{\gamma}_B \tag{13.9}$$

where $\overset{\circ}{\gamma}_B$ is the Henrian activity coefficient *at the temperature T*.

For the change of standard state

$$B_{(\text{in the Henrian standard state})} \rightarrow B_{(\text{in the 1 wt\% standard state})}$$

$$\Delta G_B^\circ(H \rightarrow 1 \text{ wt\%}) = G_{B(1 \text{ wt\%})}^\circ - G_{B(H)}^\circ = RT \ln \frac{a_{B(\text{in the 1 wt \% standard state})}}{a_{B(\text{in the Henrian standard state})}}$$

where, again, both activities are measured on the same scale:

$$\frac{a_{B(\text{in the 1 wt \% standard state})}}{a_{B(\text{in the Henrian standard state})}} = \frac{wc}{hb} = \frac{ac}{ab} = \frac{MW_A}{100MW_B}$$

and thus,

$$\Delta G^{\circ}_{B(H\rightarrow 1\text{wt\%})} = RT\ln\left(\frac{MW_A}{100MW_B}\right) \tag{13.10}$$

Combination of Equations 13.9 and 13.10 gives

$$\Delta G^{\circ}_{B(R\rightarrow 1\text{wt\%})} = RT\ln\left(\frac{\gamma^{\circ}_B MW_A}{100MW_B}\right) \tag{13.11}$$

for the change of standard-state Raoultian → 1 wt%. Using the subscript R to denote the Raoultian standard state, the subscript H to denote the Henrian standard state, and the subscript wt% to denote the 1 wt% standard state, consider again the oxidation of metal M to form the oxide MO_2 at the temperature T:

$$\text{M}_{(R)} + \text{O}_{2(g)} = \text{MO}_{2(R)}$$

For this equilibrium,

$$\Delta G^{\circ}_{(R)} = -RT\ln K_{(R)} = -RT\ln\frac{a_{\text{MO}_2}}{a_{\text{M}}p_{\text{O}_2}}$$

If M occurs in dilute solution, in which case it may be more convenient to use the Henrian standard state for M, then

$$\text{M}_{(H)} + \text{O}_{2(g)} = \text{MO}_{2(R)}$$
$$\Delta G^{\circ}_{(H)} = \Delta G^{\circ}_{(R)} - \Delta G^{\circ}_{\text{M}(R\rightarrow H)}$$

That is,

$$-RT\ln K_{(H)} = -RT\ln K_{(R)} - RT\ln\gamma^{\circ}_{\text{M}}$$

or

$$RT\ln\frac{a_{\text{MO}_2}}{h_{\text{M}}p_{\text{O}_2}} = RT\ln\frac{a_{\text{MO}_2}}{a_{\text{M}}p_{\text{O}_2}} + RT\ln\gamma^{\circ}_{\text{M}}$$

Thus,

$$a_{\text{M}} = h_{\text{M}}\gamma^{\circ}_{\text{M}} \tag{13.12}$$

which relates the activity of M in solution with respect to the Raoultian standard state to the activity of M in solution with respect to the Henrian standard state; for example, in the case of composition *m* in Figure 13.3,

$$a_B = \frac{mn}{rb} = \frac{mn}{hb}\frac{hb}{rb} = h_B\gamma^\circ_B$$

Similarly, if it is convenient to use the 1 wt% standard state for M, then

$$\mathrm{M}_{(1\ \mathrm{wt\%})} + \mathrm{O}_{2(g)} = \mathrm{MO}_{2(R)}$$
$$\Delta G^\circ_{(1\ \mathrm{wt\%})} = \Delta G^\circ_{(R)} - \Delta G^\circ_{\mathrm{M}(R\to 1\ \mathrm{wt\%})}$$

or

$$-RT\ln K_{(1\ \mathrm{wt\%})} = -RT\ln K_{(R)} - RT\ln\frac{\gamma^\circ_{\mathrm{M}} MW_{\mathrm{solvent}}}{100 MW_{\mathrm{M}}}$$

or

$$-RT\ln\frac{a_{\mathrm{MO_2}}}{f_{\mathrm{M}(1\ \mathrm{wt\%})}\times \mathrm{wt\%M}\times p_{\mathrm{O_2}}} = -RT\ln\frac{a_{\mathrm{MO_2}}}{a_{\mathrm{M}}p_{\mathrm{O_2}}} - RT\ln\frac{\gamma^\circ_{\mathrm{M}} MW_{\mathrm{solvent}}}{100 MW_{\mathrm{M}}}$$

or

$$a_{\mathrm{M}} = f_{\mathrm{M}(1\ \mathrm{wt\%})}\cdot \mathrm{wt\%\ M}\cdot\gamma^\circ_{\mathrm{M}}\cdot\frac{MW_{\mathrm{solvent}}}{100 MW_{\mathrm{M}}} \tag{13.13}$$

Example

The activity of silicon in binary Fe–Si liquid alloys, a_{Si}, is shown in Figure 13.4 at two temperatures. As is seen, Si exhibits considerable negative deviation from Raoult's law; for example, at $X_{\mathrm{Si}} = 0.1$ and 1420°C, $a_{\mathrm{Si}} = 0.00005$. Thus, in considering dilute solutions of Si in Fe, there is an advantage to using either the Henrian standard state or the 1 wt% standard state.

For the change of standard state from Raoultian to Henrian at the temperature *T*,

$$\Delta G^\circ_{\mathrm{Si}(R\to H)} = RT\ln\gamma^\circ_{\mathrm{Si}}$$

and the experimentally measured variation of log $\gamma^\circ_{\mathrm{Si}}$ with temperature is

$$\log\gamma^\circ_{\mathrm{Si}} = -\frac{6230}{T} + 0.37$$

and thus,

$$\begin{aligned}\Delta G^\circ_{\mathrm{Si}(R\to H)} &= 8.3144T\times 2.303\log\gamma^\circ_{\mathrm{Si}}\\ &= -119{,}300 + 7.08T\ \mathrm{J}\end{aligned}$$

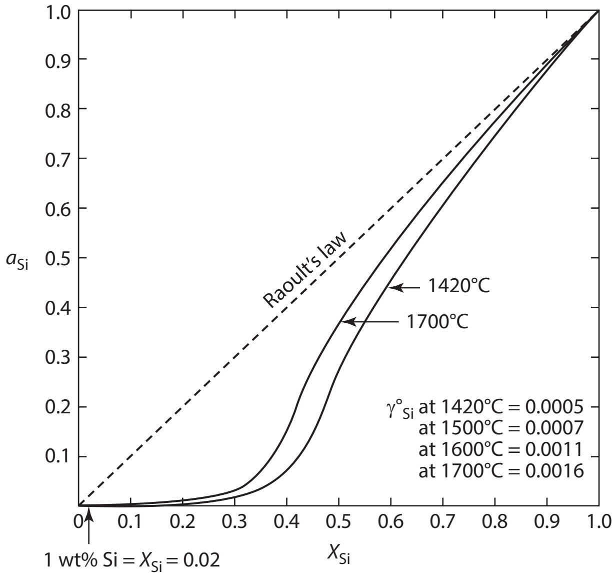

Figure 13.4 The activity of Si in Fe–Si melts at 1420°C and 1700°C.

Also, for the change of standard state from Henrian to 1 wt% in Fe at the temperature T

$$\Delta G^\circ_{\mathrm{Si}(H\to 1\ \mathrm{wt\%})} = RT\ln\frac{MW_{\mathrm{Fe}}}{100MW_{\mathrm{Si}}}$$

$$= RT\ln\left(\frac{55.85}{100\times 28.09}\right)$$

$$= -32.6T\ \mathrm{J}$$

so, for the change $\mathrm{Si}_{(R)} \rightarrow \mathrm{Si}_{(1\ \mathrm{wt\%\ in\ Fe})}$,

$$\begin{aligned}\Delta G^\circ_{(R\to 1\ \mathrm{wt\%})} &= \Delta G^\circ_{(R\to H)} + \Delta G^\circ_{(H\to 1\ \mathrm{wt\%})}\\ &= -119{,}300 - 25.5T\ \mathrm{J}\end{aligned} \qquad \text{(i)}$$

Now, given that a liquid Fe–Si alloy is in equilibrium with an SiO_2-saturated FeO–SiO_2 melt (in which $a_{SiO_2} = 1$) and an atmosphere containing oxygen, calculate the relationship between the equilibrium weight percentage of Si in the Fe–Si alloy and the oxygen pressure in the gaseous atmosphere. For the reaction

$$\mathrm{Si}_{(l)} + \mathrm{O}_{2(g)} = \mathrm{SiO}_{2(s)} \qquad \text{(ii)}$$

$\Delta G^\circ_{(\mathrm{ii})} = -952{,}700 + 204T\ \mathrm{J}$ in the temperature range 1700–2000 K. Thus, the standard Gibbs free energy for the reaction

$$\mathrm{Si}_{(1\ \mathrm{wt\%})} + \mathrm{O}_{2(g)} = \mathrm{SiO}_{2(s)} \qquad \text{(iii)}$$

is obtained as $\Delta G^{\circ}_{(\text{ii})} - \Delta G^{\circ}_{(\text{i})}$; namely

$$\begin{aligned}\Delta G^{\circ}_{(\text{iii})} &= -833{,}400 + 229.5T \text{ J}\\ &= -RT\ln\frac{a_{\text{SiO}_2}}{h_{\text{Si(1 wt\%)}}p_{\text{O}_2}}\end{aligned}$$

As $a_{\text{SiO}_2} = 1$, then

$$\ln h_{\text{Si(1 wt\%)}} = -\frac{833{,}400}{8.3144T} + \frac{229.5}{8.3144} - \ln p_{\text{O}_2}$$

If it can be assumed that Si in Fe obeys Henry's law over some initial range of composition, then, in this range, $h_{\text{Si(1 wt\%)}}$ = wt% Si, and thus,

$$\ln \text{wt\% Si} = -\frac{100{,}200}{T} + 27.60 - \ln p_{\text{O}_2}$$

Thus, to produce an equilibrium melt containing 1 wt% Si at 1600°C, the partial pressure of oxygen must be 5.57×10^{-12} atm, and the oxygen pressure for any other weight percentage of Si at 1600°C is calculated from

$$p_{\text{O}_2} = \frac{5.57\times10^{-12}}{\text{wt\% Si}}$$

The error in this calculation caused by the assumption of Henrian behavior in some initial range of composition is demonstrated when the calculation is considered again in Section 13.9.

13.4 THE GIBBS EQUILIBRIUM PHASE RULE

In Chapter 7, it was found that the number of degrees of freedom available in equilibrium in a one-component system is related to the number of phases present by means of a simple rule. This rule, the Gibbs equilibrium phase rule, was easily derived because of the simplicity of graphical representation of phase equilibria in a one-component system. However, phase relations in a multicomponent system can be complicated, and in such systems, the Gibbs equilibrium phase rule is a powerful tool in the determination of possible equilibria and the restrictions on these equilibria. The general derivation of the phase rule is as follows. Consider a system containing C chemical species, i, j, k, … (none of which enters into chemical reaction with any other). Each of the components occurs in Φ phases, α, β, γ, …. Since the thermodynamic state of each of the Φ phases is determined by the specification of its temperature, pressure, and composition (where composition is expressed in terms of $C - 1$ composition variables, such as mole fractions or weight percentages), then the state of the entire system is specified when its $\Phi(C + 1)$ variables are fixed. The conditions that the entire system be at complete equilibrium are

- $T_\alpha = T_\beta = T_\gamma = \ldots$ $(\Phi - 1)$ equalities of temperature
- $P_\alpha = P_\beta = P_\gamma = \ldots$ $(\Phi - 1)$ equalities of pressure

- $a_{i(\alpha)} = a_{i(\beta)} = a_{i(\gamma)} = \ldots$ ($\Phi - 1$) equalities of the activity of the species *i*
- $a_{j(\alpha)} = a_{j(\beta)} = a_{j(\gamma)} = \ldots$ ($\Phi - 1$) equalities of the activity of the species *j*

and so on for each of the *C* chemical species.

Thus, the total number of equilibrium conditions, given as the number of required equations among the variables of the system, is

$$(\Phi - 1)(C + 2)$$

The number of degrees of freedom, $\mathcal{F}$, which an equilibrium in the system may have is defined as the maximum number of variables which may be independently altered in value without disturbing the equilibrium. This number $\mathcal{F}$ is obtained as the difference between the total number of variables available to the system and the minimum number of equations among these variables that is required to maintain the equilibrium; that is,

$$\begin{aligned} \mathcal{F} &= \Phi(C+1) - (\Phi - 1)(C+2) \\ &= C + 2 - \Phi \end{aligned} \tag{13.14}$$

In a system of nonreacting species, the number of species *C* equals the number of components in the system. However, if some of the species enter into reaction with one another, such that the equilibrium of the system includes a number of reaction equilibria—in addition to the phase, temperature, and pressure equilibria—then the number of equations among the variables which must be specified is increased by *R*, the number of such independent reaction equilibria occurring in the system. For example, if the species *i* and *j* react to form the species *k*, then the establishment of the reaction equilibrium requires that, in each of the Φ phases,

$$\bar{G}_i + \bar{G}_j = \bar{G}_k$$

which increases the number of equations among the variables by one. Thus, if the system contains *N* species, among which there are *R* independent reaction equilibria, then

$$\begin{aligned} \mathcal{F} &= \Phi(N+1) - (\Phi - 1)(N+2) - R \\ &= (N - R) + 2 - \Phi \end{aligned}$$

In order that the phase rule, as given by Equation 13.14, be generally applicable to both reactive and nonreactive systems, the number of components in the former is defined as

$$C = N - R$$

C can be determined as either the minimum number of chemical species required to produce the system at equilibrium, or the number of species in the system minus the number of independent reaction equilibria among these species.

Example 1

Consider, again, the example discussed in Section 13.2, in which an examination was made of the conditions under which a liquid Fe–Mn solution and a liquid FeO–MnO solution can be in equilibrium with an oxygen-containing atmosphere. This is a three-component system (Fe–Mn–O) existing in three phases (metal–oxide–gas), and thus, from the phase rule, the equilibrium has two degrees of freedom, which can be selected from the variables T, p_{O_2}, $[X_{Fe}]$, $[X_{Mn}]$, (X_{FeO}), and (X_{MnO}). With five species (O_2, Fe, Mn, FeO, MnO) and three components, there are two independent reaction equilibria, which can be selected as

$$\mathrm{Fe} + \frac{1}{2}\mathrm{O_2} = \mathrm{FeO}$$

for which

$$K_{(i),T} = \frac{a_{FeO}}{a_{Fe}p_{O_2}^{1/2}} = \frac{(X_{FeO})}{[X_{Fe}]p_{O_2}^{1/2}} \tag{i}$$

and

$$\mathrm{Mn} + \frac{1}{2}\mathrm{O_2} = \mathrm{MnO}$$

for which

$$K_{(ii),T} = \frac{a_{MnO}}{a_{Mn}p_{O_2}^{1/2}} = \frac{(X_{MnO})}{[X_{Mn}]p_{O_2}^{1/2}} \tag{ii}$$

a. If T and p_{O_2} are chosen as the independent variables,

$$\frac{(X_{FeO})}{[X_{Fe}]} = K_{(i),T} \cdot p_{O_2}^{1/2}$$

is fixed by Equation (i) and

$$\frac{(X_{MnO})}{[X_{Mn}]} = \frac{1-(X_{FeO})}{1-[X_{Fe}]} = K_{(ii),T} \cdot p_{O_2}^{1/2}$$

is fixed by Equation (ii). Thus, (X_{FeO}) [and hence (X_{MnO})] and $[X_{Fe}]$ (and hence $[X_{Mn}]$) are fixed.

b. If T and $[X_{Fe}]$ are chosen as the independent variables, $[X_{Mn}] = 1 - [X_{Fe}]$ is automatically fixed.

$$\frac{(X_{MnO})}{X_{FeO}} = \frac{1-(X_{FeO})}{(X_{FeO})} = \frac{K_{(ii),T}[X_{Mn}]}{K_{(i),T}[X_{Fe}]}$$

is fixed by Equations (i) and (ii), which fixes (X_{FeO}) [and hence (X_{MnO})], and

$$p_{O_2}^{1/2} = \frac{(X_{FeO})}{[X_{Fe}]K_{(i),T}}$$

is fixed by Equation (i).

c. If p_{O_2} and $[X_{Fe}]$ are chosen as the independent variables, from Equation (i),

$$\left(X_{FeO}\right) = K_{(i),T} \cdot \left[X_{Fe}\right] \cdot p_{O_2}^{1/2} = \exp\left(\frac{-\Delta H^{\circ}_{(i)}}{RT}\right)\exp\left(\frac{\Delta S^{\circ}_{(i)}}{R}\right) \cdot \left[X_{Fe}\right] \cdot p_{O_2}^{1/2}$$

and from Equation (ii),

$$\begin{aligned}\left(X_{MnO}\right) = 1 - (X_{FeO}) &= K_{(ii),T} \cdot \left[X_{Mn}\right] \cdot p_{O_2}^{1/2} \\ &= \exp\left(\frac{-\Delta H^{\circ}_{(ii)}}{RT}\right)\exp\left(\frac{\Delta S^{\circ}_{(ii)}}{R}\right) \cdot \left[X_{Mn}\right] \cdot p_{O_2}^{1/2}\end{aligned}$$

the simultaneous solution of which fixes T and (X_{FeO}). Thus, the fixing of any two of the variables fixes the values of all of the others. In the previous discussion of this example, $T = 1800^{\circ}C$ and p_{O_2} were selected as the independent variables.

Example 2

Consider the system M–MO–O_2 in which the reaction equilibrium

$$M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$$

is established. This system has three phases (the condensed phases M and MO and the gaseous oxygen phase) and two components (M and O). The available variables are the temperature T and the total pressure P. Since, at equilibrium, the species M and MO occur in fixed states—that is, M saturated with oxygen and MO saturated with M—the activities of these two species are fixed. Thus, the total pressure P is the sum of the oxygen pressure and the saturated vapor pressures of the solid phases M and MO. Since the latter two are fixed at any given temperature, then the value of P can be varied only by varying p_{O_2}. From the phase rule, $\mathcal{F} = C + 2 - \Phi = 2 + 2 - 3 = 1$, and thus, the equilibrium has only one degree of freedom. Thus, either T can be arbitrarily fixed, in which case the equilibrium constant K_T, and hence $p_{O_2(\text{eq}T)}$, is fixed; or $P = p_{O_2}$ + (the vapor pressures of M and MO) can be arbitrarily fixed, in which case the value of K_T, and hence T, is fixed. If an inert gas is added to the system, then $P = p_{O_2} + p_{\text{inert gas}}$ + (the vapor pressures of M and MO), and so the values of p_{O_2} and $p_{\text{inert gas}}$ may be independently varied. The addition of the inert gas as the third component increases the number of degrees of freedom to two, but the additional degree of freedom is restricted to variations of the value of $p_{\text{inert gas}}$; that is, in addition to either T or p_{O_2} being independently variable, $p_{\text{inert gas}}$ may be independently varied. Consider the equilibrium

$$M_{(s)} + CO_{2(g)} = MO_{(s)} + CO_{(g)}$$

This three-component, three-phase equilibrium has two degrees of freedom which may be selected from T, P, p_{CO}, and p_{CO_2}. For example, fixing T and P uniquely fixes p_{CO} and p_{CO_2} via

$$K_T = \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \quad \text{and} \quad P = p_{\text{CO}} + p_{\text{CO}_2}$$

If the system contains the solid carbide MC, then the three-component, four-phase system (M + MO + MC + gas) has one degree of freedom, which again can be selected from T, P, p_{CO}, and p_{CO_2}. Since $R = N - C = 5 - 3 = 2$, the two independent reaction equilibria can be selected as

$$\text{M}_{(s)} + \text{CO}_{2(g)} = \text{MO}_{(s)} + \text{CO}_{(g)} \tag{i}$$

and

$$\text{M}_{(s)} + 2\text{CO}_{(g)} = \text{MC}_{(s)} + \text{CO}_{2(g)} \tag{ii}$$

Fixing T fixes

$$K_{T(\text{i})} = \frac{p_{\text{CO}}}{p_{\text{CO}_2}}$$

and

$$K_{T(\text{ii})} = \frac{p_{\text{CO}}}{p^2_{\text{CO}_2}}$$

which uniquely fixes the values of p_{CO} and p_{CO_2}, and hence $P = p_{\text{CO}} + p_{\text{CO}_2}$. If solid carbon is also present, in which case the system contains the phases M, MO, MC, C, and gaseous CO and CO_2, then the number of independent reaction equilibria is increased by one; for example, the independent equilibria

$$\text{M}_{(s)} + \text{CO}_{2(g)} = \text{MO}_{(s)} + \text{CO}_{(g)} \tag{i}$$

$$\text{M}_{(s)} + 2\text{CO}_{(g)} = \text{MC}_{(s)} + \text{CO}_{2(g)} \tag{ii}$$

and

$$\text{C}_{(s)} + \text{CO}_{2(g)} = 2\text{CO}_{(g)} \tag{iii}$$

occur, and the number of phases present is increased by one. In this case $\mathcal{F} = 0$ and the system is invariant, occurring at a unique T and at unique values of p_{CO} and p_{CO_2}. In a multiphase, multicomponent system in which several independent reaction equilibria occur, the number of such equilibria can be calculated as follows. First write a chemical reaction equation for the formation of each species present from its constituents. For example, in the preceding example,

$$\text{M} + \frac{1}{2}\text{O}_2 = \text{MO} \tag{a}$$

$$\text{M} + \text{C} = \text{MC} \tag{b}$$

$$C + \frac{1}{2}O_2 = CO \tag{c}$$

$$C + O_2 = CO_2 \tag{d}$$

Then combine these reaction equations in such a manner that those elements not considered to be present in the system are eliminated. The resulting number of reaction equations is then the number of independent reaction equilibria, *R*. In the preceding system, the species present are M, MO, MC, C, CO, and CO_2. Thus, from Equation (a):

$$\frac{1}{2}O_2 = MO - M$$

and thus, in Equation (c),

$$C + MO - M = CO \quad \text{or} \quad C + MO = CO + M \tag{iv}$$

in Equation (d),

$$C + 2MO - 2M = CO_2 \quad \text{or} \quad C + 2MO = CO_2 + 2M \tag{v}$$

and in Equation (b),

$$M + C = MC \tag{vi}$$

Thus, three independent equilibria occur, combination of which produces other equilibria which occur in the system; for example,

$$MC + 2MO = CO_2 + 3M \tag{vii}$$

$$MC + MO = CO + 2M \tag{viii}$$

$$M + CO_2 = MO + CO \tag{i}$$

$$M + 2CO = CO_2 + MC \tag{ii}$$

$$C + CO_2 = 2CO \tag{iii}$$

When any three of these five equilibria are established, the other two are also established.

13.5 PHASE STABILITY DIAGRAMS

In this section, we introduce *phase stability diagrams* (also called *predominance diagrams*). These are diagrams which are used in multicomponent, multiphase reacting systems to display regions in thermodynamic variable space where various phases in the system are likely to be found. Consider equilibrium in the ternary system Si–C–O at 1000°C. The solid phases which can exist in this system are Si, SiO_2, SiC, and C, and the gas phase is a mixture of CO and CO_2. Just as fixing the activity of one component in a binary system fixes the activity of the other, the fixing of the activities of two of the components in a ternary system fixes the activity of the third. Thus, when the activities of C and O_2 are fixed in the system Si–C–O, the activity of Si is fixed and a definite equilibrium state exists. Thus, two-dimensional representation of the phase stability can be considered in the following ways:

1. At constant temperature with a_C and p_{O_2} as the variables
2. At constant a_C (or constant p_{O_2}) with T and p_{O_2} (or a_C) as the variables

Application of the phase rule to a three-component system indicates that an equilibrium among five phases has no degrees of freedom. Thus, if a gas phase is always present,

- Four condensed phases can be in equilibrium with one another and a gas phase at an invariant state ($\mathcal{F} = 0 = C + 2 - \Phi = 3 + 2 - 5$).
- Three condensed phases can be in equilibrium with one another and a gas phase at an arbitrarily chosen temperature ($\mathcal{F} = 1 = C + 2 - \Phi = 3 + 2 - 4$).
- Two condensed phases can be in equilibrium with one another and a gas phase at an arbitrarily chosen temperature and an arbitrarily chosen value of a_C or p_{O_2} ($\mathcal{F} = 2 = C + 2 - \Phi = 3 + 2 - 3$).
- One condensed phase can be in equilibrium with the gas phase at an arbitrarily chosen temperature and arbitrarily chosen values of a_C and p_{O_2} ($\mathcal{F} = 3 = C + 2 - \Phi = 3 + 2 - 2$).

Since four solid phases can exist, there are

- Four possible equilibria involving three condensed phases and a gas phase (found by taking four solid phases three at a time, or $4!/(3! \cdot 1!) = 4$)
- Six possible equilibria involving two condensed phases and a gas phase (found by taking four solid phases two at a time, or $4!/(2! \cdot 2!) = 6$)
- Four possible equilibria involving one condensed phase and the gas phase (found by taking four solid phases one at a time, or $4!/(1! \cdot 3!) = 4$)

Consider construction of the phase stability diagram for the system Si–C–O at 1000°C using log a_C and log p_{O_2} as the variables.

As shown, there are six possible equilibria involving two condensed phases and a gas phase: namely,

1. Si–SiO_2–gas
2. Si–SiC–gas
3. SiC–SiO_2–gas
4. SiC–C–gas
5. SiO_2–C–gas
6. Si–C–gas

And the four possible equilibria involving three condensed phases and a gas phase are

1. Si–SiO_2–SiC–gas
2. Si–SiC–C–gas
3. SiO_2–SiC–C–gas
4. Si–SiO_2–C–gas

Consider the equilibria between two condensed phases and the gas phase.

1. The equilibrium Si–SiO_2–gas phase

For the reaction

$$\begin{aligned} \mathrm{Si}_{(s)} + \mathrm{O}_{2(g)} &= \mathrm{SiO}_{2(s)} \\ \Delta G^{\circ}_{(\mathrm{i})1273\ \mathrm{K}} &= -683{,}400\ \mathrm{J} \\ &= -RT \ln \frac{1}{p_{\mathrm{O}_2}} \\ &= 8.3144 \times 1273 \times 2.303 \log p_{\mathrm{O}_2} \end{aligned} \tag{i}$$

or $\log p_{O_2} = -28.04$. Thus, at 1273 K, the equilibrium between Si and SiO_2 requires $\log p_{O_2} = -28.04$, and this equilibrium, which is drawn as line *AB* in Figure 13.5a, is independent of a_C. At lower values of p_{O_2} (the abscissa), Si is stable relative to SiO_2 and, at higher values, SiO_2 is stable relative to Si.

2. The equilibrium Si–SiC–gas phase

For the reaction

$$\begin{aligned} \mathrm{Si}_{(s)} + \mathrm{C}_{(s)} &= \mathrm{SiC}_{(s)} \\ \Delta G^{\circ}_{(\mathrm{iii})1273\ \mathrm{K}} &= -63{,}300\ \mathrm{J} \\ &= -RT \ln \frac{1}{a_{\mathrm{C}}} \\ &= 8.3144 \times 1273 \times 2.303 \log a_{\mathrm{C}} \end{aligned} \tag{ii}$$

or log $a_C = -2.60$. Thus, at 1273 K, the equilibrium between Si and SiC requires log $a_C = -2.60$, and this equilibrium, which is drawn as line *CD* in Figure 13.5a, is independent of p_{O_2}. At lower values of a_C, Si is s relative to SiC and, at higher values of a_C, SiC is stable relative to Si.

3. The equilibrium SiC–SiO_2–gas phase

Lines *AB* and *CD* intersect at the point $P(\log p_{O_2} = -28.04, \log a_C = -2.60)$, which is the unique state at which the three solid phases Si, SiC, and SiO_2 are in equilibrium

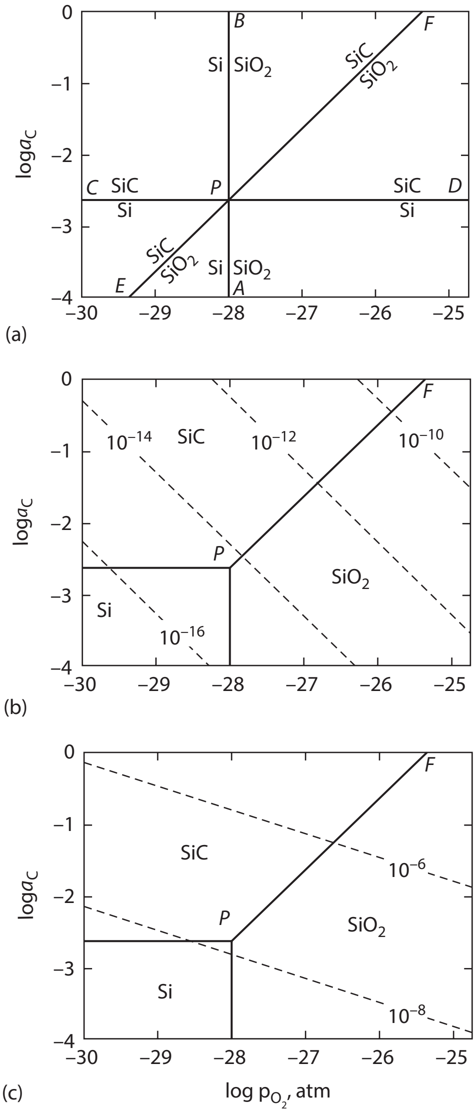

Figure 13.5 (a) Construction of the phase stability diagram for the system Si–C–O at 1273 K. (b) CO_2 isobars in the phase stability diagram for Si–C–O at 1273 K. (c) CO isobars in the phase stability diagram for Si–C–O at 1273 K.

with one another and with a gas phase at 1273 K. The variation of log a_C with log p_{O_2} required for the equilibrium SiC–SiO_2 must pass through this point. Combination of Equations (i) and (ii) gives

$$SiC_{(s)} + O_{2(g)} = SiO_{2(s)} + C_{(s)} \tag{iii}$$

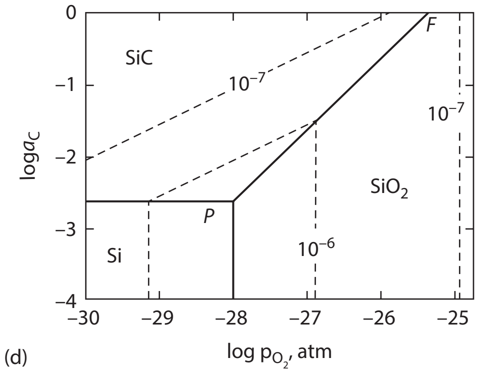

Figure 13.5 *(Continued)* (d) SiO isobars in the phase stability diagram for Si–C–O at 1273 K.

for which

$$\Delta G^{\circ}_{(\text{iii})1273\ \text{K}} = -620{,}100\ \text{J}$$

$$= -8.3144 \times 1273 \times 2.303 \log \frac{a_C}{p_{O_2}}$$

or

$$\log a_C = \log p_{O_2} + 25.44$$

which is drawn as line *EF* in Figure 13.5a. In states above this line, SiC is stable relative to SiO$_2$, and below the line, SiO$_2$ is stable relative to SiC.

4. The equilibrium SiC–C–gas phase

The equilibrium between solid SiC and solid C is a phase equilibrium which exists only at $a_C = 1$, or log $a_C = 0$. Thus, in Figure 13.5a, the equilibrium between SiC and C exists along the log $a_C = 0$ line, at values of log p_{O_2} less than –25.44, the point of intersection of line *EF* with the log $a_C = 0$ line.

5. The equilibrium SiO$_2$–C–gas phase

As with the equilibrium between SiC and C, the phase equilibrium between SiO$_2$ and C requires log $a_C = 1$, and thus occurs along the log $a_C = 0$ line at values of log p_{O_2} greater than –25.44.

6. The equilibrium Si–C–gas phase

The standard Gibbs free energy change at 1273 K for the reaction

$$\text{Si}_{(s)} + \text{C}_{(s)} = \text{SiC}_{(s)}$$

is $\Delta G^{\circ}_{(\text{ii})1273\text{ K}} = -63{,}300$ J, which, being negative, indicates that Si and C spontaneously react with one another to form SiC until either the C or the Si is consumed. Thus, Si and C cannot be in equilibrium with one another. If the molar ratio Si/C in the system is greater than 1, the C is consumed by the reaction and equilibrium between the product SiC and the remaining Si is attained, and if the ratio is less than 1, the Si is consumed by the reaction and an equilibrium is attained between the SiC produced and the remaining C. The solid carbon phase exists only along the $\log a_C = 1$ line, and thus, Figure 13.5a contains fields of stability of the single phases Si, SiO_2, and SiC. Consequently, of the six lines in the diagram radiating from point *P*, three represent stable equilibria involving two condensed phases and a gas phase, and three represent metastable equilibria involving two condensed phases and a gas phase. The problem is how to distinguish between the two types of equilibria. It is a property of such diagrams that the lines of metastable and stable equilibria radiate alternatively from a point such as *P* (see, for example, Figures 7.7 and 7.8a). Thus, one set of lines is *PA*-*PC*-*PF* and the other is *PE*-*PB*-*PD*. In Figure 13.5a, Si is stable relative to SiO_2 in states to the left of *PA* and is stable relative to SiC in states below *PC*. Thus, the line *PE* represents the metastable equilibrium between SiC and SiO_2. This identifies the stable equilibrium lines as being *PA*-*PC*-*PF* and, as shown in Figure 13.5b, defines the fields of stability of a single condensed phase with a gas phase, which, at constant temperature, have two degrees of freedom. These fields meet at lines which represent the equilibrium between two condensed phases and a gas phase (which, at constant temperature, have one degree of freedom), and the lines meet at points representing equilibrium among three condensed phases and a gas phase. The point *P* is the state of equilibrium of Si, SiC, SiO_2, and a gas phase, and the point *F* is the state of equilibrium of SiC, SiO_2, C, and a gas phase. The partial pressures of CO and CO_2 are determined by the activities of carbon and oxygen in the system, and the iso-p_{CO_2} and iso-p_{CO} lines can be placed on the stability diagram as follows. For the reaction

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \qquad \text{(iv)}$$

$$\Delta G^{\circ}_{(\text{iv})1273\text{ K}} = -395{,}200\text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{CO_2}}{a_C p_{O_2}}$$

Therefore,

$$16.21 = \log p_{CO_2} - \log a_C + \log p_{O_2}$$

or

$$\log a_C = -\log p_{O_2} - 16.21 + \log p_{CO_2}$$

Thus, as shown in Figure 13.5b, the CO_2 isobars in the phase stability diagram are lines with slopes of −1. Similarly, for

$$C_{(s)} + \frac{1}{2}O_{2(g)} = CO_{(g)} \tag{v}$$

$$\Delta G^{\circ}_{(v)1273\text{ K}} = -223{,}300\text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{CO}}{a_C p_{O_2}^{1/2}}$$

or

$$\log a_C = -\frac{1}{2}\log p_{O_2} - 9.16 + \log p_{CO}$$

and, as shown in Figure 13.5c, the CO isobars are lines with slopes of –½. The gaseous species SiO also occurs in the system Si–C–O, and SiO isobars can be drawn on the stability diagram. Since the partial pressure of SiO is determined by the activity of Si and the partial pressure of oxygen, the individual single condensed-phase stability fields have to be considered separately, and each equilibrium must involve the condensed phase of interest, SiO gas, and C and/or O_2. In the field of stability of Si, the equilibrium is

$$Si_{(s)} + \frac{1}{2}O_{2(g)} = SiO_{(g)} \tag{vi}$$

for which

$$\Delta G^{\circ}_{(vi)1273\text{ K}} = -209{,}200\text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{SiO}}{p_{O_2}}$$

or

$$\log p_{SiO} = \frac{1}{2}\log p_{O_2} + 8.59$$

Thus, as shown in Figure 13.5d, the SiO isobars in the stability field of Si are vertical lines, and p_{SiO} increases with increasing p_{O_2}. In the SiO_2 field, the equilibrium is

$$SiO_{2(s)} = SiO_{(g)} + \frac{1}{2}O_{2(g)} \tag{vii}$$

for which combination of $\Delta G^{\circ}_{(vii)1273\text{ K}}$ and $\Delta G^{\circ}_{(i)1273\text{ K}}$ gives

$$\Delta G^{\circ}_{(vii)1273\text{ K}} = -474{,}200\text{ J} = -8.3144 \times 1273 \times 2.303 \log(p_{SiO} p_{O_2}^{1/2})$$

which gives

$$\log p_{SiO} = -\frac{1}{2}\log p_{O_2} - 19.45$$

Thus, as shown in Figure 13.5d, the SiO isobars in the field of stability of SiO_2 are vertical lines and p_{SiO} decreases with increasing p_{O_2}. In the field of stability of SiC, the equilibrium is

$$SiC_{(s)} + \frac{1}{2}O_{2(g)} = SiO_{(g)} + C_{(s)} \tag{viii}$$

for which combination of $\Delta G^\circ_{(vi)1273\text{ K}}$ and $\Delta G^\circ_{(ii)1273\text{ K}}$ gives

$$\Delta G^\circ_{(viii)1273\text{ K}} = -145{,}900\text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{SiO} \cdot a_C}{p_{O_2}^{1/2}}$$

or

$$\log a_C = \frac{1}{2}\log p_{O_2} - \log p_{SiO} + 5.99$$

Thus, as shown in Figure 13.5d, the SiO isobars in the field of stability of SiC are lines with slopes of ½. At any temperature, the maximum value of p_{SiO} occurs in states in which Si and SiO_2 are in equilibrium with a gas phase. The activities of carbon and oxygen used as the variables in the construction of Figure 13.5 are determined by the individual values of p_{CO} and p_{CO_2}, which establish the equilibria

$$CO + \frac{1}{2}O_2 = CO_2$$

and

$$C + CO_2 = 2CO$$

and thus, the phase stability diagram can be constructed using p_{CO} and p_{CO_2} as the variables. The equilibrium corresponding to Equation (i) is

$$Si_{(s)} + 2CO_{2(g)} = SiO_{2(s)} + 2CO_{(g)} \tag{ix}$$

Combination of the Gibbs free energy changes for the reactions given by Equations (i), (iv), and (v) gives

$$\Delta G^\circ_{(ix)1273\text{ K}} = -339{,}600\text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{CO}^2}{p_{CO_2}^2}$$

which gives

$$\log p_{CO} = \log p_{CO_2} + 6.97$$

This is drawn as the line *AB* in Figure 13.6a (and corresponds to the line *AB* in Figure 13.5a). Above the line, Si is stable relative to SiO_2, and below the line, SiO_2 is stable relative to Si. The equivalent of the equilibrium given by Equation (ii) is

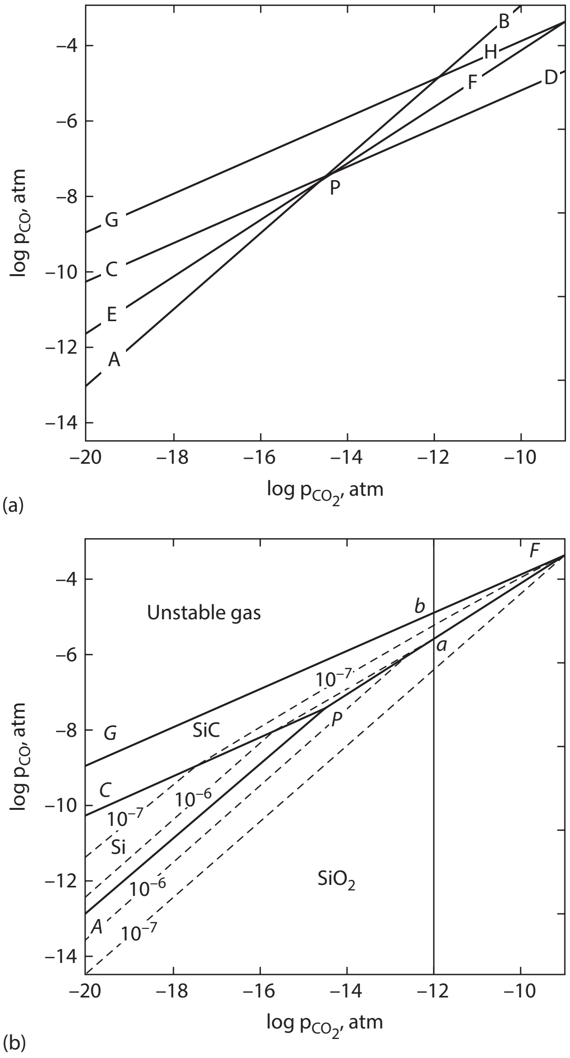

Figure 13.6 (a) Construction of the phase stability diagram for the system Si–C–O at 1273 K. (b) The phase stability diagram for the system Si–C–O at 1273 K showing the 10^{-6} and 10^{-7} atm SiO isobars.

$$\mathrm{Si}_{(s)} + 2\mathrm{CO}_{(g)} = \mathrm{SiC}_{(s)} + \mathrm{CO}_{2(g)} \tag{x}$$

for which

$$\Delta G^{\circ}_{(\mathrm{x})1273\ \mathrm{K}} = -11{,}900\ \mathrm{J} = -8.3144 \times 1273 \times 2.303 \log \frac{p_{\mathrm{CO_2}}}{p^2_{\mathrm{CO}}}$$

or

$$\log p_{\text{CO}} = \frac{1}{2}\log p_{\text{CO}_2} - 0.24$$

This is drawn as line *CD* in Figure 13.6a. Above the line, SiC is stable relative to Si, and below the line, Si is stable relative to SiC. The lines *AB* and *CD* intersect at *P*, which is thus the invariant point at which Si, SiC, SiO_2, and a gas phase are in equilibrium. The equivalent of the equilibrium given by Equation (iii) is

$$\text{SiC}_{(s)} + 3\text{CO}_{2(g)} = \text{SiO}_{2(s)} + 4\text{CO}_{(g)} \qquad \text{(xi)}$$

for which

$$\Delta G^{\circ}_{(\text{xi})1273\text{ K}} = -327{,}700 \text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p^4_{\text{CO}}}{p^3_{\text{CO}_2}}$$

or

$$\log p_{\text{CO}} = 0.75 \log p_{\text{CO}_2} + 3.36$$

This is drawn as the line *EF* in Figure 13.6a. SiC is stable relative to SiO_2 above the line, and SiO_2 is stable relative to SiC below the line.

The *carbon line*, which is equivalent to the log $a_C = 0$ line in Figure 13.5, is obtained from

$$\text{C}_{(s)} + \text{CO}_{2(g)} = 2\text{CO}_{(g)} \qquad \text{(xii)}$$

for which

$$\Delta G^{\circ}_{(\text{xii})1273\text{ K}} = -51{,}400 \text{ J} = -8.3144 \times 1273 \times 2.303 \log \frac{p^2_{\text{CO}}}{p_{\text{CO}_2}}$$

which gives

$$\log p_{\text{CO}} = \frac{1}{2}\log p_{\text{CO}_2} - 1.05$$

This is drawn as the line *GH* in Figure 13.6a. The phase stability fields, identified in the same manner as was used in Figure 13.5a, are shown in Figure 13.6b. The Si phase field is bounded by *APC*, the SiC phase field is bounded by *CPFG*, and the SiO_2 phase field lies below the line *APF*. The region above *GF* is an unstable gas. Any gas in this region precipitates carbon according to

$$2\text{CO}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{C}_{(s)}$$

until, thereby, the ratio p_{CO_2}/p_{CO} is that required for equilibrium with C at $a_C = 1$ at 1273 K. The isobars for SiO gas are calculated as follows. In the field of stability of Si, the equivalent of the equilibrium given by Equation (vi) is

$$Si_{(s)} + CO_{2(g)} = SiO_{(g)} + CO_{(g)} \qquad \text{(xiii)}$$

for which

$$\Delta G^\circ_{(xiii)1273\ K} = -37{,}300\ J = -8.3144 \times 1273 \times 2.303 \log \frac{p_{SiO}p_{CO}}{p_{CO_2}}$$

which gives

$$\log p_{CO} = \log p_{CO_2} + 1.53 - \log p_{SiO}$$

In the field of stability of SiO_2, the equivalent of the equilibrium given by Equation (vii) is

$$SiO_{2(s)} + CO_{(g)} = SiO_{(g)} + CO_{2(g)} \qquad \text{(xiv)}$$

for which

$$\Delta G^\circ_{(xiv)1273\ K} = 302{,}300\ J = -8.3144 \times 1273 \times 2.303 \log \frac{p_{CO_2}p_{SiO}}{p_{CO}}$$

which gives

$$\log p_{CO} = \log p_{CO_2} + 12.40 + \log p_{SiO}$$

In the field of stability of SiC, the equilibrium equivalent to that given by Equation (viii) is

$$SiC_{(s)} + 2CO_{2(g)} = SiO_{(g)} + 3CO_{(g)} \qquad \text{(xv)}$$

for which

$$\Delta G^\circ_{(xv)1273\ K} = -25{,}400\ J = -8.3144 \times 1273 \times 2.303 \log \frac{p^3_{CO}p_{SiO}}{p^2_{CO_2}}$$

which gives

$$\log p_{CO} = \frac{2}{3}\log p_{CO_2} - 0.35 + \frac{1}{3}\log p_{SiO}$$

The 10^{-7} and 10^{-6} atm SiO isobars are shown in Figure 13.6b, and a comparison of Figures 13.5 and 13.6 shows that the latter is produced by distorting the former such that the CO isobars are horizontal lines and the CO_2 isobars are vertical lines. The points *P* and *F* in Figure 13.6b correspond to the points *P* and *F* in Figure 13.5. The full phase stability diagram is three-dimensional, with the axes being temperature and the activities of two components (a_C and p_{O_2}) or the partial pressures of CO and CO_2. Two-dimensional phase stability diagrams which show the influence of temperature can be drawn if the activity of one component is held constant. Consider the phase stability diagram using p_{CO} and $1/T$ as coordinates and drawn for a constant partial pressure of CO_2 of 10^{-12} atm. The diagram will be drawn for temperatures in the range 1250–1990 K, and thus, since the melting temperature of Si is 1683 K, equilibria involving both solid and liquid Si will have to be considered. In Figure 13.7a, the vertical line at $T = 1685$ K represents the melting temperature of Si, and thus, liquid Si occurs to the left of the line and solid Si occurs to the right.

1. The equilibrium $Si_{(s)}$–SiO_2–gas phase

The equilibrium is

$$Si_{(s)} + 2CO_{2(g)} = SiO_{2(s)} + 2CO_{(g)} \qquad \text{(xvi)}$$

for which

$$\Delta G^\circ_{(xvi)} = -337{,}300 - 0.02T \text{ J}$$

Thus,

$$\frac{-337{,}300}{8.3144 \times 2.303T} - \frac{0.02}{8.3144 \times 2.303} = -\log \frac{p^2_{CO}}{p^2_{CO_2}}$$

which can be rearranged to give

$$\log p_{CO} = \frac{8807}{T} + 5.22 \times 10^{-4} + \log p_{CO_2}$$

This line, with $\log p_{CO_2} = -12$, is drawn as *AB* in Figure 13.7a. Silicon is stable relative to SiO_2 above the line, and SiO_2 is stable relative to Si below the line.

The equilibrium $Si_{(l)}$–SiO_2–gas phase: The equilibrium is

$$Si_{(l)} + 2CO_{2(g)} = SiO_{2(s)} + 2CO_{(g)} \qquad \text{(xvii)}$$

for which

$$\Delta G^\circ_{(xvii)} = -387{,}900 + 30.18T \text{ J}$$

Thus,

$$\frac{-387{,}900}{8.3144 \times 2.303T} + \frac{30.18}{8.3144 \times 2.303} = -\log \frac{p^2_{CO}}{p^2_{CO_2}}$$

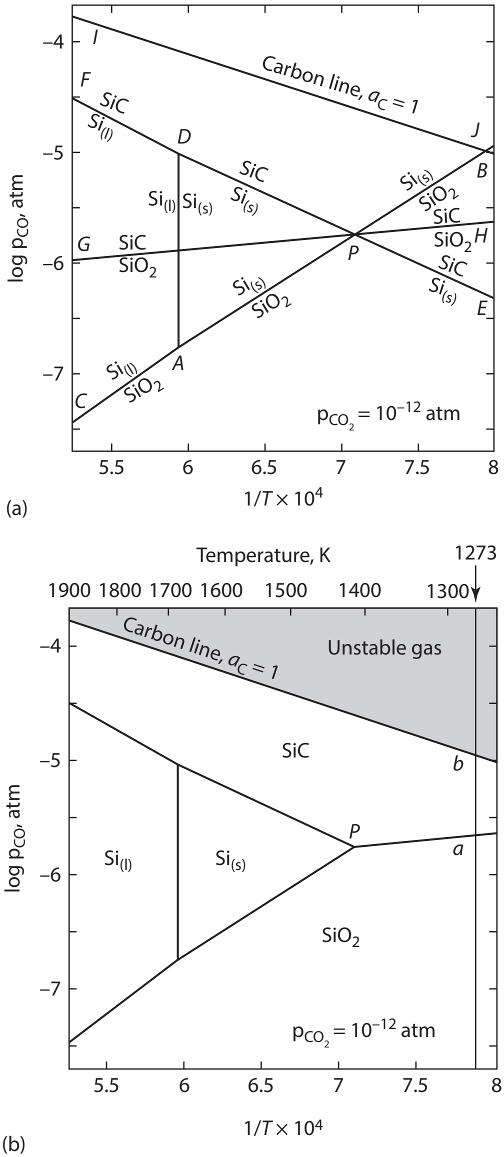

Figure 13.7 (a) Construction of the phase stability diagram for the system Si–C–O using log p_{CO} and $1/T$ as coordinates at a constant partial pressure of CO_2 of 10^{-12} atm. (b) The phase stability diagram for the system Si–C–O at a constant partial pressure of $CO_2 = 10^{-12}$ atm.

which gives

$$\log p_{CO} = \frac{10{,}130}{T} - 0.788 + \log p_{CO_2}$$

With $p_{CO_2} = 10^{-12}$ atm, this gives line *CA* in Figure 13.7a. Liquid Si is stable relative to SiO_2 above the line, and SiO_2 is stable relative to liquid Si below the line.

2. The equilibrium $Si_{(s)}$–SiC–gas phase

The equilibrium is

$$Si_{(s)} + 2CO_{(g)} = SiC_{(s)} + CO_{2(g)} \tag{xviii}$$

for which

$$\Delta G^\circ_{(xviii)} = -243{,}750 + 182.11T \text{ J}$$

which yields

$$\log p_{CO} = -\frac{6364}{T} + 4.76 + \frac{1}{2}\log p_{CO_2}$$

With $\log p_{CO_2} = -12$, this gives line *DE* in Figure 13.7a. SiC is stable relative to solid Si above the line, and Si is stable relative to SiC below the line.

3. The equilibrium $Si_{(l)}$–SiC–gas phase: The equilibrium is

$$Si_{(l)} + 2CO_{(g)} = SiC_{(s)} + CO_{2(g)} \tag{xix}$$

for which

$$\Delta G^\circ_{(xix)} = -293{,}300 + 211.5T \text{ J}$$

This gives

$$\log p_{CO} = -\frac{7659}{T} + 5.52 + \frac{1}{2}\log p_{CO_2}$$

which, with $\log p_{CO_2} = -12$, gives line *FD* in Figure 13.7a. Liquid Si is stable with respect to SiC below the line, and SiC is stable with respect to Si above the line.

4. The equilibrium SiC–SiO_2–gas phase

The equilibrium is

$$SiC_{(s)} + 3CO_{2(g)} = SiO_{2(s)} + 4CO_{(g)} \tag{xx}$$

which gives

$$\log p_{CO} = \frac{1221}{T} + 2.38 + 0.75\log p_{CO_2}$$

This is drawn, with $\log p_{CO_2} = -12$, as line *GH* in Figure 13.7a. SiC is stable relative to SiO_2 above the line, and SiO_2 is stable relative to SiC below the line.

The carbon line, at which $a_C = 1$, is determined by the equilibrium

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)}$$

for which

$$\Delta G^{\circ} = 170{,}700 - 174.5T \text{ J}$$

which gives

$$\log p_{CO} = -\frac{4457}{T} + 4.55 + \frac{1}{2}\log p_{CO_2}$$

With $p_{CO_2} = 10^{-12}$ atm, this gives line *IJ* in Figure 17.7a. States above this line represent unstable gas. The stability fields are identified as follows:

1. In the area *APD*, solid silicon is stable with respect to SiO_2 and SiC, and thus, this area is the field of stability of solid Si.
2. In the areas *FDAC*, liquid silicon is stable with respect to SiC and SiO_2, and thus, this area is the field of stability of liquid Si.
3. In the area *FDPHJI*, SiC is stable with respect to Si and SiO_2, and thus, this area is the field of stability of SiC.
4. Below the line *CAPH*, SiO_2 is stable with respect to Si and SiC, and thus, this is the field of stability of SiO_2

These fields of stability are shown in Figure 13.7b. The phase stability diagram shows that, with $p_{CO_2} = 10^{-12}$ atm, 1410 K (the point *P*) is the minimum temperature at which silicon is stable, and that, with increasing temperature, the field of stability of silicon widens at the expense of SiC and SiO_2. The slopes of the lines in Figures 13.7 are related to the standard enthalpy changes for the equilibrium reactions; for example, the slope of the line dividing the solid Si and the SiO_2 fields (the line *AB* in Figure 13.7a) is obtained as $-(\Delta H^0/(2.303 \cdot 2 \cdot R)) = 337{,}300/(2.303 \times 2 \times R) = 8807$ for the reaction given by Equation (xvi). The points *a* and *b* on the 10^{-12} atm CO_2 isobar in Figure 13.6b correspond with the points *a* and *b* on the 1273 K isotherm in Figure 13.7b.

13.6 BINARY SYSTEMS CONTAINING COMPOUNDS

The phase relationships in a two-component system can be represented on an isobaric phase diagram using temperature and composition as coordinates, and these are the phase diagrams often encountered in materials science (see Chapter 10). If

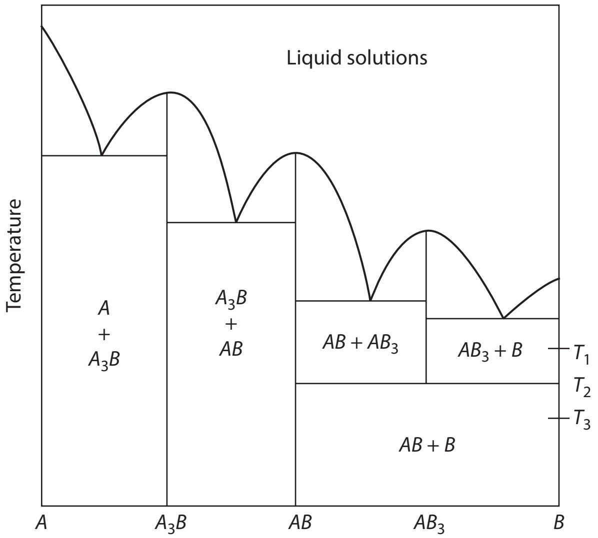

Figure 13.8 The phase diagram for the system *A*–*B* in which three stoichiometric compounds are formed.

the two components react with one another to form compounds, then, in such systems, chemical reaction equilibria and phase equilibria are synonymous. Consider the binary system *A*–*B*, the phase diagram for which is shown in Figure 13.8. The negative departures from ideality in the solid state are sufficiently large that stoichiometric compounds following the law of definite proportions are formed, with there being negligible solubility of *A* in *B*, or *B* in *A*, and negligible range of nonstoichiometry in the compounds AB_3, AB, and A_3B. The system contains the equilibria

$$3A + B = A_3B$$

$$A + B = AB,$$

$$A + 3B = AB_3$$

If one of the components (*B*) is appreciably volatile and the other (*A*) is not, then the thermodynamics of the system can be determined from knowledge of the variation of p_B with composition. The variation of p_B with composition at the temperature T_1 is shown in Figure 13.9. In the range of composition between *B* and AB_3, virtually pure *B* exists in equilibrium with AB_3 (saturated with *B*), and, since pure *B* exists, the pressure exerted by the system is p_B, the saturated vapor pressure of *B* at the temperature T_1. In the range of composition between *AB* (saturated with *B*) and AB_3 (saturated with *A*), the constant pressure exerted by the system is p'_B, in the range between A_3B (saturated with *B*) and *AB* (saturated with *A*) it is p''_B, and in the range

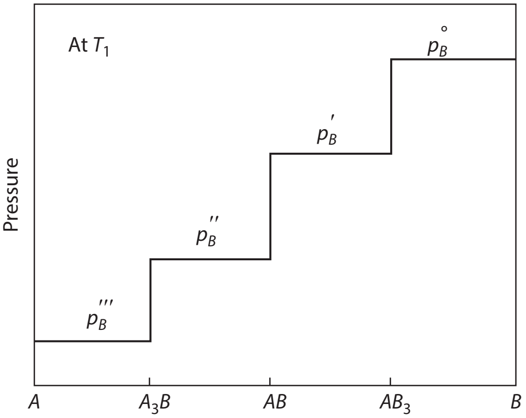

Figure 13.9 The variation, with composition, of the vapor pressure of component *B* in the system shown in Figure 13.8 at the temperature T_1.

between A (saturated with B) and A_3B (saturated with A) it is p'''_B. In each of these ranges of composition, the two-component, three-phase equilibrium has one degree of freedom, which is used when T_1 is specified, which requires that $P = p_B$ within these ranges at fixed temperature. The activity of B in the system, defined as $p_B/\overset{\circ}{p}_B$, is thus

$$\frac{\overset{\circ}{p}_B}{\overset{\circ}{p}_B} = 1 \text{ in the range } AB_3 - B$$

$$\frac{p'_B}{\overset{\circ}{p}_B} \text{ in the range } AB - AB_3$$

$$\frac{p''_B}{\overset{\circ}{p}_B} \text{ in the range } A_3B - AB$$

$$\frac{p'''_B}{\overset{\circ}{p}_B} \text{ in the range } A - A_3B$$

Thus, since $\Delta\overline{G}_B^M = \overline{G}_B - \overset{\circ}{G}_B = RT \ln p_B / \overset{\circ}{p}_B$, the Gibbs free energy–composition diagram at the temperature T_1 is as shown in Figure 13.10. Since Figure 13.10 is drawn for 1 mole of the system, then

$$hb = \Delta G_{\text{(i)}} = \Delta G \text{ for the reaction}$$
$$0.75 \text{ mole } A + 0.25 \text{ mole } B = A_{0.75}B_{0.25} \text{ or } 0.25 \text{ moles of } A_3B$$
$$gc = \Delta G_{\text{(ii)}} = \Delta G \text{ for the reaction}$$
$$0.5 \text{ mole } A + 0.5 \text{ mole } B = A_{0.5}B_{0.5} \text{ or } 0.5 \text{ moles of } AB$$
$$fd = \Delta G_{\text{(iii)}} = \Delta G \text{ for the reaction}$$
$$0.25 \text{ mole } A + 0.75 \text{ mole } B = A_{0.25}B_{0.75} \text{ or } 0.25 \text{ moles of } AB_3$$

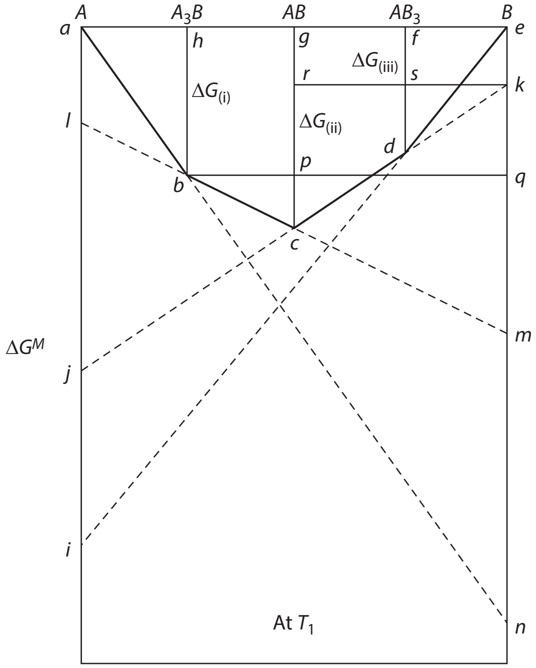

Figure 13.10 The molar Gibbs free energies at T_1 in the system shown in Figure 13.8.

These three changes in Gibbs free energy can be determined geometrically as follows:

$$ek = \Delta \bar{G}_B'^{\,M} = RT \ln \frac{p_B'}{p_B^{\circ}}$$

$$em = \Delta \bar{G}_B''^{\,M} = RT \ln \frac{p_B''}{p_B^{\circ}}$$

and

$$en = \Delta \bar{G}_B'''^{\,M} = RT \ln \frac{p_B'''}{p_B^{\circ}}$$

Thus, from consideration of the similar triangles *ahb* and *aen*,

$$\frac{\Delta G_{(\mathrm{i})}}{\Delta \bar{G}_B'''^{\,M}} = \frac{1}{4}$$

and hence,

$$\Delta G_{(\mathrm{i})} = \frac{1}{4} \Delta \bar{G}_B''^{\,M}$$

Consideration of the similar triangles *bpc* and *bqm* gives

$$\frac{pc}{qm} = \frac{bp}{bq} = \frac{1}{3}$$

But

$$pc = gc - gp = \Delta G_{\text{(ii)}} - \Delta G_{\text{(i)}}$$

and

$$qm = em - eq = \Delta \bar{G}_B''^{M} - \Delta G_{\text{(i)}}$$

Thus,

$$3(\Delta G_{\text{(ii)}} - \Delta G_{\text{(i)}}) = (\Delta \bar{G}_B''^{M} - \Delta G_{\text{(i)}})$$

or

$$\Delta G_{\text{(ii)}} = \frac{1}{3}\Delta \bar{G}_B''^{M} + \frac{2}{3}\Delta G_{\text{(i)}}$$

Consideration of the similar triangles *rck* and *sdk* gives

$$\frac{rc}{sd} = \frac{rk}{sk} = 2$$

But

$$rc = gc - gr = \Delta G_{\text{(ii)}} - \Delta \bar{G}_B'^{M}$$

and

$$sd = fd - fs = \Delta G_{\text{(iii)}} - \Delta \bar{G}_B'^{M}$$

such that

$$\Delta G_{\text{(iii)}} = \frac{1}{2}\Delta G_{\text{(ii)}} + \frac{1}{2}\Delta \bar{G}_B'^{M}$$

Thus,

$$\Delta G_{\text{(i)}} = \frac{1}{4} RT \ln \frac{p_B'''}{p_B^{\circ}}$$

$$\Delta G_{\text{(ii)}} = \frac{1}{3} RT \ln \frac{p_B''}{p_B^{\circ}} + \frac{1}{6} RT \ln \frac{p_B''}{p_B^{\circ}}$$

and

$$\Delta G_{\text{(iii)}} = \frac{1}{6}RT\ln\frac{p''_B}{p^o_B} + \frac{1}{12}RT\ln\frac{p'''_B}{p^o_B} + \frac{1}{2}RT\ln\frac{p'_B}{p^o_B}$$

and hence for

$$\begin{aligned} 3A + B = A_3B \qquad & \Delta G^{\circ}_{\text{(i)}} = 4\Delta G_{\text{(i)}} \\ A + B = AB \qquad & \Delta G^{\circ}_{\text{(ii)}} = 2\Delta G_{\text{(ii)}} = \frac{2}{3}\Delta\bar{G}''^{M}_{B} + \frac{4}{3}\Delta G_{\text{(i)}} \\ A + 3B = AB_3 \qquad & \Delta G^{\circ}_{\text{(iii)}} = 4\Delta G_{\text{(iii)}} = 2\Delta G_{\text{(ii)}} + 2\Delta\bar{G}'^{M}_{B} \end{aligned}$$

Figure 13.8 shows that, below the temperature T_2, the compound AB_3 is unstable with respect to AB and B, with the invariant equilibrium

$$AB_{(s)} + 2B_{(s)} = AB_{3(s)}$$

occurring at the temperature T_2. The standard Gibbs free energy change for this reaction is calculated as $\Delta G^{\circ}_{\text{(iii)}} - \Delta G^{\circ}_{\text{(ii)}}$, which equals $2RT\ln\ p'_B/p^{\circ}_B$. Thus, at $T > T_2$,

$$\Delta G^{\circ}_{\text{(iii)}} - \Delta G^{\circ}_{\text{(ii)}} < 0 \quad \text{and} \quad p'_B < p^{\circ}_B$$

at T_2,

$$\Delta G^{\circ}_{\text{(iii)}} - \Delta G^{\circ}_{\text{(ii)}} = 0 \quad \text{and} \quad p'_B = p^{\circ}_B$$

and at $T < T_2$,

$$\Delta G^{\circ}_{\text{(iii)}} - \Delta G^{\circ}_{\text{(ii)}} > 0 \quad \text{and} \quad p'_B > p^{\circ}_B$$

The variations of the Gibbs free energy of mixing with temperature at T_2 and T_3 are shown in Figure 13.11a and b, respectively, which illustrates graphically that at T_2,

$$\Delta G_{\text{(iii)}} = \tfrac{1}{2}\Delta G_{\text{(ii)}}$$

and at T_3,

$$\left|\Delta G_{\text{(iii)}}\right| < \left|\tfrac{1}{2}\Delta G_{\text{(ii)}}\right|$$

such that, in the range of composition B–AB, at temperatures below T_2, the system occurring as either $AB + AB_3$ or $AB_3 + B$ is metastable with respect to its occurrence as $AB + B$. In considering the thermodynamic properties of a system such as that shown in Figure 13.8, two approaches can be made: namely,

1. The consideration that the compounds are ordered solid solutions
2. The consideration that the compounds are formed by the chemical reaction of A with B

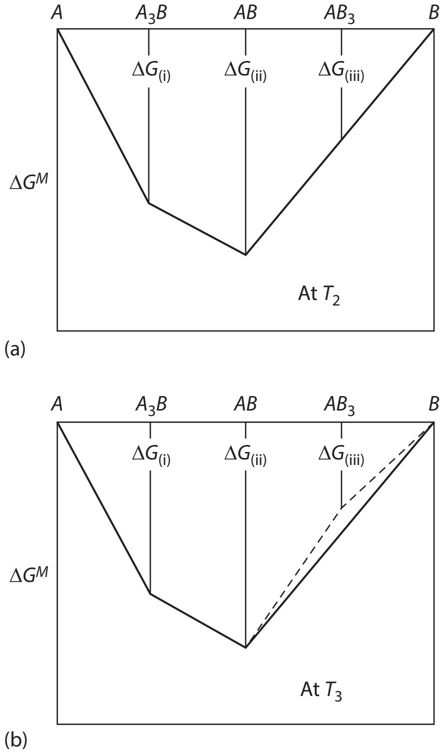

Figure 13.11 (a) The Gibbs free energies of mixing in the system shown in Figure 13.8 at the temperature T_2. (b) The Gibbs free energies of mixing in the system shown in Figure 13.8 at the temperature T_3.

1. Consider the compound AB_3 to be an ordered solid solution of A and B in the molar ratio 1/3. Then, in Figure 13.10,

$$\begin{aligned} fd &= \Delta G^M = RT(X_A \ln a_A + X_B \ln a_B) = RT(0.25 \ln a_A + 0.75 \ln a_B) \\ &= RT \ln a_A^{0.25} a_B^{0.75} \end{aligned} \tag{i}$$

2. Consider the compound AB_3 to form as the product of the reaction

$$A + 3B = AB_3$$

for which the change in the standard Gibbs free energy is $\Delta G^\circ_{(\text{iii})}$. Then,

$$\begin{aligned} fd &= 0.25 \Delta G^\circ_{(\text{iii})} = -0.25 RT \ln K_{(\text{iii})} = -RT \ln \left(\frac{a_{AB_3}}{a_A a_B^3} \right)^{0.25} \\ &= RT \ln \left(\frac{a_A^{0.25} a_B^{0.75}}{a_{AB_3}^{0.25}} \right) \end{aligned} \tag{ii}$$

Since AB_3 is a *line compound* (i.e., it has a negligible range of nonstoichiometry), it exists at a fixed composition and hence exists in a fixed state. If this fixed state is chosen as being the standard state, in which $a_{AB_3} = 1$, then Equation (ii) becomes

$$fd = 0.25\Delta G^\circ_{\text{(iii)}} = RT \ln a_A^{0.25} a_B^{0.75}$$

which is identical with Equation (i). In both Equations (i) and (ii), the standard states of A and B are the pure solid elements at the temperature T. The variations of the activities of A and B in the compound AB_3 are limited by the separation of B and AB; for example, when AB_3 is in equilibrium with B, $a_B = 1$, and thus, $a_A \exp(4\Delta G_{\text{(iii)}}/RT) = \exp(4\Delta G^\circ_{\text{(iii)}}/RT)$ ($RT \ln a_A = ai$ in Figure 13.10). If the activity of B is decreased to a value less than unity, then AB_3 is no longer saturated with B, and the activity of A in the compound increases in accordance with Equation (iv). The minimum activity of B in AB_3 is determined by the saturation of AB_3 with A, at which point the compound AB appears. The minimum activity which B may have is obtained from Figure 13.10 as $RT \ln a_B = ek$, and the corresponding maximum activity of A is obtained from $RT \ln a_A = aj$. Nonsaturation of AB_3 with either A or B occurs when the partial pressure of B exerted by the compound lies between the limits p'_B and p°_B. Similar consideration can be made with respect to the compounds AB and A_3B; for example, in Figure 13.10,

$$gc = \Delta G^M = \frac{1}{2}\Delta G^\circ_{\text{(ii)}} = RT \ln a_A^{0.5} A_B^{0.5}$$

and

$$hb = \Delta G^M = 0.25\Delta G^\circ_{(i)} = RT \ln a_A^{0.75} A_B^{0.25}$$

In the preceding discussion, it was assumed that the intermediate phases were line compounds and that there was no solubility of A in B. If A and B are partially soluble in one another and the compounds A_2B and AB_2 (identified as phases β and γ, respectively) have measurable ranges of nonstoichiometry, the phase diagram is as shown in Figure 13.12a. Again, if B is appreciably volatile and A is not, then the variation of vapor pressure with composition at the temperature T_1 is as shown in Figure 13.12b, and the corresponding variation of the Gibbs free energy is as shown in Figure 13.12c.

Example 1: The Ga–GaP System

The phase diagram for the system Ga–GaP is shown in Figure 13.13. Calculate the partial pressure of phosphorus vapor, p_{P_2}, exerted by the GaP liquidus melt at 1273 K. The standard Gibbs free energy change for the reaction

$$\text{Ga}_{(l)} + \frac{1}{2}\text{P}_{2(g)} = \text{GaP}_{(s)}$$

is

$$\Delta G^\circ = -178{,}800 + 96.2T + 3.1T \ln T - 3.61\times 10^{-3} T^2 - \frac{1.035\times 10^5}{T}$$

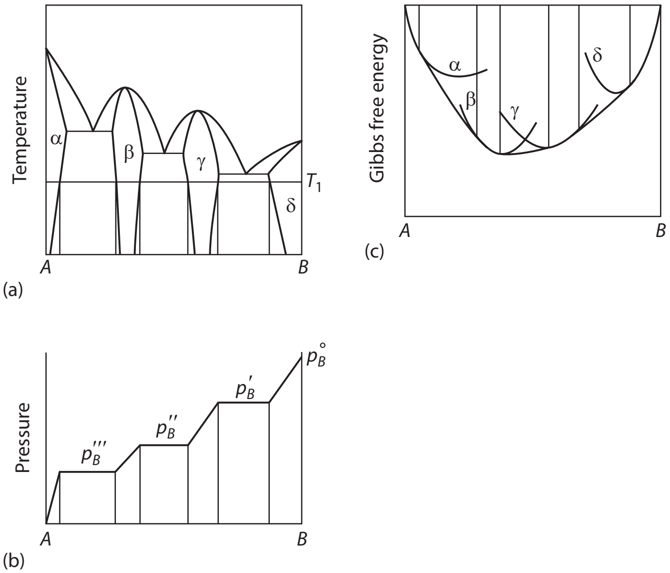

Figure 13.12 (a) The phase diagram for the system *A*–*B*. (b) The partial vapor pressure of *B* at the temperature T_1. (c) The molar Gibbs free energies of mixing at the temperature T_1.

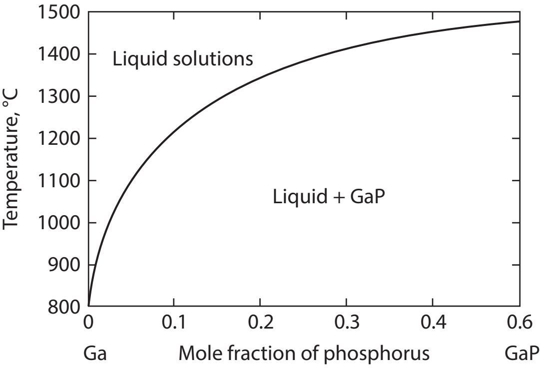

Figure 13.13 The phase diagram for the system Ga–GaP.

Solution

At 1273 K,

$$\Delta G^\circ_{1273\text{ K}} = -3.968\times10^4\text{ J} = -8.3144\times1273\ln K_{1273\text{ K}}$$

which gives

$$K_{1273\text{ K}} = 24.97 = \frac{a_{\text{GaP}}}{a_{\text{Ga}}p_{\text{P}_2}^{1/2}}$$

In the preceding expression, a_{Ga} is the activity of Ga in the liquidus melt with respect to liquid Ga as the standard state, and, since the liquidus melt is in equilibrium with pure solid GaP, the activity of GaP, a_{GaP}, is unity. The variation of the liquidus composition with temperature in the range 1173–1373 K can be expressed as

$$\ln X_{\mathrm{P}} = -\frac{16{,}550}{T} + 9.902$$

which gives the liquidus composition at 1273 K as $X_{\mathrm{P}} = 0.045$. In view of the low solubility of the solute P, it can be assumed that the solvent Ga obeys Raoult's law, in which case the activity of Ga in the liquidus melt is 0.955, and hence the partial pressure of P_2 exerted by the liquidus melt is

$$\begin{aligned} p_{\mathrm{P}_2} &= \left(\frac{1}{24.97\times 0.955}\right)^2 \\ &= 1.76\times 10^{-3} \text{ atm} \end{aligned}$$

Example 2: The Mg–Si System

The phase diagram for the system Mg–Si is shown in Figure 13.14. Determine the extent to which the phase diagram can be calculated, assuming that the liquid solutions exhibit regular solution behavior.

- Magnesium melts at 921 K and has a Gibbs free energy change on melting of $\Delta G^{\circ}_{m,\mathrm{Mg}} = 8790 - 9.54T$ J .

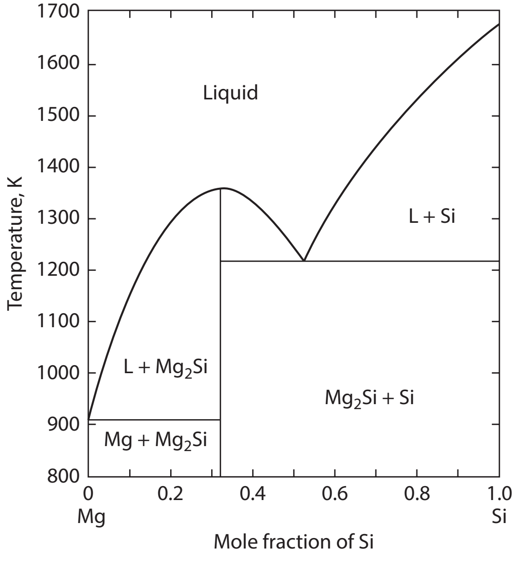

Figure 13.14 The phase diagram for the system Mg–Si.

- Silicon melts at 1688 K and has a Gibbs free energy change on melting of $\Delta G^{\circ}_{m,\mathrm{Si}} = 50{,}630 - 30.0T$ J.
- Mg_2Si melts at 1358 K and has a Gibbs free energy change on melting of $\Delta G^{\circ}_{m,\mathrm{Mg_2Si}} = 85{,}770 - 63.2T$ J.

The standard Gibbs free energy change for the reaction

$$2\mathrm{Mg}_{(l)} + \mathrm{Si}_{(s)} = \mathrm{Mg_2Si}_{(s)} \tag{i}$$

is

$$\Delta G^{\circ}_{(\mathrm{i})} = -100{,}400 + 39.3T \text{ J}$$

Solution

The Gibbs free energy diagram at 1358 K for the system, using liquid as the standard state for Mg and solid as the standard state for Si, is shown in Figure 13.15. $\Delta G^{\circ}_{(\mathrm{i})} = -47{,}030$ J at the melting temperature of Mg_2Si (1358 K), and thus, the Gibbs free energy of formation of $Mg_{2/3}Si_{1/3}$ = –47,030/3 = –15,676 J, and this is the length of the line *de* in Figure 13.15. Point *b* in Figure 13.15 represents the free energy of liquid Si relative to solid Si and lies 9890 J above the point *a*. Consequently, the length of the line *cd* is 9890/3 = 3297 J, and the length of the line *ce* is 3,297 + 15,676 = 18,973 J. Thus, the Gibbs free energy of formation of solid $Mg_{2/3}Si_{1/3}$ from liquid Mg and liquid Si is –18,919 J. However, at the melting temperature of 1358 K, $G^{\circ}_{\mathrm{Mg_2Si},(s)} = G^{\circ}_{\mathrm{Mg_2Si},(l)}$, and thus, the Gibbs free energy of formation of liquid $Mg_{2/3}Si_{1/3}$ from liquid Mg and liquid Si at 1358 K is also 973 J. Thus, the line representing the molar Gibbs free energy of formation of

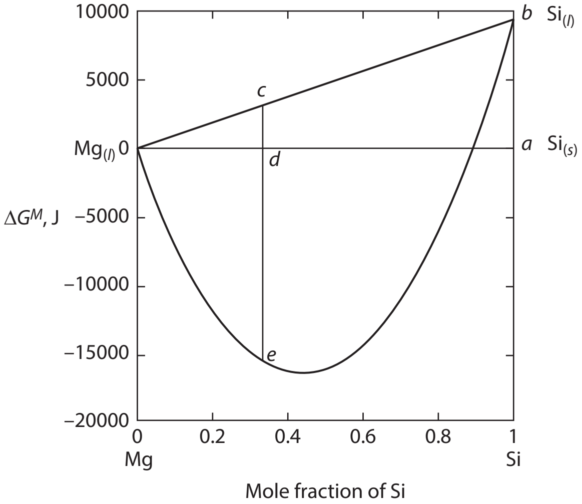

Figure 13.15 Molar Gibbs free energies of mixing in the system Mg–Si at 1358 K.

melts in the system at 1358 K passes through the point *e* and from the general expression for the formation of a regular solution

$$\Delta G^M = RT(X_{\text{Mg}}\ln X_{\text{Mg}} + X_{\text{Si}}\ln X_{\text{Si}}) + \alpha X_{\text{Mg}}X_{\text{Si}}$$

at $X_{\text{Si}} = ⅓$,

$$-18{,}973 = 8.3144 \times 1358\left(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3}\right) + \alpha\frac{1}{3}\cdot\frac{2}{3}$$

which gives $\alpha = -53{,}040$ J.

Combination of $\Delta G^\circ_{(\text{i})}$ and the Gibbs free energy change for the melting of Si gives

$$\Delta G^\circ_{(\text{ii})} = -151{,}030 + 69.3T \text{ J}$$

for the reaction

$$2\text{Mg}_{(l)} + \text{Si}_{(l)} = \text{Mg}_2\text{Si}_{(s)} \tag{ii}$$

Thus,

$$\begin{aligned}-151{,}030 + 69.3T &= -RT\ln K\\ &= -RT\ln\frac{a_{\text{Mg}_2\text{Si},(s)}}{a^2_{\text{Mg}}a_{\text{Si}}}\end{aligned}$$

Since liquids on the Mg_2Si liquidus line are saturated with Mg_2Si, $a_{\text{Mg}_2\text{Si},(s)} = 1$, the variations of the activities of Mg and Si with temperature along the Mg_2Si liquidus line are given by

$$-15{,}030 + 69.3T = 2RT\ln a_{\text{Mg}} + RT\ln a_{\text{Si}} \tag{iii}$$

In a regular solution,

$$RT\ln a_i = RT\ln X_i + \Omega(1 - X_i)^2$$

and thus, Equation (iii) becomes

$$\begin{aligned}-15{,}030 + 69.3T = 2RT\ln(1 - X_{\text{Si}}) - 2\times 53{,}040(1 - X_{\text{Si}})^2\\ +RT\ln X_{\text{Si}} - 53{,}040(1 - X_{\text{Si}})^2\end{aligned} \tag{iv}$$

Equation (iv), which is the equation of the Mg_2Si liquidus, is quadratic and gives two values of X_{Si} at each temperature, with one being the liquidus composition in the Mg–Mg_2Si sub-binary and the other being the liquidus composition in the Mg_2Si–Si sub-binary. Equation (iv) is drawn as the broken line *abc* in Figure 13.16.

The Si liquidus line is obtained from Equation 10.22 as

$$\Delta\bar{G}^M_{\text{Si}(l)} = -\Delta G^\circ_{m,\text{Si}}$$

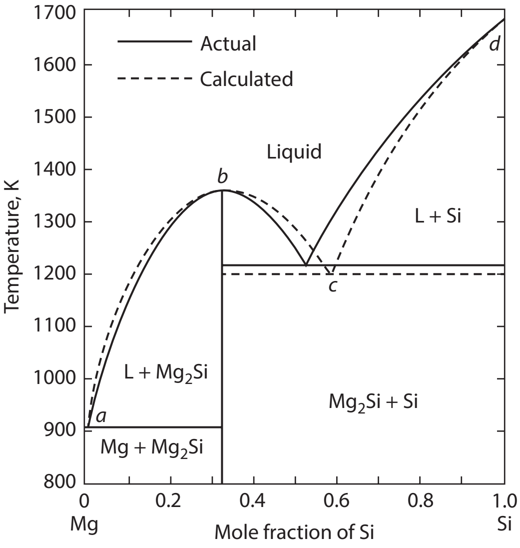

Figure 13.16 Comparison between the calculated and the actual phase diagram for the system Mg–Si.

That is,

$$RT\ln X_{\mathrm{Si}} + \alpha\left(1 - X_{\mathrm{Si}}\right)^2 = -50{,}630 + 30.0T$$

which gives

$$T = \frac{50{,}630 - 53{,}040(1 - X_{\mathrm{Si}})^2}{30.0 - 8.3144\ln X_{\mathrm{Si}}} \tag{v}$$

Equation (v) is drawn as the broken line *cd* in Figure 13.16.

Similarly, the Mg liquidus line is given by

$$RT\ln(1 - X_{\mathrm{Si}}) + \alpha X_{\mathrm{Si}}{}^2 = -8790 + 9.52T$$

which gives

$$T = \frac{8790 - 53{,}040X_{\mathrm{Si}}^2}{9.52 - 8.3144\ln(1 - X_{\mathrm{Si}})^2} \tag{vi}$$

The calculated diagram shows good agreement with the actual diagram; the calculated eutectic temperature and eutectic composition in the Mg_2Si–Si sub-binary are, respectively, 1200 K and $X_{\mathrm{Si}} = 0.58$, which are close to the actual values of 1218 K and $X_{\mathrm{Si}} = 0.53$, and the eutectic composition and temperature in the Mg–Mg_2Si sub-binary coincide with the actual values.

13.7 GRAPHICAL REPRESENTATION OF PHASE EQUILIBRIA

13.7.1 Phase Equilibria in the System Mg–Al–O

Consider the phase equilibria in the system Mg–Al–O at 1073 K. At 1073 K, liquid Mg and Al are completely miscible in one another, and MgO, Al_2O_3, and the *spinel*[*] $MgAl_2O_4$ occur as the products of oxidation of the metallic alloys. The stabilities of the oxides are determined by the activities of Al and Mg in the liquid metallic alloys and by the standard Gibbs free energies of formation of the oxides. For

$$2\mathrm{Al}_{(l)} + \frac{3}{2}\mathrm{O}_{2(g)} = \mathrm{Al_2O}_{3(s)} \tag{i}$$

$$\Delta G^{\circ}_{(\mathrm{i}),1073\ \mathrm{K}} = -1.323{,}000\ \mathrm{J} = -RT\ln\frac{a_{\mathrm{Al_2O_3}}}{a^2_{\mathrm{Al}}p^{3/2}_{\mathrm{O_2}}}$$

which gives

$$2\log a_{\mathrm{Al}} + 1.5\log p_{\mathrm{O_2}} - \log a_{\mathrm{Al_2O_3}} = -64.39 \tag{ia}$$

For

$$\mathrm{Mg}_{(l)} + \frac{1}{2}\mathrm{O}_{2(g)} = \mathrm{MgO}_{(s)} \tag{ii}$$

$$\Delta G^{\circ}_{(\mathrm{ii}),1073\ \mathrm{K}} = -\,484{,}300\ \mathrm{J} = -RT\ln\frac{a_{\mathrm{MgO}}}{a_{\mathrm{Mg}}p^{1/2}_{\mathrm{O_2}}}$$

which gives

$$\log p_{\mathrm{O_2}} = -2\log a_{\mathrm{Mg}} + \log a_{\mathrm{MgO}} - 47.14 \tag{iia}$$

For

$$\mathrm{Mg}_{(l)} + 2\mathrm{Al}_{(l)} + 2\mathrm{O}_{2(g)} = \mathrm{MgAl_2O}_{4(s)} \tag{iii}$$

$$\Delta G^{\circ}_{(\mathrm{iii}),1073\ \mathrm{K}} = -1{,}854{,}000\ \mathrm{J} = -RT\ln\frac{a_{\mathrm{MgAl_2O_4}}}{a_{\mathrm{Mg}}a^2_{\mathrm{Al}}p^2_{\mathrm{O_2}}}$$

which gives

$$\log p_{\mathrm{O_2}} = \frac{1}{2}\log a_{\mathrm{Mg}} - \log a_{\mathrm{Al}} + \log a_{\mathrm{MgAl_2O_4}} - 90.24 \tag{iiia}$$

Combination of the reactions given by Equations (i), (ii), and (iii) gives

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[*] A spinel is a cubic oxide with the general formula AB_2O_4, where A is a divalent and B is a trivalent ion.

$$MgO_{(s)} + Al_2O_{3(s)} = MgAl_2O_{4(s)} \tag{iv}$$

for which

$$\Delta G^\circ_{(\text{iv}),1073\text{ K}} = -46{,}700\text{ J} = -RT\ln\frac{a_{MgAl_2O_4}}{a_{MgO}a_{Al_2O_3}}$$

or

$$\log a_{MgO} + \log a_{Al_2O_3} - \log a_{MgAl_2O_4} = -2.273 \tag{iva}$$

The Gibbs free energy of mixing diagram for the system MgO–Al_2O_3 is shown in Figure 13.17. From $\Delta G^\circ_{(\text{iv}),1073\text{ K}}$, the Gibbs free energy of formation of $(MgO)_{1/2}(Al_2O_3)_{1/2}$ is –23,350 J, and the existence of $MgAl_2O_4$ as a stable phase requires that the activities of both MgO and Al_2O_3 have values between log a = –2.273 and log a = 0, the values of which are determined by Equation (iva). From Equation (iv*a*) and Figure 13.17, the logarithm of the activity of Al_2O_3 in $MgAl_2O_4$ (at $a_{MgAl_2O_4} = 1$) which is saturated with MgO (at a_{MgO} = 1) is –2.273, and, from symmetry, the logarithm of the activity of MgO in $MgAl_2O_4$ (at $a_{MgAl_2O_4} = 1$) which is saturated with Al_2O_3 (at $a_{Al_2O_3} = 1$) is –2.273. Thus, if the activity of either MgO or Al_2O_3 in the system is less than antilog (–2.273), the spinel of $MgAl_2O_4$ is not stable.

The measured activities of Mg and Al at 1073 K in the system Mg–Al have been fitted by the equations*

$$\log a_{Mg} = \log X_{Mg} - 0.68\left(1 - X_{Mg}\right)^3$$

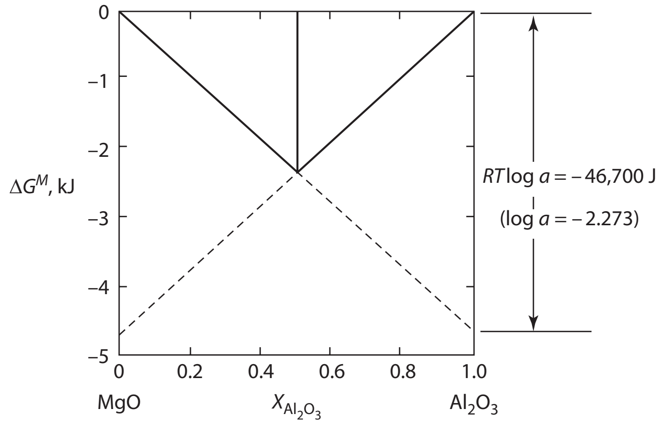

Figure 13.17 Molar Gibbs free energies of mixing in the system MgO–Al_2O_3 at 1073 K.

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* G. R. Belton and Y. K. Rao, "A Galvanic Study of Activities in Mg–Al Liquid Alloys," *Trans. Met. Soc.* (1969), vol. 245, p. 2189.

and

$$\log a_{\mathrm{Al}} = \log(1 - X_{\mathrm{Mg}}) - 1.02X_{\mathrm{Mg}}^2 + 0.68X_{\mathrm{Mg}}^3$$

The phase stability diagram for the system at 1073 K, using p_{O_2} and log a_{Mg} as coordinates, is shown in Figure 13.18a (the fixing of the activities of O_2 and Mg in the ternary system Mg–Al–O at constant temperature fixes the activity of Al). From Equation (iia), equilibrium between pure liquid Mg and MgO occurs at $\log p_{\mathrm{O}_2} = -47.17$, which is shown as the point *a* in Figure 13.18a. The three-phase equilibrium involving the Mg–Al melt, MgO, and the gas phase is determined by Equation (iia) and is shown as the line *ab* in Figure 13.18a. The addition of Al to the liquid alloy decreases a_{Mg} and hence increases the value of the pressure of oxygen required to maintain $a_{\mathrm{MgO}} = 1$. Also, in moving along *ab* from *a* toward *b*, the activity of $a_{\mathrm{Al_2O_3}}$, given by Equation (i), increases, and at the point *b*, it reaches the value of antilog (–2.273), which with $a_{\mathrm{MgO}} = 1$ makes $a_{\mathrm{MgAl_2O_4}} = 1$. Thus, the four-phase equilibrium melt–MgO–$\mathrm{MgAl_2O_4}$–gas occurs at the point *b*. The three-phase equilibrium involving the Mg–Al melt, $\mathrm{MgAl_2O_4}$, and the gas phase, determined by Equation (iiia), occurs along the line *bd*. In moving along the line from *b* to *d*, the dilution of Mg in the melt causes a_{MgO} to decrease from unity at *b* and $a_{\mathrm{Al_2O_3}}$ to increase, and at the point *d*, $a_{\mathrm{Al_2O_3}} = 1$ and $\log a_{\mathrm{MgO}} = -2.273$. Thus, *d* represents the four-phase equilibrium melt–$\mathrm{Al_2O_3}$–$\mathrm{MgAl_2O_4}$–gas. At activities of Mg less than that at *d*, the activity of MgO is less than antilog (–2.273), and thus, the spinel $\mathrm{MgAl_2O_4}$ is not stable. The line *ed* represents the equilibrium involving a melt, $\mathrm{Al_2O_3}$, and a

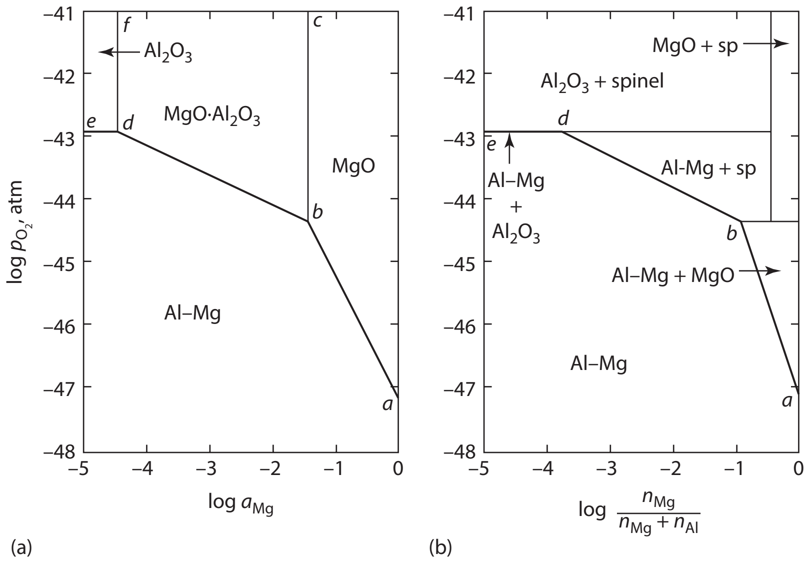


Figure 13.18 (a) The phase stability diagram for the system Al–Mg–O at 1073 K. (b) The phase diagram for the system Al–Mg–O at 1073 K.

gas phase, given by Equation (ia). However, as $a_{\mathrm{Mg}} = 5.75 \times 10^{-5}$ at the point *d*, a_{Al} is virtually unity, and thus, the line *ed* is virtually horizontal at $\log p_{\mathrm{O}_2}$ (obtained from Equation [ia]) = –42.93. The lines *df* and *bc* represent, respectively, the three-phase equilibria Al_2O_3–$MgAl_2O_4$–gas and $MgAl_2O_4$–MgO–gas. The lines in Figure 13.18a identify the fields of stability of Al–Mg liquid alloys, MgO, $MgAl_2O_4$, and Al_2O_3 at 1073 K.

The activity–composition relationships given by Equations (v) and (vi) allow the phase stability diagram presented as Figure 13.18a to be converted to the phase diagram shown in Figure 13.18b, in which $\log p_{\mathrm{O}_2}$ and $\log n_{\mathrm{Mg}}/(n_{\mathrm{Mg}} + \mathrm{n}_{\mathrm{Al}})$ (where n_{Mg} and n_{Al} are, respectively, the numbers of moles of Mg and Al in the system) are used as coordinates. The line *ab* gives the compositions of the metallic melts saturated with MgO, the line *bd* gives the compositions of the melts saturated with $MgAl_2O_4$, and the line *ed* gives the compositions of the melts saturated with Al_2O_3.

Consider the sequence of oxidation of Al–Mg alloys of $X_{\mathrm{Mg}} = 0.333$, 0.2, and 0.01 at 1073 K. With $X_{\mathrm{Mg}} = 0.333$ and $\log p_{\mathrm{O}_2} = -48$, the system exists at the state *a* in Figure 13.19. When the oxygen pressure is increased to $\log p_{\mathrm{O}_2} = -45.6$, the system exists at *b*, in which state the alloy is in equilibrium with MgO. Further increase in the oxygen pressure causes the precipitation of MgO from the melt, which decreases

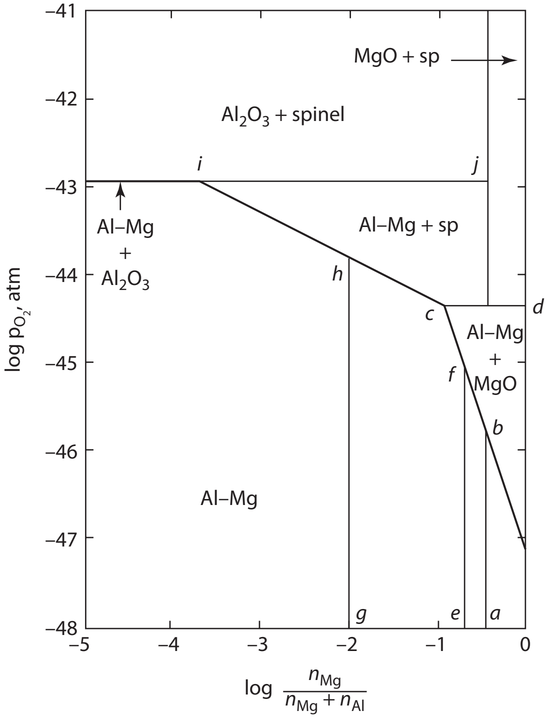


Figure 13.19 The influence of composition and oxygen pressure on the equilibrium states of existence in the system Mg–Al–O.

the mole fraction of X_{Mg} in the melt and causes its composition to move along the MgO saturation line from *b* toward *c*. At $\log p_{\mathrm{O}_2} = -44.3$, the melt of composition *c* is saturated with MgO, and further increase in the oxygen pressure causes all of the melt of composition *c* to react with all of the MgO at *d* to form the spinel $\mathrm{MgAl_2O_4}$. A melt of $X_{\mathrm{Mg}} = 0.2$ equilibrated with oxygen at $\log p_{\mathrm{O}_2} = -48$ exists at the state *e* in Figure 13.19, and increasing the oxygen pressure to $\log p_{\mathrm{O}_2} = -45.1$ brings the alloy into equilibrium with MgO at the state *f*. Further increase in the oxygen pressure to $\log p_{\mathrm{O}_2} = -44.3$ causes MgO to precipitate and moves the composition of the melt along the MgO saturation line from *f* to *c*. Further increase in the oxygen pressure causes all of the MgO to react with some of the melt to produce $\mathrm{MgAl_2O_4}$ and a melt saturated with $\mathrm{MgAl_2O_4}$. With further oxidation, $\mathrm{MgAl_2O_4}$ is precipitated from the melt, and the composition of the melt is moved along the $\mathrm{MgAl_2O_4}$ saturation line from *c* toward *i*. Although the precipitation of the spinel from the melt removes Al and Mg atoms from the melt in the ratio Al/Mg = 2, the values of X_{Mg} in the melts are low enough that the removal of Al atoms makes a negligible change in X_{Al} but causes a significant decrease in X_{Mg}. At $\log p_{\mathrm{O}_2} = -43.8$, the melt at the state *i* is doubly saturated with $\mathrm{Al_2O_3}$ and $\mathrm{MgAl_2O_4}$, and further increase in the oxygen pressure causes the disappearance of the melt. Increasing the oxygen pressure exerted on a melt of $X_{\mathrm{Mg}} = 0.01$ causes saturation of the melt with $\mathrm{MgAl_2O_4}$ at $\log p_{\mathrm{O}_2} = -43.8$ (the state *h*), and further increase in the oxygen pressure causes oxidation to proceed as described previously.

13.7.2 Phase Equilibria in the System Al–C–O–N Saturated with Carbon

We now consider phase stability in the system Al–C–O–N, saturated with carbon at 2000 K, and will identify the conditions under which AlN can be contained in a graphite crucible at 2000 K without the formation of $\mathrm{Al_4C_3}$. The solid phases which occur in the quaternary system are AlN, $\mathrm{Al_4C_3}$, $\mathrm{Al_4O_4C}$, and $\mathrm{Al_2O_3}$, and since the system is saturated with graphite, the minimum number of phases which can coexist in equilibrium with one another is three (graphite, a gas phase, and a second condensed phase). The number of degrees of freedom available to this three-phase equilibrium is

$$\mathcal{F} = C + 2 - \Phi = 4 + 2 - 3 = 3$$

which can be selected as T, p_{O_2}, and p_{N_2}. An isothermal phase stability diagram can thus be constructed using $\log p_{\mathrm{N}_2}$, and $\log p_{\mathrm{O}_2}$ as coordinates. For

$$\begin{aligned} &4\mathrm{Al}_{(l)} + 3\mathrm{C}_{(s)} = \mathrm{Al_4C}_{3(s)} \\ &\Delta G^\circ_{(\mathrm{i}),2000\ \mathrm{K}} = -74{,}060\ \mathrm{J} \end{aligned} \tag{i}$$

and thus, an equilibrium involving pure liquid Al, graphite, and solid $\mathrm{Al_4C_3}$ does not exist at 2000 K. The activity of Al in carbon-saturated $\mathrm{Al_4C_3}$ is obtained from

$$K_{(\mathrm{i}),2000\ \mathrm{K}} = \exp\left(\frac{74{,}060}{8.3144 \times 2000}\right) = 85.95 = \frac{a_{\mathrm{Al_4C_3}}}{a_{\mathrm{Al}}^4 a_{\mathrm{C}}^3} = \frac{1}{a_{\mathrm{Al}}^4}$$

which gives $a_{Al} = 0.327$, relative to pure liquid Al.

For

$$\begin{aligned} 4AlN_{(s)} + 3C_{(s)} &= Al_4C_{3(s)} + 2N_{2(g)} \\ \Delta G^{\circ}_{(ii),2000\text{ K}} &= 917{,}900\text{ J} = -2\times 8.3144\times 2000\times 2.303\log p_{N_2} \end{aligned} \qquad \text{(ii)}$$

which gives $\log p_{N_2} = -11.98$ for the equilibrium involving solid graphite, solid AlN, solid Al_4C_3, and a gas phase. The line representing this equilibrium is drawn as *ab* in Figure 13.20a. Graphite and AlN are stable relative to graphite and Al_4C_3 in

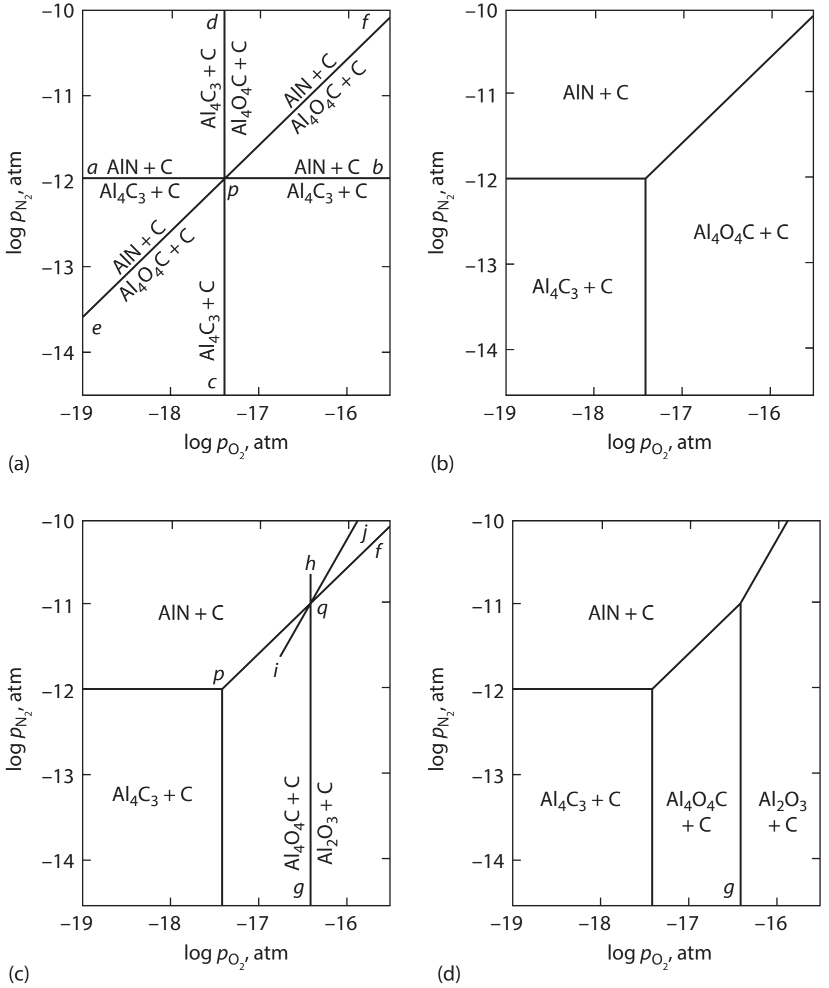


Figure 13.20 Construction of the phase stability diagram for the system Al–C–O–N saturated with carbon at 2000 K.

states above the line, and graphite and Al_4C_3 are stable relative to graphite and AlN in states below the line.

For

$$\begin{gathered} Al_4O_4C_{(s)} + 2C_{(s)} = Al_4C_{3(s)} + 2O_{2(g)} \\ \Delta G^{\circ}_{(iii),2000\text{ K}} = 1{,}333{,}000\text{ J} = -2\times 8.3144\times 2000\times 2.303\log p_{O_2} \end{gathered} \tag{iii}$$

which gives $\log p_{O_2} = -17.40$ for the equilibrium involving solid graphite, solid Al_4C_3, solid Al_4O_4C, and a gas phase. This is drawn as line *cd* in Figure 13.20a. To the left of this line, graphite and Al_4C_3 are stable relative to graphite and Al_4O_4C, and to the right of the line, the reverse is the case.

For

$$\begin{gathered} 4Al_{(l)} + 2O_{2(g)} + C_{(s)} = Al_4O_4C_{(s)} \\ \Delta G^{\circ}_{(iv),2000\text{ K}} = -1{,}407{,}000\text{ J} \end{gathered} \tag{iv}$$

and thus, for carbon-saturated Al_4O_4C,

$$K_{(iv),2000\text{ K}} = \exp\left(\frac{1{,}407{,}000}{8.3144\times 2000}\right) = 5.58\times 10^{36} = \frac{1}{a_{Al}^4 p_{O_2}^2}$$

which, with $\log p_{O_2} = -17.40$, gives $a_{Al} = 0.327$. Thus, the activity of Al in C-saturated Al_4O_4C has the same value as that in C-saturated AlN. The point of intersection of lines *ab* and *cd* is the state in which the five-phase equilibrium involving four solid phases and a gas phase occurs.

For

$$\begin{gathered} Al_4O_4C_{(s)} + 2N_{2(g)} = C_{(s)} + 2O_{2(g)} + 4AlN_{(s)} \\ \Delta G^{\circ}_{(v),2000\text{ K}} = 415{,}000\text{ J} = -2\times 8.3144\times 2000\times 2.303\log\frac{p_{O_2}}{p_{N_2}} \end{gathered} \tag{v}$$

which gives

$$\log p_{N_2} = \log p_{O_2} + 5.42$$

for the equilibrium among graphite, solid AlN, solid Al_4O_4C, and a gas phase. This is drawn as line *ef* in Figure 13.20a. Carbon-saturated AlN is stable relative to carbon-saturated Al_4O_4C above the line, with the reverse being the case below the line. Inspection of Figure 13.20a shows the following:

1. In the area below *ap* and to the left of *pc*, Al_4C_3 is stable with respect to AlN and Al_4O_4C.
2. In the area above *ap* and above *pf*, AlN is stable with respect to Al_4C_3 and Al_4O_4C.
3. In the area below *pf* and to the right of *pc*, Al_4O_4C is stable with respect to AlN and Al_4C_3.

Thus, without consideration of the stability of Al_2O_3, the fields of stability of AlN, Al_4C_3, and Al_4O_4C are as shown in Figure 13.20b.

For

$$\begin{aligned} 2Al_2O_{3(s)} + C_{(s)} &= O_{2(g)} + Al_4O_4C_{(s)} \\ \Delta G^\circ_{(vi),2000\ K} &= 630{,}800\ J = -8.3144 \times 8.3144 \times 2000 \times 2.303 \log p_{O_2} \end{aligned} \qquad \text{(vi)}$$

which gives $\log p_{O_2} = -16.47$ for the equilibrium among graphite Al_4O_4C, Al_2O_3, and a gas phase. This is drawn as the line *gh* in Figure 13.20c, and its point of intersection with *pf* is the state of the five-phase equilibrium among graphite, AlN, Al_4O_4C, Al_2O_3, and a gas phase.

For

$$\begin{aligned} Al_2O_{3(s)} + N_{2(s)} &= 2AlN_{(s)} + 1.5O_{2(g)} \\ \Delta G^\circ_{(vii),2000\ K} &= 522{,}900\ J = -8.3144 \times 2000 \times 2.303 \log \frac{p_{O_2}^{1.5}}{p_{N_2}} \end{aligned} \qquad \text{(vii)}$$

which gives

$$\log p_{N_2} = 1.5 \log p_{O_2} + 13.65$$

for the equilibrium given by Equation (vii). This line, which is independent of the activity of C in the system, is drawn as *ij* in Figure 13.20c. Since the line *pq* represents a stable equilibrium, the other two lines radiating from the point *q* which represent stable equilibria are *qg* and *gj*, and the full phase stability diagram is as shown in Figure 13.20d. The diagram shows that AlN can be heated in a graphite crucible without forming Al_4C_3 if the pressures of oxygen and nitrogen are such that the thermodynamic state lies in the field of stability of AlN.

13.8 THE FORMATION OF OXIDE PHASES OF VARIABLE COMPOSITION

Figure 13.21 shows the variation, with composition at a temperature *T*, of the molar Gibbs free energy of mixing for the metal M–oxygen system in which measurable solubility of oxygen in metallic M occurs and the oxides MO and M_3O_4 have variable compositions. Compounds with nonstoichiometric compositions are sometimes called *berthollides*, after Claude Louis Berthollet (1748–1822). Starting with pure M, increasing the pressure of oxygen causes the molar Gibbs free energy of mixing to move from *f* along the line *fi* until, at $p_{O_2} = p_{O_2(M/MO)}$, the metal is saturated with oxygen and the metal-saturated MO phase of composition M_bO_a appears. If the pure metal M and oxygen gas at 1 atm pressure at the temperature *T* are chosen as the standard states, then

$$\begin{aligned} \Delta G_{(\text{metal/saturated MO})} &= jk = RT(b \ln a_M + a \ln p_{O_2}^{1/2}) \\ &= RT \ln a_M^b p_{O_2}^{1/2a} \end{aligned}$$

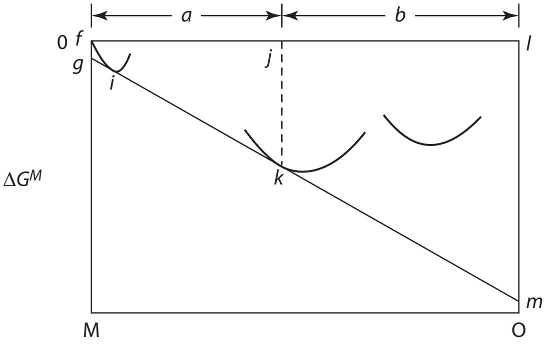


Figure 13.21 The Gibbs free energies of mixing of the system M–O which forms oxide phases of variable composition and which shows a significant solubility of oxygen in metallic M.

From Figure 13.21, $fg = RT \ln a_M$ and $lm = RT \ln p_{O_2(M/MO)}$.

We can also write for the reaction

$$bM_{(s)} + \frac{1}{2}aO_{2(g)} = M_bO_{a(s)}$$

$$\Delta G^\circ = jk = RT \ln\left(\frac{a_M^b p_{O_2}^{1/2a}}{a_{M_bO_a}}\right)$$

which, if the metal-saturated oxide is chosen as the standard state, is identical with the preceding expression. It is convenient to write the reaction of the oxidation such that an integer number of gram-atoms of oxygen are consumed. For example, for the consumption of 1 gram-atom of oxygen,

$$yM + \frac{1}{2}O_2 = M_yO, \qquad \text{where } y = \frac{b}{a}$$

$$\Delta G^\circ = RT \ln\left(\frac{a_M^y p_{O_2}^{1/2}}{a_{M_yO}}\right)$$

or, for the consumption of 1 gram-mole of oxygen (2 gram-atoms),

$$\Delta G^\circ = RT \ln\left(\frac{a_M^{2y} p_{O_2}}{a_{M_yO}^2}\right)$$

If the solubility of oxygen in the metal is virtually zero, then *fg* in Figure 13.21 shrinks to a point, and Figure 13.21 is redrawn as Figure 13.22. In this case, choosing

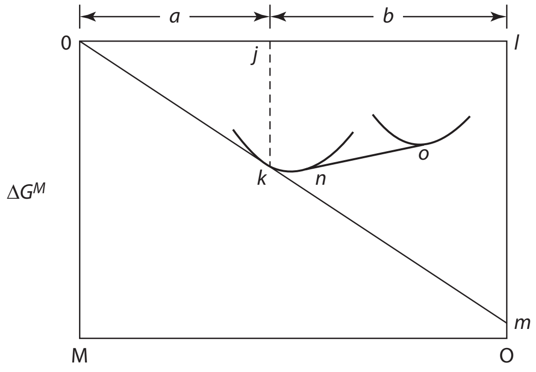


Figure 13.22 The Gibbs free energies of mixing of the system M–O which forms oxide phases of variable composition and which shows a negligible solubility of oxygen in metallic M.

pure M, oxygen gas at 1 atm pressure and the temperature T, and the oxide of composition MyO as the standard states gives, for the oxidation,

$$yM + \frac{1}{2}O_2 = M_yO$$
$$\Delta G^\circ = RT \ln p^{1/2}_{O_2(M/MO)}$$

where $p_{O_2(M/MO)}$ is the pressure of oxygen required for equilibrium between the metal M and the metal-saturated oxide MO, given by $lm = RT\ln p_{O_2(M/MO)}$.

If the oxygen pressure is increased to a value greater than $p_{O_2(M/MO)}$, the metal phase disappears, the oxygen content of the MO phase increases, the molar Gibbs free energy of mixing of the system moves along the line kn, and the activities of M and MO vary accordingly. In a classic investigation, Darken and Gurry* determined the phase relationships occurring in the system Fe–O by varying the oxygen pressure and temperature and observing the consequential changes in phase and phase composition. Their diagram, drawn for the components FeO and Fe_2O_3, is shown in Figure 13.23. Consider the wustite ("FeO")† phase field which, at 1100°C, extends from the composition m to the composition n. The variation of a_{Fe} in the wustite phase can be calculated from the experimentally determined variation of the composition of wustite with oxygen pressure using the Gibbs–Duhem equation:

$$X_{Fe}d\ln a_{Fe} + X_O d\ln a_O = 0$$

---

[*] L. S. Darken and R. W. Gurry, "The System Iron–Oxygen, I: The Wustite Field and Related Equilibria," *J. Am. Chem. Soc.* (1945), vol. 67, p. 1398; "The System Iron–Oxygen, II: Equilibria and Thermodynamics of Liquid Oxide and Other Phases," *J. Am. Chem. Soc.* (1946), vol. 68, p. 798.

[†] Quotation marks are used for wustite since the its composition is only approximately equiatomic.

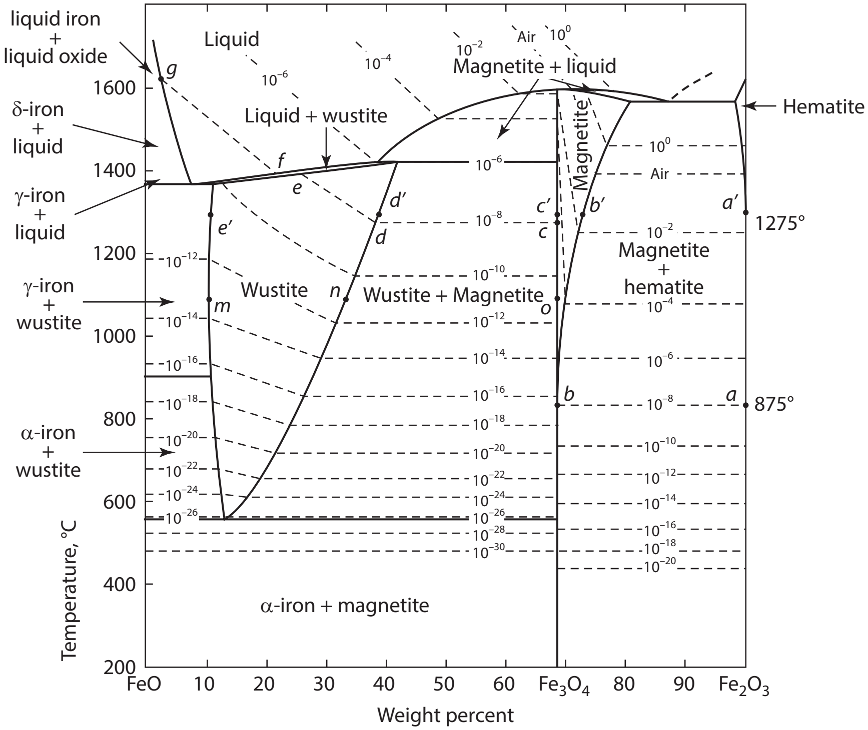


Figure 13.23 The phase diagram for the system FeO–Fe_2O_3 showing the positions of the oxygen (atm) isobars.

That is,

$$\log a_{\text{Fe}} = -\int \frac{X_{\text{O}}}{X_{\text{Fe}}}\, d\log a_{\text{O}} = -\int \frac{X_{\text{O}}}{X_{\text{Fe}}}\, d\log p_{\text{O}_2}^{1/2}$$

where the upper limit of integration is the oxygen pressure in equilibrium with the wustite composition of interest, and the lower limit is $p_{O_2(\text{Fe/"FeO"})}$ (the oxygen pressure at which wustite of composition m is in equilibrium with oxygen-saturated metallic iron), at which composition $a_{\text{Fe}} = 1$. Having thus determined the variations of a_{Fe} with composition, the corresponding variations of $a_{\text{"FeO"}}$ are determined as follows. If the standard state for oxygen gas is selected as being $p_{\text{O}_2(\text{Fe/"FeO"})}$ at the temperature of interest, then for

$$y\text{Fe}_{(s)} + \frac{1}{2}\text{O}_{2(g,\ \text{at}\ p_{O_2(\text{Fe/"FeO"})})} = \text{Fe}_y\text{O}_{(s)}$$

as the standard states are in equilibrium with one another, $\Delta G^{\circ} = 0$, and thus, $K = 1$,

$$a_{\text{"FeO"}} = a_{\text{Fe}} a_{\text{O}} \qquad \text{where } a_{\text{O}} = \left(\frac{p_{\text{O}_2}}{p_{\text{O}_2\,(\text{Fe}/\text{"FeO"})}} \right)^{1/2}$$

or

$$\begin{aligned} \log a_{\text{"FeO"}} &= \log a_{\text{Fe}} + \log a_{\text{O}} \\ &= -\int \frac{X_{\text{O}}}{X_{\text{Fe}}} d\log a_{\text{O}} + \int d\log a_{\text{O}} \\ &= -\int \left(\frac{X_{\text{O}}}{X_{\text{Fe}}} - 1 \right) d\log p_{\text{O}_2}^{1/2} \end{aligned}$$

in which the integration limits are the same as before.

The variations of a_{Fe}, $a_{\text{"FeO"}}$, and a_{O} across the wustite field at 1100°, 1200°, and 1300°C are shown in Figure 13.24, and from these variations, the molar Gibbs free energy curve for wustite, *kn* in Figure 13.22, can be determined. For a fixed

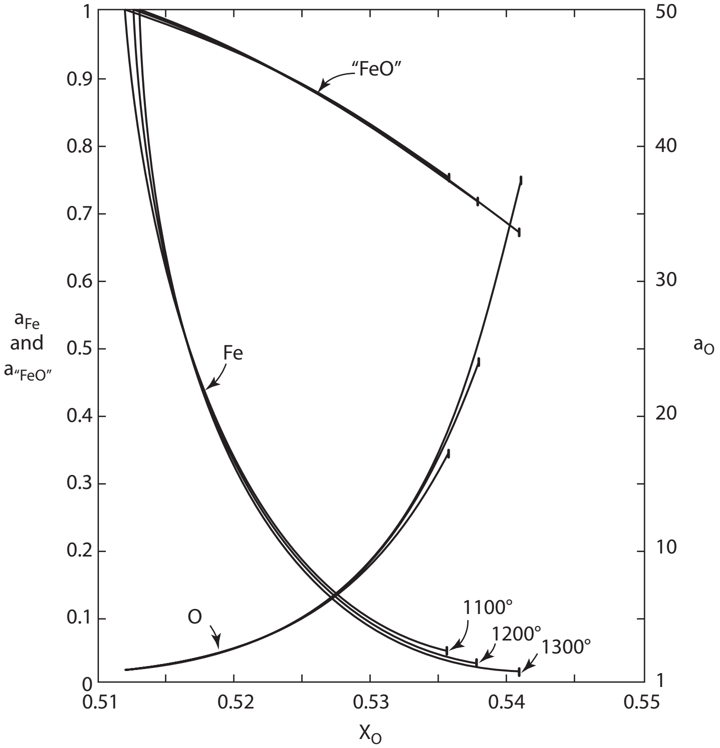


Figure 13.24 The activities of iron, oxygen, and iron-saturated wustite in the wustite phase field at several temperatures.

composition, the partial molar heats of solution of metal and oxygen in the wustite can be obtained from the Gibbs–Helmholtz relationship as

$$\Delta\overline{H}_{\mathrm{O}}^{M} = R\frac{\partial \ln p_{\mathrm{O}_2}^{1/2}}{\partial(1/T)}$$

and

$$\Delta\overline{H}_{\mathrm{Fe}}^{M} = R\frac{\partial \ln a_{\mathrm{Fe}}}{\partial(1/T)}$$

The variations of $\Delta\overline{H}_{\mathrm{O}}^{M}$ and $\Delta\overline{H}_{\mathrm{Fe}}^{M}$ with composition are shown in Figure 13.25. In Figure 13.24, at the composition of wustite $X_{\mathrm{O}} = 0.5125$, the activity of Fe is independent of temperature, and thus, as shown in Figure 13.25, the partial molar heat of mixing of Fe at this composition is zero.

At the temperature T, the limit of increase of p_{O_2} above homogeneous stable wustite is $p_{\mathrm{O}_2(\text{"FeO"}/\mathrm{Fe_3O_4})}$, the oxygen pressure at which wustite of composition n is in equilibrium with magnetite ($\mathrm{Fe_3O_4}$) of composition o (Figure 13.23), and, if these compositions are chosen as the standard states, then for

$$3\,\text{"FeO"}_{(\text{saturated with oxygen})} + \frac{1}{2}\mathrm{O}_{2(g)} = \mathrm{FeO_3O}_{4(\text{saturated with Fe})}$$

$$\Delta G^{\circ} = RT\ln p_{\mathrm{O}_2(\text{"FeO"}/\mathrm{Fe_3O_4})}^{1/2}$$

Figure 13.23 shows that the composition of wustite in equilibrium with magnetite varies significantly with temperature. Thus, the heat of formation of magnetite from wustite cannot be calculated by application of the Gibbs–Helmholtz equation to the

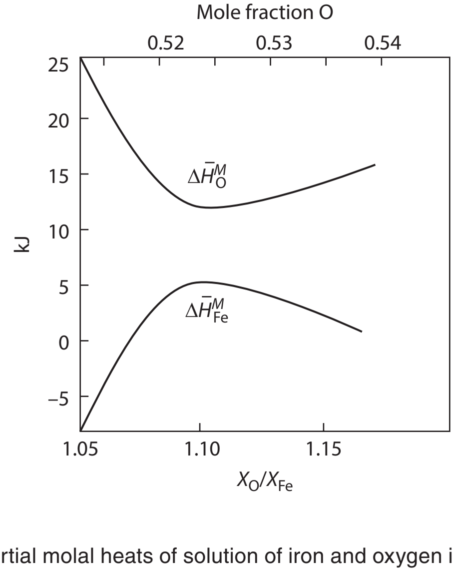


Figure 13.25 The partial molal heats of solution of iron and oxygen in wustite.

variation of $p_{O_2(\text{"FeO"}/Fe_3O_4)}$ with temperature (the Gibbs–Helmholtz partial differential is for constant total pressure and constant composition). However, since the composition of magnetite in equilibrium with wustite is independent of temperature, the change in enthalpy for the reaction

$$3Fe_{(s)} + 2O_{2(g)} = Fe_3O_{4(\text{saturated with Fe})}$$

can be obtained using the Gibbs–Helmholtz relationship; that is,

$$K = \frac{1}{a_{Fe}^3 p_{O_2}^2}$$

and thus,

$$\Delta H^\circ = -R\frac{d\ln K}{d(1/T)} = R\left[3\frac{d\ln a_{Fe}}{d(1/T)} + 2\frac{d\ln p_{O_2}}{d(1/T)}\right]$$

In this expression, a_{Fe} and p_{O_2} are the respective values for equilibrium between wustite and magnetite obtained from the data in Figure 13.24.

Below 550°C, homogeneous wustite is metastable with respect to iron and magnetite. This situation corresponds to Figure 13.11b in that, below 550°C (T_2 in Figure 13.11; see also Figure 13.8), the common tangent drawn from pure Fe (B in Figure 13.11) to the curve for the Gibbs free energy of magnetite lies below the curve for wustite. At 550°C, this common tangent becomes a "triple" common tangent and the two-component, four-phase equilibrium is invariant (Figure 13.11a).

The phase diagram at 1 atm total pressure shown in Figure 13.23 has, superimposed on it, oxygen isobars which trace the loci of variation of equilibrium composition with temperature under a fixed oxygen pressure in the system. For example, consider a small quantity of hematite (Fe_2O_3) at room temperature held in a gas reservoir of $p_{O_2} = 10^{-8}$ atm, the volume of which is sufficiently large that any oxygen gas produced by the reduction of the oxide has an insignificant effect on the pressure of oxygen in the gas reservoir. Let the oxide be heated slowly enough that equilibrium with the gas phase is maintained. From Figure 13.23, it is seen that the oxide remains as homogeneous hematite until 875°C is reached, at which temperature 10^{-8} atm is the invariant partial pressure of oxygen required for the equilibrium

$$2Fe_3O_4 + \frac{1}{2}O_2 = 3Fe_2O_3$$

At 875°C, magnetite of composition *b* is in equilibrium with hematite of composition *a*, and any increase in temperature upsets the equilibrium toward the magnetite side, with the consequent disappearance of the hematite phase. Further increase in temperature moves the composition of the oxide along the 10^{-8} atm isobar in the magnetite phase field until 1275°C is reached, at which temperature 10^{-8} atm is the invariant partial pressure of oxygen required for the equilibrium

$$3\text{"FeO"}+\frac{1}{2}O_2=Fe_2O_4$$

At 1275°C wustite of composition d is in equilibrium with magnetite of composition c. Further increase in temperature causes the disappearance of the magnetite phase, and the composition of the solid homogeneous wustite moves along the 10^{-8} atm oxygen isobar until the solidus temperature of 1400°C is reached, in which state solid wustite of composition e melts to form a liquid oxide of composition f at $p_{O_2}=10^{-8}$ atm. Continued increase in temperature moves the composition of the liquid oxide along the 10^{-8} atm isobar to saturation with iron at the temperature 1635°C, where the liquid oxide has the composition g, and oxygen-saturated liquid iron appears. In this state, the equilibrium

$$Fe_{(l)}+\frac{1}{2}O_{2(g)}=\text{"FeO"}_{(l)}$$

is established. An increase in temperature beyond 1635°C causes the disappearance of the liquid oxide phase and a decrease in the dissolved oxygen content of the liquid iron.

Similarly, isothermal reduction of hematite is achieved by decreasing the partial pressure of oxygen in the system. For example, from Figure 13.23, at 1300°C, hematite is the stable phase until the partial pressure of oxygen has been decreased to 1.34×10^{-2} atm, in which state magnetite of composition b' is in equilibrium with hematite of composition a'. Magnetite is then stable until the partial pressure of oxygen has been decreased to 2.15×10^{-8} atm, where wustite of composition d' is in equilibrium with magnetite of composition c'. Wustite is then stable until the partial pressure of oxygen has been decreased to 1.95×10^{-11} atm, where solid iron appears in equilibrium with wustite of composition e'. Further decrease in the pressure of oxygen causes the disappearance of the oxide phase. Figure 13.26 shows the phase relationships in a plot of $\log p_{O_2}$ versus temperature T, and the paths a–g and a'–e' correspond to those in Figure 13.23. In that Figure 13.26 does not contain the compositions of the coexisting oxide phases, it is less useful than the normal composition–temperature phase diagram containing oxygen isobars. Figure 13.27 shows the phase equilibria on a plot of $1/T$ versus $\log p_{O_2}$. This plot can be converted to an Ellingham diagram, as shown in Figure 13.28. In this diagram, the paths a–g and a'–e' correspond to those in Figure 13.23. Except for the Fe_3O_4–Fe_2O_3 line in Figure 13.28, the lines are drawn for oxidation reactions involving the consumption of 1 mole of oxygen—that is, of the type

$$Fe_xO_y+O_2=Fe_xO_{(2+y)}$$

in which the lower oxide of composition Fe_xO_y is in equilibrium with the higher oxide of composition $Fe_xO_{(2+y)}$. The Fe_3O_4–Fe_2O_3 line is hypothetical and applies to the stoichiometric compounds (stoichiometric Fe_3O_4 contains Fe at a higher activity

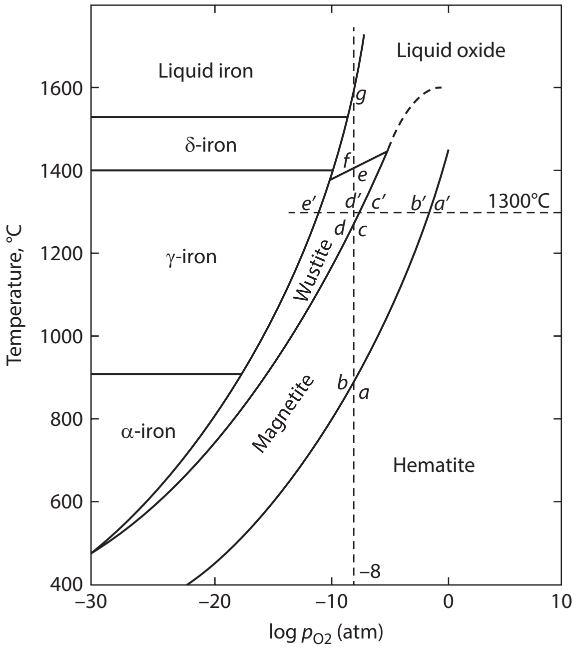


Figure 13.26 Phase stability in the system Fe–Fe_2O_3 as a function of temperature and $\log p_{O_2}$.

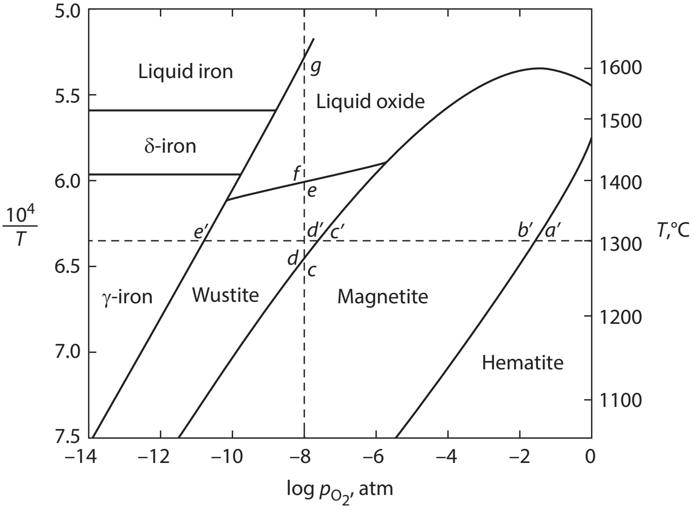


Figure 13.27 Phase stability in the system Fe–Fe_2O_3 as a function of log p_{O_2} and 1/*T*.

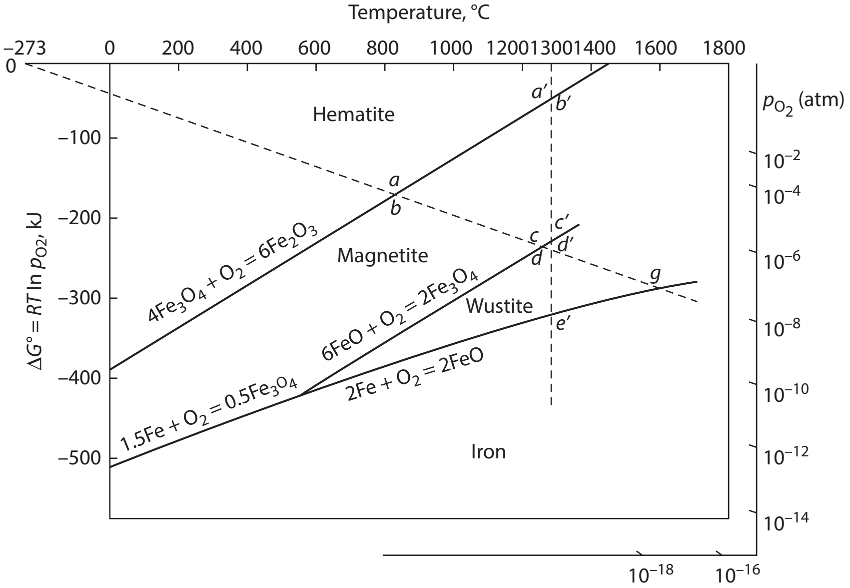


Figure 13.28 Phase stability in the system Fe–Fe_2O_3 as a function of ΔG° and temperature.

than does the composition in equilibrium with hematite). In the Ellingham diagram, lines which radiate from the origin ($\Delta G^\circ = 0$, $T = 0$ K) are oxygen isobars. The distinct advantage of the Ellingham-type representation of reaction and phase equilibria is its ability to indicate, at a glance, the relative stabilities of a large number of metal–oxygen systems, as was seen in Figure 12.13.

13.9 THE SOLUBILITY OF GASES IN METALS

It is invariably found that molecular gases dissolve in metals as atoms. For example, if pure liquid Ag is brought into contact with oxygen gas at a relatively low pressure, the following series of events occur:

1. Molecules of O_2 striking the surface of the liquid Ag become adsorbed on the surface.
2. The adsorbed molecules dissociate to form O atoms adsorbed on the surface.
3. The adsorbed O atoms diffuse from the surface into the bulk melt.

The overall reaction can be written as

$$\frac{1}{2}O_{2(g)} = [O]_{\text{in Ag}}$$

and equilibrium is attained when the partial molal Gibbs free energy of oxygen in solution in the liquid Ag, $\bar{G}_O$, is equal to the molar Gibbs free energy of oxygen in the gas phase, $\frac{1}{2}G_{O_2}$. The standard state for a gas dissolved in a metal can be chosen as the 1 wt% standard state, discussed in Section 13.3, or as the 1 atom percent (at%) standard state, which is the point on the Henry's law line at a mole fraction of solute of 0.01. Thus, the standard change in the molar Gibbs free energy which occurs when a gaseous species A_2, at 1 atm pressure and the temperature T, is dissolved in a metal at the concentration $X_A = 0.01$ (1 at%), at the temperature T, according to

$$\frac{1}{2}\mathrm{A}_{2(g,P=1\mathrm{atm})} = [\mathrm{A}]_{(1\ \mathrm{at}\%)} \tag{13.15}$$

is

$$\Delta G^\circ_{1\ \mathrm{at}\ \%} = -RT\ln K_{1\ \mathrm{at}\%} = -RT\ln\frac{[h_\mathrm{A}]_{(1\ \mathrm{at}\ \%)}}{p_{\mathrm{A}_2}^{1/2}} \tag{13.16}$$

in which $[h_A]_{(1\ \mathrm{at}\%)}$ is the activity of A in solution in the metal relative to the 1 at% standard state. If the solute obeys Henry's law,

$$K_{1\ \mathrm{at}\%} = \frac{[\mathrm{at}\%\ \mathrm{A}]}{p_{\mathrm{A}_2}^{1/2}} \tag{13.17}$$

If, however, the 1 wt% standard state is chosen for the solute, then for

$$\frac{1}{2}\mathrm{A}_{2(g,P=1\ \mathrm{atm})} = [\mathrm{A}]_{(1\ \mathrm{wt}\%)} \tag{13.18}$$

$$\Delta G^\circ_{1\ \mathrm{wt}\%} = -RT\ln K_{1\ \mathrm{wt}\%} = -RT\ln\frac{[h_\mathrm{A}]_{(1\ \mathrm{wt}\%)}}{p_{\mathrm{A}_2}^{1/2}} \tag{13.19}$$

in which $[h_A]_{(1\ \mathrm{wt}\%)}$ is the activity of A in solution relative to the 1 wt% standard state. If Henry's law is obeyed,

$$K_{1\ \mathrm{wt}\%} = \frac{[\mathrm{wt}\%\ \mathrm{A}]}{p_{\mathrm{A}_2}^{1/2}} \tag{13.20}$$

For the solution of oxygen in liquid Ag in the range 1213–1573 K,

$$\Delta G^\circ_{1\ \mathrm{at}\%} = -14{,}310 + 5.44T\ \mathrm{J} \tag{i}$$

A concentration of 1 wt% O in Ag corresponds to a mole fraction of

$$\frac{\frac{1}{16}}{\frac{1}{16}+\frac{99}{107.9}} = 0.0638$$

and thus, the change in the molar Gibbs free energy for

$$[\mathrm{O}]_{(\text{in Ag. 1 at\%})} = [\mathrm{O}]_{(\text{in Ag. 1 wt\%})}$$

is

$$\Delta G^{\circ}_{(\text{ii})} = -8.3144T \ln \frac{0.0638}{0.01} = -15.40T \text{ J}$$

The sum of $\Delta G^{\circ}_{1\text{ at\%}}$ and $\Delta G^{\circ}_{(\text{ii})}$ gives

$$\Delta G^{\circ}_{1\text{ wt\%}} = -14{,}310 - 9.96\mathrm{T} \tag{iii}$$

For the solution of oxygen in solid Ag in the range 573–1173 K,

$$\Delta G^{\circ}_{1\text{ at\%}} = 49{,}620 - 15.77T \text{ J} \tag{iv}$$

Oxygen obeys Henry's law in liquid Ag, and thus, from Equations (i), 13.16, and 13.17, the solubility of oxygen in liquid silver is

$$\text{at\% O} = p_{\mathrm{O}_2}^{1/2} \exp\left(\frac{1721}{T} - 0.654\right) \tag{v}$$

and, from Equations (iv), 13.16, and 13.17, the solubility of oxygen in solid Ag is

$$\text{at\% O} = p_{O_2}^{1/2} \exp\left(-\frac{5967}{T} + 1.90\right) \tag{vi}$$

The phase equilibria in the system Ag–O at an oxygen pressure of 1 atm are shown in Figure 13.29. Equation (i) gives $\Delta H^{\circ}_{1\,at\%}$ for the change of state

$$\frac{1}{2}\mathrm{O}_{2(g,P=1\text{ atm})} = [\mathrm{O}]_{(1\text{ at\% in liquid Ag})}$$

as −14,310 J. Thus, since the enthalpy change is negative, decreasing the temperature causes the equilibrium to shift to the right, with the consequence that, at constant oxygen pressure, the solubility of oxygen in liquid Ag increases with decreasing temperature. From Equation (v), the maximum solubility of O in liquid Ag in Figure 13.29 is 2.14 at% at 940°C (the state *b*). Equation (vi) gives the solubility of O in solid Ag at 940°C as 0.049 at% (the state *d*), and thus, the transformation

$$\mathrm{Ag}_{(l,2.14\text{ at\% O})} \rightarrow \mathrm{Ag}_{(s,0.049\text{ at\% O})} + \mathrm{O}_{2(g,P=1\text{ atm})}$$

occurs at 940°C. The evolution of oxygen during the freezing of oxygen-containing liquid Ag causes the phenomenon of *spitting*, during which droplets of liquid silver

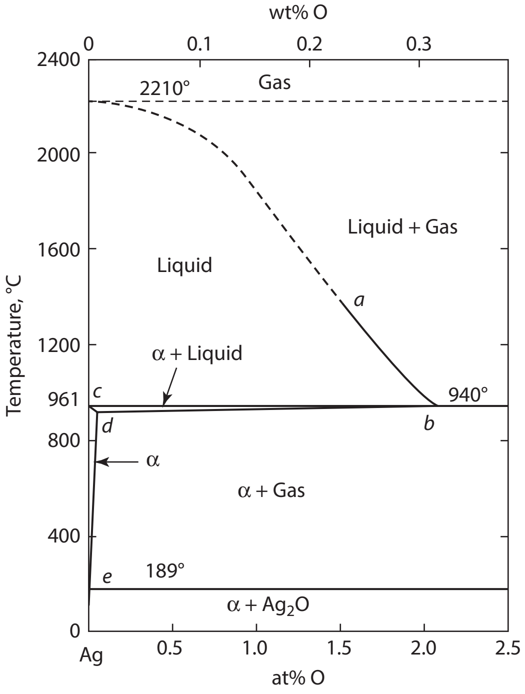


Figure 13.29 Phase equilibria in the system Ag–O at an oxygen pressure of 1 atm.

are ejected from the freezing mass of liquid. Equation (iv) gives $\Delta H^{\circ}_{1\text{at}\%}$ for the change of state

$$\frac{1}{2}\text{O}_{2(g,P=1\text{ atm})} = \text{O}_{1\text{ at\% in solid Ag}}$$

as 49,620 J, which being positive, requires that the solubility of O in solid Ag decreases with decreasing temperature. From Equation (vi), the solubility of O in solid Ag at an oxygen pressure of 1 atm decreases from 0.049 at% at 940°C to 1.7 × 10^{-5} at% at 189°C (the point *e* in Figure 13.29). ΔG° for the reaction

$$2\text{Ag}_{(s)} + \frac{1}{2}\text{O}_{2(g)} = \text{Ag}_2\text{O}_{(s)}$$

is written as

$$\Delta G^{\circ} = -30,540 + 66.11T\text{J}$$

The temperature at which $p_{\text{O}_2,\text{eq}} = 1$ atm is thus 30,540/66.11 = 462 K (189°C), and the three-phase invariant equilibrium is shown at 189°C in Figure 13.29. The solubility of oxygen in Ag is shown as a function of temperature and oxygen pressure in

Figure 13.30. On a plot of log (at% O) versus inverse temperature, the oxygen isobars in a single-phase field are parallel lines, the slopes of which are determined by the molar enthalpies of solution of oxygen. From Equation (v), the slope of the lines in the phase field of liquid silver is 1721, and from Equation (vi), the slope in the phase field of solid silver is –5967. The points *b* and *d* on the 1 atm isobar at 940°C correspond with the points *b* and *d* in Figure 13.29. Increasing the oxygen pressure decreases the temperature at which the equilibrium involving liquid Ag, solid Ag, and O_2 gas occurs and increases the temperature at which the equilibrium involving solid Ag, Ag_2O, and O_2 gas occurs. The two temperatures coincide at 508°C when the oxygen pressure is 414 atm (the state *A* in Figure 13.30). This four-phase equilibrium in a binary system has zero degrees of freedom. Recasting Equation 13.17 as

$$[\text{at\% A}] = k(T)p_{A_2}^{1/2} \tag{13.21}$$

gives an equation known as *Sieverts' law* (Adolf Sieverts, 1874–1947) and the temperature-dependent constant in Equation 13.21, *k*(*T*), which is known as *Sieverts' constant*, is evaluated as the concentration of A in the metal equilibrated, at the

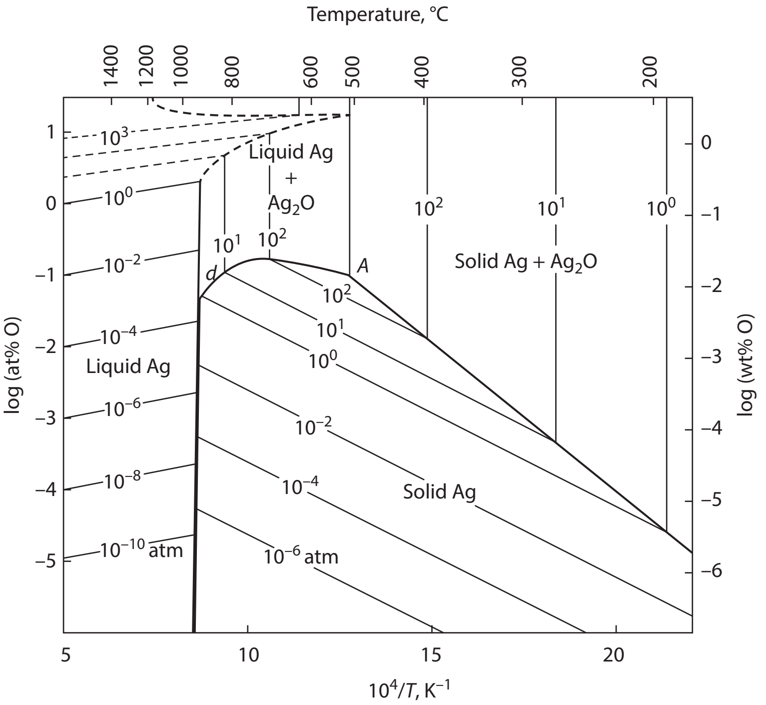


Figure 13.30 The solubility of oxygen in silver as a function of oxygen pressure and temperature.

temperature T, with gaseous A_2 at 1 atm pressure. Sieverts measured the solubility of oxygen in liquid Ag in 1907.*

13.10 SOLUTIONS CONTAINING SEVERAL DILUTE SOLUTES

The behavior of a dilute solute in a binary solution is determined by the nature and magnitude of the interactions between the solute and solvent atoms. However, when a second dilute solute is added, three types of interaction occur—namely, solvent–solute I, solvent–solute II, and solute I–solute II—and the thermodynamic behavior of the system is determined by the relative magnitudes of the three types of interaction. Consider the exposure of liquid iron to a gaseous mixture of hydrogen and oxygen. The equilibrium

$$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)} \tag{i}$$

is established in the gas phase, and thus,

$$p_{H_2} p_{O_2}^{1/1} = \frac{p_{H_2O}}{K_{(i)}}$$

Since both hydrogen and oxygen have some limited solubility in liquid iron, both gases will dissolve atomically until their respective activities in the iron, with respect to the 1 atm pressure standard state, equal the respective partial pressures in the gas phase. Alternatively, with respect to the 1 wt% in Fe standard state,

$$\frac{1}{2}O_{2(g)} = [O]_{(1\text{ wt\% in Fe})} \tag{ii}$$

and

$$\frac{1}{2}H_{2(g)} = [H]_{(1\text{ wt\% in Fe})} \tag{ii}$$

for which

$$h_{O(1\text{ wt\%})} = K_{(ii)} p_{O_2}^{1/2}$$

and

$$h_{H(1\text{ wt\%})} = K_{(iii)} p_{H_2}^{1/2}$$

Equilibrium in the metal phase is given as

---

* A. Sieverts and J. Hagenacker, “Über die Loslichkeit von Wasserstoff und Sauerstoff in festem und geschmolzenem Silber,” *Z. Phys. Chem.* (1907), vol. 68, p. 115.

$$h^2_{\text{H(1 wt\%)}} h_{\text{O(1 wt\%)}} = \frac{K^2_{\text{(iii)}} K_{\text{(ii)}}}{K_{\text{(i)}}} p_{\text{H}_2\text{O}}$$

or

$$f^2_{\text{H(1 wt\%)}} f_{\text{O(1 wt\%)}} [\text{wt\% H}]^2 [\text{wt\% O}] = \frac{K^2_{\text{(iii)}} K_{\text{(ii)}}}{K_{\text{(i)}}} p_{\text{H}_2\text{O}}$$

The solubilities of H and O (expressed as weight percentages) are thus determined by the values of the activity coefficients ($f_{\text{i (1 wt\%)}}$) of H and O, and the questions to be answered are

1. How is the activity coefficient of O in Fe influenced by the presence of H?
2. How is the activity coefficient of H in Fe influenced by the presence of O?

This problem is dealt with by the introduction of interaction coefficients and interaction parameters. In the binary A–B, the activity of B in dilute solution with respect to the Henrian standard state is given by

$$h_{\text{B}} = f^{\text{B}}_{\text{B}} X_{\text{B}}$$

If, holding the concentration of B constant, the addition of a small amount of C changes the value of the activity coefficient of B to f_{B}, then the difference between f_{B} and f^{B}_{B} is quantified by the expression

$$f_{\text{B}} = f^{\text{B}}_{\text{B}} f^{\text{C}}_{\text{B}} \tag{13.22}$$

where f^{C}_{B} is called the *interaction coefficient* of C on B and is a measure of the effect, on the behavior of B, of the presence of a specific concentration of C, at the same concentration of B. Similarly, if a small amount of D is added to the A–B solution, as a result of which the value of the activity coefficient of B changes from f^{B}_{B} to f_{B}, then

$$f_{\text{B}} = f^{\text{B}}_{\text{B}} f^{\text{D}}_{\text{B}}$$

Now consider the system A–B–C–D. Mathematical analysis of such a system is possible only if f^{D}_{B} is independent of the concentration of C and if f^{C}_{B} is independent of the concentration of D. Consider that the interaction coefficient of the solute i on the solute j is independent of the other solutes present, in which case the interaction coefficients may be combined by means of a Taylor's expansion of $\ln f_i$ as a function of the concentrations of the solutes; for example, for the binary system A–B in which A is the solvent,

$$\begin{aligned}\ln f_{\text{B}} &= \text{some function of the mole fraction of B}\\ &= \ln f^{\circ}_{\text{B}} + \left(\frac{\partial \ln f_{\text{B}}}{\partial X_{\text{B}}}\right) X_{\text{B}} + \frac{1}{2}\left(\frac{\partial^2 \ln f_{\text{B}}}{\partial X^2_{\text{B}}}\right) X^2_{\text{B}} + \cdots\end{aligned}$$

In this expression, the partial derivatives are the limiting values reached as $X_B \rightarrow 0$. For the multicomponent system A–B–C–D,

$$
\begin{aligned}
\ln f_B &= \text{some function of the fractions of B, C, and D} \\
&= \ln f_B^\circ + \left(\frac{\partial \ln f_B}{\partial X_B} X_B \right| + \frac{\partial \ln f_B}{\partial X_C} X_C + \frac{\partial \ln f_B}{\partial X_D} X_D \Bigg) \\
&\quad + \left(\frac{1}{2} \frac{\partial^2 \ln f_B}{\partial X_B^2} X_B^2 + \frac{\partial^2 \ln f_B}{\partial X_B \partial X_C} X_B X_C + \cdots \right)
\end{aligned}
$$

in which, again, the partial derivatives are the limiting values as the mole fractions of the solutes approach zero. At very low concentration, the terms containing the products of mole fractions are small enough to be ignored, and also, choice of the Henrian standard state makes $f_B^\circ = 1$. Thus,

$$
\begin{aligned}
\ln f_B &= \frac{\partial \ln f_B}{\partial X_B} X_B + \frac{\partial \ln f_B}{\partial X_C} X_C + \frac{\partial \ln f_B}{\partial X_D} X_D \\
&= \varepsilon_B^B X_B + \varepsilon_B^C X_C + \varepsilon_B^D X_D
\end{aligned}
\tag{13.23}
$$

where

$$
\varepsilon_j^j = \frac{\partial \ln f_j}{\partial X_i} \bigg|_{X_i \rightarrow 0}
$$

is called the *interaction parameter* of i on j and is obtained as the limiting slope of a plot of $\ln f_j$ against X_i at constant $X_j.\varepsilon_j^j$ and ε_j^j are related as follows. For the general system

$$
\frac{\partial^2 G}{\partial n_i \partial n_j} = \frac{\partial \bar{G}_i}{\partial n_j} = \frac{\partial \bar{G}_j}{\partial n_i}
$$

and since $\partial \bar{G}_i = RT \partial \ln a_i = RT \partial \ln f_i$, then

$$
\frac{\partial \ln f_j}{\partial n_i} = \frac{\partial \ln f_i}{\partial n_j}
$$

and thus,

$$
\varepsilon_i^j = \varepsilon_j^i \tag{13.24}
$$

It is often more convenient to consider the concentrations of the solutes in terms of weight percentages and to use logarithms to the base 10, in which case Equation 13.23 becomes

$$
\begin{aligned}
\log f_B &= \frac{\partial \log f_B}{\partial \text{ wt\% B}} \text{wt\% B} + \frac{\partial \log f_B}{\partial \text{ wt\% C}} \text{wt\% C} + \frac{\partial \log f_B}{\partial \text{ wt\% D}} \text{wt\% D} \\
\log f_B &= e_B^B \text{wt\% B} + e_B^C \text{wt\% C} + e_B^D \text{wt\% D}
\end{aligned}
\tag{13.25}
$$

Multiplying Equation 13.25 by 2.303 and comparing, term by term, with Equation 13.23 gives

$$\varepsilon_B^i X_i = 2.303\, e_B^i \text{ wt\% } i$$

and since, at small concentrations of B and i,

$$X_i \sim \frac{wt\%\, i \cdot \text{MW}_A}{100\text{MW}_i}$$

then

$$e_B^i = \frac{1}{230.3}\frac{\text{MW}_A}{\text{MW}_i}\varepsilon_B^i$$

and

$$e_B^i = \frac{\text{MW}_B}{\text{MW}_i} e_j^B$$

Pehlke and Elliott* have determined that nitrogen, dissolved in liquid iron at 1600°C, obeys Sieverts' law according to

$$[\text{wt\% N}] = k p_{N_2}^{1/2} \tag{iv}$$

where $k = 0.045$ at 1873 K, and they have measured the effects of the presence of a second dilute solute on the thermodynamics of nitrogen dissolved in liquid iron. These systems are particularly amenable to experimental study because of the ease with which the activity of nitrogen can be controlled by the gas phase. The interaction parameters, e_N^i, are determined by maintaining the nitrogen in the melt at constant activity and measuring the variation in the solubility of nitrogen with concentration of the second solute. Since nitrogen in liquid iron obeys Henry's (Sieverts') law, $f_N^N = 1$, and thus, e_N^N (and ε_N^N) are zero. Consequently, the first terms in Equations 13.23 and 13.25 are zero. If the addition of a second solute X to the Fe–N binary (equilibrated with a fixed p_{N_2}) causes a change in the dissolved nitrogen content from $[\text{wt\% N}]_{\text{Fe–N}}$ to $[\text{wt\% N}]_{\text{Fe–N–X}}$. Then, from Equation (iv),

$$k = \frac{[\text{wt\% N}]_{\text{inFe–N}}}{p_{N_2}^{1/2}} = \frac{f_N^X[\text{wt\% N}]_{\text{inFe–N–X}}}{p_{N_2}^{1/2}}$$

and thus, f_N^X is obtained experimentally as

$$f_N^X = \left(\frac{[\text{wt\% N}]_{\text{inFe–N}}}{[\text{wt\% N}]_{\text{in Fe–N–X}}}\right)_{T,p_{N_2}}$$

---

[*] R. Pehlke and J. F. Elliott, "Solubility of Nitrogen in Liquid Iron Alloys, I: Thermodynamics," *Trans. Met. Soc. AIME* (1960), vol. 218, p. 1088.

The variation of [wt% N] with [wt% X] is shown for several second solutes in Figure 13.31, and the corresponding variation of $\log f_N^X$ with [wt% X] is shown in Figure 13.32. The values of e_N^X are obtained as the slopes of the linear portions of the lines in Figure 13.32.

Thus, in a multicomponent liquid iron alloy containing several solutes including nitrogen, if the effect of any one solute on f_N is independent of the presence of any other solute, then the total effect of the solutes on f_N is the sum of their individual effects, and if $\log f_N^X$ is a linear function of [wt% X], then f_N is given by Equation 13.25. If, however, the concentrations of X are higher than the limits of linear variation of log f_N^X with [wt% X], then a graphical solution is required. In these cases, the value of log f_N^X for each value of [wt% X] is read from the graph (Figure 13.32), and log f_N is obtained as

$$\log f_N = \sum_X \log f_N^X$$

or

$$f_N = \prod_X f_N^X$$

Figure 13.32 indicates that, as a general rule, e_N^X is a negative quantity when X forms a nitride which is more stable than iron nitride, and that the order of

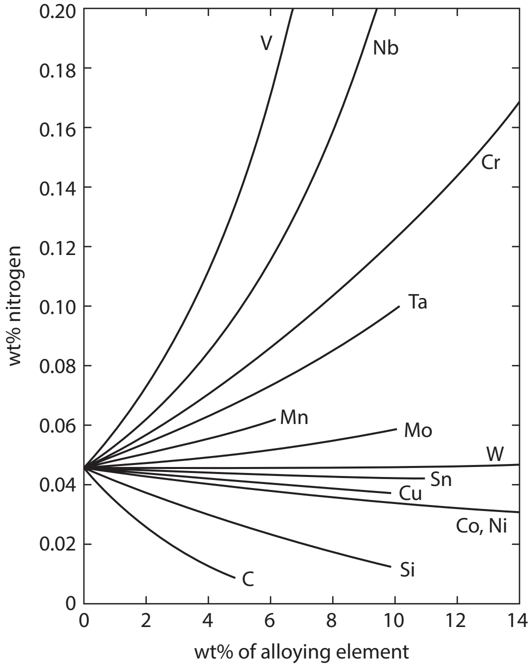


Figure 13.31 The effect of alloying elements on the solubility of nitrogen at 1 atm pressure in liquid binary iron alloys at 1600°C.

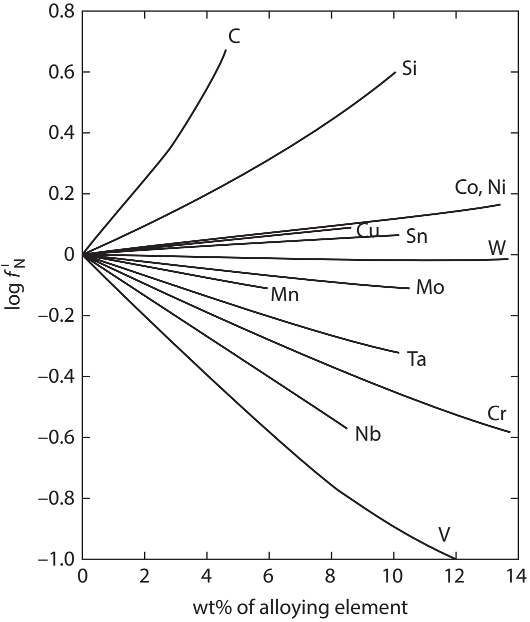


Figure 13.32 The activity coefficients of nitrogen in binary iron alloys at 1600°C.

increasing magnitude of $\left|e_N^X\right|$ follows the order of increasing magnitude of the Gibbs free energy of formation of the nitride of X. Similarly, e_N^X is a positive quantity when X has a greater affinity for iron than either X has for N or iron has for nitrogen. The values of the interaction coefficients for several elements in dilute solution in iron at 1600°C are listed in Table 13.1.

Example 1

In view of the introduction of interaction parameters, the example of the Si–O equilibrium in liquid Fe, discussed in Section 13.3, can now be reexamined. In this example, it was determined that, for

$$\mathrm{Si}_{(1\text{ wt\% in Fe})} + \mathrm{O}_{2(g)} = \mathrm{SiO}_{2(s)}$$

$$\Delta G^\circ = -833{,}400 + 229.5T \text{ J}$$

For

$$\tfrac{1}{2}\mathrm{O}_{2(g)} = [\mathrm{O}]_{(1\text{ wt\% in Fe})}$$

$$\Delta G^\circ = -111{,}300 - 6.41T \text{ J} \qquad \text{(i)}$$

and thus, for

$$\mathrm{Si}_{(1\text{ wt\% in Fe})} + 2\mathrm{O}_{(1\text{ wt\% in Fe})} = \mathrm{SiO}_{2(s)}$$

$$\Delta G^\circ = -610{,}800 + 242.32T \text{ J} \qquad \text{(ii)}$$

From Equation (i) at 1600°C,

$$\frac{h_{\mathrm{O}(1\text{ wt\%})}}{p_{\mathrm{O}_2}^{1/2}} = 2.746 \times 10^3 \qquad \text{(iii)}$$

and, from Equation (ii) at 1600°C,

$$\frac{a_{\mathrm{SiO}_2}}{h_{\mathrm{Si}(1\text{ wt\%})} h_{\mathrm{O}(1\text{ wt\%})}^2} = 2.380 \times 10^4 \qquad \text{(iv)}$$

Thus, with $p_{\mathrm{O}_2} = 5.57 \times 10^{-12}$ atm and $a_{\mathrm{SiO}_2} = 1$, Equation (iii) gives

$$h_{\mathrm{O}(1\text{ wt\%})} = 6.48 \times 10^{\ 3} \qquad \text{(v)}$$

and Equation (iv) gives

$$h_{\mathrm{O}(1\text{ wt\%})}^2 h_{\mathrm{Si}(1\text{ wt\%})} = 4.0 \times 10^{-5} \qquad \text{(vi)}$$

Division of Equation (vi) by $h_{\mathrm{O}(1\text{ wt\%})}^2$ from Equation (v) gives

$$h_{\mathrm{Si}(1\text{ wt\%})} = 1 \qquad \text{(vii)}$$

In the previous treatment the assumption that Si obeys Henry's law leads to the conclusion that

$$h_{\mathrm{Si}(1\text{ wt\%})} = \text{wt\% Si} = 1$$

At 1600°C, from Table 13.1,

$$e_{\mathrm{O}}^{\mathrm{Si}} = -0.14 \qquad e_{\mathrm{O}}^{\mathrm{O}} = -0.2$$
$$e_{\mathrm{Si}}^{\mathrm{O}} = -0.25 \qquad e_{\mathrm{Si}}^{\mathrm{Si}} = -0.32$$

Thus, from Equation (v),

$$\log f_{\mathrm{O}} + \log[\text{wt\% O}] = \log\left(6.48 \times 10^{-3}\right)$$

Table 13.1 Interaction Coefficients for Dilute Solutions of Elements Dissolved in Liquid Iron at 1600°C

Element(*i*)	Element (*j*)											
	Al	**C**	**Co**	**Cr**	**H**	**Mn**	**N**	**Ni**	**O**	**P**	**S**	**Si**
Al	4.8	11	—	—	(34)	—	(0.5)	—	−160	—	4.9	6
C	(4.8)	22	1.2	−2.4	(72)	—	(11.1)	1.2	(−9.7)	—	9	10
Co	—	(6)	—	—	(11)	—	(4.7)	—	(2.6)	—	—	—
Cr	—	(−10)	—	—	(−11)	—	(−16.6)	—	(−13)	—	(−3.55)	—
H	1.3	6.0	0.18	−0.22	0	−0.14	—	0	—	1.1	0.8	2.7
Mn	—	—	—	—	(−7.7)	—	(−7.8)	—	(0)	—	(−4.3)	(0)
N	0.3	13	1.1	−4.5	—	−2	0	1	5.0	5.1	1.3	4.7
Ni	—	(5.9)	—	—	(0)	—	(4.2)	0	(2.1)	—	(0)	(1.0)
O	−94	−13	0.7	−4.1	—	0	(5.7)	0.6	−20	7.0	−9.1	−14
P	—	—	—	—	(34)	—	(11.3)	—	(13.5)	—	(4.3)	(9.5)
S	5.8	(24)	—	−2.2	(26)	−2.5	(3.0)	0	(−18)	4.5	−2.8	6.6
Si	(6.3)	24	—	—	(76)	0	(9.3)	0.5	(−25)	8.6	(5.7)	32

Some interaction coefficients $e_i^j \times 10^2$ for dilute solutions of elements dissolved in liquid iron at 1600°C. Values in parentheses are calculated from $e_i^j = (MW_i/MW_j)e_j^i$.(From J. F. Elliott, M. Gleiser, and V. Ramakrishna, *Thermochemistry for Steelmaking*, vol. 2, Addison-Wesley, Reading, MA, 1963.)

or

$$-0.2\times\left[\text{wt\% O}\right]-0.14\times\left[\text{wt\% Si}\right]+\log\left[\text{wt\% O}\right]=-2.188 \qquad \text{(viii)}$$

and from Equation (vii),

$$\log f_{\mathrm{Si}} + \log\left[\text{wt\% Si}\right] = \log\left(1\right)$$

or

$$0.32\left[\text{wt\% Si}\right]-0.25\left[\text{wt\% O}\right]+\log\left[\text{wt\% Si}\right]=0 \qquad \text{(ix)}$$

Computer solution of Equations (viii) and (ix) gives

$$\left[\text{wt\% Si}\right] = 0.631 \text{ and } \left[\text{wt\% O}\right] = 0.00798$$

In the example in Section 13.3, in which the effect of dissolved oxygen was ignored and it was assumed that $f_{\mathrm{Si}}=1$, the equilibrium weight percentage of Si in iron when $a_{\mathrm{SiO_2}}=1$ and $p_{\mathrm{O_2}}=5.57\times10^{-12}$ atm was 1.0. It is of interest to determine which of the two initial assumptions, that (1) $e^{\mathrm{Si}}_{\mathrm{Si}}=0$ and (2) $e^{\circ}_{\mathrm{Si}}=e^{\mathrm{Si}}_{\mathrm{O}}=0$, contributes more to the error in the initial calculation. Use $e^{\mathrm{Si}}_{\mathrm{Si}}=0.32$ and assume that $e^{\mathrm{O}}_{\mathrm{Si}}$ and $e^{\mathrm{Si}}_{\mathrm{O}}$ are zero. From Equation (ix):

$$0.32\left[\text{wt\% Si}\right]+\log\left[\text{wt\% Si}\right]=0$$

which gives [wt% Si] = 0.629, and from Equation (viii),

$$-0.20\times\left[\text{wt\% O}\right]-0.24\times0.629+\log\left[\text{wt\% O}\right]=-2.188$$

which gives [wt% O] = 0.00797. The error introduced by ignoring the interaction between Si and O in solution in Fe is thus seen to be negligible in comparison with that introduced by assuming that Si obeys Henry's law over some initial range of composition.

Example 2

Calculate the equilibrium oxygen content of an Fe–C–O alloy which, at 1600°C, contains 1 wt% C and is under a pressure of 1 atm of CO.

$$\text{For } \mathrm{C}_{(gr)}+\%\mathrm{O}_{2(g)}=\mathrm{CO}_{(g)},\ \Delta G^\circ=-111{,}700-87.65T\ \mathrm{J}$$

$$\text{For } \mathrm{C}_{(gr)}=\mathrm{C}_{(1\text{ wt\% in Fe})},\ \Delta G^\circ=22{,}600-42.26T\ \mathrm{J}$$

$$\text{For } \tfrac{1}{2}\mathrm{O}_{2(g)}=\mathrm{O}_{(1\text{ wt\% in Fe})},\ \Delta G^\circ=-111{,}300-6.41T\ \mathrm{J}$$

Thus, for

$$C_{(1\text{ wt\%})} + O_{(1\text{ wt\%})} = CO_{(g)},\ \Delta G^\circ = -23{,}000 - 38.98T\text{J}$$

Therefore,

$$\Delta G^\circ_{1873\text{ K}} = -96{,}010\text{ J}$$

and

$$\frac{p_{CO}}{h_C h_O} = 476$$

Thus,

$$h_C h_O = f_C\left[\text{wt\% C}\right] f_O\left[\text{wt\% O}\right] = 2.1\times 10^{-3}\, p_{CO}$$

At 1600°C,

$$e_C^C = 0.22$$
$$e_O^O = -0.2$$
$$e_C^O = -0.097$$
$$e_O^C = -0.13$$

Thus, for 1 wt% C and p_{CO} = 1 atm,

$$\log\left[\text{wt\% O}\right] - 0.297\left[\text{wt\% O}\right] = -2.768$$

solution of which gives [wt% O] = 0.00171. If all of the interaction parameters had been ignored, the weight percentage of O would have been calculated as 0.00210.

Example 3

The partial pressure of hydrogen in the atmosphere is such that an Fe–C–Ti melt containing 1 wt% C and 3 wt% Ti contains 5 parts per million (by weight) of hydrogen at 1600°C. Calculate the vacuum which is required to decrease the hydrogen content of the melt to 1 ppm, given that $e_H^{Ti} = -0.08$, that $e_H^C = 0.06$, and that hydrogen in pure iron obeys Henry's law up to a solubility of 0.0027 wt% under a pressure of 1 atm of hydrogen at 1600°C.

For the equilibrium between gaseous hydrogen and dissolved H, given as $\frac{1}{2}H_{2(g)} = [H]_{(1\text{ wt\% in Fe})}$,

$$K = \frac{f_{H(1\text{wt\%})}[\text{wt\%H}]}{p_{H_2}^{1/2}}$$

In pure iron, as H obeys Henry's law, $f_{H(1\text{ wt\%})} = 1$, and thus,

$$K_{1873\text{ K}} = 0.0027$$

Thus,

$$\log f_{H(1\text{ wt\%})} + \log[\text{wt\% H}] - \frac{1}{2}\log p_{H_2} = \log 0.0027$$

But

$$\log f_{H(1\text{ wt\%})} = e_H^H[\text{wt\% H}] + e_H^{Ti}[\text{wt\% Ti}] + e_H^C[\text{wt\% C}]$$

As $f_{H(1\text{ wt\%})} = 1$, $e_H^H = 0$, and hence, at 1600°C,

$$e_H^{Ti}[\text{wt\% Ti}] + e_H^C[\text{wt\% C}] + \log[\text{wt\% H}] - \frac{1}{2}\log p_{H_2} = \log 0.0027$$

When [wt% H] = 5×10^{-4},

$$\begin{aligned}\log p_{H_2} &= 2\times[(-0.08\times 3) + (0.06\times 1) + \log(5\times 10^{-4}) - \log 0.0027] \\ &= -1.825\end{aligned}$$

which gives $p_{H_2} = 0.015$ atm. Similarly, when [wt% H] = 1×10^{-4}, $p_{H_2} = 6\times 10^{-4}$ atm. Thus,

$$[\text{wt\% H}] = 5\text{ ppm} \qquad \text{when } p_{H_2} = 0.015\text{ atm} \qquad \text{and } P_{(\text{total})} = 1\text{ atm}$$

and so

$$[\text{wt\% H}] = 1\text{ ppm} \qquad \text{when } p_{H_2} = 0.0006\text{ atm}$$

and

$$P_{\text{total}} = \frac{0.0006}{0.015} = 0.04\text{ atm}$$

Thus, in order to achieve the desired decrease in the content of dissolved H, the total pressure must be decreased from 1 to 0.04 atm.

13.11 SUMMARY

1. Reaction equilibrium in the reaction

$$aA + bB = cC + dD$$

is established when the reaction has proceeded to the extent that

$$a\bar{G}_A + b\bar{G}_B = c\bar{G}_C + d\bar{G}_D$$

That is, ΔG for the reaction is zero.

2. The state of reaction equilibrium is determined by the standard Gibbs free energy change for the reaction, ΔG°, via

$$\Delta G^\circ = -RT\ln K$$

where K is the equilibrium constant for the reaction given by the quotient of the activities of the reactants and products at reaction equilibrium; that is,

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

3. The Raoultian standard state of a thermodynamic component is the pure component in its stable state of existence at the temperature of interest. The Henrian standard state is obtained from consideration of Henry's law, which, strictly being a limiting law obeyed by the solute B at infinite dilution, is expressed as

$$\frac{a_B}{X_B} \to k_B \qquad \text{as } X_B \to 0$$

where a_B is the activity of B in the solution with respect to the Raoultian standard state and k is the Henry's law constant at the temperature T. Alternatively,

$$\frac{a_B}{X_B} \to \gamma_B^\circ \qquad \text{as } X_B \to 0$$

where $\gamma_B^\circ(=k_B)$ is the constant activity coefficient which quantifies the difference between Raoultian and Henrian solution behavior of B. If the solute obeys Henry's law over a finite range of composition, then, over this range,

$$a_B = \gamma_B^\circ X_B$$

The Henrian standard state is obtained by extrapolating the Henry's law line to $X_B = 1$, and the activity of B in the Henrian standard state with respect to the Raoultian standard state having unit activity is

$$a_B = \gamma_B^\circ$$

The activity of B in a solution with respect to the Henrian standard state having unit activity is given by

$$h_B = f_B X_B$$

where h_B is the Henrian activity and f_B is the Henrian activity coefficient. In the range of composition in which B obeys Henry's law, $f_B = 1$.

The 1 wt% standard state is defined as

$$\frac{h_{B(1\ \mathrm{wt\%})}}{\mathrm{wt\%}\ B} \to 1 \qquad \text{as wt\%}\ B \to 0$$

and is located at that point on the Henry's law line which corresponds to a concentration of 1 wt% B. With respect to the 1 wt% standard state having unit activity, the activity of B, $h_{B(1\ \mathrm{wt\%})}$, is given by

$$h_{B(1\ \mathrm{wt\%})} = f_{B(1\ \mathrm{wt\%})}\mathrm{wt\%}B$$

where $f_{B(1\ \mathrm{wt\%})}$ is the 1 wt% activity coefficient. The activities are related via

$$a_B = h_B \gamma_B^\circ$$

and

$$a_B = f_{B(1\ \mathrm{wt\%})} \cdot \mathrm{wt\%}B \cdot \gamma_B^\circ \cdot \frac{\mathrm{MW_{solvent}}}{100\mathrm{MW}_B}$$

4. The Gibbs equilibrium phase rule is

$$\mathcal{F} = C + 2 - \Phi$$

where:

   C is the number of components in the system

   $\mathcal{F}$ is the number of degrees of freedom available to the equilibrium involving Φ phases

With R independent reaction equilibria involving N species, the Gibbs equilibrium phase rule is

$$\mathcal{F} = (N - R) + 2 - \mathrm{P}$$

where $C = N - R$

5. In a solution of solvent A and several dilutes solutes B, C, and D,

$$\ln f_B = \varepsilon_B^B X_B + \varepsilon_B^C X_C + \varepsilon_B^D X_D$$

where

$$\varepsilon_j^i = \left.\frac{\partial \ln f_j}{\partial X_i}\right|_{X_i \to 0}$$

is the interaction parameter of i on j. The interaction parameters are related to one another by

$$\varepsilon_i^j = \varepsilon_j^i$$

If the concentrations of the dilute solutes are expressed in weight percent, then

$$\log f_B = e_B^B \text{wt\%}\ B + e_B^C \text{wt\%}\ C + e_B^D \text{wt\%}\ D$$

where

$$e_i^j = \left.\frac{\partial \log f_j}{\partial\ \text{wt\%}\ i}\right|_{\text{wt\%}\ i \to 0}$$

The two interaction parameters of i and j are related by

$$e_j^i = \frac{\text{MW}_j}{\text{MW}_i} e_i^j$$

Also

$$\varepsilon_j^i X_i = 2.303 e_j^i\ \text{wt\%}\ i$$

13.12 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 13

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Activity quotient
Adsorbed atoms
Alternate standard state
Berthollides
Components
Compound
Gibbs equilibrium phase rule
Infinite dilution
Interaction parameter
Law of definite proportions
Nonstoichiometric compound
Phase stability diagram
Sieverts’ constant
Sieverts’ law
Stoichiometric compound
Thermodynamic degree of freedom

13.13 QUALITATIVE EXAMPLE PROBLEMS

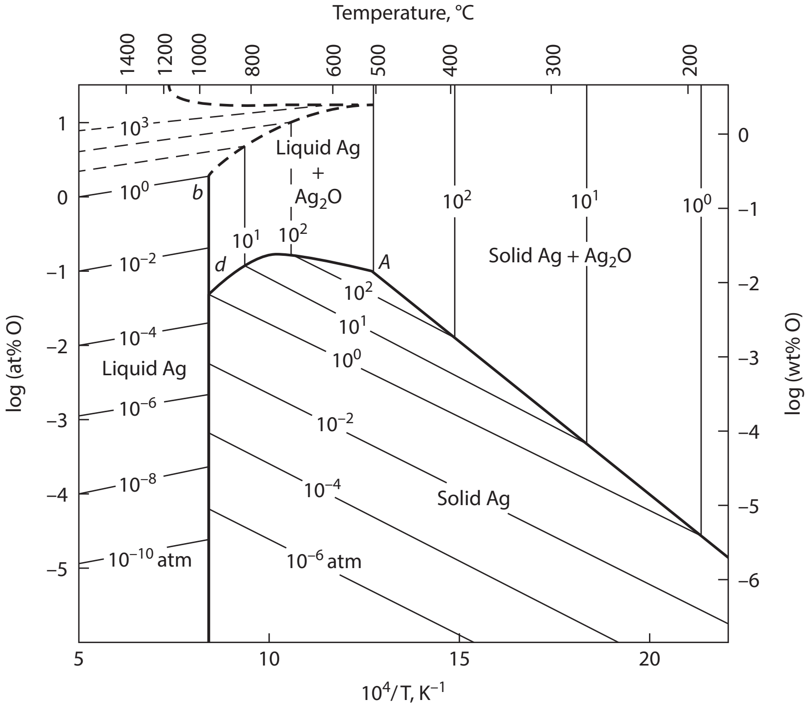
Qualitative Problem 1

a. Find the point *e* in Figure 13.29 and locate its corresponding location on Figure 13.30.
b. What phase(s) is (are) present at point *e*?

c. Apply the Gibbs equilibrium phase rule to the system at this point.
d. What phase(s) is (are) present at point *b* in Figure 13.30?
e. If the temperature is raised slightly at point *b*, what phases will be present?
f. Apply the Gibbs equilibrium phase rule to the system at this slightly higher temperature.

Solution to Qualitative Problem 1

a.



b. $Ag_{(S)}$, $Ag_2O_{(S)}$, and O_2.
c. In Figure 13.29, the pressure is fixed. There is one reaction relating the three phases: $Ag_{(S)} + O_{2(G)} \leftrightarrow Ag_2O_{(S)}$.

Thus,

$$\mathcal{F} = C - R + 1 - \Phi$$

$$\mathcal{F} = 3 - 1 + 1 - 3 = 0$$

The point *e* lies on an invariant temperature.

d. $Ag_{(L)}$, $Ag_2O_{(S)}$, and $O_{2(G)}$.
e. $Ag_{(L)}$, and $O_{2(G)}$.
f. $\mathcal{F} = C - R + 1 - \Phi = 3 - 1 + 1 - 2 = 1$ (the temperature can change or the partial pressure of O_2 can change and the state remains $Ag_{(L)}$ and $O_{2(G)}$.

Qualitative Problem 2

The molar Gibbs free energy of mixing of Al_2O_3 and MgO at 1073 K is shown in Figure 13.17. Delineate the phase fields as the composition varies from $X_{Al_2O_3} = 0$ to $X_{Al_2O_3} = 1$.

Solution to Qualitative Problem 2

$$X_{Al_2O_3} = 0 \quad \text{only } MgO$$

$$0 < X_{Al_2O_3} < 0.5 \quad MgO \text{ and } MgAl_2O_4$$

$$0.5 < X_{Al_2O_3} < 1 \quad MgAl_2O_4 \text{ and } Al_2O_3$$

$$X_{Al_2O_3} = 1 \quad \text{only } Al_2O_3$$

Note: The diagram in Figure 13.17 is only approximate. There must be some solubility (however small) of each of the components in each other as well as in the spinel phase.

13.14 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

100 g of silica and 100 g of graphite are placed in a rigid vessel of volume 20 liters, which is evacuated at room temperature and then heated to 1500°C, at which temperature the quartz and graphite react to form SiC. Calculate

a. The equilibrium partial pressures of CO and SiO in the vessel at 1500°C
b. The mass of SiC formed
c. The mass of graphite consumed to form CO and SiC

Solution to Quantitative Problem 1

The equilibrium attained in the vessel is best seen by constructing the phase stability diagram at 1773 K. In Example 2 in Section 13.4, an isothermal phase stability diagram was constructed using p_{CO} and p_{CO_2} as the independent variables. However, in the present problem, the equilibrium values of p_{CO} and p_{SiO} are required, and thus, the phase stability diagram at 1773 K will be constructed using p_{CO} and p_{SiO} as the independent variables. When CO and SiO exist at equilibrium, the activity of O in the CO equals the activity of O in the SiO. Thus, at a given partial pressure of CO, the activity of C in the CO is fixed, and at a given partial pressure of SiO the activity of Si is fixed. The condensed phases liquid silicon, solid SiC, solid SiO_2, and graphite can exist in the system, and thus, the number of possible equilibria involving two condensed phases and a gas phase is $(4 \times 3)/2 = 6$. However, as was seen in Example 2 in Section 13.4, Si and C cannot exist in equilibrium with one another. The standard molar Gibbs free energies of formation of the four compounds of interest at 1773 K are

Compound	$\Delta G^\circ_{1773\ \text{K}}$, J
$SiO_{2(s)}$	−595,900
$SiO_{(g)}$	−246,100
$SiC_{(s)}$	−56,990
$CO_{(g)}$	−266,900

Each of the five equilibria involving two condensed phases and a gas phase must include CO and SiO.

1. Equilibrium among Si, SiO_2, CO, and SiO

The equilibrium is

$$SiO_2 + C = SiO + CO \tag{i}$$

for which $\Delta G^\circ_{1773\ \text{K}} = 82{,}900$ J . Thus, for this equilibrium,

$$\log p_{\text{Sio}} = -\log p_{\text{CO}} - 2.44$$

which is drawn as line 1 in Figure 13.33. Note that, as both gases occur on the same side of the equation describing the equilibrium, determination cannot be made as to which condensed phase is stable above line 1 and which condensed phase is stable below the line.

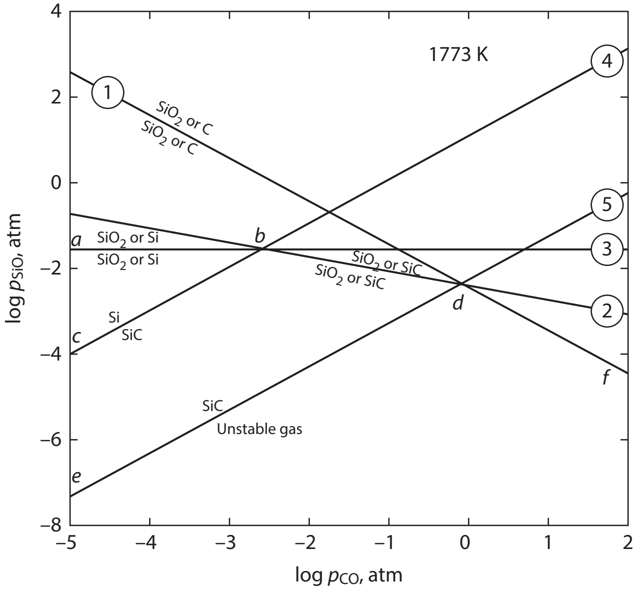


Figure 13.33 Construction of the phase stability diagram for the system Si–C–O at 1773 K.

2. Equilibrium among SiO_2, SiC, SiO, and CO

The equilibrium is

$$2SiO_2 + SiC = 3SiO + CO \tag{ii}$$

for which $\Delta G^\circ_{1773\ \mathrm{K}} = 243{,}590$ J. This gives

$$\log p_{SiO} = -\frac{1}{3}\log p_{CO} - 2.39$$

which is drawn as line 2 in Figure 13.33. Again, a determination cannot be made as to which condensed phase is stable above the line and which is stable below the line.

3. Equilibrium among SiO_2, Si, and SiO

This equilibrium is independent of the pressure of CO and is written as

$$SiO_2 + Si = 2SiO \tag{iii}$$

for which $\Delta G^\circ_{1773\ \mathrm{K}} = 103{,}700$. Thus,

$$\log p_{SiO} = -1.53$$

which is drawn as line 3 in Figure 13.33. Again, indication of the stability of the condensed phases is not given.

4. Equilibrium among Si, SiC, SiO, and CO

The equilibrium is

$$2Si + CO = SiC + SiO \tag{iv}$$

for which $\Delta G^\circ_{1773\ \mathrm{K}} = 36{,}190$ J. Thus, for the equilibrium,

$$\log p_{SiO} = \log p_{CO} + 1.06$$

which is drawn as line 4. In this equilibrium, Si is stable relative to SiC above the line, and SiC is stable relative to Si below the line.

5. Equilibrium among SiC, C, SiO, and CO

The equilibrium is

$$SiC + CO = 2C + SiO \tag{v}$$

for which $\Delta G^{\circ}_{1773,\,\mathrm{K}} = 77{,}790$ J. Thus,

$$\log p_{\mathrm{SiO}} = \log p_{\mathrm{CO}} - 2.29$$

which is drawn as line 5 in Figure 13.33. As carbon exists at unit activity along this line, SiC is stable relative to graphite above the line and an unstable gas occurs below the line.

Inspection of Figure 13.33 shows that

1. SiC is stable relative to Si below the line *bc*.
2. SiC is stable relative to graphite above the line *ed*.
3. SiC or SiO_2 are stable below the line *bd*.

This identifies the area *cbde* as the field of stability of SiC. It is then seen that (1) Si is stable relative to SiC above the line *cb*, and (2) Si or SiO_2 is stable below the line *ab*. This identifies the area *abc* as the field of stability of liquid Si. Thus, (1) SiO_2 is stable relative to Si above the line *ab*, (2) SiO_2 is stable relative to SiC above the line *bd*, and (3) SiO_2 or graphite is stable above the line *df*.

Thus, the field of stability of SiO_2 lies above the line *abdf*, and the phase stability diagram is as shown in Figure 13.34. The phase stability diagram shows that graphite and quartz react with one another to produce SiC until the SiO_2–graphite–SiC equilibrium is reached at the state *A*, which is the intersection of lines 1, 2, and 5 in

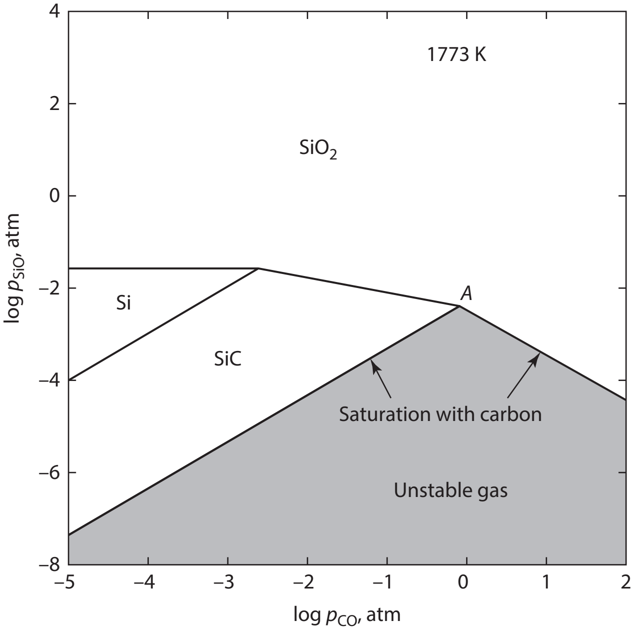


Figure 13.34 The phase stability diagram for the system Si–C–O at 1773 K.

Figure 13.33. Simultaneous solution of the equations of any two of these lines gives the state *A* as

$$\log p_{\mathrm{CO}} = -0.075 \ \left(p_{\mathrm{CO}} = 0.844 \text{ atm}\right)$$

and

$$\log p_{\mathrm{SiO}} = -0.2365 \ \left(p_{\mathrm{SiO}} = 4.32\times 10^{-3}\text{atm}\right)$$

The mass of SiC produced and the mass of graphite consumed are obtained by conducting a mass balance on Si, C, and O. The atomic weights of C, O, and Si are, respectively, 12, 16, and 28.09. Thus, before any reactions begin, the vessel contains 100/60.09 = 1.6642 moles of SiO_2 and 100/12 = 8.3333 moles of C. Thus, the vessel contains 1.6642 moles of Si, 3.3283 moles of O, and 8.3333 moles of C. When reaction equilibrium is attained at 1773 K, the number of moles of CO in the gas phase is calculated as

$$n_{\mathrm{CO}} = \frac{p_{\mathrm{CO}}V}{RT} = \frac{0.844\times 20}{0.082057\times 1773} = 0.1160 \text{ moles}$$

and the number of moles of SiO in the gas phase is

$$n_{\mathrm{SiO}} = \frac{4.315\times 10^{-3}\times 20}{0.082057\times 1773} = 5.9310\times 10^{-4} \text{ moles}$$

Thus, the gas phase contains 0.1160 moles of C, 0.1166 moles of O, and 5.9318×10^{-4} moles of Si. Consequently, at equilibrium the solid phases contain

$$1.6642 - 5.9318\times 10^{-4} = 1.6636 \text{ moles of Si}$$
$$3.3286 - 0.1166 = 3.2120 \text{ moles of O}$$

and

$$8.3333 \quad 0.1160 = 8.2173 \text{ moles of C}$$

All of the oxygen in the solids occurs in the silica, and thus, 3.2120/2 = 1.6060 moles of silicon in the solids occurs in the silica. The remaining 1.6636 – 1.6060 = 0.0576 moles of silicon in the solids occurs in the SiC. Thus, 0.0576 moles, or 0.0576 × 40.09 = 2.31 g of SiC are formed. The number of moles of graphite consumed equals the number of moles of SiC formed plus the number of moles of CO produced; that is, 0.0576 + 1160 = 0.1736 moles, or 0.1736 × 12 = 2.08 g.

The equilibrium partial pressures of CO_2 and O_2, which are, respectively, 5.9×10^{-5} and 1.3×10^{-16} atm, are small enough that the CO_2 and O_2 produced in the gas phase do not need to be included in the mass balance.

Quantitative Problem 2

Determine the conditions under which an Fe–Cr–O melt is in equilibrium with

1. Solid Cr_2O_3
2. Solid $FeO{\cdot}Cr_2O_3$

at 1600°C. For

$$2\mathrm{Cr}_{(s)}+\frac{3}{2}\mathrm{O}_{2(g)}=\mathrm{Cr}_2\mathrm{O}_{3(s)},\qquad \Delta G^{\circ}_{(\mathrm{i})}=-1{,}120{,}300+259.8T\ \mathrm{J} \tag{i}$$

and for

$$\frac{1}{2}\mathrm{O}_{2(g)}=[\mathrm{O}]_{(1\mathrm{wt\%in\,Fe})},\qquad \Delta G^{\circ}_{(\mathrm{ii})}=-111{,}070-5.87T\ \mathrm{J} \tag{ii}$$

Solution to Quantitative Problem 2

At 1600°C, Fe–Cr melts exhibit Raoultian ideality, and the molar heat of melting of Cr, at its equilibrium melting temperature of 2173 K, is 21,000 J. Thus, for $\mathrm{Cr}_{(s)}=\mathrm{Cr}_{(l)}$,

$$\Delta G^{\circ}_{m}=\Delta H^{\circ}_{m}-T\frac{\Delta H^{\circ}_{m}}{T_m}=21{,}000-9.66T\ \mathrm{J}$$

and for $\mathrm{Cr}_{(l)}=[\mathrm{Cr}]_{(1\ \mathrm{wt\%\ in\ Fe})}$,

$$\Delta G=RT\ln\frac{55.85}{100\times 52.01}=-37.70T\ \mathrm{J}$$

Therefore, for $\mathrm{Cr}_{(s)}$ — $[\mathrm{Cr}]_{(1\ \mathrm{wt\%\ in\ Fe})}$,

$$\Delta G^{\circ}_{(\mathrm{iii})}=21{,}000-47.36T\ \mathrm{J} \tag{iii}$$

The standard Gibbs free energy change for the reaction

$$2[\mathrm{Cr}]_{(1\mathrm{wt\%})}+3[\mathrm{O}]_{(1\mathrm{wt\%})}=\mathrm{Cr}_2\mathrm{O}_{3(s)} \tag{iv}$$

is thus

$$\begin{aligned}\Delta G^{\circ}_{(\mathrm{iv})}&=\Delta G^{\circ}_{(\mathrm{i})}-3\Delta G^{\circ}_{(\mathrm{ii})}-2\Delta G^{\circ}_{(\mathrm{iii})}\\&=-829{,}090+372.13T\ \mathrm{J}\\&=-RT\ln\frac{a_{\mathrm{Cr_2O_3}}}{h^2_{\mathrm{Cr(1wt\%)}}\cdot h^3_{\mathrm{O(1wt\%)}}}\end{aligned}$$

or, at 1873 K,

$$\log \frac{h^2_{\mathrm{Cr(1\ wt\%)}} \cdot h^3_{\mathrm{O(1\ wt\%)}}}{a_{\mathrm{Cr_2O_3}}} = -3.68 \tag{v}$$

Saturation of the melt with solid Cr_2O_3 occurs at $a_{\mathrm{Cr_2O_3}} = 1$, and, if the interactions between Cr and O in solution are ignored, and it is assumed that oxygen obeys Henry's law, Equation (v) can be written as

$$\log\left[\mathrm{wt\%\ Cr}\right] = -1.5\log\left[\mathrm{wt\%\ O}\right] - 1.84 \tag{vi}$$

which is the variation of [wt% Cr] with [wt% O] in liquid iron required for equilibrium with solid Cr_2O_3 at 1600°C. Equation (vi) is drawn as line (vi) in Figure 13.35.

For

$$\begin{aligned} \mathrm{Fe}_{(l)} + 2\mathrm{Cr}_{(s)} + 2\mathrm{O}_{2(g)} &= \mathrm{FeO \cdot Cr_2O_{3(s)}} \\ \Delta G^\circ_{\mathrm{(vii)}} &= -1{,}409{,}420 + 318.07T \text{ J} \end{aligned} \tag{vii}$$

and thus, for the reaction

$$\begin{aligned} \mathrm{Fe}_{(l)} + 22[\mathrm{Cr}]_{\mathrm{(1\ wt\%)}} + 4[\mathrm{O}]_{\mathrm{(1\ wt\%)}} &= \mathrm{FeO \cdot Cr_2O_{3(s)}} \\ \Delta G^\circ_{\mathrm{(viii)}} &= \Delta G^\circ_{\mathrm{(vii)}} - 2\Delta G^\circ_{\mathrm{(iii)}} - 4\Delta G^\circ_{\mathrm{(ii)}} \\ &= -1{,}007{,}140 + 436.27T \text{ J} \\ &= -RT\ln \frac{a_{\mathrm{FeO\cdot Cr_2O_3}}}{a_{\mathrm{Fe}} \cdot h^2_{\mathrm{Cr(1\ wt\%)}} \cdot h^4_{\mathrm{O(1\ wt\%)}}} \end{aligned} \tag{viii}$$

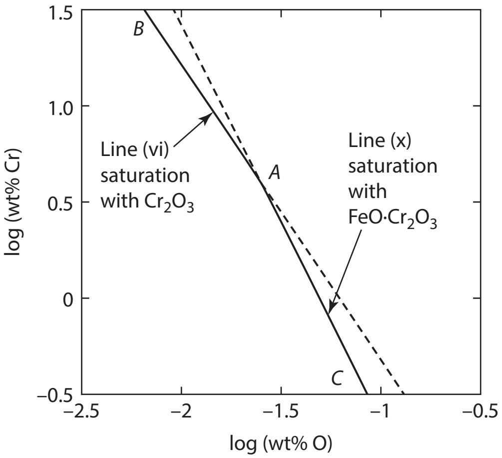


Figure 13.35 The variations of the concentrations of Cr with the concentrations of O in Fe saturated with Cr_2O_3 and $FeO\cdot Cr_2O_3$ at 1600°C.

or, at 1873 K,

$$\log \frac{a_{\mathrm{Fe}} \cdot h^2_{\mathrm{Cr(1\ wt\%)}} \cdot h^4_{\mathrm{O(1\ wt\%)}}}{a_{\mathrm{FeO\cdot Cr_2O_3}}} = -5.30 \tag{ix}$$

Saturation of the melt with $FeO \cdot Cr_2O_3$ occurs at $a_{\mathrm{FeO\cdot Cr_2O_3}} = 1$ and, with the same assumptions as before, and $a_{\mathrm{Fe}} = X_{\mathrm{Fe}} = 1 - X_{\mathrm{Cr}}$, the variation of [wt% Cr] with [wt% O] required for equilibrium with solid $FeO \cdot Cr_2O_3$ at 1600°C is

$$\log\left(1 - X_{\mathrm{Cr}}\right) + 2\log\left[\mathrm{wt\%\ Cr}\right] + 4\log\left[\mathrm{wt\%\ O}\right] = -5.30 \tag{x}$$

In solutions sufficiently dilute that $X_{\mathrm{Fe}} \sim 1$, Equation (x) can be simplified as

$$\log\left[\mathrm{wt\%\ Cr}\right] = -2\log\left[\mathrm{wt\%\ O}\right] - 2.65 \tag{xi}$$

Equation (xi) is drawn as line (x) in Figure 13.35. Lines (vi) and (x) intersect at the point *A*, log [wt% Cr] = 0.59, log [wt% O] = –1.62 (wt% O = 0.024, wt% Cr = 3.89), which is the composition of the melt which is simultaneously saturated with solid Cr_2O_3 and $FeO \cdot Cr_2O_3$. From the phase rule, equilibrium in a three-component system (Fe–Cr–O) among four phases (liquid Fe–Cr–O, solid Cr_2O_3, solid $FeO \cdot Cr_2O_3$, and a gas phase) has one degree of freedom, which, in the present case, has been used by specifying the temperature to be 1873 K. Thus, the activities of Fe, Cr, and O are uniquely fixed, and hence [wt% Cr] and [wt% O] are uniquely fixed. The equilibrium oxygen pressure in the gas phase is obtained from Equation (ii) as

$$\Delta G^\circ_{\mathrm{(ii),1873\ K}} = -122{,}065\ \mathrm{J} = -8.3144 \times 1873 \ln \frac{[\mathrm{wt\%O}]}{p^{1/2}_{O_2}}$$

which, with [wt% O] = 0.024, gives $p_{O_2\,\mathrm{(eq)}} = 8.96 \times 10^{-11}$ atm. The positions of the lines in Figure 13.35 are such that, in melts of [wt% Cr] > 3.89, Cr_2O_3 is the stable phase in equilibrium with saturated melts along the line *AB* and, in melts in which [wt% Cr] < 3.89, $FeO \cdot Cr_2O_3$ is the stable phase in equilibrium with saturated melts along the line *AC*. Alternatively, Cr_2O_3 is the stable phase in equilibrium with saturated melts of [wt% O] < 0.024, and $FeO \cdot Cr_2O_3$ is the stable phase in equilibrium with saturated melts of [wt% O] > 0.024. Consider a melt in which log [wt% Cr] = 1.5. From Figure 13.35, or Equation (vi), the oxygen content at this chromium level required for equilibrium with Cr_2O_3 (at the point *B* in Figure 13.35) is 5.93×10^{-3} wt%, or log [wt% O] = –2.25. From Equation (v), the activity of Cr_2O_3 in this melt with respect to solid Cr_2O_3 is unity, and hence the melt is saturated with respect to solid Cr_2O_3. However, from Equation (ix), in the same melt (i.e., $X_{\mathrm{Fe}} = 0.668$, [wt% Cr] = 31.6, [wt% O] = 0.00593), the activity of $FeO \cdot Cr_2O_3$ with respect to solid $FeO \cdot Cr_2O_3$ is only 0.2. Thus, the melt is saturated with respect to Cr_2O_3 and is undersaturated with respect to $FeO \cdot Cr_2O_3$. Moving along the line *BA* from *B* toward *A*, $a_{\mathrm{Cr_2O_3}} = 1$, and $a_{\mathrm{FeO\cdot Cr_2O_3}} = 1$ increases from 0.2 at *B* to unity at *A* in the doubly saturated melt. Consider a melt in which log [wt% Cr] = –0.5. From Figure 13.35, the oxygen content required for saturation with $FeO{\cdot}Cr_2O_3$ is 0.084 wt% (log [wt% O] = −1.075 at the point *C* in Figure 13.35). From Equation (ix), the activity of $FeO{\cdot}Cr_2O_3$ in this melt is unity. However, from Equation (v), the activity of Cr_2O_3 in the melt, with respect to solid Cr_2O_3, is only 0.285. Thus, this melt is saturated with $FeO{\cdot}Cr_2O_3$ and is undersaturated with Cr_2O_3. On moving along the line *CA* from *C* toward *A*, $a_{FeO\cdot Cr_2O_3}$ is unity and $a_{Cr_2O_3}$ increases from 0.285 at *C* to unity at *A*.

If the various solute–solute interactions had been considered, Equation (v), with $a_{Cr_2O_3} = 1$, would be written as

$$2\ \log h_{Cr(1\ wt\%)} + 3\ \log h_{O(1wt\%)} = -3.68$$

or

$$2\ \log f_{Cr(1\ wt\%)} + 2\ \log\left[wt\%\ Cr\right] + 3\ \log f_{O\ (1wt\%)} + 3\ \log\left[wt\%\ O\right] = -3.68$$

or

$$2e_{Cr}^{Cr}\cdot[wt\%\ Cr] + 2e_{Cr}^{O}\cdot[wt\%\ O] + 2\log[wt\%\ Cr] + 3e_{O}^{O}\cdot[wt\%\ O]$$
$$+\,3e_{O}^{Cr}[wt\%\ Cr] + 3\log[wt\%\ O] = -3.68$$

With

$$e_{Cr}^{O} = O \qquad e_{O}^{O} = -0.2 \qquad e_{O}^{Cr} = -0.041 \qquad \text{and } e_{Cr}^{O} = -0.13$$

this gives

$$-0.43[wt\%\ O] + 0.0615[wt\%\ Cr] + \log[wt\%Cr]$$
$$+\,1.5\log[wt\%\ O] = -1.84 \qquad \text{(xii)}$$

which is drawn as line (xii) in Figure 13.36.

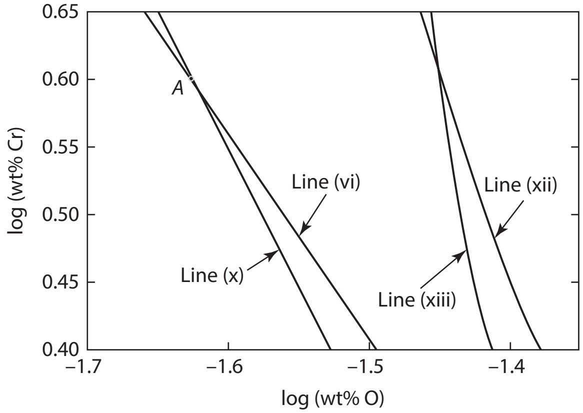


Figure 13.36 Figure 13.35 amended to take into consideration the interactions between the solutes, Cr and O, in liquid Fe.

Similarly, with $a_{\mathrm{FeO\cdot Cr_2O_3}} = 1$, Equation (ix) would be written as

$$\log X_{\mathrm{Fe}} + 2\ \log h_{\mathrm{Cr(1\ wt\%)}} + 4\ \log h_{\mathrm{O(1\ wt\%)}} = -5.30$$

or

$$\log X_{\mathrm{Fe}} + 2e_{\mathrm{Cr}}^{\mathrm{Cr}}\cdot[\mathrm{wt\%\ Cr}] + 2e_{\mathrm{Cr}}^{\mathrm{O}}\cdot[\mathrm{wt\%\ O}] + 2\log[\mathrm{wt\%\ Cr}] + 4e_{\mathrm{O}}^{\mathrm{O}}\cdot[\mathrm{wt\%\ O}]$$
$$+ 4e_{\mathrm{O}}^{\mathrm{Cr}}\cdot[\mathrm{wt\%\ Cr}] + 4\log[\mathrm{wt\%\ Cr}] = -5.30$$

or

$$\log X_{\mathrm{Fe}} - 1.06\ [\mathrm{wt\%\ O}] - 0.164\ [\mathrm{wt\%\ Cr}] + 2\log[\mathrm{wt\%\ Cr}]$$
$$+\ 4\log[\mathrm{wt\%\ O}] = -5.30$$

which is drawn as line (xiii) in Figure 13.36. Lines (xii) and (xiii) intersect at log [wt% Cr] = 0.615, log [wt% O] = −1.455 ([wt% Cr] = 4.12, [wt% O] = 0.035). When the interactions among the solute were ignored, the point of intersection, *A*, was obtained as [wt% Cr] = 3.89, [wt% O] = 0.024.

PROBLEMS

13.1 Air at atmospheric pressure is blown over a Cu-rich copper–gold liquid solution at 1500 K. If only the copper is oxidized (to form pure solid Cu_2O), calculate the minimum activity of Cu which can be obtained in the solution.

13.2 Magnesium can be removed from Mg–Al liquid solution by selectively forming the chloride $MgCl_2$. Calculate the activity of Mg in the liquid Mg–Al system which can be achieved at 800°C by reacting the solution with an H_2–HCl gas mixture containing hydrogen at essentially 1 atm pressure and $p_{\mathrm{HCl}} = 10^{-5}$ atm to form pure liquid $MgCl_2$.

13.3 The partial pressure of oxygen in equilibrium with pure liquid lead and pure liquid lead oxide at 1200 K is 2.16×10^{-9} atm. When SiO_2 is added to the liquid PbO to form a lead silicate melt, the oxygen pressure in equilibrium with pure liquid lead and the silicate melt is decreased to 5.41×10^{-10} atm. Calculate the activity of PbO in the lead silicate melt.

13.4 Copper, present as an impurity in liquid Pb, can be removed by adding PbS to the Cu–Pb alloy and allowing the exchange reaction

$$2\mathrm{Cu}_{(s)} + \mathrm{PbS}_{(s)} = \mathrm{Cu_2S}_{(s)} + \mathrm{Pb}_{(l)}$$

to come to equilibrium.

The solid sulfides are mutually immiscible, Pb is insoluble in solid Cu, and the Cu liquidus, below 850°C, can be represented by

$$\log X_{\mathrm{Cu}} = -\frac{3500}{T} + 2.261$$

where X_{Cu} is the solubility of Cu in liquid Pb. If Cu obeys Henry's law in liquid Pb, calculate the extent to which Cu can be removed from liquid Pb by this process at 800°C. Would the extent of purification of the lead be increased by increasing or by decreasing the temperature?

13.5 A CH_4–H_2 gas mixture at 1 atm total pressure, in which $p_{H_2} = 0.957$ atm, is equilibrated with an Fe–C alloy at 1000 K. Calculate the activity of C with respect to graphite in the alloy. What would the value of p_{H_2} in the gas mixture (at $P_{total} = 1$ atm) have to be in order to saturate the Fe with graphite at 1000 K?

13.6 Calculate the activity of FeO in an FeO–Al_2O_3–SiO_2 melt below which the FeO cannot be reduced to pure liquid iron by a CO–CO_2 mixture of $p_{CO}/p_{CO_2} = 10^5$ at 1600°C.

13.7 A piece of iron is to be heat treated at 1000 K in a CO–CO_2–H_2O–H_2 gas mixture at 1 atm pressure. The gas mixture is produced by mixing CO_2 and H_2 and allowing the equilibrium $CO_2 + H_2 = CO + H_2O$ to establish. Calculate (a) the minimum H_2/CO_2 ratio in the inlet gas which can be admitted to the furnace without oxidizing the iron, (b) the activity of carbon (with respect to graphite) in the equilibrated gas of this initial minimum H_2/CO_2 ratio, (c) the total pressure to which the equilibrated gas would have to be raised to saturate the iron with graphite at 1000 K, and (d) the effect, on the partial pressure of oxygen in the equilibrated gas, of this increase in total pressure.

13.8 An Fe–Mn solid solution containing $X_{Mn} = 0.001$ is in equilibrium with an FeO–MnO solid solution and an oxygen-containing gaseous atmosphere at 1000 K. How many degrees of freedom does the equilibrium have? What is the composition of the equilibrium oxide solution, and what is the partial pressure of oxygen in the gas phase? Assume that both solid solutions are Raoultian in their behavior.

13.9 The elements A and B, which are both solid at 1000°C, form two stoichiometric compounds A_2B and AB_2, which are also both solid at 1000°C. The system A–B does not contain any solid solutions. A has an immeasurably small vapor pressure at 1000°C, and, for the change of state $B_{(s)} = B_{(v)}$,

$$\Delta G^\circ = 187{,}220 - 108.80T \text{ J}$$

The vapor pressure exerted by an equilibrated AB_2–A_2B mixture is given by

$$\log p(\text{atm}) = -\frac{11{,}242}{T} + 6.53$$

and the vapor pressure exerted by an equilibrated A–A_2B mixture is given by

$$\log p(\text{atm}) = -\frac{12{,}603}{T} + 6.9$$

From these data, calculate the standard Gibbs free energies of formation of A_2B and AB_2.

13.10 For the change of standard state $V_{(s)} = V_{(1\text{ wt\% in Fe})}$

$$\Delta G^\circ = -15{,}480 - 45.61T \text{ J}$$

Calculate the value of γ_V° at 1600°C. If a liquid Fe–V solution is equilibrated with pure solid VO and a gas containing $p_{O_2} = 4.72 \times 10^{-10}$ atm, calculate the activity of V in the liquid solution (a) with respect to solid V as the standard state, (b) with respect to liquid V as the standard state, (c) with respect to the Henrian standard state, and (d) with respect to the 1 wt% in iron standard state.

13.11 When an Fe–P liquid solution is equilibrated at 1900 K with solid CaO, solid $3CaO \cdot P_2O_5$, and a gas phase containing $p_{O_2} = 10^{-10}$ atm, the activity of P in the iron, with respect to the 1 wt% in Fe standard state, is 20. Given that $\Delta G^\circ_{1900\ K} = -564{,}600$ J for

$$3CaO_{(s)} + P_2O_{5(g)} = 3CaO \cdot P_2O_{5(s)}$$

and $AG^\circ = -122{,}200 - 19.22T$ J for

$$\frac{1}{2}P_{2(g)} = P_{(1\ wt\%\ in\ Fe)}$$

calculate $\Delta G^\circ_{1900\ K}$ for the reaction

$$P_{2(g)} + \frac{5}{2}O_{2(g)} = P_2O_{5(g)}$$

13.12 Liquid iron, contained in an Al_2O_3 crucible under a gaseous atmosphere of $p_{O_2} = 3 \times 10^{-12}$ atm at 1600°C, contains its equilibrium contents of dissolved oxygen and aluminum. To what value must p_{O_2} be raised in order that solid hercynite ($FeO \cdot Al_2O_3$) appears in equilibrium with the melt and with solid Al_2O_3? What is the activity of Al (with respect to the 1 wt% in Fe standard state) in this state? How many degrees of freedom does this equilibrium have at 1600°C? Given

$$\frac{1}{2}O_{2(g)} = O_{(1\ wt\%\ in\ Fe)} \Delta G^\circ = -111{,}070 - 5.87T\ \text{J}$$

$$Al_{(l)} = Al_{(1\ wt\%\ in\ Fe)} \Delta G^\circ = -43{,}100 - 32.26T\ \text{J}$$

$$FeO \cdot Al_2O_{3(s)} = Fe_{(l)} + O_{(1\ wt\%\ in\ Fe)} + Al_2O_{3(s)}$$
$$\Delta G^\circ = 146{,}230 - 54.35T\ \text{J}$$

13.13 UC_2 can be equilibrated with UC and C at high temperature and can be equilibrated with U_2C_3 and C at lower temperatures. Calculate the maximum and minimum temperatures at which UC_2 can exist.

13.14 In the Pigeon process for the production of magnesium, dolomite ($CaO \cdot MgO$) is reduced by silicon to form magnesium vapor and $2CaO \cdot SiO_2$. Calculate the equilibrium pressure of magnesium vapor produced by this reaction at 1200°C. The Gibbs free energy of formation of dolomite from CaO and MgO is small enough that it can be ignored.

13.15 What is the minimum value that the activity of MgO can have in $MgO \cdot Al_2O_3$ at 1000°C?

13.16 A mixture of ZnO and graphite is placed in an evacuated vessel and heated to 1200 K. Calculate the partial pressures of Zn, CO, and CO_2 that are developed.

13.17 An assemblage of solid CaO, MgO, $3CaO{\cdot}Al_2O_3$, and liquid Al exerts an equilibrium vapor pressure of Mg of 0.035 atm at 1300 K. Write the equation for the appropriate reaction equilibrium. Calculate the standard Gibbs free energy of formation of $3CaO{\cdot}Al_2O_3$ from CaO and Al_2O_3 and the activity of Al_2O_3 in CaO-saturated $3CaO{\cdot}Al_2O_3$ at 1300 K.

13.18 An iron–carbon melt containing 0.5 wt% C is prepared in an alumina crucible under an atmosphere of $p_{CO} = 1$ atm at 1600°C. Calculate the equilibrium concentrations of O and Al in the melt (a) ignoring all solute–solute interactions and (b) considering the solute–solute interactions. The interaction coefficients are listed in Table 13.1.

13.19 It is required that PbO be eliminated from an ore containing PbO, PbS, and $PbSO_4$ by converting it to PbS or $PbSO_4$ by reaction with an SO_2–O_2 gas. Although the pressure of O_2 in the gas can vary within wide limits, the partial pressure of SO_2 may not be higher than 0.5 atm. Calculate the maximum temperature at which it can be guaranteed that the PbO phase will be eliminated.

13.20 Cementite, Fe_3C, is metastable with respect to carbon-saturated α-iron and graphite at 950 K and 1 atm pressure. Given that the molar volumes of α-Fe, graphite, and Fe_3C at 950 K are, respectively, 7.32, 5.40, and 23.92 cm^3/mole, calculate the pressure, at 950 K, at which Fe_3C is in equilibrium with carbon-saturated α-Fe and graphite. At what temperature, at 1 atm pressure, is carbon-saturated γ-Fe and graphite in equilibrium with cementite?

13.21 An experiment is being conducted on an equilibrated mixture of CaO and $CaCO_3$ contained in a closed vessel at 1200 K. The mixture is contaminated by iron in the form of hematite (Fe_2O_3). The contaminant would not be harmful to the experiment if it occurred as either wustite (FeO) or as cementite (Fe_3C). The necessary changes in the chemical form of the contaminant can be effected by admitting CO gas to the vessel. Calculate the allowable limits of p_{CO} in the vessel for the occurrence of the contaminant as (a) wustite and (b) cementite.

13.22 A Cu–Au alloy of $X_{Cu} = 0.5$ is being annealed at 600°C in deoxidized argon. The argon is deoxidized by being passed over heated pure copper turnings prior to its admission to the annealing furnace. The solid Cu–Au system is virtually regular in its solution behavior, with a molar Gibbs excess free energy of mixing given by

$$G^{XS} = -28{,}280 X_{Cu} X_{Au} \text{J}$$

Assuming that equilibrium is attained in the deoxidizing furnace, calculate the maximum temperature at which the deoxidizing furnace can be operated without causing oxidation of the copper in the Cu–Au alloy being annealed.

13.23 In a dew-point experiment, a Cu–Zn alloy is placed in one end of an evacuated and closed tube and is heated to 900°C. When the other end of the tube is cooled to 740° C, Zn vapor begins to condense. Calculate the activity of Zn in the alloy relative to pure zinc.

13.24 A crucible containing 100.0 g of silver at 1000°C is placed in the reaction chamber of a Sieverts' apparatus. The chamber is evacuated and filled with 50 cm^3 (STP) of argon, which measures the dead volume of the chamber. An external

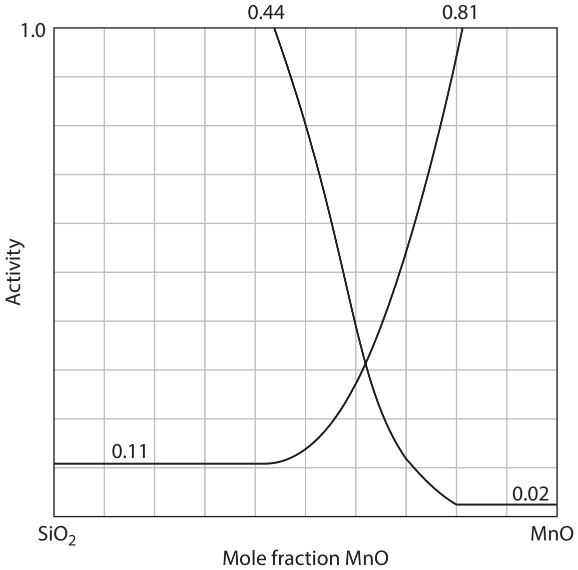


Figure 13.37 Activities in the system MnO–SiO_2 at 1600°C.

manometer reads the pressure of argon as 0.9 atm. The chamber is reevacuated and filled with oxygen, and it is found that 251.5 cm^3 (STP) are required to produce a gas pressure of 0.9 atm in the chamber. Calculate the solubility of O in the Ag (as atom percent) and calculate the value of the Sieverts' law constant at 1000°C.

13.25 Silicon and manganese are commonly used together as deoxidizers for liquid steel. At 1600°C,

$$[\mathrm{Mn}]_{(1\ \mathrm{wt\%\ in\ Fe})} + [\mathrm{O}]_{(1\ \mathrm{wt\%\ in\ Fe})} = \mathrm{MnO}_{(s)} \qquad K = 23.5$$
$$[\mathrm{Si}]_{(1\ \mathrm{wt\%\ in\ Fe})} + 2[\mathrm{O}]_{(1\ \mathrm{wt\%\ in\ Fe})} = \mathrm{SiO}_{2(s)} \qquad K = 27{,}840$$

The values of the equilibrium constants show that SiO_2 is considerably more stable than MnO. Why, then, is a mixture of Mn and Si more effective as a deoxidizing agent than Si alone? The activities of MnO and SiO_2, with respect to solids as the standard states in MnO–SiO_2 melts at 1600°C, are shown in Figure 13.37.

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CHAPTER 14

Electrochemistry

14.1 INTRODUCTION

All chemical reactions, in which products form from reactants, involve changes in the state of oxidation, or *valence state*, of some or all of the participating atoms. By convention, the valence state of an atom in a compound is determined by the number of electrons which surround the nucleus of the atom. The assignment of a valence state is not influenced by the nature of the bonding between the constituent atoms. For example, the bonding in the HF molecule is considered to be 50% ionic in character and 50% covalent in character. Here, *ionic character* implies complete electron transfer from the H atom to the F atom to form the ions H^+ and F^-, and the *covalent character* implies complete electron sharing to give a normal covalent HF molecule, which has zero electric dipole moment. Nevertheless, the valence states of H and F in HF are denoted as +1 and −1 respectively.

Changes in the valence state of an element are caused by the addition or removal of electrons, and thus, the thermodynamic driving force of any reaction must, in some way, be related to the ease with which the required changes of valence of the participating atoms can occur—that is, to the ease with which the necessary transfer of electrons can occur. For example, the reaction

$$\mathrm{AO} + \mathrm{B} = \mathrm{BO} + \mathrm{A}$$

involves a decrease in the valence state of A from +2 to 0 and an increase in the valence state of B from 0 to +2. The reaction involves the transfer of two electrons from B to A and hence can be written as

$$\mathrm{A}^{2+} + \mathrm{B} = \mathrm{B}^{2+} + \mathrm{A}$$

The change in free energy is thus a manifestation of the energetics of electron transfer. The reaction equation, written as the sum of

$$\mathrm{A}^{2+} + 2e^- = \mathrm{A}$$

and

$$B - 2e^{-} = B^{2+}$$

suggests the possibility of conducting the reaction as shown in Figure 14.1. A mixture of A + AO and a mixture of B + BO are joined by two connections *a* and *b*, where *a* is an electronic conductor through which only electrons can pass and *b* is an ionic conductor through which only oxygen ions can pass. The spontaneous reaction thus occurs in the following manner. Two electrons leave a B atom, travel from right to left along *a* and, on arrival at the A + AO mixture, convert an A^{2+} ion to an A atom. Simultaneously, an O^{2-} ion leaves the A + AO mixture and passes through *b* to the B + BO mixture. Charge neutrality in the overall system is thus maintained, and the overall reaction can be written as

$$A^{2+}O^{2-} + B = B^{2+}O^{2-} + A$$

As a result of its being conducted in an electrochemical manner, this reaction is called an *electrochemical reaction*. The driving force for the transport of electrons along *a* is manifested as an electric voltage (or difference in electric potential) which can be measured by placing an external opposing voltage in the circuit *a* and adjusting this voltage until no electric current flows, at which point the electrochemical reaction ceases. At this point, the external voltage exactly balances the voltage generated by the electrochemical system; that is, the thermodynamic driving force for the chemical reaction is exactly balanced by the externally applied electric driving force. Knowledge of the mathematical relationship between these two types of forces allows the former (ΔG for the reaction) to be measured. Furthermore, whereas in Chapter 12 it was seen that pure A, pure AO, pure B, and pure AO are in thermodynamic equilibrium only at the unique temperature at which the two Ellingham lines intersect (if, indeed, they do intersect), it is now seen that the four phases can be brought into electrochemical equilibrium at any temperature by balancing the chemical driving force with an opposing electric driving force. The properties of systems such as this are examined in this chapter.

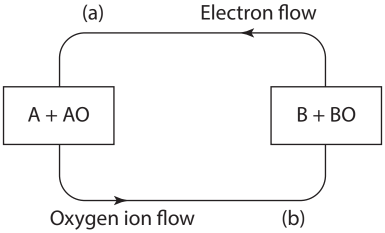

Figure 14.1 A schematic representation of an electrolytic reaction.

14.2 THE RELATIONSHIP BETWEEN CHEMICAL AND ELECTRICAL DRIVING FORCES

In Section 5.4 it was seen that when a system undergoes a reversible process at constant temperature and pressure, the decrease in the Gibbs free energy of the system equals $w'_{\max}$, the work (other than the work of expansion) done by the system. For an increment of such a process,

$$-dG' = \delta w'_{\max}$$

Consider a system which performs electrical work by transporting an electric charge across a voltage difference—that is, from one electric potential to another. The work performed is obtained as the product of the charge transported, q (coulombs), and the electric potential difference, $\Delta\phi$ (volts). The unit of such work is the joule, which is equal to a volt times a coulomb. A system which is capable of performing electrical work as the result of the occurrence of a chemical reaction is called a *galvanic cell*, and the overall chemical reaction is represented by an equation called the *cell reaction*. The charge carried by 1 g-ion (i.e., Avogadro's number of ions) of unit positive charge is 96,487 coulombs and is Faraday's constant (Michael Faraday, 1791–1867), denoted $\mathfrak{f}$. Thus, if dn g-ions of valence z are transported through a voltage difference $\Delta\phi$ maintained between the electrodes of a cell, then

$$\delta w' = z\mathfrak{f}\Delta\phi dn$$

If the transportation is conducted reversibly, in which case the electric potential difference between the electrodes of the cell is called the *electromotive force* (EMF), $\mathscr{E}$, of the cell, then

$$\delta w'_{\max} = z \cdot \mathfrak{f} \cdot \varepsilon \cdot dn = -dG' \qquad (14.1)$$

For the transportation of 1 mole of ions, Equation 14.1 becomes

$$\Delta G = -z\mathfrak{f}\varepsilon \qquad (14.2)$$

which is known as the *Nernst equation*.

Consider the familiar Daniell cell (John Frederick Daniell, 1790–1845) shown in Figure 14.2. This cell consists of a zinc electrode partially immersed into an acidified aqueous solution of $ZnSO_4$ and a copper electrode partially immersed into an acidified aqueous solution of $CuSO_4$. The two aqueous solutions, which constitute the electrolyte of the galvanic cell (i.e., the medium through which ionic current flows), are prevented from mixing by the insertion between them of a porous diaphragm. Consider the processes which occur when a metal is immersed in an electrolyte. The asymmetric forces at the interface between the metal and the electrolyte cause the rearrangement of the solvent dipoles and the charged species in such a manner that the electrolyte side of the interface becomes electrically charged. The

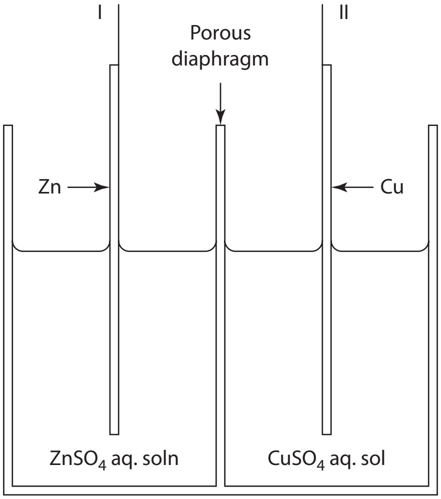

Figure 14.2 The Daniell cell.

electric field produced operates across the interface, and, depending on the direction of the field, free electrons in the metal either move toward or away from the interface until a charge is induced in the metal which is equal and opposite to that on the electrolyte side of the interface. This separation of charge causes the development of a difference in electric potential between the interface and the bulk of the electrolyte far removed from the interface. Figure 14.3a shows the nature of the variation of electric potential with distance away from the interface into the electrolyte when the

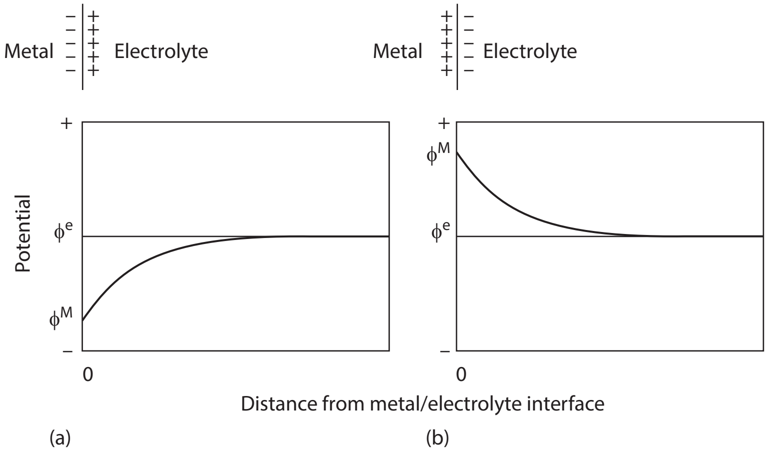

Figure 14.3 A schematic representation of the variation, with distance from a metal/electrolyte interface, of the potential when (a) the metal electrode acquires a negative charge, and (b) when the electrode acquires a positive charge.

metal acquires a negative charge. Figure 14.3b shows the corresponding variation when the metal acquires a positive charge. The difference between the potential at the metal, ϕ^M, and the potential in the bulk of the electrolyte, ϕ^e, is called the *absolute potential* of the electrode. In the Daniell cell, before external electrical contact is made between the electrodes, the zinc electrode acquires an excess of electrons, and the copper has a deficit of electrons. This causes the variation of electric potential from the zinc electrode through the electrolyte to the copper electrode to be as shown schematically in Figure 14.4. The equilibrium

$$\mathrm{Zn}^{2+} + 2e^- = \mathrm{Zn}$$

is established at the zinc–electrolyte interface when

$$\mu_{\mathrm{Zn}}{}^{2+}\left(\text{in the electrolyte}\right) = \mu_{\mathrm{Zn}}{}^{2+}\left(\text{in the electrode}\right)$$

and

$$\mu_{\mathrm{Zn}^{2+}} + 2\mu_{e^-}^{\mathrm{Zn}} = \mu_{\mathrm{Zn}}$$

where:

μ_{Zn} is the chemical potential of the zinc atoms in the electrode
$\mu_{\mathrm{Zn}^{2+}}$ is the chemical potential of the zinc ions in the solution and in the electrode
$\mu_{e^-}^{\mathrm{Zn}}$ is the chemical potential of the electrons in the zinc electrode

It is seen that the value of $\mu_{\mathrm{Zn}^{2+}(\text{in solution})}$, which is determined by the concentration of $\mathrm{ZnSO_4}$ in the solution, determines the equilibrium value of $\mu_{e^-}^{\mathrm{Zn}}$. Similarly, the equilibrium

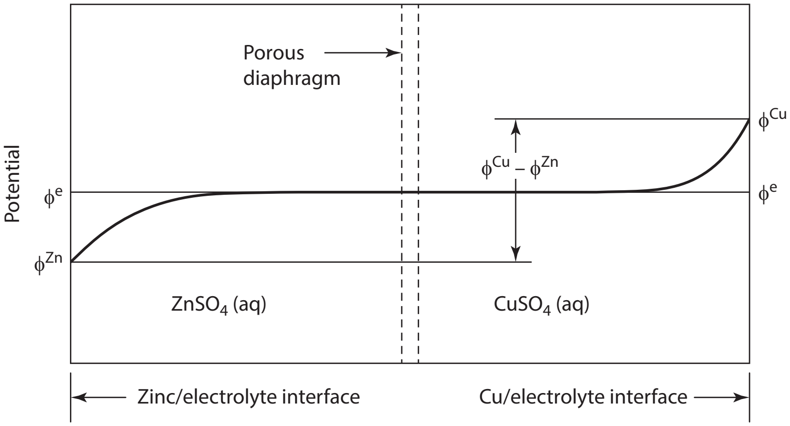

Figure 14.4 A schematic representation of the variation of potential with position in a Daniell cell. The open cell EMF of the cell is given by $\phi^{Cu} - \phi^{Zn}$.

$$\mathrm{Cu}^{2+} + 2e^{-} = \mathrm{Cu}$$

is established at the copper–electrolyte interface when

$$\mu_{\mathrm{Cu}^{2+}}(\text{in the solution}) = \mu_{\mathrm{Cu}^{2+}}(\text{in the copper electrode})$$

and

$$\mu_{\mathrm{Cu}^{2+}} + 2\mu_{e^{-}}^{\mathrm{Cu}} = \mu_{\mathrm{Cu}}$$

Again it is seen that the equilibrium value of $\mu_{e^{-}}^{\mathrm{Cu}}$ is determined by the concentration of $\mathrm{CuSO_4}$ in the electrolyte. If identical pieces of metal wire are joined to each of the electrodes as extensions, as shown in Figure 14.2, then since both the wire–Zn electrode and the wire–Cu electrode are electrical conductors,

$$\mu^{\mathrm{I}} = \mu_{e^{-}}^{\mathrm{Zn}} \quad \text{and} \quad \mu^{\mathrm{II}} = \mu_{e^{-}}^{\mathrm{Cu}}$$

The reversible transfer of *dn* moles of electrons from the electric potential ϕ^{Zn} to the electric potential ϕ^{Cu} involves the performance of work $\delta w'_{\max}$ given by

$$\delta w'_{\max} = z \cdot \mathfrak{f} \cdot (\phi^{Cu} - \phi^{Zn}) \cdot dn$$

The reversible transfer of *dn* moles of electrons from the chemical potential μ^{I} to μ^{II} at constant temperature and pressure also involves the performance of work $\delta w'_{\max}$ and a decrease in the Gibbs free energy, dG', of the system according to

$$\delta w'_{\max} = -dG' = -(\mu^{\mathrm{II}} - \mu^{\mathrm{I}})dn$$

Thus,

$$\left(\mu^{\mathrm{II}} - \mu^{\mathrm{I}}\right) = z\mathfrak{f}(\phi^{\mathrm{Cu}} - \phi^{\mathrm{Zn}}) \tag{14.3}$$

where, for electrons, z has the value of minus unity. Equation 14.3 relates the chemical potential difference and the electric potential difference for electron transfer. The difference $\phi^{\mathrm{Cu}} - \phi^{\mathrm{Zn}}$ is the *open-circuit EMF*, ε, of the Daniell cell.

When an opposing electric potential of magnitude ε is applied externally between the electrodes I and II, the entire system is at equilibrium. This is because the chemical driving force of the cell is exactly balanced by the external opposing voltage. If the magnitude of the external opposing voltage is decreased, equilibrium no longer exists and electronic current flows through the external circuit from I to II, with the equivalent ionic current flowing through the cell. In the Daniell cell, the ionic current through the cell involves the transport of $\mathrm{SO_4^{2-}}$ ions from the solution in the $\mathrm{CuSO_4}$ compartment (the catholyte) to the $\mathrm{ZnSO_4}$ compartment (the anolyte) at a rate equal to that of the addition of Zn^{2+} ions to the anolyte and, hence, equal to the rate of removal of Cu^{2+} ions from the catholyte. As the cell reaction proceeds, the concentration of $CuSO_4$ in the catholyte decreases, and the concentration of $ZnSO_4$ in the anolyte increases. As has been seen, the equilibrium values of μ^{I} and μ^{II}, and hence the value of ε, depend on the concentrations of $ZnSO_4$ and $CuSO_4$ in the electrolyte, and thus, eventually, in the absence of unfavorable kinetic factors, the EMF of the cell decreases to the value of the externally applied opposing voltage, at which point the passage of electric current ceases and a new equilibrium is established. If, however, by appropriate addition and removal, the concentrations of $ZnSO_4$ and $CuSO_4$ in their respective compartments are maintained constant, the cell reaction continues indefinitely. When the externally applied voltage is finitely less than the EMF of the cell, a finite current flows and the cell reaction proceeds irreversibly. In such a situation, less than maximum work is obtained since the electrons in the external circuit are being transported through a smaller difference in voltage. In the limit of decrease of the external voltage—that is, when the external voltage is zero and the cell is short-circuited—the degree of irreversibility of the reaction is maximized, no work is done, and the decrease in the Gibbs free energy of the system appears entirely as thermal energy. This system corresponds to that of placing a piece of zinc in an aqueous solution of $CuSO_4$. For the production of maximum work, the cell must be operated reversibly, in which case the externally applied voltage must be only infinitesimally smaller than the EMF of the cell, giving an infinitesimal flow of current in the forward direction. If the cell can be operated reversibly, then an infinitesimal increase in the magnitude of the external voltage reverses the direction of the current flow and the direction of the cell reaction. The cell thus becomes current consuming rather than current producing; that is, it becomes an electrolysis cell instead of a galvanic cell. This scheme is illustrated in Figure 14.5.

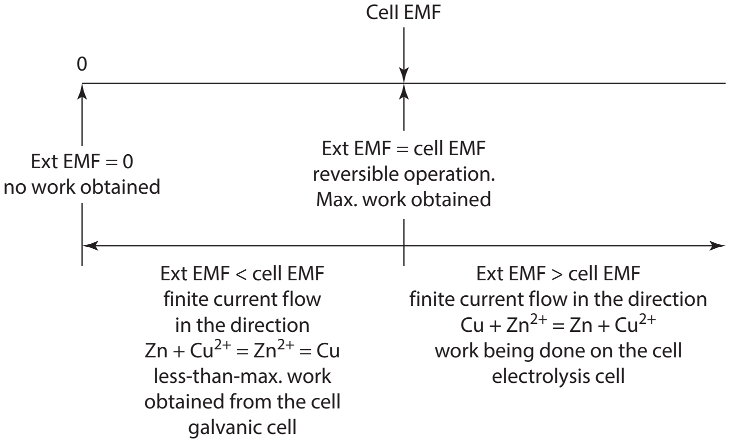

Figure 14.5 The relationship of a current-producing cell (a galvanic cell) to a current-consuming cell (an electrolysis cell).

When operating as a galvanic cell, the anodic oxidation reaction

$$\mathrm{Zn} = \mathrm{Zn}^{2+} + 2e^-$$

occurs at the Zn anode and the cathodic reduction reaction

$$\mathrm{Cu}^{2+} + 2e^- = \mathrm{Cu}$$

occurs at the Cu cathode. The overall cell reaction is the sum of these, which gives

$$\mathrm{Zn} + \mathrm{CuSO_4} = \mathrm{Cu} + \mathrm{ZnSO_4}$$

In shorthand notation, this is written as

$$\mathrm{Zn}\ \Big|\ \mathrm{Zn}^{2+}(\text{aqueous solution})\ \vdots\ \mathrm{Cu}^{2+}(\text{aqueous solution})\ \Big|\ \mathrm{Cu}$$

where the full vertical lines indicate phase boundaries in the cell and the dashed vertical line represents the porous diaphragm separating the two aqueous solutions.

14.3 THE EFFECT OF CONCENTRATION ON EMF

In the preceding section, it was seen that the EMF of a Daniell cell is dependent on the concentrations of $CuSO_4$ and $ZnSO_4$ in the catholyte and anolyte, respectively. The quantitative relationship between the concentration, or correctly, the activity, and the EMF can be introduced as follows. Consider the reaction

$$\mathrm{Zn} + \mathrm{CuSO_4} = \mathrm{Cu} + \mathrm{ZnSO_4}$$

Although it was assumed that the reaction, as written, proceeds spontaneously from left to right, the direction depends on the states of the reactants and products. Consider the reactants and products to occur in their standard states at 298 K. Then,

$$\mathrm{Zn}_{(s)} + \mathrm{CuSO_4}(\text{saturated aqueous solution})$$

$$= \mathrm{Cu}_{(s)} + \mathrm{ZnSO_4}(\text{saturated aqueous solution})$$

which is thermodynamically equivalent to

$$\mathrm{Zn}_{(s)} + \mathrm{CuSO4}_{(s)} = \mathrm{Cu}_{(s)} + \mathrm{ZnSO4}_{(s)}$$

At 298 K, $\Delta G = \Delta G^\circ_{298\ \mathrm{K}} = -213{,}040\ \mathrm{J}$, and thus, from Equation 14.2,

$$\varepsilon^\circ = -\frac{\Delta G^\circ}{z\mathfrak{f}} = \frac{213{,}040}{2 \times 96{,}487} = 1.104 \text{ volts}$$

where ε°, being the EMF of the cell when the reactants and products occur in their designated standard states, is termed the *standard EMF* of the cell. Thus, when Zn is immersed in a saturated aqueous solution of $ZnSO_4$ and Cu is immersed into a saturated aqueous solution of $CuSO_4$, the externally applied voltage which is required to balance the chemical driving force of the cell reaction at 298 K is 1.104 volts.

For the general reaction

$$aA + bB = cC + dD$$

when the reactants and products do not occur in their standard states,

$$\Delta G' = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \tag{13.4}$$

and, from Equation 14.2, the EMF of the cell in which the preceding reaction is occurring electrochemically is

$$\varepsilon = \varepsilon^\circ - \frac{RT}{z\mathfrak{f}} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \tag{14.4}$$

Thus, with pure Zn and Cu in the Daniell cell, the EMF is given as

$$\varepsilon = \varepsilon^\circ - \frac{RT}{2\mathfrak{f}} \ln \frac{a_{\mathrm{ZnSO_4}}}{a_{\mathrm{CuSO_4}}}$$

which, at 298 K, gives

$$\varepsilon = 1.104 - 0.0296 \log \frac{a_{\mathrm{ZnSO_4}}}{a_{\mathrm{CuSO_4}}}$$

In order that the EMF of the cell be zero, the activity quotient must be

$$10^{\frac{1.104}{0.0296}} = 1.98 \cdot 10^{37}$$

Thus, if the $ZnSO_4$ solution is saturated (i.e., $a_{\mathrm{ZnSO_4}} = 1$), then it is required that the activity of $CuSO_4$ in the catholyte, with respect to the saturated solution as the standard state, be 5×10^{-38} in order that the occurrence of equilibrium does not require a backing EMF in the external circuit between the electrodes. The concentration gradient which exists across the porous diaphragm causes the diffusion of ions from one compartment to the other, and since diffusion is an irreversible process, the concentration gradient gives rise to a potential known as the *liquid junction potential*. This liquid junction potential must be minimized by such means as the use of a *salt bridge* between the anolyte and the catholyte.

14.4 FORMATION CELLS

An example of a cell without a liquid junction is the cell

$$Pb_{(l)}\big|\,PbO_{(l)}\big|\;O_{2(g)},(Pt)$$

in which the anode is liquid lead, the cathode is oxygen gas bubbled over an inert platinum wire immersed into the electrolyte, and the electrolyte is liquid lead oxide. In this cell, the driving force of the cell reaction

$$Pb_{(l)} + \frac{1}{2}O_{2(g)} = PbO_{(l)}$$

can be balanced by application of an opposing voltage between the electrodes. Such a cell, which is an example of a formation cell, is illustrated in Figure 14.6.*

At the liquid lead anode,

$$Pb = Pb^{2+} + 2e^{-}$$

and at the oxygen cathode,

$$\frac{1}{2}O_2 + 2e^{-} = O^{2-}$$

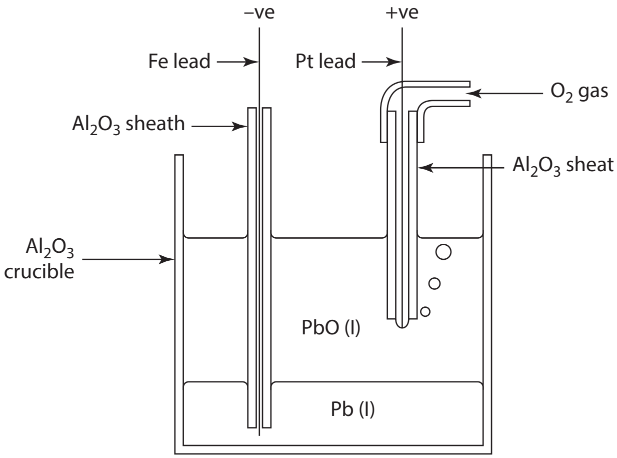

Figure 14.6 A lead oxide formation cell.

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* R. Sridhar and J. H. E. Jeffes, "Thermodynamics of PbO and PbO–SiO$_2$ Melts," *Trans. Inst. Mining Met.* (1967), vol. 76, p. C44.

With a pure liquid lead anode, pure liquid PbO electrolyte, and oxygen gas at 1 atm pressure at the cathode, the standard Gibbs free energy of formation of lead oxide is obtained as

$$\Delta G^\circ = -2\mathfrak{F}\varepsilon^\circ$$

Maintaining the oxygen pressure constant at 1 atm and varying the temperature of the cell facilitate the determination of the variation of ΔG° with T. The addition to the electrolyte of a second oxide which

1. Must be chemically more stable than PbO and
2. Must not introduce any electronic conductivity (e.g., SiO_2)

influences the EMF of the cell according to

$$\varepsilon = \varepsilon^\circ - \frac{RT}{2\mathfrak{F}} \ln \frac{a_{\mathrm{PbO(in\ PbO-SiO_2)}}}{p_{O_2}^{1/2}}$$

Thus, measurement of the EMF of the cell as a function of the concentration of PbO in the lead silicate from pure PbO to saturation with SiO_2 allows the determination of the variation of a_{PbO} with composition. Hence, via the Gibbs–Duhem relationship, the variation of $a_{\mathrm{SiO_2}}$ with composition can also be determined. The variation of ε° with temperature and composition of the lead silicate melts, obtained by Sridhar and Jeffes, are shown in Figure 14.7. The variation of ε° with temperature (the line in Figure 14.7 for $X_{\mathrm{PbO}} = 1$) gives

$$\Delta G^\circ = -191{,}600 + 79.08T \text{ J}$$

for the cell reaction

$$\mathrm{Pb}_{(l)} + \frac{1}{2}\mathrm{O}_{2(g)} = \mathrm{PbO}_{(l)}$$

14.5 CONCENTRATION CELLS

A cell which has identical electrodes inserted into solutions differing only in concentration is called a *concentration cell*. Consider the cell

Cu | $CuSO_4$ (aq. sol'n, low concentration) | $CuSO_4$ (aq. sol'n, high concentration) | Cu

The cell reaction is

$$\mathrm{CuSO_4}\left(\text{at high concentration}\right) \rightarrow \mathrm{CuSO_4}\left(\text{at low concentration}\right)$$

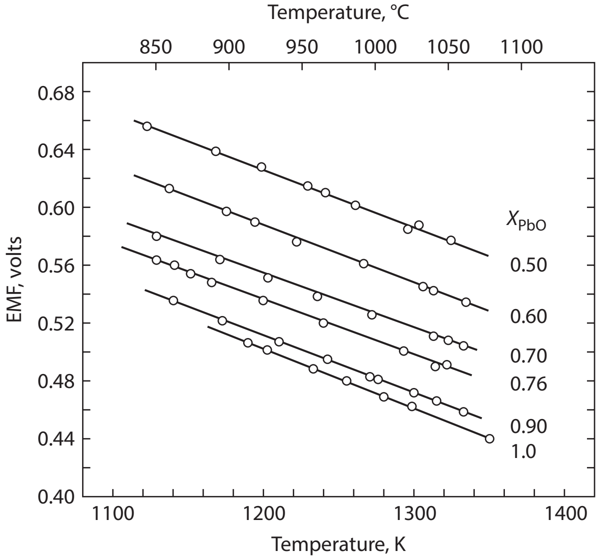

Figure 14.7 The variation, with temperature and silica of the electrolyte, of the EMF of the cell $PbO_{(l)}$ | $PbO–SiO_{2(l)}$ | $O_{2(1\ atm)}$, Pt. (R. Sridhar and J. H. E. Jeffes, op. cit.)

that is, the spontaneous process is the dilution of $CuSO_4$. The standard EMF of such a cell is zero, and thus, the EMF is

$$\varepsilon = -\frac{RT}{2\mathfrak{f}}\ln\frac{a_{CuSO_4}(\text{low concentration})}{a_{CuSO_4}(\text{high concentration})}$$

If one of the aqueous solutions (say the high-concentration solution) contains $CuSO_4$ in its standard state, then

$$\varepsilon = -\frac{RT}{2\mathfrak{f}}\ln a_{CuSo_4(\text{low concentration})} = \frac{\Delta\bar{G}^M_{CuSO_4}}{2\mathfrak{f}}$$

Thus, an electrochemical measurement allows the determination of the partial molal Gibbs free energy of solution of $CuSO_4$ in water. Such a cell suffers from the disadvantage of having a liquid junction potential.

A form of concentration cell of considerable importance in materials applications is the oxygen concentration cell which uses lime-stabilized zirconia as a solid electrolyte. The phase diagram for the system ZrO_2–CaO, presented as Figure 14.8, shows that the substitution of Ca^{2+} ions for Zr^{4+} ions stabilizes the high-temperature cubic polymorph of ZrO_2, and solid solutions containing up to 20 mole percent CaO can be formed. Electroneutrality in the solid solution requires that an oxygen vacancy be formed in the crystal lattice for every substitution of Ca^{2+} for Zr^{4+}, and

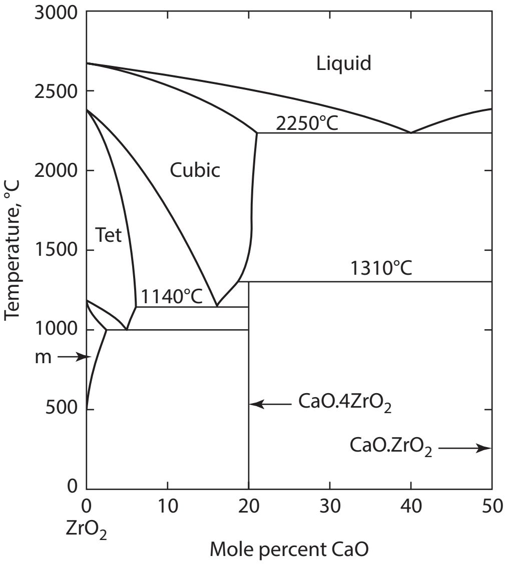

Figure 14.8 The phase diagram for the system ZrO_2–CaO (m = monoclinic polymorph, tet = tetragonal polymorph).

thus, when the stabilized cubic zirconia contains x mole percent of CaO, $0.5x\%$ of the oxygen lattice sites are vacant; for example, with 20 mole percent CaO, 10% of the oxygen sites in the crystal lattice are vacant. This causes the diffusivity of oxygen in the solid solution to be high enough that, within certain ranges of oxygen pressure and temperature, the cubic solid solution is an ionic conductor in which the oxygen ion is the only mobile species. Thus, a cell constructed as follows:

$$O_2\left(g,\ \text{lower pressure I}\right),\ \text{Pt}\ \middle|\ \text{CaO}-\text{ZrO}_2\middle|\ \text{Pt},\ O_2\ \left(g,\ \text{higher pressure II}\right)$$

in which the cell reaction is

$$O_2\left(g,\ \text{pressure II}\right) \rightarrow O_2\left(g,\ \text{pressure I}\right)$$

has the EMF

$$\varepsilon = -\frac{RT}{4\mathfrak{f}}\ln\frac{p_{O_2(\mathrm{I})}}{p_{O_2(\mathrm{II})}}$$

In the operation of the cell, oxygen ions are transported through the electrolyte from the cathode to the anode (or oxygen vacancies diffuse in the reverse direction), and electrons are transported through the external circuit from the anode to the cathode.

The oxygen pressures at the electrodes can be fixed by using metal–metal oxide couples; for example, using the couples X–XO and Y–YO, the cell becomes

$$\mathrm{X}\,\big|\,\mathrm{XO}\,\big|\,\mathrm{CaO-ZrO_2}\,\big|\,\mathrm{YO}\,\big|\,\mathrm{Y}$$

At the temperature *T*, the lower anode oxygen pressure $p_{\mathrm{O_2\,(X/XO)}}$ is fixed by the establishment of the chemical equilibrium

$$\mathrm{X}_{(s)}+\frac{1}{2}\mathrm{O}_{2(g)}=\mathrm{XO}_{(s)}$$

and the higher cathode oxygen pressure $p_{\mathrm{O_2\,(Y/YO)}}$ is fixed by the establishment of the chemical equilibrium

$$\mathrm{Y}_{(s)}+\frac{1}{2}\mathrm{O}_{2(g)}=\mathrm{YO}_{(s)}$$

Thus, the anode half-cell reaction can equivalently be regarded as being

$$\mathrm{X}+\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,X/XO)}})=\mathrm{XO}$$

or

$$\mathrm{O}^{2-}-2e^{-}=\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,X/XO)}})$$

and, similarly, the cathode half-cell reaction can equivalently be regarded as being

$$\mathrm{YO}=\mathrm{Y}+\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,Y/YO)}})$$

or

$$\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,Y/YO)}})+2e^{-}=\mathrm{O}^{2-}$$

The cell reaction is thus

$$\mathrm{YO}+\mathrm{X}=\mathrm{XO}+\mathrm{Y} \tag{i}$$

or

$$\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,Y/YO)}})=\frac{1}{2}\mathrm{O_2}(\mathrm{at}\;p_{\mathrm{O_2\,(eq.}T\mathrm{,X/XO)}}) \tag{ii}$$

Thus, whereas the chemical equilibrium between the pure reactants and products

$$\mathrm{YO}+\mathrm{X}=\mathrm{XO}+\mathrm{Y}$$

could be obtained only at the single invariant temperature (e.g, at T_E in Figure 12.4) in which state

$$p_{O_2(\mathrm{eq.}T,\mathrm{X/XO})} = p_{O_2(\mathrm{eq.}T,\mathrm{Y/YO})}$$

the electrochemical equilibrium

$$\mathrm{YO} + \mathrm{X} = \mathrm{XO} + \mathrm{Y}$$

can be obtained at any temperature (within the limits imposed by the performance of the ZrO_2–CaO electrolyte) by placing an external voltage in opposition to the chemical driving force of the cell. For either Equation (i) or (ii), the chemical driving force is

$$\Delta G = RT \ln \frac{p^{1/2}{}_{O_2(\mathrm{eq.}T,\mathrm{X/XO})}}{p^{1/2}_{O_2(\mathrm{eq.}T,\mathrm{Y/YO})}}$$

and hence the cell EMF is

$$\varepsilon = -\frac{RT}{2\mathfrak{F}} \ln \frac{p^{1/2}_{O_2(\mathrm{eq.}T,\mathrm{X/XO})}}{p^{1/2}_{O_2(\mathrm{eq.}T,\mathrm{Y/YO})}}$$

or

$$\varepsilon = -\frac{RT}{4\mathfrak{F}} \ln \frac{p_{O_2(\mathrm{eq.}T,\mathrm{X/XO})}}{p_{O_2(\mathrm{eq.}T,\mathrm{Y/YO})}} \tag{iii}$$

If one of the metals—say, X—is dissolved in an inert solvent, where the requirement for “inertness” is that the equilibrium oxygen pressure for the solvent metal–solvent metal oxide equilibrium is considerably higher than $p_{O_2(\mathrm{eq.}T,\mathrm{X/XO})}$, then the activity of X in the alloy can be obtained as follows. If X in solution is denoted $\underline{\mathrm{X}}$, then the EMF of the cell

$$\mathrm{X} \mid \mathrm{XO} \mid \mathrm{CaO} - \mathrm{ZrO_2} \mid \mathrm{Y} \mid \mathrm{YO}$$

is

$$\varepsilon' = -\frac{RT}{4\mathfrak{F}} \ln \frac{p_{O_2(\mathrm{eq.}T,\underline{\mathrm{X}}/\mathrm{XO})}}{p_{O_2(\mathrm{eq.}T,\mathrm{Y/YO})}} \tag{iv}$$

At the temperature T,

$$a_{\mathrm{X}} p^{1/2}_{O_2(\underline{\mathrm{X}},\mathrm{XO})} = p^{1/2}_{O_2(\mathrm{X},\mathrm{XO})}$$

combination of Equations (iii) and (iv) gives

$$\varepsilon - \varepsilon' = -\frac{RT}{4\mathfrak{F}} \ln a_{\mathrm{X}}$$

and thus, measurement of the variation of ε' with composition of the alloy allows the determination of the activity–composition relationship of X in the alloy. More simply, if the cell is

$$\mathrm{X} \mid \mathrm{XO} \mid \mathrm{CaO-ZrO_2} \mid \underline{\mathrm{X}} \mid \mathrm{XO}$$

then

$$\varepsilon = \frac{RT}{2\mathfrak{F}} \ln \frac{p^{1/2}_{\mathrm{O_2}(\mathrm{eq}.T,\underline{\mathrm{X/XO}})}}{p^{1/2}_{\mathrm{O_2}(\mathrm{eq.T,X/XO})}} = -\frac{RT}{2\mathfrak{F}} \ln a_{\mathrm{X}} = -\frac{\Delta \overline{G}^{M}_{X}}{2\mathfrak{F}}$$

Similarly, if the metal oxide XO is dissolved in an inert oxide solvent, then, denoting dissolved XO as XO, for the cell

$$\mathrm{X} \mid \underline{\mathrm{XO}} \mid \mathrm{CaO-ZrO_2} \mid \mathrm{X} \mid \mathrm{XO}$$

$$\varepsilon = -\frac{RT}{2\mathfrak{F}} \ln \frac{p^{1/2}_{\mathrm{O_2}(\mathrm{eq}.T,\mathrm{X}/\underline{\mathrm{XO}})}}{p^{1/2}_{\mathrm{O_2}(\mathrm{eq}.T,\mathrm{X}/\underline{\mathrm{XO}})}}$$

and, as

$$a_{\mathrm{XO}} = \frac{p^{1/2}_{\mathrm{O_2}(\mathrm{eq}.T,\mathrm{X}/\underline{\mathrm{XO}})}}{p^{1/2}_{\mathrm{O_2}(\mathrm{eq}.T,\mathrm{X/XO})}}$$

then

$$\varepsilon = -\frac{RT}{2\mathfrak{F}} \ln a_{\mathrm{XO}}$$

This technique has been used by Kozuka and Samis* to measure the activities of PbO in the melt in the system PbO–SiO_2 using the cell

$$\mathrm{Pb}_{(l)} \mid \mathrm{PbO}_{(l,\mathrm{in\ pbO-SiO_2})} \mid \mathrm{CaO-ZrO_2} \mid \mathrm{Pb}_{(l)} \mid \mathrm{PbO}_{(l)}$$

Their experimental cell is illustrated in Figure 14.9, and their results, at 1000°C, are shown, in comparison with those obtained by Sridhar and Jeffes, in Figure 14.10.

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* Z. Kozuka and C. S. Samis, "Thermodynamic Properties of Molten PbO–SiO_2 Systems," *Met. Trans. AIME* (1970), vol. 1, p. 871.

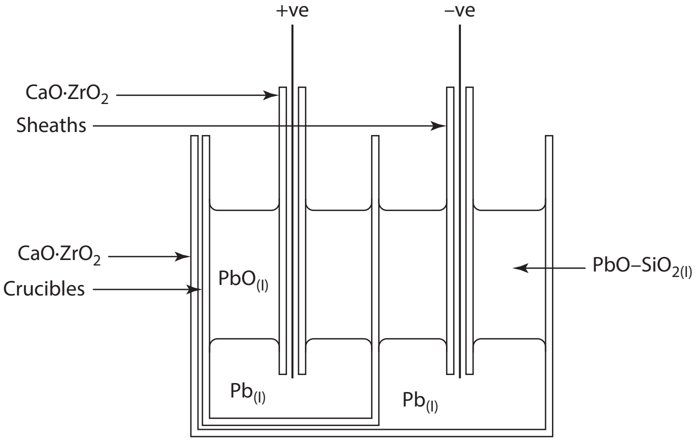

Figure 14.9 A lead oxide concentration cell using stabilized zirconia as the solid-state electrolyte.

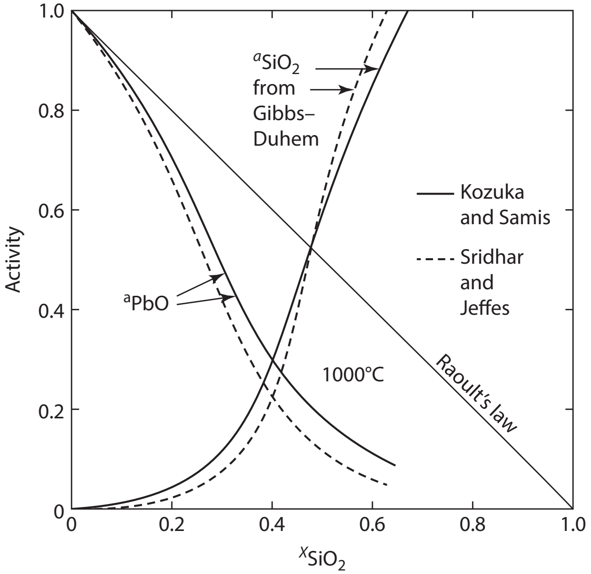

Figure 14.10 The activities of PbO in liquid PbO–SiO$_2$ determined from a PbO concentration cell. (From: Z. Kozuka and C. S. Samis, op. cit.

14.6 THE TEMPERATURE COEFFICIENT OF THE EMF

For any cell reaction at constant temperature and pressure,

$$\Delta G = -z\mathfrak{F}\varepsilon$$

Differentiation with respect to temperature at constant pressure gives

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -z\mathfrak{F}\left(\frac{\partial \varepsilon}{\partial T}\right)_P = -\Delta S$$

Thus, for the cell reaction,

$$\Delta S = z\mathfrak{F}\left(\frac{\partial \varepsilon}{\partial T}\right)_P \tag{14.5}$$

and

$$\Delta H = -z\mathfrak{F}\varepsilon + z\mathfrak{F}T\left(\frac{\partial \varepsilon}{\partial T}\right)_P \tag{14.6}$$

Thus, from Equation 14.5, the slopes of the lines in Figure 14.7 are equal to $\Delta S/2\mathfrak{F}$ for the cell reaction in the formation cell Pb + ½O_2 = PbO. The slope of the line for $X_{\text{PbO}} = 1$ gives

$$\Delta S_{(a)} = S^\circ_{\text{PbO}(l)} - S^\circ_{\text{Pb}(l)} - \frac{1}{2}S^\circ_{\text{O}_2(g)}$$

and the slopes of the lines for melts of $X_{\text{PbO}} < 1$ give

$$\Delta S_{(b)} = \bar{S}_{\text{PbO at } X_{\text{PbO}}} - S^\circ_{\text{Pb}(l)} - \frac{1}{2}S^\circ_{\text{O}_2(g)}$$

Thus, the partial molal entropy of mixing of PbO in a melt of composition X_{PbO}, $\Delta\bar{S}^M_{\text{PbO}}$, is given by $\Delta S_{(b)} - \Delta S_{(a)}$.

In concentration cells such as

$$\text{A} \,\Big|\, \text{A}^{z+}\text{X}^{z-} \Big|\, \text{A}\ (\text{in an A} - \text{B alloy})$$

since

$$\varepsilon = -\frac{RT}{z\mathfrak{F}}\ln a_{\text{A}}$$

the partial molar properties of A in the A–B alloy are obtained as

$$\Delta\overline{S}_A^M = z\Im\frac{\partial\varepsilon}{\partial T}$$

and

$$\Delta\overline{H}_A^M = -z\Im\varepsilon + z\Im T\frac{\partial\varepsilon}{dT}$$

Alternatively, from measurements on formation cells of the type

$$\mathrm{A}\;\Big|\;\mathrm{A}^{2+}\mathrm{x}^{2-}\Big|\,X_{2(g,1\ \mathrm{atm})}$$

for which

$$\varepsilon_{(\mathrm{i})} = \varepsilon^\circ$$

and measurements on cells of the type

$$\mathrm{A}\ (\mathrm{in\ A-B\ alloy})\;\Big|\;\mathrm{A}^{2+}\mathrm{X}^{2-}\Big|\;\mathrm{X}_{2(g,1\ \mathrm{atm})}$$

for which

$$\varepsilon_{(\mathrm{ii})} = \varepsilon^\circ - \frac{RT}{2\Im}\ln\left(\frac{1}{a_\mathrm{A}}\right)$$

the value of a_A is obtained from

$$\varepsilon_{(\mathrm{ii})} - \varepsilon_{(\mathrm{i})} = \frac{RT}{2\Im}\ln a_\mathrm{A}$$

Variation with temperature then gives

$$\Delta\overline{S}_A^M = 2\Im\frac{\partial}{\partial T}(\varepsilon_{(\mathrm{i})} - \varepsilon_{(\mathrm{ii})})$$

and

$$\Delta\overline{H}_A^M = 2\Im(\varepsilon_{(\mathrm{ii})} - \varepsilon_{(\mathrm{i})}) - 2\Im T\frac{\partial}{\partial T}(\varepsilon_{(\mathrm{ii})} - \varepsilon_{(\mathrm{i})})$$

Belton and Rao* measured the EMFs of the cells

$$\mathrm{Mg}_{(l)}\Big|\;\mathrm{MgCl}_{2(l)}\Big|\;\mathrm{Cl}_{2(g,1\ \mathrm{atm})}$$

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* G. R. Belton and Y. K. Rao, "A Galvanic Cell Study of Activities in Mg–Al Liquid Alloys," *Trans. Met. Soc. AIME* (1969), vol. 245, p. 2189.

and

$$\mathrm{Mg}\left(\mathrm{in\ Mg-Al}\right)_{(l)}\left|\ \mathrm{MgCl}_{2(l)}\right|\ \mathrm{Cl}_{2(g,1\,\mathrm{atm})}$$

in the range of temperature 700°C–1000°C with Mg–Al alloys in the range X_{Mg} = 0.096–0.969. With pure Mg as the anode, they obtained

$$\varepsilon^\circ = 3.135 - 6.5\times10^{-4}T\ \text{(volts)}$$

which gives, for the reaction

$$\mathrm{Mg}_{(l)} + \mathrm{Cl}_{2(g)} = \mathrm{MgCl}_{2(l)}$$

$$\Delta G^\circ = -604{,}970 + 125.4T\ \mathrm{J}$$

They fitted their activities, measured at 1073 K, to Equations (v) and (vi) in Section 13.6.2.

14.7 THERMAL ENERGY (HEAT) EFFECTS

In examining the properties of enthalpy, H, in Chapter 5, it was noted that the change in the enthalpy of a system equals the thermal energy entering or leaving the system during a constant-pressure process only if the work of volume change is the sole form of work performed on or by the system. If an electrochemical reaction is conducted in a galvanic cell, as a result of which electrical work is performed, $\Delta H \neq q_P$.

For a change of state at constant temperature and pressure, Equation 5.6 gave

$$\Delta G = q - w + P\Delta V - T\Delta S$$

$$= q - w' - T\Delta S$$

If $w' = 0$, then, $q = \Delta G + T\Delta S = \Delta H$. But, if the process, which involves the performance of work w', is conducted reversibly, in which case $-w' = -w'_{\max} = \Delta G,$ then

$$q = T\Delta S$$

(Recall that w' is the sum of all non-PV work)

Consider the Daniel cell reaction $\mathrm{Zn} + \mathrm{CuSO_4} = \mathrm{Cu} + \mathrm{ZnSO_4}$. When the reactants and products are in their standard states (pure metals and saturated aqueous solutions), the change in the Gibbs free energy for the cell reaction is

$$\Delta G^\circ = -208{,}800 - 13.9T\ \mathrm{J}$$

If the reaction occurs as a result of placing pure solid zinc into a saturated copper sulfate solution at 25°C, in which case the reaction proceeds spontaneously and w' is zero, then, for the formation of saturated zinc sulfate solid and copper, per mole of the reaction,

$$\Delta H^\circ = -208{,}800 \text{ J}$$

is the thermal energy which *flows from* the system into the constant-temperature heat reservoir. However, if the reaction is conducted reversibly in a Daniell cell, in which case

$$w' = -\Delta G^\circ = 208{,}800 + 13.9 \times 298$$

then $q = T\Delta S = 13.9 \times 298 = +4140$ J is the thermal energy that *is transferred into* the system from the constant-temperature reservoir.

14.8 THE THERMODYNAMICS OF AQUEOUS SOLUTIONS

The composition of an aqueous solution is usually expressed in terms of the molality, m, or the molarity, M, where the molality is the number of moles of solute present per 1000 g of water, and the molarity is the number of moles of solute present in 1 liter of solution. Mole fraction, molality, and molarity are related as follows. Consider an aqueous solution of m_i moles of solute i in 1000 g of H_2O, such that the solution is m_i molal. Since the molecular weight of H_2O is 18, 1000 g of H_2O contains 1000/18 g-moles, and hence,

$$X_i = \frac{n_i}{n_i + n_{H_2O}} = \frac{m_i}{m_i + 1000/18}$$

Consider an M_i molar solution which contains Mi moles of solute i per liter of solution—that is, in 1000ρ g of the solution, where ρ is the density of the solution in g/cm³. The number of g-moles of H_2O in the liter of solutions is $(1000\rho - M_i\mathrm{MW}_i)/18$, where MW_i is the molecular weight of i, and thus,

$$X_i = \frac{n_i}{n_i + n_{H_2O}} = \frac{M_i}{M_i + (1000\rho - M_i\mathrm{MW}_i)/18}$$

As the solution tends toward infinite dilution,

$$m_i \to \frac{1000X_i}{18} \quad \text{and} \quad M_i \to \frac{1000\rho X_i}{18}$$

In dilute solutions, molality and molarity are essentially equal to one another; for example, an aqueous solution of NaCl of $X_{\mathrm{NaCl}} = 10^{-3}$ is 0.0556 molal and 0.0554 molar.

In the case of dilute solutes in liquid metals, it was convenient to define the 1 wt% standard state, and hence the 1 wt% activity scale, as

$$h_{i(1\ wt\%)} \rightarrow [\text{wt\% } i] \quad \text{as} \quad [\text{wt\% } i] \rightarrow 0$$

with the 1 wt% standard state located on the Henry's law line at 1 wt%. It is also convenient, in aqueous solutions, to define the analogous unit molality standard state, and hence unit molality activity scale, as

$$a_{\mathbf{i}(m)} \rightarrow m_i \text{ as } m_i \rightarrow 0$$

where $a_{i(m)}$ is the activity of the solute with respect to the unit molality standard state, and the unit molality standard state is located on the Henry's law line at $m_i = 1$. As before, deviations from ideality are accommodated by introducing an activity coefficient defined as

$$\gamma_{i(m)} = \frac{a_{i(m)}}{m_i}$$

Consider the electrolyte (or salt) A_aY_y, which, when dissolved in water, dissociates to form A^{z+} cations and Y^{z-} cations according to

$$A_aY_y = aA^{z+} + yY^{z-}$$

When m moles of A_aY_y are dissolved in n moles of H_2O, the solution formed can be considered either

1. A solution containing m moles of the component A_aY_y and n moles of H_2O
2. A solution of am moles of A^{z+} and ym moles of Y^{z-} in n moles of H_2O

In case 1, the variation of the Gibbs free energy of the solution with composition at constant T and P is given by Equation 9.16 as

$$dG' = \bar{G}_{A_aY_y}dm + \bar{G}_{H_2O}dn \tag{i}$$

In case 2, the stoichiometry of the dissociation is such that the number of moles of A^{z+}, $m_{A^{z+}}$, is am and the number of moles of Y^{z-}, $m_{Y^{z-}}$, $^{-}$is ym. Thus,

$$dm_{A}{}^{z+} = a\ dm \quad \text{and} \quad dm_{Y^{z-}} = zdm$$

and, at constant T and P,

$$\begin{aligned} dG' \quad &= \bar{G}_{A^{z+}}dm_{A^{z+}} + \bar{G}_{A^{z+}}dm_{A^{z+}} + \bar{G}_{H_2O}dn \\ &= (a\bar{G}_{A^{z+}} + y\bar{G}_{A^{z+}})dm + \bar{G}_{H_2O}dn \end{aligned}$$

By definition,

$$\overline{G}_{\mathrm{A}_a\mathrm{Y}_y} = \left(\frac{\partial G'}{\partial m} \right)_{T,P,n}$$

$$\overline{G}_{\mathrm{A}^{z+}} = \left(\frac{\partial G'}{\partial m_{\mathrm{A}^{z+}}} \right)_{T,P,n,m_{\mathrm{Y}^{z-}}}$$

and

$$\overline{G}_{\mathrm{Y}^{z-}} = \left(\frac{\partial G'}{\partial m_{\mathrm{Y}^{z-}}} \right)_{T,P,n,m_{\mathrm{A}^{z+}}}$$

Since m can be varied at constant n, $\overline{G}_{\mathrm{A}_a\mathrm{Y}_y}$ can be determined experimentally. However, since $m_{\mathrm{A}}{}^{z+}$ an $m_{\mathrm{Y}}{}^{z-}$ cannot be varied independently, neither $\overline{G}_{\mathrm{A}^{z+}}$ nor $\overline{G}_{\mathrm{Y}^{z-}}$ can be measured. Combination of Equation (i) and (ii) gives

$$\overline{G}_{\mathrm{A}_a\mathrm{Y}_y} = a\overline{G}_{\mathrm{A}^{z+}} + y\overline{G}_{\mathrm{Y}^{z-}} \tag{iii}$$

which shows that, although neither $\overline{G}_{\mathrm{A}^{z+}}$ nor $y\overline{G}_{\mathrm{Y}^{z-}}$ can be measured, the combination given by Equation (iii) can be measured.

If the component $\mathrm{A}_a\mathrm{Y}_y$ occurs in the unit molality standard state, Equation (iii) is written as

$$G^{\circ}_{\mathrm{A}_a\mathrm{Y}_y} = aG^{\circ}_{\mathrm{A}^{z+}} + yG^{\circ}_{\mathrm{Y}^{z-}} \tag{iv}$$

and subtraction of Equations (iv) from (iii), noting that

$$\overline{G}_i - G_i^{\circ} = RT \ln a_i$$

gives, on rearrangement,

$$a_{\mathrm{A}_a\mathrm{Y}_y} = a^{a}_{A^{z+}} + a^{y}_{\mathrm{Y}^{z-}} \tag{v}$$

Thus, again, although neither $a_{A^{z+}}$ nor $a_{\mathrm{Y}^{z-}}$ can be measured experimentally, which necessarily means that neither $a_{A^{z+}}$ nor $a_{\mathrm{Y}^{z-}}$ has any physical significance, the product given by Equation (v) can be measured and does have a physical significance. Equation (v) can be written as

$$\begin{aligned} a_{\mathrm{A}_a\mathrm{Y}_y} &= (\gamma_{\mathrm{A}^{z+}} m_{\mathrm{A}^{z+}})^a \left(\gamma_{\mathrm{Y}^{z-}} m_{\mathrm{Y}^{z-}}\right)^y \\ &= \gamma^{a}_{\mathrm{A}^{z+}} \gamma^{y}_{\mathrm{A}^{z-}} m^{a}_{\mathrm{A}^{z+}} m^{y}_{\mathrm{Y}^{z-}} \end{aligned} \tag{vi}$$

The mean ionic molality, $m_\pm$, is defined as

$$m_\pm = (m^a_{A^{z+}} m^y_{Y^{z-}})^{\frac{1}{(a+y)}} \tag{vii}$$

and the mean ion activity coefficient, $\gamma_\pm$, is defined as

$$\gamma_\pm = (\gamma^a_{A^{z+}} \gamma^y_{Y^{z-}})^{\frac{1}{(a+y)}} \tag{viii}$$

Thus, substitution of Equation (vii) and (viii) into Equation (vi) gives

$$a_{A_aY_y} = (\gamma_\pm m_\pm)^{a+y} \tag{ix}$$

Consider an m molar solution of NaCl. Since $|z^+|$ and $|z^-| = 1$ and $a = y = 1$, Equation (ix) gives

$$a_{\mathrm{NaCl}(m)} = (\gamma_\pm m_\pm)^2$$

and Equation (vii) gives

$$m_\pm = \left(mm\right)^{1/2}$$

Thus,

$$a_{\mathrm{NaCl}(m)} = (\gamma_\pm m_{\mathrm{NaCl}})^2$$

and Henrian behavior follows

$$a_{\mathrm{NaCl}(m)} = m^2_{\mathrm{NaCl}}$$

In an m molal solution of $CaCl_2$, since $|z^+| = 2,\ |z^-| = 1,\ a = 1,$ and $y = 2,$

$$\begin{aligned} a_{\mathrm{CaCl}_2(m)} &= (\gamma_\pm m_\pm)^3 \\ m_\pm &= [m(2m)^2]^{1/3} \end{aligned}$$

and thus,

$$a_{\mathrm{CaCl}_2(m)} = 4(\gamma_\pm m_{\mathrm{CaCl}_2})^3$$

Similarly, in an m molal solution of $Fe_2(SO_4)_3$,

$$a_{\mathrm{Fe}_2(\mathrm{SO}_4)_{(m)}} = 36(\gamma_\pm m_{\mathrm{Fe}_2(\mathrm{SO}_4)_3})^5$$

14.9 THE GIBBS FREE ENERGY OF FORMATION OF IONS AND STANDARD REDUCTION POTENTIALS

Consider the cell

$$\mathrm{Pt,H_{2(g)}}\,\Big|\,\mathrm{HCl_{(aqueous)}}\,\Big|\,\mathrm{Hg_2Cl_{2(\mathit{s})}}\mid\mathrm{Hg_{(\mathit{l})}}$$

set up as shown in Figure 14.11. The half-cell reaction at the anode is

$$\frac{1}{2}\mathrm{H_2} = \mathrm{H^+} + e^-$$

and the Hg_2Cl_2 half-cell reaction at the cathode is

$$\frac{1}{2}\mathrm{Hg_2Cl_2} + e^- = \mathrm{Hg} + \mathrm{Cl^-}$$

The overall reaction is thus

$$\frac{1}{2}\mathrm{H_{2(\mathit{g})}} + \frac{1}{2}\mathrm{Hg_2Cl_{2(\mathit{s})}} = \mathrm{Hg_{(\mathit{l})}} + \mathrm{HCl_{(\mathit{m})}} \tag{i}$$

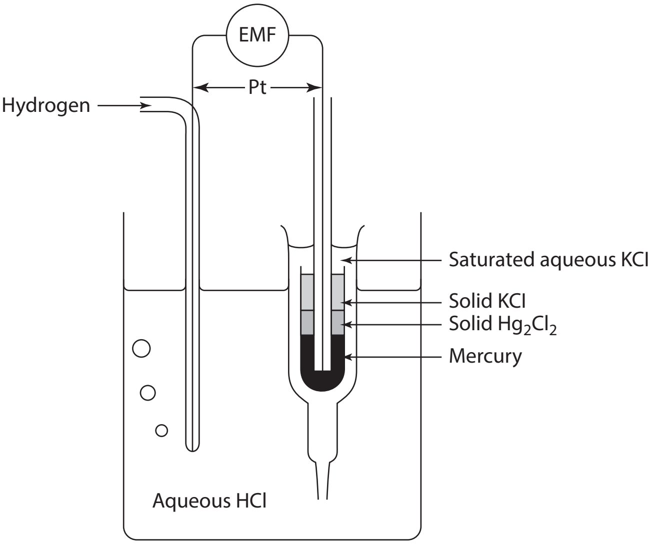


Figure 14.11 The calomel cell, $Pt,H_{2(g)} \mid HC1_{(aq)} \mid Hg_2Cl_2(s) \mid Hg_{(l)}$.

with Hg and Hg_2Cl_2 occurring at unit activity and $p_{H_2} = 1$ atm. The EMF of the cell is

$$\varepsilon = \varepsilon^\circ - \frac{RT}{\mathfrak{f}} \ln a_{\mathrm{HCl}(m)}$$

$$= \varepsilon^\circ - \frac{RT}{\mathfrak{f}} \ln(\gamma_\pm m_{\mathrm{HCl}})^2$$

This expression can be rearranged as

$$\varepsilon + \frac{2RT}{\mathfrak{f}} \ln m_{\mathrm{HCl}} = \varepsilon^\circ - \frac{2RT}{\mathfrak{f}} \ln \gamma \pm \tag{ii}$$

in which the measurable quantities occur on the left-hand side. Extrapolation of the term $\varepsilon + 2RT/\mathfrak{f} \ln m_{\mathrm{HCl}}$ to infinite dilution, where $\gamma_\pm \to 1$, allows the calculation of ε° and hence, from Equation (ii), the calculation of the variation of $\gamma_\pm$ with m_{HCl}. The value of ε° at 298 K has been determined to be 0.26796 volts, and the variation of $a_{\mathrm{HCl}(m)}$ with m^2_{HCl} is as shown in Figure 14.12. Since $\varepsilon^\circ = 0.26796$ volts,

$$\Delta G^\circ_{(i),298\ \mathrm{K}} = -\mathfrak{f}\varepsilon^\circ = -96{,}487 \times 0.26796 = -25{,}855\ \mathrm{J}$$

For

$$\mathrm{Hg}_{(l)} + \frac{1}{2}\mathrm{Cl}_{2(g)} = \frac{1}{2}\mathrm{Hg_2Cl}_{2(s)} \tag{iii}$$

$$\Delta G^\circ_{(\mathrm{iii}),298\ \mathrm{K}} = -105{,}320\ \mathrm{J}$$

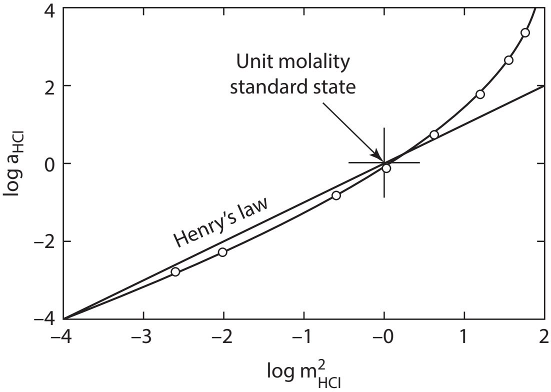


Figure 14.12 The activity of HCl in aqueous solution.

and thus, for

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} = HCl_{(m)}$$

$$\begin{aligned} \Delta G^{\circ}_{(\mathrm{iv})} &= \Delta G^{\circ}_{(i)} + \Delta G^{\circ}_{(\mathrm{iii})} \\ &= -25{,}855 - 105{,}320 \text{ J} \qquad \text{(iv)} \\ &= -131{,}175 \text{ J} \end{aligned}$$

Thus, the standard Gibbs free energy of formation of HCl in aqueous solution at unit activity from H_2 gas and Cl_2 gas, each at 1 atm pressure, is –131,175 J at 298 K. For

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} = HCl_{(g)} \qquad \text{(v)}$$

$$\Delta G^{\circ}_{(\mathrm{v}),298\text{ K}} = -94{,}540 \text{ J}$$

and hence, for the change of state

$$HCl_{(g)} = HCl_{(m)}$$

$$\begin{aligned} \Delta G^{\circ}_{298\mathrm{K}} &= -131{,}175 + 94{,}540 \\ &= -36{,}635 \text{ J} \\ &= -8.3144 \times 298 \ln \frac{a_{HCl_{(m)}}}{p_{HCl}} \end{aligned}$$

Thus, at 298 K, an aqueous solution of HCl at unit activity exerts a partial vapor pressure of HCl of 3.79×10^{-7} atm.

From Equation (iv), the standard EMF of the cell

$$Pt, H_{2(g)} \,|\, HCl_{(m)} \,|\, Cl_{2(g)}, Pt$$

is

$$\varepsilon^{\circ} = \frac{-\Delta G^{\circ}_{(\mathrm{iv})}}{\mathfrak{F}} = \frac{131{,}175}{96{,}487} = 1.3595 \text{ volts}$$

and the cell reaction

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} = HCl_{(m)}$$

or

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} = H^+_{(m)} + Cl^-_{(m)} \tag{vi}$$

is the sum of the half-cell reactions

$$\frac{1}{2}H_{2(g)} = H^+ + e^- \tag{vii}$$

and

$$\frac{1}{2}Cl_2 + e^- = Cl^- \tag{viii}$$

It is now convenient to introduce the concept of a *half-cell*, or *single electrode potential*, the sum of which, in any cell, equals the EMF of the cell. This concept is useful in spite of the fact that it is impossible to construct, and hence to measure the potential of, a cell with a single electrode. In order to give meaning to the concept, it is necessary to choose a particular standard single electrode and arbitrarily assign it a potential of zero. In aqueous solutions, this standard single electrode is the *standard hydrogen electrode* (SHE), in which hydrogen gas at 1 atm pressure, in contact with a platinum wire, is bubbled through an aqueous solution containing hydrogen ions at unit activity. In the SHE, hydrogen gas in its standard state is arbitrarily placed at the same potential as hydrogen ions in their standard state in aqueous solution. Consider the cell

$$Pt,H_{2(g,1\text{ atm})} \mid H^+_{(m)}Cl^-_{(m)} \mid Cl_{2(g,1\text{ atm})},Pt$$

The variation of the potential with distance from the hydrogen gas–electrolyte interface to the chlorine gas–electrolyte interface is shown schematically in Figure 14.13.

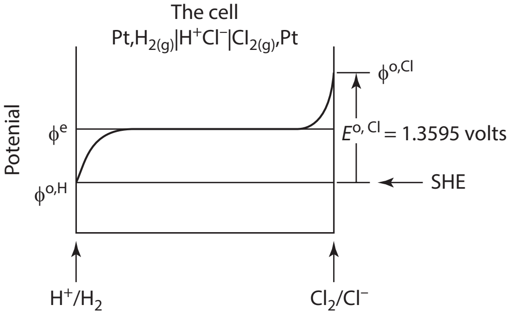


Figure 14.13 The relationship of the standard reduction potential of Cl to the standard hydrogen electrode and the absolute potentials in the cell $Pt,H_{2(g,1\text{ atm})} \mid H^+_{(m)}Cl^-_{(m)} \mid Cl_{2(g,1\text{ atm})},Pt$.

Although the value of $\phi^{\circ,e}$ is not known, the difference between $\phi^{\circ,\mathrm{Cl}}$ and $\phi^{\circ,\mathrm{H}}$ is experimentally measured as 1.3595 volts. Thus, if the absolute potential $\phi^{\circ,\mathrm{H}}$ is arbitrarily assigned the value zero, the standard electrode potential at which the reduction of ½Cl_2 to Cl^- occurs at the cathode is 1.3595 volts. Thus, with the standard oxidation (and hence reduction) potential of hydrogen being zero, then, algebraically, from Figure 14.13, the standard EMF of the cell, ε°, is obtained as the standard reduction potential of the cathode minus the standard reduction potential at the anode; that is,

$$\varepsilon^\circ = \varepsilon^{\circ,\mathrm{Cl}} - \varepsilon^{\circ,\mathrm{H}}$$

$$= 1.3595 \text{ volts}$$

Consider, again, the Daniell cell with pure Zn and Cu as electrodes and Zn^{2+} and Cu^{2+} ions at unity molality. Figure 14.14a shows a schematic variation of the potential through the electrolyte in the subcell which has the cell reaction

$$Zn_{(s)} + 2\mathrm{H}^+_{(m)} = 2\mathrm{n}^{2+}_{(m)} + \mathrm{H}_{2(g)}$$

and Figure 14.14b shows the corresponding variation through the subcell which has the cell reaction

$$\mathrm{H}_{2(g)} + \mathrm{Cu}^{2+}_{(m)} = 2\mathrm{H}^+_{(m)} + \mathrm{Cu}_{(s)}$$

With reference to the SHE, as shown, the standard reduction potential for Cu^{2+} is given by $\phi^{\circ,\mathrm{Cu}} - \phi^{\circ,\mathrm{H}}$, which is experimentally measured as 0.337 volts. The standard reduction potential of copper is thus 0.337 volts. Also, with respect to the SHE,

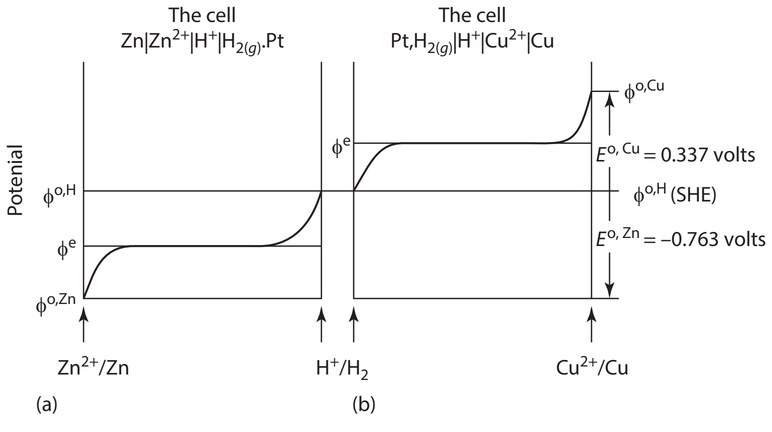


Figure 14.14 The relationship of the standard reduction potentials of Zn and Cu to the standard hydrogen electrode and the absolute potentials in the cells Zn | Zn^{2+} | H^+ | $H_{2(g)}$,Pt, and Pt,$H_{2(g)}$ | H^+ | Cu^{2+} | Cu.

the standard oxidation potential for Zn is measured experimentally as $\phi^{\circ,H} - \phi^{\circ,Zn} = 0.763$. Thus, the standard reduction potential of Zn, $\varepsilon^{\circ,Zn}$, is –0.763 volts, and the standard EMF of the Daniell cell is the standard reduction potential of Cu minus the standard reduction potential of Zn; that is,

$$\varepsilon^{\circ} = 0.337 - (-0.763) = 1.100 \text{ volts}$$

The systematic list of standard reduction potentials, part of which is presented as Table 14.1, is called the *electrochemical series*.

14.9.1 Solubility Products

From Table 14.1, the standard reduction potential for sodium, $\varepsilon^{\circ,Na}$, is –2.714 volts, and the standard reduction potential for chlorine, $\varepsilon^{\circ,Cl}$, is 1.3595 volts. Thus, for the equilibrium

$$\text{Na} = \text{Na}^{+} + e^{-}$$

$$\Delta G^{\circ} = -\mathfrak{f}\varepsilon^{\circ,\text{Na}} = -96{,}487 \times 2.714 = -261{,}870 \text{ J}$$

and for

$$\frac{1}{2}\text{Cl}_2 + e^{-} = \text{Cl}^{-}$$

$$\Delta G^{\circ} = -\mathfrak{f}\varepsilon^{\circ\text{Cl}} = -96{,}487 \times 1.3595 = -131{,}170 \text{ J}$$

Summing gives

$$\Delta G^{\circ}_{(\text{i})} = -261{,}870 - 131{,}170 = -393{,}040 \text{ J}$$

for the reaction

$$\text{Na}_{(s)} + \frac{1}{2}\text{Cl}_{2(g)} = \text{Na}^{+}_{(m)} + Cl^{-}_{(m)} \qquad \text{(i)}$$

For the reaction

$$\text{Na}_{(s)} + \frac{1}{2}\text{Cl}_2(g) = \text{NaCl}_{(s)} \qquad \text{(ii)}$$

$$\Delta G^{\circ}_{(\text{ii}),298\text{K}} = -385{,}310 \text{ J}$$

Table 14.1 Standard Electrode Potentials at 298 K, 1 atm

Electrode Reaction	$\varepsilon^{\circ,x}$, volts
Acid Solutions	
$F_2 + 2e^- = 2F^-$	2.65
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	1.98
$Co^{3+} + e^- = Co^{2+}$	1.82
$Ce^{4+} + e^- = Ce^{3+}$	1.61
$\frac{1}{2}Cl_2 + e^- = Cl^-$	1.3595
$Cr_2O_7^{2-} + 14H^+ + e^- = 2Cr^3 + 7H_2O$	1.33
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23
$Br_2(l) + 2e^- = 2Br^-$	1.0652
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.92
$Hg^{2+} + 2e^- = Hg$	0.854
$Ag^+ + e^- = Ag$	0.7991
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$I_2 + 2e^- = 2I^-$	0.5355
$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^- = Cu$	0.337
$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-}$	0.17
$Cu^{2+} + e^- = Cu^+$	0.153
$Sn^{4+} + 2e^- = Sn^{2+}$	0.15
$S + 2H^+ + e^- = H_2S$	0.141
$2H^+ + e^- = H_2$	0.000
$Fe^{3+} + 3e^- = Fe$	−0.036
$Pb^{2+} + 2e^- = Pb$	−0.126
$Sn^{2+} + 2e^- = Sn$	−0.136
$Cd^{2+} + 2e^- = Cd$	−0.403
$Cr^{3+} + e^- = Cr^{2+}$	−0.41
$Fe^{2+} + 2e^- = Fe$	−0.440
$Zn^{2+} + 2e^- = Zn$	−0.763
$Al^{3+} + 3e^- = Al$	−1.66
$\frac{1}{2}H_2 + e^- = H^-$	−2.25
$Mg^{2+} + 2e^- = Mg$	−2.37
$Na^+ + e^- = Na$	−2.714
$Ca^{2+} + 2e^- = Ca$	−2.87
$Ba^{2+} + 2e^- = Ba$	−2.90
$Cs^+ + e^- = Cs$	−2.923
$K^+ + e^- = K$	−2.925
$Li^+ + e^- = Li$	−3.045
Basic Solutions	
$O_3 + H_2O + 2e^- = O_2 + 2OH^-$	1.24
$Fe(OH)_3 + e^- = OH^- + Fe(OH)_2$	−0.56

(*Continued*)

Table 14.1 (Continued) Standard Electrode Potentials at 298 K, 1 atm

Electrode Reaction	**$\varepsilon^{\circ,x}$, volts**
$Ni(OH)_2 + 2e^- = Ni + 2OH^-$	−0.72
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
$SO_4^{2-} + H_2O + 2e^- = 2OH^- + SO_3^{2-}$	−0.93
$CNO^- + H_2O + 2e^- = 2OH^- + CN^-$	−0.97
$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$	−1.216
$Cr(OH)_3 + 3e^- = Cr + 3OH^-$	−1.3
$Ca(OH)_2 + 2e^- = Ca + 2OH^+$	−3.03

Note: Standard state is 1 molal.

and combination of Equations (i) and (ii) gives

$$\mathrm{NaCl}_{(s)} = \mathrm{Na}^+_{(m)} + \mathrm{Cl}^- \qquad \text{(iii)}$$

for which

$$\begin{aligned}\Delta G^\circ_{\text{(iii)}} &= \Delta G^\circ_{(i)} - \Delta G^\circ_{\text{(ii)}} \\ &= -393{,}040 + 385{,}310 \\ &= -8.3144 \times 298 \ln \frac{(\gamma_\pm m_{\mathrm{NaCl}})^2}{a_{\mathrm{NaCl}}}\end{aligned}$$

In Equation (iii), the standard state on the left-hand side is pure solid NaCl, and the standard state on the right-hand side is the unit molality standard state. Saturation of the aqueous solution occurs when NaCl has dissolved to the extent that the activity of NaCl in the solution, with respect to solid NaCl as the standard state, is unity. In this state,

$$\left(\gamma_\pm m_{\mathrm{NaCl}}\right)^2 = 22.6$$

or

$$\gamma_\pm m_{\mathrm{NaCl}} = 4.76$$

Thus, if the ions in solution are behaving ideally, the saturated aqueous solution of NaCl at 298 K is 4.76 molal. When the activity of NaCl in the solution is unity with respect to solid NaCl as the standard state, the term $(\gamma_\pm m_{\mathrm{NaCl}})^2$ is called the *solubility product*, K_{sp}. Thus, generally, for the salt $A_a Y_y$,

$$K_{\mathrm{sp}} = (\gamma_\pm m_\pm)^{a+y} = \exp \frac{-\Delta G^\circ_{298\mathrm{K}}}{298R}$$

where $\Delta G^{\circ}_{298\text{ K}}$ is the standard Gibbs free energy change for the change of state

$$\mathrm{A}_a\mathrm{Y}_{y(\text{Raoultian})} = a\mathrm{A}^{z+}_{(m)} + y\mathrm{Y}^{z-}_{(m)}$$

Example

Calculate the molalities of H^+ and OH^- in water at 298 K.

Solution

In Table 14.1, the standard reduction potential for the half-cell reaction

$$\mathrm{H_2O}_{(l)} + e^- = \frac{1}{2}\mathrm{H}_{2(g)} + \mathrm{OH}^-_{(m)}$$

is –0.828 volts, and the standard reduction potential for the reaction

$$\mathrm{H}_{(m)} + e^- = \frac{1}{2}\mathrm{H}_{2(g)}$$

is zero. Summing gives

$$\mathrm{H_2O}_{(l)} = H^+_{(m)} + \mathrm{OH}^-_{(m)}$$

for which

$$\begin{aligned}\Delta G^{\circ}_{298\mathrm{K}} \quad &= -\mathfrak{F}\varepsilon^{\circ} = -96487 \times (-0.828)\\ &= 79{,}900\ \mathrm{J}\\ &= -8.3144 \times 298\ \ln\,(\gamma_{\pm} m_{\mathrm{H+}} m_{\mathrm{OH-}})\end{aligned}$$

Thus, presuming that $\gamma_{\pm} = 1$,

$$m_{\mathrm{H^+}} m_{\mathrm{OH^-}} = 0.97 \times 10^{-5}$$

or, from the stoichiometry of the dissociation, as $m_{\mathrm{H^+}} = m_{\mathrm{OH^-}}$,

$$m_{\mathrm{H^+}} = m_{\mathrm{OH^-}} = 10^{-7}$$

At a molality of 10^{-7}, the assumption that $\gamma_{\pm} = 1$ is reasonable.

14.9.2 The Influence of Acidity

The single electrode potential for the half-cell reaction

$$\mathrm{H}^+_{(m)} + e^- = \frac{1}{2}\mathrm{H}_{2(g)}$$

is

$$\varepsilon^{H} = \varepsilon^{\circ,H} - \frac{RT}{\mathfrak{f}} \ln \frac{p_{H_2}^{1/2}}{m_{H^+}}$$

$\varepsilon^{\circ,H} = 0$ and thus,

$$\varepsilon^{H} = -\frac{RT}{\mathfrak{f}} \ln \frac{p_{H_2}^{1/2}}{m_{H^+}} \tag{i}$$

that is, for a fixed pressure of hydrogen gas, ε^{H} is a linear function of the logarithm of the molality of the hydrogen ions. The concentration of hydrogen ions in an aqueous solution determines the acidity of the solution, and, conventionally, acidity is quantified by the definition of pH, as

$$\text{pH} = -\log\left[\text{H}^+\right] \tag{ii}$$

$[H^+]$ is the *molarity* of the hydrogen ions—that is, the number of moles of H^+ per liter of solution. Substitution of Equation (ii) into Equation (i) would require that either the half-cell reduction potential be determined with reference to the unit molarity standard state, or that pH be defined as $-\log(m_{H}^{+})$. Since in dilute solutions, molality and molarity are virtually identical, this theoretical difficulty is of no practical significance. In the following discussions, the unit molarity standard state will be used for ions in solution. This standard state is defined as

$$a_{A^{z+}} \rightarrow \quad [A^{z+}] \quad \text{as} \quad [A^{z+}] \rightarrow 0$$

Furthermore, in the following discussions, it will be assumed that all ions in aqueous solutions behave ideally, in which case

$$a_{A^{z+}} = [A^{z+}] \sim m_{A^{z+}}$$

With this understanding, Equation (i) becomes

$$\varepsilon^{H} = -\frac{RT}{\mathfrak{f}} \ln \frac{p_{H_2}^{1/2}}{[H^+]}$$

which, with Equation (ii), becomes

$$\begin{aligned}\varepsilon^{H} &= -\frac{2.303\times 8.3144\times 298}{2\times 96{,}487}\log p_{H_2} \qquad + \frac{2.303\times 8.314\times 298}{96{,}487}\log[H^+] \\ &= -0.0591(\text{pH}) - 0.0296\log p_{H_2}\end{aligned}$$

or, with $p_{H_2} = 1$ atm, the reduction potential of hydrogen varies with pH as

$$\varepsilon^{H} = -0.0591(\text{pH})$$

In the previous example, it was found that the molality (and hence the molarity) of H^+ in H_2O at 298 K is 10^{-7}. Thus, the pH of H_2O at 298 K is 7, and the reduction potential of hydrogen in water is $-0.0591 \times 7 = -0.414$ volts. The hydrogen electrode has its standard reduction potential of 0 at pH = 0—that is, at $[H^+] = 1$.

14.10 POURBAIX DIAGRAMS

Pourbaix diagrams,[*] or *potential-pH* diagrams, are graphical representations of thermodynamic and electrochemical equilibria occurring in aqueous systems. They are thus the electrochemical analogues of the chemical phase stability diagrams discussed in Section 13.5. Consider the cell

$$\mathrm{Pt}, \mathrm{H}_{2(g)} \,\big|\, \mathrm{H_2O} \,\big|\, \mathrm{O}_{2(g)}, \mathrm{Pt}$$

The galvanic cell reaction

$$\mathrm{H}_{2(g)} + \frac{1}{2}\mathrm{O}_{2(g)} = \mathrm{H_2O}_{(l)} \tag{i}$$

is the sum of the half-cell reactions

$$\mathrm{H_2} = 2\mathrm{H}^+ + 2e^- \tag{ii}$$

and

$$\frac{1}{2}\mathrm{O_2} + 2\mathrm{H}^+ + 2e^- = \mathrm{H_2O} \tag{iii}$$

Thus,

$$\Delta G^\circ_{(i)} = \Delta G^\circ_{(\mathrm{ii})} + \Delta G^\circ_{(\mathrm{iii})}$$

$\Delta G^\circ_{(i)298\,\mathrm{K}} = -237{,}190$ J, and by convention, $\Delta G^\circ_{(\mathrm{ii})298\,\mathrm{K}} = 0$. Thus, the standard reduction potential for the reaction given by Equation (iii) is

$$\begin{aligned} \mathcal{E}^\circ_{(\mathrm{iii})} &= \frac{-\Delta G^\circ_{(\mathrm{iii})}}{2\mathcal{F}} \\ &= \frac{237{,}190}{2\mathcal{F}} \\ &= 1.229 \text{ volts} \end{aligned}$$

---

[*] M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," National Association of Corrosion Engineers, Houston, TX, 1974.

With all of the reactants and products occurring in their standard states, electrochemical equilibrium is established when the backing EMF applied to the cell is 1.229 volts. If the backing EMF is less than this value, the cell is a current-producing galvanic cell and the cell reaction occurring is

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

with the oxidation $2H_2 \rightarrow 2H^+ + 2e^-$ occurring at the anode and the reduction reaction $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ occurring at the cathode. However, if the backing EMF is greater than 1.229 volts, the cell is a current-consuming electrolysis cell and the cell reaction occurring is

$$H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$$

with the oxidation reaction $H_2O \rightarrow \frac{1}{2}\ O_2 + 2H^+ + 2e^-$ occurring at the anode and the reduction reaction $2H^+ + 2e^- \rightarrow H_2$ occurring at the cathode. Thus, with hydrogen gas and hydrogen ions at unit activity, electrochemical equilibrium is established at the hydrogen electrode when the electrode is at zero potential. If the potential of the electrode is increased to a value above zero, the anodic reaction $H_2 \rightarrow 2H^+ + 2e^-$occurs, and if the potential of the electrode is decreased to a value less than zero, the cathodic reaction $2H^+ + 2e^- \rightarrow H_2$ occurs. Similarly, with oxygen at unit pressure and hydrogen ions at unit activity, electrochemical equilibrium at the oxygen electrode is established when the electrode potential is 1.229 volts. If the potential of the electrode is increased above 1.229 volts, the anodic reaction $H_2 \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ occurs, and if the potential of the electrode is decreased below 1.229 volts, the cathodic reaction $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ occurs. Thus, generally, if the potential, ε, of an electrode at equilibrium with the electrolyte is increased, an anodic oxidation reaction occurs, and if it is decreased, a cathodic reduction reaction occurs.

Since both half-cell reactions (i) and (ii) involve hydrogen ions, the half-cell potentials are functions of the pH of the aqueous solution. At the hydrogen electrode, at 298 K, the electrochemical equilibrium

$$H^+ + e^- = \frac{1}{2}H_2 \tag{a}$$

is established at

$$\begin{aligned} \varepsilon_{(a)} &= -\frac{RT}{\mathcal{F}}\ln\frac{p_{H_2}^{1/2}}{[H^+]} \\ &= -0.0591(\mathrm{pH}) - 0.0298\log p_{H_2} \end{aligned}$$

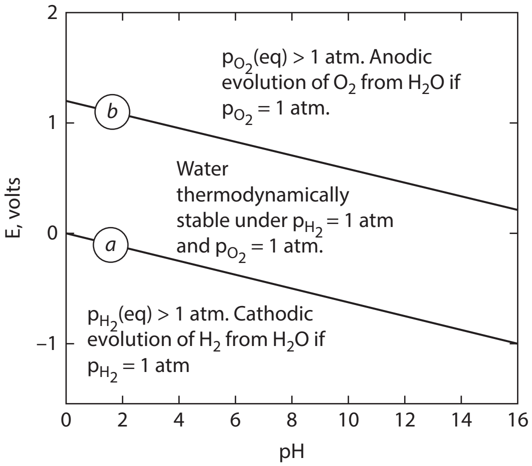


Figure 14.15 The domain of thermodynamic stability of water.

which, with $p_{H_2} = 1$ atm, is drawn as line *a* in Figure 14.15. At the oxygen electrode, at 298 K, the electrochemical equilibrium

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \tag{b}$$

is established at

$$\varepsilon_{(b)} = 1.299 - \frac{RT}{2\mathcal{F}} \ln \frac{1}{[H^+]^2 p_{O_2}^{1/2}}$$

$$= 1.229 - 0.0591\text{pH} + 0.0148 \log p_{O_2}$$

which, with $p_{O_2} = 1$ atm, is drawn as line *b* in Figure 14.15. Lines *a* and *b* in Figure 14.15 define the *domain of thermodynamic stability of water* in aqueous solutions under a pressure of 1 atm of H_2 and 1 atm of O_2. Below line *a*, the equilibrium pressure of hydrogen gas is greater than 1 atm, and thus, hydrogen is cathodically evolved from an aqueous solution, the potential of which is moved below line *a* when the pressure of hydrogen at the electrode is 1 atm. Similarly, above line *b*, the equilibrium pressure of oxygen gas is greater than 1 atm, and thus, oxygen gas is anodically evolved from an aqueous solution at an electrode, the potential of which is moved above line *b* when the oxygen pressure at the electrode is 1 atm. Water is thermodynamically stable between lines *a* and *b* with oxygen and hydrogen pressures of 1 atm.

14.10.1 The Pourbaix Diagram for Aluminum

The species participating in the various chemical and electrochemical equilibria are the solids Al and Al_2O_3 and the ions Al^{3+} and AlO_2^-. The pertinent standard Gibbs free energies of formation are

Reaction	$\Delta G^{\circ}_{298\ \mathrm{K},}$ J
Al	0
$\frac{1}{2}\mathrm{H}_{2(g)} = \mathrm{H}^{+}_{(m)} + e^{-}$	0
$2\mathrm{Al}_{(s)} + 1.50_{2(g)} = \mathrm{Al}_2\mathrm{O}_{3(2)}$	$-1{,}608{,}900$
$\mathrm{Al}_{(s)} = Al^{3+}_{(m)} + 3e^{-}$	$-481{,}200$
$\mathrm{Al}_{(s)} + \mathrm{O}_{2(g)} + e^{-} = \mathrm{AlO}^{-}_{2(m)}$	$-839{,}800$
$\mathrm{H}_{2(g)} + \frac{1}{2}\mathrm{O}_{2(g)} = \mathrm{H}_2\mathrm{O}_{(l)}$	$-237{,}200$

Consider first the equilibrium which occurs between the ions in solution. Since reduction potentials are being used, the equations for the electrochemical equilibria are set up with the higher oxidation state on the left and the lower oxidation state on the right—that is, with the balancing electronic charge on the left-hand side of the equation.

14.10.2 The Equilibrium between the Two Dissolved Substances

The equilibrium between Al^{3+} *and* AlO_2^-:

$$\mathrm{Al}^{3+} \longleftrightarrow \mathrm{AlO}_2^-$$

The procedure for deriving the expression for the equilibrium is as follows:

1. Balance the oxygen with H_2O; that is,

$$\mathrm{Al}^{3+} + 2\mathrm{H}_2\mathrm{O} \longleftrightarrow \mathrm{AlO}_2^-$$

2. Balance the hydrogen with H^+; that is,

$$\mathrm{Al}^{3+} + 2\mathrm{H}_2\mathrm{O} \longleftrightarrow \mathrm{AlO}_2^- + 4\mathrm{H}^+$$

3. If necessary, balance the charge with e^-.

This step is not necessary with Al^{3+} and AlO_2^-, as the equilibrium is not electrochemical. The desired expression is thus

$$\mathrm{Al}^{3+} + 2\mathrm{H}_2\mathrm{O} = \mathrm{AlO}_2^- + 4\mathrm{H}^+ \tag{i}$$

for which

$$\begin{aligned}\Delta G^{\circ}_{(\mathrm{i})} &= (-839{,}800) - (2\times -237{,}200) - (-481{,}200)\\ &= 115{,}800\ \mathrm{J}\\ &= -8.3144\times 298\times 2.303\log\frac{[\mathrm{H}^+]^4[\mathrm{AlO}_2^-]}{[\mathrm{Al}^{3+}]}\end{aligned}$$

Thus,

$$-20.29 = 4\log\ [\mathrm{H}^+] + \log\frac{[\mathrm{AlO}_2^-]}{[\mathrm{Al}^{3+}]}$$

or

$$\log\frac{[\mathrm{Al}^{3+}]}{[\mathrm{AlO}_2^-]} = 20.29 - 4\mathrm{pH}$$

Thus, $[\mathrm{Al}^{3+}] = [\mathrm{AlO}_2^-]$ at pH = 5.07 and pH = 5.07 is drawn as line 1 in Figure 14.16a. At values of pH greater than 5.07, $[\mathrm{AlO}_2^-] > [\mathrm{Al}^{3+}]$, and at values of pH less than 5.07, $[\mathrm{Al}^{3+}] > [\mathrm{AlO}_2^-]$.

14.10.3 The Equilibrium between the Two Solids

The equilibrium between Al and Al_2O_3: With the higher oxidation state on the left and the lower oxidation state on the right, the procedure for deriving the expression for the equilibrium begins with

$$\mathrm{Al_2O_3} \longleftrightarrow 2\mathrm{Al}c$$

Then, as before, balance the oxygen with H_2O; that is,

$$\mathrm{Al_2O_3} \longleftrightarrow 2\mathrm{Al} + 3\mathrm{H_2O}$$

balance the hydrogen with H^+; that is,

$$\mathrm{Al_2O_3} + 6\mathrm{H}^+ \longleftrightarrow 2\mathrm{Al} + 3\mathrm{H_2O}$$

and balance the charge with e^-; that is,

$$\mathrm{Al_2O_3} + 6\mathrm{H}^+ + 6\mathrm{e}^- \longleftrightarrow 3\mathrm{H_2O} + 2\mathrm{Al}$$

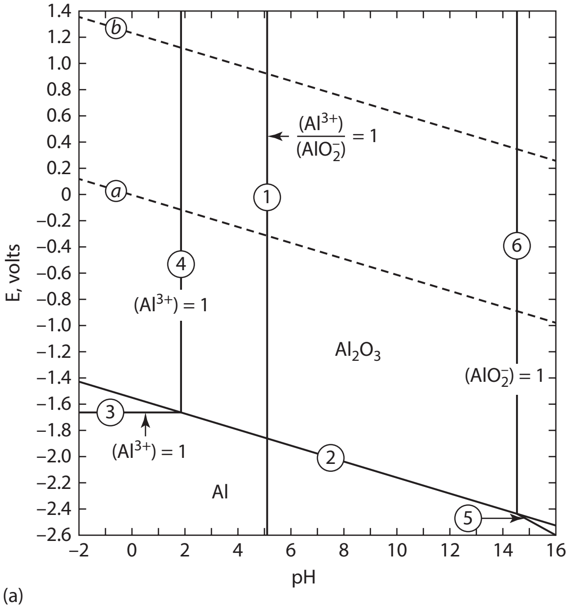
The required equilibrium is thus

$$\mathrm{Al_2O_3} + 6\mathrm{H}^+ + 6\mathrm{e}^- = 3\mathrm{H_2O} + 2\mathrm{Al} \qquad \text{(ii)}$$

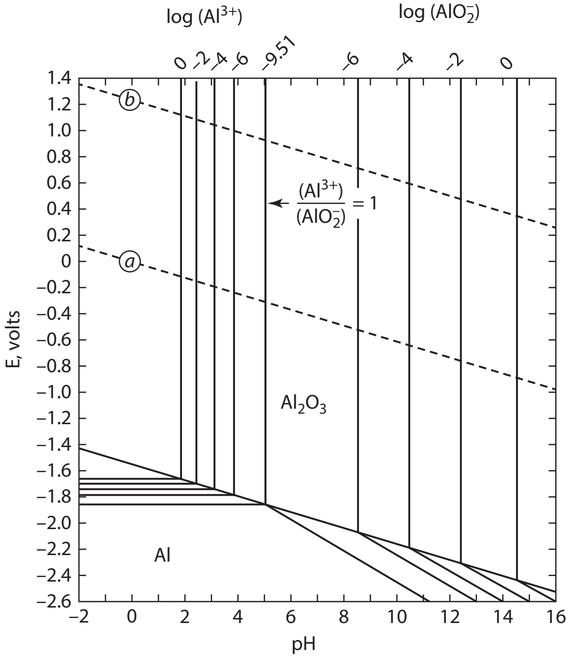
for which

$$\begin{aligned}\Delta G^\circ_{\text{(ii)}} &= (3 \times -237{,}200) - (-1{,}608{,}900)\\ &= 897{,}300\ \mathrm{J}\\ &= -z\mathfrak{F}\varepsilon^\circ_{\text{(ii)}} = -6 \times 96{,}487\varepsilon^\circ_{\text{(ii)}}\end{aligned}$$

Thus, $\varepsilon^\circ_{\text{(ii)}} = -1.55$ volts and, with $a_{\mathrm{Al}} = a_{\mathrm{Al_2O_3}} = 1$,



(a)



(b)

Figure 14.16 (a) Construction of the Pourbaix diagram for Al. (b) The Pourbaix diagram for Al.

$$\begin{aligned}\varepsilon_{(\mathrm{iii})} &= \varepsilon^{\circ}_{(\mathrm{ii})} - \frac{RT}{z\mathfrak{f}}\ln\frac{1}{[\mathrm{H}^+]^6}\\ &= -1.55 + \frac{8.3144\times 298\times 2.303\times 6}{6\times 96{,}487}\log\ [\mathrm{H}^+]\\ &= -1.55 - 0.0591\ \mathrm{pH\ volts}\end{aligned}$$

This is drawn as line 2 in Figure 14.16a and is the line along which Al is in equilibrium with Al_2O_3. Al is the stable solid phase in states below line 2 (at lower values of pH and at more negative electrode potentials), and Al_2O_3 is the stable solid in states above the line.

14.10.4 One Solid in Equilibrium with a Dissolved Substance

The equilibrium between Al and Al^{3+}:

The equilibrium is

$$\mathrm{Al}^{3+} + 3e^- = \mathrm{Al} \tag{iii}$$

for which

$$\Delta G^{\circ}_{(\mathrm{iii})} = 481{,}200\ \mathrm{J}$$

Thus,

$$\varepsilon^{\circ}_{(\mathrm{iii})} = \frac{-481{,}200}{3\times 96{,}487} = -1.66\ \mathrm{volts}$$

Then, with $a_{\mathrm{Al}} = 1$,

$$\varepsilon_{(\mathrm{iii})} = -1.66 - \frac{8.3144\times 298\times 2.303}{3\times 96{,}487}\log\frac{1}{[\mathrm{Al}^{3+}]}$$

The variation of the concentration of Al^3+ ions in equilibrium with Al is thus

$$\varepsilon_{(\mathrm{iii})} = -1.66 + 1.971\times 10^{-2}\log\left[\mathrm{Al}^{3+}\right]$$

With $[Al^3+]$ = 1 mole per liter, this equation is drawn as line 3 in Figure 14.16a. The concentration of Al^3+ in equilibrium is independent of pH and decreases with increasingly negative values of ε.

The equilibrium between Al_2O_3 *and* Al^{3+}: The sequence in the derivation of the equilibrium equation is

$$\mathrm{Al_2O_3} \leftarrow\ \rightarrow 2\mathrm{Al}^{3+}$$

$$\mathrm{Al_2O_3} \leftarrow\ \rightarrow 2\mathrm{Al}^{3+} + 3\mathrm{H_2O}$$

$$6\mathrm{H}^+ + \mathrm{Al_2O_3} \leftarrow\ \rightarrow 2\mathrm{Al}^{3+} + 3\mathrm{H_2O}$$

Balancing the charge with e^- is not necessary, and the required expression is thus

$$6\text{H}^+ + \text{Al}_2\text{O}_3 = 2\text{Al}^{3+} + 3\text{H}_2\text{O} \tag{iv}$$

for which

$$\begin{aligned}\Delta G^\circ_{(\text{iv})} &= (3\times -237{,}200) + (2\times -481{,}200) - (-1{,}608{,}900)\\ &= -65{,}100 \text{ J}\end{aligned}$$

which, with $a_{\text{Al}_2\text{O}_3} = 1$, gives

$$-65{,}100 = -8.3144\times 298\times 2.303\log\frac{[\text{Al}^{3+}]^2}{[\text{H}^+]^6}$$

or

$$\log\left[\text{Al}^{3+}\right] = 5.70 - 3\text{pH}$$

which is the variation of the concentration of Al^{3+} ions in equilibrium with Al_2O_3. This equilibrium is independent of the electrode potential, and line 4 in Figure 14.16a, at pH = 1.9, represents a concentration of Al^{3+} of 1 mole per liter in equilibrium with Al_2O_3.

The equilibrium between Al and AlO_2^-:

$$\begin{gathered}\text{AlO}_2^- \longleftrightarrow \text{Al}\\ \text{AlO}_2^- \longleftrightarrow \text{Al} + 2\text{H}_2\text{O}\\ \text{AlO}_2^- + 4\text{H}^+ \longleftrightarrow \text{Al} + 2\text{H}_2\text{O}\\ \text{AlO}_2^- + 4\text{H}^+ + 3e^- \longleftrightarrow \text{Al} + 2\text{H}_2\text{O}\end{gathered}$$

The equilibrium is thus

$$\text{AlO}_2^- + 4\text{H}^+ + 3e^- = \text{Al} + 2\text{H}_2\text{O} \tag{v}$$

for which

$$\begin{aligned}\Delta G^\circ_{(\text{v})} &= (2\times -237{,}200) + 839{,}800\\ &= 365{,}400 \text{ J}\end{aligned}$$

Thus,

$$\varepsilon^\circ_{(\text{v})} = \frac{-365{,}400}{3\times 96{,}487} = -1.26 \text{ volts}$$

With $a_{\text{Al}} = 1$,

$$\varepsilon_{(\text{v})} = -1.26 - \frac{8.3144\times 298\times 2.303}{3\times 96{,}487}\log\frac{1}{[\text{H}^+]^4[\text{AlO}_2^-]}$$

which gives the variation of the concentration of AlO_2^- ions in equilibrium with Al as

$$\varepsilon_{(v)} = -1.26 - 0.0789\ \text{pH} + 0.0198 \log[AlO_2^-]$$

This equation, with $[AlO_2^-] = 1$ mole per liter, is drawn as line 5 in Figure 14.16a. The equilibrium is dependent on both pH and ε.

The equilibrium between Al_2O_3 and AlO_2^-:

$$Al_2O_3 \longleftrightarrow 2AlO_2^-$$
$$H_2O + Al_2O_3 \longleftrightarrow 2AlO_2^-$$
$$H_2O + Al_2O_3 \longleftrightarrow 2AlO_2^- + 2H^+$$

The equilibrium is thus

$$H_2O + Al_2O_3 = 2AlO_2^- + 2H^+ \tag{vi}$$

for which

$$\Delta G^{\circ}_{(vi)} = 166{,}500\ \text{J}$$

This gives

$$\log[AlO_2^-] = \text{pH} - 14.59$$

as the variation of the concentration of AlO_2^- in equilibrium with Al_2O_3. This equation, with $[AlO_2^-] = 1$ mole per liter is drawn as line 6 in Figure 14.16a at pH = 14.59.

The Pourbaix diagram for Al, containing iso-concentrations lines for Al^{3+} and AlO_2^- in the fields of stability of Al and Al_2O_3, is shown in Figure 14.16b. At pH = 5.07 in the Al_2O_3 field of stability $[Al^{3+}] = [AlO_2^-] = 3.10 \times 10^{-10}$ moles per liter. However, in the Al stability field, the 3×10^{-10} moles of Al^{3+} per liter iso-concentration line occurs at ε = −1.85 volts, and the 3×10^{-10} moles of AlO_2^- per liter iso-concentration lines lies at ε = −1.45 − 0.0789 pH. The domain of thermodynamic stability of water at hydrogen and oxygen pressures of 1 atm is defined by the lines *a* and *b*, and the position of line *a* relative to line 2 in Figure 14.16a illustrates why Al metal cannot be produced by electrolysis of aqueous solutions. With a hydrogen pressure of 1 atm, attempts to decrease the potential of an electrode to a value less than that given by line *a* cause the cathodic evolution of hydrogen gas from the electrolyte.

14.10.5 The Solubility of Alumina in Aqueous Solutions

Alumina dissolves in aqueous solutions to form Al^{3+} ions according to

$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O$$

and to form AlO_2^- ions according to

$$Al_2O_3 + H_2O = 2AlO_2^- + 2H^+$$

The solubility, as Al^{3+}, which varies with pH as

$$\log\left[Al^{3+}\right] = 5.70 - 3pH$$

and as AlO_2^-, which varies with pH as

$$\log\,[AlO_2^-] = pH - 14.59$$

is shown in Figure 14.17. The solubility of Al_2O_3 as AlO_2^- decreases by 10 orders of magnitude when the pH is decreased from 14 to 5, and this behavior is made use of in the Bayer process for the separation of Al_2O_3 from bauxite. Bauxite, which is the principal aluminum ore, is a mixture of aluminum monohydrate and aluminum trihydrate containing up to 60% Al_2O_3 with Fe_2O_3 as the main impurity. The ore is digested in a strong caustic solution at a temperature between 150°C and 250°C and a pressure high enough to suppress boiling. The alumina dissolves as AlO_2^-, and the insoluble residue of Fe_2O_3 (red mud) is removed from the solution by filtration. The pH of the solution is then increased by adding water, and seed crystals of $Al(OH)_3$ are added. The decreasing solubility causes the precipitation of $Al(OH)_3$ by the hydrolysis reaction

$$NaAlO_2 + 2H_2O = NaOH + Al(OH)_3$$

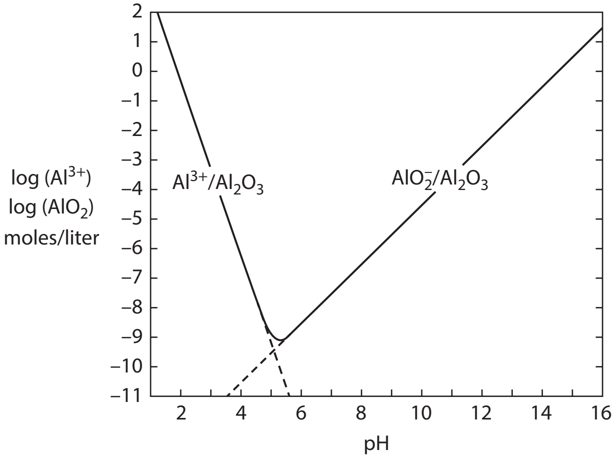


Figure 14.17 The solubility of Al_2O_3 in aqueous solution.

The strong caustic solution is regenerated by the removal of water by boiling, and the precipitated hydrate is then calcined at 1200°C–1350°C to form α-Al_2O_3.

14.11 SUMMARY

1. A system which is capable of performing electrical work as the result of the occurrence of a chemical reaction is called a galvanic cell, and the overall chemical reaction is represented by an equation called the cell reaction.

- If, in such a reaction, dn g-ions of valence z are transported through a voltage difference $\Delta\phi$ maintained between the electrodes of the cell, then

$$\delta w' = z\mathfrak{F}\Delta\phi dn$$

where $\mathfrak{F}$ is Faraday's constant (= 96,487 coulombs/mole).
- If the transportation is conducted reversibly, in which case the electric potential difference between the electrodes of the cell is called the electromotive force (EMF), ε, of the cell, then

$$\delta w'_{\max} = z\mathfrak{F}\varepsilon dn = -dG'$$

and, for the transportation of 1 mole of ions,

$$\Delta G = -z\mathfrak{F}\varepsilon$$

2. If the reaction

$$aA + bB = cC + dD$$

is conducted in an electrochemical cell, the EMF of the cell is given by

$$\varepsilon = \varepsilon^\circ - \frac{RT}{z\mathfrak{F}} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where the standard EMF of the cell, ε°, is given by

$$\varepsilon^\circ = -\frac{\Delta G^\circ}{z\mathfrak{F}}$$

3. For any cell reaction at constant temperature and pressure,

$$\Delta G = -z\mathfrak{F}\varepsilon$$

Thus, the molar entropy change for the cell reaction is

$$\Delta S = z\mathfrak{F}\left(\frac{\partial \varepsilon}{\partial T}\right)_P$$

and the molar enthalpy change for the cell reaction is

$$\Delta H = -z\mathfrak{F}\varepsilon + z\mathfrak{F}T\left(\frac{\partial \varepsilon}{\partial T}\right)_P$$

4. The composition of an aqueous solution is usually expressed in terms of the molality, m, or the molarity, M, where molality is the number of moles of solute present per 1000 g of water and molarity is the number of moles of solute present in 1 liter of solution. The unit molality activity scale (which is analogous with the 1 wt% activity scale) is defined as

   $$a_{i(m)} \rightarrow m_i \quad \text{as} \quad m_i \rightarrow 0$$

   where $a_{i(m)}$ is the activity of the solute with respect the unit molality standard state, and the unit molality standard state is located on the Henry's law line at $m_i = 1$. Deviation from ideality is accommodated by an activity coefficient defined as

   $$\gamma_{i(m)} = \frac{a_{i(m)}}{m_i}$$

5. The mean ionic molality, $m_{\pm}$, of the electrolyte (or salt) A_aY_y when dissolved in water is defined by

   $$m_{\pm} = \left(m^a_{A^{z+}} m^y_{Y^{z-}}\right)^{\frac{1}{a+y}}$$

   and the mean ion activity coefficient, $\gamma_{\pm}$, is defined as

   $$\gamma_{\pm} = \left(\gamma^a_{A^{z+}} \gamma^y_{Y^{z-}}\right)^{\frac{1}{a+y}}$$

   The activity of the dissolved salt is thus

   $$a_{A_aY_y} = \left(\gamma_{\pm} m_{\pm}\right)^{a+y}$$

6. Any cell reaction is the sum of two half-cell reactions, and the SHE, at which the half-cell reaction

   $$H^+_{(\text{aqueous},m=1)} + e^- = \frac{1}{2}\mathrm{H}_{2(g,P=1\text{ atm})}$$

   occurs is assigned a potential of zero. This facilitates the assignment of standard reduction half-cell potentials to all other half-cell reactions. The electrochemical series is produced by listing the half-cell reactions in decreasing order of the magnitudes of their standard reduction half-cell potentials.
7. The influence of electrode potential and pH on the phase equilibria and solubilities in aqueous electrochemical systems can be presented graphically by Pourbaix diagrams.

14.12 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 14

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Absolute potential
Anodic oxidation reaction
Anolyte
Cathodic reduction reaction
Catholyte
Cell reaction
Charge neutrality
Concentration cell
Covalent character
Daniell cell
Electric potential
Electric work
Electrochemical reaction
Electrochemical series
Electrode
Electrolysis
Electrolyte
Electromotive force (EMF)
Faraday's constant ($\mathfrak{F}$; 96,487 coulombs/mole)
Formation cell
Galvanic cell
Ionic character
Liquid junction potential
Molality
Molarity
Nernst equation
Open-circuit EMF
Salt bridge
Single electrode potential
Solubility product
Standard EMF of the cell
Standard hydrogen electrode (SHE)

14.13 QUALITATIVE EXAMPLE PROBLEM

Qualitative Problem

Calculate the solubility of AgBr in water at 298 K.

Solution to Qualitative Problem

From Table 14.1, $\varepsilon^{\circ,\mathrm{Ag}} = 0.7991$ volts and $\varepsilon^{\circ,\mathrm{Br}} = 1.0652$ volts. Therefore, for the reaction

$$Ag_{(s)} + \frac{1}{2}Br_{2(l)} = Ag^{+}_{(m)} + Br^{-}_{(m)}$$

$$\Delta G^{\circ}_{298\text{ K}} = -\mathcal{F}(-0.7991 + 1.0652) = 25{,}775\text{ J}$$

For

$$Ag_{(s)} + \frac{1}{2}Br_{2(l)} = AgBr_{(s)}$$

$$\Delta G^{\circ}_{298\text{ K}} = -95{,}670\text{ J}$$

and hence for

$$AgBr_{(s)} = Ag^{+}_{(m)} + Br^{-}_{(m)}$$

$$\begin{aligned}\Delta G^{\circ}_{298\text{ K}} &= 25{,}675 + 95{,}670\\ &= 121{,}345\text{ J}\\ &= -8.3144 \times 298 \ln K_{\text{sp}}\end{aligned}$$

Thus, $K_{sp} = (\gamma_{\pm} m_{\text{AgBr}})^2 = 5.4 \times 10^{-22}$ or $m_{\text{AgBr}} = 2.3 \times 10^{-11}$, which indicates that AgBr is virtually insoluble in water.

14.14 QUANTITATIVE EXAMPLE PROBLEMS

Quantitative Problem 1

Fayalite, $2FeO{\cdot}SiO_2$, is the only iron silicate compound formed by reaction of FeO with SiO_2 at a total pressure of 1 atm, and the standard Gibbs free energy change for the reaction

$$2FeO_{(s)} + SiO_{2(s)} = 2FeO \cdot SiO_{2(s)}$$

is −11,070 J at 1200 K. Calculate the EMF of the cell

$$Fe \mid SiO_2 \mid 2FeO \cdot SiO_2 \mid CaO - ZrO_2 \mid FeO \mid Fe$$

at 1200 K.

Solution to Quantitative Problem 1

This is an oxygen concentration cell in which the cell reaction can be written as

$$O_2\left(\text{higher pressure at the cathode}\right) \rightarrow O_2\left(\text{lower pressure at the anode}\right) \quad \text{(i)}$$

for which the EMF is

$$\varepsilon = -\frac{RT}{4\mathfrak{f}}\ln\frac{p_{O_2}(\text{at the anode})}{p_{O_2}(\text{at the cathode})} \tag{ii}$$

The oxygen pressure at the electrodes are fixed by the chemical equilibrium

$$\text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO} \tag{iii}$$

for which

$$K_{(\text{iii})} = \frac{a_{\text{FeO}}}{a_{\text{Fe}}p_{O_2}^{1/2}}$$

At the cathode, the activity of FeO with respect to Fe-saturated pure FeO is unity, and at the anode, the activity of FeO is that occurring in $2\text{FeO}\cdot\text{SiO}_2$ saturated with Fe and SiO_2. As

$$K_{(\text{iii})} = \frac{a_{\text{FeO(cathode)}}}{a_{\text{Fe(cathode)}}p_{O_2\,(\text{cathode})}^{1/2}} = \frac{a_{\text{FeO(anode)}}}{a_{\text{Fe(anode)}}p_{O_2\,(\text{anode})}}$$

and

$$a_{\text{Fe(anode)}} = a_{\text{Fe(cathode)}} = a_{\text{FeO(cathode)}} = 1$$

$$\frac{p_{O_2\,(\text{anode})}}{p_{O_2\,(\text{cathode})}} = a_{\text{FeO(anode)}}^2$$

and hence, in Equation (ii),

$$\varepsilon = -\frac{RT}{4\mathfrak{f}}\ln a_{\text{FeO(anode)}}^2$$

For $2\text{FeO} + \text{SiO}_2 = 2\text{FeO}\cdot\text{SiO}_2$,

$$\begin{aligned}\Delta G^{\circ}_{1200\text{ K}} &= -11{,}070\text{ J}\\ &= -8.3144\times 1200\ln\frac{a_{2\text{FeO}\cdot\text{SiO}_2}}{a_{\text{FeO}}^2 a_{\text{SiO}_2}}\end{aligned}$$

Thus, at the anode, with $a_{2\text{FeO}\cdot\text{SiO}_2} = a_{\text{SiO}_2} = 1$,

$$a_{\text{FeO(anode)}} = 0.574$$

and thus,

$$\begin{aligned}\varepsilon &= -\frac{8.3144\times 1200}{4\times 96,487}\ln\ (0.574)^2\\ &= 0.0287 \text{ volts}\end{aligned}$$

Alternatively, the anode half-cell reaction can be written as

$$\mathrm{O}^{2-} = \frac{1}{2}\mathrm{O}_{2(\mathrm{eq.Fe}/\underline{\mathrm{FeO}})} + 2e^-$$

and the cathode half-cell reaction can be written as

$$\frac{1}{2}\mathrm{O}_{2(\mathrm{eq.Fe/FeO})} + 2e^- = \mathrm{O}^{2-}$$

or, at the anode,

$$2\mathrm{Fe} + 2\mathrm{O}^{2-} + \mathrm{SiO}_2 = 2\mathrm{FeO}\cdot\mathrm{SiO}_2 + 4e^-$$

and, at the cathode,

$$2\mathrm{FeO} + 4e^- = 2\mathrm{Fe} + 2\mathrm{O}^{2-}$$

summation of which gives the cell reaction as

$$2\mathrm{FeO} + \mathrm{SiO}_2 = 2\mathrm{FeO}\cdot\mathrm{SiO}_2$$

The Gibbs free energy change for the cell reaction is

$$\Delta G^\circ = -z\mathfrak{f}\varepsilon^\circ = -11,070 \text{ J}$$

and thus,

$$\varepsilon = \frac{-\Delta G^\circ}{4\mathfrak{f}} = \frac{11,070}{4\times 96,487} = 0.0287 \text{ volts}$$

Quantitative Problem 2

A waste liquor consists of a 0.5 molal solution of $CaCl_2$ in water. Calculate the minimum work, per mole of $CaCl_2$, required to separate the liquor into anhydrous $CaCl_2$ and pure water at atmospheric temperature and pressure. The mean ionic activity coefficient of 0.5 molal $CaCl_2$ is 0.448.

Solution to Quantitative Problem 2

The minimum work is that required when the separation is conducted reversibly; that is, $w = -\Delta G$ for the process. Further, 0.5 molal $CaCl_2$ comprises 0.5 moles of $CaCl_2$ and 1000 g of H_2O or 0.5 moles of $CaCl_2$ and 1000/18 = 55.55 moles of water. Thus, 1 mole of $CaCl_2$ exists in 111.1 moles of water, and the mole fraction of water is 111.1/112.1 = 0.991.

1. Move 1 mole of dissolved $CaCl_2$ from a concentration of 0.5 molar to the 1 molal standard state.

$$\begin{aligned}\Delta G_{(1)} &= RT\ln\frac{a_{\mathrm{CaCl_2}(m\,=\,1)}}{a_{\mathrm{CaCl_2}(m\,=\,0.5)}}\\ &= -RT\ln 4\left(\gamma_{\pm}m_{\mathrm{CaCl_2}}\right)^3\\ &= -8.3144\times 298\ln\ [4\times(0.448\times 0.5)^3] = 7686\ \mathrm{J}\end{aligned}$$

2. Transfer the 1 mole of Ca^{2+} ions from the 1 molal standard state to solid Ca at 298 K. From Table 14.1, $\varepsilon^{\circ,\mathrm{Ca}} = -2.87$ volts. Therefore, for the reaction

$$\mathrm{Ca}^{2+}_{(m)} + 2e^- = \mathrm{Ca}_{(s)}$$
$$\Delta G_{(2)} = -(2\times 96{,}487\times -2.87) = 553{,}835\ \mathrm{J}$$

3. Transfer the 2 moles of Cl^{2-} ions from the 1 molal standard state to Cl_2 gas at 1 atm pressure at 298 K. From Table 14.1, $\varepsilon^{\circ,\mathrm{Cl}} = 1.3595$ volts. Therefore, for the reaction

$$2C1^-_{(m)} = C1_{2(g)} + 2e^-$$
$$\Delta G_{(3)} = -(2\times 96{,}487\times -1.3595) = 262{,}348\ \mathrm{J}$$

4. Transfer 111.1 moles of H_2O from a mole fraction of 0.991 to a mole fraction of 1.0. Assuming Raoultian behavior,

$$\begin{aligned}\Delta G_{(4)} &= -n_{\mathrm{H_2O}}RT\ln X_{\mathrm{H_2O}}\\ &= -111.1\times 8.3144\times 298\ln 0.991 = 2486\ \mathrm{J}\end{aligned}$$

5. Allow the 1 mole of solid Ca to react with the mole of gaseous Cl_2 to form 1 mole of solid $CaCl_2$ at 298 K. For the reaction

$$\mathrm{Ca}_{(s)} + \mathrm{Cl}_{2(g)} = \mathrm{CaCl}_{2(s)}$$
$$\Delta G_{(5)} = \Delta G^{\circ}_{298\ \mathrm{K}} = -752{,}100\ \mathrm{J}$$

Thus, the change in the Gibbs free energy for the separation process is

$$\Delta G_{(1)} + \Delta G_{(2)} + \Delta G_{(3)} + \Delta G_{(4)} + \Delta G_{(5)} = 74{,}255\ \mathrm{J}$$

which is the minimum amount of work required per mole of $CaCl_2$ separated.

PROBLEMS

14.1 The EMF of the galvanic cell

$$\mathrm{Pb}_{(s)}\big|\mathrm{PbCl}_{2(s)}\big|\mathrm{HCl}_{(\mathrm{aqueous})}\big|\mathrm{AgCl}_{(s)}\big|\mathrm{Ag}_{(s)}$$

where all of the components are present as pure solids in contact with an HCl electrolyte, is 0.490 volts at 25°C and, at that temperature, the temperature coefficient of the EMF is -1.84×10^{-4} volts/degree. Write the cell reaction and calculate the Gibbs free energy change and the change in enthropy for the cell reaction at 298 K.

14.2 At 298 K, the EMF of the cell

$$\mathrm{Pb}\,\big|\,\mathrm{PbCl}_2\big|\,\mathrm{Hg}_2\mathrm{Cl}_2 \mid \mathrm{Hg}$$

is +0.5357 volts and the temperature coefficient of the EMF is 1.45×10^{-4} volts/degree. Calculate (a) the maximum work available from the cell at 298 K per mole of Pb reacted, (b) the change in entropy for the cell reaction, and (c) the heat absorbed by the cell at 298 K per mole of Pb reacted when the cell is operating reversibly.

The Hg electrode in the cell is replaced by an Hg–X alloy in which $X_{\mathrm{Hg}} = 0.3$ and where X is inert. The EMF of the cell at 298 K is found to increase by 0.0089 volts. Calculate (d) the activity of Hg in the alloy at 298 K.

14.3 The solid-state electrochemical cell

$$\left(\mathrm{Pt}\right),\mathrm{O}_2(\text{gas at } p_{\mathrm{O}_2})\big|\mathrm{CaO}-\mathrm{ZrO}_2\big|\mathrm{Fe}\big|\mathrm{FeO},(\mathrm{Pt})$$

is built to measure the partial pressure of oxygen in gases. Write an equation relating the oxygen pressure and temperature of the gas to the EMF to the cell.

14.4 The EMF of the cell

$$\mathrm{Ag}_{(s)}\big|\mathrm{AgCl}_{(s)}\big|\mathrm{Cl}_{2(g,1\ \mathrm{atm})},\mathrm{Pt}$$

is found to be

$$\varepsilon\left(\text{volts}\right) = 0.977 + 57\times10^{-4}(350-t) - 4.8\times10^{-7}\left(350-t\right)^2$$

in the temperature range 100°C–450°C. Calculate the value of Δc_p for the cell reaction.

14.5 A galvanic cell is set up with electrodes of solid aluminum and solid aluminum–zinc alloy and an electrolyte of molten AlCl_3–NaCl. When the mole fraction of Al in the alloy electrode is 0.38, the EMF of the cell is 7.43 millivolts at 380°C, and the temperature coefficient of the EMF is 2.9×10^{-5} volts/degree. Calculate (a) the activity of Al in the alloy, (b) the partial molar Gibbs free energy of mixing of Al in the alloy, and (c) the partial molar enthalpy of mixing of Al in the alloy.

14.6 By measuring the EMFs of cells of the type

$$Ni_{(s)} \mid NiO_{(s)} \mid CaO\text{–}ZrO_2 \mid Cu_{(l)} \text{ containing dissolved oxygen}$$

it has been established that e_O^O in liquid copper at 1363 K is –0.16 and that the standard Gibbs free energy change for

$$\frac{1}{2}O_{2(g)} = [O]_{1\text{ wt\% in Cu}}$$

is $\Delta G° = -74{,}105 + 10.76T$ J. If the EMF of such a cell is 0.222 volts at 1363 K, calculate (a) the activity of oxygen in the liquid copper cathode with respect to a standard state of oxygen gas at 1 atm pressure, (b) the activity of Cu_2O in the cathode metal with respect to Cu-saturated pure solid Cu_2O, (c) the weight percentage of oxygen dissolved in the copper cathode, (d) the maximum solubility of oxygen in liquid copper at 1363 K.

14.7 Calculate the conditions under which an aqueous solution of $[Pb^{2+}]$ = 1 mole/liter is in equilibrium with metallic Pb and solid PbO at 298 K. Is any other lead ion present in significant concentration in this solution?

Species	$\Delta G^\circ_{298\text{ K}}$ J
$PbO_{(s)}$	−189,300
$Pb^{2+}_{(m)}$	–24,310
$Pb^{4+}_{(m)}$	+302,500
$HPbO^{-}_{2(m)}$	–339,000
$PbO^{2-}_{3(m)}$	–277,570
$PbO^{4-}_{4(m)}$	–28,210
$H_2O_{(l)}$	–237,190

14.8 Aluminum can be produced by the electrolysis of Al_2O_3 dissolved in molten cryolite, $3NaF \cdot A1F_3$. If inert electrodes are used in an electrolysis cell and the cryolite is saturated with Al_2O_3 at 1000°C, what is the decomposition voltage of the Al_2O_3? The Hall–Heroult process for the electrolysis of Al_2O_3 uses graphite as the anode material, and the gas which is evolved at the anode is essentially pure CO_2 at 1 atm pressure. Calculate the decomposition voltage of Al_2O_3 in an Al_2O_3-saturated $3NaF \cdot AlF_3$ electrolyte at 1000°C in the Hall–Heroult cell.

14.9 At 298 K, the solubility of Cl_2 in H_2O, under a partial pressure of Cl_2 = 1 atm, is 0.0618 molal. Calculate the standard Gibbs free energy of formation of an aqueous solution of chlorine and calculate the change in the Gibbs free energy to form a solution of chlorine which is 0.01 molal. Ideal solution behavior can be assumed.

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CHAPTER 15

Thermodynamics of Phase Transformations

This chapter is about phase transformations in closed thermodynamic systems. It is appropriate to first define the terms *phase* and *phase transformation*.

> A phase is a physically distinct homogeneous portion of a thermodynamic system delineated in space by a bounding surface, called an interphase interface, and distinguished by its state of aggregation (solid, liquid or gas), crystal structure, composition and/or degree of order. Each phase in a material system generally exhibits a characteristic set of physical, mechanical and chemical properties and is, in principle, mechanically separable from the whole.*
>
> A phase transformation in a material system occurs when one or more of the phases in a system changes their state of aggregation, crystal structure, degree of order or composition resulting from a reconfiguration of the constituent particles (atoms, molecules, ions, electrons, etc.) comprising the phase. This reconfiguration is a change in the thermodynamic state leading to a more stable condition described by appropriate thermodynamic potentials such as a decrease in the Gibbs free energy (G) at constant temperature (T) and pressure (P). Whether describing the freezing of a metal or the onset of ferromagnetism in iron (Fe), a change in phase is indicated when small changes in relevant thermodynamic variables produce marked changes and sometimes dramatic qualitative changes in the nature of the system. These changes can occur abruptly (discontinuously) or gradually (continuously) at critical values of certain thermodynamic variables. The decrease in free energy accompanying the reconfiguration is often referred to as the thermodynamic "driving force" for the phase change.†

One can see that most of the topics of the preceding chapters lead very nicely into the field of study of phase transformations. This chapter will briefly discuss selected aspects of the thermodynamics of phase transformations.‡

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* W. A. Soffa and D. E. Laughlin, "Diffusional Phase Transformations in the Solid State," in *Physical Metallurgy*, vol. 1, edited by D. E. Laughlin and K. Hono, Elsevier, Waltham, MA, 2014, pp. 851–1019.

† Ibid.

‡ For more in-depth discussion, see Soffa and Laughlin (ibid.).

15.1 THERMODYNAMICS AND DRIVING FORCE

15.1.1 Phase Transformations with No Change in Composition

A phase transformation that does not involve a change in composition and occurs in a single-component system (an element or a compound) is the first one we will examine. Figure 15.1 shows two Gibbs free energy curves for competing phases in a one-component system at constant pressure. We use the units of J/m^3 (molar free energy divided by the molar mass, G_M/V_M) for the volume-extensive Gibbs free energy for reasons that will become apparent later. The liquid is the high-temperature equilibrium phase and the solid is the low-temperature equilibrium phase. The intersection of the two Gibbs free energy curves denotes the equilibrium melting point of the single-component material. We have already discussed the slopes and curvatures of similar Gibbs free energy versus temperature curves and how those geometric features are related to the heat capacities of the two phases (see Chapter 7). Now we look in more detail at what happens in the liquid phase as the temperature of the system is lowered, starting from above the melting point.

By looking into the details of the transformation, we deviate somewhat from our previous discussions of phase diagrams (Chapters 7 and 10), where we spoke only of equilibrium states of the system. During the transformation of a liquid to a crystal, there will be *transition states* which in themselves may not be equilibrium states in the strictest sense. Indeed, to even discuss the "initiation" of a heterogeneous transformation, we must include a discussion of the finite regions in which the new phase forms and bring into the discussion a new entity: namely, the interface between the liquid phase and the evolving solid phase, with its attendant *excess free energy*.

Above the melting temperature, T_M, any fluctuation of the equilibrium liquid phase into a state resembling that of the solid brings with it an increase in the free energy of the system. Such fluctuations are therefore unstable and will dissolve back into the

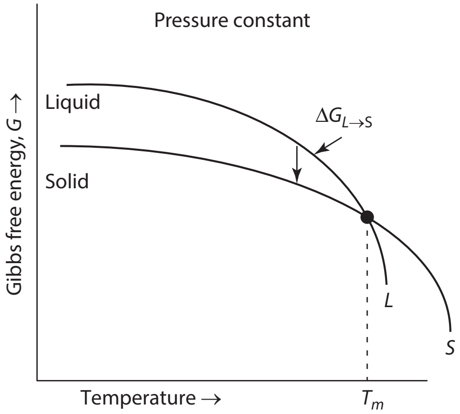

Figure 15.1 Gibbs free energy vs. temperature plot of the solid and liquid phase in a one-component system. T_M is the melting point.

liquid. At the melting point, both phases have the same Gibbs free energy and both are equilibrium phases. Since they have the same free energy at the melting point, there is no driving force (decrease in Gibbs free energy) for the formation of the solid from the liquid. If a fluctuation in the liquid produces a small region of the solid phase, since there is no increase in the volume free energy, we may think that such a fluctuation would also be stable. However, it is at this point that the new feature of the system—namely, the interface between the incipient solid phase and the existing liquid phase—must be taken into account. The interface between the liquid phase and the emerging solid phase has a positive excess energy associated with it and it therefore presents a barrier to the formation of the solid phase. At the melting temperature, the change in Gibbs free energy of a volume of liquid into a volume of solid is positive because of this excess surface energy. Undercooling of the liquid must occur in order to form the solid phase. This is true for first-order phase transformations (see Chapter 7).

Let us examine what happens when a small, spherically shaped solid phase forms within an *undercooled* liquid. Since the system is below the melting point, the volume Gibbs free energy change of the liquid to solid, $\Delta G_{L\to S}$, is negative. However, we must account for the surface energy between the solid and liquid as well. Taking these two energies into account, we write for the total change in Gibbs free energy, $\Delta g_{L\to S}$, to form a sphere of the solid phase of radius r:

$$\Delta g_{L\to S} = \frac{4\pi}{3} r^3 \Delta G_{L\to S} + 4\pi r^2 \gamma_{S/L} \tag{15.1}$$

where $\gamma_{S/L}$ is the excess surface free energy between the solid and the liquid.

The change in the Gibbs free energy, $\Delta g_{L\to S}$, as a function of its size, is shown in Figure 15.2. It is seen to have two components, where one is negative (the volume term)

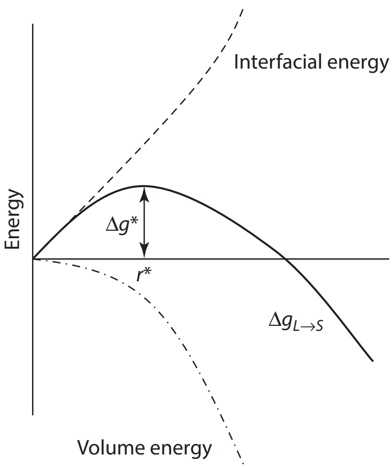

Figure 15.2 The free energy to form a critical size nucleus of solid from a liquid phase plotted against its radius, along with its volume energy and surface energy contributions.

and the second one is positive, since it represents the positive excess surface energy term. For very small solid particles, the surface term dominates and the sign of the change in free energy is positive.

In order for a stable solid to form (nucleate), the region in which it is to form must undergo fluctuations in its configuration such that it becomes more like a solid than a liquid. If the region is large enough, the decrease in the free energy due to the volume of the new phase will be greater than the increase in the free energy due to the interface term. In such a case, the change in free energy will be negative and the nucleus of the solid phase will be stable.

By taking the derivative of Equation 15.1 with respect to radius and setting the result equal to zero, the critical radius for the initiation of the transformation is obtained.

$$r^* = -\frac{2\gamma_{S/L}}{\Delta G_{L\to S}} \tag{15.2}$$

This is the size of a fluctuation where the change in the Gibbs free energy accompanying the formation of the solid begins to decrease. Substituting the value of this critical radius into Equation 15.1 yields the critical activation energy which must be overcome in order that the fluctuation can grow.

$$\Delta g^*_{L\to S} = \frac{16\pi\gamma^3_{S/L}}{3\Delta G^2_{L\to S}} \tag{15.3}$$

From Figure 15.1, it can be seen that the larger is the undercooling (ΔT), the larger is the magnitude of the value of $\Delta G_{L\to S}$, and hence, as can be seen in Equation 15.2, the smaller is the size of the new solid phase that can grow into a stable particle. Note the cubic dependence of critical activation energy on the excess surface free energy.

15.1.2 Phase Transformations with Change in Composition

The formation of a new phase in a multicomponent alloy system is somewhat more complicated. Let us examine this case for the binary system shown in Figure 15.3. An alloy of composition X_0 initially is held a temperature T_1. At equilibrium, the state of the system at T_1 is a single phase of the solid α. Consider now what happens when the temperature is suddenly lowered to the temperature T_2. The alloy is now in the α + β two-phase region of the phase diagram. Figure 15.4 shows the Gibbs free energy curves for the α + β phases at the temperature T_2. A common tangent is drawn between the two curves, and the equilibrium compositions of the two phases are indicated as X_e^α and X_e^β. Also indicated on the plot is the total decrease in the Gibbs free energy for the formation of the amount of β phase in equilibrium with α. In this case, the final state is a two-phase state and the composition of the new β phase (X^β), is different from that of the original phase (X_0). The lever rule

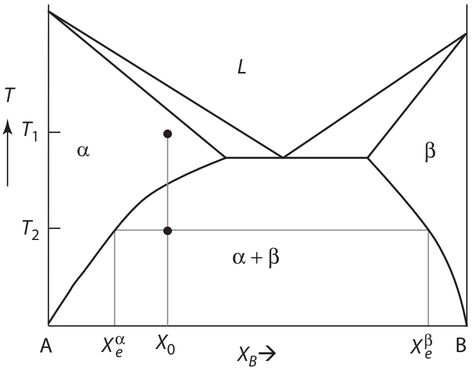

Figure 15.3 Binary eutectic phase diagram. The equilibrium state at T_1 of an alloy of composition X_0 is the solid α phase. At T_2 the equilibrium state is two-phase α and β with their compositions shown on the phase diagram.

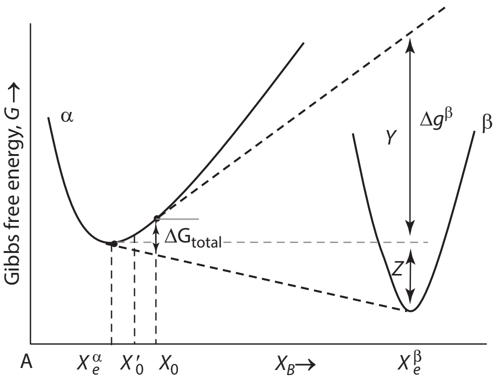

Figure 15.4 Free energy curves for the α and β phases at T_2. When a small amount of β forms, the overall composition of the alloy changes from X_0 to X_0. The driving force for the formation of the β phase is shown as Δg.

(Section 1.7) can be used to determine the fractional amounts of the two phases at equilibrium. For example, the fractional amount of the β phase is given by

$$\%\beta = \frac{X_0 - X_e^\alpha}{X_e^\beta - X_e^\alpha}$$

If we are to utilize Equation 15.2 to determine the critical size of the new phase, we need to determine the driving force for the formation of the critical nucleus of the new phase. This is not the value of ΔG_{total}, shown in Figure 15.4, since that is the total change in the Gibbs free energy after equilibrium has been attained.

We must determine Δg^β when a small amount of β with composition X^β forms from matrix of composition X_0 changing the composition of the matrix to X'_0. The value X_0' is less than that of the original alloy, since the new phase is richer in β, depleting the original phase. The change in free energy of a mole of the phase when a fraction of β has formed is

$$\Delta G = G_\beta f_\beta + G_{\alpha'} f_\alpha - G_\alpha$$

where:

ΔG is the change in free energy for the formation of f_β of β

$f_\beta = \dfrac{X_0 - X_0'}{X_\beta - X_0'}$ is the fraction of β formed

$$\Delta g^\beta = \frac{\Delta G}{f_\beta} = G_\beta - G_{\alpha'} + \frac{G_{\alpha'} - G_\alpha}{f_\beta}$$

But

$$G_{\alpha'} \approx G_\alpha - \left(X_0 - X_0'\right)\left(\frac{\partial G}{\partial X}\right)_{X_0}$$

which after some algebra yields

$$\Delta g^\beta \approx G_\beta - G_{\alpha'} - \left(X_\beta - X_0\right)\left(\frac{\partial G}{\partial X}\right)_{x=x} < 0 \qquad (15.4)$$

This is shown in Figure 15.4, where Δg^β can be seen to be found by first constructing a tangent to the α free energy curve at X_0 and then by dropping down to the free energy curve at the composition of the formation of the new β phase. This is the value of the change in free energy which is substituted into Equations 15.2 and 15.3 to obtain the critical size and critical barrier to the formation of the solid phase since this is the driving force for the nucleation of the solid.

15.2 USE OF THE T_0 CURVES

In one-component systems, the temperature where two free energy curves intersect is the equilibrium temperature of the phase transition between the two phases. This is not so for a binary system. Consider the phase diagram of Figure 15.5 and the Gibbs free energy curves that produce the equilibrium at T' (Figure 15.6). Included on the phase diagram are dashed curves which represent the locus of all points where the α and γ and β and γ phases have equal free energies as a function of temperature—that is, where the free energy curves intersect.

Now consider the phase changes which can occur when a phase of composition X_1 is quenched from the γ phase stability region to the temperature T'. The following two transformations are possible:

- The γ phase could transform directly to the α phase without a change in composition.
- The γ phase could decompose into the equilibrium two-phase mixture of α + β.

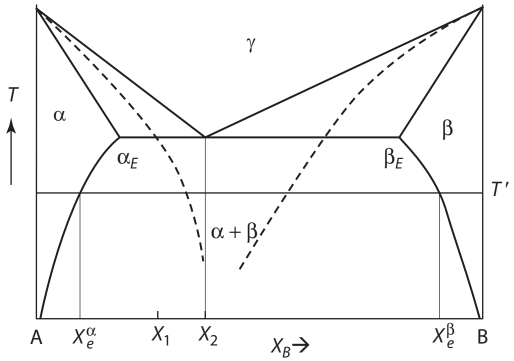

Figure 15.5 A eutectoid phase diagram displaying its T_0 curves for the α/γ and γ/β phases.

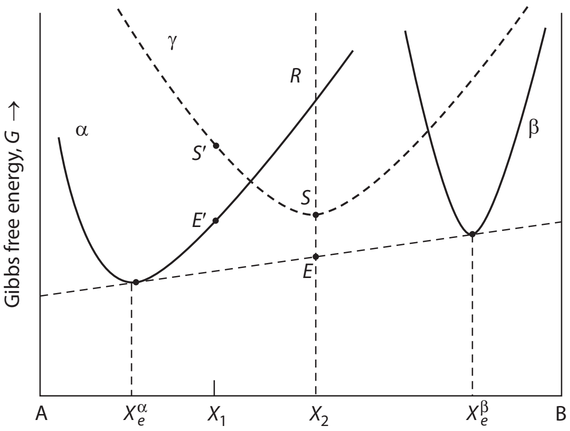

Figure 15.6 The free energy curves for the diagram shown in Figure 15.5. The alloy X_1 has a free energy of S' at T' and the alloy of composition X_2 has a free energy of S at T'.

Now consider the phase change(s) which can occur when a phase of composition X_2 is quenched from the γ region to the temperature T'. Only the following transformation is possible:

- The γ phase decomposes into the equilibrium two-phase mixture of α + β.

The reason for this difference is easily seen from the free energy curves of Figure 15.6. For the first case, the free energy of γ is shown as point S' and is above the Gibbs free energy curve of that of α at the composition in question. The γ phase can therefore transform directly to α with a decrease in free energy, arriving at point E'. Thus, the γ phase has changed into the α phase without a change in its composition. Such phase transformations are known as diffusionless transformations because no long-range atomic diffusion is necessary for the transformation to complete. Since the two phases are distinguished from each other, there must be a change in crystal structure in such transformations.

In the second case, however, the free energy of the γ phase is less than that of the α phase at the composition being considered (points *S* and *R*, respectively). Therefore, γ cannot transform to the α phase of the same composition.

The loci of the T_0 points on a phase diagram therefore denote which compositions of the high-temperature phase can transform into a low-temperature phase of the same composition but a different crystal structure. This analysis is important for the following solid-state transformations:

- The martensite transformation in steels
- The massive transformations in a variety of binary alloys

15.2.1 Martensitic Transformation

In steels of certain compositions, the alloys are held at temperatures within the high-temperature face-centered cubic (FCC) *austenite* (γ) phase field (named after Sir William Chandler Roberts-Austen, 1843–1902) and rapidly quenched to lower temperatures. The resulting phase is a tetragonal phase, α′, which is related to the body-centered cubic (BCC) α phase, but somewhat distorted due to trapped carbon atoms in specific sites of the new phase, which lowers its symmetry. This lower-symmetry α′ phase (called *martensite*, after Adolf Martens, 1850–1914) greatly increases the strength of the alloy. Immediately after the quench, the α′ phase is a single phase of the same composition as the austenite phase from which it formed. The α′ martensite is not an equilibrium phase and will decompose into the equilibrium $\alpha + \text{Fe}_3\text{C}$ phases if given enough thermal energy.

15.2.2 Massive Transformations

Another type of solid-state transformation that can be investigated using the T_0 curves is the *massive transformation*, named for its characteristic "massive" microstructure. The massive transformation is a solid-state phase transformation involving a compositionally invariant nucleation and growth process, producing a change in crystal structure. The transformation was first documented in studies of Cu–Zn and Cu–Al alloys during the 1930s.

Consider again the free energy curves displayed in Figure 15.6. The low-temperature α phase can only form from the high-temperature γ phase if the composition of γ is less than that of the intersection of the α and γ free energy curves (i.e., T_0) composition. For example, the γ phase of composition *S′* can directly form the α phase of the same composition (*E′*). The same can be said about the formation of the β phase from the high-temperature γ phase of the diagram. In this case, β can only be formed if the γ phase has a composition which is greater than that of the intersection of the γ and β free energy curves.

15.2.3 The Formation of Amorphous Phases from the Liquid

Another application of the T_0 curves is understanding which alloys are likely to form amorphous phases when rapidly quenched from the liquid state. Amorphous phases can be considered supercooled liquids which have been frozen by the rapid increase of their viscosity on cooling.

Consider the binary eutectic phase diagram of Figure 15.7a and its accompanying Gibbs free energy plots in Figure 15.7b. If a liquid of composition S' is rapidly quenched to T', it can do one of the following:

1. Transform into the equilibrium mixture of the α and β phases
2. Become an amorphous solid
3. Transform into the α solid phase of the same composition

Case 1 is not likely to occur, because the quench does not allow sufficient time for the decomposition to occur and to form the two solid phases of very different compositions. Such a transformation is therefore kinetically unlikely.

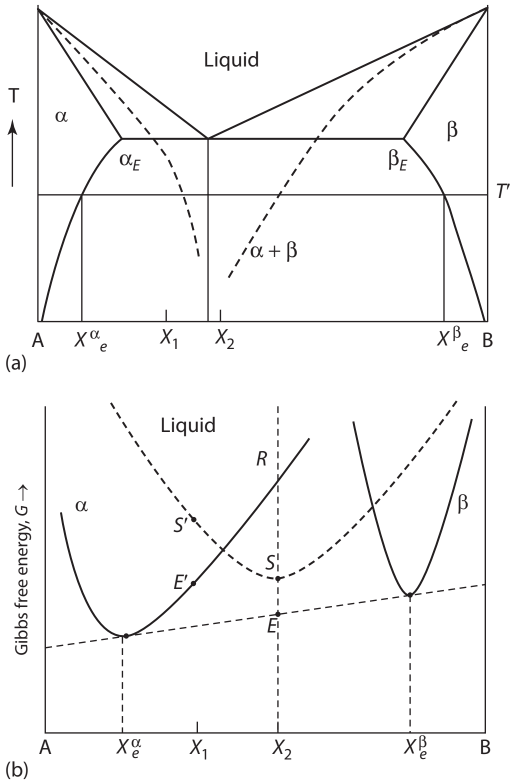

Figure 15.7 (a) A binary eutectic phase diagram with its T_0 curves. (b) The free energy curves at T' for the phase diagram in (a).

Either Case 2 or Case 3 may occur. Since there is a greater change in the free energy for the liquid to transform directly to a crystalline solid phase of the same composition, this is more likely. Such a process is sometimes denoted a *congruent solidification*.

Now consider the rapid cooling of the liquid phase of composition X_E. The liquid of this composition cannot transform into a solid of the same composition because of its location with respect to the T_0 points. A liquid of such composition thus has only two possible transformations:

1. Transform into the equilibrium mixture of the α and β phases
2. Become an amorphous solid

Once again, the option of transforming into the equilibrium mixture is unlikely because of the lack of time for it to occur. This leaves the option of the liquid phase of remaining in its undercooled liquid state and becoming a solid with an amorphous structure as its viscosity increases. Such will be the case if the temperature to which the liquid was rapidly cooled is below its glass transition temperature. An amorphous solid composed of metallic elements is sometimes called a *metallic glass*.

Once again, the T_0 curves play an important role in understanding and predicting what kind of phase transformation can occur. In the case of the formation of an amorphous solid, the liquid should be in a position relative to the T_0 points which does not allow for the formation of a solid phase of the same composition. In the case of the eutectic phase diagram, this means liquids of composition between the two T_0 curves are able to form amorphous solids.

15.3 SURFACE ENERGY

15.3.1 Equilibrium Shape

In the previous discussion of the determination of critical values for the size of the critical nuclei, we assumed a spherical shape for the solid phase when it nucleated. This may be true if the surface energy of the solid is isotropic, since this is the shape which minimizes the ratio of the surface area to volume of a solid and therefore minimizes the effect of the surface energy. If the surface energy is not isotropic, the shape will be that which produces low-energy facets, which usually means the nuclei will have the shapes of polyhedrons. For cubic symmetry, the surface energy versus the normal to the facet in question must display $m\bar{3}m$ point group symmetry, following Neumann's principle.*

For example, if the surface energy of the (100) planes is much less than that of the (111) planes, the equilibrium shape of the crystal would be that of a cube (Figure 15.8a). On the other hand, if the reverse is true and the (111) surface energy is much

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* "The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal." J. F. Nye, *Physical Properties of Crystals*, Oxford University Press, Oxford, UK, 1957, pp. 20–24.

less than (100) surface energy, a particle with the shape of an octahedron would form (Figure 15.8b). The anisotropy of the surface energy of a crystal can be understood in terms of *broken bonds*. In general, minimizing the number of broken bonds at the surface minimizes the surface free energy for those orientations.

Of course, intermediate cases of anisotropy could exist and can be illustrated using the polar plot shown in Figure 15.9. This polar plot can be used to establish the

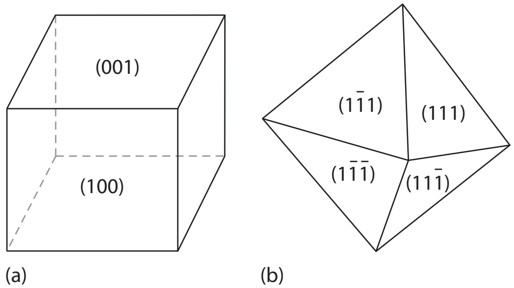


Figure 15.8 Particle shapes for crystals with cubic symmetry. (a) Cube, when (100) planes have very small surface energies. (b) Octagon, when the (111) planes have very low surface energies.

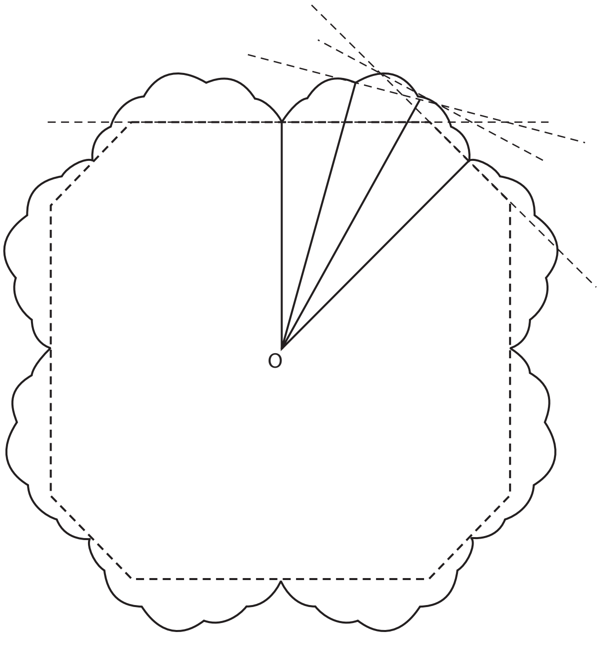


Figure 15.9 A polar plot of the excess surface energy of a crystal with a fourfold axis. The Gibbs–Wulff construction produces the equilibrium shape of the crystal. (From J. W. Christian, *The Theory of Transformations in Metals and Alloys*, Pergamon Press, Oxford, UK, 1965.)

equilibrium shape of a crystal through the Gibbs–Wulff (George Yuri Viktorovich Wulff, 1863–1925) construction. In the plot, $\mathbf{n}$ is the normal to a $\{hkl\}$ plane, and the distance from the origin to the solid curve is proportional to the value of the surface energy of the plane in question. The Gibbs–Wulff construction generates an envelope of planes as a function of position which has the lowest value of surface energy by minimizing $\int \sigma(n)dA$. This shape defines the equilibrium shape of the crystal.

15.4 NUCLEATION AND SURFACE ENERGY

15.4.1 Homogeneous Nucleation

Where the solid phase first forms within the liquid phase is often of interest. One possibility is that it can form anywhere within the liquid phase. This is what is usually termed *homogeneous nucleation*. In principle, the new phase can form at any of the sites where a atom in the liquid exists. With time, the liquid will be uniformly transformed into the solid phase, with the grains of the solid phase which formed first being the largest.

15.4.2 Heterogeneous Nucleation

The most likely nucleation method is by what is called *heterogeneous nucleation*, which means that the initiation of transformation from the liquid to the solid occurs at very specific sites. In this section, we will only consider the formation of a solid on the walls of the container of the liquid.

The reason that heterogeneous nucleation is more frequently observed to occur is that the energy barrier to the formation of the solid is reduced at the specific site at which the nucleation occurs. For example, consider the nucleation of the solid β phase on the wall of the vessel containing the liquid phase in Figure 15.10. The shape of the nucleus is constrained by the wall, and importantly, the wall itself has a surface with the liquid and thereby exhibits a surface energy. When the β phase nucleates on the wall, the wall–liquid surface (and hence its surface energy) is replaced with the surface of the β phase and the wall (and hence its surface energy). The wall–β phase surface energy is usually less than that of the wall–liquid, and therefore, there

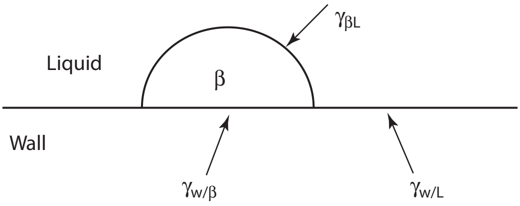


Figure 15.10 Schematic of a semispherical β particle forming on the wall of the container of the liquid phase, showing the various interface energies.

is an energetic advantage for the β phase to form there. This effectively reduces the free energy barrier to nucleation Δg^*, allowing for the formation of the new phase at substantially lower undercoolings.

The thermodynamics details of the process is as follows.

We saw in Equation 15.1 that the change in free energy in forming a nucleus by homogeneous nucleation is given as

$$\Delta g_{L\to S} = \frac{4\pi}{3} r^3 \Delta G_{L\to S} + 4\pi r^2 \gamma_{S/L}$$

The barrier to homogeneous nucleation is given as

$$\Delta g^*_{L\to S} = \frac{16\pi\gamma^3_{S/L}}{3\Delta G^2_{L\to S}}$$

If a sphere one-half the volume of one nucleated homogeneously is formed on the wall of the vessel which contains the liquid (Figure 15.10), we write the following for the energy changes:

$$\Delta g^{\text{het}}_{L\to\beta} = \frac{2}{3}\pi r^3 \Delta G_{L\to S} + 2\pi r^2 \gamma_{\beta/L} + \pi r^2 (\gamma_{\beta/W} - \gamma_{L/W})$$

$$r^{\text{het}*} = -\frac{2\gamma_{\beta/L} - \gamma_{\beta/W} + \gamma_{L/W}}{\Delta g_{L->\beta}}$$

$$\Delta g^{\text{het},*}_{L\to\beta} = -\frac{\pi(-2\gamma_{\beta/L} - \gamma_{\beta/W} + \gamma_{W/L})^3}{3\Delta g^2_{L\to\beta}}$$

The ratio of the barrier to form the new phase heterogeneously to that to form the same volume of the phase homogeneously is found to be

$$\frac{\Delta g^{\text{het},*}_{L\to\beta}}{\frac{1}{2}(\text{hom.})\Delta g^*_{L\to\beta}} = -\left(\frac{1}{8}\right)\frac{(-2\gamma_{\beta/L} - \gamma_{\beta/W} + \gamma_{W/L})^3}{\gamma^3_{\beta/L}}$$

If the surface energy $\gamma_{\beta/\mathrm{w}}$ equals that of the surface energy $\gamma_{\mathrm{w/L}}$, the ratio goes to unity, meaning there is no advantage to form on the wall. If, however, $\gamma_{W/L} > \gamma_{\beta/W}$, the ratio of the two barriers is less than unity, and therefore, there is an smaller barrier for the heterogeneous formation of the β phase on the wall of the vessel.

A similar effect can be demonstrated for other interfacial defects (e.g., grain boundaries in solid–solid phase transformations) as well as defects that have strain energies associated with them (e.g., dislocations). In the case of dislocations, the new phase diminishes the local strain energy, thereby effectively lowering the barrier to nucleation.

The preceding discussion demonstrates the *thermodynamics* of heterogeneous nucleation. It is the value of the thermodynamic barrier which is put into an exponential expression for the rate of nucleation. So, small changes in the magnitude of the barrier to nucleation yield large effects on the kinetics of the transformation.

15.5 CAPILLARITY AND LOCAL EQUILIBRIUM

The phase diagram shown in Figure 15.6 is an equilibrium diagram. The construction of an equilibrium diagram assumes that the α and β phases are large, so that the effect of surface energy is negligible. It is of interest to examine what happens if this is not the case, and the β phase is small with respect to the matrix (α) phase.

The free energy curve of the large β phase shown in Figure 15.7 must be modified to show that the Gibbs free energy of formation of the small β phase is less negative than that of the large ($r = \infty$) β phase (Figure 15.11).

The increase in the Gibbs free energy, $\Delta\mu$, must be known in order to estimate the change in the composition of the α phase due to size of the particle. The Gibbs free energy of the β particle including its surface energy is written as

$$dG' = \Delta\mu dn = -S'dT + PdV' + \sigma dA'$$

For equilibrium, at constant temperature and pressure this reduces to

$$\Delta\mu dn = \sigma dA'$$

For spherical particles, the surface area $\mathrm{A} = 4\pi r^2$ and $n = 4\pi r^3/3V_M$.

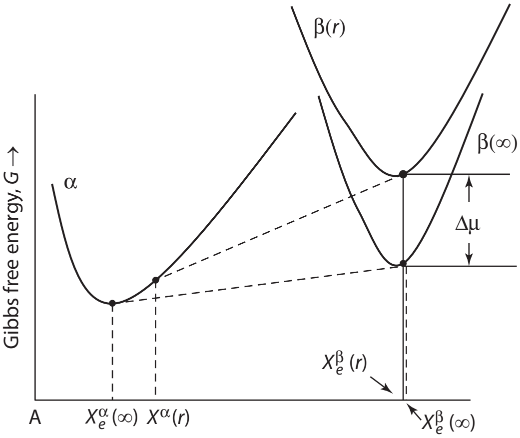


Figure 15.11 Schematic of the free energy curves of a β particle of very large size and one of very small size, showing that the solubility of the components in each of the phases depends on the size of the particle.

Thus, $dA = 8\pi r$ and $dn = 4\pi r^2/V_M$. This leads to

$$\Delta\mu = \frac{\sigma dA'}{dn} = \frac{\sigma 8\pi r}{4\pi r^2/V_M} = \frac{2\sigma V_M}{r}$$

It can be seen from the figure that this increase in the Gibbs free energy changes the location of its common tangent with the α phase. The change of the composition of the α phase which is in equilibrium with a particle of radius r_i and the composition of the α phase which is in equilibrium with a very large ($r = \infty$) particle is seen to be $X^{\alpha}(r_i) - X_e^{\alpha}(r = \infty)$.

The difference is related to value of the two slopes:

$$\Delta \text{ slopes} \approx \frac{\Delta\mu}{X_e^{\beta} - X_e^{\alpha}} \approx \frac{\partial^2 G}{\partial X^2}(X^{\alpha}(r) - X_e^{\alpha})$$

$$\frac{2V_M\sigma}{r(X_e^{\beta} - X_e^{\alpha})} \approx \frac{RT}{X_e^{\alpha}(1 - X_e^{\alpha})}(X^{\alpha}(r) - X_e^{\alpha})$$

If X^{α} is small with reference to X^{β},

$$1 - X_e^{\alpha} \approx 1$$

$$X^{\alpha}(r) - X_e^{\alpha} = \frac{2V_M\sigma X_e^{\alpha}}{rRT} \tag{15.5}$$

Equation 15.5 is a form of the Gibbs–Thomson equation.

Now consider two particles, one of radius r_1 and the other of radius r_2 (Figure 15.12). It can be seen that the composition of the α phase in equilibrium with the smaller particle, $X^{\alpha}(r_1)$, is greater than that in equilibrium with the larger particle, $X^{\alpha}(r_2)$. This gives rise to a gradient in the composition (and therefore, a gradient in the chemical potential, which is the driving force for diffusion). Therefore, β atoms will leave the smaller particle and be added to the larger one. This process

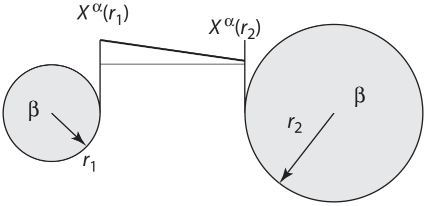


Figure 15.12 Schematic showing that the solubility of the β component in the α phase is greater when the α phase is in local equilibrium with a smaller β particle. A composition gradient is produced between small and large β particles.

is known as *particle coarsening* or *Ostwald ripening* (Friedrich Wilhelm Ostwald, 1853–1932). The end effect of coarsening is to have large particles thereby lowering the total surface energy of the system.

15.6 THERMODYNAMICS OF THE LANDAU THEORY OF PHASE TRANSFORMATIONS

We saw in Chapter 8 that the van der Waals equation for a nonideal gas gave rise to a phase change in the system and that such a change could be either a first-order one or a continuous one. We have also discussed the Ehrenfest designation of transitions being either first order or second (higher) order. In this section, we introduce another model of the thermodynamics of a phase that predicts phase transitions and also allows for both first- and higher-order transitions. This model is the Landau model of phase transitions.

In the late 1930s, Lev Davidovich Landau (1908–1968) proposed that many phase transitions can be characterized by a parameter, η, which describes an important property that is characteristic of the system under study (spin, moment, density, strain, etc.). This parameter has nonzero values below a certain critical temperature, T_C, and is zero above this temperature. It is called an *order parameter*, and it describes the evolution of the system in terms of measurable physical parameters and has an equilibrium value for a given system which is a function of temperature and pressure. It is usually normalized such that in the ordered state it approaches unity ($\eta = 1$) as T approaches zero, and above the transition temperature it is equal to zero. The way that it varies in the vicinity of the critical point serves as a useful basis for classifying the nature of the phase transition/transformation. Both first-order and higher-order transitions can be modeled, though the original model was focused on the higher-order transitions. In Section 9.10, we utilized the atomic order parameter to investigate equilibrium states in regular solutions that exhibit negative deviations from ideality. Figure 9.19 is a plot of the atomic order parameter versus temperature for such systems.

The effect of order parameter on the thermodynamics of a system is tracked as an excess term in the free energy. Landau's model is that the excess free energy between the ordered ($\eta > 0$) and disordered states ($\eta = 0$), $G^{\text{XS}}(\eta)$, can be expanded in a power series in the order parameter in the neighborhood of the critical point.

Landau wrote the excess free energy as

$$G^{\text{XS}}(\eta) = G(\eta \neq 0) - G(\eta = 0)$$

$$G^{\text{XS}}(\eta) = A\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 \ldots \tag{15.6}$$

where the coefficients $A, B, C, \ldots$ may be functions of temperature, T, and pressure, P. At constant pressure, the term A can be taken as a linear function of temperature given by

$$A = a\left(T - T_C\right) \tag{15.7}$$

with the coefficient a being a positive constant. B, C, D, and E are taken as constant in the first approximation. It can be seen that A changes sign on passing through the temperature T_C.

- When $T > T_C, A > 0$.
- When $T = T_C, A = 0$.
- When $T < T_C, A < 0$.

The coefficient A is proportional to the curvature of the $G^{\text{XS}}(\eta)$ versus η plot at $\eta = 0$. Above T_C, since $A > 0$, the curvature of the plot is positive. At T_C, the coefficient becomes 0, signifying an impending instability of the high-temperature phase. Below T_C, the disordered phase is unstable and the ordered phase forms.

We will now investigate three cases of the Landau expansion.

Case (i): The 2-4 Case

In this case, $B = 0$, $C > 0$, and $D = E = 0$

When $B = D = 0$, $G^{\text{XS}}(\eta)$ is an even function of η; that is,

$$G^{\text{XS}}(+\eta) = G^{\text{XS}}(-\eta) \tag{15.8}$$

As mentioned previously, $A = a(T - T_C)$ changes sign at $T = T_C$.

The behavior of $G^{\text{XS}}(\eta)$ as a function of temperature and the variation of the order parameter with temperature are shown in Figure 15.13. Above T_C (T_1 and T_2), $G^{\text{XS}}(0)$ is the only minimum, and therefore, the equilibrium state is disordered. At T_C, the curvature of $G^{\text{XS}}(0)$ equals zero, which means that the disordered phase is about to become unstable. Below T_C (T_3 and T_4), there are two states with nonzero order parameters. It can be seen from the figure that the minimum in $G^{\text{XS}}(\eta)$ occurs at larger η as the temperature is decreased.

We now will look at other thermodynamic aspects of this system.

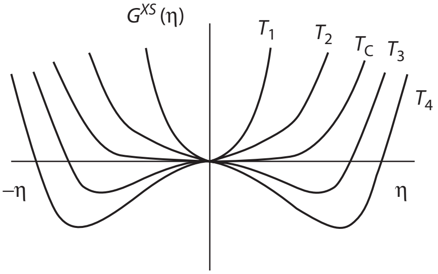


Figure 15.13 The excess Gibbs free energy for the 2-4 case (A and $C \neq 0$) of the Landau expansion. At T_C the disordered phase becomes unstable (curvature = 0). In the figure, $T_1 > T_2 > T_C > T_3 > T_4$.

First, we write the excess free energy:

$$G^{\mathrm{XS}}(\eta) = a(T - T_C)\eta^2 + C\eta^4 \tag{15.9}$$

For equilibrium, we minimize the excess free energy with respect to η by taking the first derivative and setting it equal to zero.

$$\frac{\partial G^{\mathrm{XS}}(\eta)}{\partial \eta} = 2a(T - T_C)\eta + 4C\eta^3 = 0$$

The solutions to this equation are:

$$\eta_{\mathrm{eq}} = 0 \text{ and } \eta_{\mathrm{eq}}^2 = -\frac{a(T - T_C)}{2C}$$

Furthermore, if we set $\eta = 1$ at $T = 0$ (a Third Law criterion), we obtain $T_C = 2C/A$ and thus, for the nonzero solutions,

$$\eta_{\mathrm{eq}}^2 = \frac{T_C - T}{T_C} = 1 - \frac{T}{T_C} \tag{15.10}$$

The two solutions $+\eta_{\mathrm{eq}}$ and $-\eta_{\mathrm{eq}}$ have equal absolute values (Figure 15.13) and correspond to different domains of the low-temperature phase.

If $T > T_C$, there is only one real solution to the equation: namely, $\eta = 0$. By taking the second derivative of $G^{\mathrm{XS}}(\eta)$, we get an expression which is proportional to the curvature of the plot.

$$\frac{\partial^2 G^{\mathrm{XS}}(\eta)}{\partial \eta^2} = 2a(T - T_C) + 12C\eta^2$$

At $\eta = 0$,

$$\left(\frac{\partial^2 G^{\mathrm{XS}}(\eta)}{\partial \eta^2}\right)_{\eta=0} = 2a(T - T_C) > 0, \text{ for } T > T_C$$

The positive curvature shows the disordered phase is stable above T_C.

It is only when the temperature falls below T_C that the other extrema values are real and thus appear in the plot. Since at T_C the curvature is zero at $\eta = 0$, the high-temperature phase becomes unstable and any further drop in temperature will commence the continuous phase transition to the ordered phase.

The equilibrium plot of the order parameter is shown in Figure 15.14.

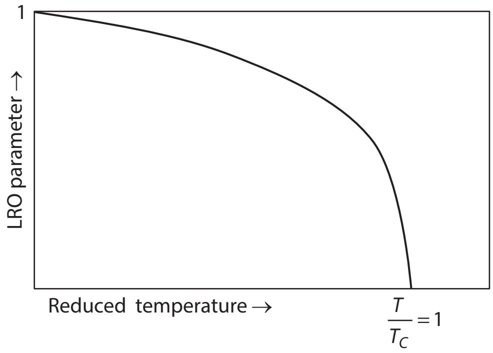


Figure 15.14 The order parameter vs. reduced temperature (T/T_C) plot for the Landau 2-4 case of Figure 15.13. Note that the slope at $T = 0$ is not zero in the Landau model.

This is an example of a continuous phase transition. The behavior is essentially identical to that of the Ehrenfest second-order transition.

The excess Gibbs free energy, G^{XS}, for $T < T_C$ is found by substituting the equilibrium value of η into Equation 14.1. We thus obtain

$$G^{\text{XS}} = -\frac{a(T_C - T)^2}{2T_C}$$

Since $a > 0$, $G^{\text{XS}} < 0$ for all $T < T_C$. A negative excess value of G^{XS} is expected for the stable low-temperature-ordered phase.

Now the excess entropy of the system can be found as

$$S^{\text{XS}} = -\frac{\partial G^{\text{XS}}}{\partial T} = -a\frac{(T_C - T)}{T_C}$$

This varies continuously through the transition temperature, as should be the case for a continuous transition. Below T_C, its sign is negative since the excess is with respect to the disordered phase, and the configurational entropy of the ordered phase is *less than* that of the disordered one.

The excess heat capacity of the ordered phase relative to the disordered phase at constant pressure for $T < T_C$ is given as

$$C_P^{\text{XS}} = T\left(\frac{\partial S^{\text{XS}}}{\partial T}\right) = \frac{aT}{T_C}$$

and is plotted in Figure 15.15.

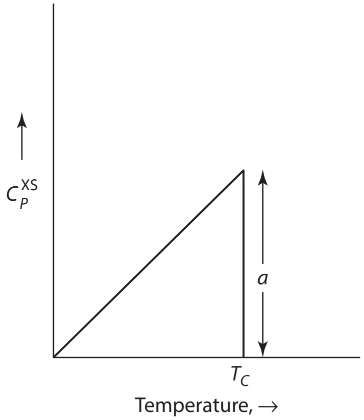


Figure 15.15 Plot of excess heat capacity vs. temperature for the Landau 2-4 case of Figure 15.12. Note the finite discontinuity at the critical temperature.

At T_C, the value of C_P^{XS} is a, and just above T_C, the excess value drops to zero. This produces a finite discontinuity in the heat capacity, consistent with the transition being *second order* since it is the second derivative of the energy term ($C_P = T\left(\partial^2 G/\partial T^2\right)$), which first becomes discontinuous at the transition temperature. The excess heat capacity is positive because it takes more thermal energy to increase the temperature of the low-temperature-ordered phase since the thermal energy must also be utilized to decrease the order of the system. The heat capacity above T_C is that of the high-temperature phase.

Finally, the excess enthalpy H^{XS} can be shown (see Problem 3) to be

$$H^{XS} = \frac{a}{2}\frac{(T^2 - T_C^2)}{T_C}$$

The transition has no latent enthalpy of transformation, which is another signature of a second-order transition.

Case (ii): The 2-3-4 Case

First-order transitions can also be modeled by the Landau expansion. If the expression for G^{XS} is truncated beyond the fourth order but B and $C \neq 0$ and $A = a\,(T - T_0)$, a first-order phase transition results.

The excess free energy is written as

$$G^{XS}(\eta) = a(T - T_C)\eta^2 + B\eta^3 + C\eta^4$$

Taking the first derivative of G^{XS} with respect to η yields three possible equilibrium solutions:

$$\eta_{\mathrm{eq}} = 0 \text{ and } \eta_{\mathrm{eq}} = \frac{-3B \pm \sqrt{9B^2 - 32aC(T - T_C)}}{8C}$$

At very high temperatures, the only real solution to the equation is $\eta_{\varepsilon\theta} = 0$. Since

$$\left(\frac{\partial^2 G^{XS}(\eta)}{\partial \eta^2} \right)_{\eta=0} = 2a(T - T_C) + 6B\eta + 12C\eta^2 = 2a(T - T_C) > 0$$

this is a minimum for G^{XS} (Figure 15.16).

As the temperature is lowered a temperature is reached (T_0) where the free energy of the disordered phase ($\eta = 0$) equals that of the ordered phase (see Figure 15.16). This two phase equilibrium is a signature of a first order phase transition. As the temperature continues to be lowered, there are two *minima* in the free energy curve, one for the ordered phase and one for the disordered phase. However, the one for the disordered phase is metastable. Finally, at lower temperatures the *minima* at $\eta = 0$ becomes a maximum: if the disordered phase could have been supercooled to this temperature it becomes unstable and the phase orders. This is the T_C temperature of the phase. Sometimes this is called the instability of temperature on cooling.

There is a clear discontinuity of the excess free energy on cooling: at T_C, the ordered state with a finite order parameter becomes the stable state. The order parameter versus temperature plot of this case is shown in Figure 15.17. The discontinuity is apparent.

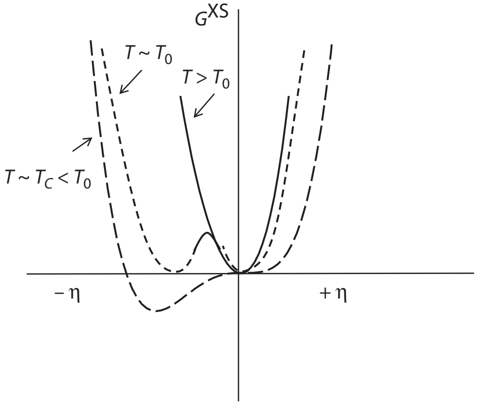


Figure 15.16 G^{XS} for the Landau 2-3-4 model above T_0, near T_0, and below T_0 and at T_C. The nonsymmetrical first-order character of the transition is apparent. (Courtesy of Ms Caroline Gorham.)

Case (iii): The 2-4-6 Case

For this case, $A \neq 0$, $C \neq 0$, and $E \neq 0$.

Like the 2-4 case, the free energy in this case is symmetrical about $\eta = 0$. As previously, only the quadric term is given a temperature dependence, and $C < 0$ and $E > 0$ are taken to be independent of T and P. The sixth-order term insures the proper thermodynamic behavior at low temperatures, yielding real solutions for the order parameter (Figure 15.18).

The interesting feature of this case is that even though the symmetry of the excess free energy of the low-temperature phase is symmetric about $\eta = 0$, the phase transition is first order. At $T = T_C$ there are three minima: two at nonzero order parameters and one at the disordered state ($\eta = 0$). Note that in this case, at low enough temperatures (e.g., T_4), the disordered phase becomes unstable (negative curvature at $\eta = 0$) and the ordered state could form continuously from a supercooled disordered state. As in the 2-3-4 case, the instability temperature of the disordered phase is less than the transition temperature.

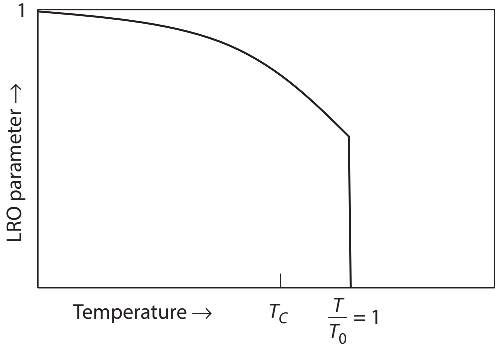


Figure 15.17 The order parameter versus reduced temperature (T/T_C) plot for Landau 2-3-4 case displaying a first order phase transition.

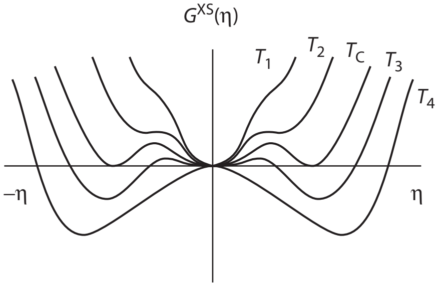


Figure 15.18 The excess Gibbs free energy for the Landau 2-4-6 case (A, C, and $E \neq 0$, but $C < 0$). At T_0, the disordered phase has the same free energy as the two variants of the ordered phase. $T_1 > T_2 > T_C > T_3 > T_4$. This is the case of a symmetrical first-order phase transition.

In each of the preceding three cases, it can be seen that the η versus T plot has a nonzero slope as T approaches absolute zero (Figures 15.4 and 15.17). This is discussed further in Qualitative Problem 1 of this chapter.

Although this approach to the modeling of phase transformations is simple, some important aspects of the thermodynamics are present (the order of the transition, the stability of phases, entropy, etc.). The Landau model is used in many fields and can be extended to nonhomogeneous phases by adding gradient terms of the order parameter. In addition, two or more order parameters may be included in the expansion and the interaction of the different types of order can be examined (see Qualitative Problem 2).

15.7 SUMMARY

In this chapter, several direct applications of the thermodynamics presented in the first 10 chapters of the text were applied to phase transformations. In the chapter, we

- Defined the terms *phase* and *phase transformation*
- Saw how to determine the driving force for nucleation with and without composition changes
- Discussed the importance of T_0 curves in the equilibrium phase diagram to the understanding of phase transformations
- Discussed the importance of surface energy in determining the equilibrium shape of crystals as well how surface energy effects can favor certain sites for heterogeneous nucleation
- Discussed how capillarity effects local compositional equilibrium and how surface energy produces the driving force for particle coarsening
- Introduced the Landau model of the excess free energy and showed that it leads to two distinct types of phase transitions

15.8 CONCEPTS AND TERMS INTRODUCED IN CHAPTER 15

The reader should write out brief definitions or descriptions of the following terms. Where appropriate, equations may be used.

Amorphous solid
Barrier to nucleation
Capillarity
Congruent transformation
Critical nucleus
Diffusionless transformation
Driving force
Equilibrium shapes
Facets
Gibbs–Wulff construction
Heterogeneous nucleation

Homogeneous nucleation
Instability
Landau model of free energy
Martensite
Massive transformation
Metallic glass
Nucleation
Particle coarsening
Surface energy
T_0 curves

15.9 QUALITATIVE EXAMPLE PROBLEMS

Qualitative Example Problem 1

Calculate the slope of the η versus temperature plot for the 2-4 model of a transition as the temperature approaches 0 K. Discuss this in terms of the Third Law prediction.

Solution to Qualitative Problem 1

$$\eta = \left(1 - \frac{T}{T_C}\right)^{\frac{1}{2}} \text{ (see Equation 15.10)}$$

$$\frac{\partial \eta}{\partial T} = -\frac{1}{2T_C}\left(1 - \frac{T}{T_C}\right)^{-\frac{1}{2}}$$

$$\text{The limit of } \frac{\partial \eta}{\partial T} \text{ as } T \to 0 = -\frac{1}{2T_C}\left(1 - \frac{T}{T_C}\right)^{-\frac{1}{2}} = -\frac{1}{2T_C} < 0$$

The slope of the variation of the order parameter η with temperature as η → 1 at $T = 0$ K is negative in this model, which is at variance with the predicted slope of zero according to the requirements of the Third Law of Thermodynamics.

See also Qualitative Problem 2 of Chapter 9, where the slope of the curve is shown to be zero as the temperature approaches absolute zero for systems which conform to the Third Law.

Qualitative Example Problem 2

The Landau expansion for a higher-order transition is written as

$$G^{\mathrm{XS}} = A\eta^2 + C\eta^4 \quad (\mathrm{C} > 0)$$

The Landau expansion that includes a second-order parameter (strain) can be written as:

$$G^{XS} = A\eta^2 + C\eta^4 + \lambda\varepsilon_S\eta^2 + \frac{1}{2}\,C_{El}\varepsilon_S^2 \quad (C > 0)$$

where:

ε_S is the strain in the phase

λ is the coupling constant between the strain and the order parameter η

C_{El} is an elastic constant

Show that this coupling can change the phase transition into a first-order transition and delineate under what conditions this occurs.

Solution to Qualitative Problem 2

First we minimize the free energy with respect to the strain

$$\frac{\partial G^{XS}}{\partial \varepsilon_S} = 0 = \lambda\eta^2 + C_{El}\varepsilon_S$$

$$\varepsilon_S^* = -\frac{\lambda\eta^2}{C_{El}}$$

Now we substitute this value in the free energy and obtain

$$G^{XS} = A\eta^2 + C\eta^4 + \lambda\left(-\frac{\lambda\eta^2}{C_{El}}\right)\eta^2 + \frac{1}{2}C_{El}\left(-\frac{\lambda\eta^2}{C_{El}}\right)^2$$

$$G^{XS} = A\eta^2 + \left(C + \lambda^2\left(-\frac{1}{C_{El}}\right) + \frac{\lambda^2}{2C_{El}}\right)\eta^4$$

$$G^{XS} = A\eta^2 + \left(C - \frac{\lambda^2}{2C_{El}}\right)\eta^4$$

If the coupling term λ is positive and large or if the elastic constant is small, the term multiplying η^4 may become negative. This is no longer a higher-order transition. When the second term becomes negative, we must include an η^6 term for stability.

PROBLEMS

15.1* 2-4 Landau Case:

The excess Gibbs free energy as a function of order parameter for a solution is written as

$$G^{XS} = G_{\mathrm{ord}} - G_{\mathrm{dis}} = a(T - T_C)\eta^2 + C\eta^4$$

where G_{dis} is the free energy of the disordered phase and a and C are positive constants.

a. Obtain an expression for the excess entropy of the equilibrium ordered phase as a function of temperature.
b. Determine the value of $\Delta C_P = C_P^{\text{ord}} - C_P^{\text{dis}}$ at the transition temperature T_C.

15.2* 2-4-6 Landau Case

The Gibbs energy as a function of order parameter for a solution is written as

$$G = a(T - T_C)\eta^2 + C\eta^4 + E\eta^6$$

For this case, assume $C < 0$ and a and E are positive.

a. Find the nonzero value of the order parameter of the solution that has the same Gibbs energy as that of the disordered solution.
b. Sketch the Gibbs energy versus η curve for the temperature in question in (a). This temperature can be called T_0.
c. Determine if the transformation for this alloy is first order. Explain.
d. Calculate the heat of transformation, ΔH_0, for this disorder/order transformation in terms of (a), η_0 and T_{tr}, where η_0 is the order parameter at the equilibrium transition temperature T_0.
e. What is the significance of the sign of ΔH_{tr} for this transformation?

15.3* 2-4 Landau Case

Using the equation

$$G^{\text{XS}}(\eta) = a(T - T_0)\eta^2 + C\eta^4$$

show that the excess enthalpy for the Landau model with $B = 0$ and $C > 0$ is

$$\Delta H^{\text{XS}} = \frac{a}{2}\frac{(T^2 - T_C^2)}{T_C}$$

15.4* A solid is held at high temperature until equilibrium is attained. Its surface displays grooves, as shown in Figure 15.19.

a. Write an expression for the relationships between the grain boundary energy of α_1 and α_2.
b. Which grain boundary has the largest energy, α_1/α_2 or α_2/α_3?
c. If ϕ_{ij} goes to π, what is the value of the grain boundary energy?
d. If ϕ_{ij} goes to 0, what is the value of the grain boundary energy?

15.5* Small cylindrical particles have been observed to nucleate in certain alloy systems.

a. What values of r and ℓ will minimize the energy barrier to the formation of these particles?
b. What surface energies favor the formation of long, thin cylinders? Explain.
    - γ_1 is the surface energy of the circular face.
    - γ_2 is the surface energy along the length of the cylinder.

Note: Assume the volume of the particle is constant.

15.6* 2-6 Landau Case

The Gibbs energy of a phase can be written in terms of its order parameter as

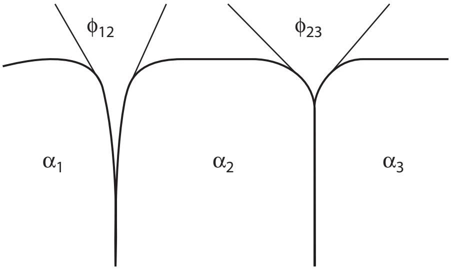


Figure 15.19 Grain boundary grooves arising from grain boundaries with different grain boundary energies.

$$G = a(T - T_C)\eta^2 + E\eta^6$$

where $a > 0$ and $E > 0$

a. What is the temperature T_0 where the disordered phase has the same Gibbs energy as the equilibrium ordered phase? Show work.
b. What is the value of the order parameter at T_0?
c. Is this a first-order or higher-order phase transition? Explain.
d. Show mathematically that, for $T < T_C$, the disordered phase is unstable.

APPENDIX A

Selected Thermodynamic and Thermochemical Data

TABLE A.1: THE STANDARD GIBBS FREE ENERGY CHANGES FOR SEVERAL REACTIONS

Table A.1 lists the standard Gibbs free energy changes for selected reactions in the form

$$\Delta G_T^\circ = A + BT \text{ J}$$

or

$$\Delta G_T^\circ = A + BT \ln T + CT \text{ J}$$

and lists the range of temperature in which the expression is valid.

Example: For the oxidation of solid copper to form solid cuprous oxide according to

$$2\text{Cu}_{(s)} + \frac{1}{2}\text{O}_{2(g)} = \text{Cu}_2\text{O}_{(s)}$$

$$\Delta G^\circ = -162{,}200 + 69.24T \text{ J}$$

in the range 298–1356 K. Thus, at the melting temperature of Cu, 1356 K,

$$\begin{aligned}\Delta G_{1356\text{ K}}^\circ &= -162{,}200 + 69.24 \times 1{,}356 \\ &= -68{,}311 \text{ J}\end{aligned}$$

For the oxidation of liquid copper to form solid cuprous oxide according to

$$2\text{Cu}_{(l)} + \frac{1}{2}\text{O}_{2(g)} = \text{Cu}_2\text{O}_{(s)}$$

$$\Delta G_T^\circ = -188{,}300 + 88.48T \text{ J}$$

in the range 1356–1509 K. Thus, at 1356 K,

$$\begin{aligned}\Delta G_{1356\text{ K}}^\circ &= -188{,}300 + 88.48 \times 1{,}356 \text{ J} \\ &= -68{,}321 \text{ J}\end{aligned}$$

Table A.1 The Standard Gibbs Free Energy Changes for Several Reactions

Reaction	$\Delta G°$, J	Range, K
$2Ag_{(s)} + \frac{1}{2}O_{2(g)} = Ag_2O_{(s)}$	$-30{,}540 + 66.11\,T$	298–463
$Al_{(l)} = [Al]_{(1\text{ wt\% in Fe})}$	$-43{,}100 - 32.26\,T$	
$2Al_{(l)} + 1.5O_{2(g)} = Al_2O_{3(s)}$	$-1{,}687{,}200 + 326.8\,T$	993–2327
$C_{(s)} + \frac{1}{2}O_{2(g)} = CO_{(g)}$	$-111{,}700 - 87.65\,T$	298–2000
$C_{(s)} + O_{2(g)} = CO_{2(g)}$	$-394{,}100 - 0.84\,T$	298–2000
$C_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}S_{2(g)} = COS_{(g)}$	$-202{,}800 - 9.96\,T$	773–2000
$C_{(gr)} + 2H_{2(g)} = CH_{4(g)}$	$-91{,}040 + 110.7\,T$	773–2000
$C_{(gr)} = [C]_{(1\text{ wt\% in Fe})}$	$22{,}600 - 42.26\,T$	
$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)}$	$-168{,}400 + 144\,T$	449–1150
$2CaO_{(s)} + SiO_{2(s)} = 2CaO{\cdot}SiO_{2(s)}$	$-118{,}800 - 11.30\,T$	298–2400
$CoO_{(s)} + SO_{3(g)} = CoSO_{4(s)}$	$-227{,}860 + 165.3\,T$	298–1230
$2Cr_{(s)} + 1.5O_{2(g)} = Cr_2O_{3(s)}$	$-1{,}110{,}100 + 247.3\,T$	298–1793
$2Cu_{(s)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$	$-162{,}200 + 69.24\,T$	298–1356
$2Cu_{(l)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$	$-188{,}300 + 88.48\,T$	1356–1509
$2Cu_{(s)} + \frac{1}{2}S_{2(g)} = Cu_2S_{(s)}$	$-131{,}800 + 30.79\,T$	708–1356
$3Fe_{(\alpha)} + C_{(gr)} = Fe_3C_{(s)}$	$29{,}040 - 28.03\,T$	298–1000
$3Fe_{(\gamma)} + C_{(gr)} = Fe_3C_{(s)}$	$11{,}234 - 11.00\,T$	1000–1137
$Fe_{(s)} + \frac{1}{2}O_{2(g)} = FeO_{(s)}$	$-263{,}700 + 64.35\,T$	298–1644
$Fe_{(l)} + \frac{1}{2}O_{2(g)} = FeO_{(s)}$	$-256{,}000 + 53.68\,T$	1808–2000
$3Fe_{(s)} + 2O_{2(g)} = Fe_3O_{4(s)}$	$-1.102{,}200 + 307.4\,T$	298–1808
$Fe_{(s)} + \frac{1}{2}S_{2(g)} = FeS_{(s)}$	$-150{,}200 + 52.55\,T$	412–1179
$H_{2(g)} + Cl_{2(g)} = 2HCl_{(g)}$	$-188{,}200 - 12.80\,T$	298–2000
$H_{2(g)} + I_{2(g)} = 2HI_{(g)}$	$-8{,}370 - 17.65\,T$	298–2000
$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)}$	$-247{,}500 + 55.85\,T$	298–2000
$Hg_{(v)} + \frac{1}{2}O_{2(g)} = Hg0_{(s)}$	$-152{,}200 + 207.2\,T$	
$Li_{(g)} + \frac{1}{2}Br_{2(g)} = LiBr_{(g)}$	$-333{,}900 + 42.09\,T$	1289–2000
$Mg_{(l)} + Cl_{2(g)} = MgCl_{2(l)}$	$-603{,}200 + 121.43\,T$	987–1368
$Mg_{(g)} + \frac{1}{2}O_{2(g)} = MgO_{(s)}$	$-729{,}600 + 204\,T$	1363–2200
$2MgO_{(s)} + SiO_{2(s)} = Mg_2SiO_{4(s)}$	$-67{,}200 + 4.31\,T$	298–2171
$MgO_{(s)} + CO_{2(g)} = MgCO_{3(s)}$	$-117{,}600 + 170\,T$	298–1000
$MgO_{(s)} + Al_2O_{3(s)} = MgO{\cdot}Al_2O_{3(s)}$	$-35{,}560 - 2.09\,T$	298–1698
$Mn_{(s)} + \frac{1}{2}O_{2(g)} = MnO_{(s)}$	$-388{,}900 + 76.32\,T$	298–1517
$N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$	$-87{,}030 + 25.8\,T \ln T + 31.7\,T$	298–2000
$2Ni_{(s)} + O_{2(g)} = 2NiO_{(s)}$	$-471{,}200 + 172\,T$	298–1726
$2Ni_{(l)} + O_{2(g)} = 2NiO_{(s)}$	$-506{,}180 + 192.2\,T$	1726–2200
$\frac{1}{2}O_{2(g)} = [O]_{(1\text{ wt\% in Fe})}$	$-111{,}070 - 5.87\,T$	
$Pb_{(l)} + \frac{1}{2}O_{2(g)} = PbO_{(s)}$	$-208{,}700 + 91.75\,T$	600–1158
$Pb_{(l)} + \frac{1}{2}O_{2(g)} = PbO_{(l)}$	$-181{,}200 + 68.03\,T$	1158–1808
$Pb_{(l)} + \frac{1}{2}S_{2(g)} = PbS_{(s)}$	$-163{,}200 + 88.03\,T$	600–1386

(*Continued*)

TableA.1 (Continued) The Standard Gibbs Free Energy Changes for Several Reactions

Reaction	$\Delta G°$, J	Range, K
$PbO_{(s)} + SO_{2(g)} + ½O_{2(g)} = PbSO_{4(s)}$	−401,200 + 261.5 T	298–1158
$PCl_{3(g)} + Cl_{2(g)} = PCl_{5(g)}$	−95,600 − 7.94 $T \ln T$ + 235.2 T	298–1000
$½S_{2(g)} + O_{2(g)} = SO_{2(g)}$	−361,700 + 76.68 T	718–2000
$Si_{(s)} + O_{2(g)} = SiO_{2(s)}$	−907,100 + 175 T	298–1685
$3Si_{(s)} + 2N_{2(g)} = Si_3N_{4(s)}$	−723,800 + 315.1 T	298–1685
$Sn(l) + Cl_{2(g)} = SnCl_{2(l)}$	−333,000 + 118.4 T	520–925
$SO_{2(g)} + ½O_{2(g)} = SO_{3(g)}$	−94,600 + 89.37 T	298–2000
$U_{(l)} + C_{(gr)} = UC_{(s)}$	−102,900 + 5.02 T	1408–2500
$2U_{(l)} + 3C_{(gr)} = U_2C_{3(s)}$	−236,800 + 25.1 T	1408–2500
$U_{(l)} + 2C_{(gr)} = UC_{2(s)}$	−115,900 + 10.9 T	1408–2500
$V_{(s)} + ½O_{2(g)} = VO_{(s)}$	−424,700 + 80.04 T	298–2000
$Zn_{(v)} + ½O_{2(g)} = ZnO_{(s)}$	−460,200 + 198 T	1243–1973

Note: Standard states are noted by subscript.

TABLE A.2: THE CONSTANT-PRESSURE MOLAR HEAT CAPACITIES OF VARIOUS SUBSTANCES

The constant-pressure molar heat capacities are presented as

$$c_p = a + bT + cT^{-2} \text{ J/K}$$

or as

$$c_p = a + bT + cT^{-2} + dT^2 \text{ J/K}$$

and Table A.2 includes the ranges of temperature in which the expressions are valid.

Example: For Ag in the range 298–1234 K,

$$c_p = 21.30 + 8.54\times10^{-3}T + 1.51\times10^5 T^{-2} \text{ J/K}$$

and for graphite in the range 298–1100 K,

$$c_p = 0.11 + 38.94\times10^{-3}T - 1.48\times10^5 T^{-2} - 17.38\times10^{-6}T^2 \text{ J/K}$$

Table A.2 The Constant-Pressure Molar Heat Capacities of Various Substances ($c_p = a + bT + cT^{-2}$ J/mole·K)

Substance	a	$b \times 10^3$	$c \times 10^{-5}$	Range, K	Remarks
Ag	21.30	8.54	1.51	298–1234 (T_m)	
$Ag_{(l)}$	30.50	—	—	1234–1600	
$Al_{(s)}$	20.67	12.38	—	298–933(T_m)	
$Al_{(l)}$	31.76	—	—	933–1600	
Al_2O_3	106.6	17.78	–28.53	298–2325(T_m)	
$Ba_{(\alpha)}$	–473.2	1587.0	128.2	298–648	
$Ba_{(\beta)}$	–5.69	80.33	—	648–1003	
BaO	53.30	4.35	–8.30	298–2286(T_m)	
$BaTiO_3$	121.46	8.54	–19.16	298–1800	
$C_{(graphite)}$	0.11	38.94	–1.48	298–1100	$-17.38 \times 10^{-6}T^2$
$C_{(graphite)}$	24.43	0.44	–31.63	1100–4000	
$C_{(diamond)}$	9.12	13.22	–6.19	298–1200	
CO	28.41	4.10	–0.46	298–2500	
CO_2	44.14	9.04	–8.54	298–2500	
$Ca_{(\alpha)}$	25.37	–7.26	—	298–716	$23.72 \times 10^{-6}T^2$
$Ca_{(\beta)}$	–0.36	41.25	—	716–1115	
CaO	49.62	4.51	–6.95	298–1177	
$CaTiO_3$	127.49	5.69	–27.99	298–1530	
$Cr_{(s)}$	24.43	9.87	–3.68	298–2130(T_m)	
Cr_2O_3	119.37	9.30	–15.65	298–1800	
$Cu_{(s)}$	22.64	6.28	—	298–1356(T_m)	
$Fe_{(\alpha/\delta)}$	37.12	6.17	—	298–1183/1664–1809	
$Fe_{(\gamma)}$	24.47	8.45	—	1187–1664	
$Fe_{(l)}$	41.8	—	—	1809–1873	
$H_2O_{(g)}$	30.00	10.71	0.33	298–2500	
$O_{2(g)}$	29.96	4.18	–1.67	298–3000	
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	626.34	91.21	–200.83	298–1738(T_m)	
N_2	27.87	4.27	—	298–2500	
Si_3N_4	70.54	98.74	—	298–900	
$SiO_{2(\alpha\text{-quartz})}$	43.89	1.00	–6.02	298–847	
Ti	22.09	10.46	—	298–1155	
$TiO_{2(rutile)}$	75.19	1.17	–18.20	298–1800	
$Zr_{(\alpha)}$	21.97	11.63	—	298–1136	
$Zr_{(\beta)}$	23.22	4.64	—	1136–2128	
$ZrO_{2(\alpha)}$	69.62	7.53	–14.06	298–1478	
$ZrO_{2(\beta)}$	74.48	—	—	1478–2950(T_m)	

TABLE A.3: THE STANDARD MOLAR HEATS OF FORMATION AND MOLAR ENTROPIES OF VARIOUS SUBSTANCES AT 298 K

Example: For the reaction

$$2\mathrm{Al}_{(s)} + \frac{3}{2}\mathrm{O}_{2(g)} = \mathrm{Al}_2\mathrm{O}_{3(s)}$$

$$\Delta H^\circ_{298\ \mathrm{K}} = -1{,}675{,}700\ \mathrm{J}$$

which is thus the standard molar heat of formation of Al_2O_3 at 298 K. The molar entropy of Al_2O_3 at 298 K is 50.9 J/K. By convention, the standard molar enthalpies of elements in their standard states at 298 K are assigned the value of zero.

Table A.3 The Standard Molar Heats of Formation and Molar Entropies of Various Substances at 298 K

Substance	ΔH°_{298}, J	S°_{298}, J/K
Al_2O_3	–1,675,700	50.9
Ba	—	62.4
BaO	–548,100	72.1
$BaTiO_3$	–1,653,100	107.9
$C_{(\mathrm{graphite})}$	—	5.73
$C_{(\mathrm{diamond})}$	1,900	2.43
CH_4	–74,800	186.3
CO	–110,500	197.5
CO_2	–393,500	213.7
Ca	—	41.6
CaO	–634,900	38.1
$CaTiO_3$	–1,660,600	93.7
$3CaO{\cdot}Al_2O_3{\cdot}3SiO_2$	–6,646,300	241.4
$CaO{\cdot}Al_2O_3{\cdot}SiO_2$	–3,293,200	144.8
$CaO{\cdot}Al_3O_3{\cdot}2SiO_2$	–4,223,700	202.5
$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$	–3,989,400	198.3
Cr_2O_3	–1,134,700	81.2
$H_2O_{(g)}$	–241,800	232.9
N_2	—	191.5
O_2	—	205.1
$SiO_{2,(\alpha\text{-quartz})}$	–910,900	41.5
Si_3N_4	–744,800	113.0
Ti	—	30.7
TiO	–543,000	34.7
Ti_2O_3	–1,521,000	77.2
Ti_3O_5	–2,459,000	129.4
TiO_2	–944,000	50.6
Zr	—	39.0
ZrO_2	–1,100,800	50.4

TABLE A.4: THE SATURATED VAPOR PRESSURES OF VARIOUS SUBSTANCES

The saturated (equilibrium) vapor pressures of substances, in the stated ranges of temperatures, are presented in the form

$$\ln p \text{ (atm)} = -\frac{A}{T} + B \ln T + C$$

Example: The saturated vapor pressure exerted by liquid CaF_2 in the range of temperature 1691–2783 K is given by

$$\ln p \text{ (atm)} = -\frac{50,200}{T} - 4.525 \ln T + 53.96$$

Thus, at its normal boiling temperature of 2783 K, the saturated vapor pressure of liquid CaF_2 is

$$\begin{aligned} \ln p \text{ (atm)} \quad &= -\frac{50,200}{2,783} - 4.525 \ln(2,783) + 53.96 \\ &= 0 \end{aligned}$$

That is, at the normal boiling temperature, the saturated vapor pressure is 1 atm.

Table A.4 The Saturated Vapor Pressures of Various Substances
$[\ln p \text{ (atm)} = -A/T + B \ln T + C]$

Substance	A	B	C	Range, K
$CaF_{2(\alpha)}$	54,350	–4.525	56.57	298–1430
$CaF_{2(\beta)}$	53,780	–4.525	56.08	1430–1691 (T_m)
$CaF_{2(l)}$	50,200	–4.525	53.96	1691–2783 (T_b)
$Fe_{(l)}$	45,390	–1.27	23.93	1809 (T_m)–3330 (T_b)
$Hg_{(l)}$	7,611	–0.795	17.168	298–630 (T_b)
$Mn_{(l)}$	33,440	–3.02	37.68	1517 (T_m)–2348 (T_b)
$SiCl_{4(l)}$	3,620	—	10.96	273–333 (T_b)
$Zn_{(l)}$	15,250	–1.255	21.79	693 (T_m)–1177 (T_b)

TABLE A.5: MOLAR HEATS OF MELTING AND TRANSFORMATION

Example: At the melting temperature of Ag (1234 K), the enthalpy change for

$$Ag_{(s)} \rightarrow Ag_{(l)}$$

is 11.090 J. Thus, at 1234 K, the molar heat of melting of Ag is 11,090 J. The change in molar entropy due to melting at 1234 K is thus

$$\frac{\Delta H_m}{T_m} = \frac{11{,}090}{1234} = 8.987 \text{ J/K}$$

At 1187 K, the enthalpy change for the transformation

$$Fe_{(\alpha)} \rightarrow Fe_{(\gamma)}$$

is 670 J. The corresponding change in the molar entropy at 1187 K is thus

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} = \frac{670}{1187} = 0.56 \text{ J/K}$$

Table A.5 Molar Heats of Melting and Transformation

Substance	Trans.	ΔH_{trans}, J	T_{trans}, K
Ag	$s \rightarrow l$	11,090	1,234
Al	$s \rightarrow l$	10,700	934
Al_2O_3	$s \rightarrow l$	107,500	2,324
Au	$s \rightarrow l$	12,600	1,338
Ba	$\alpha \rightarrow \beta$	630	648
Ba	$\beta \rightarrow l$	7,650	1,003
Cu	$s \rightarrow l$	12,970	1,356
Ca	$\alpha \rightarrow \beta$	900	716
CaF_2	$s \rightarrow l$	31,200	1,691
Fe	$\alpha \rightarrow \gamma$	670	1,187
Fe	$\gamma \rightarrow \delta$	840	1,664
Fe	$\delta \rightarrow l$	13,770	1,809
H_2O	$s \rightarrow l$	6,008	273
$K_2O\cdot B_2O_3$	$s \rightarrow l$	62,800	1,220
MgF_3	$s \rightarrow l$	58,160	1,563
$Na_2O\cdot B_2O3$	$s \rightarrow l$	67,000	1,240
Pb	$s \rightarrow l$	4,810	600
PbO	$s \rightarrow l$	27,480	1,158
Si	$s \rightarrow l$	50,200	1,685
V	$s \rightarrow l$	22,840	2,193
Zr	$\alpha \rightarrow \beta$	3,900	1,136
ZrO_2	$\alpha \rightarrow \beta$	5,900	1,478

APPENDIX B

Exact Differential Equations

Consider an initial state of a system defined by the parameters x, y, z and a final state at an infinitesimal distance $x + dx$, $y + dy$, $z + dz$. Movement from the initial to the final state causes a change in its dependent variables, such as the volume of the system dV, given by

$$dV = V(x+dx, y+dy, z+dz) - V(x, y, \mathrm{z}) \tag{B.1}$$

which corresponds to

$$dV = \left(\frac{\partial V}{\partial x}\right)_{y,z} dx + \left(\frac{\partial V}{\partial y}\right)_{x,z} dy + \left(\frac{\partial V}{\partial z}\right)_{x,y} dz \tag{B.2}$$

Each function in parentheses in Equation B.2 is a *partial derivative* of the function $V(x,y,z)$ with respect to one of the variables—that is, the derivative of V with respect to one variable at constant values of the other two variables. The differential dV, which is the sum of the partial derivatives, is called a total differential and it is an exact differential if V is as state function.

Consider the function

$$V\left(x, y, z\right) = x^2 y^3 + xz$$

Its partial differentials are

$$\left(\frac{\partial V}{\partial x}\right)_{y,x} = 2xy^3 + z; \quad \left(\frac{\partial V}{\partial y}\right)_{x,z} = 3x^2 y^2; \quad \left(\frac{\partial V}{\partial z}\right)_{x,y} = x$$

and the exact differential is

$$dV = \left(2xy^3 + z\right)dx + 3x^2 y^2 dy + xdz \tag{B.3}$$

The exact differential given by Equation B.2 has the properties

$$\left(\frac{\partial^2 V}{\partial x \partial y}\right) = \left(\frac{\partial^2 V}{\partial y \partial x}\right); \quad \left(\frac{\partial^2 V}{\partial y \partial z}\right) = \left(\frac{\partial^2 V}{\partial z \partial y}\right); \quad \left(\frac{\partial^2 V}{\partial z \partial x}\right) = \left(\frac{\partial^2 V}{\partial x \partial z}\right) \tag{B.4}$$

Conversely, the differential

$$dV = Xdx + Ydy + Zdz \tag{B.5}$$

is exact if there exists a function $V(x,y,z)$ for which

$$X = \left(\frac{\partial V}{\partial x}\right)_{yz}; \quad Y = \left(\frac{\partial V}{\partial y}\right)_{xz}; \quad Z = \left(\frac{\partial V}{\partial z}\right)_{xy} \tag{B.6}$$

and thus, from Equation B.4, it follows that

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}; \quad \frac{\partial Y}{\partial z} = \frac{\partial Z}{\partial y}; \quad \frac{\partial Z}{\partial x} = \frac{\partial X}{\partial z} \tag{B.7}$$

The relationships given by Equation B.7 are a necessary and sufficient condition for Equation B.5 to be an exact differential. The application of Equation B.7 shows Equation B.3 to be an exact differential as follows:

$$\frac{\partial(2xy^3 + Z)}{\partial y} = 6xy^2; \quad \frac{\partial(3x^2y^2)}{\partial x} = 6xy^2$$

$$\frac{\partial(3x^2y^2)}{\partial z} = 0; \quad \frac{\partial(x)}{\partial y} = 0$$

$$\frac{\partial(x)}{\partial x} = 1; \quad \frac{\partial(2xy^3 + z)}{\partial z} = 1$$

Thermodynamic functions that are exact are called *thermodynamic state functions*. State functions do not depend on the path that is taken to change them. Their equilibrium values at any state do not depend on the history of the paths taken, only the values of their independent variables.

APPENDIX C

The Generation of Additional Thermodynamic Potentials as Legendre Transformations

We have found for a simple thermodynamic system that the internal energy U is a function of the independent variables entropy and volume; that is, $U = U(S, V)$. This appendix details the mathematical method used in Chapter 5 to obtain the other thermodynamic potentials of the simple system. We also give a method to obtain all of the thermodynamic potentials for any number of dependent variables.

The variation of the dependent variable y with the independent variable x can be represented as the locus of points satisfying the relation $y = y(x)$, as shown in Figure C.1. It can also be shown as the envelope of a family of tangent lines shown in Figure C.2. In Figure C.1, every point in the plane is described by two coordinates, x and y, and every line in the plane in Figure C.2 can be described by two numbers, m and ψ, where m is the slope of the line and ψ is the intercept of the line with the y-axis. Then, just as the relation $y = y(x)$ selects a subset of all possible points (x,y), a relation $\psi = \psi(m)$ selects a subset of all possible lines (m,ψ). Knowledge of the intercept ψ of the tangent lines as a function of the slopes m allows the construction of the family of tangent lines and thus the curve for which they are the envelope. Thus, the relationship

$$\psi = \psi(m) \tag{C.1}$$

is equivalent to the relation $y = y(x)$, and in Equation C.1, m is the independent variable. The computation of the relation $\psi = \psi(m)$ from the known relation $y = y(x)$ is known as a *Legendre transformation* (Adrien-Marie Legendre, 1752–1833). Figure C.3 shows a tangent line of slope m going through the point x,y. If the intercept with the y axis is ψ, then

$$m = \frac{y - \psi}{x - 0} \tag{C.2}$$

or

$$\psi = y - mx \tag{C.3}$$

Differentiation of the known equation $y = y(x)$ gives $m = m(x)$, and elimination of x and y gives the desired relation ψ and m. The function ψ is known as the Legendre transform of y.

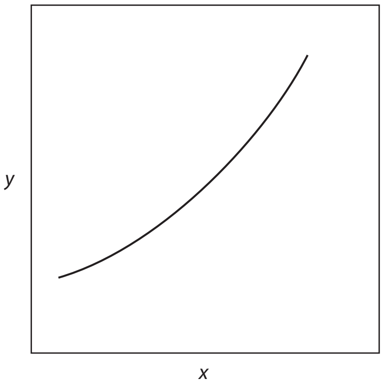


Figure C.1 The locus of points satisfying the relation $y = y(x)$.

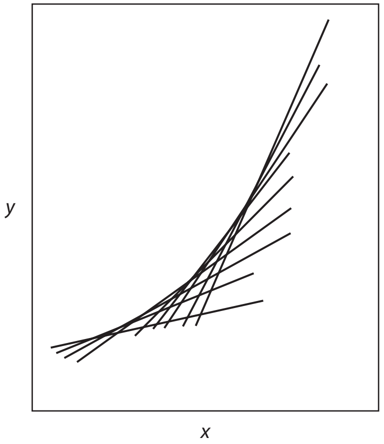


Figure C.2 The family of tangent lines $\psi = \psi(m)$.

Equation 3.12 gives the variation of the dependent variable U on the independent variables S and V for one mole of a closed system which is undergoing a process involving a change of volume against the external pressure as the only form of work performed on, or by, the system.

$$dU = TdS - PdV \tag{3.12}$$

A schematic variation of U with V at constant S is shown in Figure C.4. Using the geometry procedure outlined in Figure C.3 gives

$$m = \frac{U - \psi}{V - 0}$$

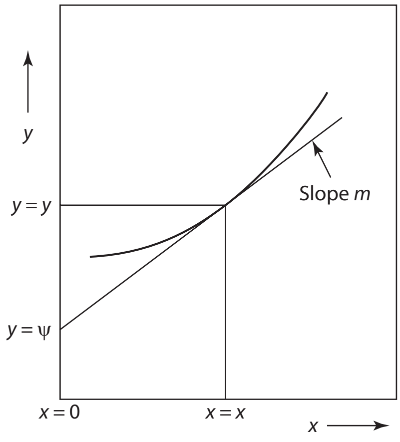


Figure C.3 Geometry procedure for obtaining ψ, the Legendre transform of *y*.

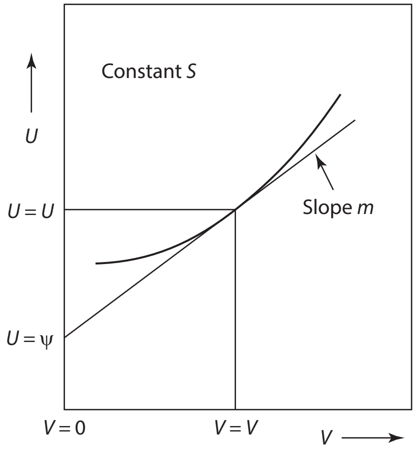


Figure C.4 Geometry procedure for obtaining ψ, the Legendre transform of *U* at constant *S*.

which rearranges to give

$$\psi = U - mV \tag{C.4}$$

From Equation 3.12, the slope of the line, m, is

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

and thus, Equation C.4 becomes

$$\psi = U + PV$$

This thermodynamic potential is called the *enthalpy*, H (see Equation 2.4). The enthalpy is thus a Legendre transform of the internal energy, U, given as

$$H = U + PV \tag{C.5}$$

Differentiation of Equation C.5 gives

$$dH = dU + PdV + VdP$$

which in combination with Equation 3.12 gives

$$dH = TdS + VdP \tag{C.6}$$

which is an expression for the variation of the dependent variable H with the independent variables S and P. Since H is a state function, we can write

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Comparison of this equation with Equation C.6 gives the thermodynamic definitions of T and V as

$$T = \left(\frac{\partial H}{\partial S}\right)_P$$

and

$$V = \left(\frac{\partial H}{\partial P}\right)_S$$

Figure C.5 shows a schematic variation of U with S at constant V, and the geometry procedure gives

$$m = \frac{U - \psi}{S - 0}$$

or

$$\psi = U - mS \tag{C.7}$$

From Equation 3.12, the slope of the line, m, is

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

and thus, Equation C.7 becomes

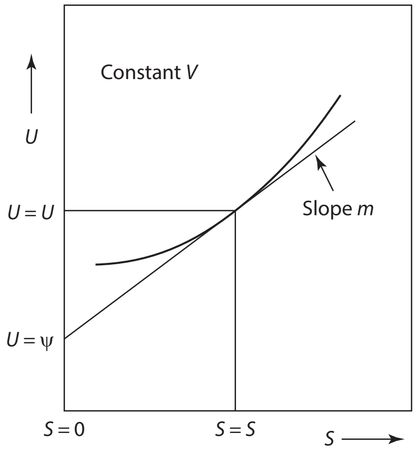


Figure C.5 Geometry procedure for obtaining ψ, the Legendre transform of U at constant V.

$$\psi = U - TS \tag{C.8}$$

which is called the Helmholtz free energy, A (see Equation 5.1). The Helmholtz free energy is thus *another* Legendre transform of the internal energy, U, given as

$$A = U - TS \tag{C.9}$$

Differentiation of Equation C.9 gives

$$dA = dU - TdS - SdT$$

which, in combination with Equation 3.12, gives

$$dA = -SdT - PdV \tag{C.10}$$

which is an expression for the variation of A, as the dependent variable, with the independent variables T and V. Since A is a state function (and therefore an exact differential), we can write

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

Comparison of this equation with Equation C.10 gives the thermodynamic definition of S and P as

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

and

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

The thermodynamic variable which is dependent on T and P is obtained as a Legendre transform of A in which V in Equation C.10 is replaced by P. The variation of A with V at constant T gives

$$m = \left(\frac{A - \psi}{V - 0}\right)$$

or

$$\psi = A - mV \tag{C.11}$$

From Equation C.10,

$$m = \left(\frac{\partial A}{\partial V}\right)_T = -P$$

Thus, Equation C.11 becomes

$$\psi = A + PV = U - TS + PV = H - TS$$

which is called the *Gibbs free energy*, G (defined in Section 5.4).

$$G = H - TS \tag{C.12}$$

Differentiation of Equation C.12 gives

$$dG = dH - TdS - SdT$$

which, in combination with Equation C.6 gives

$$dG = -SdT + VdP \tag{C.13}$$

which is an expression for the variation of G, the dependent variable, on T and P as the independent variables. Comparison of Equation C.13 with

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

gives the thermodynamic definitions of S and V as

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

and

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

Thus, starting with the First Law as

$$dU = TdS - PdV \tag{3.12}$$

we have

$$U = U(S,V)$$

$$H = H(S,P)$$

$$A = A(T,V)$$

and

$$G = G(T,P)$$

Now suppose the First Law is written to include another form of work which may be performed on or by the system.

$$dU = TdS - PdV + Xdy$$

where:

X	is the force applied by or on the system
y	is the resulting displacement

We now have

$$U = U(S,V,y)$$

$$H = H(S,P,y)$$

$$A = A(T,V,y)$$

and

$$G = G(T,P,y)$$

From this, the following additional fundamental equations can be obtained.

$$\begin{aligned} dH &= TdS + VdP + Xdy \\ dA &= -SdT - PdV + Xdy \\ dG &= -SdT + VdP + Xdy \end{aligned} \tag{C.14}$$

We may also form the Legendre transforms of the internal energy by considering the additional work terms*

$$\begin{aligned} dU'' &= TdS - PdV - ydX \\ dH'' &= TdS + VdP - ydX \\ dA'' &= -SdT - PdV - ydX \\ dG'' &= -SdT + VdP - ydX \end{aligned} \tag{C.15}$$

These have been primed to distinguish them from Equation C.14. We see that the addition of another independent variable to the First Law increases the number of fundamental equations to eight. Since each member of the thermodynamic conjugate pairs of variables in the First Law may be considered a dependent variable, there will be 2^n fundamental equations for the First Law, written with n terms.

We now look at a specific application of the three-term First Law: namely, the equation that includes magnetic terms. We have seen that the magnetic work done on or by the system can be written as

$$\delta w_{\text{mag}} = \mu_0 V \boldsymbol{\mathcal{H}} dM$$

where V is the volume and we assume $\vec{\boldsymbol{\mathcal{H}}} // \vec{M}$.

We write the First Law as

$$dU_{\text{mag}} = TdS - PdV + \mu_0 V \boldsymbol{\mathcal{H}}\, dM$$

and obtain the other three magnetic fundamental equations as

$$\begin{aligned} dH_{\text{mag}} &= TdS + VdP + \mu_0 V \boldsymbol{\mathcal{H}}\, dM \\ dA_{\text{mag}} &= -SdT - PdV + \mu_0 V \boldsymbol{\mathcal{H}}\, dM \\ dG_{\text{mag}} &= -SdT + VdP + \mu_0 V \boldsymbol{\mathcal{H}}\, dM \end{aligned} \tag{C.16}$$

---

* The double prime is used to distinguish these terms from dU, dH, dA and dG.

As above, we also get the following additional fundamental equations:

$$dU''_{\text{mag}} = TdS - PdV - \mu_0 VMd\mathcal{H}$$

$$dH''_{\text{mag}} = TdS + VdP - \mu_0 VMd\mathcal{H} \tag{C.17}$$

$$dA''_{\text{mag}} = \ \ -SdT - PdV - \mu_0 VMd\mathcal{H}$$

$$dG''_{\text{mag}} = -SdT + VdP - \mu_0 VMd\mathcal{H}$$

Which fundamental equation one uses in dealing with a magnetic system depends on which of the thermodynamic variables are the independent ones (see Equation 5.11).

Nomenclature

LIST OF SYMBOLS

a	van der Waals constant
a_i	the activity of species *i* with reference to a specified standard state
A	Helmholtz free energy (or work function)
b	van der Waals constant
C	the number of components
C	heat capacity
c_p	constant-pressure molar heat capacity
c_v	constant-volume molar heat capacity
$\boldsymbol{e}_j^i$	the interaction parameter of *i* on *j*
$\boldsymbol{\mathcal{F}}$	the number of degrees of freedom of an equilibrium
$\mathfrak{f}$	Faraday's constant
f	fugacity
f_i	the Henrian activity coefficient of the species *i*
$f_{i(\text{wt}\%)}$	the activity coefficient of the species *i* with respect to the 1 weight percent standard state
f_j^i	the interaction coefficient of *i* on *j*
G	Gibbs free energy
$\boldsymbol{\mathcal{H}}$	magnetic field
H	enthalpy
h_i	the Henrian activity of the species *i*
$h_i(_{\text{wt}}\%)$	the activity of the species *i* with respect to the 1 weight percent standard state
K	the equilibrium constant
k_B	Boltzmann's constant
$\boldsymbol{M}$	magnetization
m	mass
n	the number of moles
n_i	the number of moles of the species *i*
N_o	Avogadro's number
P	pressure
p_i	the partial pressure of the species *i*
p_i°	the saturated vapor pressure of the species *i*
q	heat
R	the gas constant
S	entropy
T	temperature
T_m	melting temperature
T_b	boiling temperature
U	internal energy
V	volume

w	work
X_i	the mole fraction of the species i
$\mathcal{Z}$	partition function
Z	the compressibility factor
α	coefficient of thermal expansion
α	the regular solution constant
β_S	adiabatic compressibility
β_{T}	coefficient of isothermal compressibility
β	is equal to $(\mathrm{k_B T})^{-1}$
γ	ratio of c_p to c_v
γ_i	the activity coefficient of the species i
γ_i°	the Henry's law constant
ε_i	the energy of the ith energy level
ε_j^i	the interaction parameter of i on j
ε	electromotive force
$\varepsilon^{\mathrm{o,A}}$	standard reduction potential of the species A
γ	surface energy
η	efficiency of heat engine
η	generalized order parameter
μ_0	permeability of vacuum
μ_i	the chemical potential of the species i
σ	stress
ϕ	the number of phases occurring in a system
Ω	possible number of arrangements of microstates
(s)	solid
(l)	liquid
(g)	gas

NOTATION FOR EXTENSIVE THERMODYNAMIC PROPERTIES (EXEMPLIFIED BY *G*, THE GIBBS FREE ENERGY)

G'	the Gibbs free energy of the system containing n moles
G	the Gibbs free energy per mole of the system
ΔG	the change in G due to a specified change in the state of the system
ΔG^M	the integral molar Gibbs free energy change due to mixing of the components to form a solution
$\Delta G^{M,id}$	the integral molar Gibbs free energy change due to mixing of the components to form an ideal solution the molar Gibbs free energy of the species i
G_i°	the molar Gibbs free energy of the species i in its designated standard state
$\bar{G}_i$	the partial molar Gibbs free energy of i in some specified solution
ΔG_i^M	$= \bar{G}_i - G_i^\circ$, the partial molar Gibbs free energy of mixing of i
G^{XS}	$= \Delta G^M - \Delta G^{M,\mathrm{id}}$, the integral excess molar Gibbs free energy of a solution
$\bar{G}_i^{\mathrm{xs}}$	the partial molar excess Gibbs free energy of mixing of i
ΔG_m	the molar Gibbs free energy of melting
ΔG_b	the molar Gibbs free energy of boiling
ΔG_0	the standard Gibbs free energy change for reaction as written

Answers to Selected Problems

Chapter 1

1.1* The curvatures are proportional to the second derivatives:

$$\left(\frac{\partial^2 V}{\partial P^2}\right)_T = \beta_T^2 V > 0 \text{ and } \left(\frac{\partial^2 V}{\partial T^2}\right)_P = \alpha^2 V > 0\,.$$

The surface is convex.

1.4 adiabatic compressibility $\frac{\alpha}{\beta_T} = \frac{R}{V}$

Chapter Two

2.1 (la) 22.5 liters, (2a) $w = 9244$ J, (3a) $q = 9244$ J, (4a) $\Delta U = 0$, (5a) $\Delta H = 0$, (lb) 19.13 liters, (2b) $w = 5130$ J, (3b) $q = 0$, (4b) $\Delta U = -5130$ J, (5b) $\Delta H = -8549$ J

2.2 (a) $w = 2270$ J, $q = 5675$ J; (b) $w = 0$, $q = 6809$ J; (c) $w = -3278$ J, $q = -13.492$ J; w Total = q Total = –1008 J

2.3 $V = 1.52$ liters, $w = 8.7$ J

2.4 $T = 1620$ K

2.5 (a) $P = 1$ atm, V = 30.61 liters, $T = 373$ K; (b) $\Delta U = 2168$ J, $\Delta H = 3000$ J; (c) $c_v = 21.7$ J/mole·K, $c_p = 30$ J/mole·K

2.6 (a) +123.4 kJ, (b) –22.5 kJ, (c) 0. Total work = 100.9 kJ done by the system.

2.7 $p = 0.3$ atm

2.8*

$$\Delta U = 0 \text{ (a state function)}$$

$$\sum w_i = RT_A - 2RT_A \ln(2)$$

$$\sum q_i = (C_V + R)T_A - 2RT_A \ln(2) - C_V T_A = RT_A - 2RT_A \ln(2)$$

2.9*

$$w = \int_0^{M_f} \mu_0 V \mathcal{H} \cdot dM = \int_0^{M_f} \mu_0 V \frac{TM}{C} \cdot dM = \mu_0 V \frac{TM_f^2}{2C} = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$$

2.12*

$$\gamma_{gb} = 2\gamma_{\alpha/L} \cos(\frac{\theta_{groove}}{2})$$

Chapter Three

3.1 (a) 5.76 J/K, (b) 0 J/K. (c) –8.65 J/K

3.2

a. $\Delta U = \Delta H = q = w = 0, \Delta S = 9.13$ J/K

b. $\Delta U = q = 1247$ J, $\Delta H = 2079$ J, $w = 0, \Delta S = 3.59$ J/K

c. $\Delta U = \Delta H = 0, q = w = 3654$ J, $\Delta S = 9.13$ J/K

d. $\Delta U = -1247$ J, $\Delta H = q = -2079$ J, $w = -831$ J, $\Delta S = 5.98$ J/K

totals: $\Delta U = \Delta H = 0, w = q = 2322$ J, $\Delta S = 15.88$ J/K

3.3 $T_1 = 300$ K, $T_2 = 600$ K. The isothermal expansion is conducted at 300 K.

3.4 $\Delta H = 42750$ J, $\Delta S = 59.7$ J/K

3.5 The final temperature is 323.32 K, which is greater than 323 K because the heat capacity increases with increasing temperature. Thus the decrease in temperature caused by withdrawing heat q from hot copper is less than the increase in temperature caused by adding heat q to cold copper. The quantity of heat transferred is 1233 J and $\Delta S_{\text{irr}} = 0.6$ J/K.

3.6

$$T_{\text{f}} = \left(T_1^{C_1} T_2^{C_2}\right)^{\frac{1}{c_1 + c_2'}}, w = q_2 - q_1 = [-C_2(T_{\text{f}} - T_2)] - [C_1(T_{\text{f}} - T_1)]$$

3.8*

a. $-21.23 \dfrac{J}{K}$

b. $-19.4 \dfrac{J}{K}$

3.9* $w = (t_2 - t_1)\Delta S$, the area of the box in the T-S plot

Chapter Four

4.1 $R \ln 4$, $R \ln 8$, 0, $R \ln (32/27)$

4.2 The total number of distinguishable complexions is

$$\frac{(2n)!}{n!n!}$$

and, with n being a multiple of 4, the number of complexions in the most probable distribution is

$$\left[\frac{n!}{(0.5n)!(0.5n)!}\right]\left[\frac{n!}{(0.5n)!(0.5n)!}\right] \tag{ii}$$

The ratio of (ii) to (i) decreases with increasing n.

4.3 $\Delta S_{\text{conf}} = 1.02$ J/K

4.4 65.0 grams

4.5*

$$S = nk_B \ln \mathcal{Z} + nk_B T \frac{\partial \ln \mathcal{Z}}{\partial T}$$

4.6*

a. $$\mathcal{Z} = \sum \exp\left(\frac{\varepsilon_i}{k_B T}\right) = \exp\left(\frac{\varepsilon^{\uparrow}}{k_B T}\right) + \exp\left(\frac{\varepsilon^{\downarrow}}{k_B T}\right)$$

b. at high T: equal numbers up and down
at low temperatures: all up

Chapter Five

5.1

$$dU = TdS - PdV$$

$$\therefore dS = \frac{dU}{T} + \frac{P}{T} dV$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_P + \frac{P}{T}$$

$$U = H - PV$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial H}{\partial V}\right)_P - P$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_P$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\therefore \left(\frac{\partial H}{\partial V}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{c_p}{V\alpha}$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_P = \frac{c_p}{T\alpha V}$$

5.2

$$dU = TdS - PdV$$

$$\therefore dS = \frac{dU}{T} + \frac{P}{T}dV$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{-\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\beta_T}{\alpha} \quad \text{and} \quad \left(\frac{\partial U}{\partial T}\right)_V = c$$

$$\therefore \left(\frac{\partial U}{\partial P}\right)_V = \frac{c_v\beta}{\alpha} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_V = \frac{c_v\beta_T}{T\alpha}$$

$$c_p - c_v = \frac{VT\alpha^2}{\beta} \therefore c_v = c_p - \frac{VT\alpha^2}{\beta_T}$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_V = \frac{c_p\beta}{T\alpha} - V\alpha$$

5.3

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial A}{\partial P}\right)_V = \left(\frac{\partial A}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{\beta_T}{\alpha}$$

$$\therefore \left(\frac{\partial A}{\partial P}\right)_V = \frac{-S\beta_T}{\alpha}$$

5.4

$$dA = \left(\frac{\partial A}{\partial T}\right)_P dT + \left(\frac{\partial A}{\partial P}\right)_T dP$$

$$\therefore \left(\frac{\partial A}{\partial V}\right)_P = \left(\frac{\partial A}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{\partial A}{\partial T}\right)_P \frac{1}{\alpha V}$$

$$dA = -SdT - PdV$$

$$\therefore \left(\frac{\partial A}{\partial T}\right)_P = -S - P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial A}{\partial V}\right)_P = \left(-S - P\alpha V\right)\frac{1}{\alpha V}$$

$$= -\left(\frac{S}{\alpha V} + P\right)$$

5.5

$$dH = \left(\frac{\partial H}{\partial T}\right)_V dT = \left(\frac{\partial H}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial H}{\partial S}\right)_V = \left(\frac{\partial H}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

$$TdS + \delta q_v = c_v dT \ \therefore \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{c_v}$$

$$H = U + PV$$

$$\therefore \left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

$$= c_v + \frac{V\alpha}{\beta_T}$$

$$\therefore \left(\frac{\partial H}{\partial S}\right)_V = \frac{T}{c_v}\left[c_v + \frac{V\alpha}{\beta_T}\right] = T\left[1 + \frac{V\alpha}{c_v\beta_T}\right]$$

5.6

$$dH = TdS + VdP$$

$$\therefore \left(\frac{\partial H}{\partial V}\right)_S = V\left(\frac{\partial P}{\partial V}\right)_S$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_V}$$

From problem 5.1:

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{c_p}{TV\alpha}$$

From problem 5.2:

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{c_v\beta_T}{T\alpha}$$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_S = \frac{c_p}{Vc_v\beta_T}$$

$$\therefore \left(\frac{\partial H}{\partial V}\right)_S = -\frac{c_p}{c_v\beta_T}$$

5.7

$$c_p = \left(\frac{\partial H}{\partial T}\right)_P \therefore \left(\frac{\partial c_p}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right]_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \text{ and } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial c_p}{\partial P}\right)_T = \frac{\partial}{\partial T}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]_P$$

$$= \frac{\partial}{\partial T}\left[-T\alpha V + V\right]_P$$

$$= -\alpha V - TV\frac{d\alpha}{dT} - T\alpha^2 V + \alpha V$$

$$= -TV\left(\alpha^2 + \frac{d\alpha}{dT}\right)$$

5.8

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{c_p}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{\alpha V T}{c_p}$$

5.9

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_V}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \frac{c_v}{T}\frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{c_v}{T} \times \frac{\beta_T V}{\alpha V} = \frac{c_v \beta_T}{T\alpha}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{c_p}{T}\frac{1}{\alpha V}$$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_S = -\frac{c_p}{c_v V \beta_T}$$

5.10

$$dG = -SdT + VdP$$

$$\therefore \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T$$

$$dA = -SdT - PdV$$

$$\therefore \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\left(\frac{\partial^2 G}{\partial P^2}\right)_T}$$

5.11 The process is adiabatic. Therefore $q = 0$ and work done by the gas, $w = P_2v_2 - P_1v_1$. Thus $\Delta H = q - w + (P_2V_2 - P_lV_l) = 0$:

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H$$

but

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{1}{c_p}\left(\frac{\partial H}{\partial P}\right)_T$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -T\alpha V + V$$

$$\therefore \mu_{J-T} = -\frac{1}{c_p}(-\alpha TV + V) = \frac{V}{c_p}(\alpha T - 1)$$

For an ideal gas

$$\alpha = \frac{1}{T}, \quad \text{so} \quad \alpha T = 1 \quad \text{and} \quad \mu_{J-1} = 0$$

5.12

a. 1. $\Delta U = \Delta H = 0,\ \Delta S = R \ln 4,\ \Delta A = \Delta G = -T\Delta S = -RT \ln 4$

2. $\Delta U = \Delta H = 0,\ \Delta S = R \ln 8,\ \Delta A = \Delta G = -RT \ln 8$

3. $\Delta U = \Delta H = \Delta S = \Delta A = \Delta H = 0$

4. $\Delta U = \Delta H = 0,\ \Delta S = R\ln(32/27),\ \Delta A = \Delta G = -RT\ln(32/27)$

b. $\Delta U = \Delta H = 0,\ \Delta S = R\ln(V_2/V_1) = R\ln 2,\ \Delta A = \Delta G = -RT\ln 2$

c. $\Delta U = c_v(T_2 - T_1),\ \Delta H = c_p(T_2 - T_1),\ \Delta S = 0,\ \Delta A = \Delta U - S(T_2 - T_1),$

$$\Delta G = \Delta H - S(T_2 - T_1)$$

d. $\Delta U = c_v(T_2 - T_1), \Delta H = c_p(T_2 - T_1), \Delta S = c_p\ln(T_2/T_1),$

$$\Delta A = \Delta U - (T_2 - T_1)S_1 - T_2\Delta S,\ \Delta G = \Delta H - (T_2 - T_1)S_1 - T_2\Delta S$$

e. $$\Delta U = c_v(T_2 - T_1), \Delta H = c_p(T_2 - T_1), \Delta S = c_v \ln\left(T_2 / T_1\right),$$

$$\Delta A = \Delta U - \left(T_2 - T_1\right)S_1 - T_2\Delta S,\ \Delta G = \Delta H - \left(T_2 - T_1\right)S_1 - T_2\Delta S$$

5.14*

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mathcal{H}} = \left(\frac{\partial V}{\partial S}\right)_{P,\mathcal{H}}$$

$$\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{S,P} = -\mu_0 V\left(\frac{\partial M}{\partial P}\right)_{S,\mathcal{H}}$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{S,P} = -\mu_0 V\left(\frac{\partial M}{\partial S}\right)_{P,\mathcal{H}}$$

5.15*

$$\left(\frac{\partial S}{\partial V}\right)_{T,M} = \left(\frac{\partial P}{\partial T}\right)_{V,M}$$

$$\left(\frac{\partial S}{\partial M}\right)_{T,V} = -\mu_0 V\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{M,V}$$

$$\left(\frac{\partial P}{\partial M}\right)_{V,T} = -\mu_0 V\left(\frac{\partial \mathcal{H}}{\partial V}\right)_{M,T}$$

Chapter Six

6.1 $\Delta H_{1600} = -1.086 \times 10^6$ J, $\Delta S_{1600} = -178.5$ J/K

6.2 $H_{\text{diamond, 1000}} - H_{\text{graphite, 1000}} = 1037$ J. Thus the oxidation of diamond at 1000 K is 1037 J/mole more exothermic than the oxidation of graphite.

6.3 $\Delta H_{1000} = -80{,}500$ J, $\Delta S_{1000} = 6.6$ J/K

6.4 Increasing the pressure to 1000 atm increases the molar enthalpy by 612 J. This increase in molar enthalpy is achieved by increasing the temperature of Cu from 298 to 327 K at a pressure of 1 atm.

6.5 (a) $\Delta H = -435{,}000$ J, $\Delta S = -94.75$ J/K; (b) $\Delta H = -355{,}000$ J, $\Delta S = -75.35$ J/K; (c) $\Delta H = -373{,}000$ J, $\Delta S = -80.15$ J/K

6.6 15.1 kg

6.7 (a) 4745 K, (b) 2330 K

6.8 $\Delta G_{800} = -1.817 \times 10^6$ J. If it is assumed that Δc_p for the reaction is zero, $\Delta G_{800} = \Delta H_{298} - 800\Delta S$ is calculated as -1.811×10^6 J, which involves a 0.3% error.

6.9 $a = 3$, $b = c = 2$, $\Delta H_{298} = 99{,}700$ J, $\Delta S_{298} = 125.8$ J/K, $\Delta G_{298} = 62{,}210$ J

6.10 1675 kJ

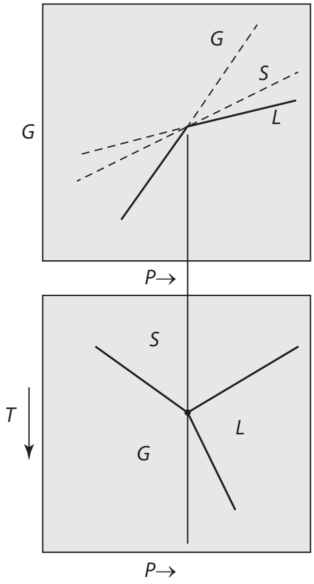
6.11*

$$d\,\Omega = SdT + PdV + Nd\mu$$

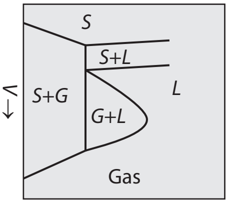
$$\Omega = \Omega\ (T, V, m)$$

Chapter Seven

7.1 (a) The triple point for α-β-vapor is T = 1163 K, $p = 2.52 \times 10^{-10}$ atm, and the triple point for β-liquid-vapor is T = 1689 K, $p = 8.35 \times 10^{-5}$ atm. (b) T_b = 2776 K. (c) $\Delta H_{(\alpha\rightarrow\beta)} = 4739$ J, ΔH_m = 29,770 J.
7.2 $p_{\text{Hg.373 K}} = 3.55 \times 10^{-4}$ atm
7.3 Condensation begins at 328 K; at 280 K 82.5% of the $SiCl_4$ has condensed.
7.4 Eq. (I) gives the vapor pressure of solid zinc.
7.5 $\Delta H_{b},_{\text{Fe,3330 K}} = 342$ kJ
7.6 $p_{CO_2,298\text{ K},(l)} = 73.3$ atm. The triple-point pressure is 5.14 atm, and, as the 1 atm isobar does not pass through the liquid-phase field, liquid CO_2 is not stable at atmospheric pressure.
7.7 P = 2822 atm
7.8 The slopes of the lines at the triple-point are obtained from $dP/dT = \Delta S/\Delta V$.
7.9 T_b = 523 K
7.12*



7.13*



Chapter Eight

8.1 The van der Waals equation containing the reduced variables is

$$\left(P_R + \frac{3}{V_R^2}\right)(3V_R - 1) = 8T_R$$

$Z_{\mathrm{cr}} = 0.375$; $(\partial U/\partial V)_T = a/V^2$

8.2 $n_A/n_B = 1$, $P = 1.414$ atm

8.3 The tank contains 565 moles of van der Waals oxygen and 511 moles of ideal gas oxygen. As the gas is purchased by the tank-load, the same price purchases more moles of a van der Waals gas than it does an ideal gas.

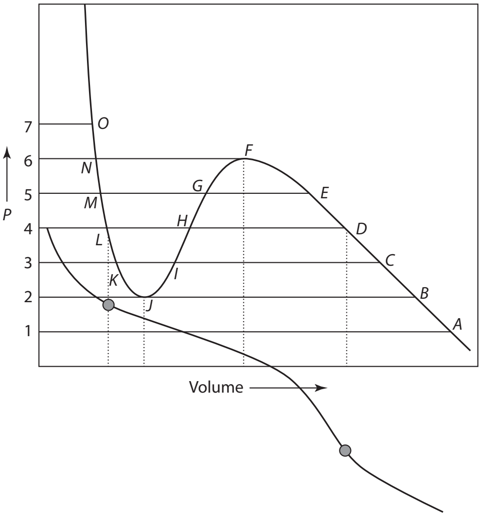
8.4 $w = -1384$ J

8.5 (a) $b = 0.0567$ 1/mole, $a = 6.771^2$·atm/mole^2; (b) 0.170 1/mole; (c) P (van der Waals) = 65.5 atm, P (ideal gas) = 82.1 atm

8.6 With the virial equation $w = -301$ kJ, with the van der Waals equation $w = -309$ kJ, with the ideal gas law $w = -272$ kJ.

8.7 (a) $f = 688$ atm, (b) $P = 1083$ atm, (c) $\Delta G = 16{,}190$ J with an nonideal contribution of 790 J

8.9*



8.10*

$$dP = \frac{R}{V-b}dT - \left(\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right)dV$$

8.12*

$$Z_{cr} = \frac{P_{cr}V_{cr}}{RT_{cr}} = \frac{a}{27b^2} \cdot 3b \cdot \frac{1}{R} \cdot \frac{27bR}{8a} = \frac{3}{8} = 0.375$$

Chapter Nine

9.1 $\Delta H = 117{,}400$ J, $\Delta S = 59.63$ J/K

9.2 $\gamma_{\mathrm{Mn}} = 1.08$

9.3 (a) The average value of α is 4396 ± 6 J which indicates that, with respect to the behavior of G^{xs}, the solution is regular. (b) $\bar{G}^{\mathrm{xs}}_{\mathrm{Fe}} = 1583$ J and $\bar{G}^{\mathrm{xs}}_{\mathrm{Mn}} = 703$ (c) $\Delta G^M = -9.370$ J. (d) $p_{\mathrm{Mn}} = 0.0118$ atm and $p_{\mathrm{Fe}} = 3.68 \times 10^{-5}$ atm.

9.4 73,380 J

9.5 $\alpha = -4578$ J, $a_{\mathrm{Sn}} = 0.418$

9.6*

a.

$$\Delta \bar{G}_B = RTa_B = -5763J$$

$$a_B(X_B = 0.5) = \exp\left(-\frac{5763}{8314}\right) = 0.5$$

b.

$$\Delta \bar{G}_B = RTa_B = -1609\ J$$

$$a_B = \exp\left(-\frac{1609}{8314}\right) = .844$$

9.8 The temperature is increased by 2.37 degrees (K).

9.10 $\ln \gamma_{\mathrm{Cd}} = 0.425\ X^2_{\mathrm{Zn}} + 0.30X^3_{\mathrm{Zn}}$, $a_{\mathrm{Cd}} = 0.577$

9.11 $a_{\mathrm{Au}} = 0.695$, $a_{\mathrm{Ni}} = 0.85$

9.14 $a_0'' < a_0'$

9.15* $a_B = 0.824$

Chapter Ten

10.1 $T = 1317$ K, $X_{\mathrm{CaF2}} = 0.53$

10.2 (a) – 11,140 J, (b) zero

10.3 (a) 2418 K, (b) $X_{\mathrm{Al_2O_3}} = 0.62$, (c) 2444 K, (d) $X_{\mathrm{Al_2O_3}} = 0.38$

10.4 – 814 J

10.5 $\alpha_l = 38{,}096$ J, $T_{\mathrm{cr}} = 2291$ K

10.6 (a) $\Delta H^\circ_{m,\mathrm{Ge}}$ from liquidus = 21,527 J, (b) $\Delta H^\circ_{m,\mathrm{Ge}}$ from solidus = 33,111 J

10.7 The maximum solubility of CaO in MgO is $X_{\mathrm{CaO}} = 0.066$, and the maximum solubility of MgO in CaO is $X_{\mathrm{MgO}} = 0.15$.

Chapter Eleven

11.1 $X_{\mathrm{CO_2}} = X_{\mathrm{H_2}} = 0.182,\ X_{\mathrm{H_2O}} = 0.0677,\ X_{\mathrm{CO}} = 0.568$
11.2 43,800 J
11.3 $CO_2/H_2 = 1.276$
11.4 1771 K
11.5 $P_T = 0.192$ atm, $T = 792$ K
11.6 (a) $p_N = 5.94 \times 10^{-6}$ atm, (b) $P_T = 3.18 \times 10^{-9}$ atm
11.7 13.3 atm, $\Delta H^\circ_{573\ \mathrm{K}} = -50{,}900$ J, $\Delta H^\circ_{573\ \mathrm{K}} = -1107$ J/K
11.8 $PCl_5/PCl_3 = 0.371$
11.9 At $P_T = 1$ atm, $p_{\mathrm{H_2}} = 1.05\times10^{-8}$ atm, $p_{\mathrm{O_2}} = 0.0756$ atm. At $P_T = 10$ atm, $p_{\mathrm{H_2}} = 3.31\times10^{-8}$ atm, $p_{\mathrm{O_2}} = 0.756$ atm.
11.10

$$X_{\mathrm{H_2}} = X_{\mathrm{I_2}} = 0.165,\ X_{\mathrm{HI}} = 0.669,\ T = 906\ \mathrm{K}$$

11.11*

$$p_{CO} = \frac{1}{(K_P^{\frac{1}{4}} + 1)} \qquad p_{CO_2} = \frac{K_P^{\frac{1}{4}}}{(K_P^{\frac{1}{4}} + 1)}$$

Chapter Twelve

12.1 $T = 565$ K
12.2 $T_{m,\mathrm{Ni}} = 1731$ K, $\Delta H^\circ_{m,\mathrm{Ni}} = 17{,}490$ J, $\Delta S^\circ_{m,\mathrm{Ni}} = 10.1$ J/K
12.3 (a) $T = 462$ K, (b) $T = 421$ K
12.4 $p_{\mathrm{H_2O}} = 1.32\times10^{-3}$ atm, and the oxidation reaction is exothermic.
12.5 Equilibrium would produce a gas containing 11.4% HCl, 46.6% H_2, and 42% Ar. Therefore equilibrium is not attained.
12.6 The FeO disappears.
12.7 $p_{\mathrm{Mg}} = 2.42 \times 10^{-2}$ atm
12.8 (a) $T = 1173$ K, (b) $p_{\mathrm{CO_2}} = 0.055$ atm, (c) $p_{\mathrm{CO_2}} = 1.23$ atm
12.9 $P = 1$ atm $(p_{\mathrm{SO_3}} = 7.99\times10^{-2}$ atm, $p_{\mathrm{SO_2}} = 0.612$ atm, $p_{\mathrm{O_2}} = 0.306$ atm$)$
12.10 99.1% of the sulfur is removed, and $p_{\mathrm{S_2}}$ in the effluent gas is 6.3×10^{-11} atm
12.11 $\Delta G^\circ = 282{,}000 - 123T$ J
12.12 0.76 moles of CH_4 are consumed per mole of Fe produced.
12.13 Eq. (i) for solid Mg, Eq. (ii) for gaseous Mg, Eq. (iii) for liquid Mg, $T_{m,\mathrm{Mg}} = 930$ K, $T_{b,\mathrm{Mg}} = 1372$ K

12.14 54.92 g of Zn are oxidized to form ZnO and 29.78 g of Zn are evaporated, which leaves 115.3 g of metallic Zn in the crucible.

12.15 4.76 moles of $CaCO_3$ are decomposed per mole of CH_4 burned

12.16 $X_{Hg} = 0.0152$, $X_{O2} = 0.0071$

12.17 $P_T = 1.651$ atm, $p_{CO} = 1.009$ atm, $p_{CO_2} = 0.642$ atm

Chapter Thirteen

13.1 $a_{Cu} = 0.159$

13.2 $a_{Mg} = 6.4 \times 10^{-4}$

13.3 $a_{PbO} = 0.5$

13.4 $X_{Cu} = 0.018$. Increasing T decreases the extent to which Cu is removed.

13.5 $a_C = 0.5$ $p_{H_2} = 0.92$ atm

13.6 $a_{FeO} = 9.9 \times 10^{-5}$

13.7 (a) $p_{H_2}/p_{CO_2} = 2.15$, (b) $a_C = 0.194$, (c) $P_T = 5.16$ atm, (d) the total pressure does not influence p_{O_2}.

13.8 With $C = 3$ and $P = 3$, $\mathcal{F} = 2$, which are used by specifying $T = 1000$ K and $[X_{Mn}] = 0.001$. $(X_{FeO}) = 1.22 \times 10^{-3}$, $p_{O_2} = 2.33 \times 10^{-27}$ atm.

13.9 For 2A + B = A_2B, $\Delta G^\circ_{1273\ K} = -24{,}370$ J; for A + 2B = A_2B, $\Delta G^\circ_{1273\ K} = -23{,}190$ J.

13.10 (a) 10^{-3}, (b) 8.07×10^{-4}, (c) 7.14×10^{-3}, (d) 0.65

13.11 AG° = −567,500 J

13.12 $p_{O_2} = 5.17 \times 10^{-10}$ atm; $h_{Al(1\ wt\%\ in\ Fe)} = 7.2 \times 10^{-6}$; $C = 3$, $P = 4$, therefore $\mathcal{F} = 1$ which is fixed by specifying $T = 1600$°C

13.13 $T_{max} = 2211$ K, $T_{min} = 1515$ K

13.14 $p_{Mg} = 0.053$ atm

13.15 $a_{MgO}(\text{min}) = 0.027$

13.16 $p_{CO} = 0.739$ atm, $p_{CO_2} = 0.0117$ atm, $p_{Zn} = 0.763$ atm

13.17 $a_{Al_2O_3} = 0.129$

13.18 (a) wt% Al = 0.00042, wt% O = 0.0039; (b) wt% Al = 0.00054, wt% O = 0.0035

13.19 $T_{max} = 1108$ K

13.20 $P = 6917$ atm

13.21 Wustite $0.904 < p_{CO} < 3.196$ atm, cementite $7.43 < p_{CO} < 8.14$ atm

13.22 $T_{max} = 1026$ K

13.23 $a_{Zn} = 0.154$

13.24 [wt% O] = 1.9, $k(1273\ K) = 2.0$

13.25 The formation of a manganese silicate melt as the deoxidation product decreases the activity of SiO_2 to a value less than unity and thus shifts the equilibrium [Si] + 2[O] = (SiO_2) to the right. For any given value of [wt% Si], the extent of deoxidation is maximized when the product of deoxidation is an MnO-saturated silicate melt in which a_{SiO_2} has its minimum value of 0.02.

Chapter Fourteen

14.1 $Pb_{(s)} + 2AgCl_{(s)} = 2Ag_{(s)} + PbCl_{2(s)}$, $\Delta G^\circ = -94{,}560$ J, $\Delta S^\circ = -35.5$ J/K
14.2 (a) –103,400 J, (b) 27.98 J/K, (c) 8338 J/mole of Pb, (d) $a_{\mathrm{Hg}} = 0.71$
14.3

$$\ln p_{O_2}(\mathrm{atm}) = \frac{46{,}620E}{T} + \frac{63{,}440}{T} - 15.48$$

14.4 $\Delta c_p = -0.093$ J/K
14.5 (a) $a_{\mathrm{Al}} = 0.673$, (b) $\Delta \bar{G}^M_{\mathrm{Al}} = -2150\ \mathrm{J}$, (c) $\Delta \bar{H}^M_{\mathrm{Al}} = 3329\ \mathrm{J}$
14.6 (a) 1.62×10^{-6}, (b) 0.5, (c) 0.266 wt%, (d) 0.602 wt%
14.7 pH = 6.33, $\mathscr{E} = -0.126$ volts, $[Pb^{4}+] = 3.1 \times 10^{-62}$ moles/liter, $HPbO_2^- = 10^{-9}$ moles/liter, $PbO_3^{2-} = 2.5 \times 10^{-47}$ moles/liter, $[PbO_4^{4-}] = 6 \times = 10^{-221}$ moles/liter
14.8 2.20 volts, 1.17 volts
14.9 +6897 J, –4513 J

Chapter Fifteen

15.1*

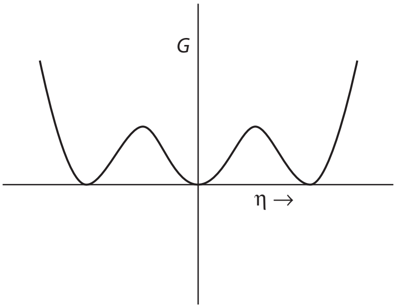
a. $$S^{XS} = \frac{a^2(T - T_C)}{2C}$$

b. $$C_P^{ord} - C_P^{dis} = a$$

15.2*

$$T = T_C + \frac{C^2}{4aE}$$

b.



c. First order

d. $\Delta H = T_0 a\left(\frac{C}{2E}\right) < 0 \quad \text{since } C < 0$

e. Exothermic

15.4*

a. $\gamma_{gb/1-2} = 2\gamma_{\alpha_1/\alpha 2}\cos\left(\frac{\phi_{12}}{2}\right)$

b. α_1/α_2

c. zero

d. $2\gamma_{\alpha_i/\alpha_j}$

Index