Gabriel Plascencia · David Jaramillo

Basic Thermochemistry in Materials Processing

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To Priscila with love;
Til Torstein
G.P.

Preface

This book is the result of the experience gained over the years on the learning and teaching the subject of thermodynamics in metal and materials systems. The authors still remember how painful it is to do well in such courses, and are sympathetic to those students currently undergoing such ordeal.

On the other hand, the authors have realized over the years that thermodynamics is not a nightmare; and in fact they have come to a realization that this subject is not as complex as many believe it to be.

Hence, this text was created. It is designed to serve as a complement to more extensive textbooks. The main idea is to show full solutions of problems commonly taught in chemical thermodynamics, thermochemistry or simple thermodynamics courses. The fully solved problems presented in this manuscript are not only found in academics, some of them are also found (quite frequently) in major metallurgical operations. It has been sought as a balance between merely academic problems and industry-related ones. The problems shown in the text are to ease the understanding of key concepts and help students overcome their fear to this simple yet powerful tool for process analysis.

The book also includes some theory; however, we tried to keep the concepts described in the text as simple as possible and it has been attempted to use a friendly language appealing to students.

In the end, we expect that the students and those who have an opportunity to check on the book might experience a pleasant time learning this subject manner.

Most of the examples in the book were modified versions of those taken from *Collection of problems in chemical metallurgy and materials science* by Toguri et al. The data used to solve the problems were taken from HSC Chemistry V6.1 by A. Roine, Hultgren's et al. book *Selected values of thermodynamic properties of metals and alloys* and from Alcock and Kubaschewski's *Materials Thermochemistry, 6th Edition.* The phase diagrams shown in Chap. 5 were drawn using TAPP V2.2 software.

Mexico City, Mexico
November 2016

Gabriel Plascencia
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Introduction

Thermodynamics developed from studying the efficiency of early steam engines. Thermodynamics deals with energy exchange or energy transformation in a given system without considering any molecular mechanism. At its core, thermodynamics relates heat and temperature to energy and mechanical work.

From its beginnings, thermodynamics extended to chemical systems. Chemical thermodynamics or thermochemistry developed into a powerful tool for chemical engineers, metallurgists, and materials science specialists to predict the macroscopic behavior of the system under study.

Thermochemistry relates to the amount of energy needed to undergo any sort of chemical or physical transformation. In materials processing, process engineers usually look for specific chemical reactions (oxidation, reduction, etc.) or for phase changes, i.e., fusion or solidification. In either case, it is imperative to estimate the energy exchange involved in such changes.

The importance of quantifying the energy required to incur in any of these transformations allows for establishing energy and mass balances which in turn help in sizing up the different equipments used to produce the materials that we end up using every day.

To be able to calculate the energy exchange, thermochemistry heavily relies on basic thermodynamic principles. In this chapter, we will define some quantities and functions based on the laws of thermodynamics. These quantities will be used throughout the entire text to help us calculate the energy needed to carry over any chemical reaction, phase change, or to form solutions over different composition ranges.

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The First Law of Thermodynamics and the Enthalpy Function

The first law of thermodynamics is a conservation law that defines energy as a constant in a system of fixed mass. This law states that energy can be transformed form one kind into another and even some of the energy can be converted into mechanical work.

The total energy of a system can be associated to the internal energy (E) which is comprised of: (i) The kinetic energy associated with atom motions, (ii) the energy stored in chemical bonds of the molecules within the system, (iii) the potential energy of the system.

It is nearly impossible account for each of these contributions to determine the absolute energy of the system; that is why we only concern about the change in the energy of the system (ΔE). This simplifies our calculations because:

- If the temperature remains constant, the kinetic energy of the atoms can be neglected.
- If no bonds are broken, the chemical energy of the system can be ignored.
- If the system does not change location (height), its potential energy is discarded.

In a chemical reaction, the internal energy of the reactants is E_{initial} and the heat of the products is E_{final}.

In terms of work, in thermodynamic systems the most common one is in the form of PV work, which is conducted by gases behaving ideally. Depending on process conditions, PV work can be expressed in different ways using process variables, as seen in Table 1.2. In addition to PV work, other types of work such as gravitational ($w = Mgh$), electrical ($E_{\text{i}} \cdot \text{d}t$) and that to create an interfacial area ($\text{d}w = -P\text{d}V + \gamma\text{d}A$) among others are also attainable.

Based on this, the change of internal energy in a system can be expressed in terms of the heat or energy (q) and the work (w) that can be exchanged as any transformation takes place (Table 1.1):

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = q - w \tag{1.1}$$

Table 1.1 Sign convention for heat and work

Quantity	Sign	Condition
Heat	Positive	Energy taken INTO the system
	Negative	Energy taken OUT of the system
Work	Positive	Work done BY the system
	Negative	Work done UPON the system

The Enthalpy Function

Table 1.2 shows that when the pressure remains fixed, the first law of thermodynamics takes the form:

$$E_{\text{final}} - E_{\text{initial}} = q - P(V_{\text{final}} - V_{\text{initial}}) \tag{1.2}$$

Solving for q in Eq. (1.2) yields:

$$q = (E + PV)_{\text{final}} - (E + PV)_{\text{initial}} = H \tag{1.3}$$

The terms (E + PV) are called ENTHALPY or heat content (H). Thus the total heat exchanged from/to a system under constant pressure conditions is defined by this quantity, so:

$$q = H_{\text{final}} - H_{\text{initial}} = \Delta H \tag{1.4}$$

Taking differentials in Eq. (1.4) results in:

$$\mathrm{d}q = \mathrm{d}H \tag{1.5}$$

Enthalpy as internal energy is an extensive property of a system. It depends on the mass present in the system and like internal energy; H is a state function since it only depends on the final and initial states of the system. If during the chemical reaction or transformation heat is released, then the process is called exothermic; whereas if energy is applied to complete the reaction or the transformation, it is called endothermic.

As mentioned before, enthalpy relates to the heat involved in chemical reactions, phase changes, and solution formation. Each of these phenomena can be associated to a specific type of heat:

Heat of formation: Is the heat evolved or absorbed per mole when a mole of a compound is obtained from its constituent elements. The heat of formation depends on the thermodynamic state of reactants and products as well as to their chemical state. For this reason, this heat is expressed in terms of "*standard heat of formation*". Based on that, it is necessary to define the standard state.

The standard state of an element is the most stable form of that element under the chosen standard conditions. IUPAC recognizes the standard state as an arbitrary

Table 1.2 ΔE and its relation to PV work and heat

Fixed variable	Work	Heat	Internal energy
P (Isobaric)	$w = P(V_{\text{final}} - V_{\text{initial}})$	$q = nCp(T_{\text{final}} - T_{\text{inital}})$	$\Delta E = q - w$
T (Isothermic)	$w = nRT \ln\left(\frac{V_{\text{final}}}{V_{\text{inital}}}\right)$	$q = w$	$\Delta E = 0$
V (Isometric)	$w = 0$	$q = \Delta E$	$\Delta E = nCv(T_{\text{final}} - T_{\text{initial}})$
Q (Adiabatic)	$w = nCv(T_{\text{final}} - T_{\text{initial}})$	$q = 0$	$\Delta E = -w$

one, but it recommends setting the standard pressure as 10^5 Pa. On the other hand, most thermodynamic databases report data with a standard state of 1.01325×10^5 Pa (1 atm) and 298 K (25 °C); it is seldom found the standard state as 1 atm and 273 K (0 °C). In this text, we will adopt the standard state as 1.01325×10^5 Pa (1 atm) and 298 K (25 °C). Furthermore, by convention, the standard enthalpy of formation for a pure element in its standard state is zero.

Heat of reaction: Is the heat released or absorbed when reactants fully transform into products. This heat can be expressed in terms of the number of moles of any reactant or any product.

To evaluate the heat of reaction it is necessary to account for the enthalpies of all the reactants and products, thus for any reaction, its heat of reaction is given by:

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \tag{1.6}$$

If both reactants and products are in their respective standard state, Eq. (1.6) can be rewritten as:

$$\Delta H^{\circ}_{\text{reaction}} = \sum \Delta H^{\circ}_{\text{products}} - \sum \Delta H^{\circ}_{\text{reactants}}, \tag{1.6a}$$

where the superscript "°" denotes the standard state.

Heat of combustion: The heat of combustion is the amount of energy released when one mole of a substance is fully burnt in oxygen.

Heat of solution: It is the energy exchange when a substance dissolved into another one, and it depends on the concentration of the solution.

Heat of transformation: It is also known as "Latent heat" and it is the energy released or absorbed by an element or a compound as it undergoes a phase change such as melting, solidification, or any solid state transformation.

As systems differ, some of them may be able to store more energy than others. Thus the enthalpy is related to the heat capacity (C) of a system:

$$C = \frac{q}{\Delta T} \tag{1.7}$$

Under constant pressure conditions and using the definition (1.5), Eq. (1.7) transforms into:

$$Cp = \frac{\mathrm{d}H}{\mathrm{d}T}, \tag{1.8}$$

where Cp is the heat capacity at constant pressure. Analogously, under constant volume conditions, the heat capacity (Cv) is defined as a function of the internal energy of the system ($Cv = \mathrm{d}E/\mathrm{d}T$).

From relationship (1.8), it is evident that it is possible to estimate the enthalpy change from the heat capacity:

$$\mathrm{d}H = nCp\,\mathrm{d}T, \tag{1.9}$$

where n is the number of moles in the system. Heat capacity is also an extensive property of any system that depends on the amount of substance present. Cp strongly depends on the temperature and is generally expressed by polynomials with the temperature as independent variable:

$$Cp = a + bT + \frac{c}{T^2} + dT^2 + \cdots \tag{1.10}$$

Figure 1.1 shows the Cp of iron and silver as a function of temperature. Each of the iron phases in the solid state is represented in such figure. It can be noticed that there is a discontinuity in the Cp when a phase transformation occurs; this means that every single phase of an element or a compound has its own heat capacity. This is an inherent property of every material that has to be measured experimentally.

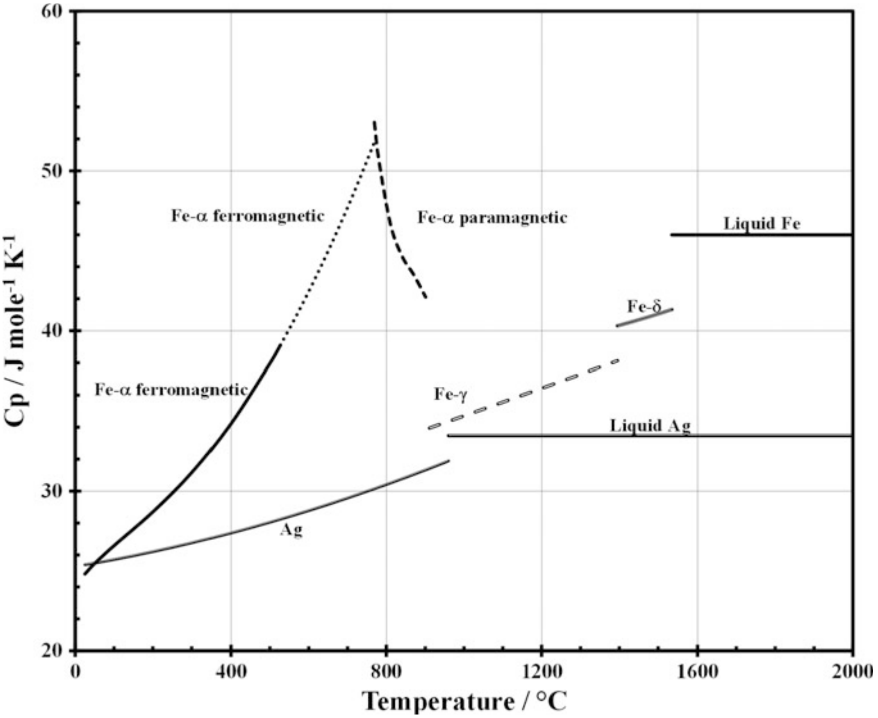

Fig. 1.1 Heat capacity at constant pressure (Cp) of iron and silver as a function of temperature

Hess's Law

This law states that for any chemical reaction, the total energy exchange is the same whether it takes place in one or in several steps as long as the temperature of the system and either the pressure or the volume remains constant.

The Second Law of Thermodynamics and the Entropy Function

The first law of thermodynamics establishes that the energy needed to undergo any transformation remains constant and it can only be transformed into another form of energy or into any sort of work. This law does not provide with any indication of how efficiently the energy is used; furthermore the first law only quantifies the amount of energy required. Additionally, it can be deducted from the first law if the system releases or absorbs heat as it transforms, but it does not provide insight into how easily the transformation will take place or even more if under given conditions, the transformation will or will not occur. Thus it is necessary to define a thermodynamic quantity which can provide information regarding to the spontaneity of a reaction.

The second law of thermodynamics was the first to be recognized; this law evidences an imbalance in natural systems; for example, hot objects cool down spontaneously, but cold objects do not become hot by themselves. Despite the total energy must be preserved in any process, the distribution of that energy changes irreversibly. Thus the second law relates to the natural direction of how energy is distributed, which is independent of the total amount of energy available.[1]

The second law lacks of a universal statement, but according to Smith[2] this law can be postulated as: "*Spontaneous changes are those which, if carried out under the proper conditions, can be made to do work. If carried out reversibly they yield a maximum amount of work. In natural processes, the maximum work is never obtained.*"

According to this assertion, changes can be spontaneous (occurring in nature) or reversible (non-spontaneous). Those spontaneous changes absorb less energy and do less work than reversible changes. In reversible systems the maximum amount of work is attainable.

Based on this, the internal energy cannot totally transform into work; which is defined by the potential energy of the system, while the equilibrium condition is set by the minimum level of potential energy. Therefore, it is needed to define a quantity that accounts for the capacity of a system to do work, and it is also required to define a state function that reflects the loss in the ability to do work.

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[1] Atkins P.W., The second law. Scientific American Books, New York, 1984.

[2] Smith E.B., Basic chemical thermodynamics. Imperial College Press, London, 2004.

If we consider a reversible process that absorbs an infinitesimal amount of heat δq at temperature T, the term $\frac{\delta q}{T}$ is called ENTROPY (S). δq itself is not a state property, but the ratio $\frac{\delta q}{T}$ is. Thus:

$$\mathrm{d}S = \frac{\delta q}{T} \tag{1.11}$$

Entropy also is an extensive property as it depends on the mass of the system. Additionally, entropy is a state function since it is defined by the thermodynamic state of the system. However, when using entropy as a criterion to determine the state of equilibrium of a system, it is necessary to evaluate both the system and its surroundings. The combination of these two constitutes an isolated system.

For reversible processes, the sum of the entropy change of a system and its surroundings is always zero:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \tag{1.12}$$

Therefore, the entropy change in an isolated system undergoing a reversible change is always zero.

In irreversible (spontaneous) processes, the sum of the entropy change of the system and its surroundings is always a positive quantity:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \tag{1.13}$$

Thus, isolated systems going through spontaneous transformations will result in an entropy increase. That entropy increase will eventually reach a maximum value at such point the system will be in equilibrium and the entropy will remain constant at its maximum value. This is represented in Fig. 1.2.

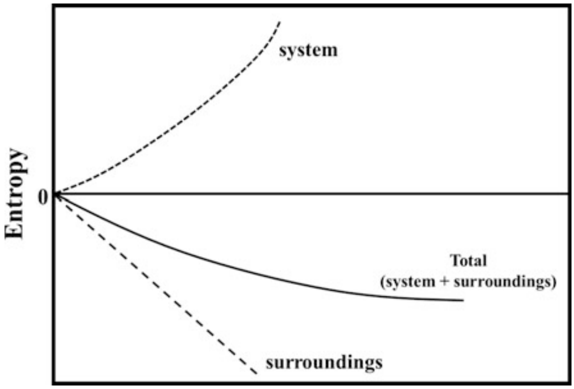

Fig. 1.2 Total entropy of a system considering the system itself and its surroundings

Table 1.3 Entropy criteria to reach equilibrium conditions

Criterion	Condition
$\Delta S_{\mathrm{Total}} = 0$	The system is at equilibrium and no spontaneous transformations will occur
$\Delta S_{\mathrm{Total}} > 0$	Any transformation will tend to take place spontaneously from initial state 1 to final state 2
$\Delta S_{\mathrm{Total}} < 0$	Any transformation will tend to take place spontaneously in the inverse direction from initial state 2 to final state 1

To define the equilibrium condition for a system going from the initial state 1 to the final state 2, the total entropy change (system + surroundings) is:

$$\Delta S_{\mathrm{Total}} = \Delta S_{2,\mathrm{total}} - \Delta S_{1,\mathrm{total}} \tag{1.14}$$

Under conditions of constant internal energy and volume or constant enthalpy and pressure, spontaneous transformations will occur accordingly to Table 1.3.

In spite of clearly defining the equilibrium condition and also predicting in which direction a transformation will take place, entropy presents a major setback. The surroundings must be examined before deciding if a change may occur either reversibly or irreversibly. Since the surroundings are vast, they are difficult to evaluate. This limits the utility of entropy to define equilibrium conditions.

Entropy itself is a primitive concept that has no explicit definition and was developed from efficiency analysis of heat engines. However entropy is useful in determining how energy spreads.

In summary, the second law of thermodynamics is a conservation law only for reversible (nonnatural) processes. This law can be stated in two parts:

- the entropy of a system is a state function. If the state of a system changes reversibly by heat flow, the entropy change is given by: $\mathrm{d}S = \frac{\mathrm{d}q}{T}$
- in spontaneous processes, the entropy change in the universe is given by: $\mathrm{d}S_{\mathrm{universe}} \geq 0 = \mathrm{d}S_{\mathrm{system}} + \mathrm{d}S_{\mathrm{surroundings}}$.

Third and Zeroth Laws of Thermodynamics

Entropy not only defines the state of equilibrium of a system; it also relates to the degree of randomness or lack of uniformity within systems. Such randomness results from either compositional or thermal gradients.

From Eqs. (1.8) and (1.11), it is clear that under constant pressure conditions, the entropy of any substance can be calculated by:

$$\mathrm{d}S = \frac{Cp}{T}\mathrm{d}T \tag{1.15}$$

After integration it yields:

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{Cp}{T} \mathrm{d}T \tag{1.16}$$

Equation (1.15) shows the dependency between entropy and temperature, however, unlike enthalpy, entropy has an absolute value, which can be estimated by defining the entropy of a perfect crystal as zero at the absolute zero temperature. This is stated by the third law of thermodynamics. Most pure substances may form perfect crystals at the lowest temperatures, which allow us to assume $S_{T_1} = 0$. Therefore Eq. (1.16) turns into:

$$S_T = \int_0^T \frac{Cp}{T} \mathrm{d}T \tag{1.17}$$

As with enthalpy, the entropy change for a chemical reaction with all products and reactants in their respective standard state is given by:

$$\Delta S^\circ_{\text{reaction}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}} \tag{1.18}$$

The third law deals with properties of the matter at very low temperatures; it basically states that it is not possible to bring any substance to the absolute zero in a finite number of steps. Aside this, the third law might not even be considered a law, but solely a definition.

On the other hand, heat measurements are not simple to make. Process engineers usually measure temperature and then relate such variable to the amount of heat exchanged. Based on the strong relationship between heat and temperature, the zeroth law was conceived as an afterthought of the three other laws. This law simply defines the temperature by making the observation that when two objects are separately in thermal equilibrium with a third one, they are in equilibrium with each other. Objects in thermodynamic equilibrium have the same temperature.

Free Energy and Auxiliary Functions

The first and second laws of thermodynamics basically state that energy is a constant and how it is utilized, however we still need to define a criterion which allows us in a simple, yet effective manner to stablish whether or not a transformation will take place.

Entropy could be used as criterion for reaching the equilibrium state, however to be useful, it is necessary to evaluate both the system and the surroundings, which may not be very practical.

It is necessary to define a new thermodynamic function that will allow us to predict the equilibrium state of any given system. From the first law and the definition of entropy, we can determine the work done in a reversible process as:

$$\mathrm{d}w_{\text{reversible}} = \mathrm{d}E - T\mathrm{d}S \tag{1.19}$$

This expression defines reversible work as the difference between internal energy and the not-available energy; therefore, reversible work is the free energy of the system. Such free energy clearly defines the state of equilibrium. If the value of the free energy is zero, then the system is under equilibrium; otherwise, the system needs additional work to keep the equilibrium condition.

Most reactions in materials processing occur under constant pressure and temperature. Any system under these conditions is considered closed and energy is exchanged through its boundaries. Because of this, it is highly desirable to develop a criterion for spontaneity based on a thermodynamic quantity/function that can be used under fixed pressure and temperature conditions. Such criterion can be developed based on the concept of Free energy.

If we combine both the enthalpy and the entropy, we can define a new thermodynamic function named Gibbs free energy (G):

$$G = H - TS \tag{1.20}$$

Since we are interested in evaluating the change in Gibbs free energy, Eq. (1.18) can be rewritten as:

$$\Delta G = \Delta H - T\Delta S \tag{1.21}$$

The free energy change for any reaction is the difference between the sum of the free energies of the products and those of the reactants; thus at a temperature T, the standard Gibbs free energy change is:

$$\begin{aligned}
\Delta G^\circ &= \sum G^\circ_{\text{products}} - \sum G^\circ_{\text{reactants}} \\
&= \left(\sum H^\circ_{\text{products}} - T\sum S^\circ_{\text{products}}\right) - \left(\sum H^\circ_{\text{reactants}} - T\sum S^\circ_{\text{reactants}}\right) \\
&= \left(\sum H^\circ_{\text{products}} - \sum H^\circ_{\text{reactants}}\right) - T\left(\sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}\right) \\
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ
\end{aligned} \tag{1.22}$$

For a reaction to occur, it is necessary that the Gibbs free energy has a negative value; the more negative the ΔG value, the more spontaneous the reaction will be. As temperature increases, the entropy term in Eqs. (1.20)–(1.22) becomes more

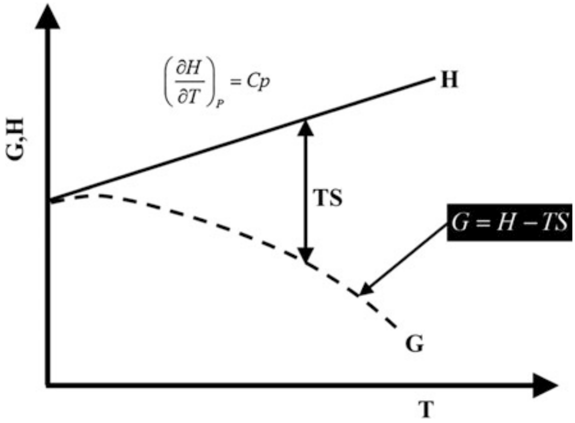

Fig. 1.3 Effect of entropy on the Gibbs free energy function

Table 1.4 Spontaneity of reactions based on the enthalpy and entropy contributions attached to them

Spontaneity	ΔH	ΔS	ΔG	Comments
Always	−	+	−	ΔG always (−)
Never	+	−	+	ΔG always (+)
Enthalpy driven	−	−	−	Occurs at low T
Entropy driven	+	+	−	Occurs at high T

important, so at higher temperatures it is more likely that Gibbs free energy will have a negative value (see Fig. 1.3). If the free energy has a value of zero, then the system is in equilibrium. Additionally, all exothermic reactions will occur. Table 1.4 summarizes under which conditions the Gibbs free energy will be negative and positive.

Thermodynamic data is usually reported in the form of standard enthalpies and entropies at 25 °C (298 K), which allows for an easy calculation of the standard free energy change at the reference temperature; however, if it is of interest calculating the free energy change at a different temperature, it is possible to do so by integrating the respective Cp's:

$$\Delta G_T^\circ = \left[\Delta H_{298}^\circ + \int_{298}^{T} \Delta Cp\, \mathrm{d}T\right] - T\left[\Delta S_{298}^\circ + \int_{298}^{T} \frac{\Delta Cp}{T}\, \mathrm{d}T\right] \qquad (1.23)$$

Equation (1.23) allows calculating the standard free energy change at any temperature using the standard enthalpy (ΔH_{298}°) and the standard entropy (ΔS_{298}°) changes (heat and entropy of reaction) at 298 K and ΔCp values. The ΔCp values are the difference between the sum of products Cp's and reactants Cp's. If any phase transformation occurs in the temperature interval (298 to T), enthalpy and entropy terms must be added to Eq. (1.23) accordingly.

Gibbs Free Energy and Chemical Equilibrium

As chemical reactions proceed, the concentration of reactants decrease as that of the reaction products increase; this happen until the chemical equilibrium is attained (see Fig. 1.4). Once this condition is reached, the concentration of both products and reactants remains constant.

The concentration of all species participating in a chemical reaction (reactants and products) can be related through a reaction quotient (Q). For example, consider the general chemical reaction:

$$aA + bB \rightleftarrows cC + dD \tag{1.24}$$

The reaction quotient associated to reaction (1.24) will be:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{1.25}$$

In Eq. (1.25) the square brackets indicate the concentration of the different chemicals in the reaction. The concentration itself can be expressed in several ways; in material systems and for convenience it can be expressed in terms of the chemical activity of the ith chemical (a_i) in the reaction. In the case of gases, their partial pressure can be used as well. The chemical activity will be discussed later in the text. At this point the activity of any species should be considered as 1 if such species is pure.

The reaction quotient measures the relative amounts of products and reactants in a chemical reaction at any point in time. This ratio indicates in which direction the reaction is going to proceed. When the chemical equilibrium has been reached, the reaction quotient is called equilibrium constant (K); K is defined by the concentration of products and reactants in equilibrium. Thus under chemical equilibrium conditions, we can rewrite Eq. (1.25) as:

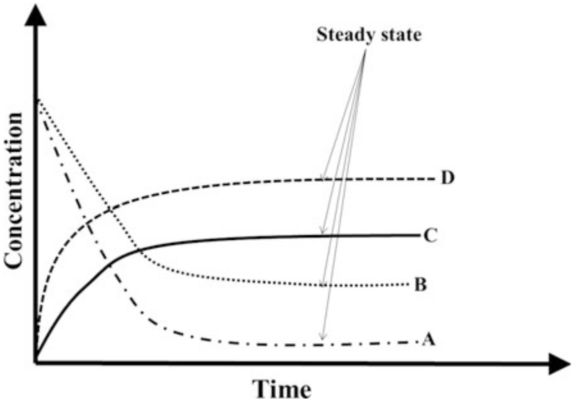

Fig. 1.4 Advancement of a chemical reaction until reaching the equilibrium condition (steady state)

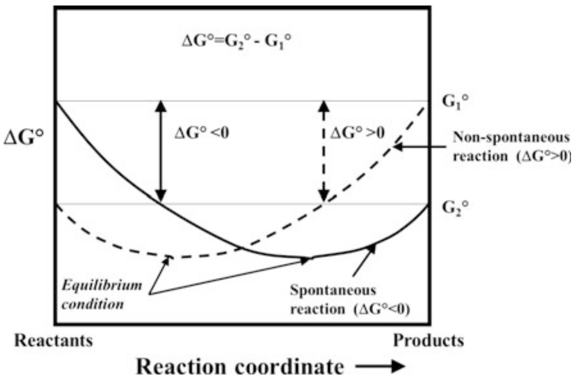

Fig. 1.5 Chemical equilibrium condition and its relationship with ΔG°

$$K = \frac{a_A^a a_B^b}{a_C^c a_D^d} \tag{1.25a}$$

If $Q < K$ the reaction proceeds toward the products, whereas if $Q > K$ the reaction proceeds toward the reactants, this is illustrated in Fig. 1.5.

Relationship Between *K* and Δ*G*

Equation (1.22) indicates that the Gibbs free energy change for a chemical reaction consists in subtracting the free energy of reactants from that of the products; similarly K relates the relative concentrations of reaction products to reactants, therefore, there should exist a relationship between the equilibrium constant and ΔG for any reaction.

Combining Eqs. (1.3) and (1.20), we can define Gibbs free energy as:

$$G = E + PV - TS \tag{1.26}$$

After taking differentials in Eq. (1.24) we obtain:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{1.27}$$

Since chemical reactions take place at constant temperature, Eq. (1.27) reduces to:

$$\mathrm{d}G = V\mathrm{d}P \tag{1.28}$$

Using the ideal gases law, we can rewrite Eq. (1.28) as:

$$\mathrm{d}G = RT\frac{\mathrm{d}P}{P} \tag{1.29}$$

It is evident that for gaseous species, integration of Eq. (1.29) between limits $G = 0$ when $P = 1$ atm, and $G = G$ when $P = P$ atm, will result in:

$$G = RT \ln P \tag{1.30}$$

For condensed phases (liquids and solids), we can exchange the pressure for the activity[3] of each participant in the chemical reaction, thus Eq. (1.29) can be integrated as follows:

$$\begin{aligned} \int_{G^\circ}^{G} \mathrm{d}G &= RT \int_{a^\circ}^{a} \frac{\mathrm{d}a}{a} \\ G - G^\circ &= RT \ln\left(\frac{a}{a^\circ}\right) \end{aligned} \tag{1.31}$$

In this case a° is the activity in standard state of the ith component in the reaction, this standard activity has a value of 1, thus Eq. (1.31) simplifies to:

$$G - G^\circ = RT \ln a \tag{1.32}$$

We can establish a clear relationship between the equilibrium constant (K) and the free energy change for any chemical reaction through Eq. (1.32). Take for example reaction (1.24). From definition (1.22), we have:

$$\Delta G = cG_C + dG_D - (aG_A + bG_B) \tag{1.33a}$$

Similarly, assuming that all participants in the reaction are in their respective standard state:

$$\Delta G^\circ = cG_C^\circ + dG_D^\circ - \left(aG_A^\circ + bG_B^\circ\right) \tag{1.33b}$$

Subtracting Eq. (1.33b) from (1.33a):

$$\Delta G - \Delta G^\circ = c\left(G_C - G_C^\circ\right) + d\left(G_D - G_D^\circ\right) - \left[a\left(G_A - G_A^\circ\right) + b\left(G_B - G_B^\circ\right)\right] \tag{1.34}$$

Substituting Eq. (1.32) into (1.34) results in:

$$\Delta G - \Delta G^\circ = RT(c \ln a_C + d \ln a_D) - RT(a \ln a_A + b \ln a_B) \tag{1.35}$$

---

[3] This concept will be further discussed in Chap. 4.

Simplification of (1.35) yields:

$$\Delta G - \Delta G^\circ = RT \ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right] \tag{1.36}$$

Substitution of expression (1.25a) into (1.36) gives the relationship between the equilibrium constant and the Gibbs free energy change associated to any chemical reaction:

$$\Delta G - \Delta G^\circ = RT \ln K \tag{1.37}$$

or

$$\Delta G = \Delta G^\circ + RT \ln K \tag{1.37a}$$

Furthermore, K indicates that the reaction has reached its equilibrium; therefore, $\Delta G = 0$ and Eq. (1.37a) reduces to:

$$\Delta G^\circ = -RT \ln K \tag{1.38}$$

It is clear now from Eq. (1.38) that we can relate the standard free energy change to the equilibrium constant of any chemical reaction.

Table 1.5 relates the possible values of K to those of ΔG°.

Table 1.6 summarizes the relationship between the different thermodynamic quantities that we have developed up to this point. It is evident from this table that all the quantities involved are interrelated. We will keep using these relationships throughout the rest of the text to determine energy changes in single component as well as in multicomponent systems.

As Table 1.6 suggests, it is possible to combine the different thermodynamic quantities in order to obtain information about the effect of temperature on either ΔG° or K without having to calculate the enthalpy and entropy changes that accompany the chemical reactions as they take place.

Table 1.5 Relationship between K and ΔG°

K	ln (K)	ΔG°	Comments
>1	+	−	Products are favored over reactants. The reaction takes place
=1	0	0	Products and reactants are equally favored, true equilibrium
<1	−	+	Reactants are favored over products. Reaction is favorable in reverse direction

Table 1.6 Relationships between the different thermodynamic functions

Quantity to determine	Quantity needed	Relationship
K	ΔG°	$\Delta G^\circ = -RT\ln(K)$ $\Delta G^\circ = -2.303RT\log(K)$
ΔG°	ΔH°, ΔS°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta G^\circ = V\mathrm{d}P - S\mathrm{d}T$
ΔH°	ΔH°_{298}, Cp	$\Delta H^\circ = \sum \Delta H^\circ_{\mathrm{products},298} - \sum \Delta H^\circ_{\mathrm{reactants},298}$ $\Delta H = n\int_{\mathrm{T_1}}^{\mathrm{T_2}} Cp\mathrm{d}T + \Delta H^\circ_{\mathrm{transformation}}$
ΔS°	ΔS°_{298}, Cp	$\Delta S^\circ = \sum \Delta S^\circ_{\mathrm{products},298} - \sum \Delta S^\circ_{\mathrm{reactants},298}$ $\Delta H = n\int_{\mathrm{T_1}}^{\mathrm{T_2}} \frac{Cp}{T}\mathrm{d}T + \frac{\Delta H^\circ_{\mathrm{transformation}}}{T_{\mathrm{transformation}}}$ $\left[\frac{\partial G}{\partial T}\right]_P = -S$
Cp	Experimental measurements	

Gibbs–Helmholtz Equation

Gibbs–Helmholtz equation allows calculating ΔG° for a reaction at any temperature from its value at a different temperature..

If we substitute the relationship:

$$-\Delta S = \left[\frac{\partial \Delta G}{\partial T}\right]_P \tag{1.39}$$

into Eq. (1.19), we obtain:

$$\Delta G^\circ = \Delta H^\circ + T\left[\frac{\partial \Delta G^\circ}{\partial T}\right] \tag{1.40}$$

Dividing (1.40) by $-1/T^2$ and taking the partial derivative with respect of $1/T$ of results in:

$$\left(\frac{\partial\left[\frac{\Delta G^\circ}{T}\right]}{\partial\left[\frac{1}{T}\right]}\right)_P = \Delta H^\circ \tag{1.41}$$

Equation (1.41) is the differential form of Gibbs–Helmholtz equation. It can be seen from this last expression that plotting $\frac{\Delta G^\circ}{T}$ versus $\frac{1}{T}$ gives a straight line whose slope is the enthalpy of reaction. Figure 1.6 shows a schematic representation of these plots.

Assuming that the heat of formation remains constant, the slope of the resulting line represents the standard heat of formation at 298 K. Furthermore, if the slope of this plot is positive, then the reaction is endothermic since $\Delta H^\circ > 0$. If the slope is negative, the reaction is exothermic ($\Delta H^\circ < 0$).

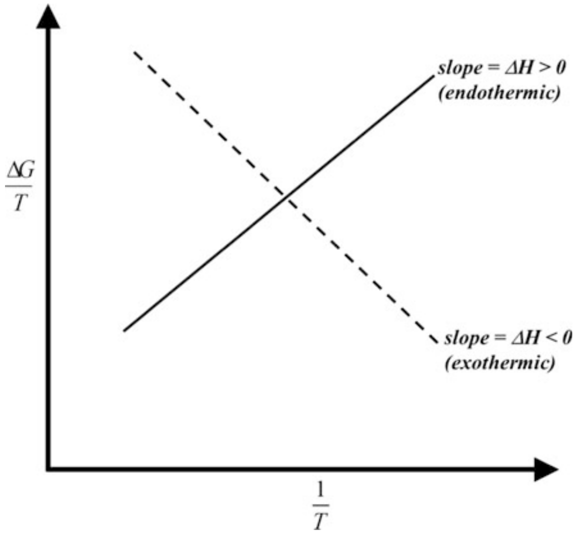

Fig. 1.6 Schematic plot of Gibbs–Helmholtz equation

Integration of Eq. (1.41) between $1/T_2$ and $1/T_1$ yields:

$$\left(\frac{\Delta G^\circ_{T_2}}{T_2}\right) - \left(\frac{\Delta G^\circ_{T_1}}{T_1}\right) = \Delta H^\circ\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.42}$$

Van't Hoff Equation

Van't Hoff equation allows to obtain information about the dependency of the equilibrium constant on temperature. This equation can be derived from Gibbs–Helmholtz equation (1.41).

Substitution of Eq. (1.38) into (1.41) yields:

$$\left[\frac{\partial \ln K}{\partial\left(\frac{1}{T}\right)}\right] = -\frac{\Delta H^\circ}{R} \tag{1.43}$$

Equation (1.43) is the differential form of Van't Hoff equation. Integration of this expression between limits $1/T_2$ and $1/T_1$ yields:

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1.44}$$

Similar to Eq. (1.41), plotting $\ln K$ versus $1/T$ results in a straight line whose slope is $-\frac{\Delta H^\circ}{R}$. As with Gibbs–Helmholtz equation, it is possible to evaluate the nature of the reaction under study by examining the slope of the resulting curve. For endothermic reactions, the slope is negative and the equilibrium constant increases

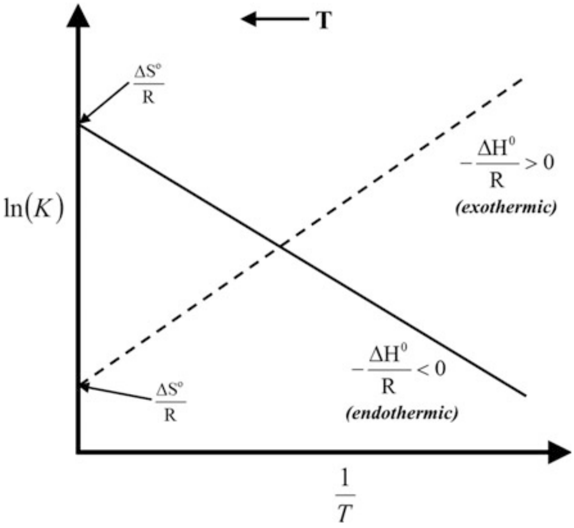

Fig. 1.7 Schematic plot of Van't Hoff equation

as temperature does so. For exothermic reactions, the slope is positive and the equilibrium constant decreases as the temperature increases. Additionally from Van't Hoff's curve, it is also possible to evaluate the entropy contribution to the reaction. This entropy can be directly found at the interception of Van't Hoff line with the $\ln(K)$ axis (Fig. 1.7).

Finally substitution of Eq. (1.38) into (1.21) results in:

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{1.45}$$

This last equation relates the equilibrium constant to both enthalpy and entropy contributions at a given temperature.

Helmholtz Free Energy

Similar to Gibbs free energy, Helmholtz free energy is a thermodynamic potential that measures the maximum amount of work that the system can perform in a thermodynamic process in which temperature is held constant.

If the volume within the system is not held constant, part of this work will be performed as boundary work. The Helmholtz energy is commonly used for systems held at constant volume. Since in this case no work is performed on the environment, the drop in the Helmholtz energy is equal to the maximum amount of useful work that can be extracted from the system. For a system at constant temperature and volume, the Helmholtz energy is minimized at equilibrium.

While Gibbs free energy is most commonly used as a measure of thermodynamic potential; it is inconvenient for some applications that do not occur under constant pressure to use the Helmholtz free energy. For example, in explosives research, Helmholtz free energy is often used since explosive reactions by their nature induce pressure changes. This function is also frequently used to define fundamental equations of state of pure substances.

Again, similar to Gibbs free energy, the Helmholtz free energy can be defined as a function of entropy, but also as a function of the internal energy, thus the change in Helmholtz free energy can be expressed as:

$$\Delta \mathrm{A} = \Delta \mathrm{E} - \mathrm{T}\Delta \mathrm{S} \tag{1.46}$$

For an isothermal change from one state to another, the condition for a spontaneous change to occur is that ΔA is less than zero and analogous to the Gibbs free energy, the condition for equilibrium is that $\Delta A = 0$ (constant T and V). If ΔA is greater than zero a process is not spontaneous.

If work is done on the system, the Helmholtz free energy has an important physical interpretation. Since the heat for reversible processes is related to entropy (Eq. 1.11), then we have:

$$q_{\mathrm{rev}} = T\Delta S \tag{1.47}$$

Inserting this last expression into Eq. (1.48), we obtain:

$$\Delta A = \Delta E - q_{\mathrm{rev}} \tag{1.48}$$

From Eq. (1.1), we can see that under reversible isothermal conditions the Helmholtz free energy becomes the maximum reversible work that can be extracted from the system:

$$\Delta A = -w_{\mathrm{rev}} \tag{1.49}$$

In a system at constant pressure and temperature, Gibbs free energy will decrease continuously for spontaneous processes until the system reaches the equilibrium condition, where $dG = 0$.

Direct comparison between Helmholtz and Gibbs free energies reveals that $A = A(V, T)$ and $G = G(P, T)$; in other words these energies are completely analogous except that A is valid at constant V and G is valid at constant P.

Moreover, these energies can be directly related:

$$\Delta G = \Delta A + PV \tag{1.50}$$

Equation (1.50) is analogous to the definition of enthalpy (Eq. 1.3):

$$\Delta H = \Delta E + PV \tag{1.3a}$$

From these last two equations, it is clear that there is a direct relationship between these four quantities (ΔE, ΔH, ΔG and ΔA), such link is illustrated in

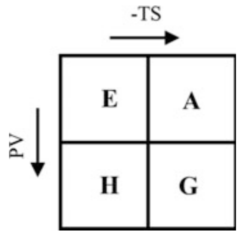

Fig. 1.8 Relationship between ΔE, ΔH, ΔG, and ΔA

Fig. 1.8. The thermodynamic quantities before mentioned are related by offsets of the *TS* and *PV* terms.

Examples of Calculations

Example 1 First Law of Thermodynamics (Energy conservation).

A mass of 50 kg attached to a stirrer through a pulley, falls 25 m at constant velocity. The stirrer is placed in an isolated container filled with 1 L of water at 20 °C. As the mass falls, the stirrer stirs the water. Assume adiabatic conditions and $Cv \approx Cp$ and linear.

Calculate the change in internal energy and temperature of the water after the mass has fallen 5, 10, 15, 20, and 25 m.

Plot the change in internal energy and that in potential energy versus water temperature.

Data:

$$Cp_{\text{water}} = 75.258\ \text{J/mol/K};\quad \rho_{\text{water}} = 1\ \text{kg/L};\quad g = 9.8\ \text{m/s}^2;\quad M_{\text{water}} = 18\ \text{g/mol}$$

Solution

The energy balance establishes that the change in potential energy has to be equal to the change in internal energy, thus the balance is:

$$\Delta E_{\text{potential}} = \Delta E_{\text{internal}} \tag{E1.1}$$

The potential energy is defined as: $E_{\text{potential}} = mgh$; since the system is adiabatic and $Cv \approx Cp$, the internal energy is defined by: $\Delta E_{\text{internal}} = nCp(T_2 - T_1)$, additionally, since $q = 0$ (adiabatic), $\Delta E_{\text{internal}} = -w$.

The total amount of energy available to stir the water is when the mass is at the highest point (25 m); at that location, the total potential energy is:

$$E_{\text{potential,total}} = (50)(9.8)(25) = 12{,}250\ \text{J}.$$

As the mass falls, the potential energy decreases, by increasing the internal energy of the system from 0 J at 25 m to 12,250 J at 0 m. At the highest point, the mass has fallen 0 m, then:

$$E_{\text{potential}} = (50)(9.8)(25) = 12{,}250\ \text{J}.$$

Since the mass has not moved, no energy has exchanged, and $E_{\text{internal}} = 0 = -w$; finally, the water temperature remains at 20° since no work was performed on the water.

When the mass fell 5 m, the change in potential energy is $(50)(9.8)(20) - 12{,}250 = -2450$ J.

$E_{\text{internal}} = 2450 = (55.56\ \text{mol})(75.258\ \text{J/mol/K})(T_2 - T_1)$, solving for T_2, yields a value of 20.6 °C.

This calculation is repeated until the mass reaches the ground level. Table 1.7 summarizes the computations.

Plotting the energy exchange versus water temperature yields straight lines which is expected since constant *Cp* was used during the calculations. It can also be noticed from the table and the figure that adding the potential energy to the internal energy gives a constant of 12,250 J which is the total energy available (Fig. 1.9).

Example 2 Effect of Temperature on *Cp*.

One mole of gold at uniform temperature (0 °C) is placed in thermal contact with a second mole of gold which is a 100 °C. Calculate the temperature of the

Table 1.7 Water temperature increase as result of energy exchange

Fallen distance (m)	Potential energy (J)	Internal energy (J)	Water temperature (°C)
0	12,250	0	20.0
5	9800	2450	20.6
10	7350	4900	21.2
15	4900	7350	21.8
20	2450	9800	22.3
25	0	12,250	22.9

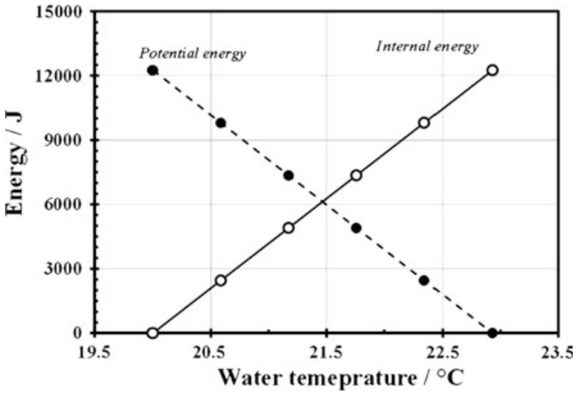

Fig. 1.9 Water temperature increase as a function energy exchange

2 mol system, which is contained in an adiabatic enclosure when thermal equilibrium is attained. Why not the common temperature of the moles is 50 °C? How much heat is transferred? The heat capacity of gold is:

$$Cp_{\mathrm{Au}} = 23.7 + 5.19 \times 10^{-3}T\ \mathrm{J/mol/K}$$

Repeat the calculations if cobalt or magnesium is used instead of gold, using the following data:

$$Cp_{\mathrm{Co}} = 21.4 + 1.43 \times 10^{-2}T - \frac{0.88 \times 10^{5}}{T^{2}}\ \mathrm{J/mol/K}$$
$$Cp_{\mathrm{Mg}} = 22.3 + 1.03 \times 10^{-2}T - \frac{4.31 \times 10^{4}}{T^{2}}\ \mathrm{J/mol/K}$$

Solution

The energy balance establishes that $q_{\mathrm{total}} = q_{\mathrm{hot}} + q_{\mathrm{cold}} = 0$. The energy exchange has to be expressed in terms of the Cp of the metal:

Energy Balance:

$$q_{\mathrm{net}} = \Delta H_{\mathrm{total}} = \Delta H_{\mathrm{Au,hot}} + \Delta H_{\mathrm{Au,cold}} = 0$$

$$\Delta H_{\mathrm{Au,hot}} = \int_{373}^{T} Cp_{\mathrm{Au}}\mathrm{d}T = \int_{373}^{T} \left(23.7 + 5.19 \times 10^{-3}T\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Au,hot}} = 23.7(T - 373) + 2.6 \times 10^{-3}\left(T^{2} - 373^{2}\right)$$

similarly for the cold gold

$$\Delta H_{\mathrm{Au,cold}} = \int_{273}^{T} Cp_{\mathrm{Au}}\mathrm{d}T = \int_{273}^{T} \left(23.7 + 5.19 \times 10^{-3}T\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Au,cold}} = 23.7(T - 273) + 2.6 \times 10^{-3}\left(T^{2} - 273^{2}\right)$$

adding $\Delta H_{\mathrm{Au,cold}}$ to $\Delta H_{\mathrm{Au,hot}}$

$$q_{\mathrm{net}} = 23.7(T - 373) + 2.6 \times 10^{-3}\left(T^{2} - 373^{2}\right) + 23.7(T - 273) + 2.6 \times 10^{-3}\left(T^{2} - 273^{2}\right)$$
$$q_{\mathrm{net}} = 47.4T + 5.19 \times 10^{-3}T^{2} - 15{,}865.7 = 0$$

solving for T

$$T = 323.27\ \mathrm{K};\quad T = 50.27\ ^{\circ}\mathrm{C}$$

Since Cp increases with T, the temperature change caused by adding heat to the system is imposed over that withdrawing it.

Total heat transferred:

$$\Delta H_{\mathrm{Au,hot}} = 23.7(T - 373) + 2.6 \times 10^{-3}\left(T^2 - 373^2\right)$$
$$\Delta H_{\mathrm{Au,hot}} = 23.7(323.27 - 373) + 2.6 \times 10^{-3}\left(323.27^2 - 373^2\right) \Rightarrow \Delta H_{\mathrm{Au,hot}} = -1269\ \mathrm{J}$$

or

$$\Delta H_{\mathrm{Au,cold}} = 23.7(T - 273) + 2.6 \times 10^{-3}\left(T^2 - 273^2\right)$$
$$\Delta H_{\mathrm{Au,cold}} = 23.7(323.27 - 273) + 2.6 \times 10^{-3}\left(323.27^2 - 273^2\right) \Rightarrow \Delta H_{\mathrm{Au,cold}} = 1269\ \mathrm{J}$$

For cobalt, we have the following energy balance:

$$q_{\mathrm{total}} = \Delta H_{\mathrm{total}} = \Delta H_{\mathrm{Co,hot}} + \Delta H_{\mathrm{Co,cold}} = 0$$

hot Co:

$$\Delta H_{\mathrm{Co,hot}} = \int_{373}^{T} Cp\mathrm{d}T = \int_{373}^{T} \left(21.4 + 1.43 \times 10^{-2}T - \frac{0.88 \times 10^5}{T}\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Co,hot}} = 21.4(T - 373) + 7.15 \times 10^{-3}\left(T^2 - 373^2\right) + 0.88 \times 10^5\left(\frac{1}{T} - \frac{1}{373}\right)$$

cold Co:

$$\Delta H_{\mathrm{Co,cold}} = \int_{273}^{T} Cp\mathrm{d}T = \int_{273}^{T} \left(21.4 + 7.15 \times 10^{-3}T - \frac{0.88 \times 10^5}{T}\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Co,cold}} = 21.4(T - 273) + 7.15 \times 10^{-3}\left(T^2 - 273^2\right) + 0.88 \times 10^5\left(\frac{1}{T} - \frac{1}{273}\right)$$

Adding both contributions:

$$\Delta H_{\mathrm{Co,hot}} + \Delta H_{\mathrm{Co,cold}} = 42.8T + 1.43 \times 10^{-2}T^2 + \frac{1.76 \times 10^5}{T} - 15{,}910.3 = 0$$

Solving for T

$$T = 323.97\ \mathrm{K}; \quad T = 50.97\,^{\circ}\mathrm{C}$$

The total energy transferred is:

$$\Delta H_{\mathrm{Co,hot}} = 21.4(323.97 - 373) + 7.15 \times 10^{-3}\left(323.97^2 - 373^2\right) + 0.88 \times 10^5\left(\frac{1}{323.97} - \frac{1}{373}\right)$$
$$\Delta H_{\mathrm{Co,hot}} = -1258\ \mathrm{J}$$
$$\Delta H_{\mathrm{Co,cold}} = 21.4(323.97 - 273) + 7.15 \times 10^{-3}\left(323.97^2 - 273^2\right) + 0.88 \times 10^5\left(\frac{1}{323.97} - \frac{1}{273}\right)$$
$$\Delta H_{\mathrm{Co,cold}} = 1258\ \mathrm{J}$$

Similar to gold and cobalt, an energy balance is needed:

$$q_{\mathrm{total}} = \Delta H_{\mathrm{total}} = \Delta H_{\mathrm{Mg,hot}} + \Delta H_{\mathrm{Mg,cold}} = 0$$

hot Co:

$$\Delta H_{\mathrm{Mg,hot}} = \int_{373}^{T} Cp\mathrm{d}T = \int_{373}^{T} \left(22.3 + 1.03 \times 10^{-2}T - \frac{4.31 \times 10^4}{T}\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Mg,hot}} = 22.3(T - 373) + 5.15 \times 10^{-3}\left(T^2 - 373^2\right) + 4.31 \times 10^4\left(\frac{1}{T} - \frac{1}{373}\right)$$

Cold Mg:

$$\Delta H_{\mathrm{Mg,cold}} = \int_{273}^{T} Cp\mathrm{d}T = \int_{273}^{T} \left(22.3 + 1.03 \times 10^{-2}T - \frac{4.31 \times 10^4}{T}\right)\mathrm{d}T$$
$$\Delta H_{\mathrm{Mg,cold}} = 22.3(T - 273) + 5.15 \times 10^{-3}\left(T^2 - 273^2\right) + 4.31 \times 10^4\left(\frac{1}{T} - \frac{1}{273}\right)$$

Adding both contributions:

$$\Delta H_{\mathrm{Mg,hot}} + \Delta H_{\mathrm{Mg,cold}} = 44.6T + 1.03 \times 10^{-2}T^2 + \frac{8.62 \times 10^4}{T} - 15{,}779.56 = 0$$

Solving for T:

$$T = 323.65\ \mathrm{K}; \quad T = 50.65\,^{\circ}\mathrm{C}$$

The total energy transferred is:

$$\Delta H_{\text{Mg,hot}} = 22.3(323.65 - 373) + 5.15 \times 10^{-3}\left(323.65^2 - 373^2\right) + 4.31 \times 10^4\left(\frac{1}{323.65} - \frac{1}{373}\right)$$

$$\Delta H_{\text{Mg,hot}} = -1260 \text{ J}$$

$$\Delta H_{\text{Mg,cold}} = 22.3(323.65 - 273) + 5.15 \times 10^{-3}\left(323.65^2 - 273^2\right) + 4.31 \times 10^4\left(\frac{1}{323.65} - \frac{1}{273}\right)$$

$$\Delta H_{\text{Mg,cold}} = 1260 \text{ J}$$

It is worth noticing that when calculating the heat exchange, we get the same numerical value, but the change in sign indicates that the hot metal releases energy as it cools while the cold metal takes that energy to heat up until reaching the equilibrium point which is slightly over 50 °C. This indicates the strong influence of Temperature on the Heat Capacity (*Cp*).

Example 3 Calculation of heat of reaction at 298 K and at different temperatures. Use of *Cp*'s and application of Hess's Law.

Part (a) Iron for steelmaking is sometimes processed in a blast furnace. The main reaction in this furnace is the reduction of iron ore (Fe_2O_3) with carbon monoxide to produce iron (with some impurities) and CO_2 gas. Using the data for the following reactions:

$$\begin{array}{ll} 3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 & \Delta H^\circ_{298} = -53.1 \text{ kJ} \\ Fe_3O_4 + CO \rightarrow 3FeO + CO_2 & \Delta H^\circ_{298} = 41.0 \text{ kJ} \\ FeO + CO \rightarrow Fe + CO_2 & \Delta H^\circ_{298} = -18.4 \text{ kJ} \end{array}$$

Calculate $\Delta H^\circ{}_{298}$ for the reaction:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + CO_2$$

Solution

Hess's law states that it is possible to combine as many reactions as needed to calculate the heat of reaction of any particular chemical transformation. Based on this, we can combine the chemical reactions given to us:

$$\begin{array}{lll} 3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 & \Delta H^\circ_{298} = -53.1 \text{ kJ} & (1) \\ Fe_3O_4 + CO \rightarrow 3FeO + CO_2 & \Delta H^\circ_{298} = 41.0 \text{ kJ} & (2) \\ FeO + CO \rightarrow Fe + CO_2 & \Delta H^\circ_{298} = -18.0 \text{ kJ} & (3) \end{array}$$

To get to the solution of this problem, we need to follow some steps:

Step 1. Multiply reaction (2) by 2 and add it to reaction (1):

$$\begin{array}{lll} 3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 & \Delta H^\circ_{298} = -53.1\ \text{kJ} & (1) \\ 2Fe_3O_4 + 2CO \rightarrow 6FeO + 2CO_2 & \Delta H^\circ_{298} = 82.0\ \text{kJ} & (2) \\ 3Fe_2O_3 + 3CO \rightarrow 6FeO + 3CO_2 & \Delta H^\circ_{298} = 28.9\ \text{kJ} & (4) \end{array}$$

As it can be seen, in this step, by multiplying Eq. (2) by 2, the Fe_3O_4 has been eliminated, since the oxide appears as product (Eq. 1) and reactant (Eq. 2) in the same amount. Also by doubling Eq. (2), its heat of reaction has to double as well. As a result we obtain reaction (4) with $\Delta H^\circ{}_{298}$ of 28.9 kJ.

Step 2. Multiply reaction (3) by 6 and add it to reaction (4):

$$\begin{array}{lll} 3Fe_2O_3 + CO \rightarrow 6FeO + 3CO_2 & \Delta H^\circ_{298} = 28.9\ \text{kJ} & (4) \\ 6FeO + 6CO \rightarrow 6Fe + 6CO_2 & \Delta H^\circ_{298} = -110.4\ \text{kJ} & (3) \\ 3Fe_2O_3 + 9CO \rightarrow 6Fe + 9CO_2 & \Delta H^\circ_{298} = -81.5\ \text{kJ} & (5) \end{array}$$

Similar to Step 1, reaction (3) has been multiplied by 6, so the FeO can be eliminated. The heat of reaction of Eq. (3) has been multiplied by 6 as well. The result is reaction (5), which has the chemical species that we are looking for, but we still need to express this reaction in terms of one mole of Fe_2O_3.

Step 3. Multiply reaction (5) by 1/3:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \quad \Delta H^\circ_{298} = -27.17\ \text{kJ}$$

We obtain the reaction we are seeking for. The heat of formation of iron from Fe_2O_3 is −27.17 kJ.

Part (b) In this example, we are going to manipulate the *Cp*'s of the chemical species involved to (i) express the heat of reaction as a function of temperature and (ii) calculate it at a Temperature different than 298 K:

The heat of formation of FeO at 25 °C (298 K) is −267.3 kJ/mol. Obtain an expression for $\Delta H^\circ{}_{298}$ of FeO as a function of temperature and evaluate it at 800 K, using the following data:

$$\begin{aligned} O_2;\ Cp &= 27.73 + 12.97 \times 10^{-3}T \\ Fe;\ Cp &= 16.32 + 28.45 \times 10^{-3}T \\ FeO;\ Cp &= 52.80 + 6.23 \times 10^{-3}T \end{aligned}$$

Solution

We need to calculate the heat of reaction of the iron oxide from its constitutive elements; thus the reaction we are looking for is:

$$Fe + \frac{1}{2}O_2 = FeO \qquad (1)$$

For this reaction, its heat of formation has been already given, so $\Delta H^\circ_{298,\mathrm{FeO}} = -267.3\ \mathrm{kJ/mol}$. We need to calculate the heat of reaction (1) at 800 K; to do so, we need to use the Cp's provided, to set up ΔH° as a function of temperature. We need to use the definitions:

$$\Delta H^\circ_{298-T} = n \int_{298}^{T} Cp\,\mathrm{d}T \tag{2}$$

and

$$\Delta H^\circ = \sum \Delta H^\circ_{\mathrm{products}} - \sum \Delta H^\circ_{\mathrm{reactants}} \tag{3}$$

Substituting (2) into (3):

$$\Delta H^\circ_{298-T} = \int_{298}^{T} Cp_{\mathrm{FeO}}\,\mathrm{d}T - \left(\int_{298}^{T} Cp_{\mathrm{Fe}}\,\mathrm{d}T + 0.5 \int_{298}^{T} Cp_{\mathrm{O_2}}\,\mathrm{d}T \right) \tag{4}$$

Substituting the Cp's into (4):

$$\Delta H^\circ_{298-T} = \int_{298}^{T} \left(52.8 + 6.23 \times 10^{-3}T\right)\mathrm{d}T - \int_{298}^{T} \left(16.32 + 28.45 \times 10^{-3}T\right)\mathrm{d}T$$
$$- 0.5 \int_{298}^{T} \left(27.73 + 12.97 \times 10^{-3}T\right)\mathrm{d}T$$

$$\Delta H^\circ_{298-T} = \int_{298}^{T} \left(22.62 - 2.871 \times 10^{-2}T\right)\mathrm{d}T$$

$$\Delta H^\circ_{298-T} = 22.62(T - 298) - 1.436 \times 10^{-2}\left(T^2 - 298^2\right)$$
$$\Delta H^\circ_{298-T} = 22.62T - 1.436 \times 10^{-2}T^2 - 5465.5$$

Finally, to find ΔH°_{800}, we need to add ΔH°_{298} to ΔH°_{298-T}, and substitute $T = 800$ in the resulting equation:

$$\Delta H^\circ_{800} = \Delta H^\circ_{298-T} + \Delta H^\circ_{298} = 22.62T - 1.436 \times 10^{-2}T^2 - 5465.5 - 267{,}300$$

Substituting $T = 800$ K

$$\Delta H^\circ_{800} = 22.62(800) - 1.436 \times 10^{-2}(800)^2 - 5465.5 - 267{,}300$$

$$\Delta H^\circ_{800} = -263{,}860\ \text{J}$$
$$\Delta H^\circ_{800} = -263.86\ \text{kJ}$$

The heat of reaction (1) at 800 K is −263.86 kJ. The negative sign indicates that the reaction is exothermic which is expected since all oxidation reactions release energy.

Part (c) This example is similar to part (b) in this case we need to take into account a phase transformation as we calculate the heat contribution from the reaction products:

Calculate the heat of reaction of the Hall–Héroult process for refining aluminum:

$$Al_2O_3\ +\ 3C = 2Al + 3CO$$

At 25 and 1200 °C from the following data:

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \quad \Delta H^\circ_{298} = -30,962\ \text{J/gAl}$$
$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H^\circ_{298} = -9414\ \text{J/gC}$$
$$Cp_{\text{Al,s}} = 20.67 + 12.38 \times 10^{-3}T\ \text{J/mol}$$
$$Cp_{\text{Al,l}} = 29.29\ \text{J/mol}$$
$$Cp_{\text{Al}_2\text{O}_3} = 106.67 + 17.78 \times 10^{-3}T - \frac{28.53 \times 10^5}{T^2}\ \text{J/mol}$$
$$Cp_{\text{C}} = 17.15 + 4.27 \times 10^{-3}T - \frac{8.8 \times 10^5}{T^2}\ \text{J/mol}$$
$$Cp_{\text{CO}} = 29.29 + 4.18 \times 10^{-3}T - \frac{2.1 \times 10^5}{\text{T}^2}\ \text{J/mol}$$
$$\Delta H^\circ_{\text{fus,Al}} = 10,460\ \text{J/mol}$$
$$\text{Melting point of aluminum} = 660\ ^\circ\text{C}$$

Solution

(1) Heat of reaction at 298 K.

To calculate the heat of reaction at 298 K (25 °C), it is necessary to manipulate the reactions provided:

$$2Al + \tfrac{3}{2}O_2 = Al_2O_3 \quad \Delta H^\circ_{298} = -30,962\frac{\text{J}}{\text{gAl}} \quad (1)$$
$$C + \tfrac{1}{2}O_2 = CO \quad \Delta H^\circ_{298} = -9414\frac{\text{J}}{\text{gC}} \quad (2)$$

To obtain ΔH°_{298}, we need to multiply reaction (2) by 3 and subtract reaction (1) from it:

$$Al_2O_3 + 3C = 2Al + 3CO \quad \Delta H^\circ_{298} = -9414 \times 3 + 309,062\ \text{J}$$

To obtain the value of the heat of reaction at 298 K, it is necessary to multiply the heat contribution from reaction 1 by 54 (2 moles of aluminum are involved) and also is necessary to multiply the heat contribution from reaction 2 by 12 (3 moles of carbon react), since this reaction has already been augmented by 3; additionally, since 1 mole of alumina is reacted, the heat of reaction is expressed in terms of the mole of Al_2O_3.

$$\begin{aligned} &Al_2O_3 + 3C = 2Al + 3CO \\ &\qquad \Delta H^\circ_{298} = -28,242 \times 12 + 30,962 \times 54 \frac{\text{J}}{\text{mol}Al_2O_3} \\ &Al_2O_3 + 3C = 2Al + 3CO \\ &\qquad \Delta H^o_{298} = 1,333,044\ \text{J/mol}Al_2O_3 = 1333.04\ \text{kJ/mol}\ Al_2O_3 \end{aligned}$$

It takes 1333.04 kJ/mol Al_2O_3 to reduce alumina to aluminum at 298 K. Notice that this is a reduction reaction. Since reduction reactions are opposite to oxidation reactions, the enthalpy change in these kinds of transformations will always be positive.

To calculate the heat of reaction at 1200 K, we need to consider the *Cp*'s of all the species involved. To help visualize how to set up the energy balance involved, the following scheme can be followed up (Fig. 1.10):

The heat balance in this problem is: $\Delta H^\circ_1 + \Delta H^\circ_2 - \Delta H^\circ_3 - \Delta H^\circ_4 = 0$. We are looking for calculating ΔH°_3 which is the heat of reaction at 1473 K. To calculate this heat, we already have ΔH°_1, since $\Delta H^\circ_{298} = \Delta H^\circ_1$. The remaining two paths, i.e., ΔH°_2 and ΔH°_4 need to be calculated by means of the respective *Cp*'s. The negative sign in ΔH°_3 indicates that the reaction is "assumed" backwards, whereas the path ΔH°_4 indicates that the reactants have to be subtracted from the reaction products. With this, we can establish these paths:

ΔH°_2 takes into account the heating of solid and liquid Al; also the phase transitions from solid to liquid has to be accounted for. Additionally, the heating of CO gas is considered. Each contribution has to be affected by the number of moles of each participating species:

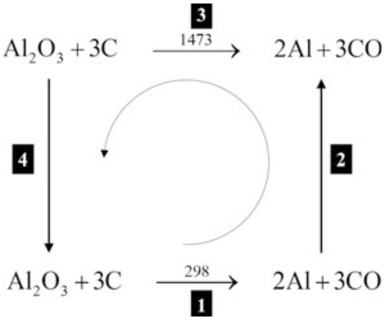

Fig. 1.10 Estimation of the heat of reaction for the reduction of aluminum

$$\Delta H_2^\circ = 2\Delta H^\circ_{\text{Al},298-1473} + 3\Delta H^\circ_{\text{CO},298-1473}$$

$$\Delta H_2^\circ = 2\left(\int_{298}^{933} Cp_{\text{Al,solid}}\text{d}T + \Delta H^\circ_{\text{Fusion,Al}} + \int_{933}^{1473} Cp_{\text{Al,liquid}}\text{d}T\right) + 3\int_{298}^{1473} Cp_{\text{CO}}\text{d}T$$

$$\Delta H_2^\circ = 2\left(\int_{298}^{933} \left(20.67 + 12.38 \times 10^{-3}T\right)\text{d}T + 10{,}460 + \int_{933}^{1473} 29.29\,\text{d}T\right)$$
$$+3\int_{298}^{1473}\left(29.29 + 4.18 \times 10^{-3}T - \frac{2.1 \times 10^5}{T^2}\right)\text{d}T$$

$$\Delta H_2^\circ = 2(17{,}964.08 + 10{,}460 + 15{,}816.6) + 3(38{,}202.75)$$
$$\Delta H_2^\circ = 203{,}089.61 \text{ J}$$

To calculate ΔH_4°, we can simply exchange the integration limits of the reactants *Cp*'s from 1473 to 298 K, or we can integrate from 298 to 1473 K and change signs accordingly. Either case will give the same value regardless of the sign. In this example, we are going to change the integration limits.

$$\Delta H_4^\circ = \Delta H^\circ_{\text{Al}_2\text{O}_3,1473-298} + 3\Delta H^\circ_{\text{C},1473-298}$$

$$\Delta H_4^\circ = \int_{1473}^{298} Cp_{\text{Al}_2\text{O}_3}\text{d}T + 3\int_{1473}^{298} Cp_{\text{C}}\text{d}T$$

$$\Delta H_4^\circ = \int_{1473}^{298}\left(106.67 + 17.78 \times 10^{-3}T - \frac{28.53 \times 10^5}{T^2}\right)\text{d}T$$
$$+3\int_{1473}^{298}\left(17.15 + 4.27 \times 10^{-3}T - \frac{8.8 \times 10^5}{T^2}\right)\text{d}T$$

$$\Delta H_4^\circ = -136{,}199.71 + 3(-22{,}248.83)$$
$$\Delta H_4^\circ = -202{,}946.2 \text{ J}$$

Finally, the heat of reaction at 1473 K can be calculated as:

$$\Delta H^\circ_{1473} = \Delta H_3^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_4^\circ$$

$$\Delta H^\circ_{1473} = 1{,}333{,}044 + 203{,}089.6 - 202{,}946.2$$

$$\Delta H^{\circ}_{1473} = 1{,}333{,}187.4\ \mathrm{J/molAl_2O_3}$$

or

$$\Delta H^{\circ}_{1473} = 1333.19\ \mathrm{kJ/molAl_2O_3}$$

Example 4 Calculation of entropy.

Part (a) Find the entropy of element “X” at 273 and 298 K from the following data:

T/K	*Cp*/J $\mathrm{mol^{-1}\ K^{-1}}$
10	0.04
25	0.29
50	2.97
100	11.8
150	18.12
200	21.63
298	25.23

Solution

To solve this problem, we need to express the *Cp* as a function of temperature. To do so, we need to plot the data (*Cp* vs. *T*) and fit (least squares) to find an appropriate polynomial. Figure 1.11 shows the data fitted.

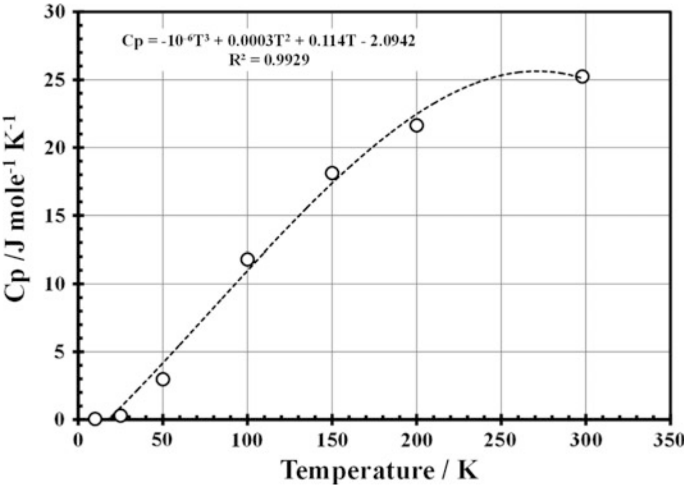

Fig. 1.11 *Cp* data fitting as a function of temperature

From Fig. 1.11, the heat capacity of element X is:

$$Cp = -10^{-6}T^3 + 0.0003T^2 + 0.114T - 2.092$$

To find the entropy, we need to use the definition:

$$\Delta S = \int_0^T \frac{Cp}{T} \mathrm{d}T$$

Remember that $S = 0$ at $T = 0$ K. Thus substituting the Cp into ΔS expression, we have:

$$\Delta S = \int_0^T \frac{-10^{-6}T^3 + 0.0003T^2 + 0.114T - 2.092}{T} \mathrm{d}T$$

$$\Delta S = \int_0^T \left(-10^{-6}T^2 + 0.0003T + 0.114 - \frac{2.092}{T}\right) \mathrm{d}T$$

$$\Delta S = -\frac{10^{-6}}{3}T^3 + \frac{0.0003}{2}T^2 + 0.114T - 2.092 \ln T$$

Substituting the values of $T = 273$ and $T = 298$ into the last expression, we get $\Delta S_{273} = 23.78$ J mol^{-1} K^{-1} and $\Delta S_{298} = 26.55$ J mol^{-1} K^{-1}, respectively. Notice that these values may change depending on the fitting of the data.

Part (b) The heat capacity of an element is:

$$Cp = 22.64 + 6.28 \times 10^{-3}T$$

If the entropy of this element at 300 K is 33.5 J mol^{-1} K^{-1}, what is the entropy at 1073 °C?

Solution

In this problem, we already have an entropy value up to 300 K; to estimate the entropy at the indicated temperature, we need to divide the Cp by T and integrate it from 300 to 1346 K:

$$\Delta S = \Delta S_{300} + \int_{300}^{1346} \frac{Cp}{T} \mathrm{d}T$$

$$\Delta S = \Delta S_{300} + \int_{300}^{1346} \left(\frac{22.64}{T} + 6.28 \times 10^{-3}\right) \mathrm{d}T$$

$$\Delta S = 33.5 + 22.64 \ln\left(\frac{1346}{300}\right) + 6.28 \times 10^{-3}(1346 - 300)$$

$$\Delta S = 33.5 + 34 + 6.6$$

$$\Delta S = 74.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

Part (c) Zinc melts at 420 °C and its standard entropy at 25 °C is 41.63 J mol^{-1} K^{-1}. Calculate the standard entropy of this metal at 750 °C, given that: $\Delta H^{\circ}_{\mathrm{fusion,\,Zn}} = 7.28$ kJ mol^{-1}, $Cp_{\mathrm{Zn,solid}} = 22.38 + 10.04 \times 10^{-3}T$ J mol^{-1} K^{-1}, $Cp_{\mathrm{Zn,liquid}} = 31.38$ J mol^{-1} K^{-1}.

Solution

To calculate the entropy change, we need to take into account the entropy contribution from the solid and the liquid zinc and also the entropy change due to the melting process.

$$\Delta S^{\circ}_{\mathrm{Zn},1023} = \Delta S^{\circ}_{\mathrm{Zn},298} + \int_{298}^{693} \frac{Cp_{\mathrm{Zn,solid}}}{T}\mathrm{d}T + \frac{\Delta H^{\circ}_{\mathrm{Zn,fusion}}}{T_{\mathrm{fusion}}} + \int_{693}^{1023} \frac{Cp_{\mathrm{Zn,liquid}}}{T}\mathrm{d}T$$

$$\Delta S^{\circ}_{\mathrm{Zn},1023} = 41.63 + \int_{298}^{693} \left(\frac{22.38}{T} + 10.04 \times 10^{-3}\right)\mathrm{d}T + \frac{7280}{693} + \int_{693}^{1023} \frac{31.38}{T}\mathrm{d}T$$

$$\Delta S^{o}_{\mathrm{Zn},1023} = 41.63 + (18.89 + 3.97) + 10.51 + 12.22$$

$$\Delta S^{o}_{\mathrm{Zn},1023} = 87.22\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

Part (d) Calculate the standard entropy change at 298 K for the reaction:

$$\mathrm{Cr_2O_3} + 3\mathrm{C} = 2\mathrm{Cr} + 3\mathrm{CO},$$

Given $\Delta S^{\circ}_{\mathrm{Cr_2O_3}} = 81.17$ J mol^{-1} K^{-1}, $\Delta S^{\circ}_{\mathrm{C}} = 5.69$ J mol^{-1} K^{-1}, $\Delta S^{\circ}_{\mathrm{Cr}} = 23.76$ J mol^{-1} K^{-1}, $\Delta S^{\circ}_{\mathrm{CO}} = 197.90$ J mol^{-1} K^{-1}.

Solution

To solve this problem, we need to alter the entropy of each component by its stoichiometric coefficient and then we need to subtract the entropy of reactants from that of products:

$$\mathrm{Cr_2O_3 + 3C = 2Cr + 3CO}$$

$$\Delta S^\circ_{298} = \sum n\Delta S^\circ_{\text{products}} - \sum n\Delta S^\circ_{\text{reactants}}$$
$$\Delta S^\circ_{298} = \left(2\Delta S^\circ_{\mathrm{Cr}} + 3\Delta S^\circ_{\mathrm{CO}}\right) - \left(\Delta S^\circ_{\mathrm{Cr_2O_3}} + 3\Delta S^\circ_{\mathrm{C}}\right)$$
$$\Delta S^\circ_{298} = (2 \times 23.76 + 3 \times 197.9) - (81.17 + 3 \times 5.69)$$
$$\Delta S^\circ_{298} = (641.22) - (98.24)$$
$$\Delta S^\circ_{298} = 543\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Example 5 Calculation of the free energy change in chemical reactions.

ΔG° for the reaction: $\mathrm{Ni} + {}^1\!/\!{}_2\mathrm{O_2} = \mathrm{NiO}$ at 25 °C is −211,585 J.

Calculate ΔG° at 400 °C for the nickel oxide reaction using the following data:

$$Cp_{\mathrm{NiO}} = 54.01\ \mathrm{J\,mol^{-1}\,K^{-1}}$$
$$Cp_{\mathrm{O_2}} = 29.96 + 4.184 \times 10^{-3}T - \frac{1.67 \times 10^5}{T^2}\ \mathrm{J\,mol^{-1}\,K^{-1}}$$
$$Cp_{\mathrm{Ni}} = 25.23 - 10.46 \times 10^{-3}T + \frac{43.68 \times 10^6}{T^2}\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

Solution

To solve this problem, we need to use the Cp's given in order to estimate the enthalpy and entropy contributions of the nickel oxide and the reactants as they are heated up from 298 to the desired temperature. Once we have done that, we will add the value of ΔG°_{298}, so we can calculate the free energy change at 673 K (400 °C).

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NiO} \quad \Delta G^\circ_{298} = -211{,}585\ \mathrm{J\,mol^{-1}}$$

$$\Delta G^\circ_{673} = \Delta G^\circ_{298} + \Delta G^\circ_{298-673}$$

$$\Delta G^\circ_{298-673} = \Delta H^\circ_{298-673} - T\Delta S^\circ_{298-673}$$

$$\Delta G^\circ_{298-673} = \int_{298}^{673} \Delta Cp\mathrm{d}T - T\int_{298}^{673} \frac{\Delta Cp}{T}\mathrm{d}T$$

ΔCp is the difference in Cp's between products and reactants, thus from the data given, we can calculate this function:

$$\Delta Cp = \sum nCp_{\text{products}} - \sum nCp_{\text{reactants}}$$

$$\Delta Cp = Cp_{\text{NiO}} - \left(Cp_{\text{Ni}} + 0.5Cp_{\text{O}_2}\right)$$

$$\Delta Cp = 54.01 - 25.23 - 14.98 + \left(10.46 \times 10^{-3} - 2.092 \times 10^{-3}\right)T + \frac{\left(0.835 \times 10^5 - 43.68 \times 10^6\right)}{T^2}$$

$$\Delta Cp = 13.8 + 8.368 \times 10^{-3}T - \frac{46.6 \times 10^6}{T^2}$$

With this Cp, we can calculate both the enthalpy and the entropy contributions:

$$\Delta H^\circ_{298-673} = \int_{298}^{673} \left(13.8 + 8.368 \times 10^{-3}T - \frac{46.6 \times 10^5}{T^2}\right)\mathrm{d}T$$

$$\Delta H^\circ_{298-673} = 13.8(673 - 298) + 0.5 \times 8.368 \times 10^{-3}\left(673^2 - 298^2\right) + 46.6 \times 10^5\left(\frac{1}{673} - \frac{1}{298}\right)$$

$$\Delta H^\circ_{298-673} = -80{,}435.1 \text{ J}$$

$$\Delta S^\circ_{298-673} = \int_{298}^{673} \left(\frac{13.8}{T} + 8.368 \times 10^{-3} - \frac{46.6 \times 10^5}{T^3}\right)\mathrm{d}T$$

$$\Delta S^\circ_{298-673} = 13.8\ln\left(\frac{673}{298}\right) + 8.368 \times 10^{-3}(673 - 298) + + \frac{46.6 \times 10^5}{2}\left(\frac{1}{673^2} - \frac{1}{298^2}\right)$$

$$\Delta S^\circ_{298-673} = -196.55 \text{ J K}^{-1}$$

To calculate ΔG° for the formation of nickel oxide at 673 K, we substitute values:

$$\Delta G^\circ_{673} = \Delta G^\circ_{298} + \left(\Delta H^\circ_{298-673} - T\Delta S^\circ_{298-673}\right)$$
$$\Delta G^\circ_{673} = -211{,}585 + (-80{,}435.1 - 673 \times -196.55)$$

$$\Delta G^{\circ}_{673} = -159,742 \text{ J} \quad \text{or} \quad -160 \text{ kJ}$$

Example 6 Equilibrium constant and free energy.

A gaseous mixture consisting of 75 mol% H_2 and 25 mol% CO_2 at a total pressure of 1 atm is passed through a furnace at 1000 K. Calculate the equilibrium composition of the mix made up of H_2, H_2O, CO_2, and CO gases, given the following data:

$$\begin{array}{lll} C + \frac{1}{2}O_2 = CO & \Delta G^{\circ} = -111,713 - 87.65T \text{ J} & (1) \\ C + O_2 = CO_2 & \Delta G^{\circ} = -394,133 - 0.84T \text{ J} & (2) \\ H_2 + \frac{1}{2}O_2 = H_2O & \Delta G^{\circ} = -246,856 + 55.98T \text{ J} & (3) \end{array}$$

Solution

We need to combine reactions (1) to (3) obtain the reaction:

$$H_2 + CO_2 = H_2O + CO \quad (4)$$

To obtain reaction (4) we have to do the following operation between reactions: (1) + (3) − (2). The corresponding ΔG° for reaction (4) is: ***ΔG° = 35564 − 30.83T***

The equilibrium constant of reaction (4) is:

$$K = \frac{P_{H_2O} P_{CO}}{P_{H_2} P_{CO_2}}.$$

Since the reaction takes place at 1000 K, the free energy change is: $\Delta G^{\circ} = 35,564 - 30.83(1000) = 4734$ J. With this value, we can calculate now that of the equilibrium constant:

$$\Delta G^{\circ} = -RT \ln(K)$$
$$K = \exp\left\{-\frac{\Delta G^{\circ}}{RT}\right\}$$
$$K = \exp\left\{-\frac{4734}{8.314 \times 1000}\right\}$$
$$K = 0.566$$

We need to relate the partial pressure of each gas with the value of the equilibrium constant:

$$0.566 = \frac{P_{H_2O} P_{CO}}{P_{H_2} P_{CO_2}}$$

Initially (before the reaction takes place), there are 0.75 atm H_2 and 0.25 atm CO_2, as they begin to react they form H_2O and CO gases in a proportion of 1 mol. Thus we can establish the following balance:

Species	Initial conditions	Equilibrium conditions
H_2	0.75	$0.75 - x$
CO_2	0.25	$0.25 - x$
H_2O	0.00	x
CO	0.00	x

Substituting the equilibrium conditions into the expression for the equilibrium constant:

$$0.566 = \frac{P_{H_2O}P_{CO}}{P_{H_2}P_{CO_2}}$$

$$0.566 = \frac{(0.75 - x)(0.25 - x)}{(x)(x)}$$

$$0.566x^2 = 0.1875 - x + x^2$$

$$0.434x^2 - x + 0.1875 = 0$$

Solving for x, we get $x = 0.206$. Thus the equilibrium composition of the gas mixture is:

Species	Equilibrium composition (atm)
H_2	0.544
CO_2	0.044
H_2O	0.206
CO	0.206

Example 7 Use of Gibbs–Helmholtz equation.

Part (a) Calculate the free energy change at 425 °C for the reaction:

$$H_2 + \frac{1}{2}O_2 = H_2O$$

With the data available: $\Delta G^\circ_{298,H_2O} = -237.141$ kJ/mol, and $\Delta H^\circ_{298,H_2O} = -285.83$ kJ/mol.

Solution

Using the integrated form of Gibbs–Helmholtz equation:

$$\frac{\Delta G^\circ_{T_2}}{T_2} - \frac{\Delta G^\circ_{T_1}}{T_1} = \Delta H^\circ \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Taking $T_2 = 698$ K, $T_1 = 298$ K, and substituting the known values for ΔH° and ΔG°_{298} into the latest equation, it is possible to find ΔG°_{698}:

$$\frac{\Delta G^\circ_{698}}{698} - \frac{\Delta G^\circ_{298}}{298} = \Delta H^\circ \left(\frac{1}{698} - \frac{1}{298} \right)$$

$$\Delta G^\circ_{698} = \left[\Delta H^\circ \left(\frac{1}{698} - \frac{1}{298} \right) + \frac{\Delta G^\circ_{298}}{298} \right] 698$$

$$\Delta G^\circ_{698} = \left[-285.83 \left(\frac{1}{698} - \frac{1}{298} \right) - \frac{237.141}{298} \right] 698$$
$$\Delta G^\circ_{698} = -171.778 \text{ kJ mol}^{-1}$$

Part (b) Calculate the free energy change at 1000 °C for the reaction:

$$\mathrm{CaCO_3 = CaO + CO_2}$$

For this reaction, the following data is available: $\Delta G^\circ_{298,\mathrm{CaCO_3}} = 130.423$ kJ/mol, and $\Delta H^\circ_{298,\mathrm{CaCO_3}} = 178.175$ kJ/mol.

Solution

Similar to part (a); use the integrated form of Gibbs–Helmholtz equation, consider $T_2 = 1273$ K, $T_1 = 298$ K and substitute known values to find ΔG°_{1273}:

$$\frac{\Delta G^\circ_{1273}}{1273} - \frac{\Delta G^\circ_{298}}{298} = \Delta H^\circ \left(\frac{1}{1273} - \frac{1}{298} \right)$$
$$\Delta G^\circ_{1273} = 1273 \left[178.175 \left(\frac{1}{1273} - \frac{1}{298} \right) + \frac{130.423}{298} \right]$$
$$\Delta G^\circ_{698} = -25.71 \text{ kJ mol}^{-1}$$

From this example it is evident the behavior of endothermic and exothermic reactions. As predicted, temperature increments result in increasing the free energy value of the exothermic reaction (water reaction); whereas for the endothermic carbonate decomposition, increasing the temperature results in lowering its free

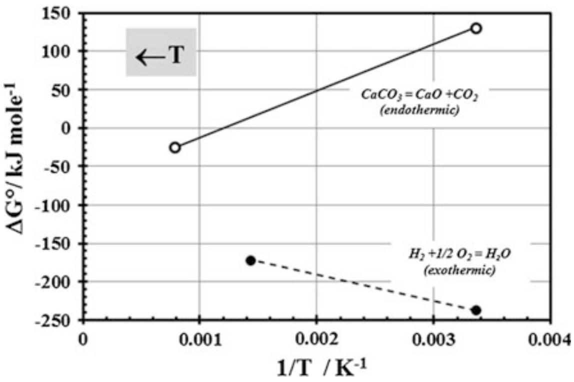

Fig. 1.12 Use of Gibbs–Helmholtz equation

energy, thus making the reaction barely feasible at 1000 °C. This can be better seen in Fig. 1.12.

Example 8 Use of Van't Hoff equation

The following data for Boudouard reaction:

$$C + CO_2 = 2CO \tag{1}$$

is presented at 800 and 900 °C

Temperature/°C	P_{total}/atm	% CO in gas
800	2.57	74.55
900	2.30	93.08

Additionally, for the equilibrium:

$$2CO_2 = 2CO + O_2 \tag{2}$$

Its equilibrium constant at 900 °C is 8.33×10^{-17}. On the other hand, it was determined that the heat of formation of CO_2 at 1173 K is -394.96 kJ mol^{-1}.

With this information, determine $\Delta H°$ and $\Delta S°$ for reaction (2) at 900 °C.

Solution

From reaction (1), we can obtain an expression for K in terms of the partial pressures of CO and CO_2. These pressures can be easily calculated since the total pressure and the CO content are provided.

$$C + CO_2 = 2CO; \quad K = \frac{P_{CO}^2}{P_{CO_2} \times a_C}$$

Table 1.8 Computed values for the equilibrium constant at 800 and 900 °C

T/°C	T/K	P_{tot}/atm	P_{CO}/atm	P_{CO_2}/atm	K
800	1073	2.57	1.92	0.65	5.61
900	1173	2.30	2.14	0.16	28.80

To simplify our calculations, we can assume pure solid carbon reacting with CO_2 gas, thus the activity of carbon has a value of 1, so we can express the equilibrium constant as:

$$K = \frac{P_{CO}^2}{P_{CO_2}}$$

From the data given and the expression for K, we obtained the following results (Table 1.8).

If we make $T_2 = 1173$ K, $K_{T_2} = 28.80$, $T_1 = 1073$ K and $K_{T_1} = 5.61$; and substitute these values into Van't Hoff's equation, to calculate $\Delta H°$ for reaction (1):

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{28.80}{5.61}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{1173} - \frac{1}{1073}\right)$$

$$-8.314 \times 1.635 = \Delta H°\left(-7.95 \times 10^{-5}\right)$$

$$\Delta H° = 171.12 \text{ kJ mol}^{-1}$$

Now we need to combine reaction (1) with that of the CO_2 formation:

$$C + O_2 = CO_2 \quad \Delta H° = -394.96 \text{ kJ mol}^{-1}$$

To obtain reaction (2), we have to apply Hess's law by reversing the CO_2 reaction and add it to reaction (1):

$$\begin{array}{ll} C + CO_2 = 2CO & \Delta H° = 171.12 \\ \underline{CO_2 = C + O_2} & \underline{\Delta H° = 394.96} \\ 2CO_2 = 2CO + O_2 & \Delta H^o = 566.08 \text{ kJ mol}^{-1} \end{array}$$

So far we have computed the heat of reaction (2) at 1173 K, whose value is $\Delta H°_{1173} = 566.08$ kJ mol^{-1}. To calculate the entropy for this reaction, we can use the value given for its equilibrium constant:

$$\Delta G^\circ = -RT \ln K$$
$$\Delta G^\circ = -8.314(1173) \ln\left(8.33 \times 10^{-17}\right)$$
$$\Delta G^\circ = 361.07 \text{ kJ mol}^{-1}$$

Knowing both ΔG° and ΔH°, it is possible to calculate ΔS°:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{566.08 - 361.07}{1173}$$
$$\Delta S^\circ = 0.175 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Phase Equilibria I

2

Introduction

In the previous chapter, it was discussed the thermodynamics principles that are the basis of thermochemistry. It was shown how to calculate the energy involved in any chemical or physical transformation. Additionally, it was established the Gibbs free energy as a criterion to know whether or not such transformations would take place under a given set of conditions.

Furthermore based on the sign of the enthalpy change associated to any of these transformations, it is possible to distinguish if we need to supply heat to the system or to withdraw it.

As chemical reactions occur, they occasionally involve phase transitions such as allotropy, melting, boiling, etc. As they take place, their requirement of energy can be easily accounted, but more importantly, it is possible to relate such energy demands to determine specific conditions under which two or more phases can coexist simultaneously in equilibrium.

Heat and Phase Changes

To boil water, it is necessary to provide heat, as heat is supplied to the liquid, the water temperature increases in inverse proportion to the heat capacity of the liquid.

This happens until the normal boiling point of the liquid is reached. At that point, boiling begins and the temperature of the water remains constant while the heat supplied to the system boils the liquid. The water temperature does not increase again until all the liquid has fully transformed into vapor. Once the liquid has disappeared, the temperature of the system again increases, this time in inverse proportion to the heat capacity of the gas. If we plot this experiment over a wide enough range of temperature to go from solid to liquid to vapor, the plot would look something like Fig. 2.1.

G. Plascencia and D. Jaramillo, *Basic Thermochemistry in Materials Processing*,
DOI 10.1007/978-3-319-53815-0_2

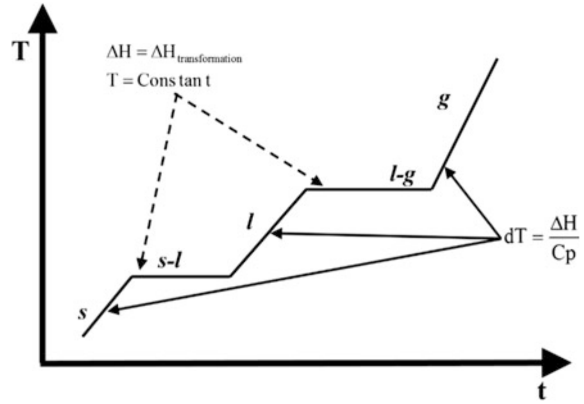

Fig. 2.1 Heat exchange during heating of a substance, phase transformations occur at constant temperature

In such plot, time directly relates to the energy supplied in the form of heat since it is assumed that heat is added at a constant rate. This graph is somewhat idealistic; the slopes (temperature increase) for the solid, liquid and gas will not be equal (each slope will be the inverse of the heat capacity for that particular phase) nor will they be linear since we know that heat capacity increases with temperature. Still, over a short enough range, the heat capacities of each phase can be assumed as constant.

The heat that must be supplied to convert one phase into another (solid to liquid, liquid to vapor) is just the enthalpy of the phase transition (ΔH_{fusion}, $\Delta H_{\text{vaporization}}$, etc.), adjusted appropriately for the number of moles of substance present at the moment of the transformation. Because this amount of energy has to be supplied to the lower temperature phase to convert it into the higher temperature phase, it is called the latent heat of the phase transition.

For phase transitions with latent heat, the corresponding entropy of the phase change is:

$$\Delta S_{\text{transformation}} = \frac{\Delta H_{\text{transformation}}}{T_{\text{transformation}}} \tag{2.1}$$

Phase transitions with latent heats are called first-order transitions. The phase jump from one state to the other is discontinuous with temperature. In second-order transition, such as the demagnetization of iron, the change is continuous over a range of temperatures.

Gibbs Rule of Phases

Chemical systems are made of elements and/or molecules whose masses cannot be taken arbitrarily; there exist certain mass relationships among them. For example, if we have a system with magnesium carbonate, magnesium oxide and carbon dioxide, the system is composed of C, Mg, and oxygen. We can randomly pick the mass of two of these elements, but the third one will be determined by itself without any doubt. Thus, it is possible to choose in many different ways the number of components (C) in any system.

On the other hand, we usually face heterogeneous systems. In general, it is quite simple to enumerate the distinct phases that are present in a given system. For example, a system formed by liquid water and water vapor has two phases. A system containing salt crystals and an aqueous solution of this salt has likewise two phases (the salt and the solution). In general, the number of phases comprising a system is denoted by (P). It is clear now that any system is characterized by the number of components (C) and that of the phases (P) into which the system is divided.

If we define process variables (temperature, pressure, composition) of each phase within the system, then it is possible to estimate the number of physical variables that can be changed, without varying the number of phases present. The number of process variables to change is known as degrees of freedom (F) and these are related to the number of components and phases by:

$$F = C - P + 2 \tag{2.2}$$

Equation (2.2) is known as Gibbs rule of phases.

One Component Systems

If we plot the pressure versus the temperature for an element or a molecule like water, the system is comprised by a single component; such diagram, like the one sketched in Fig. 2.2, reveals phase stability regions as well as phase boundaries. As we know, water can exist as solid, liquid or gas, therefore fields corresponding to these phases are properly labeled in the diagram, we also know that depending on atmospheric or process conditions two of these phases can coexist, like ice and water in a pond during wintertime or steam and liquid water in dry cleaning shops. The phases can coexist along the lines (boundaries) delimiting them. Also, there is a well-defined point in which the three phases can coexist; this point is named the triple point. This triple point is unique for each system/compound.

Direct application of Gibbs rule of phases (Eq. 2.2) to any unary system represented in a pressure—temperature (PT) diagram, results in (Table 2.1).

In those regions containing any of the S, L or G phases, we have two degrees of freedom which means that both pressure and temperature can vary freely, without altering the corresponding phase. Along phase boundaries, there is only one degree of freedom; this means that along any of these lines we can define arbitrarily either the pressure or the temperature; then the second variable will be fixed by itself. At the triple point, the three phases coexist in equilibrium; this means that there is a specific P-T combination at which the phases can be present simultaneously. Thus, at this point there are no degrees of freedom.

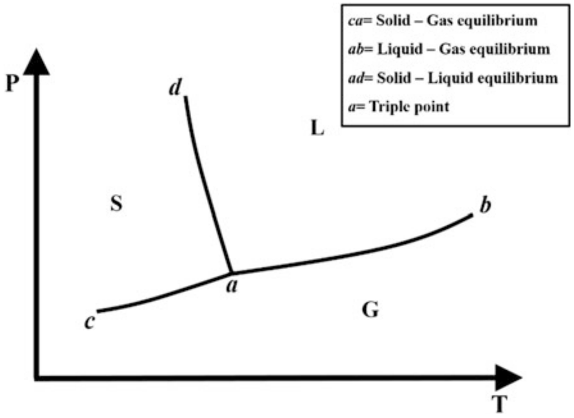

Fig. 2.2 Pressure—temperature diagram for water (schematic)

Table 2.1 Gibbs rule of phases in mono component systems

Region in P-T diagram	C	P	F
Phase field	1	1	2
Phase boundary	1	2	1
Triple point	1	3	0

Since it is possible for the different phases to coexist, then we should be able to relate the free energy of each phase in a way to find correlations between process variables and the corresponding energy change.

Thermodynamics of One Component Systems

In Chap. 1, it was shown that it is possible to express Gibbs free energy as a function of temperature and pressure:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T. \tag{1.27}$$

Taking partial derivatives of expression (1.27) with respect of pressure and temperature; the following relationships are obtained:

$$\left(\frac{\partial G}{\partial T}\right)_{\mathrm{P}} = -S \tag{2.3a}$$

$$\left(\frac{\partial G}{\partial P}\right)_{\mathrm{T}} = V. \tag{2.3b}$$

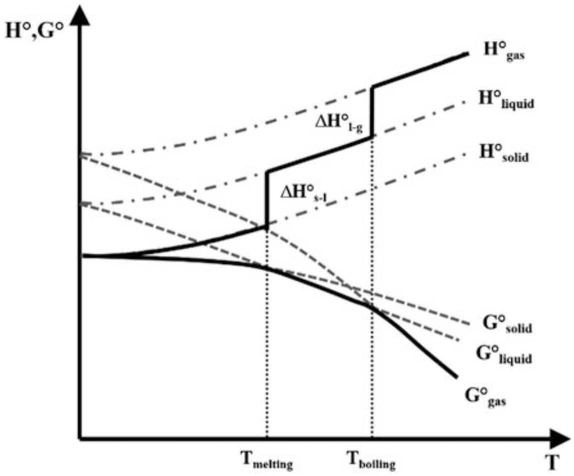

Fig. 2.3 Gibbs free energy and enthalpy changes for phases in equilibrium as a function of temperature

Plotting *G* and *H* for each phase at constant pressure, show that as temperature increases, Gibbs free energy of each phase becomes more negative, and the most stable phase at higher temperature is the one with larger specific heat, this is illustrated in Fig. 2.3.

As seen in Fig. 2.3, the free energy curve can be crossed in more than one occasion this lead to entropy ratios $\frac{S_{\text{phase2}}}{S_{\text{phase1}}}$, these ratios are larger than unity and increase as temperature does. This confirms the effect of temperature on the free energy. As temperature increases, the entropy contribution to ΔG becomes more important. Furthermore if we follow phase transitions as more energy is supplied to any system, we can easily observe the change of entropy as a solid transforms into a liquid and the liquid boils into a gas. Not surprisingly, the entropy of each phase progressively increases from the solid to the gaseous state; this can be seen in Fig. 2.4.

Clapeyron Equation

Figures 2.3 and 2.4 show the effect of enthalpy and entropy, respectively, on Gibbs free energy during phase transitions. With this, it is possible to associate this free energy to any of the phase boundaries in Fig. 2.2. To do so, we need to equate the free energy of the phases in equilibrium. For example, consider a solid—gas equilibrium. We can represent such equilibrium as a chemical reaction:

$$\text{Solid} \rightarrow \text{Liquid} \tag{2.4}$$

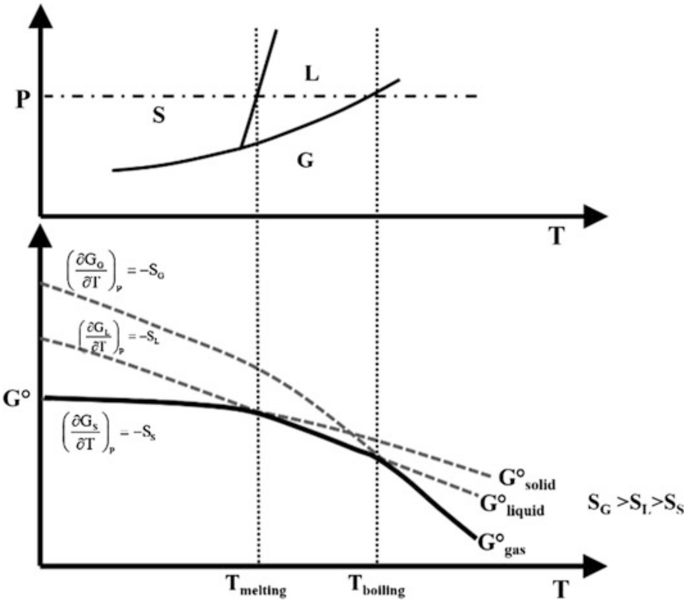

Fig. 2.4 Effect of entropy on Gibbs free energy during phase transitions

From Eq. (2.4), we have that at the phase boundary; the corresponding free energies are equated:

$$G_S = G_L \tag{2.5}$$

Substituting Eq. (1.27) into (2.5), results in:

$$V_S dP - S_S dT = V_L dP - S_L dT. \tag{2.6}$$

Accommodating terms in expression (2.6)

$$G_S - G_L = (V_S - V_L)dP - (S_S - S_L)dT. \tag{2.7}$$

Since at the phase boundary both phases are in equilibrium, then G_S-G_L should be zero, therefore, Eq. (2.7) can be written as:

$$\Delta G_{S-L} = \Delta V_{S-L} dP - \Delta S_{S-L} dT = 0. \tag{2.8}$$

From Eq. (2.8), we have:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \tag{2.9}$$

Equation (2.9) is known as Clapeyron equation. This equation can be modified if we substitute expression (1.11) into (2.9), to obtain:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}. \tag{2.9a}$$

Clapeyron equation applies to any phase change in a one-component system. This equation, only determines the slope of the equilibrium boundary, not the actual position of the reaction in the pressure–temperature domain. That position must be determined by further thermodynamic calculations or by experiments.

For example, a reaction with shallow dP/dT slope is more sensitive to pressure changes, whereas a reaction with a steep (nearly vertical) slope is sensitive to temperature.

Additionally, if we collect experimental data on any reaction at a given temperature (or pressure), we can determine the slope and extrapolate to other conditions, rather than doing more time-consuming experiments.

Clapeyron equation helps determining thermodynamic values for reactions or phases. When combined with volume data, we can use the slope of an experimentally determined reaction to calculate the entropy change of the reaction, and to calculate the entropy of formation of a particular phase. Often the volume of a phase is well known, but the entropy data may have considerable uncertainties.

In some instances, volume changes are quite large, especially if a gas phase is involved in the transformation we are interested in, thus the ΔV term in Clapeyron equation can be assumed as the volume of the gas phase; by doing so, we can modify Eq. (2.9) using the ideal gas equation, resulting in:

$$\frac{dP}{dT} = \frac{\Delta H}{\mathrm{R}T^2}P. \tag{2.10}$$

Variable separation in expression (2.10) results in:

$$\frac{dP}{P} = \frac{\Delta H}{R}\frac{dT}{T^2}. \tag{2.11}$$

Equation (2.11) is the differential form of Clausius—Clapeyron equation. Integration of this expression results in:

$$\ln(P) = -\frac{\Delta H}{R}\frac{1}{T} + C. \tag{2.12}$$

C is an integration constant that should be evaluated depending on the system properties. Clausius—Clapeyron equation can be applied to any phase transformation (melting, boiling, sublimation, allotropy). It is also worth noting that plotting ln (P) versus $(1/T)$, would yield a straight line whose slope is equal to $-\Delta H/R$; from this slope it can be calculated the enthalpy change associated to the transformation under

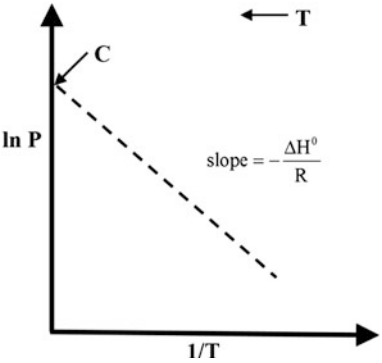

Fig. 2.5 Graphical representation of Clausius—Clapeyron equation

study. The intersection of this line with the ln (P) axis will give the value of C constant. This is illustrated in Fig. 2.5.

Equation (2.11) can also be integrated between limits P_1 and P_2 corresponding to T_1 and T_2, respectively; if such is the case, Eq. (2.12) results in:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{2.13}$$

This last expression is the integrated form of Clausius–Clapeyron equation. Relation (2.13) is often used to estimate the vapor pressures of pure liquids or solids. ΔH is the enthalpy of vaporization if the substance is a liquid or the enthalpy of sublimation if it is a solid. The enthalpy of vaporization (or sublimation) is assumed to be constant over the temperature range of interest. This is not true, but actual changes in ΔH values are negligible at low and moderate pressures. The vapor phase can be assumed as an ideal gas, since the external pressure does not significantly affect its pressure.

On the other hand, and in order to simplify calculations, the latent heat of evaporation can be estimated using Trouton's rule. This rule states that the ratio of latent heat of evaporation to the normal point is constant for many liquids:

$$\frac{\Delta H^{\circ}_{\text{vap}}}{T_{\text{vap}}} = 88\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}. \tag{2.14}$$

This rule is an approximate one. However, it is useful to estimate near values for the heat of evaporation. Data in Fig. 2.6 from Kubaschewski and Alcock[1] reveal the departure from this law, especially at higher boiling points.

The departure from Trouton's rule can be explained by the presence of several gaseous species during boiling; for example, when PbF_2 boils, its vapor not only

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[1] Kubascheeski, O., Alcock, C.B., Metallurgical Thermochemistry 5th Ed., Pergamon Press, Oxford, 1979.

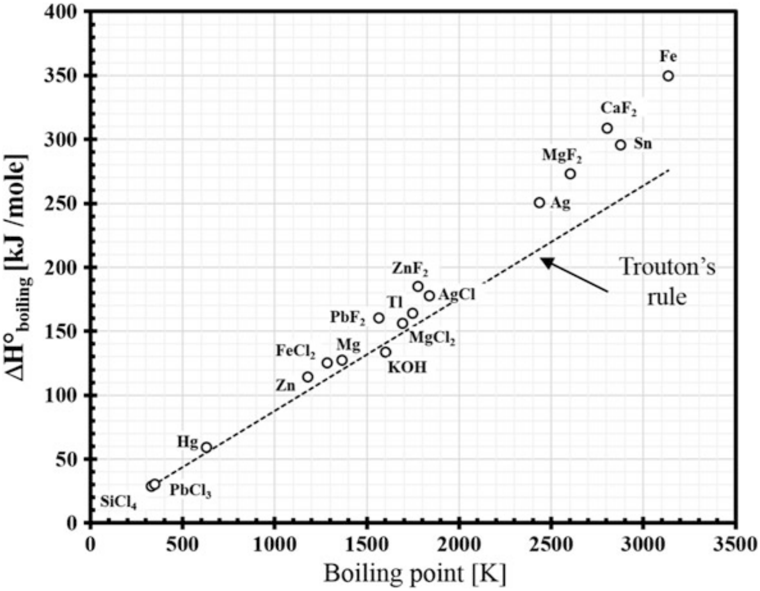

Fig. 2.6 Trouton's rule and deviation from this rule of some elements and compounds. Data from Kubaschewski and Alcock

contains such fluoride, but also contains minor amounts of other species such as PbF, PbF_4, and Pb.

In some applications, it is important to know the vapor pressure of metals and alloys. Vapor of solids or liquids results from the dissociation of the substance in the gaseous state as a consequence of thermal movement of atoms or molecules. Vaporization is a reversible process highly sensitive on temperature; a small variation in temperature produces condensation of the vapor phase. Therefore, vaporization strongly depends on the pressure and temperature to which the system is kept.

The enthalpy of vaporization $\Delta H^\circ_{\text{vap}}$ is equal in magnitude but opposite in sign to the enthalpy of condensation; however, the value of the enthalpy of vaporization changes with the temperature. Furthermore, it has been observed that $\Delta H^\circ_{\text{vap}}$ increases with the atomic weight (mass).

Using Calusius—Clapeyron equation (Eq. 2.11) to relate the vapor pressure of metals or alloys to the temperature:

$$\frac{\mathrm{d}P}{P} = \frac{\Delta H^\circ_{\text{vap}}}{R}\frac{\mathrm{d}T}{T^2}. \tag{2.11}$$

Integration between limits P_1, P_2 and T_1, T_2 yields Eq. (2.13); setting P_1 as 1 atmosphere and T_1 as the boiling point (T_{boiling}) and approximating using Trouton's rule (Eq. 2.14):

$$\ln(P_2) - \ln(1) = \frac{\Delta H^\circ_{\text{vap}}}{\text{RT}_{\text{boiling}}} - \frac{\Delta H^{\text{o}}_{\text{vap}}}{\text{RT}_2}. \tag{2.15}$$

Reduces to:

$$\ln(P_2) = \frac{88}{8.314} - \frac{\Delta H^\circ_{\text{vap}}}{\text{RT}_2}. \tag{2.15a}$$

It is customary to represent vapor pressure data in terms of the log function rather than the ln one, thus, Eq. (2.15a) has to be altered by a factor of 2.303:

$$\log(P_2) = 4.6 - \frac{\Delta H^\circ_{\text{vap}}}{19.147T_2}. \tag{2.15b}$$

This last result allows for a good approximation of the vapor partial pressure of a metal or alloy; additionally it is evident that vapor pressure data can be estimated by a general relation:

$$\log P = \frac{A}{T} + B. \tag{2.16}$$

Plotting log P versus $1/T$ results in a straight line whose slope equals $-\Delta H^\circ_{\text{vap}}/19.147$. This is illustrated in Fig. 2.7.

If sublimation (solid transforming into a gas) takes place, a similar expression for the vapor pressure over a solid can be deducted. The entropy associated to sublimation can be assumed[2] as 96 J mole^{-1} K^{-1}. With such value the following relation

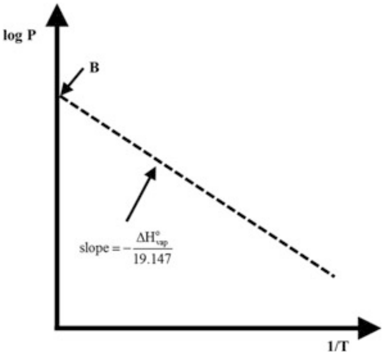

Fig. 2.7 Relationship between log P and $1/T$

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[2] Biswas A.K., Bashforth G.R., The Physical Chemistry of Metallurgical Processes, Chapman and Hall, London, 1962.

between the partial pressure of the solid and its enthalpy of sublimation $\Delta H^{\circ}_{\text{sub}}$ can be obtained:

$$\log P = -\frac{\Delta H^{\circ}_{\text{sub}}}{19.147T} + B'. \tag{2.17a}$$

Substituting the entropy of sublimation in (2.17a) gives:

$$\log P = 5.0 - \frac{\Delta H^{\circ}_{\text{sub}}}{19.147T}. \tag{2.17b}$$

Therefore knowing the vapor pressure expression for the liquid phase, the melting point and the heat of fusion it is then possible to obtain a general equation valid for the solid phase; moreover, it is then concluded the validity of the following relation:

$$\Delta H^{\circ}_{\text{sub}} = \Delta H^{\circ}_{\text{vap}} + \Delta H^{\circ}_{\text{fusion}}. \tag{2.18}$$

Example of Calculations

Example 1 Gibbs rule of phases

Part (A)

An equimolar mixture of H_2 and O_2 is contained in a pressurized cylinder. A spark causes a reaction resulting in the formation of water droplets. List the degrees of freedom before and after the water forming reaction.

Solution

In this case we have a gaseous mixture (1 phase, two components) transforming chemically into 1 phase and one component.

Gibbs rule of phases: $F = C - P + 2$

$H_2 + 0.5\ O_2$			H_2O		
C	P	**F**	C	P	**F**
2	1	**3**	1	1	**2**

Part (B)

Evaluate P, C and F for each of the following systems/reactions:

a. A mixture of five gases enclosed in a cylinder
b. $2HI = H_2 + I_2$ in vapor phase, starting with various mixtures of hydrogen and iodine

c. H_2, O_2 and H_2O enclosed in a vessel at room temperature
d. $2H_2O = 2H_2 + O_2$ at high temperature starting with water
e. Solid carbon, CO, CO_2 and O_2 in equilibrium at 600 °C
f. $(CH_3\ COOH)_{2\ \text{liquid}} = (CH_3\ COOH)_{2\ \text{gas}}$

Solution

System	C	P	F	Comments
a	5	1	6	This is a gaseous solution with 5 components. No chemical interaction between components
b	2	1	3	This systems considers the decomposition of HI into H_2 and I_2 gases; therefore there are two components mixed in one phase
c	3	2	3	At room temperature liquid water is the most stable phase. This is in equilibrium with a gaseous mixture made of H_2 and O_2
d	1	1	2	In this case water is expected to be in the gaseous phase, therefore there are 3 components mixed together in a single phase
e	4	2	4	Two phases (1 solid, 1 gas) coexist. 3 components are present in the gas and 1 component in the solid
f	1	2	1	There is a single component existing in two distinct phases

Part (C)

At high temperature, magnesium carbonate dissociates and can exist in equilibrium with the decomposition products:

$$MgCO_3 = MgO + CO_2$$

(a) State the number of phases and components in this system
(b) Would the number of components be changed by adding CO_2 from an external source?
(c) Would the number of phases be altered?

Solution

(a) At equilibrium, there are 3 phases, 2 solids ($MgCO_3$ and MgO) and one gas (CO_2). The number of components is also 3, the carbonate, the oxide and the gas.
(b) No it would not change, since CO_2 is already in the system.
(c) No, because CO_2 is in the gas phase and already is in the system.

Part (D)

Ammonium chloride vaporizes upon heating.

(a) State the number of components in a system consisting of solid ammonium chloride and its vapor
(b) Would the number of components be changed by admitting ammonia gas into the system?
(c) Would the number of phases be altered?
(d) Would equilibrium be still possible?

Solution

(a) There is one component (NH_4Cl) and two phases (1 solid, 1 gas)
(b) Yes, there would be 2 components (NH_4Cl, NH_3)
(c) No, there would still be a gaseous phase and a solid one
(d) Yes, it would.

Example 2 Clausius—Clapeyron equation The vapor pressures of sodium are written as:

$$\log P = 10.304 - \frac{5603}{T} \tag{E2.1}$$

and

$$\log P = 9.710 - \frac{5377}{T} \tag{E2.2}$$

Where P is in Pa and T in K. Which of the two equations is for solid sodium?

Solution

We need to convert log P into ln P ($\ln P = 2.303 \log P$) in order to be able to use Clausius–Clapeyron equation:

$$\begin{aligned} \ln P &= 2.303\left[10.304 - \frac{5603}{T}\right] \\ \ln P &= 23.730 - \frac{12903.709}{T} \end{aligned} \tag{E2.1a}$$

and,

$$\begin{aligned} \ln P &= 2.303\left[9.710 - \frac{5377}{T}\right] \\ \ln P &= 22.362 - \frac{12383.231}{T} \end{aligned} \tag{E2.2a}$$

Using Clausius–Clapeyron Eq. (2.11) witgh the form:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{i}}^{\circ}}{\mathrm{R}T^{2}} \tag{E2.3}$$

Applying equation (E2.3) to expressions (E2.1a) and (E2.2a) results in:

$$\begin{aligned} \frac{\mathrm{d}\ln P}{\mathrm{d}T} &= \frac{\mathrm{d}}{\mathrm{d}T}\left(23.730 - \frac{12903.709}{T}\right) \\ \frac{\mathrm{d}\ln \mathrm{P}}{\mathrm{d}T} &= \frac{12903.709}{T^{2}} = \frac{\Delta H_{1}}{\mathrm{RT}} \end{aligned} \tag{E2.1b}$$

and

$$\begin{aligned} \frac{\mathrm{d}\ln P}{\mathrm{d}T} &= \frac{\mathrm{d}}{\mathrm{d}T}\left(22.362 - \frac{12383.231}{T}\right) \\ \frac{\mathrm{d}\ln P}{\mathrm{d}T} &= \frac{12383.231}{T^{2}} = \frac{\Delta H_{2}}{\mathrm{R}T} \end{aligned} \tag{E2.2b}$$

From expressions (E2.1b) and (E2.2b) it is evident that $\Delta H_1 > \Delta H_2$, therefore, equation (E2.1) corresponds to solid sodium.

Example 3 Use of Clapeyron equation Calculate the pressure that must be applied to silver to increase its melting temperature by 10 and 20 K, using the following data:

Property	Value
Atomic mass (M)	107.87 g mole^{-1}
Melting point (T_{fus})	961.8 °C
Solid density (ρ_s)	10.50 g cm^{-3}
Liquid density (ρ_l)	9.32 g cm^{-3}
Heat of melting ($\Delta H_{\mathrm{fus}}^{\circ}$)	11280 J mole^{-1s}

Solution

We need to calculate the molar volume of both solid and liquid silver:

$V_{\mathrm{molar}} = \frac{M}{\rho}$; for each phase we have:

$$\begin{aligned} V_{\mathrm{m,solid}} &= \frac{\mathrm{M_{Ag}}}{\rho_{\mathrm{Ag,s}}} = \frac{107.87\frac{\mathrm{g}}{\mathrm{mole}}}{10.50\frac{\mathrm{g}}{\mathrm{cm^3}}} = 10.27\,\frac{\mathrm{cm}^3}{\mathrm{mole}} \\ V_{\mathrm{m,liquid}} &= \frac{\mathrm{M_{Ag}}}{\rho_{\mathrm{Ag,l}}} = \frac{107.87\frac{\mathrm{g}}{\mathrm{mole}}}{9.32\frac{\mathrm{g}}{\mathrm{cm^3}}} = 11.57\,\frac{\mathrm{cm}^3}{\mathrm{mole}}. \end{aligned}$$

From these molar volumes, we can calculate the volume change due to silver melting:

$$\Delta V = V_{\text{m. liquid}} - V_{\text{m, solid}} = 11.57 - 10.27 = 1.3\frac{\text{cm}^3}{\text{mole}} \quad \text{or} \quad 1.3 \times 10^{-6}\frac{\text{m}^3}{\text{mole}}$$

We can integrate Clapeyron's equation between limits 1.01325×10^5 Pa at T_{fus} and P at T:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{\Delta V}\frac{1}{T}$$

$$\int_{1.01325 \times 10^5}^{P} \mathrm{d}P = \frac{\Delta H}{\Delta V}\int_{1234.8}^{T}\frac{\mathrm{d}T}{T}$$

$$P = \frac{\Delta H}{\Delta V}\ln\left(\frac{T}{1234.8}\right) + 1.01325 \times 10^5$$

$$P = \frac{11280}{1.3\times 10^{-6}}\ln\left(\frac{T}{1234.8}\right) + 1.01325 \times 10^5$$

Substituting the corresponding temperature values (in *K*) in the last equation, we can calculate the pressure increase needed to melt silver:

T (°C)	P (atm)
961.8	1
971.8	691.7
981.8	1376.9
991.8	2056.6

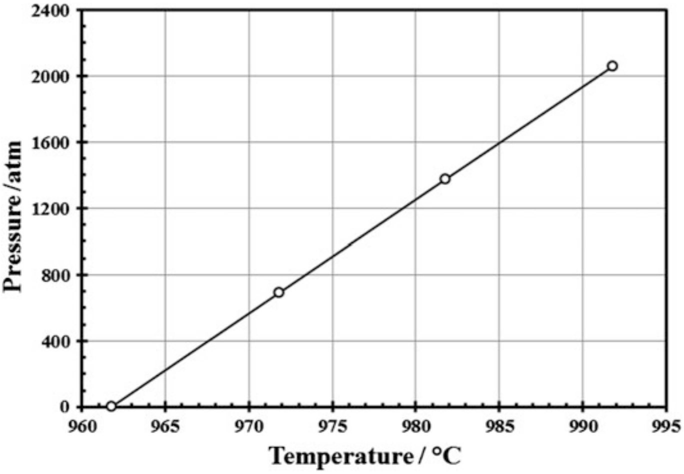


Fig. 2.8 Pressure increase to augment the meltin1 g point of silver

The relationship between the temperature (°C) increase and the corresponding pressure (atm) increment is shown in the figure below (Fig. 2.8).

Example 4 Calculation of phase boundary line The dissociation of Na_2O at 1000 °C can be represented by:

$$2\mathrm{Na_2O_{(solid)}} = 4\mathrm{Na_{(gas)}} + \mathrm{O_{2,(gas)}}$$

For this reaction, $\Delta G°_{1273} = 450.77$ kJ. Graphically determine under which conditions, sodium oxide would not decompose:

Solution

For this problem, $\Delta G°$ is given, therefore we can relate the equilibrium constant to the partial pressures of the gases resulting from the oxide decomposition

$$\begin{aligned}&\Delta G^{o}_{1273} = -\mathrm{RT}\ln(K)\\&K = \exp\left(-\frac{\Delta G^{o}_{1273}}{\mathrm{RT}}\right) = \exp\left(-\frac{450770}{8.314\times 1273}\right).\\&K = 3.18\times 10^{-19}\end{aligned}$$

On the other hand, form the dissociation reaction we can express the equilibrium constant in terms of partial pressure of sodium and oxygen:

$$\begin{aligned}&K = \mathrm{p_{O_2}}\times \mathrm{p^4_{Na}}\\&3.18\times 10^{-19} = \mathrm{p_{O_2}}\times \mathrm{p^4_{Na}}.\end{aligned}$$

The logarithm of the previous equation, allow us to express the partial pressure of sodium as a function of that of the oxygen evolving from the oxide:

$$\begin{aligned}&\log(3.18\times 10^{-19}) = \log(\mathrm{p_{O_2}}) + 4\log(\mathrm{p_{Na}})\\&\log(\mathrm{p_{Na}}) = \frac{-18.5-\log(\mathrm{p_{O_2}})}{4}.\end{aligned}$$

We can assign values to the partial pressure of oxygen so we can calculate the equilibrium value for that of sodium and thus define the equilibrium line between the oxide and its dissociation products; this is illustrated in the figure below (Fig. 2.9).

Example 5 Determination of the heat of sublimation of water using the heat of vaporization and that of melting along with Clasius–Clapeyron equation The heats of vaporization and of fusion of water are 45.054 kJ $\mathrm{mole^{-1}}$ and 6.01 kJ $\mathrm{mole^{-1}}$ at 0 °C, respectively. The vapor pressure of water at 0 °C is 0.006 atm. Calculate the sublimation pressure of ice at −15 °C, assuming that the enthalpies of transformation do not change with temperature.

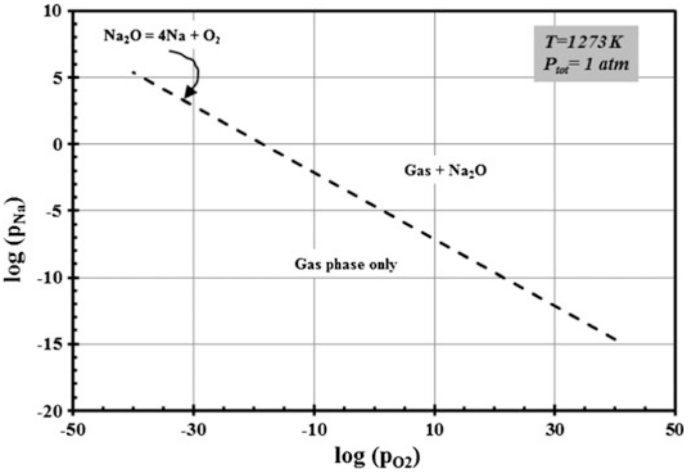
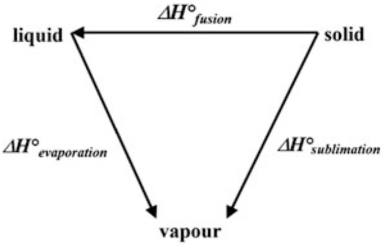


Fig. 2.9 Phase stability in the dissociation of Na_2O



$$\Delta H^\circ_{\text{sublimation}} = \Delta H^\circ_{\text{evaporation}} + \Delta H^\circ_{\text{fusion}}$$

Fig. 2.10 Relationship between the standard heat of evaporation, sublimation and fusion

Solution

The heats of transformation are related as indicated in the sketch below. According to this figure, we can calculate the heat of sublimation of water at 0 °C by combining the heats of evaporation and melting at the same temperature. With that heat, then we can use Clausius–Clapeyron equation to calculate the pressure for transforming solid water into vapor at −15 °C (Fig. 2.10).

To calculate the heat of sublimation at 273 K, we can use Eq. (2.18):

$$\Delta H^\circ_{\text{sub},273} = \Delta H^\circ_{\text{evap},273} + \Delta H^\circ_{\text{fus},273}$$
$$\Delta H^\circ_{\text{sub},273} = 45.054 + 6.010 \quad \text{kJ mole}^{-1}$$
$$\Delta H^\circ_{\text{sub},273} = 51.064 \quad \text{kJ mole}^{-1}.$$

Assuming that this value is independent of temperature, we can calculate the sublimation pressure at a lower temperature:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{\circ}_{\text{sub}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Solving for P_2, and substituting the corresponding values:

$$P_2 = P_1 \exp\left[-\frac{\Delta H^{\circ}_{\text{sub}}}{R}\left(T_2^{-1} - T_1^{-1}\right)\right]$$
$$P_2 = 0.006 \exp\left[-\frac{51064}{8.314}\left(258^{-1} - 273^{-1}\right)\right]$$
$$P_2 = 0.0017\,\text{atm}.$$

As temperature drops 15 °C, the pressure to transform solid water into vapor decreases as well. This is observed in the P-T plot below (Fig. 2.11).

Example 6 Estimation of vapor pressure by combining Trouton's rule and Clausius–Clapeyron equation Mercury evaporates at 357 °C (630 K) under 1 atm of pressure. Calculate its approximate vapor pressure at 100 °C, assuming that it follows Trouton's rule.

Solution

First, we need to find $\Delta H^{\circ}{}_{\text{vap}}$ from Trouton's rule:

$$\frac{\Delta H^{\circ}_{\text{vap}}}{T_{\text{evaporation}}} = 88 \quad \text{J}\,\text{mole}^{-1}\text{K}^{-1};$$
$$\Delta H^{\circ}_{\text{vap,Hg}} = 88(T_{\text{evaporation,Hg}})$$
$$\Delta H^{\circ}_{\text{vap,Hg}} = 88(630)$$
$$\Delta H^{\circ}_{\text{vap,Hg}} = 55440 \quad \text{J}\,\text{mole}^{-1}.$$

Substituting this $\Delta H^{\circ}{}_{\text{vap, Hg}}$ value, into Clausius–Clapeyron equation, and solving for the gas pressure at the desired temperature:

$$\ln\left(\tfrac{P_2}{P_1}\right) = -\tfrac{\Delta H^{\circ}_{\text{vap}}}{R}\left(\tfrac{1}{T_2} - \tfrac{1}{T_1}\right)$$
$$P_2 = P_1 \times \exp\left[-\tfrac{\Delta H^{\circ}_{\text{vap}}}{R}\left(\tfrac{1}{T_2} - \tfrac{1}{T_1}\right)\right]$$
$$P_2 = 1 \times \exp\left[-\tfrac{55440}{8.314}\left(\tfrac{1}{373} - \tfrac{1}{630}\right)\right]$$
$$P_2 = \exp[-7.293]$$
$$P_2 = 0.0007 \quad \text{atm}; \qquad P_2 = 70.9 \quad \text{Pa}.$$

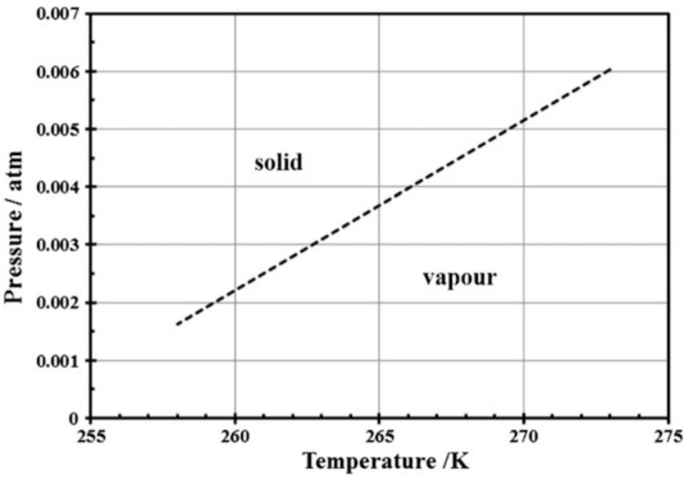


Fig. 2.11 Solid–vapor equilibrium for water

Example 7 Estimation of the heat of transformation from raw temperature and pressure data Calculate the mean heat of vaporization of palladium from the following data:

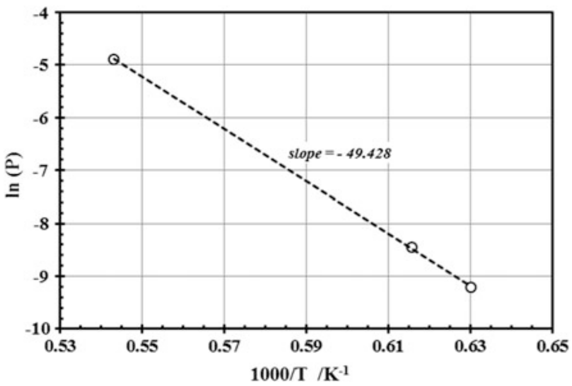
T (°C)	P (Pa)
1314	1.00×10^{-4}
1351	2.15×10^{-4}
1568	7.50×10^{-3}

Solution

To find the heat of vaporization, we need to work out the raw data to obtain the logarithm of the pressure and the inverse of the temperature in absolute scale, such manipulation results in:

P (Pa)	ln P	T (°C)	T (K)	$10^3/T$ (1/K)
1.00×10^{-4}	−9.210	1314	1587	0.630
2.15×10^{-4}	−8.445	1351	1624	0.616
7.50×10^{-3}	−4.893	1568	1841	0.543

Fig. 2.12 Vapor pressure of palladium as a function of the inverse of temperature



Accordingly with Clausius–Calpeyron equation, plotting ln (P) versus $10^3/T$, would result in a straight line whose slope is equivalent to $-\frac{\Delta H^\circ_{vap}}{R}$. By taking $10^3/T$, the resulting heat of evaporation will be expressed in kJ mole^{-1}. This is shown in (Fig. 2.12).

From the slope, the heat of evaporation of palladium becomes:

$$\Delta H^\circ_{\text{vap}} = -\text{slope} \times R$$
$$\Delta H^\circ_{\text{vap}} = 49.428 \times 8.314$$
$$\Delta H^\circ_{\text{vap}} = 411\,\text{kJ mole}^{-1}.$$

Example 8 Use of Clapeyron and Clausius–Clapeyron equations to solve every day problems

Part (A)

How much a speed skater, who is 70 kg by weight, decreases the melting point of ice? The skating iron is 1 by 400 mm. Assume all his weight is on one skate at a time. Data: $\Delta S^\circ_{\text{fus}} = 21.97$ J mole^{-1} K^{-1}; $\Delta V_{\text{fus}} = -1.49$ cm3 mol^{-1}.

Solution

For this problem, we need to use Clapeyron equation

$$\frac{dP}{dT} \approx \frac{\Delta P}{\Delta T} = \frac{\Delta S^\circ_{\text{melting}}}{\Delta V_{\text{melting}}}$$
$$\Delta T = \Delta P \frac{\Delta V_{\text{melting}}}{\Delta S^\circ_{\text{melting}}} \tag{E7.1}$$

It is necessary to calculate the pressure exerted by the skater on the ice surface:

$$\Delta P = \frac{F}{A} = \frac{70 \times 9.8}{10^{-3} \times 0.4} = 1.715 \times 10^6 \text{ Pa.} \tag{E7.2}$$

Substituting this pressure value into equation (E7.1):

$$\Delta T = 1.715 \times 10^6 \times \frac{-1.49 \times 10^{-6}}{21.97}; \quad \Delta T = -0.12\,\mathrm{K}.$$

Therefore, the melting point of ice drops by 0.12 K

Part (B)

The spouse of an engineer showed scientific interest in asking:

(i) What is the temperature in our pressure cooker?
(ii) Why does it cook faster than in an ordinary saucepan?

Given: Pressure regulator weighs 78 g and sits on a 2.618 mm outer diameter opening; $\Delta H^\circ_{\mathrm{vap}}$ for water at 1 atm and 100 °C is 40585 J mole^{-1}. What would your answers be for (i) and (ii) above?

Solution

For this problem, we have to calculate the pressure inside the cooker using Clausius–Clapeyron equation. To do so, we need to multiply the weight of the regulator by 9.8 to find the force that it exerts over the area defined by the gage opening:

$$P_{\mathrm{cooker}} = \frac{F}{A} = \frac{78 \times 10^{-3} \times 9.8 \quad [\mathrm{N}]}{0.25\pi \times (2.618 \times 10^{-3})^2 [\mathrm{m}^2]} = 1.42 \times 10^5\,\mathrm{Pa}.$$

With the cooker pressure, we can fix the following conditions: $P_1 = 1.01325 \times 10^5$ Pa (1 atm), $P_2 = 1.42 \times 10^5$ Pa, $T_1 = 373$ K (100 °C), and T_2 = cooker temperature at the cooker pressure P_2. These values along with that of the heat of vaporization can be inserted now in Clausius–Clapeyron equation and solve for T_2:

$$\begin{aligned} \ln\left(\frac{P_2}{P_1}\right) &= -\frac{\Delta H^\circ_{\mathrm{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ \ln\left(\frac{1.42}{1.01325}\right) &= -\frac{40585}{8.314}\left(\frac{1}{T_2} - \frac{1}{373}\right) \\ -\frac{0.3375}{4881.53} &= \frac{1}{T_2} - \frac{1}{373} \\ T_2 = 383\,\mathrm{K}; &\quad T_2 = 110^\circ\mathrm{C}. \end{aligned}$$

Thus answering to the engineer's spouse we have that (i) the cooker reaches 110 °C and (ii) since the pressure increases so does the boiling temperature, then meals are cooked faster.

Electrochemistry

3

Introduction

In chapter one, it was stated that energy can transform into different forms; one of such useful transformations is when electrical energy converts into chemical one or vice versa. Batteries transform the energy released by a chemical reaction into electricity, so we can run different devices like cell phones, computers, personal media players, and even some vehicles.

Electrochemistry not only deals with this energy conversion, it is also useful in determining thermodynamic properties of different systems at elevated temperatures, it can be used to decrease corrosion rates among other applications.

In this chapter we will be establishing those energy–voltage relationships, so we can calculate thermodynamic quantities from voltage measurements; additionally, some techniques to measure the chemical activity of components in solution will be described.

Also it will be illustrated how to calculate the amount of metal deposited in coatings or in the electrorefining of some nonferrous metals such as copper or aluminum.

Electrolysis

The use of electricity to promote chemical reactions has many different applications; for example, plating a thin film of metal on surfaces of other metals to improve their appearance or to prevent corrosion. Another use of electricity can be found in the extraction of reactive metals such as sodium and aluminum from their ores. It can also be considered the industrial production of sodium hydroxide, copper, chlorine gas and hydrogen gas, or recharging car batteries and other rechargeable cells, such as lithium batteries.

G. Plascencia and D. Jaramillo, *Basic Thermochemistry in Materials Processing*,
DOI 10.1007/978-3-319-53815-0_3

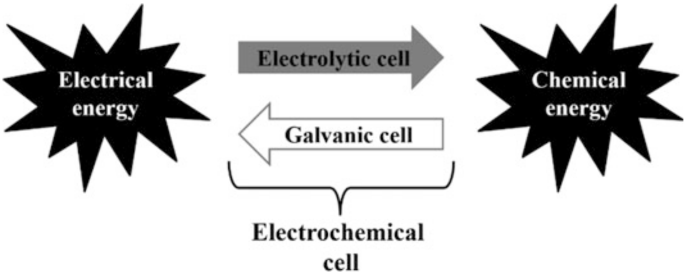


Fig. 3.1 Energy transformation in galvanic and electrolytic cells

Electrolysis is the passing of an electric (direct) current through a conductive medium (electrolyte) bearing ionic species; as the electricity flows, ions break down into elements. During electrolysis, ions with positive charge move toward the negative electrode known as cathode, while simultaneously the negatively charged ions move to the positive electrode or anode.

At the cathode, the positive charged ions gain electrons, thus a reduction reaction takes place; whereas at the anode negative ions give up (lose) electrons, therefore oxidation reactions take place at this electrode.

Those chemical reactions occurring by electrolysis would not normally happen without the application of electrical energy, and so they are non-spontaneous. Thus the chemicals obtained by electrolysis are often difficult to obtain by other means.

Electrolysis takes place in electrolytic cells; these cells are comprised of a positive electrode (anode), a negative one (cathode), and an electrolyte. Similarly, the energy released by a chemical reaction can be transformed into electricity; for this process, galvanic cells are the apparatuses used to achieve this goal. Galvanic cells also contain two electrodes (one positive, one negative) and an electrolyte (Fig. 3.1).

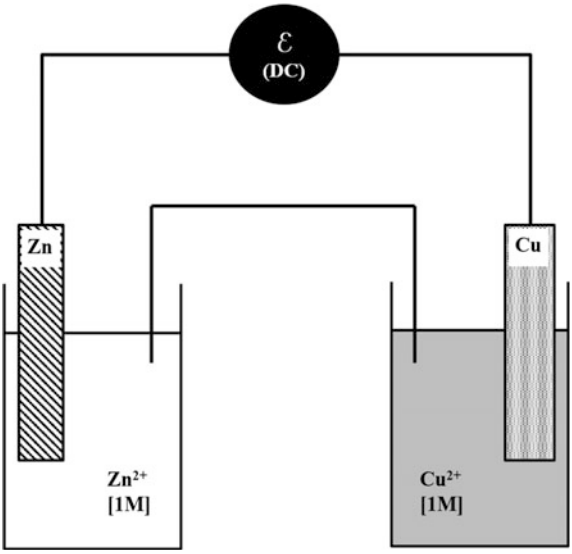
Electrochemical Cell

If a piece of solid metal is placed in a solution made of its own ions, an electromotive force or potential difference develops between the metal and the solution. Such system constitutes an electrode and the potential difference is known as electrode potential.

The potential develops from passing of the metal into the solution forming its own ions, or by depositing metal ions from the solution onto the metal surface. If two of such electrodes are connected, they result in an electrochemical cell, which is a device where electrical energy is obtained from a chemical reaction.

For example, the Daniell cell consists of an electrode made of zinc in contact with a zinc ions solution, coupled through a porous membrane or a wire to a copper electrode made of copper in contact to Cu^{2+} ions solution. This cell can be represented as: $Zn \mid ZnSO_4 \mathrel{\vdots} CuSO_4 \mid Cu$, and it is sketched in Fig. 3.2.

Fig. 3.2 Schematics of a Daniell cell



If the zinc and copper are connected through an external circuit, an electrical current flows between them as a consequence of the reactions taking place at each electrode:

$$Zn = Zn^{2+} + 2e^- \tag{3.1}$$

and

$$Cu^{2+} + 2e^- = Cu \tag{3.2}$$

Combining these reactions, results in the overall cell reaction:

$$Zn + Cu^{2+} = Zn^{2+} + Cu \tag{3.3}$$

The electrodes not necessarily need to be made of a metal and its ions. For example, if hydrogen gas is bubbled into a solution bearing hydrogen ions (acidic solution), equilibrium between the gas and the ions can be obtained:

$$H_2 = 2H^+ + 2e^- \tag{3.4}$$

In such case, it is necessary to introduce a metallic conductor to pick up the electrons released; the hydrogen electrode can be written as $PtH_2 \mid H^+$.

The voltage of the electrochemical cell is the combination of the two electrode potentials. The cell voltage is proportional to the energy required to drive the electrons from one electrode to the other and will be maximum when the resistance of the circuit is infinite. This maximum voltage (E) is related to the free energy change associated to the cell reaction.

Electrical energy is the result of the product Volts × Coulombs which is equivalent to Joules. The stoichiometry of a reaction involving electron transfer relates to the electrical charge supplied. For a cell reaction, in which n Faradays pass through a cell of voltage E volts, and one Faraday is given by F Coulombs ($F = 96{,}500$ C mole^{-1}), then the electrical energy associated to the cell reaction under reversible conditions is:

$$\text{Energy} = nFE \tag{3.5}$$

As an example, in Daniell's cell two electrons are transferred between the zinc and the copper electrodes, thus $n = 2$; this means that the energy associated to this cell would be $2FE$. This energy when expressed as work, does not involve work of expansion and therefore, it is a direct measurement of the free energy change for the cell reaction. If the cell reaction proceeds, then ΔG must be negative and hence equating it to the electrical energy:

$$\Delta G = -nFE. \tag{3.6}$$

Therefore, the potential of a working cell must be positive. This relationship between ΔG and the cell potential is very important, since it allows to obtain thermodynamic data for many different chemical reactions.

Additionally, since ΔG is related to both ΔH and ΔS, these quantities associated to any electrochemical cell can be estimated.

Recalling that entropy can be defined as the first derivative of ΔG with respect of T at constant pressure:

$$\Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_P. \tag{3.7}$$

Substituting back Eqs. (3.7) into (3.6):

$$\Delta S = -\left[\frac{\partial(-nFE)}{\partial T}\right]_P.$$

This expression simplifies to:

$$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_P. \tag{3.8}$$

The term $\left[\frac{\partial E}{\partial T}\right]_P$ is known as the temperature coefficient of the cell. This coefficient has to be found from experimental measurements by plotting the cell voltage versus its temperature. The slope of the resulting curve at the desired temperature is the temperature coefficient.

Since we know both the free energy and the entropy changes as a function of the cell voltage, we can now estimate the corresponding enthalpy change. To do so, we need to use Eq. (1.21):

$$\Delta G = \Delta H - T\Delta S \tag{1.21}$$

Substituting Eqs. (3.6) and (3.8) into (1.21), results in:

$$-nFE = \Delta H - T\left(nF\left[\frac{\partial E}{\partial T}\right]_P\right)$$

$$\Delta H = T\left(nF\left[\frac{\partial E}{\partial T}\right]_P\right) - nFE.$$

Simplifying:

$$\Delta H = nF\left(T\left[\frac{\partial E}{\partial T}\right]_P - E\right). \tag{3.9}$$

By using Eq. (1.8), it is possible to determine the heat capacity by means of an electrochemical cell:

$$\Delta C_p = \frac{\partial \Delta H}{\partial T} \tag{1.8}$$

$$\Delta C_\mathrm{p} = nFT\left[\frac{\partial^2 E}{\partial T^2}\right]. \tag{3.10}$$

Nernst Equation

Recalling Eq. (1.37a), which relates the Gibbs free energy of any given reaction to its equilibrium constant:

$$\Delta G = \Delta G^\mathrm{o} + RT\ \ln(K). \tag{1.37a}$$

By substituting Eq. (3.6) into expression (1.37a) results in a new expression that relates the equilibrium constant to the voltage supplied to the electrochemical cell:

$$-nFE = -nFE^\mathrm{o} + RT\ \ln(K). \tag{3.11}$$

Dividing (3.11) by $-nF$:

$$E = E^\mathrm{o} - \frac{RT}{nF}\ln(K). \tag{3.11a}$$

Equation (3.11a) is known as Nernst equation. As mentioned, this equation relates the concentration (chemical) gradient to the electric gradient in a reaction. In dilute solutions, actual concentrations can be inserted into Eq. (3.11a) since activity coefficients are close to unity. As solutions become more concentrated, chemical activities should be used; to do so, it is necessary to measure these activities. Nernst equation is only useful when no current flows through the electrode. This is because the ionic activity may change at the electrode's surface when current is supplied; additionally, over potentials or resistive terms may arise with the current, thus altering the actual potential measurements.

Going back to the Daniell cell example, we can apply relation (3.11a) to the negative zinc electrode: $\mathrm{Zn} = \mathrm{Zn}^{2+} + 2\mathrm{e}^-$ (oxidation of zinc):

$$E_{\mathrm{Zn(ox)}} = E^{\mathrm{o}}_{\mathrm{Zn(ox)}} - \frac{RT}{2F} \times \ln\left(\frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Zn}}}\right) \tag{3.12}$$

were $E_{\mathrm{Zn(ox)}}$ is the electrode potential in volts, $E^{o}_{\mathrm{Zn(ox)}}$ is the standard oxidation potential, $a_{\mathrm{Zn}}{}^{2+}$, and a_{Zn} are the chemical activities of zinc ions and metallic zinc, respectively. The activity of the later can be taken as unity, since it is a pure metal in solid state, thus the electrode potential becomes:

$$E_{\mathrm{Zn(ox)}} = E^{\mathrm{o}}_{\mathrm{Zn(ox)}} - \frac{RT}{2F} \times \ln(a_{\mathrm{Zn}^{2+}}). \tag{3.13}$$

Similarly, for the positive copper electrode in this cell, the ions reduce to metal: $\mathrm{Cu}^{2+} + 2\mathrm{e}^- = \mathrm{Cu}$, the electrode potential is now expressed as:

$$E_{\mathrm{Cu(red)}} = E^{\mathrm{o}}_{\mathrm{Cu(red)}} - \frac{RT}{2F} \times \ln\left(\frac{1}{a_{\mathrm{Cu}^{2+}}}\right) \tag{3.14}$$

As already mentioned, the overall cell reaction results of adding the oxidation and reduction reactions; this allows for calculating the total cell potential which can be obtained by adding the oxidation voltage of zinc to the reduction voltage of copper, this is:

$$E = E_{\mathrm{Zn(ox)}} + E_{\mathrm{Cu(red)}}$$

$$E = E^{\mathrm{o}}_{\mathrm{Zn(ox)}} - \frac{RT}{2F}\ln(a_{\mathrm{Zn}^{2+}}) + E^{\mathrm{o}}_{\mathrm{Cu(red)}} - \frac{RT}{2F}\ln\left(\frac{1}{a_{\mathrm{Cu}^{2+}}}\right)$$

$$E = E^{\mathrm{o}}_{\mathrm{Zn(ox)}} + E^{\mathrm{o}}_{\mathrm{Cu(red)}} - \frac{RT}{2F}\ln\left(\frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Cu}^{2+}}}\right). \tag{3.15}$$

Defining $E^{o} = E^{o}_{\mathrm{Zn(ox)}} + E^{o}_{\mathrm{Cu(red)}}$, we finally obtain:

$$E = E^{o} - \frac{RT}{2F} \ln\left(\frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Cu}^{2+}}}\right). \tag{3.16}$$

Table 3.1 shows the standard potentials for several oxidation and reduction reactions. The voltages shown in this table are in reference to the standard hydrogen electrode depicted in Fig. 3.3.

The standard potential of any cell can be evaluated by either:

- Doing direct measurements of E^{o} under standard conditions.
- Doing measurements of E under nonstandard conditions and calculating E^{o} using Nernst equation.

To express the tendency to oxidize (release electrons) or to reduce (gain electrons) of individual electrodes, it is necessary to use a reference electrode. The most common reference electrode in use is that of hydrogen. The standard voltage for the hydrogen electrode is 0 V.

Table 3.1 Standard potentials for the oxidation or reduction of chemical elements

Half-reaction	E^{o} [V]
$Li^+ + e^- = Li$	−3.04
$K^+ + e^- = K$	−2.92
$Ca^{2+} + 2e^- = Ca$	−2.76
$Na^+ + e^- = Na$	−2.71
$Mg^{2+} + 2e^- = Mg$	−2.38
$Al^{3+} + 3e^- = Al$	−1.66
$Ce^{3+} = Ce^{4+} + e^-$	−1.61
$V^{2+} + 2e^- = V$	−1.19
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.83
$Zn^{2+} + 2e^- = Zn$	−0.76
$Cr^{3+} + 3e^- = Cr$	−0.74
$Fe^{2+} + 2e^- = Fe$	−0.41
$Cd^{2+} + 2e^- = Cd$	−0.40
$Ni^{2+} + 2e^- = Ni$	−0.23
$Sn^{2+} + 2e^- = Sn$	−0.14
$Pb^{2+} + 2e^- = Pb$	−0.13
$Fe^{3+} + 3e^- = Fe$	−0.04
$2H^+ + 2e^- = H_2$	0.00
$Sn^{4+} + 2e^- = Sn^{2+}$	0.15
$Cu^{2+} + e^- = Cu^+$	0.16
$ClO_4^- + H_2O + 2e^- = ClO_3^- + 2OH^-$	0.17
$AgCl + e^- = Ag + Cl^-$	0.22

(continued)

Table 3.1 (continued)

Half-reaction	E° [V]
$Cu^{2+} + 2e^- = Cu$	0.34
$ClO_3^- + H_2O + 2e^- = ClO_2^- + 2OH^-$	0.35
$IO^- + H_2O + 2e^- = I^- + 2OH^-$	0.49
$Cu^+ + e^- = Cu$	0.52
$I_2 + 2e^- = 2I^-$	0.54
$ClO_2^- + H_2O + 2e^- = ClO^- + 2OH^-$	0.59
$Fe^{3+} + e^- = Fe^{2+}$	0.77
$Hg_2^{2+} + 2e^- = 2Hg$	0.80
$Ag^+ + e^- = Ag$	0.80
$Hg^{2+} + 2e^- = Hg$	0.85
$ClO^- + H_2O + 2e^- = Cl^- + 2OH^-$	0.90
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.90
$NO_3^- + 4H^+ + 3e^- = NO(g) + 2H_2O$	0.96
$Br_2 + 2e^- = 2Br^-$	1.07
$O_2 + 4H^+ + 4e^- = 2H_2O$	1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33
$Cl_2 + 2e^- = 2Cl^-$	1.36
$Ce^{4+} + e^- = Ce^{3+}$	1.44
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.49
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.78
$Co^{3+} + e^- = Co^{2+}$	1.82
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	2.01
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07
$F_2 + 2e^- = 2F^-$	2.87

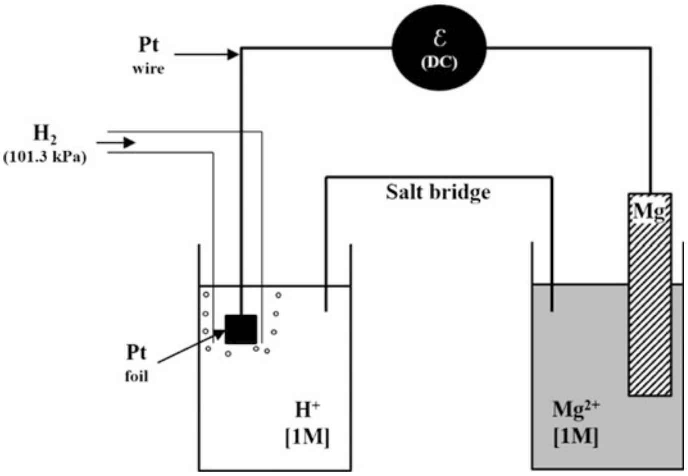


Fig. 3.3 Sketch of a standard hydrogen electrode

The more negative the half-cell potential, the greater the tendency of the reductant to donate electrons, and the smaller the tendency of the oxidant to accept electrons. Furthermore, Given the E^o values for two half-reactions, it can easily predict the potential difference of the corresponding cell by simply adding the reduction potential of the reduction half-cell to the negative of the reduction potential (that is, to the oxidation potential) of the oxidation reaction.

For example, to find the standard potential of the cell:

$$\mathrm{Cu}\big|\mathrm{Cu}^{2+}\big|\big|\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}$$

and predict the electron flow when the two electrodes are connected, it is necessary to rewrite the cell to show the half-reactions at each electrode, thus:

$$\begin{array}{ll} \mathrm{Cu} = \mathrm{Cu}^{2+} + 2\mathrm{e}^- & E^o = +0.337\,\mathrm{V} \\ \mathrm{AgCl} + \mathrm{e}^- = \mathrm{Ag} + \mathrm{Cl}^- & E^o = +0.222\,\mathrm{V} \end{array}.$$

The cell indicates that copper oxidizes, releasing electrons; those electrons are collected by the Ag^+ ions contained within AgCl. Reduction of Ag^+ ion to metallic Ag is accompanied by the release of Cl^- ions into solution. Thus, the overall cell reaction must be written as:

$$2\mathrm{AgCl} + \mathrm{Cu} = 2\mathrm{Ag} + 2\mathrm{Cl}^- + \mathrm{Cu}^{2+}$$

Because Cu is being oxidized, the negative of the standard reduction potential should be used; additionally, the silver reaction has to multiply by 2 to balance out electrons, thus the standard cell voltage is:

$$E^o_{\mathrm{cell}} = (-0.337 + 0.222)\mathrm{V} = -0.115\,\mathrm{V}$$

Because this potential is negative, we know that the overall cell reaction proceed in the reverse direction to those depicted above. Thus, when the two electrodes are connected, electrons pass from the silver electrode through the external circuit to the copper electrode. AgCl acts as an oxidizing agent to metallic copper.

It is also worth noting that the cell potential of the AgCl/Ag electrode was not multiplied by two, the reason for this is that voltage represents the energy produced per quantity of charge passing through the cell. Because voltage is the quotient of two extensive quantities, it is intensive itself. When we multiply the anodic and cathodic half-reactions by the stoichiometric factors required to ensure that each involves the same quantity of charge, the free energy change and the number of Coulombs both increase by the same factor, leaving the potential (voltage) unchanged. This explains why we do not have to multiply the standard potentials of anodic and cathodic reactions by stoichiometric factors when calculating potentials of complete cells.

Chemical Activity

It was mentioned the concept of activity. This quantity measures the propensity of a given material to contribute to a chemical reaction. To determine how "active" this material is in a reaction compared to how it would behave if it were present in its standard state, it is necessary to determine the activity by either its concentration or its partial pressure:

$$a_i = \frac{C}{C^{\mathrm{o}}} = \frac{P}{P^{\mathrm{o}}}. \tag{3.17}$$

However, some intermolecular interactions in multicomponent systems result in deviations from a direct correspondence with pressure or concentration, to account for these deviations, it is necessary to introduce the concept of activity coefficient (γ). The activity coefficient is close to unity for dilute solutions and in gaseous systems at low partial pressures; however, this coefficient changes rapidly with concentration, temperature, etc., and it can be expressed in a very complex manner as the number of components in a given system grows.

In its simpler way, the activity coefficient for the *i*th component in a multicomponent system can be defined as:

$$a_i = \gamma_i \frac{C_i}{\mathrm{C}_i^{\mathrm{o}}}. \tag{3.18}$$

Using the definition of molar fraction $\left(x_i = \frac{n_i}{n_t} = \frac{\text{moles of } i}{\text{total moles}}\right)$, expression (3.18) can be written as:

$$a_i = \gamma_i x_i. \tag{3.19}$$

More importantly, the activity is related to the chemical potential of the different species in the system under study.

The chemical potential of the *i*th substance is the partial derivative of the free energy G with respect of its number of moles in the system:

$$\mu_i = \left[\frac{\partial G_i}{\partial n_i}\right]_{P,T,n_j}. \tag{3.20}$$

As matter flows spontaneously from a region of high chemical potential to a region of low chemical potential; this quantity can be used to determine whether or not a system is in equilibrium. When the system is at the state of equilibrium, the chemical potential of each substance will be the same in all the phases appearing in the system.

This will be discussed in the upcoming chapters.

Experimental Determination of Thermodynamic Data

The determination of thermodynamic data (either in standard state or not) and the activity of components in mixtures are paramount in materials research. Several methods are used to accomplish such determinations. Of these methods, the electrochemical ones are quite useful and easy to implement.

Electrochemical methods are commonly used to determine the standard Gibbs free energy of formation of a compound as well as the activity of a component in solution.

To determine the standard free energy of formation, consider an electrochemical cell made of a metal *M* and a nonmetal X (X = N,O,S,Cl,F, etc.). The cell can be represented as M|MX|X. At the electrodes, the metal *M* is reduced, whereas X oxidizes according to the general reactions:

$$\mathrm{M}^{+} + \mathrm{e}^{-} = M \quad E_{\mathrm{M}} = E^{\mathrm{o}}_{\mathrm{M}} - \frac{\mathrm{RT}}{nF}\ln\left(\frac{1}{a_{\mathrm{M}^{+}}}\right) \tag{3.21}$$

$$1/2\,\mathrm{X}_2 + \mathrm{e}^{-} = \mathrm{X}^{-} \quad E_{\mathrm{X}_2} = E^{\mathrm{o}}_{\mathrm{X}_2} - \frac{\mathrm{RT}}{nF}\ln\left(\frac{a_{\mathrm{X}}}{P^{0.5}_{\mathrm{X}_2}}\right). \tag{3.22}$$

Combining these electrode reactions, the overall cell reaction becomes:

$$M + 1/2\,\mathrm{X}_2 = \mathrm{M}^{+} + \mathrm{X}^{-}. \tag{3.23}$$

And the total cell voltage under reversible conditions becomes:

$$E = E^{\mathrm{o}} - \frac{\mathrm{RT}}{nF}\ln\left[\frac{a_{\mathrm{X}^-}a_{\mathrm{M}^+}}{\sqrt{P_{\mathrm{X}_2}}}\right] = -\frac{\Delta G}{nF} \tag{3.24}$$

If the MX electrolyte is in equilibrium with its ions, it is possible to consider MX to be in its standard state; thus the cell reaction can be rewritten as:

$$M + 1/2\,\mathrm{X}_2 = \mathrm{MX} \tag{3.25}$$

Then the Gibbs free energy of the cell reaction is given by:

$$\Delta G = -nFE = \Delta G^{\mathrm{o}} + \mathrm{RT}\ \ln\left[\frac{a_{\mathrm{MX}}}{a_{\mathrm{M}}\sqrt{P_{\mathrm{X}_2}}}\right]. \tag{3.26}$$

When both MX and *M* are pure and the partial pressure of X_2 reaches 1 atm (at the electrode), the Gibbs free energy of reaction (3.25), represents the standard Gibbs free energy change and is equal to $-nFE^{\mathrm{o}}$. Therefore, it is sufficient to measure the cell potential to determine the standard Gibbs free energy of formation of the MX compound.

Depending on whether M or MX forms a solution, we may have an electrode or an electrolyte concentration cell.

In the concentration cell, the voltage of two cells whose electrodes are different, one being pure M and the other M dissolved in N metal, the overall reaction would be:

$$M = (M)_N. \tag{3.27}$$

This reaction produces a voltage which corresponds to the Gibbs free energy of mixing of M:

$$E = -\frac{G_{\text{mix}}}{nF} = -\frac{RT}{nF}\ln(a_{\text{M}}). \tag{3.28}$$

Thus, the activity of M in solution is found by directly measuring the cell potential. Furthermore, by changing the temperature of the cell, it is possible to determine the entropy of mixing:

$$S_{\text{mix}} = -\frac{\mathrm{d}G_{\text{mix}}}{\mathrm{d}T} = nF\frac{\mathrm{d}E}{\mathrm{d}T}, \tag{3.29}$$

which is analogous to Eq. (3.8)

On the other hand, the electrolyte concentration cell allows estimating the activity of the MX compound in solution with an NX salt. To do so, it is necessary to compare the potential of the MX and $(\text{MX})_{\text{NX}}$ bearing cells:

$$M|\text{MX}|\text{X}_2 \tag{3.30}$$

$$M\big|(\text{MX})_{\text{NX}}\big|\text{X}_2. \tag{3.31}$$

In cell (3.30), MX is obtained from pure elements, thus:

$$E_{(3.30)} = E^{\text{o}}_{(3.30)} = -\frac{G^{\text{o}}_{(3.30)}}{nF}. \tag{3.32}$$

Meanwhile, in cell (3.31) MX is dissolved into NX. Therefore, the voltage for this cell depends on the activity of MX in the solution:

$$E_{(3.31)} = -\frac{G_{(3.31)}}{nF} = E^{\text{o}}_{(3.31)} - \frac{RT}{nF}\ln\left(a_{(\text{MX})_{\text{NX}}}\right). \tag{3.33}$$

The voltage difference $E_{(3.31)}$–$E_{(3.30)}$ sets the activity of the MX salt dissolved into NX:

$$E_{(3.31)} - E_{(3.30)} = \frac{RT}{nF}\ln\left(a_{(\text{MX})_{\text{NX}}}\right). \tag{3.34}$$

In spite of being very useful, electrochemical methods have some limitations. To perform accurate activity measurements certain conditions must be met:

- The electrolyte conductivity must be ionic, or have limited electronic contributions.
- The valency of the metallic ion in the electrolyte must be unique. It must be known, since it is essential for calculating the activity of the electrolyte or that of the metal (electrode).
- In electrode concentration cells, the metal in the electrolyte must be more active than the electrode one otherwise; a displacement reaction will take place, resulting in measuring the activity of different element.

If these conditions are not fulfilled, the composition of the electrolyte will change at the electrode–electrolyte interface resulting in instable voltage readings.

Faraday's Laws of Electrolysis

As mentioned before, electrolysis is quite useful in obtaining many metallic materials that are quite different to refine by other means. It is possible to relate the amount of metal recovered to the current and voltage supplied to the electrolytic cell used for reduction.

The amount of metal that is reduced can be estimated by means of Faraday's electrolysis laws; these laws state that:

- The mass of a substance formed at an electrode during electrolysis is directly proportional to the quantity of electricity that passes through the electrolyte.
- The masses of different substances formed by passing the same quantity of electricity are proportional to the equivalent weight of each substance.

The equivalent weight of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance. Thus one mole of Al^{3+} corresponds to three equivalents of this species, and will require three Faradays (F) of charge to deposit it as metallic aluminum.

These laws can be expressed mathematically as:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{n}\right), \tag{3.35}$$

where m is the mass of the substance liberated/deposited at the electrode; Q is the total electric charge passed through the substance (C); F is Faraday's constant (96,500 C/mole); M is the molecular mass of the deposited substance and n is the valence number of ions (electrons transferred per ion).

For Faraday's 1st law, M, F, and z are constant, so that the larger the value of Q the larger m will be; whereas for Faraday's 2nd law, Q, F, and z are constants, so that the larger the value of M/z (equivalent weight) the larger m will be.

If the supplied current does no change, the total charge is equal to the product between current and time:

$$Q = i \times t \tag{3.36}$$

Substituting Eqs. (3.36) into (3.35), results in:

$$m = \frac{i \times t}{F} \times \frac{M}{z}$$

$$m = \frac{i \times t}{F} \frac{M}{z}. \tag{3.37}$$

If we are only interested in calculating the amount of moles of substance deposited at the electrode, then Eq. (3.37) can be written as:

$$n = \frac{i \times t}{F} \frac{1}{z}. \tag{3.38}$$

This last set of equations is useful in estimating production rates of metals obtained by electrolysis.

From the practical point of view, electrolysis of metals is conducted using as electrolyte either aqueous solutions or molten salt mixtures. Regardless of the electrolyte, the processes have some similarities:

1. Electrical energy does the chemical work and heat is generated due to the resistance in the electrolyte.
2. Low metal production rate per unit or floor area.
3. Large space requirements, capital intensive, and labor intensive.

Also these processes have some major differences:

1. Molten salt electrolysis is more energy intensive.
2. Current density may be a factor of 10–50 times higher in molten salt electrolysis, due to the higher ionic conductivity of the bath. Further, because a liquid product is formed, there is no problem with dendrite formation.
3. In molten salt electrolysis, the raw materials are added directly to the individual cells and no recirculation is possible.
4. In molten salt electrolysis, most metal products are tapped as liquids.
5. Molten salt electrowinning is used to produce the most reactive metals Al, Mg, Na, also Li, K, Ca and Be, and also very reactive gases (F_2).

Additionally, it is desired no chemical interaction of the electrolyte during the refining (winning) of metals so an "inert" electrolyte is highly desired. Such electrolyte must meet the following requirements:

(a) Stability

1. The electrolyte has to have a higher dissociation voltage than the salt from which the metal is produced.
2. The vapor pressure should be as low as possible.

(b) Solubility

1. The salt from which the product is formed, should have a reasonable solubility in the electrolyte.
2. The products formed should have as low as solubility as possible to prevent back-reactions.

(c) Physical–Chemical properties

1. The melt should have a low viscosity
2. The melt should have a high electrical conductivity
3. The melt should have a melting point as low as possible, but it should generally be slightly above that of the metal in order to produce the metal in a liquid form
4. The melt and the products formed should have a sufficient density difference to facilitate a rapid phase separation.

Due to different operational reasons, the actual metal production rate is only a fraction of the expected value; this difference is known current efficiency (η):

$$\eta = \frac{\text{actual metal production}}{\text{theoretical production}} \times 100 \tag{3.39}$$

Examples of Calculations

Example 1 Calculation of cell potentials

Determine the cell potential for the following reactions:

(a) $2Au^{+} + Cu = Cu^{2+} + 2Au$
(b) $Sn^{4+} + 2Ce^{3+} = Sn^{2+} + 2Ce^{4+}$
(c) $Fe^{2+} + V = Fe + V^{2+}$
(d) $2Ag^{+} + Sn = 2Ag + Sn^{2+}$.

Solution

By using the potentials in Table 3.1, we have:

For part (a)

The reaction: $2Au^+ + Cu = Cu^{2+} + 2Au$ can be decomposed into two half-cell reactions as:

$$\begin{array}{ll} Au^+ + e^- = Au; & E^o = 1.69\,V \\ Cu = Cu^{2+} + 2e^-; & E^o = -0.34\,V \end{array}.$$

Thus the cell voltage is: 1.69 − 0.34 = 1.35 V

For part (b)

The reaction: $Sn^{4+} + 2Ce^{3+} = Sn^{2+} + 2Ce^{4+}$ can be decomposed into:

$$\begin{array}{ll} Sn^{4+} + 2e^- = Sn^{2+}; & E^o = 0.15\,V \\ Ce^{3+} = Ce^{4+} + e^-; & E^o = -1.61\,V \end{array}.$$

Thus the cell voltage is: 0.15 − 1.61 = −1.46 V

For part (c)

The reaction: $Fe^{2+} + V = Fe + V^{2+}$ can be decomposed into:

$$\begin{array}{ll} Fe^{2+} + 2e^- = Fe; & E^o = -0.41\,V \\ V^{2+} + 2e^- = V; & E^o = -1.19\,V \end{array}$$

Thus the cell voltage is: −0.41 − (−1.19) = 0.78 V

For part (d)

The reaction $2Ag^+ + Sn = 2Ag + Sn^{2+}$ results from adding the reactions:

$$\begin{array}{ll} Sn^{2+} + 2e^- = Sn; & E^o = -0.14\,V \\ 2Ag^+ + e^- = 2Ag; & E^o = 0.80\,V \end{array}$$

Thus the cell voltage is: 0.80 − (−0.14) = 0.94 V

Example 2 Calculation of the equilibrium constant from standard cell voltage

Use the table of standard potentials to calculate the equilibrium constant at 25 °C for the reaction:

$$2Cu+ = Cu2+ + Cu.$$

Solution

From Table 3.1, we have the following half-reactions:

$$\begin{array}{ll} Cu^+ = Cu^{2+} + e^-; & E^o = -0.16\,V \\ Cu^+ + e^- = Cu; & E^o = 0.52\,V \end{array}.$$

Adding up these two reactions results in:

$$2Cu^{+} = Cu^{2+} + Cu; \quad E^{o} = -0.16 + 0.52 = 0.36\,V.$$

The free energy of the cell becomes:

$$\Delta G^{o} = -nFE^{o}. \tag{E2.1}$$

On the other hand, we also know that:

$$\Delta G^{o} = -RT\ \ln(K). \tag{E2.2}$$

Equating these expressions and noting that $n = 1$; thus the equilibrium constant becomes:

$$\begin{aligned} -nFE^{o} &= -RT\ \ln(K) \\ \ln(K) = \frac{FE^{o}}{RT} &= \frac{96,500 \times 0.36}{8.314 \times 298} \\ \ln(K) &= 14.02 \\ K &= 1.23 \times 10^{6}. \end{aligned}$$

Example 3 Calculation of the free energy and entropy of an electrochemical cell

The cell:

$$Pb|PbCl_2|HCl|AgCl|Ag,$$

where all components are pure solids are in contact with an electrolyte made of HCl. The cell voltage is 0.49 V at 298 K. The temperature coefficient of this cell at the given temperature is -1.84×10^{-4} VK^{-1}. Calculate the free energy and the entropy changes of the cell reaction at 25 °C.

Solution

To calculate the free energy of the cell reaction, we use Eq. (3.6):

$$\begin{aligned} \Delta G &= -nFE \\ \Delta G &= -2 \times 96,500 \times 0.49 \\ \Delta G &= -94,570 \quad J. \end{aligned}$$

To determine the entropy change, we use expression (3.7):

$$\begin{aligned} \Delta S &= nF\left[\frac{\partial E}{\partial T}\right]_P \\ \Delta S &= 2 \times 96,500 \times -1.84 \times 10^{-14} \\ \Delta S &= -35.5\,JK^{-1}. \end{aligned}$$

Example 4 Estimation of thermodynamic quantities for an electrochemical cell.

The reaction of a cadmium–calomel cell is represented by:

$$Cd + Hg_2Cl_2 = Cd^{2+} + 2Cl^{-} + 2Hg.$$

All components are in their standard state. The reversible cell voltage (E^o) varies with temperature, according to:

$$E^o = 0.67 - 1.062 \times 10^{-4}(T - 298) - 2.4 \times 10^{-6}(T - 298)^2. \tag{E4.1}$$

Calculate the values of ΔG^o, ΔS^o, and ΔH^o for the cell reaction at 40 °C.

Solution We need to determine the temperature coefficient of the cell. To do so, we must take the first derivative of E^o with respect of T:

$$\left[\frac{\partial E^o}{\partial T}\right]_P = \frac{\partial}{\partial T}\left(0.67 - 1.062 \times 10^{-4}(T - 298) - 2.4 \times 10^{-6}(T - 298)^2\right)$$

$$\left[\frac{\partial E^o}{\partial T}\right]_P = 1.324 \times 10^{-3} - 4.8 \times 10^{-6}T. \tag{E4.2}$$

Now it is necessary to calculate the cell voltage (E^o) at 40 °C (313 K) which is the test temperature. From equation (E4.1):

$$\begin{aligned} E^o &= 0.67 - 1.062 \times 10^{-4}(T - 298) - 2.4 \times 10^{-6}(T - 298)^2 \\ E^o &= 0.67 - 1.062 \times 10^{-4}(313 - 298) - 2.4 \times 10^{-6}(313 - 298)^2 \\ E^o &= 0.667\,\mathrm{V}. \end{aligned}$$

Since both the standard potential and the temperature coefficient of the cell are known, it is possible to calculate ΔG^o, ΔS^o and ΔH^o:

$$\begin{aligned} \Delta G^o &= -nFE^o \\ \Delta G^o &= -2 \times 96{,}500 \times 0.667 = -128{,}731\,\mathrm{J} \\ \Delta S^o &= nF\left[\frac{\partial E^o}{\partial T}\right]_P \\ \Delta S^o &= 2 \times 96{,}500 \times \left(1.324 \times 10^{-3} - 4.8 \times 10^{-6} \times 313\right) = -34.4\,\mathrm{JK^{-1}} \\ \Delta H^o &= nF\left[T\left[\frac{\partial E^o}{\partial T}\right]_P - E^o\right] \\ \Delta H^o &= 2 \times 96{,}500 \times \left(313\left(1.324 \times 10^{-3} - 4.8 \times 10^{-6} \times 313\right) - 0.667\right) = -139{,}539\,\mathrm{J}. \end{aligned}$$

It is worth noticing that from the computed enthalpy and entropy changes it is possible to calculate the Gibbs free energy associated to the cell using Eq. (1.21):

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -139,539 - 313 \times -34.4$$
$$\Delta G^{o} = -128,772\,\mathrm{J}.$$

This value differs 41 J from the one computed using Eq. (3.6). This error can be attributed to rounding off; additionally such small difference is not significant given the order of magnitude of the Gibbs free energy value.

Example 5 Use of experimental data to calculate the thermodynamic quantities associated to a cell.

For the cell:

$$\mathrm{Zn}|\mathrm{ZnCl_2}(x = 0.6) + \mathrm{KCl}(x = 0.4)|\mathrm{Cl_2C}.$$

The following data has been recorded:

T (°C)	*E* (V)
435	1.6447
436	1.6435
440	1.6420
453	1.6338
456	1.6325
461	1.6295
468	1.6235
469	1.6230
477	1.6178
490	1.6098
497	1.6052
525	1.5870
545	1.5750
546	1.5741
551	1.5695
561	1.5642
575	1.5540
583	1.5502

For this cell, E^{o} is 1.5635 V at 500 °C. Answer:

(a) What is the cell reaction?
(b) Plot the cell voltage vs temperature and determine E at 500 °C by interpolation
(c) Calculate the free energy, entropy and enthalpy of the cell reaction at 500 °C
(d) Calculate the activity and the activity coefficient of $\mathrm{ZnCl_2}$ in the electrolyte.

Solution

Part (a):

An electrochemical cell is represented by: anode | electrolyte | cathode; in this example we have: Zn | $ZnCl_2$(x = 0.6) + KCl(x = 0.4) | Cl_2 C, which means than zinc and chlorine gas are isolated at each electrode, but are in electrical contact trough the chlorides mixture. In view of this the overall cell reaction is:

$$\mathrm{Zn} + 2\mathrm{Cl}^- = \mathrm{Zn}^{2+} + \mathrm{Cl}_2 \uparrow + 2\mathrm{e}^-$$

Part (b)

Plotting the data provided: (Fig. 3.4)

To determine the cell potential at 500 °C, we can use the data provided to interpolate this value. To do so, we need the data at 497 and 525 °C, with these points, we have:

$$\frac{1.5870 - 1.6052}{525 - 497}\frac{\mathrm{V}}{^{\mathrm{o}}\mathrm{C}} = \frac{1.5870 - E_{500}}{525 - 500}\frac{\mathrm{V}}{^{\mathrm{o}}\mathrm{C}}$$

$$E_{500} = 1.587 - \frac{25}{28}(-0.0182) = 1.6033\,\mathrm{V}.$$

Thus the cell potential at 500 °C is 1.6033 V.

Another option is to run a linear regression on the data so we can estimate the slope of the corresponding line and its distance to the origin. Using this second approach, the calculated the cell voltage at 500 °C is 1.6029 V. This value is also plotted in the graph above (black triangle). There is good agreement between the computed values.

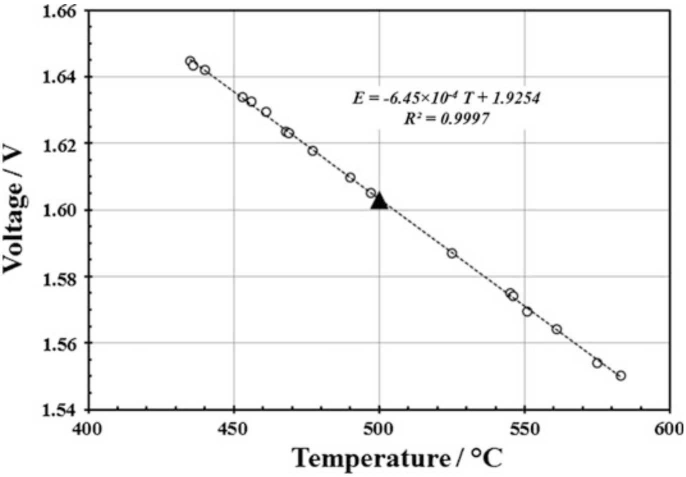


Fig. 3.4 Voltage versus temperature plot

Part (c)

Form the linear regression on the data supplied, we can express the cell voltage as a function of the temperature and thus calculate the cell temperature coefficient:

$$E = -6.45 \times 10^{-4} T + 1.9254$$
$$\left[\frac{\partial E}{\partial T}\right]_P = -6.45 \times 10^{-4}.$$

The cell free energy at 500 °C is:

$$\Delta G = -nFE$$
$$\Delta G = -2 \times 96{,}500 \times 1.6029 = -309{,}360\,\mathrm{J}.$$

At 500 °C the cell entropy is:

$$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]$$
$$\Delta S = 2 \times 96{,}500 \times -6.45 \times 10^{-4} = -124.5\,\mathrm{JK}^{-1}.$$

The enthalpy of the cell at 500 °C is:

$$\Delta H = nF\left[T\left[\frac{\partial E}{\partial T}\right]_P - E\right]$$
$$\Delta H = 2 \times 96{,}500\left(773 \times -6.45 \times 10^{-4} - 1.6029\right) = -405{,}587\,\mathrm{J}.$$

Part (d)

The standard free energy of the cell is given by:

$$\begin{array}{l} \Delta G_{\mathrm{cell}} = G_{\mathrm{cell}} - G^{\mathrm{o}}_{\mathrm{cell}} \\ \Delta G_{\mathrm{cell}} = -nFE_{\mathrm{cell}} - \left(-nFE^{\mathrm{o}}_{\mathrm{cell}}\right) \\ \Delta G_{\mathrm{cell}} = nF\left(E^{\mathrm{o}}_{\mathrm{cell}} - E_{\mathrm{cell}}\right) \\ \Delta G_{\mathrm{cell}} = 2 \times 96{,}500(1.5635 - 1.6029) = -7604 \end{array}.$$

With the cell free energy change, we can now estimate the activity coefficient of $ZnCl_2$:

$$\Delta G_{\mathrm{cell}} = RT\,\ln\left(\gamma_{\mathrm{ZnCl_2}}\right)$$
$$\gamma_{\mathrm{ZnCl_2}} = \exp\left(\frac{\Delta G_{\mathrm{cell}}}{RT}\right) = \exp\left(-\frac{7604}{8.314 \times 773}\right)$$
$$\gamma_{\mathrm{ZnCl_2}} = 0.306.$$

Having this value, it is possible to compute the activity of zinc chloride:

$$a_{ZnCl_2} = x_{ZnCl_2} \times \gamma_{ZnCl_2}$$
$$a_{ZnCl_2} = 0.6 \times 0.306$$
$$a_{ZnCl_2} = 0.184.$$

Further discussion on how to calculate the activity or the activity coefficient of a component in a mixture as a function of Gibbs free energy will be presented in the next chapter. In the meantime, we advise the reader to accept these formulae as shown.

Example 6 Use of experimental data to calculate thermodynamic quantities in an electrolytic cell

The cell:

$$\mathrm{Pb}|\mathrm{PbCl_2} + \mathrm{LiCl}|\mathrm{Pb} - \mathrm{Bi}$$

Yielded the following data at 700 K

x_{Pb}	E [V]	dE/dT [V K^{-1}]
0.848	0.00532	7.40×10^{-6}
0.720	0.01148	1.44×10^{-5}
0.600	0.01929	2.08×10^{-5}
0.496	0.02782	2.78×10^{-5}
0.414	0.03594	3.76×10^{-5}
0.328	0.0454	4.64×10^{-5}
0.230	0.05976	6.44×10^{-5}
0.111	0.08615	1.02×10^{-4}

(a) Calculate the values of a_{Pb}, ΔS_{Pb} and ΔH_{Pb} for each of these compositions.
(b) At the composition $x_{Pb} = 0.6$, if a potential of 19.29001 mV were applied to the cell so as to oppose the measured e.m.f. would the cell generate or absorb heat?

Solution

In this cell lead is dissolved into a Pb–Bi alloy; as more lead is mixed with the bismuth, the activity of the former should increase from zero (unmixed bismuth) toward unity (unmixed lead). As the solution gets richer in lead, the associated entropy and enthalpy should change accordingly.

To calculate the activity of lead in the Pb–Bi alloy, we need to use Eq. (3.6) along with Eq. (1.38):

$$\Delta G^{o} = -nFE^{o} \tag{3.6}$$

$$\Delta G^{o} = -RT \ln K. \tag{1.38}$$

The dissolution of lead in bismuth can be expressed as:

$$\mathrm{Pb} = \mathrm{Pb}_{\mathrm{Bi}} \tag{E6.1}$$

From this expression, we can write down the equilibrium constant as:

$$K = \frac{a_{\mathrm{Pb_{Bi}}}}{a_{\mathrm{Pb}}}. \tag{E6.2}$$

The activity of pure lead is 1, therefore the equilibrium constant becomes the activity of lead in solution with bismuth, and therefore we have:

$$-RT\ \ln\left(a_{\mathrm{Pb_{Bi}}}\right) = -nFE^{\mathrm{o}}. \tag{E6.3}$$

From the given data, we have that $T = 700$ K, $n = 2$. Substituting the corresponding voltage values in expression (E6.3) would yield the activity of the dissolved lead. This is shown in the table below.

To calculate the entropy of the cell as the lead content in the mixture changes, we need to take the same approach as before. In this case the values of the cell temperature coefficient must be inserted in Eq. (3.8) to compute the entropy change associated to lead dissolution in bismuth. Results are shown in the table below. The same procedure is taken to compute the enthalpy change.

Table (3.2) summarizes all the calculations of these thermodynamic quantities as a function of lead concentration in the Pb–Bi mix.

Plotting the data in Table 3.2, results in: (Fig. 3.5)

For part (b)

ΔH_{Pb} at $x_{\mathrm{Pb}} = 0.6$ is negative, the cell would release heat.

Example 7 Estimation of energy consumption in copper deposition.

Copper refining can be done by depositing Cu^{2+} from an acidic $\mathrm{CuSO_4}$ solution onto copper cathodes by applying an electric current.

Determine:

(a) How many kWh are required for the electrolytic refining of 1 ton of copper if 0.4 V are applied to the electrolysis cell and all the current supplied is used to deposit the metal.

Table 3.2 Activity of lead and thermodynamic quantities as a function of lead content in bismuth

x_{Pb}	a_{Pb}	ΔS_{Pb} [J K^{-1}]	ΔH_{Pb} [J]
0.848	0.8383	1.43	−27.02
0.720	0.6834	2.78	−270.2
0.600	0.5274	4.01	−912.89
0.496	0.3975	5.37	−1613.48
0.414	0.3037	7.26	−1856.66
0.328	0.2219	8.96	−2493.56
0.230	0.1378	12.43	−2833.24
0.111	0.0574	19.69	−2846.75

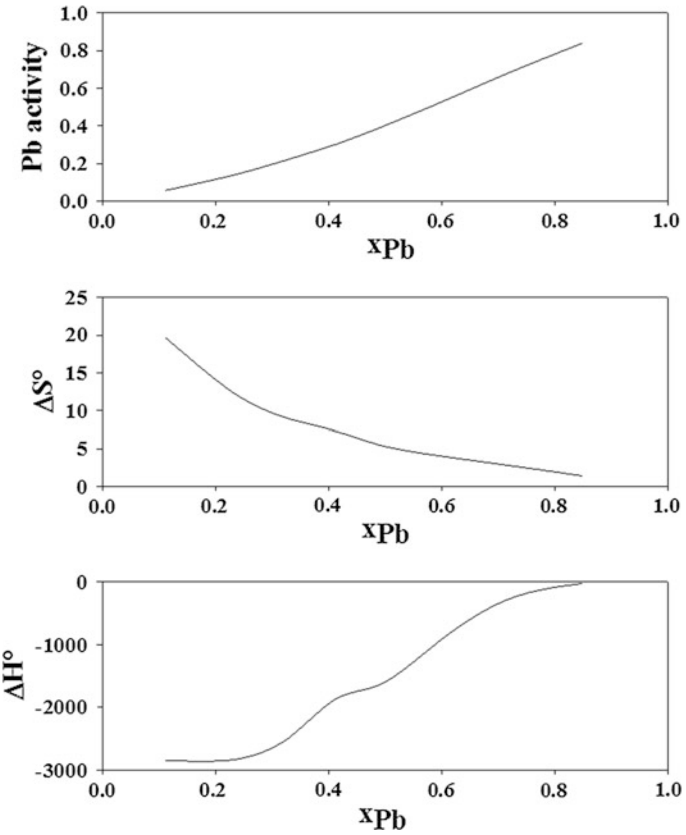


Fig. 3.5 Thermodynamic quantities as lead dissolves in bismuth at 700 K (427 °C)

(b) How would the energy requirements would change if the voltage is lowered to 0.2 V?

(c) How much heat is liberated in each case?

Solution

For part (a):

We need to use Eq. (3.37) to determine the current supplied to the cell:

$$m = \frac{i \times t}{F}\frac{M}{z}$$

Assuming an hour of operation and solving for i:

$$i = \frac{Fzm}{tM}$$

Substituting values: $F = 96{,}500$ A s mole^{-1}, $t = 3600$ s, $z = 2$, $m = 10^6$ g, $M = 63.54$ g mole^{-1}; we obtain:

$$i = \frac{(96{,}500)(2)\left(10^6\right)}{(3600)(63.54)} = 8.44 \times 10^5\,\mathrm{A}$$

Since we know the amount of current circulating through the cell as well as the voltage supplied, we can calculate the power required:

$$P = i\mathrm{V} = \left(8.44 \times 10^5\right)(0.4) = 3.376 \times 10^5\,\mathrm{W}.$$

Since the current was supplied for an hour, then the power needed is 337.6 kWh.

For part (b)

Since we cut the voltage by a half, the power needed when using only 0.2 V is 168.8 kWh.

For part (c)

All the energy supplied to the cell via electric current has to be released eventually, therefore from the First law of Thermodynamics, we can estimate the heat losses from the power supplied. Just remember that 1 kWh = 3.6 MJ, thus the liberated heat when applying 0.4 V is (337.6 kWh × 3.6 MJ kWh^{-1}) 1215.4 MJ: Similarly when 0.2 V are used, the heat released is 607.7 MJ.

Example 8 Estimation of current efficiency in a cell for copper deposition.

A set up for copper refining consists of 4 cells. After running a test for 7.33 h, with an average current of 34.2 A, results in 1089 g of deposited copper. What is the current efficiency of the process?

Solution

We need to use Eq. (3.37) to determine the theoretical amount of current needed to deposit the specified amount of copper:

$$m = \frac{itM}{zF}.$$

Substituting values: $m = 1089$ g, $t = 26{,}388$ s, $M = 63.54$ g mole^{-1}, $F = 96{,}500$ A s mole^{-1}, $z = 2$ into Eq. (3.37) and solving for i:

$$i\mathrm{th} = \frac{mzF}{tM} = \frac{1089 \times 2 \times 96{,}500}{26{,}388 \times 63.54} = 125.3\,\mathrm{A}.$$

Each cell uses 34.2 A; therefore the total amount of current supplied to the cells is 136.8 A. To deposit the copper the cells would only utilize 125.3 A, thus the current efficiency (η) is defined by the ratio of theoretical current used to actual current used:

$$\eta = \frac{i\mathrm{th}}{i_{\mathrm{supl}}} \times 100$$

$$\eta = \frac{125.3\,\mathrm{A}}{136.8\,\mathrm{A}} \times 100 = 91.6\%.$$

Example 9 Effect of process variables on the acidity of an electrolyte.

It has been suggested to produce metallic nickel powders by hydrogen reduction of a nickel sulfate solution. The reduction reaction would be:

$$\mathrm{Ni}^{2+} + \mathrm{H}_2 = \mathrm{Ni} + 2\mathrm{H}^{+}.$$

For this reaction, its standard free energy change is:ΔG^{o} = 640,15 − 58.948 T/J mole^{-1}.

Discuss the effect of the following variables and calculate the final value of the solution pH for the given variables.

(a) Temperature: 100 and 200 °C
(b) P_{H_2}: 10 and 100 atm
(c) $a_{\mathrm{Ni}}{}^{2+}$: 10^{-2} and 10^{-3}

Solution

We need to determine the equilibrium constant (K) of the nickel reduction reaction:

$$\mathrm{Ni}^{2+} + \mathrm{H}_2 = \mathrm{Ni} + 2\mathrm{H}^{+}; \quad \mathrm{K} = \frac{a_{\mathrm{Ni}} \times a^2_{\mathrm{H}^+}}{a_{\mathrm{Ni}^{2+}} \times P_{\mathrm{H}_2}}. \tag{E9.1}$$

As seen, the K value depends on the activities (concentration) of the different species involved in the reaction. In addition, we know we can express the equilibrium constant in terms of the free energy change:

$$\Delta G^{\mathrm{o}} = -RT\,\ln(K).$$

With this information, we can discuss the effect of the variables on the acidity of the resulting solution:

For part (a):

Since we are looking to estimate the effect of process temperature on the acidity of the final solution, we need to keep fixed a_{Ni}, a^{2+}_{Ni} and P_{H2} and solve for a^{+}_{H} as a function of temperature. To simplify our calculations the fixed variables are set as 1, thus we can establish how temperature influences the acidity of the electrolyte:

If T = 100 °C = 373 K

$$\Delta G^{o} = 64,015 - 58.948\,\mathrm{T}$$
$$\Delta G^{o} = 64,015 - 58.948(373) = 42027.4\,\mathrm{J}$$
$$K = \exp\left(-\frac{\Delta \mathrm{G}^{o}}{\mathrm{RT}}\right) = \exp\left(-\frac{42027.4}{8.314(373)}\right)$$
$$K = 1.3 \times 10^{-6}$$
$$a_{\mathrm{H}^+} = \sqrt{\frac{K \times a_{\mathrm{Ni}^{2+}} \times P_{\mathrm{H}_2}}{a_{\mathrm{Ni}}}}; \quad a_{\mathrm{Ni}^{2+}}, P_{\mathrm{H}_2}, a_{\mathrm{Ni}} = 1$$
$$a_{\mathrm{H}^+} = \sqrt{K} = \sqrt{1.3 \times 10^{-6}} = 1.14 \times 10^{-3}.$$

From this, we can calculate the final pH since: pH ≈ −log ($a_{\mathrm{H}}{}^{+}$)

$$\mathrm{pH} \approx -\log(a_{\mathrm{H}^+})$$
$$\mathrm{pH} \approx -\log\left(1.14 \times 10^{-3}\right)$$
$$\mathrm{pH} \approx 2.94.$$

If we now increase the temperature to 200 °C (473 K), we need to repeat the calculations to obtain the final pH:

$$\Delta G^{o} = 64,015 - 58.948(473) = 36,132.6\,\mathrm{J}$$
$$\ln K = -9.19$$
$$K = 1.02 \times 10^{-4}$$
$$a_{\mathrm{H}^+} = \sqrt{K} = \sqrt{1.02 \times 10^{-4}} = 1.01 \times 10^{-2}$$
$$\mathrm{pH} \approx -\log\left(1.01 \times 10^{-2}\right) = 1.99.$$

Therefore, as temperature increases, so does the acidity in the electrolyte.

For part (b):

We need to keep T, a_{Ni}, and a_{Ni}^{2+} fixed. The Temperature is set at 100 °C and the latter two variables are kept as one. By fixing the temperature, we have set the equilibrium constant as well. With this information we can estimate how the partial pressure of hydrogen affects the final acidity:

$$\text{if}\, P_{\mathrm{H}_2} = 10\,\mathrm{atm};$$
$$a_{\mathrm{H}^+} = \sqrt{\frac{K \times a_{\mathrm{Ni}^{2+}} \times P_{\mathrm{H}_2}}{a_{\mathrm{Ni}}}}; \quad a_{\mathrm{Ni}^{2+}} = a_{\mathrm{Ni}} = 1$$
$$a_{\mathrm{H}^+} = \sqrt{K \times P_{\mathrm{H}_2}} = \sqrt{1.3 \times 10^{-6}(10)} = 3.61 \times 10^{-3}$$
$$\mathrm{pH} \approx -\log\left(3.61 \times 10^{-3}\right) = 2.44$$
$$\text{if}\, P_{\mathrm{H}_2} = 100\,\mathrm{atm};$$
$$a_{\mathrm{H}^+} = \sqrt{1.3 \times 10^{-6}(100)} = 0.0114$$
$$\mathrm{pH} \approx -\log(0.0114) = 1.94.$$

From these calculations, it is clear that when partial pressure of hydrogen gas increases, the solution becomes more acidic.

Part (c):

In this case, the activity of nickel ions vary, which means that temperature, hydrogen pressure and concentration of H^+ ions must be fixed. Again choosing $T = 100$ °C, results in setting the equilibrium constant ($K = 1.3 \times 10^{-6}$), thus:

$$\begin{aligned}
&\text{if}\, a_{Ni^{2+}} = 10^{-2};\\
&a_{H^+} = \sqrt{K \times a_{Ni^{2+}}}\\
&a_{H^+} = \sqrt{1.3 \times 10^{-6}(10^{-2})} = 1.14 \times 10^{-4}\\
&\mathrm{pH} \approx -\log\left(1.14 \times 10^{-4}\right) = 3.94\\
&\text{if}\, a_{Ni^{2+}} = 10^{-3};\\
&a_{H^+} = \sqrt{1.3 \times 10^{-6}(10^{-3})} = 3.6 \times 10^{-5}\\
&\mathrm{pH} \approx -\log\left(3.6 \times 10^{-5}\right) = 4.44.
\end{aligned}$$

Therefore if the amount of nickel ions decrease, the less acidic the solution becomes.

Example 10 Calculation of a copper electrolytic refining plant capacity

1. An electrolytic copper refinery has 458 tanks of which 42 are used to produce starting sheets. Anodes weigh 240 kg. Each tank has 22 anodes and 23 cathodes. There are three pulls of cathodes per anode. The current in each tank is 5400 A, and its efficiency is 92%. 11% of the anodes are turned into scrap.

Calculate: (a) The mass of each cathode. (b) The capacity of the refinery.

2. A second refinery has 39 cathodes (0.95 m × 0.95 m) and 38 anodes to a cell. The anode weighs 240 kg and lasts 28 days. There are two pulls of cathodes per 28 days. The starting sheets weigh 4.54 kg. The current efficiency is of 93% and 2 V are applied to this cell.

Calculate: (c) What is the mass of the copper deposited on the cathode when pulled. (d) What is the percentage of anode scrap? (e) What is the cathode current density? (f) How many kg of copper are produces by kilowatt-day?

Solution

For part (a)

There are 22 cathodes in each tank whose weight is 240 kg. From this mass, 89% is concerted into copper cathodes, and 3 anodes are needed to obtain a cathode. Since the mass of the starting anodes is given, and the ratio anode/cathode is also known, we do not need to use Faraday's laws to estimate the weight of each cathode.

Therefore the mass of a cathode is:

$$240\,\mathrm{kg_{anodes}} \times 0.89 \times \frac{1_{\mathrm{cathode}}}{3_{\mathrm{anodes}}} = 71.2\,\mathrm{kg_{cathode}}$$

For part (b)

To produce the copper cathodes there are 416 tanks available. The mass of copper that is produced in a daily basis is given by Fraday's law. We need to assume a processing time of 24 h:

$$\mathrm{m_{Cu}} = n_{\tan\,\mathrm{ks}} \times \frac{i \times t \times M}{z \times F},$$

where $\mathrm{m_{Cu}}$ is the mass of copper in g/day; i is the current (5400 A × 0.92); t is the time (3600 s/h × 24 h); $M = 63.54$ g/mole; $z = 2$; $F = 96{,}500$ C/mole; $n_{\tan\,\mathrm{ks}}$ = number of tanks for electrolysis. Substituting these values:

$$\mathrm{m_{Cu}} = 416 \times \frac{(5400 \times 0.92) \times (3600 \times 24) \times 63.54}{2 \times 96500} = 59 \times 10^6\,\frac{\mathrm{g_{Cu}}}{\mathrm{day}}.$$

Therefore the plant can produce 59 tons of copper per day.

For part (c):

In this case, two anodes are needed to produce a cathode, assuming 93% current efficiency and subtracting the mass of the initial sheet (4.5 kg), gives the weight of each cathode:

$$240\,\mathrm{kg_{anode}} \times 0.93 \times \frac{1_{\mathrm{cathode}}}{2_{\mathrm{anodes}}} = 111.6\,\mathrm{kg_{cathode}}$$

$$w_{\mathrm{cathode}} = 111.6 - 4.5 = 107\,\mathrm{kg}.$$

For part (d)

Since two anodes are needed to produce a cathode. The amount of copper consumed from the each anode is 107 kg × 2 = 214 kg; then the percentage of anode scrap is:

$$\%\mathrm{scrap} = 100 \times \left(1 - \frac{\mathrm{w_{Cu,\,deposited}}}{\mathrm{w_{Cu,\,anode}}}\right)$$

$$\%\mathrm{scrap} = 100 \times \left(1 - \frac{214}{240}\right) = 10.8\%.$$

Therefore 10.8% or 26 kg of the anode is thrown away as scrap.

For part (e):

To estimate the current density, first we need to know the amount of current applied to the cell:

$$i = \frac{m \times z \times F}{t \times M} \times \frac{1}{\eta} = \frac{(107 \times 10^3) \times 2 \times 96500}{(3600 \times 24 \times 28) \times 63.54} \times \frac{1}{0.93}$$

$$i = 144.5\,\mathrm{A}.$$

The current density is the ratio current/cathode area, therefore:

$$\text{current density} = \frac{i}{\mathrm{A}} = \frac{144.5}{0.95^2} = 160\,\frac{\mathrm{A}}{\mathrm{m}^2}.$$

For part (f)
The power supplied to the cell is:

$$P = i \times \mathrm{V} = 144.5 \times 2 = 289\,\mathrm{W}.$$

The amount of copper produced daily is:

$$\mathrm{m_{Cu}} = \frac{i \times \eta \times t \times M}{z \times F} = \frac{144.5 \times 0.93 \times (3600 \times 24) \times 63.54}{2 \times 96{,}500}$$

$$\mathrm{m_{Cu}} = 3823\,\mathrm{g_{Cu}}.$$

The amount of copper produced per unit of power is:

$$\frac{\mathrm{m_{Cu}}}{P} = \frac{3823\,\mathrm{g_{Cu}}}{289\,\mathrm{W}} = 13.22\,\frac{\mathrm{kg_{Cu}}}{\mathrm{kW}}.$$

Therefore 13.22 kg of copper are produced per kW per day.

Mixing and Solution Thermodynamics

4

Introduction

In nature, we rarely find pure components or elements. We live in a world made of mixtures; therefore, we should shift our attention to mixtures components in solids, liquids, and gases. Because of this, we are more interested in the thermodynamics of mixing.

Solution thermodynamics has three properties that are of primary importance: heats, entropies, and Gibbs free energies of mixing. These properties can be expressed in terms of integral and differential (partial molar) quantities.

Integral properties are related to processes in which solutions are obtained from pure components. Take, for example, pure elements A and B. To form a mixture of these elements at constant pressure and temperature.

The mixing of n_A moles of A with n_B moles of B can be represented in the form of a chemical reaction:

$$n_A A + n_B B = \left((A)_{n_A} (B)_{n_B} \right) \tag{4.1a}$$

If instead of using the actual number of moles, we define the molar fraction as: $x_i = n_i/(n_A + n_B)$ with i = A or B, then expression (4.1a) can be rewritten as:

$$x_A A + x_B B = (x_A x_B) \tag{4.1b}$$

This process is sketched in Fig. 4.1.

G. Plascencia and D. Jaramillo, *Basic Thermochemistry in Materials Processing*,
DOI 10.1007/978-3-319-53815-0_4

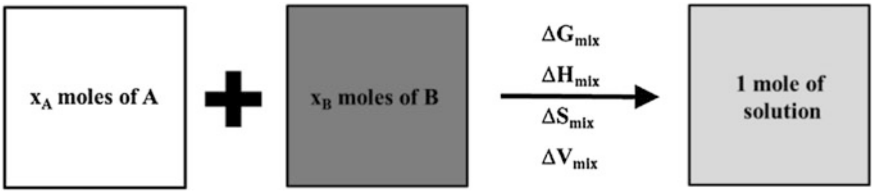


Fig. 4.1 The making of a binary mix (solution) from components A and B

In order to continue our discussion of solution thermodynamics, we need to define the term solution. A possible definition would be[1]:

A solution whether it be gaseous, liquid, or solid is a homogeneous mixture of two or more substances (components); it constitutes a single phase.

The Concept of Activity

In Chap. 3 it was introduced by the term of activity, more precisely this term should be called chemical activity. In the next paragraphs we are going to define such quantity and how it relates to chemical equilibria in solutions and in phase transitions.

Consider any chemical reaction such as:

$$aA + bB = cC + dD \tag{4.2}$$

The equilibrium constant of reaction (4.2) is the ratio of the product of the concentrations of reaction products over that of the reactants taking place in it:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{4.3}$$

The larger the value of K, the larger the concentration of reaction products and the less the concentration of the reactants. Thus, the rate of a chemical reaction is proportional to the active mass taking place in the reaction. This is known as molecular concentration of the chemicals involved.

However, if there are mutual inter atomic interactions (collisions/repulsions), atoms, or molecules are less free to interact among them, therefore, the apparent concentration either decrease or increase, respectively. To overcome this, the actual concentrations of the species taking part in chemical reactions or any transformation can be substituted by the "activity" of each of them. Henceforth, the equilibrium constant now becomes:

---

[1] Parker R.H., An introduction to chemical metallurgy, Pregamon Press, London, 1967.

$$\mathrm{K} = \frac{a_{\mathrm{A}}^{a} \times a_{\mathrm{B}}^{b}}{a_{\mathrm{C}}^{c} \times a_{\mathrm{D}}^{d}} \tag{4.4}$$

It should be emphasized that the equilibrium constant strongly depends on the temperature and the pressure of the system under study. Because of this feature, the activity (and activity coefficients) is directly related to the change in Gibbs free energy.

In its simpler form, the activity of a component can be defined as the ratio of its vapor pressure (P_i) over a solution, to the vapor pressure of the pure component ($P_i°$) at the same temperature, and assuming ideal gas behavior in the vapor phase:

$$a_i = \frac{P_i}{P_i^{\circ}} \tag{4.5}$$

From definition (4.5) it is evident that the activity of any component may vary from 0 to 1 and is a dimensionless quantity.

In addition to that, in the case of gaseous species, it is possible to relate the gas concentration to the total pressure of the system through their partial pressure (Dalton's Law), i.e.,

$$P_i = x_i \times P \tag{4.6}$$

where P_i is the partial pressure of the *i*th gaseous component in solution, x_i is its molar fraction, and P is the total pressure of the system.

The molar fraction of any component in any solution is the number of moles of that component (n_i) divided by the total number of moles $\left(n = \sum_{1}^{j} n_i\right)$ in the solution, i.e.

$$x_i = \frac{n_i}{n} \tag{4.7}$$

In the case of pure condensed species (solids and liquids) their activities can be considered as the unity.

Under ideal conditions, all components in a solution act independently of one another; however, in real situations this simply does not happen, and all components in a mixture interact between each other up to some extent. Such interactions would reduce the availability of any component for other chemical reactions, and the rate of reactions would no longer depend on the concentration of the components, but on a fraction of that concentration; this fraction is the activity; therefore, the activity of a substance in a solution is expected to vary with composition of the solution and with the temperature.

Partial Molar Quantities

The total value of any thermodynamic quantity, such as volume, enthalpy, entropy, Gibbs free energy, or Helmholtz free energy of a solution consisting of n_1, n_2, …, n_n moles of components 1, 2, …, n, might be expressed in terms of pressure, temperature, and the amount of moles of each component in solution as:

$$\Psi = \Psi(P, T, n_1, n_2, \ldots, n_n) \tag{4.8}$$

With Ψ being V, H, S, G, A, etc. The total derivative of expression (4.8) is:

$$\begin{aligned} d\Psi = {} & \left(\frac{\partial \Psi}{\partial P}\right)_{T,n_1,n_2,n_n} + \left(\frac{\partial \Psi}{\partial T}\right)_{P,n_1,n_2,n_n} + \left(\frac{\partial \Psi}{\partial n_1}\right)_{P,T,n_2,n_n} \\ & + \ldots + \left(\frac{\partial \Psi}{\partial n_n}\right)_{P,T,n_1,n_2} \end{aligned} \tag{4.9}$$

Or simply:

$$d\Psi = \left(\frac{\partial \Psi}{\partial P}\right)_{T,n_1,n_2,n_n} + \left(\frac{\partial \Psi}{\partial T}\right)_{P,n_1,n_2,n_n} + \overline{\Psi}_1 + \overline{\Psi}_2 + \ldots + \overline{\Psi}_n \tag{4.9a}$$

In general, form these last two equations, it can be defined:

$$\overline{\Psi}_i = \left[\frac{\partial \Psi}{\partial n_i}\right]_{P,T,n_1,n_2,\ldots n_{i-1},n_{i+1},n_n} \tag{4.10}$$

The term $\overline{\Psi}_i$ is known as the partial molar property (V, H, S, G, A, etc.) of the ith component in solution. These quantities are defined as the rate of change of the quantity (extensive) Ψ when an infinitesimal amount of component i is added to the system while keeping, the pressure, the temperature, and the amounts of all other components in the mixture fixed.

Partial molar properties are intensive. In any system, at constant pressure and temperature, the total value of the extensive property Ψ is:

$$\Psi = \sum_{i=1}^{n} n_i \overline{\Psi}_i \tag{4.11}$$

The value of the extensive property per mole of solution is:

$$\Psi = \sum_{i=1}^{n} x_i \overline{\Psi}_i \tag{4.12}$$

Thus, we have the following relationships for the different thermodynamic quantities thus far discussed:

$$
\begin{aligned}
V &= x_1\overline{V}_1 + x_2\overline{V}_2 + \ldots + x_n\overline{V}_n \\
H &= x_1\overline{H}_1 + x_2\overline{H}_2 + \ldots + x_n\overline{H}_n \\
S &= x_1\overline{S}_1 + x_2\overline{S}_2 + \ldots + x_n\overline{S}_n \\
G &= x_1\overline{G}_1 + x_2\overline{G}_2 + \ldots x_n\overline{G}_n \\
A &= x_1\overline{A}_1 + x_2\overline{A}_2 + \ldots x_n\overline{A}_n
\end{aligned}
\tag{4.13}
$$

where *V*, *H*, *S*, *G,* and *A* represent the molar volume, enthalpy, entropy, Gibbs free energy, and Helmholtz free energy, respectively. The partial molar Gibbs free energy is also known as the chemical potential (μ).

The various partial molar quantities are related to each other by some of the relationships developed in Chap. 1:

$$
\begin{aligned}
&\overline{G}_i = \overline{H}_i - T\overline{S}_i \\
&\left(\frac{\partial \overline{G}_i}{\partial T}\right)_P = -\overline{S}_i \\
&\left[\frac{\partial\left(\frac{\overline{G}_i}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right] = \overline{H}_i \\
&\left(\frac{\partial \overline{G}_i}{\partial P}\right)_T = \overline{V}_i
\end{aligned}
\tag{4.14}
$$

The Concept of Chemical Potential

Recalling expression (1.27), the Gibbs free energy for a system comprised by a single component is defined as:

$$
\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{1.27}
$$

This implies that Gibbs free energy solely depends on pressure and temperature, i.e., $G = G(P, T)$.

However, in systems with more than a single component, where the amount of the substances present continuously change due to the advance of a chemical reaction or because a given species is present in different concentrations in several phases simultaneously (ice and water, water and vapor, etc.), results in extending the dependency of Gibbs free energy to the number of moles of each component present in the system; using Eq. (4.8), it results in:

$$
G = G(P, T, n_1, n_2, \ldots, n_n) \tag{4.15}
$$

Taking the derivative of expression (4.15), results in:

$$G = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_n} + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,n_n} + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2,n_n} + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1,n_n} + \left(\frac{\partial G}{\partial n_n}\right)_{P,T,n_1,n_2} \tag{4.16}$$

Expression (4.16) shows that the variation of Gibbs free energy with respect to the number of moles of the *i*th substance in the mixture is:

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \tag{4.17}$$

The quantity in expression (4.17) is called chemical potential of the *i*th component in the mixture, thus we can rewrite Eq. (4.17) as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \tag{4.17a}$$

The chemical potential of a substance defines the rate of change of Gibbs free energy per mole of substance present and it is an intensive quantity since it depends on the mass of the system.

From definition (4.17a) we can see that under fixed temperature and pressure, the rate of change in the amount of the other components while the system is:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \times \mathrm{d}n_i = \mu_i \mathrm{d}n_i \tag{4.18}$$

Integrating (4.18) after adding 1 mol of material, results in:

$$G = \mu_i n_i \tag{4.19}$$

Equation (4.19) means that multiplying the chemical potential by the amount of substance within the system gives the free energy (Gibbs) of that pure component. Now dividing (4.19) by the number of moles of the *i*th component in the system gives:

$$\mu_i = \frac{G}{n_i} \tag{4.20}$$

Equation (4.20) signifies that the chemical potential (μ) represents the Gibbs free energy per mole of a pure substance.

The chemical potentials are applicable to phase transformations and chemical equilibria for pure substances and mixtures.

Also, form Eq. (4.17a) we notice that the chemical potential of a substance in solution is defined as the partial derivative of the Gibbs free energy with respect of the number of moles of that particular component in solution, thus we can now define the partial Gibbs free energy of the *i*th component in solution:

$$\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i \tag{4.21}$$

On the other hand, we can express the Gibbs free energy change in terms of the chemical potential of any component in solution. Recalling Eq. (1.32) we have:

$$G - G^\circ = RT \ln a \tag{1.32}$$

Substituting definition (4.21) into expression (1.32)

$$\overline{G}_i - \overline{G}_i^\circ = RT\ \ln(a_i) = \Delta\overline{G}_i \tag{4.22}$$

Equation (4.22) represents the relative partial molar Gibbs free energy of the *i*th component in solution.

Two problems arise from this definition: (1) the selection of the appropriate species and (2) the selection of the proper standard state.

The properties of the selected species usually have been already measured (heat and entropy content, heat capacity, etc.). Whereas the standard state is selected in such a way that it is the most convenient for calculation purposes.

Conversely, the activity of a component can also be defined as the ratio of the fugacity[2] of a substance to its fugacity in the standard state. This fugacity (*f*) can be approached in terms of pressure, as previously shown.

From this discussion, we can also define the chemical activity of a component in solution as:

$$\ln a_i \equiv \frac{\mu_i - \mu_i^o}{RT} \tag{4.23}$$

where μ_i is the chemical potential of species *i* in solution and $\mu_i{}^\circ$ is the standard state of *i* at the same temperature and pressure as the solution.

In those systems where the amounts of the substances constituting them change because of a chemical reaction or by the formation of a solution, the free energy in addition to temperature, and pressure will also depend on the amounts of the components within the system. Take, for example, a system made of components *i* and *j*; the free energy of such system can be defined as:

---

[2] Fugacity can be defined as a measure of the tendency of a gas to escape or expand. It is the activity of a gas. Fugacity is not the same as pressure but it is closely related to it. The need for the fugacity is to have a form for the chemical potential that looks like that of an ideal gas but still obeys the rule that: $\left(\frac{\partial \mu}{\partial P}\right)_T = V$.

$$G = G(T, P, n_i, n_j) \tag{4.24}$$

By assuming this functionality, the free energy of the system now becomes:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \mu_i \mathrm{d}n_i + \mu_j \mathrm{d}n_j \tag{4.25}$$

If both the temperature and the pressure of the system are fixed, then the Gibbs free energy only relates to the chemical potential of the components:

$$\mathrm{d}G = \mu_i \mathrm{d}n_i + \mu_j \mathrm{d}n_j = \sum_{i=1}^{n} \mu_i \mathrm{d}n_i \tag{4.26}$$

As systems grow in terms of the number of components, the variation in Gibbs free energy becomes:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{n} \mu_i \mathrm{d}n_i \tag{4.27}$$

Because of the relationship between G and μ, it becomes evident that likewise the Gibbs free energy, the chemical potential can be regarded as the driving force which determines if a component would transfer within the system or move away from it or simply undergo a chemical reaction.

Moreover, if a system is comprised of different phases (say A and B), the chemical potential of the *i*th component relates to Gibbs free energy of each of these phases by:

$$\mathrm{d}G_\mathrm{A} = \mu_i^{(\mathrm{A})} \mathrm{d}n_i \tag{4.28a}$$

$$\mathrm{d}G_\mathrm{B} = \mu_i^{(\mathrm{B})} \mathrm{d}n_i \tag{4.28b}$$

If phase equilibrium has not been attained, *i*th component will be transferred from the phase with higher chemical potential to the phase with lower chemical potential, until reaching the equilibrium condition. In view of this, assuming that the molar transfer occurs from phase A to phase B as indicates Fig. 4.2. Equations (4.28a) and (4.28b) can be rewritten as:

$$\mathrm{d}G_\mathrm{A} = \mu_i^{(\mathrm{A})} \times -\mathrm{d}n_i \tag{4.29a}$$

$$\mathrm{d}G_\mathrm{B} = \mu_i^{(\mathrm{B})} \times \mathrm{d}n_i \tag{4.29b}$$

The total Gibbs free energy change due to transferring the *i*th component from phase A to phase B becomes:

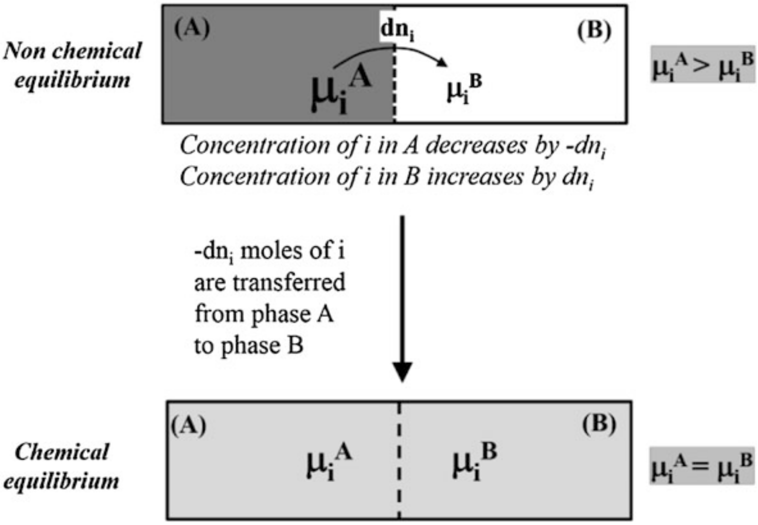


Fig. 4.2 Reaching the chemical equilibrium between phases A & B as component i is transferred from the former to the later

$$dG = dG_A + dG_B = -\mu_i^{(A)}dn_i + \mu_i^{(B)}dn_i = \left(\mu_i^{(B)} - \mu_i^{(A)}\right)dn_i \tag{4.30}$$

Therefore it is expected that $\mu_i^{(B)} < \mu_i^{(A)}$. This condition means that in order to achieve the equilibrium condition, a component always will transfer to a region where its chemical potential is the lowest.

This principle confirms that the phase with the lower free energy always is going to be the more stable in any system.

In reaching the equilibrium condition, the overall change in free energy must be zero ($dG = 0$), thus to satisfy this condition, the chemical potential for the *i*th component between phases must be equalized, i.e., $\mu_i^{(B)} = \mu_i^{(A)}$.

Equation (4.26) allows us to determine in a multicomponent system the amount of moles that will be present in each individual phase along with the chemical potential of each component present in every phase.

Take, for example, closed system made of components i and j and a single phase (α). The chemical potential of each species would be μ_i^α and μ_j^α, respectively; because the system is closed, no matter is exchanged, therefore the Gibbs free energy of the system is:

$$dG^\alpha = \mu_i^\alpha dn_i^\alpha + \mu_j^\alpha dn_j^\alpha \tag{4.31}$$

Since there is no mass exchange, we have:

$$dn_i^\alpha = dn_j^\alpha = 0 \tag{4.32}$$

Therefore $dG^\alpha = 0$, which means that the system is in equilibrium.

In open systems where matter can be exchanged, mass transfer may occur freely between the phases coexisting within the system. Thus for a three phase (α, β, γ) system containing components i and j, the total Gibbs free energy change would be:

$$dG = dG^\alpha + dG^\beta + dG^\gamma \tag{4.33}$$

or

$$dG = \left[\mu_i^\alpha dn_i^\alpha + \mu_j^\alpha dn_j^\alpha\right] + \left[\mu_i^\beta dn_i^\beta + \mu_j^\beta dn_j^\beta\right] + \left[\mu_i^\gamma dn_i^\gamma + \mu_j^\gamma dn_j^\gamma\right] = 0 \tag{4.34}$$

Consequently, for a system comprised of n components allocated in m phases, the total mass transfer between phases is conditioned by the chemical equilibrium that must be attained between phases, i.e., $dG = dG^\alpha + dG^\beta + \cdots + dG^m = 0$; and that the chemical potential of each component must be the same in every phase at fixed temperature and pressure, so $\mu_i^\alpha = \mu_i^\beta = \cdots = \mu_i^m$, for all components $i = 1, 2, \ldots, n$.

If we now consider the equilibrium between a liquid and its vapor, we have a mono component system comprised by two phases; thereupon for this equilibrium we have:

$$\mu^{\text{liquid}} = \mu^{\text{vapor}} \tag{4.35}$$

And from Eq. (1.29), the Gibbs free energy for this system becomes:

$$G = G^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \tag{4.36}$$

where G° is the standard Gibbs free energy of the vapor under standard pressure conditions (P°) and this pressure is chosen in such a way that it has a value of 1 atm.

If we now mix the vapor with different chemical species, then the Gibbs free energy of the ith component in the gas mixture becomes:

$$G_i = G_i^\circ + nRT \ln\left(\frac{P_i}{P^\circ}\right) \tag{4.37}$$

where P_i is the partial pressure of component i in the mixture. If we divide Eq. (4.30) by the number of moles in the system:

$$\frac{G_i}{n} = \frac{G_i^\circ}{n} + RT \ln\left(\frac{P_i}{P^\circ}\right) \tag{4.38}$$

And from the definition of chemical potential, given by Eq. (4.21), it is possible to rewrite expression (4.31) as:

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{P_i}{P^\circ}\right) \tag{4.39}$$

Notice that if $P_i = P^\circ$ results in $\mu_i = \mu_i^\circ$.

Now, going back to the equilibrium between the liquid phase with its vapor as defined by expression (4.35), we have the following relationship:

$$\mu^{\text{liquid}} = \mu^\circ + RT \ln\left(\frac{P_i}{P^\circ}\right) \tag{4.40}$$

This last relationship is valid because whenever there is a liquid (pure or mixed), it is always in equilibrium with a vapor (gas) phase. Because of this, Eq. (4.39) becomes fundamental in discussing the majority of systems, since invariably they are equilibrated with a gas phase.

Considering a more complex system in which a mixture of different liquids is present, the partial pressure of each component in the gas phase can be expressed as:

$$P_i = x_i \times P_{\text{total}} \tag{4.6}$$

Relating this pressure to that in the standard state results in:

$$\frac{P_i}{P^\circ} = \frac{x_i \times P_{\text{total}}}{P^\circ} \tag{4.41}$$

x_i represents the molar fraction of the ith component in the liquid mix; henceforth, the chemical potential for this species becomes:

$$\mu_i^{\text{liquid mix}} = \mu_i^{\text{gas}} \tag{4.42}$$

Combining Eqs. (4.40), (4.41), and (4.42) results in:

$$\mu_i^{\text{liquid mix}} = \mu_i^{\circ,\text{gas}} + RT \ln\left(\frac{P_{\text{Total}}}{P^\circ}\right) + RT \ln(x_i) \tag{4.43}$$

It is evident that in mono component systems $x_i = 1$, so the last term in Eq. (4.43) becomes zero.

Solutions

As mixing takes place to form a solution, different interactions between components take place. As a result of such interactions, different thermodynamic effects occur, consequently different types of solutions can be found. The solutions described in this text are illustrated in Fig. 4.3.

To obtain a solution made of components i and j, a two staged process must be completed:

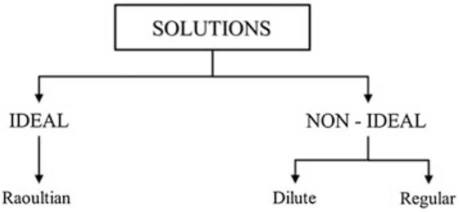


Fig. 4.3 Classification of solutions

1. Bring together components *i* and *j*.
2. Mix *i* and *j* together until forming a homogeneous solution.

The Gibbs free energy of mixing two components into a solution can be estimated by using the free energies of each pure component.

Additionally, to obtain one mole of solution, it is necessary to mix x_i moles of *i* and x_j moles of *j*. Since one mole of solution is formed, the mass balance must be:

$$x_i + x_j = 1 \tag{4.44}$$

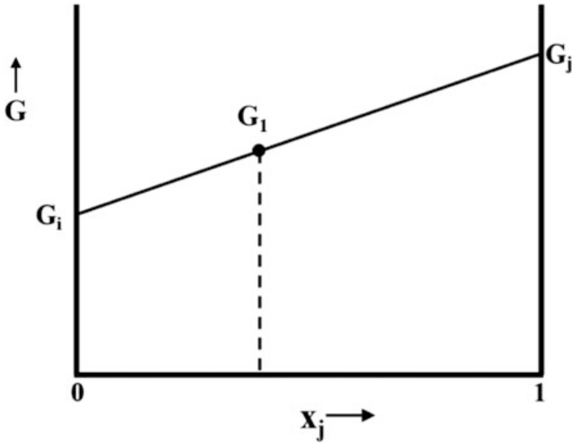
The Gibbs free energy associated to step 1 can be calculated from the molar free energies of i and j, respectively:

$$G_1 = x_i G_i + x_j G_j \tag{4.45}$$

Graphically, we can represent Eq. (4.45) by plotting the molar free energy as a function of x_i or x_j (Fig. 4.4).

Whereas for stage 2, the free energy of the system will change as *i* and *j* atoms mix until forming a solution; for this reason, the free energy at this stage (G_2) should consider both G_1 and the change in free energy due to mixing:

Fig. 4.4 Gibbs free energy content of components i and j before mixing takes place



$$G_2 = G_1 + \Delta G_{\text{mix}} \tag{4.46}$$

From this expression, we can define the free energy change during mixing as:

$$\Delta G_{\text{mix}} = G_2 - G_1 \tag{4.47}$$

Similarly, we can expect the same relations for both the enthalpy and the entropy of mixing:

$$\Delta H_{\text{mix}} = H_2 - H_1 \tag{4.47a}$$

$$\Delta S_{\text{mix}} = S_2 - S_1 \tag{4.47b}$$

Consequently:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{4.48}$$

Solution Models

From the previous discussion it can be argued that the heat associated to the mixing process as shown in Fig. 4.5 can be estimated by:

$$\Delta H_{\text{mix}} = H_{\text{solution}} - \left(x_i H_i^{\circ} + x_j H_j^{\circ}\right) \tag{4.49}$$

When the components of a mixture are mixed together, there is a Gibbs free energy change and entropy change associated to mixing as well. This results in absorbing or releasing heat from the solution. The amount of heat exchange in Eq. (4.49) defines the character of the solution at hand.

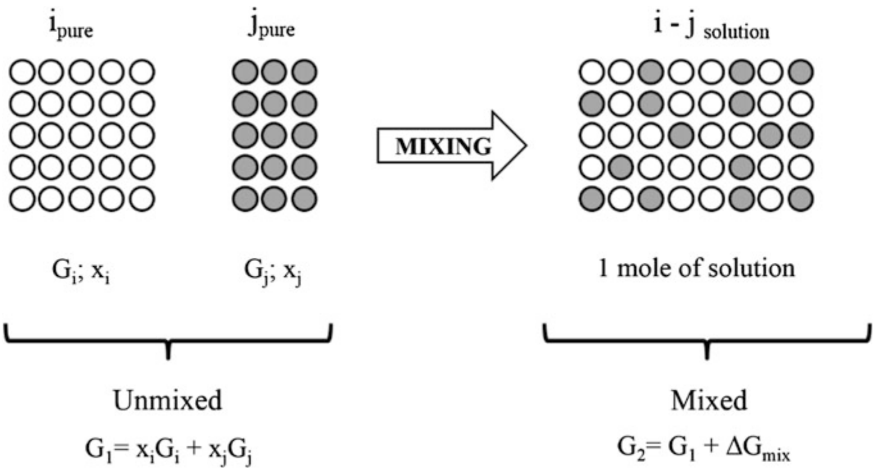


Fig. 4.5 Gibbs free energy change associated to mixing

Ideal Solutions

To exemplify the ideal solution behavior, consider a liquid in equilibrium with its vapor. To determine the strength of molecular bonding in the liquid, we should look at its vapor pressure. The stronger the bonding, the lower the pressure the vapor exerts over the liquid. If a solute is added to the liquid, then the vapor pressure exerted by the solvent will be lowered accordingly; but the solute itself will also exert its own vapor pressure. Thus, the vapor pressure of the solution will be the sum of the pressures of the solvent and that of the solute.

Raoult's Law states that the relative lowering of the solvent's vapor pressure due to solute additions is equal to the molar fraction of the solute in the solution. If the solution is made of components *i* and *j*, each of them will exert its own vapor pressure, thus the total pressure of the solution becomes:

$$P = P_i + P_j \tag{4.50}$$

Additionally, for the pure components, their respective vapor pressure would be P_i° and P_i°. Thus according to Raoult's Law:

$$\begin{aligned} x_i &= \frac{P_i}{P_i^\circ} \\ x_j &= \frac{P_j}{P_j^\circ} \end{aligned} \tag{4.51}$$

This means that the vapor pressure of one of the components in solution is directly proportional to the molar fraction of that component, thus the proportionality constant is the vapor pressure of the component in its pure state (P_i°). Figure 4.6 depicts this.

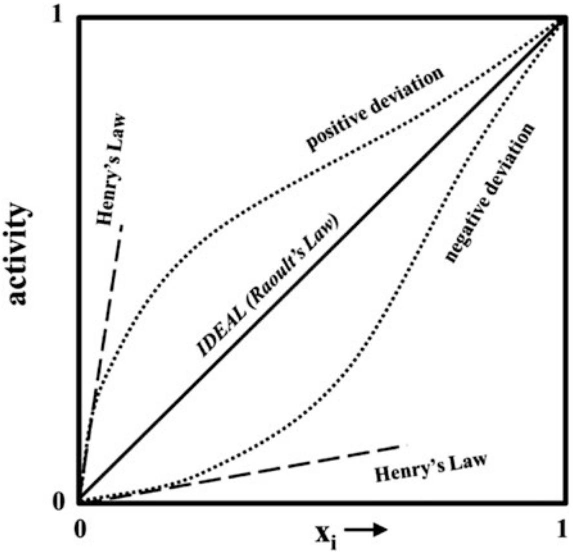


Fig. 4.6 Graphical representation of Raoult's Law. Deviations from this law are also shown

Any solution obeying Raoult's Law is known as an "ideal" solution. These solutions are found when their components are similar in size (atomic, molecular) and must attract one another with the same force as their own molecules. Also the vapor phase should follow the ideal gas Law.

Enthalpy Change Associated to Ideal Mixing

In assuming ideal behavior in the gas phase, we can set P_{total} in Eq. (4.6) equal to the standard pressure, i.e., P°. Substitution of this into Eqs. (4.41) and (4.5) results in:

$$a_i = \frac{P_i}{P_i^\circ} = \frac{x_i P_i^\circ}{P_i^\circ} \tag{4.52}$$

From this, it becomes evident that in ideal solutions, the activity of the *i*th component in the mixture equals its own molar fraction in the solution:

$$a_i = x_i \tag{4.52a}$$

For binary solution made of species i and j, we can estimate the Gibbs free energy of mixing incorporating definition (4.52a) into Eq. (4.45):

$$\Delta G_{\text{mix}}^{\text{ideal}} = x_i G_i + x_j G_j \tag{4.53}$$

Using (4.36) into the last equation we obtain:

$$\begin{aligned} \Delta G_{\text{mix}}^{\text{ideal}} &= x_i(RT\ln(x_i)) + x_j\left(RT\ln\left(x_j\right)\right) \\ \Delta G_{\text{mix}}^{\text{ideal}} &= RT\left(x_i\ln(x_i) + x_j\ln\left(x_j\right)\right) \end{aligned} \tag{4.54}$$

Similarly, we can compute the entropy associated to ideal mixing. To do so, we need to use the second equation in (4.14):

$$\Delta S_{\text{mix}}^{\text{ideal}} = -\frac{\mathrm{d}\left(\Delta G_{\text{mix}}^{\text{ideal}}\right)}{\mathrm{d}T} \tag{4.14}$$

Thus taking the derivative with respect of the temperature of Eq. (4.54) results in:

$$\Delta S_{\text{mix}}^{\text{ideal}} = -\frac{\mathrm{d}}{\mathrm{d}T}\left[RT\left(x_i\ln(x_i) + x_j\ln\left(x_j\right)\right)\right] \tag{4.55}$$

It is obvious that the entropy change due to ideal mixing is:

$$\Delta S_{\text{mix}}^{\text{ideal}} = -R\left(x_i\ln(x_i) + x_j\ln\left(x_j\right)\right) \tag{4.55a}$$

Since we now have computed the Gibbs free energy and the entropy changes associated to ideal mixing, we can calculate the enthalpy change related to this mixing process; to do so, the first relationship in Eq. (4.14) will be used:

$$\Delta G_{\mathrm{mix}}^{\mathrm{ideal}} = \Delta H_{\mathrm{mix}}^{\mathrm{ideal}} - T\Delta S_{\mathrm{mix}}^{\mathrm{ideal}} \tag{4.14}$$

Substituting Eqs. (4.54) and (4.55a) into (4.14) gives:

$$RT\left(x_i \ln(x_i) + x_j \ln\left(x_j\right)\right) = \Delta H_{\mathrm{mix}}^{\mathrm{ideal}} - T\left(-R\left(x_i \ln(x_i) + x_j \ln\left(x_j\right)\right)\right)$$

Solving for the ideal mixing enthalpy:

$$\Delta H_{\mathrm{mix}}^{\mathrm{ideal}} = RT\left(x_i \ln(x_i) + x_j \ln\left(x_j\right)\right) - RT\left(x_i \ln(x_i) + x_j \ln\left(x_j\right)\right) \tag{4.56}$$

$$\Delta H_{\mathrm{mix}}^{\mathrm{ideal}} = 0 \tag{4.56a}$$

This result is very important. The fact that no heat evolves or it is absorbed means that there are no strong interactions between atoms or molecules of those components that are getting mixed. Moreover, the entropy change due to mixing is the parameter that determines the chemical potential of the system since the Gibbs free energy becomes exclusively dependent on that quantity. This is illustrated in Fig. 4.7.

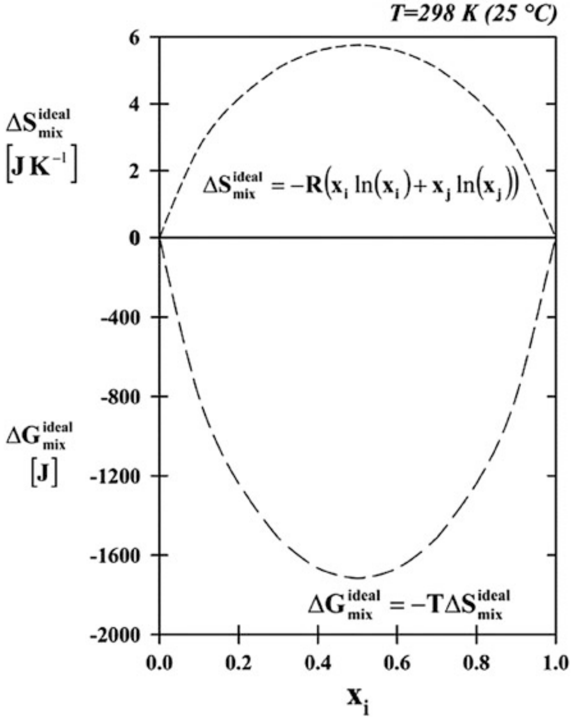


Fig. 4.7 Effect of ideal entropy of mixing on the Gibbs free energy of mixing

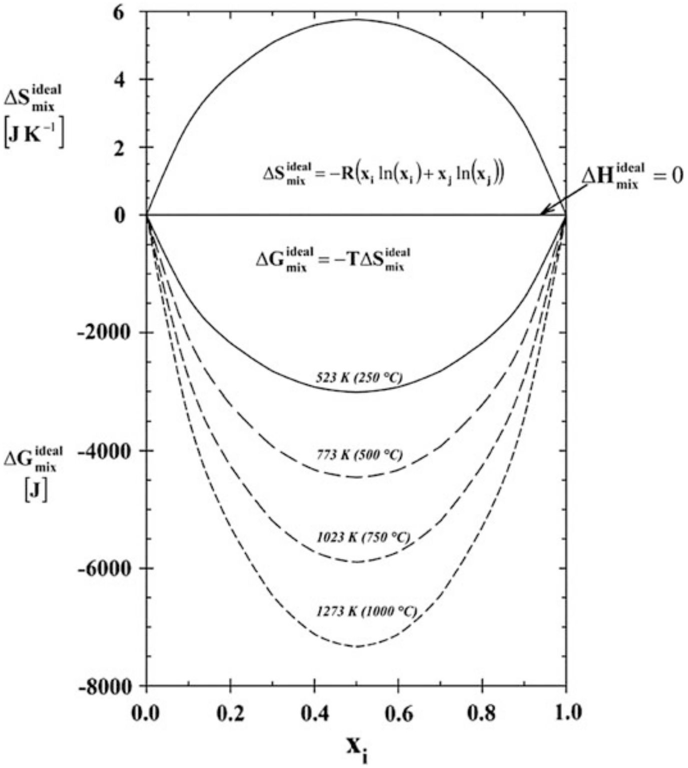


Fig. 4.8 Effect of temperature increase on Gibbs free energy of ideal mixing

Temperature on the other hand becomes a multiple of the entropy of mixing. This is shown in Fig. 4.8.

It is evident from these two figures that the parabolas describing the Gibbs free energy are symmetrical and their lowest point occurs when $x_i = x_j = 0.5$. This condition indicates that there is no heat exchange involved in ideal mixing. This feature also indicates that the activity of each component is equal to their own molar fraction in the solution. Departures from ideal behavior should show asymmetrical features in the curves obtained for the thermodynamic quantities shown, therefore the equations already obtained should change accordingly.

Nonideal Solutions

A nonideal solution shows a deviation from the Raoultian behavior, i.e., the activity of the *i*th component in solution differs from its molar fraction. This is illustrated in Fig. 4.6.

To account for such deviation, a correction factor known as activity coefficient has to be included, so it would allow for computing the activity of any component in solution; therefore, the activity of the *i*th component in a nonideal solution can

$$a_i = \gamma_i x_i \tag{4.57}$$

γ_i Is the activity coefficient of component i in solution. This coefficient depends on pressure, temperature, and chemical composition of the mixture. Form the definition of this coefficient; it is evident that in ideal solutions, its value is 1.

Dilute Solutions (Henrian Behavior)

In dilute solutions, Henry's Law states that over a narrow composition interval, the vapor pressure of a solute in solution is proportional to its mole fraction.

Considering a solution made of components A and B, with the solute being component A, from applying Henry´s Law, the partial pressure of this component is:

$$P_{\mathrm{A}} = h_{\mathrm{A}} x_{\mathrm{A}} \tag{4.58}$$

In this last equation, h_{A} is a constant under a given temperature. Using expressions (4.5), (4.6), and (4.57), we obtain from (4.58):

$$a_{\mathrm{A}} = \gamma^{\circ}_{\mathrm{A}} x_{\mathrm{A}} \tag{4.59}$$

In (4.59) $\gamma^{\circ}{}_{\mathrm{A}}$ is a constant and represents the slope of the activity—composition (molar fraction) plot at infinite dilution; it also represents the slope of such curve at zero concentration of A.

Henry's Law only applies over a concentration interval whose extent changes from system to system. But its validity only occurs at very low solute concentrations.

Alternative Standard States

Since the activity of a component in nonideal solutions differs from the molar fraction, it becomes convenient in some instances to use a different standard state then the pure substance.

Henry's Law allows for using two alternative standard states[3]:

1. Infinitely diluted molar fraction.
2. Infinitely diluted weight percent.

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[3] Upadhyaya, G.S., Problems in metallurgical thermodynamics and kinetics, Pergamon, Oxford, UK, 1977.

The former is defined in such a way that Henrian activity approaches the molar fraction at infinite dilution:

$$h_{\mathrm{A}} = x_{\mathrm{A}} \quad \text{as} \quad x_{\mathrm{A}} \to 0 \tag{4.60}$$

And h_{A} is the Henrian activity of component A. This means that in the concentration range where Henry's Law is valid, the molar fraction equals the activity. Beyond such composition interval, the activity can be calculated by the following relationship:

$$h_{\mathrm{A}} = f_{\mathrm{A}} x_{\mathrm{A}} \tag{4.61}$$

f_{A} is the Henrian activity coefficient of component A, relative to the infinitely diluted molar fraction standard state. The relation between the activity coefficient of A with respect of the pure substance standard state and the activity of A relative to the infinitely diluted molar fraction standard state is:

$$\gamma_{\mathrm{A}}^{\circ} = \left.\frac{\text{activity of A relative to pure substance SS}}{\text{activity of A relative to diluted molar fraction SS}}\right|_{x_{\mathrm{A}} = \text{constant}} \tag{4.62}$$

The Gibbs free energy change associated to this change in standard state is:

$$\Delta \mathrm{G}^{\circ} = RT \ln\left(\gamma_{\mathrm{A}}^{\circ}\right) \tag{4.63}$$

For the infinitely diluted weight percent standard state, this is the most widely used in metallurgy. In this standard state, the Henrian activity approaches the weight percent at infinite dilution:

$$h_{\mathrm{A}} = \mathrm{wt\%_A} \quad \text{as} \quad \mathrm{wt\%_A} \to 0 \tag{4.64}$$

In this case, it is customary to assume that Henry's Law is observed up to 1 wt% of A, then h_{A} is has a value of one at this concentration, and the standard state is called the 1 wt% solution. Deviations from the activity using this standard state are estimated in terms of the Henrian activity coefficient relative to the infinitely dilute wt% standard state.

$$h_{\mathrm{A}} = f_{\mathrm{A}}(\mathrm{wt\%_A}) \tag{4.65}$$

Similar to the diluted molar fraction standard state, there is a relationship between the activity referred to the pure substance standard state and that of the infinitely diluted wt% standard state:

$$\gamma_{\mathrm{A}}^{\circ} \frac{x_{\mathrm{A}}}{\mathrm{wt\%_A}} = \left.\frac{\text{activity of A relative to pure substance SS}}{\text{activity of A relative to diluted wt \% fraction SS}}\right|_{\mathrm{X_A} = \text{constant}} \tag{4.66}$$

Gibbs free energy associated to this change in standard state is:

$$\Delta G^{\circ} = RT \ln\left(\gamma_{\mathrm{A}}^{\circ} \frac{x_{\mathrm{A}}}{\mathrm{wt}\%_{\mathrm{A}}}\right) \tag{4.67}$$

In very small concentrations of solute A in A-B solutions, we have the following approximation:

$$\frac{x_{\mathrm{A}}}{\mathrm{wt}\%_{\mathrm{A}}} \approx \frac{M_{\mathrm{B}}}{100 M_{\mathrm{A}}} \tag{4.68}$$

M_{A} and M_{B} are the molecular (atomic) masses of A and B components, respectively. Substituting (4.68) into (4.67) yields:

$$\Delta G^{\circ} = RT\left(\ln\left(\gamma_{\mathrm{A}}^{\circ}\right) + \ln\left(\frac{M_{\mathrm{B}}}{100 M_{\mathrm{A}}}\right)\right) \tag{4.68a}$$

Regardless of the standard state selected to perform calculations, Eq. (1.38) still holds; but the numerical values of ΔG° and K will depend upon the selected standard state.

Sievert's Law

A particular application of Henry's Law in metallurgy relates to the dissociation of gases (H_2, S_2, O_2, N_2) in molten metals. Chemically, the decomposition of the any of these gases can be represented as:

$$G_2 = 2G \tag{4.69}$$

where G represents any of the gases mentioned. According to expression (4.69), Henry's Law takes the form:

$$P_G = k_S x_G^2 \tag{4.70}$$

This relationship fits well with the solubility (S_G) of these gases in the majority of molten metals; this observation is known as Sievert's Law and since the molar fraction of the dissolved gas is proportional to its own solubility in the metal, Sievert's Law can be written as:

$$S_G = k_S \sqrt{P_G} \tag{4.71}$$

k_S represents a constant which is determined for every gas–metal system. If the dissolving gas is not diatomic, (4.71) still is valid as long as $\mathrm{P_G}$ is expressed as the partial gas pressure of the diatomic species.

Regular Solutions

It has been discussed that when components A and B are mixed together changes in thermodynamic quantities like *V*, *H*, *S*, *G*, *A*, etc. occur. Assuming an ideal behavior resulted in that the enthalpy change associated to mixing is zero and the entropy and Gibbs free energy of ideal mixing are functions of the composition and temperature.

But in dealing with real, non-diluted solutions, beg the questions of how these thermodynamic quantities change?, and how are they related to the activity or activity coefficients of the components in solution?

We need to refer to Fig. 4.5. It is evident that in order to go from state 1 (premixed) to state 2 (mixed) the change of the thermodynamic quantities directly relates to this state change. Also we can distinguish between real and ideal behaviors during mixing, thus we can establish that the departure from the ideality is accompanied by excesses in the thermodynamic functions as mixing occurs.

Such excess may be defined as the difference between thermodynamic function for the real solution and that of the ideal solution, thus:

$$\Psi^{xs} = \Psi_{\text{real}} - \Psi_{\text{ideal}} \tag{4.72}$$

With this definition, we can compute the excess Gibbs free energy of mixing for a binary A-B solution. To do so, we need expressions (4.72), (4.59), and (4.54):

$$\begin{aligned}
G^{xs} &= \Delta G^{\text{real}}_{\text{mixing}} - \Delta G^{\text{ideal}}_{\text{mixing}}\\
G^{xs} &= RT[x_{\text{A}}\ln(a_{\text{A}}) + x_{\text{B}}\ln(a_{\text{B}})] - RT[x_{\text{A}}\ln(x_{\text{A}}) + x_{\text{B}}\ln(x_{\text{B}})]\\
G^{xs} &= RT[x_{\text{A}}\ln(\gamma_{\text{A}}x_{\text{A}}) + x_{\text{B}}\ln(\gamma_{\text{B}}x_{\text{B}})] - RT[x_{\text{A}}\ln(x_{\text{A}}) + x_{\text{B}}\ln(x_{\text{B}})]
\end{aligned}$$

This results in:

$$G^{xs} = RT[x_{\text{A}}\ln(\gamma_{\text{A}}) + x_{\text{B}}\ln(\gamma_{\text{B}})] \tag{4.73}$$

Similarly, it is possible to compute the excess entropy and enthalpy of mixing:

$$S^{xs} = -\text{R}(x_{\text{A}}\ln\gamma_{\text{A}} + x_{\text{B}}\ln\gamma_{\text{B}}) - RT\left[x_{\text{A}}\left(\frac{\partial\ln\gamma_{\text{A}}}{\partial T}\right)_{P.x_{\text{A}}} + x_{\text{B}}\left(\frac{\partial\ln\gamma_{\text{B}}}{\partial T}\right)_{P.x\text{B}}\right] \tag{4.74}$$

$$H^{xs} = -RT^2\left[x_{\text{A}}\left(\frac{\partial\ln\gamma_{\text{A}}}{\partial T}\right)_{P,x_{\text{A}}} + x_{\text{B}}\left(\frac{\partial\ln\gamma_{\text{B}}}{\partial T}\right)_{P,x_{\text{B}}}\right] \tag{4.75}$$

From (4.75), the partial molar enthalpy for a component in solution is:

$$\overline{H}_i = R\left(\frac{\partial\ln(\gamma_i)}{\partial\left(\frac{1}{T}\right)}\right)_P \tag{4.75a}$$

These last equations, show that in order to compute both the excess entropy and enthalpy is necessary to calculate the partial derivatives of the activity coefficients contained in them. To avoid such calculation, the regular solution model was created; such model states that the entropy of mixing is equal to that of an ideal solution and that the enthalpy of mixing is different from zero. Under these conditions, for a binary solution, the associated mixing thermodynamic properties are:

$$\Delta G_{\mathrm{mix}} = RT(x_{\mathrm{A}} \ln(a_{\mathrm{A}}) + x_{\mathrm{B}} \ln(a_{\mathrm{B}})) \tag{4.76}$$

$$\Delta S_{\mathrm{mix}} = -R(x_{\mathrm{A}} \ln(x_{\mathrm{A}}) + x_{\mathrm{B}} \ln(x_{\mathrm{B}})) \tag{4.77}$$

$$\Delta H_{\mathrm{mix}} = RT(x_{\mathrm{A}} \ln(\gamma_{\mathrm{A}}) + x_{\mathrm{B}} \ln(\gamma_{\mathrm{B}})) = \Delta G^{xs}_{\mathrm{mix}} \tag{4.78}$$

From Eqs. (4.76) to (4.78), it is evident that the enthalpy of mixing in a regular solution is equal to the Gibbs free energy associated to this type of mixing. Also to identify if a solution behaves regularly, it should be calculated the interaction parameter (Ω). Such parameter is constant and independent of the solution composition; furthermore it has the same value for all the components within the system.

$$\Omega = \frac{RT \ln(\gamma_{\mathrm{A}})}{x_{\mathrm{B}}^2} = \frac{RT \ln(\gamma_{\mathrm{B}})}{x_{\mathrm{A}}^2} \tag{4.79}$$

Excess properties can also be used to determine partial molar quantities; for example, the excess partial molar Gibbs free energy of component i in solution is:

$$\overline{G}^{xs}_i = RT \ln(\gamma_i) \tag{4.80}$$

Hence for an A–B solution:

$$G^{xs} = x_{\mathrm{A}} \overline{G}^{xs}_{\mathrm{A}} + x_{\mathrm{B}} \overline{G}^{xs}_{\mathrm{B}} \tag{4.81}$$

Similarly:

$$\overline{G}^{xs}_i = \overline{H}^{xs}_i - T\overline{S}^{xs}_i \tag{4.82}$$

and so on.

The effect of the interaction parameter Ω can be seen in the sketches in Fig. 4.9.

Gibbs–Duhem Equation

With the use of Eq. (4.12), it is possible to express any extensive thermodynamic quantity as:

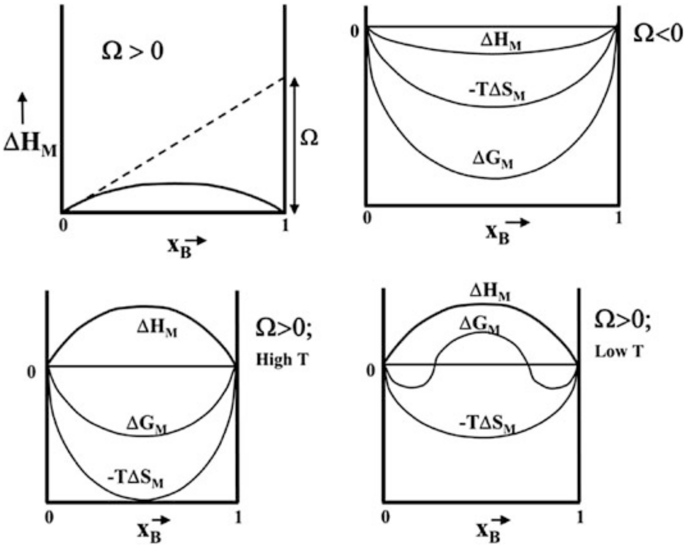

Fig. 4.9 Effect of the interaction parameters on the different thermodynamic properties

$$\sum_{i=1}^{n} x_i \mathrm{d}\overline{\Psi}_i = 0 \tag{4.83}$$

Equation (4.83) is known as Gibbs–Duhem equation. This equation is used to calculate partial molar quantities of a component when those quantities from the other components in solution are known. Also it is possible to compute activities and activity coefficients of an unknown component when data form other components in solution are known. To do so, Gibbs –Duhem equation in a binary system takes the form:

$$\mathrm{d}\overline{\Psi}_\mathrm{A} = -\frac{x_\mathrm{B}}{x_\mathrm{A}}\mathrm{d}\overline{\Psi}_\mathrm{B} \tag{4.84}$$

To solve this equation, it is necessary to integrate. It is customary to set the upper integration limit as $x_\mathrm{A} = x_\mathrm{A}$. The lower integration limit should be set in a way that the value of $\overline{\Psi}_\mathrm{A}$ is known. However, it is also convenient to set the lower limit as $x_\mathrm{A} = 1$, i.e., when no solution is formed:

$$\int_{x_\mathrm{A}=1}^{x_\mathrm{A}=x_\mathrm{A}} \mathrm{d}\overline{\Psi}_\mathrm{A} = -\int_{x_\mathrm{A}=1}^{x_\mathrm{A}=x_\mathrm{A}} \frac{x_\mathrm{B}}{x_\mathrm{A}}\mathrm{d}\overline{\Psi}_\mathrm{B} \tag{4.85}$$

Equation (4.85) is solved numerically.

To exemplify the use of this equation, consider computing the activity of component A in a binary solution if the activity of component B is known:

$$\begin{aligned}
&x_{\mathrm{A}}\mathrm{d}\overline{G}_{\mathrm{A}}+x_{\mathrm{B}}\mathrm{d}\overline{G}_{\mathrm{B}}=0\\
&x_{\mathrm{A}}\mathrm{d}RT\ln a_{\mathrm{A}}+x_{\mathrm{B}}\mathrm{d}RT\ln a_{\mathrm{B}}=0\\
&x_{\mathrm{A}}\mathrm{d}\ln a_{\mathrm{A}}+x_{\mathrm{B}}\mathrm{d}\ln a_{\mathrm{B}}=0\\
&\int_{1}^{x_{\mathrm{A}}}\mathrm{d}\ln a_{\mathrm{A}}=-\int_{1}^{x_{\mathrm{A}}}\tfrac{x_{\mathrm{B}}}{x_{\mathrm{A}}}\mathrm{d}\ln a_{\mathrm{B}}
\end{aligned}\tag{4.86}$$

Similarly, the activity coefficient of a can be computed:

$$\int_{1}^{x_{\mathrm{A}}}\mathrm{d}\ln\gamma_{\mathrm{A}}=-\int_{1}^{x_{\mathrm{A}}}\frac{x_{\mathrm{B}}}{x_{\mathrm{A}}}\mathrm{d}\ln\gamma_{\mathrm{B}}\tag{4.87}$$

Examples of Calculations

Example 1 Estimation of Partial Molar Quantities

Part (a) The following data for liquid Zn–Sn alloys at 710 K is available

x_{Zn}	$\Delta\overline{H}_{\mathrm{mix}}$ (J)	$\Delta\overline{S}_{\mathrm{mix}}$ (J/K)
0	0	0
0.1	9121	25.94
0.2	7950	18.87
0.3	6736	15.48
0.4	5648	11.8
0.5	4184	8.54
0.6	3180	6.11
0.7	2008	4.1
0.8	1088	2.3
0.9	259	1.05
1	0	0

Calculate:

i. The partial molar Gibbs free energies and the integral free energies at all compositions
ii. Plot all the calculated data as a function of the composition

Table 4.1 Gibbs free energy of mixing after Eq. (1.21)

x_{Zn}	$\Delta\overline{G}_{mix}$ (J)
0	0
0.1	−9296.4
0.2	−5447.7
0.3	−4254.8
0.4	−2730
0.5	−1879.4
0.6	−1158.1
0.7	−903
0.8	−545
0.9	−486.5
1	0

iii. Calculate the activities and activities coefficients of both Zn and Sn at all compositions

Solution

To calculate the partial molar Gibbs free energies of the components, first, we need to calculate the Gibbs free energy of mixing. To so, we use Eq. 1.21.

$$\Delta\overline{G}_{\mathrm{mix}} = \Delta\overline{H}_{\mathrm{mix}} - T\Delta\overline{S}_{\mathrm{mix}} \tag{1.21}$$

Results from this operation are shown in the Table 4.1.

With the tabulated Gibbs free energy of mixing, we can compute the partial molar Gibbs free energy for both the zinc and the tin. To do so, we need to plot $\Delta\overline{G}_{\mathrm{mix}}$ versus the molar fraction of zinc (or that of tin). This is shown in Fig. 4.10.

To determine the partial molar Gibbs free energy at every composition, a tangent line is drawn over each composition point and then the partial molar Gibbs free energy of tin is read directly from the graph on the left axis. Similarly, the partial molar Gibbs free energy of zinc is read on the left axis. This is illustrated in the plot below shown in Fig. 4.11. The results after repeating this procedure at every composition are shown in Table 4.2.

The last column in Table 4.2 is the result of using expression (4.13):

$$\Delta\overline{G}_{\mathrm{mix}} = x_{\mathrm{Zn}}\overline{G}_{\mathrm{Zn}} + x_{\mathrm{Sn}}\overline{G}_{\mathrm{Sn}} \tag{4.13}$$

As seen from this column there is good agreement between the Gibbs free energy of mixing.

Since each partial molar Gibbs free energy is known, it is possible to calculate the activity and the activity coefficient of each component by using Eq. (4.22) in the following form:

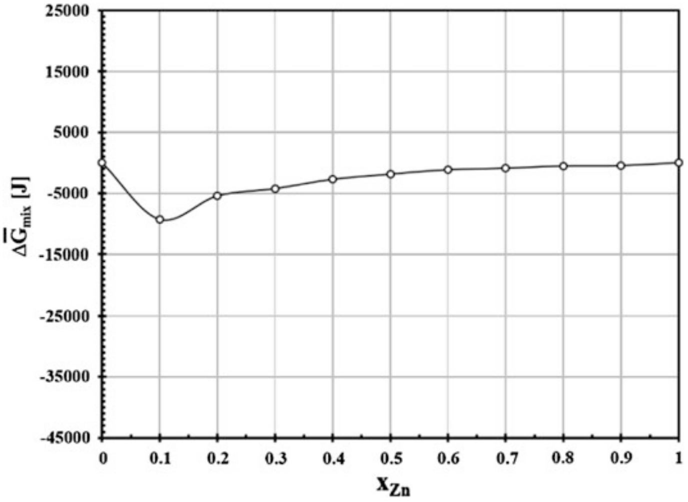

Fig. 4.10 Gibbs free energy of mixing in the Zn–Sn system at 710 K

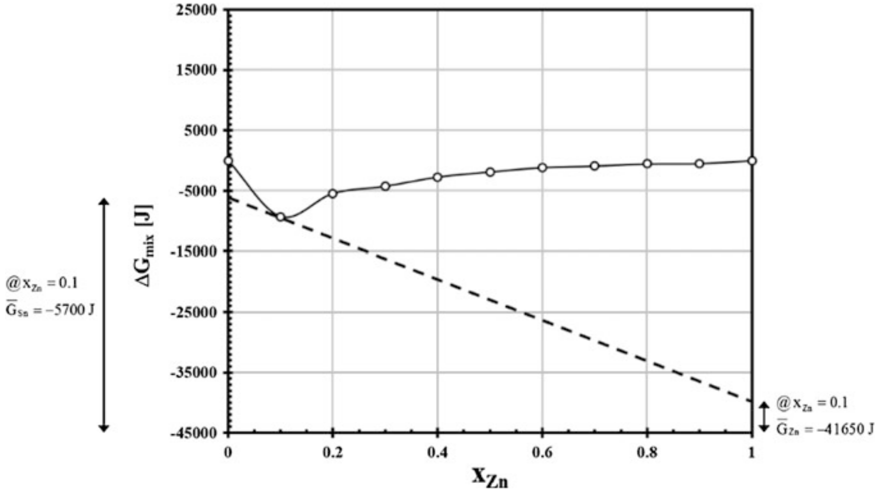

Fig. 4.11 Determination of the partial molar Gibbs free energy of zinc and tin in a binary Zn–Sn alloy

$$\overline{G}_i = RT\ \ln(a_i) \tag{4.22}$$

And because the molar fraction for each component is known, the corresponding activity coefficients can be computed easily:

Table 4.2 Partial molar Gibbs free energy in the Zn–Sn system

x_{Zn}	G_{Sn} (J)	G_{Zn} (J)	G_{mix} (J)
0	0	0	0
0.1	−5700	−41,650	−9295
0.2	−12,200	21,600	−5440
0.3	−8350	5300	−4255
0.4	−7750	4800	−2730
0.5	−7000	3250	−1875
0.6	−5150	1500	−1160
0.7	−1975	−450	−907.5
0.8	−1175	−390	−547
0.9	−4000	−100	−490
1	0	0	0

Table 4.3 Computed values of the activity and activity coefficients for Zn and Sn in the Zn–Sn system at 710 K

x_{Zn}	a_{Sn}	γ_{Sn}	a_{Zn}	γ_{Zn}
0.1	0.38	0.42	0.00086	0.01
0.2	0.13	0.16	38.83	194.15
0.3	0.24	0.35	2.45	8.18
0.4	0.27	0.45	2.26	5.64
0.5	0.31	0.61	1.73	3.47
0.6	0.42	1.04	1.29	2.15
0.7	0.72	2.39	0.93	1.32
0.8	0.82	4.10	0.94	1.17
0.9	0.51	5.08	0.98	1.09

$$\gamma_i = \frac{a_i}{x_i}$$

Results for these calculations are shown in Table 4.3.

In the case of the activities of zinc, it is noticeable the extremely high values for this quantity, especially at $x_{Zn} = 0.2$. The reason for such numerical values is that the partial molar Gibbs free energy for this metal is positive in the interval $0.6 > x_{Zn} > 0.2$. Although numerically consistent, activity values larger than unity lack of any physical sense.

Part (b) The enthalpies of mixing of Cd-Sn alloys at 773 K are given in the table below

x_{Cd}	ΔH_{mix} (J/mole)
0	0
0.1	1247.7
0.3	2729.6

(continued)

(continued)

x_{Cd}	ΔH_{mix} (J/mole)
0.5	3347.2
0.7	2596.2
0.9	1052.3
1	0

Calculate the values of the partial molar enthalpies of mixing of cadmium and tin in a mixture containing 60% molar Cd.

Solution

Similar to part (a), we need to plot the data given and at the composition (60% Cd, 40% Sn) draw a tangent line crossing the mixing enthalpy curve. The tangent line must cross each axis and then read the values for the partial molar enthalpy of each element.

The partial molar enthalpy of Zn at 773 K in a Zn-60% mole Cd alloy is 5600 J/mole, whereas that of Cd is 1400 J/mole.

Part (c) Ag–Cu alloys exhibit a regular behavior in the solid state. The enthalpies of mixing at 500 °C (773 K) are given as a function of the copper content

x_{Cu}	ΔH_{mix}
0.1	−1402
0.2	−2740
0.3	−3807
0.4	−4686
0.5	−5146
0.6	−5188
0.7	−4728
0.8	−3598

Find:

i. ΔH_{Cu} and ΔH_{Au} at $x_{Cu} = 0.3$
ii. ΔG_{mix} at $x_{Cu} = 0.3$

Solution

For part (i), we need to proceed like in the previous examples (Figs. 4.12 and 4.13):

From the figure, the partial molar enthalpy of gold at 0.3 mol of copper is −1000 J/mole, whereas for copper that value is −10,500 J/mole.

For part (ii), since the solution exhibits a regular behavior, the Gibbs free energy of mixing can be calculated using Eq. (4.72), thus:

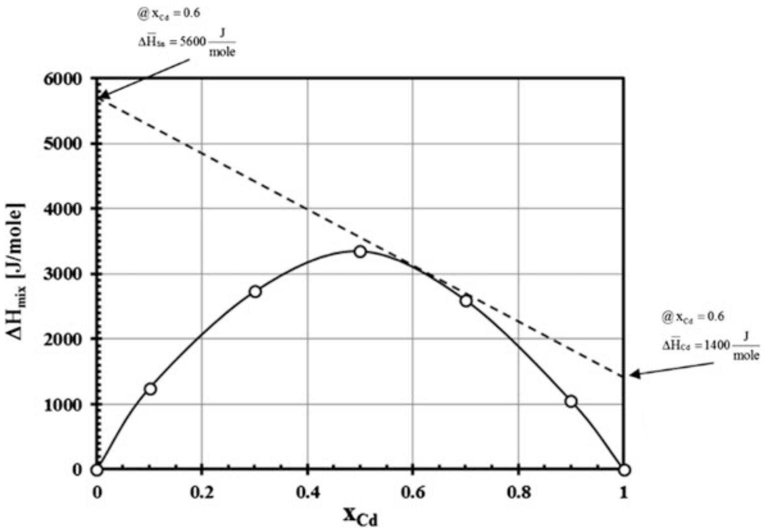

Fig. 4.12 Estimation of the partial molar enthalpies of Zn and Cd in a Zn—60% mole Cd alloy at 773 K

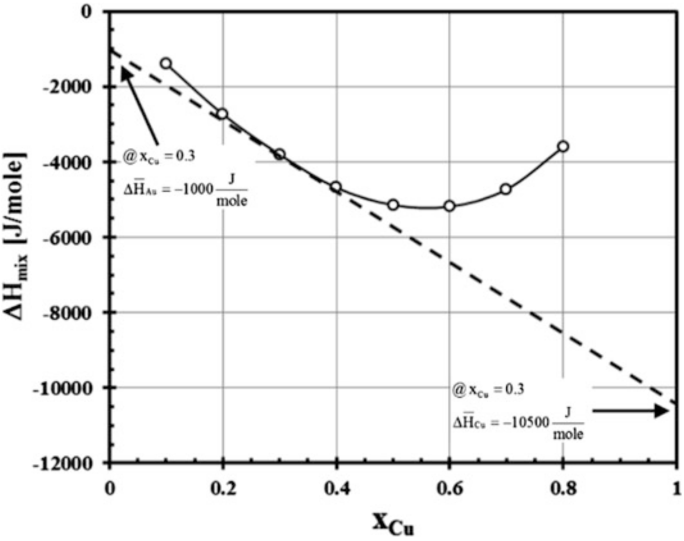

Fig. 4.13 Estimation of the partial molar enthalpies of gold and copper in a Au—30% mole Cu alloy at 773 K

$$\Delta\overline{G}_{\text{mix}} = \Delta\overline{H}^{xs}_{\text{mix}} - T\Delta\overline{S}^{\text{ideal}}_{\text{mix}}$$
$$\Delta\overline{G}_{\text{mix}} = 3807 - 773[-8.314(0.3\ln(0.3) + 0.7\ln(0.7))]$$
$$\Delta\overline{G}_{\text{mix}} = -7733\ \frac{\text{J}}{\text{mole}}$$

Example 2 Calculation of Activity Coefficient

Part (a). The activities of aluminum at different concentrations in Al–Cu solutions at 1373 K (1100 °C) are provided below:

x_{Al}	a_{Al}
0.90	0.890
0.75	0.690
0.63	0.500
0.53	0.310
0.45	0.200
0.38	0.100
0.30	0.030
0.20	0.005
0.10	0.008

Calculate the activity coefficient of aluminum in a solution containing 49 mol% aluminum.

Solution

To solve this problem, we need to calculate the activity coefficient of aluminum:

$$\gamma_{Al} = \frac{a_{Al}}{x_{Al}}$$

From the data provided, we can calculate the activity coefficient and then plot it against the molar (atomic) fraction of aluminum. From that resulting plot, we can directly find the value for such coefficient (Table 4.4).

From the plot below (see insert), the value of the activity coefficient of aluminum is 0.515 (Fig. 4.14).

Part (b). The following data is available for the Fe–Si system at 1600 °C (1873 K)

x_{Fe}	$\log \gamma_{Si}$
0.1	−0.01
0.2	−0.02
0.3	−0.06

(continued)

Table 4.4 Activity coefficient of aluminum in Al–Cu alloys at 1373 K

x_{Al}	a_{Al}	γ_{Al}
0.90	0.890	0.989
0.75	0.690	0.920
0.63	0.500	0.794
0.53	0.310	0.585
0.45	0.200	0.444
0.38	0.100	0.263
0.30	0.030	0.100
0.20	0.005	0.025
0.10	0.008	0.080

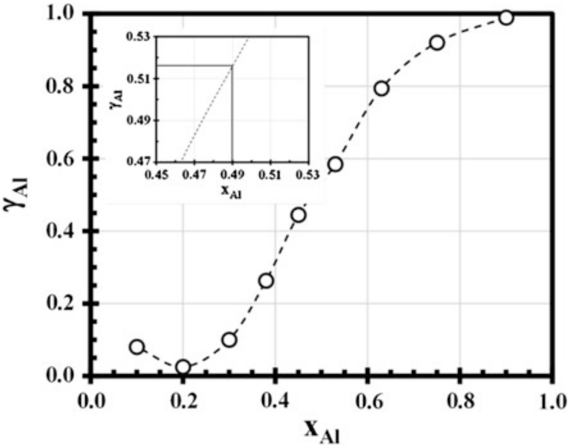

Fig. 4.14 Estimation of the activity coefficient of Al in Al–Cu alloys at 1100 °C

(continued)

x_{Fe}	$\log \gamma_{Si}$
0.4	−0.14
0.5	−0.7
0.6	−1.2
0.7	−1.45
0.8	−1.56
0.9	−1.62
1	−1.65

Determine:

i. The change in the activity of silicon over the Fe–Si system.
ii. The correction required to change from pure silicon standard state to the 1 wt% Si standard state in iron at the indicated temperature.

Table 4.5 Silicon content, activity, and activity coefficient in Si–Fe alloys at 1600 °C

x_{Fe}	$\log \gamma_{Si}$	x_{Si}	γ_{Si}	a_{Si}
0.1	−0.01	0.9	0.977	0.87951
0.2	−0.02	0.8	0.955	0.76399
0.3	−0.06	0.7	0.871	0.60967
0.4	−0.14	0.6	0.724	0.43466
0.5	−0.7	0.5	0.200	0.09976
0.6	−1.2	0.4	0.063	0.02524
0.7	−1.45	0.3	0.035	0.01064
0.8	−1.56	0.2	0.028	0.00551
0.9	−1.62	0.1	0.024	0.0024
1	−1.65	0	0.022	0

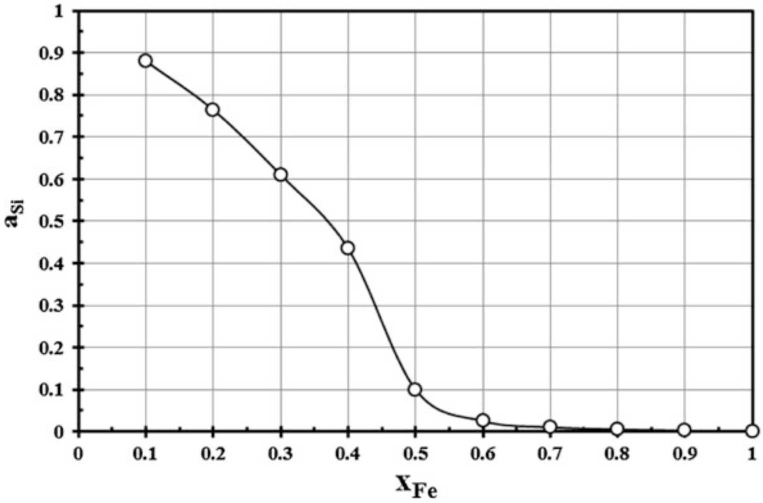

Fig. 4.15 Activity of silicon as a function of iron content in Si–Fe alloys at 1600 °C

In part (i), from the given data, we need to compute both the molar fraction of silicon as well as its activity coefficient. To determine the molar fraction of silicon we must subtract from one the molar fraction of iron. To calculate the activity coefficient of silicon, we must take the antilogarithm (base 10) of such coefficient from the provided data. Once these quantities are known, we can determine the value of the activity of silicon at every composition by multiplying the activity coefficient and the molar fraction of silicon (Table 4.5).

Plotting the activity of silicon versus the iron content in the melt results in Fig. 4.15.

From this figure, it is clear that at high concentrations of iron, the activity of silicon is very low, thus we can assume Henrian behavior. Now plotting the activity of silicon as a function of the silicon content at very low Si concentrations would allow us to compute Henry's constant for silicon (γ°_{Si}); this is illustrated in Fig. 4.16.

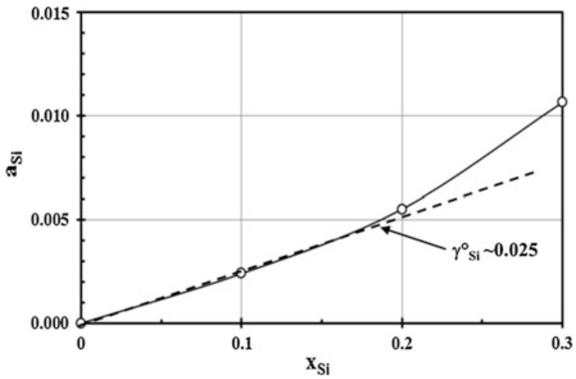

Fig. 4.16 Estimation of Henry's constant in diluted Si–Fe alloys at 1600 °C

With Henry's constant, we can calculate the correction factor by using Eq. (4.67):

$$\Delta G^\circ = RT\,\ln\left[\gamma^\circ_{\mathrm{Si}}\frac{M_{\mathrm{Fe}}}{100M_{\mathrm{Si}}}\right] \tag{4.67}$$

Substituting values:

$$\Delta G^\circ = 8.314(1873)\ln\left[0.025\frac{55.85}{100\times 28}\right] = -118404\ \mathrm{J}$$

The correction for changing standard state from pure silicon to 1 wt% Si in iron at 1600 °C is −118.4 kJ.

Part (c) A stream of nitrogen gas is passed over mercury at 100 °C. The flow rate is such that the gas becomes saturated with Hg vapor. The total volume of nitrogen used was 22 L, measured at 20°C and 1 atm of pressure.

Calculate the vapor pressure of Hg (200 g/mole) at 100 °C, if 0.067 g of mercury were found in the nitrogen.

The same experiment was carried out using a sodium–mercury mixture with $x_{\mathrm{Hg}} = 0.878$. The 22 L of nitrogen contained 0.0471 g of mercury. Determine the activity of mercury and its activity coefficient. Also find the Gibbs free energy of mixing of mercury.

Solution

We need to calculate the number of moles of nitrogen in the experiment. To do so, we must assume an ideal gas behavior form the nitrogen:

$$n_{\mathrm{N}_2} = \frac{PV}{RT} = \frac{1.01325\times 10^5(22\times 10^{-3})}{8.314(373)}$$

$$n_{\mathrm{N}_2} = 0.915\ \text{moles N}_2$$

We need to determine the molar fraction of mercury in the gas phase. To do so we need to calculate the number of moles of mercury and from the number of moles of Hg and N_2 compute the molar fraction of mercury:

$$n_{\mathrm{Hg}} = 0.067\ \mathrm{g\ Hg} \times \frac{1\ \mathrm{mole}}{200\ \mathrm{g\ Hg}} = 3.35 \times 10^{-4} \mathrm{moles\ Hg}$$

$$x_{\mathrm{Hg}} = \frac{n_{\mathrm{Hg}}}{n_{\mathrm{Hg}} + n_{\mathrm{N_2}}} = \frac{3.35 \times 10^{-4}}{3.35 \times 10^{-4} + 0.915} = 3.66 \times 10^{-4}$$

Since the total pressure is 1 atm (1.01325×10^5 Pa):

$$P_{\mathrm{Hg}} = x_{\mathrm{Hg}} P_{\mathrm{Total}} = 3.66 \times 10^{-4}(1)$$
$$P_{\mathrm{Hg}} = 3.66 \times 10^{-4}\ \mathrm{atm}$$

For the second part, we need to calculate the mole fraction of mercury in the gas phase after repeating the experiment:

$$n_{\mathrm{Hg}} = 0.0471\ \mathrm{g\ Hg} \times \frac{1\ \mathrm{mole}}{200\ \mathrm{g\ Hg}} = 2.36 \times 10^{-4} \mathrm{moles\ Hg}$$

$$x_{\mathrm{Hg}} = \frac{n_{\mathrm{Hg}}}{n_{\mathrm{Hg}} + n_{\mathrm{N_2}}} = \frac{2.36 \times 10^{-4}}{2.36 \times 10^{-4} + 0.915} = 2.58 \times 10^{-4}$$

With this result, the partial pressure of mercury over the mixture is 2.58×10^{-4} atm.

The activity of mercury in the Na–Hg mixture can be calculated using Eq. (4.52), making $P^{\circ}_{\mathrm{Hg}} = 3.66 \times 10^{-4}$ atm and $P_{\mathrm{Hg}} = 2.58 \times 10^{-4}$ atm:

$$a_{\mathrm{Hg}} = \frac{P_{\mathrm{Hg}}}{P^{\circ}_{\mathrm{Hg}}} = \frac{2.58 \times 10^{-4}}{3.66 \times 10^{-4}} = 0.705$$

To calculate the activity coefficient of mercury in the Hg–Na mixture, we need to use the molar fraction of mercury in the mix, thus using Eq. (4.57) we have:

$$a_{\mathrm{Hg}} = \gamma_{\mathrm{Hg}} x_{\mathrm{Hg}}$$
$$\gamma_{\mathrm{Hg}} = \frac{a_{\mathrm{Hg}}}{x_{\mathrm{Hg}}} = \frac{0.705}{0.878} = 0.8$$

To determine the Gibbs free energy of solution in the mixture, we use Eq. (4.36)

$$\Delta G_{\mathrm{Hg}} = RT \ln\left(a_{\mathrm{Hg}}\right)$$
$$\Delta G_{\mathrm{Hg}} = 8.314(374)\ln(0.705) = -1084\ \mathrm{J}$$

Part (d) In AgCl–KCl solutions at 800 °C, the activity of AgCl is 0.409 when x_{AgCl} = 0.5; additionally, the molar partial enthalpy of AgCl is−1793 J. This quantity can be assumed independent of temperature. Calculate the activity of AgCl at 1000 °C in an equimolar AgCl–KCl mixture.

Solution

To solve this problem, we need to combine Eqs. (4.78) and (4.10), this results in:

$$\Delta\overline{H}_{\mathrm{AgCl}} = RT\ln\left(\gamma_{\mathrm{AgCl}}\right)$$

Since the enthalpy of the silver chloride in independent of temperature, we can substitute its given value into last equation as well as those of the gas constant and the temperature, thus:

$$-1793 = 8.314(1273)\ln\left(\gamma_{\mathrm{AgCl}}\right)$$

$$\gamma_{\mathrm{AgCl}} = \exp\left[\frac{-1793}{8.314(1273)}\right] = 0.8442$$

Since the composition of the binary mixture is known, we use the activity coefficient and the molar fraction of the silver chloride to compute its activity at 1000 °C:

$$a_{\mathrm{AgCl}} = \gamma_{\mathrm{AgCl}}\, x_{\mathrm{AgCl}}$$

$$a_{\mathrm{AgCl}} = 0.8442 \times 0.5$$

$$a_{\mathrm{AgCl}} = 0.422$$

Example 3 Ideal solutions (Raoult's Law)

Part (a) Calculate:

i. The heat effect after dissolving 1 mol of nickel (solid) in 9 mol of copper (liquid) at 1200 °C (1473 K), assuming these metals form an ideal solution
ii. The entropy change for this process

Solution

Part (i):

Since the solution is ideal, the enthalpy of mixing associated to the dissolution of nickel in copper is zero.

Part (ii):

To compute the entropy change, we need to use Eq. (4.55a):

$$\Delta S_{\mathrm{mix}}^{\mathrm{ideal}} = -R\left[x_{\mathrm{Cu}}\ln(x_{\mathrm{Cu}}) + x_{\mathrm{Ni}}\ln(x_{\mathrm{Ni}})\right]$$

$$x_{\mathrm{Cu}} = \frac{9}{1+9} = 0.9;\, x_{\mathrm{Ni}} = \frac{1}{1+9} = 0.1$$

$$\Delta S_{\text{mix}}^{\text{ideal}} = -8.314[0.9 \ln(0.9) + 0.1 \ln(0.1)]$$

$$\Delta S_{\text{mix}}^{\text{ideal}} s = 2.7 \frac{\text{J}}{\text{mole K}}$$

Part (b) A metal (M) can be removed from molten lead by selective oxidation at 900 °C (1173 K). Assuming that M forms an ideal solution with lead, determine the limiting concentration to which M can be removed from lead.

Use the following data:

$$\begin{array}{ll} 2\text{Pb} + \text{O}_2 = 2\text{PbO} & \Delta \text{G}_{1173}^{\circ} = -200832 \text{ J} \\ 2\text{M} + \frac{3}{2}\text{O}_2 = \text{M}_2\text{O}_3 & \Delta \text{G}_{1173}^{\circ} = -334720 \text{ J} \end{array}$$

Atomic weight of M = 122 g/mole
Atomic weight of Pb = 207 g/mole

Solution

To eliminate M from the molten lead, we are seeking for the reaction:

$$3\text{PbO} + 2\text{M} = 3\text{Pb} + \text{M}_2\text{O}_3$$

The Gibbs free energy for this reaction is obtained by reversing the lead oxidation reaction and to multiply it by 1.5 and then add that result to the Gibbs free energy for the oxidation of M. As a result of this the Gibbs free energy for the lead refining reaction is −33472 J.

In addition, we need to determine an expression for the equilibrium constant of the lead refining reaction in terms of the concentration of M and need to calculate a numerical value for such constant:

$$\text{K} = \frac{a_{\text{M}_2\text{O}_3} a_{\text{Pb}}^3}{a_{\text{M}}^2 a_{\text{PbO}}^3}$$

and

$$\Delta \text{G}^{\circ} = -RT \ln(\text{K}) = -RT \ln\left(\frac{a_{\text{M}_2\text{O}_3} a_{\text{Pb}}^3}{a_{\text{M}}^2 a_{\text{PbO}}^3}\right)$$

In the expression of the equilibrium constant, since an ideal behavior is assumed, the activities of lead and those of the oxides can be considered as one, additionally, the activity of the metal M equals to its molar fraction. Thus we obtain:

$$\Delta G^{\circ} = -RT \ln\left(\frac{1 \times 1^3}{x_M^2 \times 1^3}\right)$$

substituting numerical values :

$$-33472 = -8.314 \times 1173 \times \ln\left(\frac{1}{x_M^2}\right)$$

Solving for x_M:

$$x_M = \sqrt{\frac{1}{30.94}} = 0.18 \text{ mole of M}$$

This means that there are 0.18 mol of M and 0.82 mol of Pb. With such molar fractions we need to compute the masses of each metal, i.e.:

$$0.18 \text{ mole M} \times 122 \frac{\text{g M}}{\text{mole M}} = 21.96 \text{ g}$$

$$0.82 \text{ mole Pb} \times 207 \frac{\text{g Pb}}{\text{mole Pb}} = 169.74 \text{ g}$$

concentration of M :

$$\%\text{M} = \frac{21.94}{21.94 + 169.74} \times 100$$

$$\%\text{M} = 11.5\ \%$$

Therefore, M can be removed from the lead up to 11.5 weight %.

Part (c) In lead refining, antimony is removed from liquid lead by selective oxidation with air at 900 °C (air does not oxidize lead). Assuming Raoult's Law, estimate the minimum amount of antimony in (mass%) dissolved in lead after purification.

Use the following data:

ΔG_{Sb2O3} @ 1100 K = −417,563 J/mole; ΔG_{Sb2O3} @ 1200 K = −394,970 J/mole
M_{Sb} = 121.75 g/mole; M_{Pb} = 207.2 g/mole

Solution

The oxidation of antimony can be represented by the following chemical reaction:

$$2\text{Sb}_{\text{Pb}} + \frac{3}{2}\text{O}_2 = \text{Sb}_2\text{O}_3$$

Assuming a lineal dependency between Gibbs free energy for the antimony reaction and temperature, allow us to estimate the free energy at 1173 K (900 °C):

$$\Delta G^{\circ}_{Sb2O3,\,1173} = \frac{-417563 + 394970}{1100 - 1200}(1173 - 1200) - 394970$$
$$\Delta G^{\text{o}}_{\text{Sb2O3},\,1173} = -401070$$

The equilibrium constant for antimony oxidation reaction is:

$$K = \frac{a_{\text{Sb}_2\text{O}_3}}{a^2_{\text{Sb}} \times P^{1.5}_{\text{O}_2}}$$

To use this constant, we need to do some considerations:

- Sb_2O_3 is a pure oxide, thus its activity is 1
- Since antimony is forming an ideal solution, its activity equals its molar fraction
- Air contains 0.21 mol%, thus the partial pressure of oxygen in air is 0.21.

With these assumptions, we can rewrite the equilibrium constant as:

$$K = \frac{1}{x_{\mathrm{Sb}}^2 (0.21)^{1.5}}$$

To solve for x_{Sb}, first we need to calculate the value of K, to do so, we use Eq. (1)

$$\Delta G^\circ_{1173} = -RT\ \ln(K)$$
$$K = \exp\left(\tfrac{-401070}{-8.314 \times 1173}\right)$$
$$\mathrm{K} = 7.25 \times 10^{17}$$

With this value, we can calculate the molar fraction of antimony:

$$x_{\mathrm{Sb}} = \sqrt{\frac{1}{7.25 \times 10^{17} (0.21)^{1.5}}}; \quad x_{\mathrm{Sb}} = 3.79 \times 10^{-9}$$

The mass of the remaining Sb in solution is:

$$m_{\mathrm{Sb}} = x_{\mathrm{Sb}} M_{\mathrm{Sb}}$$
$$m_{\mathrm{Sb}} = 3.79 \times 10^{-9} (121.75)$$
$$m_{\mathrm{Sb}} = 4.61 \times 10^{-7} g_{\mathrm{Sb}}$$

To calculate the mass% of antimony, we need to add the mass of the lead. Since the mole fraction of antimony is very small, we can consider x_{Pb} as 1. Thus there are 207.2 g of lead and 4.61×10^{-7} g of antimony. Therefore, the mass percentage of remaining antimony is: 2.22×10^{-7} mass% of Sb.

Part (d)

The standard Gibbs free energy for the reaction:

$$CO_2 + C = 2CO$$

Is

$$\Delta G^\circ = 170700 - 174.5T\ (\mathrm{J})$$

The equilibrium ratio P_{CO}/P_{CO_2} over molten steel containing 1 wt% C at 1600 °C (1873 K) under 1 atm is 1003. Determine the activity of carbon in the steel with respect of pure solid carbon.

Solution
For the given reaction, the equilibrium constant is:

$$K = \frac{P_{CO}^2}{a_C P_{CO_2}}$$

To compute the activity of carbon, we need to calculate the numerical value of the equilibrium constant and that of the partial pressures of CO and CO_2:

The equilibrium constant is given by:

$$\begin{aligned}
&170700 - 174.5\,T = \Delta G^\circ = -RT\ \ln K\\
&170700 - 174.5(1873) = -8.314(1873)\ln K\\
&\ln K = 10.03\\
&K = 2.262 \times 10^4
\end{aligned}$$

From the P_{CO}/P_{CO_2} ratio given, we can express the partial pressure of CO in terms of that of CO_2:

$$\frac{P_{CO}}{P_{CO_2}} = 1003 \quad \Rightarrow \quad P_{CO} = 1003 P_{CO_2}$$

Substituting this relationship in the expression for K:

$$K = \frac{P_{CO}^2}{P_{CO_2}}\frac{1}{a_C} = \frac{1003^2 P_{CO_2}^2}{P_{CO_2}}\frac{1}{a_C} = \frac{1003^2 P_{CO_2}}{a_C}$$

$$P_{CO} + P_{CO_2} = 1;$$

$$1003 P_{CO_2} + P_{CO_2} = 1$$

$$P_{CO_2} = \frac{1}{1004} = 9.96 \times 10^{-4}$$

Thus :

$$K = \frac{1003^2 P_{CO_2}}{a_C} = \frac{1003^2\left(9.96 \times 10^{-4}\right)}{a_C}$$

Substituting the numerical value of K and solving for the activity of carbon:

$$a_C = \frac{1003^2(9.96 \times 10^{-4})}{2.262 \times 10^4} = 0.044$$

The activity of carbon in molten steel at 1600 °C is 0.044.

Part (e) At 150 °C, component A has a vapor pressure of 1.4 atm and that of component B is 0.6 atm. A solution of A and B is prepared and allowed to reach the equilibrium with its vapor. The vapor is equimolar. What is the molar fraction of A in the solution?

Solution

Assuming an ideal mixing, we have from Eq. (4.6):

$$P_i = x_i P_i^{\circ}$$

Since the vapor over the mixture contains the same amount of moles of A and B, then we have that $P_A = P_B$. Because of this condition, we can use Eq. (4.6) as follows:

$$x_A P_A^{\circ} = x_B P_B^{\circ}$$
$$x_A P_A^{\circ} = (1 - x_A) P_B^{\circ}$$

Solving for x_A:

$$x_A = \frac{1}{\frac{P_A^{\circ}}{P_B^{\circ}} + 1} = \frac{1}{\frac{1.4}{0.6} + 1} = 0.3$$

The initial mole fraction of a in the solution is 0.3.

Part (f) The vapor pressure over an aqueous solution contains 21 mg of water per liter at 25 °C, what is the concentration of the solute? The vapor pressure of water at 25 °C is 0.031 atm.

Solution

We need to determine the number of moles of water in the vapor over the solution:

$$\frac{0.021\ \text{g}}{18\text{g/mole}} = 0.0012\ \text{mole H}_2\text{O}$$

Using the ideal gas law, we can calculate the pressure exerted by the water vapor over the solution:

$$P = \frac{nRT}{V} = \frac{0.0012\text{mole}\left(0.08206\frac{\text{atmL}}{\text{moleK}}\right)\left(298\text{K}\right)}{1\text{L}} = 0.029\ \text{atm}$$

Assuming an ideal behavior, the molar fraction of the water can be calculated from Eq. (4.6):

$$P_{\text{water}} = x_{\text{water}} P_{\text{water}}^{\circ}$$
$$x_{\text{water}} = \frac{P_{\text{water}}}{P_{\text{water}}^{\circ}} = \frac{0.029}{0.031} = 0.94$$

The solute content is then $1 - x_{water} = 0.06$

Example 4 Diluted solutions (Henry's Law)

Part (a) Data was recorded in measuring the vapor pressure of mercury over Bi–Hg alloys at 321 °C. At that temperature, the vapor pressure of mercury is 0.5039 atm.

With the given data:

i. Plot P_{Hg} vs x_{Hg}
ii. Calculate the activity of mercury for each alloy with respect of pure liquid mercury as standard state. Also calculate the activity coefficients of mercury. Plot the results.
iii. Recalculate the activities of mercury, but now use the infinitely diluted molar fraction standard state.

Data:

x_{Bi}	P_{Hg} (atm)
0.1486	0.4579
0.247	0.4237
0.347	0.3855
0.463	0.3276
0.563	0.2737
0.67	0.2171
0.793	0.1395
0.937	0.0463

Solution

Part (i). We need to compute the molar fraction of mercury ($x_{Hg} = 1 - x_{Bi}$) and the plot the pressure of mercury vs its molar fraction (Fig. 4.17).

Part (ii). To determine the activities of mercury in the different alloys, we must use Eq. (4.5). In this particular case, P°_{Hg} has been given, and its value is 0.5039 atm. Since the molar fractions and the activities of mercury are known, we can compute the activity coefficients of mercury (γ_{Hg}) using Eq. (4.57). Results of these calculations are shown in the Fig. 4.18.

For part (iii), we need to change the standard state from pure mercury to the infinitely diluted molar fraction. To do so, we need to calculate the value of the Henrian activity coefficient for mercury (γ°_{Hg}). To do this, we need to determine the slope in the a_{Hg} versus x_{Hg} plot at very low mercury content. Such value should be utilized to determine the Henrian activity of mercury (h_{Hg}) according to Eq. (4.62), since the activity of mercury is already known. This means that in order to compute the new activities of mercury, we must multiply the activities calculated in part (ii) by γ°_{Hg}. The estimation of γ°_{Hg} is shown in Fig. 4.12.

Table 4.6 summarizes the results of this problem; whereas Fig. 4.20 compares the different activities computed in this problem (Fig. 4.19).

Fig. 4.17 Partial pressure of mercury vs its molar fraction in Hg–Bi mixtures at 321 °C

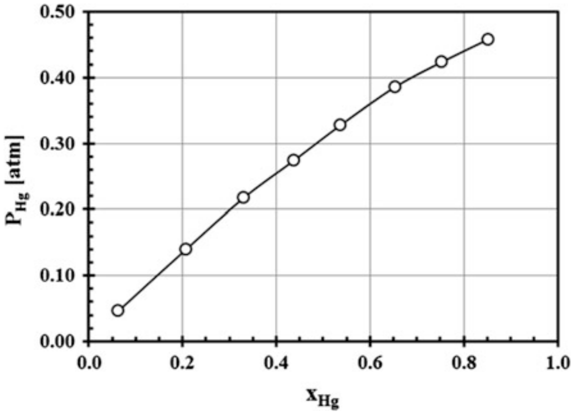

Fig. 4.18 Activities and activity coefficients of mercury in Hg–Bi alloys at 321 °C as a function of composition

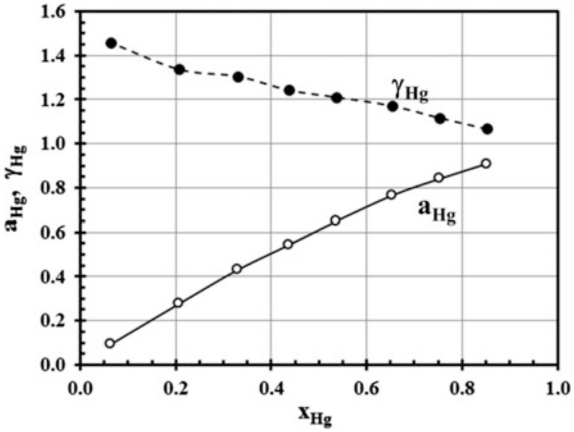

Fig. 4.19 H's constant for Hg in diluted Hg–Bi alloys at 321 °C

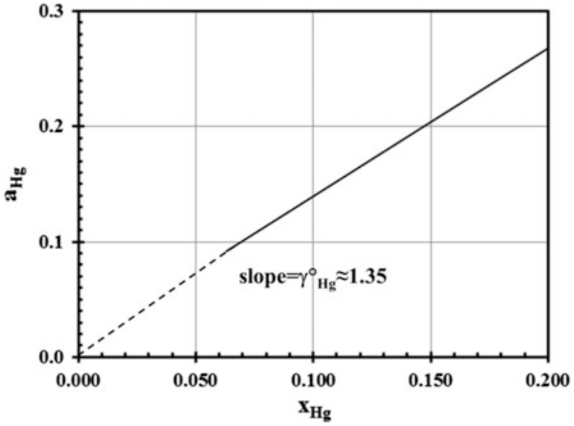

Table 4.6 Activity and Henrian activity of mercury in Hg–Bi alloys at 321 °C

x_{Bi}	P_{Hg} (atm)	x_{Hg}	a_{Hg}	γ_{Hg}	h_{Hg}
0.1486	0.4579	0.8514	0.9086	1.0672	0.673
0.247	0.4237	0.7530	0.8407	1.1165	0.623
0.347	0.3855	0.6530	0.7650	1.1715	0.567
0.463	0.3276	0.5370	0.6501	1.2107	0.482
0.563	0.2737	0.4370	0.5431	1.2427	0.402
0.67	0.2171	0.3300	0.4308	1.3055	0.319
0.793	0.1395	0.2070	0.2768	1.3370	0.205
0.937	0.0463	0.0630	0.0919	1.4588	0.068

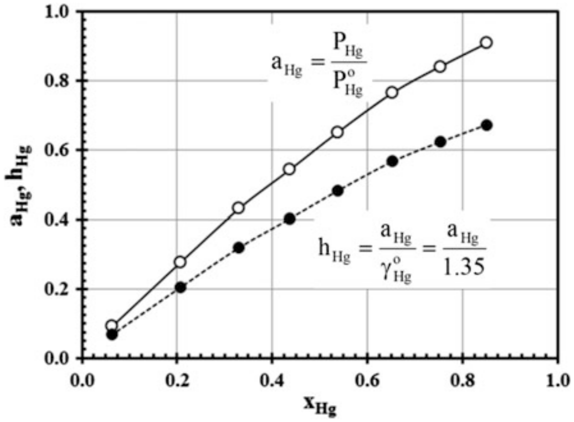

Fig. 4.20 Comparison between activity and Henrian activity of mercury in Hg–Bi alloys at 321 °C

Part (b) Zinc vapor pressure over α and β brasses at 800 °C was recorded:

Phase	x_{Zn}	P_{Zn} (mm Hg)
α	0.1	2
	0.2	7.4
	0.3	22
	0.35	35
β	0.4	37
	0.45	56
	0.5	93

The vapor pressure of pure zinc (in mmHg) can be estimated with the equation:

$$\log P^{\circ}_{Zn} = -1.255\ \log(T) + 12.34 - \frac{6620}{T}$$

i. Calculate the activity of Zn in α and β brasses, and plot the activity vs the molar fraction of zinc
ii. Calculate the activity coefficients of zinc and plot them vs molar fractions.
iii. Draw the curve for the ideal solution
iv. How is the behavior of these alloys with respect of an ideal solution?

Solution

First, we need to determine the pressure of pure zinc at the test temperature:

$$\log P^{\circ}_{\mathrm{Zn}} = -1.255\log(1073) + 12.34 - \tfrac{6620}{1073}$$

$$\log P^{\circ}_{\mathrm{Zn}} = 2.367$$

$$P^{\circ}_{\mathrm{Zn}} = 232.8\,\mathrm{mm\,Hg}$$

Since we now have the pressure of zinc at the different compositions and that of the pure element, we now can compute the activity of zinc in the different compositions, according to Eq. (4.5). Also, having already determined the activities of zinc, we can calculate the corresponding activity coefficients by using Eq. (4.57). Finally, if an ideal behavior is assumed, then we should plot x_{Zn} versus x_{Zn}. This is shown in Fig. 4.21, next:

As seen from the previous image, the line of the activity of zinc lies below that of the ideal behavior, henceforth, these solutions have a negative deviation with respect of the ideality.

Table 4.7 summarizes the computed values of the different quantities used in this example.

Part (c) Newhouse et al.[4] measured the electromotive force in Ca–Mg alloys at 500 °C. The measurements were made over mixtures with different calcium contents. The following data is provided:

x_{Ca}	E_{Ca} (mV)	a_{Mg}
0.01	167	0.990
0.05	163	0.990
0.1	161	0.990
0.19	161	0.990
0.31	157	0.940
0.49	7.5	0.046
0.6	3	0.039
0.69	1	0.035
0.8	−4.3	0.032

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[4] Newhouse J.M., Poizeau S., Kim H., Spatocco B.L., Sadoway D.R., Electrochimica Acta. 91, 2013, 293–301.

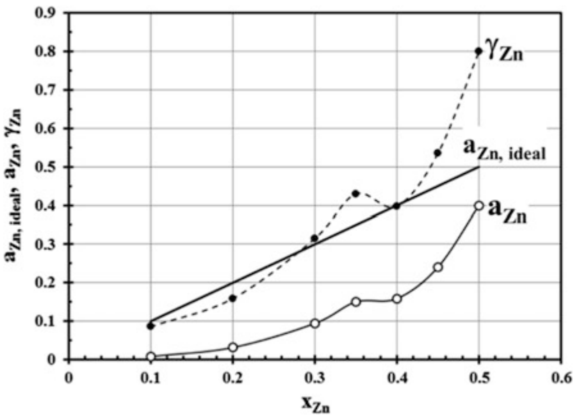

Fig. 4.21 Comparison of ideal and nonideal activity of zinc over different brasses

Table 4.7 Activities (ideal and nonideal) over different brasses at 800 °C

Phase	x_{Zn}	P_{Zn} (mm Hg)	a_{Zn}	γ_{Zn}	$a_{Zn, ideal}$
α	0.1	2	0.008591	0.085911	0.1
	0.2	7.4	0.031787	0.158936	0.2
	0.3	22	0.094502	0.315008	0.3
	0.35	35	0.150345	0.429557	0.35
β	0.4	37	0.158936	0.39734	0.4
	0.45	56	0.240552	0.53456	0.45
	0.5	93	0.399488	0.798976	0.5

Calculate:

i. The activity of calcium at the different composition tested
ii. The partial molar Gibbs free energies of calcium and magnesium
iii. The molar Gibbs free energy of mixing and how it departs from the ideal behavior.

Solution

To determine the activity of calcium in the mixtures, we need to use Eq. (3.28):

$$E = -\frac{RT}{nF}\ln(a_{Ca}) \tag{3.28}$$

Solving for the activity of calcium, yields:

$$a_{Ca} = \exp\left(-\frac{nFE}{RT}\right)$$

Table 4.8 Computed activity of calcium, partial molar Gibbs free energy of Ca and Mg, and Gibbs free energy of mixing

x_{Ca}	E (mV)	a_{Ca}	a_{Mg}	ΔG_{Ca} (kJ/mole)	ΔG_{Mg} (kJ/mole)	ΔG_{mix} (kJ/mole)	$\Delta G_{\mathrm{mix,\ ideal}}$ (kJ/mole)
0.01	167.0	0.0066	0.990	−32.231	−0.06459	−0.38625	−0.35991
0.05	163.0	0.0075	0.990	−31.459	−0.06459	−1.63431	−1.2758
0.10	161.0	0.0079	0.990	−31.073	−0.06459	−3.16543	−2.08922
0.19	161.0	0.0079	0.990	−31.073	−0.06459	−5.95619	−3.12482
0.31	157.0	0.0090	0.940	−30.301	−0.39766	−9.66769	−3.97879
0.49	7.5	0.7983	0.046	−1.4475	−19.7886	−10.8015	−4.45338
0.60	3.0	0.9138	0.039	−0.579	−20.8495	−8.68721	−4.32526
0.69	1.0	0.9704	0.035	−0.193	−21.545	−6.81212	−3.97879
0.80	−4.3	1.1378	0.032	0.8299	−22.1209	−3.76026	−3.21595

With $n = 2$ eq/mole, $F = 96{,}500$ J/V/eq, $R = 8.314$ J/mole/K, $T = 773$ K and E the voltage readings. Substituting the constant terms in the previous equation:

$$a_{Ca} = \exp(-30.031E)$$

The results for the calculated activities of calcium are shown in Table 4.8, along with the activity of magnesium (provided). These activities are plotted together and compared to the activities of these metals if Raoultian behavior were exhibited. See Fig. 4.22a.

Since the activity of both calcium and magnesium are known, we can compute the partial molar Gibbs free energy of each element according to Eq. (4.22):

$$\Delta\overline{G}_i = RT\ln(a_i) \tag{4.22}$$

Results are shown in Fig. 4.22b. Once we have the partial molar Gibbs free energies, we can compute the partial molar Gibbs free energy of the mixture according to Eq. (4.45):

$$\Delta\overline{G}_{\mathrm{mix}} = x_{\mathrm{Ca}}\Delta\overline{G}_{\mathrm{Ca}} + x_{\mathrm{Mg}}\Delta\overline{G}_{\mathrm{Mg}} \tag{4.45}$$

Finally, the Gibbs free energy of mixing was calculated following Eq. (4.54):

$$\Delta G_{\mathrm{mix}}^{\mathrm{ideal}} = RT\left(x_{\mathrm{Ca}}\ln(x_{\mathrm{Ca}}) + x_{\mathrm{Mg}}\ln\left(x_{\mathrm{Mg}}\right)\right) \tag{4.54}$$

Figure 4.22c compares the Gibbs free energy of ideal mixing with that of the nonideal solution.

Results for the calculated activities and Gibbs free energies are shown in Table 4.8.

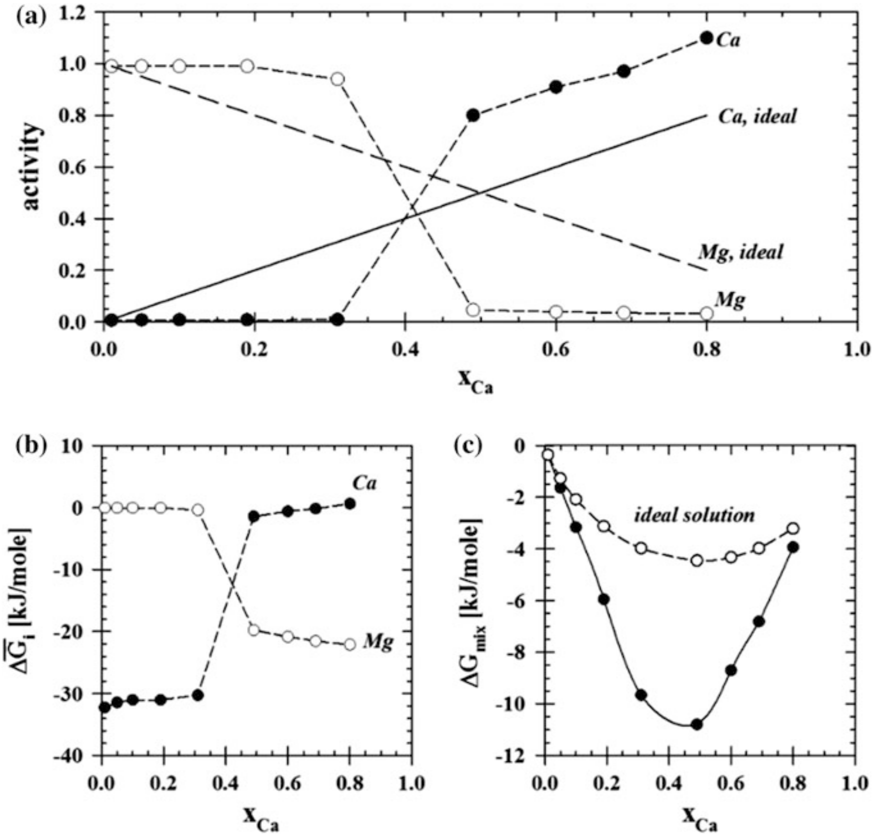

Fig. 4.22 **a** Computed activities (ideal and nonideal) of Ca and Mg at 773 K; **b** Partial molar Gibbs free energy of Ca and Mg at 773 K; **c** Gibbs free energy of mixing (ideal and nonideal) in the Ca–Mg alloy at 773 K

Part (d) Considerable amounts of magnesium are produced by molten salt electrolysis. The salts used for electrolysis contain NaCl; this results in magnesium bearing sodium with typical concentrations lying between 2 and 200 ppm (parts per million). Because of these extreme low concentrations, reliable determination of the activity of sodium becomes an issue.

Determine if sodium–magnesium mixtures with high Mg contents obey Henry's Law. If so, determine the value of Henry's constant fore sodium (γ°_{Na}), if the electrolysis takes place at 735 °C.

The following data is available:

$$\begin{aligned} &MgCl_2 = Mg + Cl_2; \\ &\Delta G^{\circ} = 618604.4 + 56.819T\ \log(T) - 304.5T\ \mathrm{J/mole} \end{aligned} \tag{1}$$

$$\begin{aligned}&NaCl = Na + 0.5 \cdot Cl_2;\\&\Delta G^\circ = 478231.2 - 149.8\,T\,\mathrm{J/mole}\end{aligned} \tag{2}$$

Also experimental data from Rosenkilde et al.[5] is available:

x_{Na}	a_{NaCl}	a_{MgCl2}
3.40×10^{-7}	0	1
1.80×10^{-7}	0.024	0.757
4.80×10^{-7}	0.089	0.427
4.00×10^{-6}	0.477	0.05
9.30×10^{-6}	0.693	0.016
1.37×10^{-5}	0.753	0.011
3.1×10^{-7}	0	1
1.9×10^{-7}	0.024	0.757
3.7×10^{-7}	0.089	0.427
1.5×10^{-6}	0.289	0.128
3.9×10^{-6}	0.477	0.05
6.6×10^{-6}	0.693	0.016
9.2×10^{-6}	0.753	0.011

Solution

We need to combine reactions (1) and (2) to obtain the equilibrium between magnesium sodium and their respective chlorides. To do so, we must multiply reaction (2) by two and subtract Eq. (1) from the modified reaction (2):

$$\begin{aligned}&2NaCl = 2Na + Cl_2 && \Delta G^\circ = 2[478231.2 - 149.8T]\\&Cl_2 + Mg = MgCl_2 && \Delta G^\circ = -618604.4 - 56.819T\,\log(T) + 304.5T\end{aligned}$$

This results in:

$$\begin{aligned}&2NaCl + Mg = 2Na + MgCl_2\\&\Delta G^\circ = 337858 - 56.819T\,\log(T) + 4.9\mathrm{T}\end{aligned} \tag{3}$$

At the test temperature of 735 °C (1008 K), the Gibbs free energy of formation is:

$$\Delta G^\circ = 170778\,\mathrm{J/mole}$$

On the other hand, we can relate this Gibbs free energy of formation to the equilibrium constant by using Eq. (1.38):

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[5] Rosenkilde C., Arnesen L.H., Wallevik O., J. Phase Equilibria. 21(6), 2000, 521–527.

$$\Delta G^{\circ} = -RT\ln(K)$$

Solving for the equilibrium constant K results in:

$$K = \exp\left[-\frac{\Delta G^{\circ}}{RT}\right] = \exp\left[-\frac{170778}{8.314 \times 1008}\right] = 1.41 \times 10^{-9}$$

According to reaction (3), the equilibrium constant can be expressed as:

$$K = \frac{a_{\mathrm{Na}}^{2}\, a_{\mathrm{MgCl_2}}}{a_{\mathrm{NaCl}}^{2}\, a_{\mathrm{Mg}}}$$

Since the concentration of sodium in magnesium is very low, we can assume that the activity of magnesium is fixed at one. Substituting Rosenkilde's data, we can compute the activity of sodium:

$$a_{\mathrm{Na}} = \sqrt{\frac{K \times a_{\mathrm{NaCl}}^{2} \times a_{\mathrm{Mg}}}{a_{\mathrm{MgCl_2}}}} = \sqrt{\frac{K \times a_{\mathrm{NaCl}}^{2}}{a_{\mathrm{MgCl_2}}}}$$

Plotting the activity of sodium versus the molar fraction of this component yields the following graph (Fig. 4.23).

As seen in this figure, the activity of sodium may be represented by a straight line at very low concentrations, therefore, sodium forms solutions (low Na contents) with magnesium that follow Henry's law. The Henrian activity coefficient of sodium in magnesium is 0.041.

Example 5 Regular solutions

Part (a) The enthalpies of mixing in various Cd–Zn alloys were measured at 800 K. Such measurements are shown next:

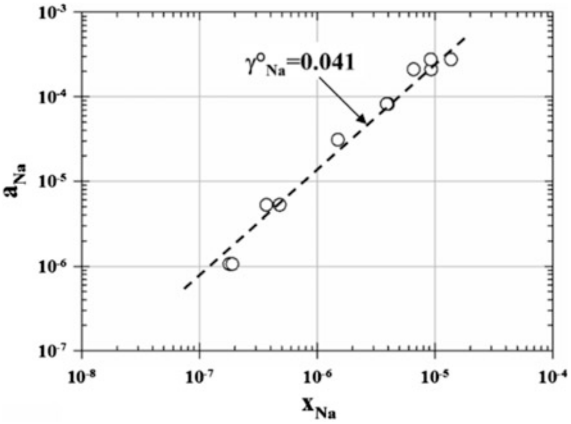


Fig. 4.23 Activity of sodium in diluted Na–Mg mixtures at 735 °C

x_{Zn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
ΔH_{mix} (J/mole)	774	1372	1761	2008	2092	2025	1799	1397	803

i. Plot the concentration dependence of the integral heat of mixing of these alloys and by the method of tangents determine the partial molar heats for each component.
ii. Find a_{Cd} for each composition
iii. Do these solutions exhibit a regular behavior?

Solution

Part (i), plotting the data gives the following figure.

Repeating the procedure described in example 1 part a, the following enthalpies of mixing were found from Fig. 4.24.

The last column of Table 4.9 is in good agreement with the data provided. The little variations between the computed ΔH_{mix} and that gives is attributed to the reading from the plot in Fig. 4.24.

For part (ii)

Since the partial molar enthalpy of mixing of cadmium is known and by assuming regular behavior in the Cd–Zn alloys, the activity of cadmium can be calculated from Eq. (4.80) since for a regular solution the enthalpy of mixing equals to the Gibbs free energy of mixing, thus:

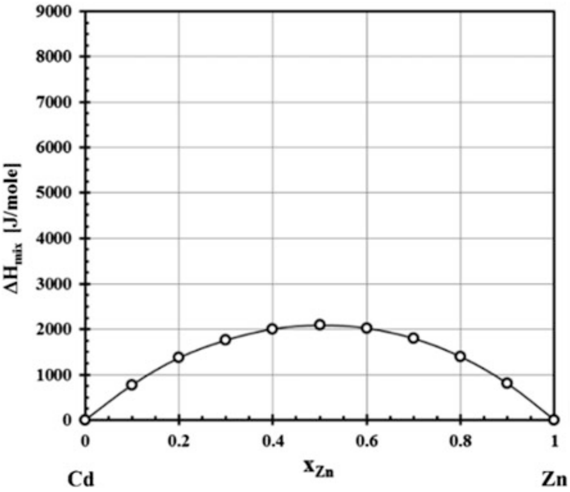


Fig. 4.24 Enthalpy of mixing in Cd–Zn alloys at 800 K

Table 4.9 Molar partial enthalpies of zinc and cadmium and mixing enthalpy in the Zn–Cd system at 800 K

x_{Zn}	H_{Zn} (J/mole)	x_{Cd}	H_{Cd} (J/mole)	H_{mix} (J/mole)
0	8750	1	0	0
0.1	6000	0.9	200	780
0.2	4800	0.8	510	1368
0.3	3760	0.7	905	1761.5
0.4	3150	0.6	1250	2010
0.5	2200	0.5	2000	2100
0.6	1440	0.4	2900	2024
0.7	900	0.3	3900	1800
0.8	500	0.2	5050	1410
0.9	200	0.1	6300	810
1	0	0	8000	0

$$\begin{aligned}\Delta G_{Cd} &= \Delta H_{Cd} = RT\ln\gamma_{Cd}\\ \gamma_{Cd} &= \exp\left[\frac{\Delta H_{Cd}}{RT}\right]\end{aligned} \tag{4.80}$$

Once the activity coefficient of cadmium is calculated, its activity can be estimated by multiplying this coefficient by the molar fraction of Cd in the solution.

To verify the assumption of the regular solution behavior, we need to compute the interaction parameter Ω as indicated by Eq. (4.79):

$$\Omega = \frac{RT\ \ln\gamma_{Cd}}{(1 - x_{Cd})^2} \tag{4.79}$$

Results of these calculations are shown in Table 4.10.

Table 4.10 Interaction parameter (Ω) in Zn–Cd alloys at 800 K

x_{Cd}	γ_{Cd}	a_{Cd}	Ω
1	1.00	1.00	
0.9	1.03	0.93	20000.00
0.8	1.08	0.86	12750.00
0.7	1.15	0.80	10055.56
0.6	1.21	0.72	7812.50
0.5	1.35	0.68	8000.00
0.4	1.55	0.62	8055.56
0.3	1.80	0.54	7959.18
0.2	2.14	0.43	7890.63
0.1	2.58	0.26	7777.78
0	3.33	0.00	

From the table, it can be seen that the Ω parameter exhibits some variation especially at high Cd contents, however, up to $x_{\mathrm{Cd}} = 0.6$, the interaction parameter shows little variability, thus we can affirm that the Cd–Zn solutions have regular conduct.

Part (b) For an AgCl–KCl liquid solution, the activity of silver chloride is 0.409 at the equimolar composition and 800 °C. It was also found that the molar partial enthalpy of mixing of this chloride is −1793 J. This quantity is independent of temperature. Calculate the activity of silver chloride at the equimolar composition but at 1000 °C.

Solution

Since there is a value for the partial molar enthalpy of mixing for the silver chloride, we can assume a regular behavior for the AgCl–KCl mixture; then to solve this problem, we can use Eq. (4.75a) to first calculate the activity coefficient of the chloride and then its activity:

$$\begin{gathered}\Delta\overline{H}_{\mathrm{AgCl}} = RT\ln\left(\gamma_{\mathrm{AgCl}}\right)\\ \gamma_{\mathrm{AgCl}} = \exp\left(\frac{\Delta\overline{H}_{\mathrm{AgCl}}}{RT}\right)\end{gathered} \tag{4.75a}$$

Substituting values:

$$\gamma_{\mathrm{AgCl}} = \exp\left(-\frac{1793}{8.314\times(1000+273)}\right) = 0.8442$$

With this coefficient, we now can calculate the activity of silver chloride:

$$a_{\mathrm{AgCl}} = \gamma_{\mathrm{AgCl}}x_{\mathrm{AgCl}} = 0.8842\times 0.5 = 0.422$$

At 1000 °C, the activity of silver chloride in an equimolar AgCl–KCl solution is 0.422.

Part (c) A and B form regular solutions with an interaction parameter of −4184 J. What is the activity of component A at 1000 K in an equimolar mixture.

Solution

From Eq. 4.79, we can calculate the activity coefficient of A and then its activity:

$$\Omega = \frac{RT\ \ln(\gamma_{\mathrm{A}})}{x_{\mathrm{B}}^2} = \frac{RT\ \ln(\gamma_{\mathrm{A}})}{(1-x_{\mathrm{A}})^2}$$

Substituting values and solving for γ_{A}:

$$\ln(\gamma_A) = \frac{(1 - x_A)^2 \Omega}{RT} = -\frac{(0.5)^2(4184)}{8.314(1000)} = -0.1258$$

$$\gamma_A = 0.88$$

And the activity of A is then:

$$a_A = \gamma_A x_A = 0.88(0.5) = 0.44$$

Part (d) Gold-copper solutions are regular at 500 °C. At such temperature the enthalpy of mixing is given below.

x_{Cu}	ΔH_{mix} (J/mole)
0.1	−1402
0.2	−2740
0.3	−3807
0.4	−4686
0.5	−5146
0.6	−5188
0.7	−4728
0.8	−3598

Find:

i. ΔH_{Cu} and ΔH_{Au} at $x_{Cu} = 0.3$
ii. ΔG_{mix} at $x_{Cu} = 0.3$

Solution

We need to plot the data given, and graphically determine the partial molar enthalpies of mixing for gold and copper (part (i)); this is illustrated in Fig. 4.25.

For part (ii), to calculate Gibbs free energy of mixing, we need to apply Eq. (4.82):

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{4.82}$$

The enthalpy of mixing at the composition is already given (−3807 J/mole). Assuming regular behavior, the entropy term should be calculated using Eq. (4.77), thus, substituting values in (4.82), we have:

$$\Delta G_{mix} = -3807 - 773(-8.314(0.3\ \ln 0.3 + 0.7\ \ln 0.7))$$

$$\Delta G_{mix} = -3807 - 3926 = -7733\ \frac{\text{J}}{\text{mole}}$$

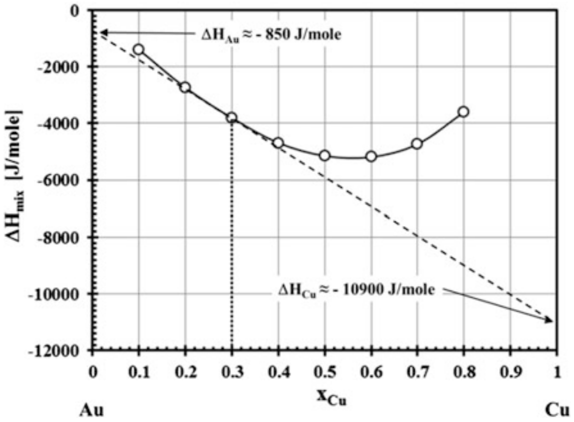


Fig. 4.25 enthalpy of mixing in the Au–Cu system at 500 °C

The Gibbs free energy of mixing at $x_{\mathrm{Cu}} = 0.3$ is −7733 J/mole.

Part (e) The activities and heats of solution are reported for PbO–SiO$_2$ binary mixtures at 1200 °C.

$x_{\mathrm{SiO_2}}$	a_{PbO}	$a_{\mathrm{SiO_2}}$	ΔH_{PbO} (kJ/mole)	$\Delta H_{\mathrm{SiO_2}}$ (kJ/mole)
0.1	0.85	0.0068	−0.42	−45.2
0.2	0.66	0.031	−1.7	−41.8
0.3	0.45	0.095	−9.6	−18.8
0.4	0.27	0.25	−18.0	−2.93
0.5	0.14	0.55	−23.0	4.20
0.6	0.079	0.88	−25.1	6.30

i. Construct the heat of formation curve for one mole of mixture
ii. Construct the integral free energy curve
iii. Construct the integral ΔS curve
iv. What are the values of ΔG_{PbO}, ΔH_{PbO}, ΔS_{PbO}, and a_{PbO} for a solution in which $x_{\mathrm{PbO}} = 0.53$

Solution

To solve part (i), we need to calculate the activity coefficients of lead oxide and silicon oxide by using Eq. (4.57). Once these coefficients are known, their respective values are inserted in Eq. (4.78) to determine the enthalpy of mixing at 1473 K (1200 °C) as the silicon oxide contents increases. The resulting plot is shown in Fig. 4.26.

Additionally, in part (ii), to compute the Gibbs free energy of mixing, we must insert the activities (given data) of both oxides into Eq. (4.76) at 1473 K; results of this operation are also plotted in Fig. 4.26.

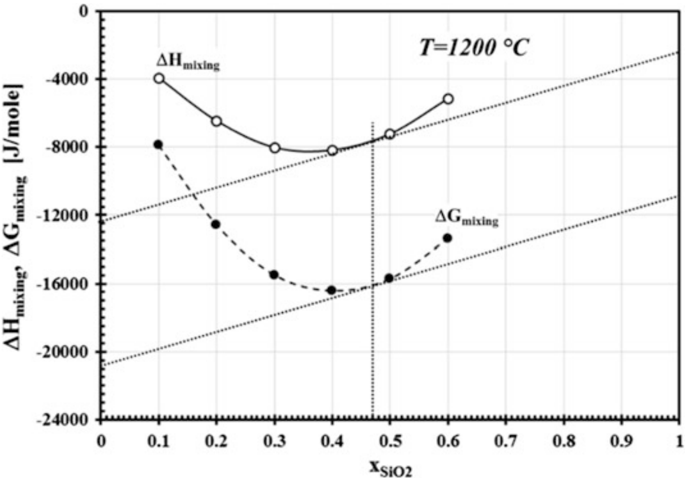


Fig. 4.26 Gibbs free energy and enthalpy of mixing at 1200 °C in the PbO–SiO_2 system

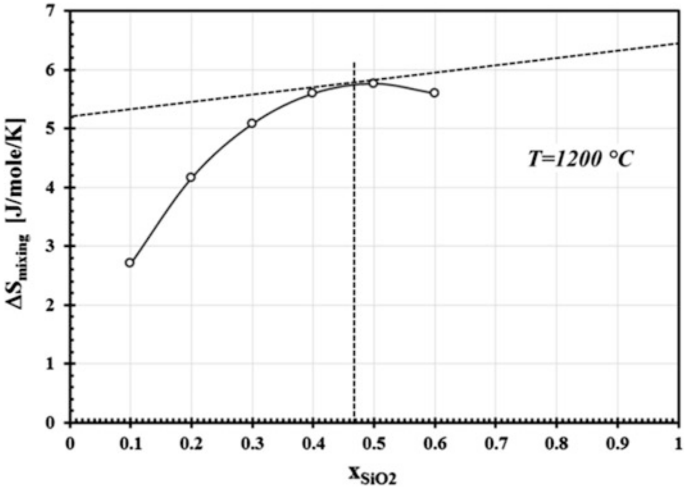


Fig. 4.27 Entropy of mixing at 1200 °C in the PbO–SiO_2 system

Similarly, to determine the entropy of mixing (part iii), we need to substitute the molar fractions provided in the data (determine x_{PbO} from x_{SiO_2}), into Eq. (4.77) at 1473 K. Results are shown in Fig. 4.27.

To solve part (iv) we need to read directly the values of the quantities referred in the problem at the ordinate axis when x_{SiO_2} is 0 (pure PbO), either in Fig. 4.26 or 4.27. Form these plots we have:

Table 4.11 computed values for the Gibbs free energy, the enthalpy and the entropy of mixing in the PbO–SiO_2 system at 1200 °C

x_{SiO_2}	a_{PbO}	a_{SiO_2}	γ_{PbO}	γ_{SiO2}	G_{mix} (J/mole)	H_{mix} (J/mole)	S_{mix} (J/mole/K)
0.1	0.85	0.0068	0.944	0.068	−7903.30	−3922.16	2.70
0.2	0.66	0.031	0.825	0.155	−12579.21	−6451.02	4.16
0.3	0.45	0.095	0.643	0.317	−15493.31	−8012.34	5.08
0.4	0.27	0.25	0.450	0.625	−16411.78	−8169.73	5.60
0.5	0.14	0.55	0.280	1.100	−15699.73	−7211.09	5.76
0.6	0.079	0.88	0.198	1.467	−13373.48	−5131.43	5.60

Quantity	Value
$\Delta\overline{H}_{PbO}$	−12,500 J/mole
$\Delta\overline{G}_{PbO}$	−20,750 J/mole
$\Delta\overline{S}_{PbO}$	5.2 J/mole/K
a_{PbO}	0.184

The activity of PbO was calculated using the Gibbs free energy of the oxide by means of Eq. (4.22). Table 4.11 summarizes the results plotted in the previous two figures.

Part (f) For a binary regular solution, Gibbs free energy of mixing is expressed as:

$$\Delta G_{mix} = \Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$

The first term in the previous equation is related to the enthalpy of mixing, whereas the second term relates to the entropy. Determine the effect of the interaction parameter (Ω) on the Gibbs free energy of mixing and that of the entropy of mixing.

Solution

To solve this problem, first we need to fix the temperature (entropy term) and vary the interaction parameter. Second, we need to fix the interaction parameter and vary the temperature. This is shown in the Fig. 4.28.

Example 6 Application of Sievert's Law

It was found the following solubilities of oxygen in liquid silver (100 g) at 962 °C:

P_{O_2} (atm)	0.58	1.00	1.32	1.58
$g_{O_2}/100\,g\,Ag$	0.232	0.305	0.35	0.383

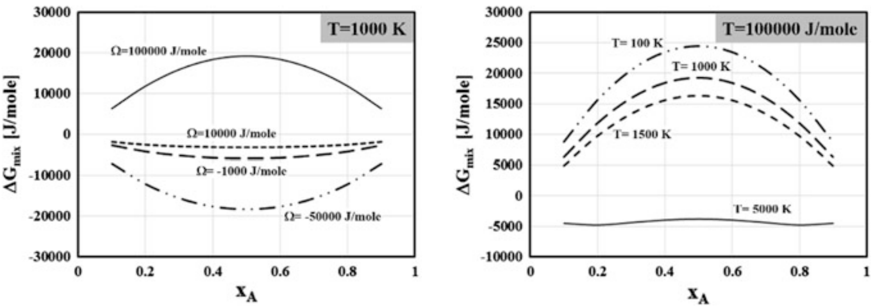
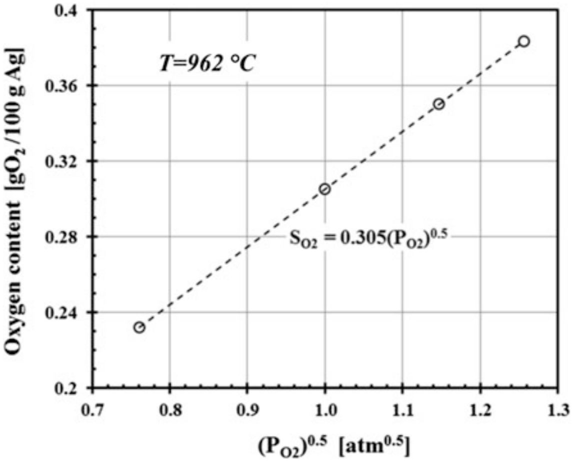


Fig. 4.28 Effect of the interaction parameter, and that of the ideal entropy on the Gibbs free energy of mixing in regular solutions

Fig. 4.29 Solubility of oxygen in silver at 962 °C



Show that the data fits Sievert's Law. Calculate how much oxygen silver absorbs at the test temperature from ambient air.

Solution

To solve this problem, we need to plot the data given; in this case the oxygen content must be plotted against the square root of the partial pressure of oxygen.

Form the graph in Fig. 4.29, the slope of the resulting line is 0.305. The oxygen content in the air is 0.21 atm and its square root is 0.458 $\text{atm}^{0.5}$. Substitution of this value in the equation found from the data results in that the oxygen tat silver can pick up from atmospheric air is 0.14 g O_2/100 g Ag.

Example 7 Application of Gibbs–Duhem equation

Part (a) It has been found that the activity coefficient of zinc in Zn–Cd alloys at 435 °C can be represented by the equation:

$$\ln \gamma_{Zn} = 0.87(1 - x_{Zn})^2 - 0.30(1 - x_{Zn})^3$$

Find an expression for the activity coefficient of cadmium, and calculate the activity of this metal in 30 and 50 molar% Cd alloys at 435 °C.

Solution

We need to use Gibbs–Duhem Eq. (4.86) to solve this problem. Such equation takes the following form:

$$x_{Cd}\mathrm{d}\ \ln \gamma_{Cd} + x_{Zn}\mathrm{d}\ \ln \gamma_{Zn} = 0 \tag{1}$$

Solving for the logarithm of cadmium activity coefficient:

$$\mathrm{d}\ \ln \gamma_{Cd} = -\frac{x_{Zn}}{x_{Cd}}\mathrm{d}\ \ln \gamma_{Zn} \tag{2}$$

To obtain the activity coefficient of cadmium in (2), we need to take the differential of $\ln\gamma_{Zn}$:

$$\begin{aligned}
\ln \gamma_{Zn} &= 0.87(1 - x_{Zn})^2 - 0.30(1 - x_{Zn})^3 \\
\mathrm{d}\ \ln \gamma_{Zn} &= \mathrm{d}\left[0.87(1 - x_{Zn})^2 - 0.30(1 - x_{Zn})^3\right] \\
\mathrm{d}\ \ln \gamma_{Zn} &= 0.87d(1 - x_{Zn})^2 - 0.30d(1 - x_{Zn})^3 \\
\mathrm{d}\ \ln \gamma_{Zn} &= 2 \times 0.87(1 - x_{Zn})(-\mathrm{d}x_{Zn}) - 3 \times 0.30(1 - x_{Zn})^2(-\mathrm{d}x_{Zn})
\end{aligned}$$

$$\mathrm{d}\ln \gamma_{Zn} = -1.74(1 - x_{Zn})(\mathrm{d}x_{Zn}) + 0.90(1 - x_{Zn})^2(\mathrm{d}x_{Zn}) \tag{3}$$

Inserting (3) into (2):

$$\begin{aligned}
\mathrm{d}\ \ln \gamma_{Cd} &= -\frac{x_{Zn}}{x_{Cd}}\left[-1.74(1 - x_{Zn})\mathrm{d}x_{Zn} + 0.9(1 - x_{Zn})^2\mathrm{d}x_{Zn}\right] \\
\mathrm{d}\ \ln \gamma_{Cd} &= -\frac{x_{Zn}}{1 - x_{Zn}}\left[-1.74(1 - x_{Zn})\mathrm{d}x_{Zn} + 0.9(1 - x_{Zn})^2\mathrm{d}x_{Zn}\right] \\
\mathrm{d}\ \ln \gamma_{Cd} &= -x_{Zn}[-1.74\mathrm{d}x_{Zn} + 0.9(1 - x_{Zn})\mathrm{d}x_{Zn}] \\
\mathrm{d}\ \ln \gamma_{Cd} &= -x_{Zn}[-1.74dx_{Zn} + 0.9\mathrm{d}x_{Zn} - 0.9x_{Zn}\mathrm{d}x_{Zn}] \\
\mathrm{d}\ \ln \gamma_{Cd} &= -x_{Zn}[-0.84\mathrm{d}x_{Zn} - 0.9x_{Zn}\mathrm{d}x_{Zn}]
\end{aligned}$$

$$\mathrm{d}\ln \gamma_{Cd} = \left[0.84x_{Zn}\mathrm{d}x_{Zn} + 0.9x_{Zn}^2\mathrm{d}x_{Zn}\right] \tag{4}$$

To obtain the expression for the activity coefficient of cadmium we need to integrate equation (E7.4), to do so, we need to use the following limits to perform the integration: @ $x_{\mathrm{Cd}} = 1$, $x_{\mathrm{Zn}} = 0$, $\gamma_{\mathrm{Cd}} = 1$, and @ $x_{\mathrm{Cd}} = x_{\mathrm{Cd}}$, $x_{\mathrm{Zn}} = (1 - x_{\mathrm{Cd}})$, $\gamma_{\mathrm{Cd}} = \gamma_{\mathrm{Cd}}$.

$$\int_{1}^{\gamma_{\mathrm{Cd}}} \mathrm{d}\ln\gamma_{\mathrm{Cd}} = \int_{0}^{1-x_{\mathrm{Cd}}} \left[0.84 x_{\mathrm{Zn}} \mathrm{d}x_{\mathrm{Zn}} + 0.9 x_{\mathrm{Zn}}^2 \mathrm{d}x_{\mathrm{Zn}}\right]$$

$$\ln\gamma_{\mathrm{Cd}}\Big|_{1}^{\gamma_{\mathrm{Cd}}} = \left[\frac{0.84}{2} x_{\mathrm{Zn}}^2 + \frac{0.9}{3} x_{\mathrm{Zn}}^3\right]\Bigg|_{0}^{1-x_{\mathrm{Cd}}}$$

Thus the logarithm of the activity coefficient of cadmium is:

$$\ln\gamma_{\mathrm{Cd}} = 0.42(1 - x_{\mathrm{Cd}})^2 + 0.3(1 - x_{\mathrm{Cd}})^3 \tag{5}$$

To find the activity of cadmium at 0.3 and 0.5 mol fraction; we need to substitute these values into (5) to first calculate the respective activity coefficients and then the activities:

x_{Cd}	γ_{Cd}	a_{Cd}
0.3	1.3617	0.408
0.5	1.1532	0.577

Part (b) Data for Cr–Ti alloys were collected at 1250 °C:

x_{Cr}	0.090	0.190	0.270	0.370	0.470	0.670	0.780	0.890
a_{Cr}	0.302	0.532	0.660	0.778	0.800	0.863	0.863	0.906

Determine the activity of titanium in a Cr–Ti solution containing 60 mol% Ti.

Solution

To solve this problem, we need to use Gibbs–Duhem equation:

$$\mathrm{x_{Cr} d\ln a_{Cr} + x_{Ti} d\ln a_{Ti}}$$

$$\int_{1}^{\mathrm{x_{Ti}}} \mathrm{d\ln a_{Ti}} = -\frac{\mathrm{X_{Cr}}}{\mathrm{X_{Ti}}} \int_{1}^{\mathrm{x_{Ti}}} \mathrm{d\ln a_{Cr}}$$

This last should be integrated at $x_{\mathrm{Ti}} = 0.6$ ($x_{\mathrm{Cr}} = 0.4$). The integration should be performed graphically after plotting $x_{\mathrm{Cr}}/x_{\mathrm{Ti}}$ versus $-\ln(a_{\mathrm{Cr}})$; such plot is shown in Fig. 4.30.

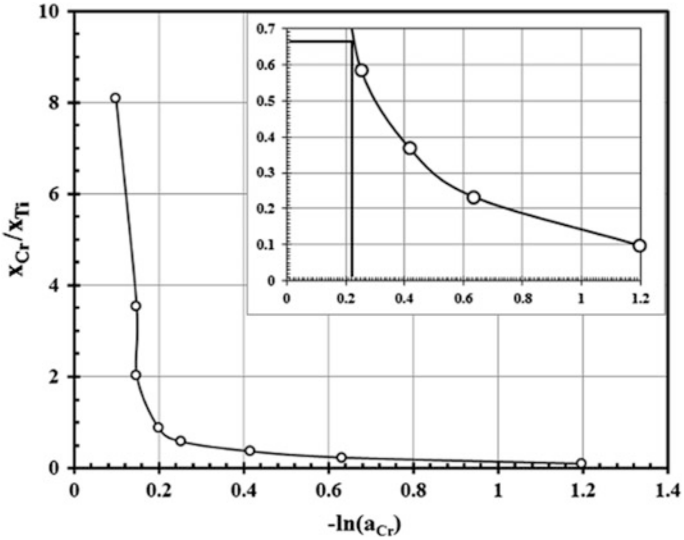


Fig. 4.30 Plot of x_{Cr}/x_{Ti} versus $-\ln(a_{Cr})$ to determine the activity of titanium at $x_{Ti} = 0.6$ (*insert*)

As seen in the insert of Fig. 4.30 the area to integrate is defined between $x_{Cr}/x_{Ti} = 0.4/0.6 = 0.667$, and $x_{Cr}/x_{Ti} = 0$. Such area equals -0.2546, thus $\ln(a_{Ti}) = -0.2546$ and the activity of titanium becomes 0.775.

Phase Equilibria II

5

Introduction

In the last chapter, interactions between components forming mixtures were discussed. As more constituents were added to the system, the equations describing the thermodynamic quantities become more complex. However, it was shown in the examples section that graphical representation of such equations is very useful in determining those quantities.

In this chapter, we will be discussing how these graphic representations can be utilized to perform rapid calculations and what is meant of them in a very practical manner.

Equilibrium Among Phases and Compounds

When several substances (compounds and elements) are mixed together, several reactions may take place and consequently, the overall chemical composition of the mixture will change with time, until no more chemical changes occur. At this point the system is said to be in equilibrium.

This seems to be an ideal situation, however for metallurgical systems; chemical reactions at high temperatures take place fairly quickly so the chemical composition of the system under study may approach the equilibrium condition. By knowing the equilibrium condition, it is possible to evaluate different processes and determine if further improvements in terms of selectivity and recovery are possible.

To determine the equilibrium condition, it is clear from our previous discussions that the key thermodynamic quantity to do so is the Gibbs free energy. The manner in which we may determine this quantity depends on the situation we are in

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- Standard Gibbs free energies from constituents in solutions: $\Delta G^\circ = \Sigma x_i \mu^\circ{}_i(T)$
- From absolute entropies and enthalpies of formation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- From electrode potentials: $\Delta G^\circ = -nFE^\circ$

Once the Gibbs free energy has been determined, the equilibrium constant associated to the transformation under study is also determined. Such constant is calculated from compositions based on activity ratios. Depending on the system, the activity of the components may take different expressions, for example, consider the general reaction

$$aA + bB = cC + dD \tag{5.1}$$

The equilibrium constant for reaction (5.1) is

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} \tag{5.2}$$

For many specific situations in metallurgy, one or several of the following relations may apply:

The activity coefficient (γ) depends both on temperature and composition. Values for this coefficient are available for several systems. Also, it has been observed that systems with strong chemical interactions exhibit activity coefficients with very low values (0.001 and below). Elements and compounds that have little mixing capacity (form immiscible phases), show very large values for their activity coefficients ($\gamma_i > 300$). (Table 5.1).

Consequently, since there is a direct relationship between the activity, the equilibrium constant and the Gibbs free energy, it is expected that for a given system, the equilibrium constant varies as temperature does. Take for example the following equilibrium:

$$\begin{aligned} &H_2 + CO_2 = H_2O + CO \\ &K = \frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}} \end{aligned} \tag{5.3}$$

Data on the value of both the equilibrium constant and the associated Gibbs free energy for reaction (5.3) are shown in Table 5.2

Table 5.1 Activity of a component in relation to its occurrence

Occurrence of i	Activity of i
i is a gas	$a_i = P_i$ (atm)
i is a pure solid or liquid compound or element	$a_i = 1$
i forms an ideal solution	$a_i = x_i$
i forms a non-ideal solution	$a_i = \gamma_i x_i$
i forms an ideal aqueous solution	$a_i = c_i$ (moles of i/L = molarity of i)
i forms a non-ideal dilute solution	$a_i = f_i(\%wt_i)$

Table 5.2 Temperature effect on Gibbs free energy and equilibrium constant for reaction (5.3)

T [°C]	$\Delta G°$ [kJ/mole]	Log(K)
0.000	29.656	−5.672
250.000	19.523	−1.949
500.000	10.387	−0.702
750.000	2.092	−0.107
1000.000	−5.576	0.229
1250.000	−12.790	0.439
1500.000	−19.672	0.580
1750.000	−26.300	0.679
2000.000	−32.728	0.752

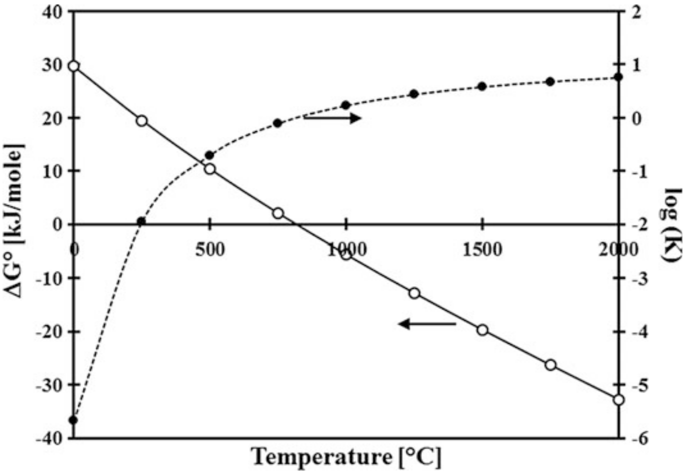

Fig. 5.1 Variation of Gibbs free energy and the equilibrium constant with temperature for reaction (5.3)

From the data in Table 5.2, it is evident that as temperature increases to 1000 °C, reaction (5.3) proceeds from right to left ($\Delta G° < 0$). Below such temperature, it proceeds from left to right ($\Delta G° > 0$). This is better illustrated in Fig. 5.1:

In view of this example, it seems quite helpful to express thermodynamic data graphically; this would assist in making fast accurate calculations.

Ellingham Diagrams

In Chap. 1 it was shown that the standard Gibbs free energy for a reaction may be given by Eq. (1.22):

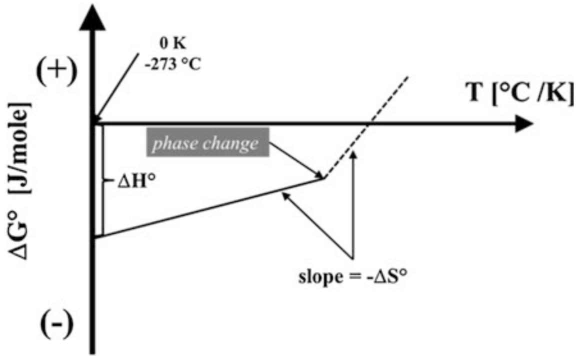

Fig. 5.2 Schematics of an Ellingham diagram

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1.22}$$

A second look to Eq. (1.22) suggests a linear relationship between Gibbs free energy and the temperature, where the slope is defined by the entropy term (ΔS°) and the intercept with Gibbs free energy is ΔH°. Plots of Gibbs free energy versus temperature are called Ellingham diagrams. A sketch of such diagram is shown in Fig. 5.2:

Each plot in an Ellingham diagram represents a specific reaction, thus it is possible to compare different reactions if Gibbs free energy lines corresponding to similar reactions are plotted together. For example, consider that you want to know the relative stability of various oxides. To be able to plot those oxidation reactions, first every reaction must be related to a mole of oxygen consumed, thus the general relationship can be written

$$2\frac{x}{y}\mathrm{Me} + \mathrm{O_2} = \frac{2}{y}\mathrm{Me}_x\mathrm{O}_y \tag{5.4}$$

The equilibrium constant for this reaction is

$$K = \frac{a_{\mathrm{Me}_x\mathrm{O}_y}^{\frac{2}{y}}}{a_{\mathrm{Me}}^{2\frac{x}{y}} P_{\mathrm{O_2}}} \tag{5.5}$$

The system described by reaction (5.4) is comprised by two components (Me and O_2) and three phases (Me, O_2 and $\mathrm{Me}_x\mathrm{O}_y$); thus applying the rule of phases to this systems it results in $F = 1$, which means that at equilibrium only one variable can be allowed to vary freely. If we consider that the temperature is fixed and that the pure metal is oxidized to form a pure oxide, then the activity of these substances is one; therefore at equilibrium, the standard Gibbs free energy of metal oxidation only depends on the partial pressure of oxygen:

$$K = \frac{1}{P_{O_2}}$$
$$\Delta G^\circ = -\mathrm{RT}\ \ln K = \mathrm{RT}\ \ln P_{O_2} = 2.303\mathrm{RT}\ \log P_{O_2} \qquad (5.6)$$

The quantity RT ln P_{O2} is called "oxygen potential".

Important Features of Ellingham Diagrams

For a given reaction line on the diagram, Me and Me_xO_y coexist in equilibrium with oxygen (at the equilibrium oxygen pressure) at a particular temperature. Below the equilibrium line, at lower oxygen pressures, Me exists, whereas above the line at higher oxygen contents (pressure), only Me_xO_y exists. The equilibrium oxygen pressure can be found by extrapolating a straight line that goes from point O at 0 K (−273 °C) through the intersection of the Me/Me_xO_y line with the temperature of interest, until it reaches the P_{O2} scale on the right side of the diagram (Fig. 5.3).

In metallurgy reduction–oxidation reactions are quite common, since in order to obtain a pure metal, oxides must be reduced, to accomplish this gaseous reducing agents such as CO and H_2 gases are frequently used. Thus it is possible to determine

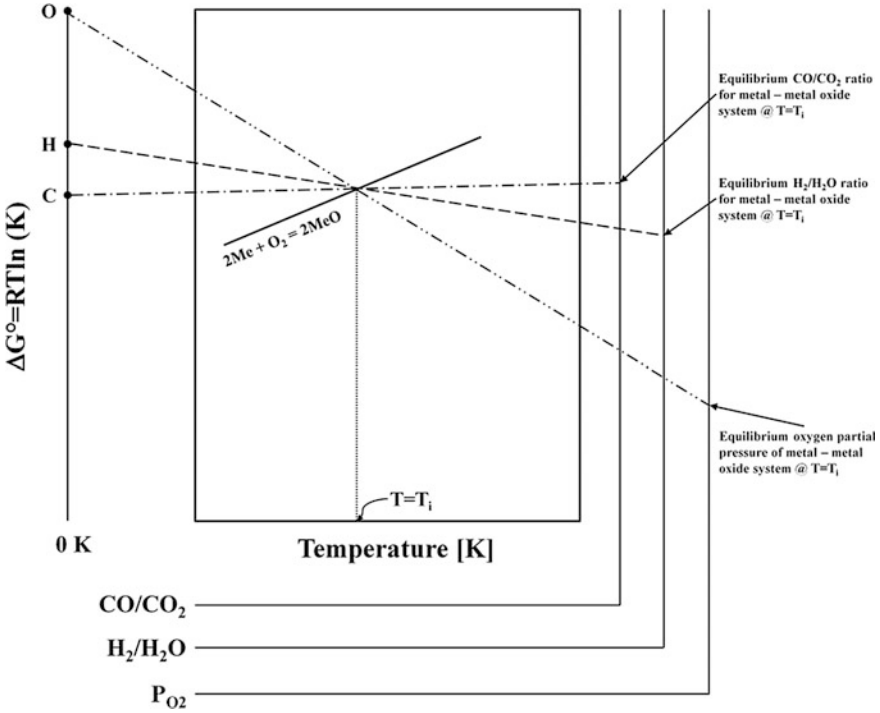

Fig. 5.3 Estimation of the equilibrium pressure of oxygen and the CO/CO_2 and H_2/H_2O ratios in equilibrium with a metal/metal oxide pair (schematic representation)

the CO/CO_2 and H_2/H_2O ratios in equilibrium with a metal/metal oxide pair, by reading them directly in the Ellingham diagram. Similar to finding the equilibrium oxygen pressure, the CO/CO_2 ratio is obtained by drawing a straight line from point C on the left axis, through the point on the Me/Me_xO_y line at the temperature of interest, and to the CO/CO_2 ratio scale on the right side of the diagram (Fig. 5.3). This scale is calculated from

$$\begin{aligned}&2CO + O_2 = 2CO_2\\&\Delta G^\circ = -RT\ \ln\left(\frac{P^2_{CO_2}}{P^2_{CO}P_{O_2}}\right)\\&RT\ \ln(P_{O_2}) = \Delta G^\circ + RT\ \ln\left(\frac{P^2_{CO_2}}{P^2_{CO}}\right)\end{aligned} \tag{5.7}$$

The H_2/H_2O is obtained in similar fashion as the CO/CO_2 one. The starting point to read this ratio is point H in the left side of the diagram (Fig. 5.3). The scale of the H_2/H_2O ratio is calculated from

$$\begin{aligned}&2H_2 + O_2 = 2H_2O\\&\Delta G^\circ = -RT\ \ln\left(\frac{P^2_{H_2O}}{P^2_{H_2}\mathrm{P}_{O_2}}\right)\\&RT\ \ln(P_{O_2}) = \Delta G^\circ + RT\ \ln\left(\frac{P^2_{H_2O}}{P^2_{H_2}}\right)\end{aligned} \tag{5.8}$$

In terms of thermal stability, most oxides are thermodynamically very stable. Only noble metals silver, gold, copper, and the platinum group metals are found in the native state. However, as temperature is raised, all oxides become less stable and at sufficient high temperature they all decompose. This is due to an entropy increase upon the decomposition into a metal and oxygen gas.

The trend of stability is from noble metals, through transition metals (iron to tungsten), to the light reactive metals (Ti, Al, Mg). In Ellingham diagrams, this can be seen by the relative position of the reaction lines. The most stable oxides are at the bottom of the diagram, while the least stable oxides are found at the upper part. If a metal located at the upper part of the diagram is in contact with metal oxides located at the bottom of the chart, no reactions will take place; however, if a reactive metal is in contact with an oxide of a more noble metal, an exchange reaction will occur and the reactive metal will react with the less stable oxide.

In spite of not displaying the effect of activity changes in the equilibrium constant, they can be evaluated; consider the equilibrium

$$2Fe + O_2 = 2FeO \tag{5.9}$$

The Gibbs free energy change associated to reaction (5.9) is

$$\Delta G^\circ = -\mathrm{RT}\ \ln\left(\frac{a_{\mathrm{FeO}}^2}{a_{\mathrm{Fe}}^2 P_{\mathrm{O}_2}}\right) \tag{5.10}$$

If pure iron is oxidized, its activity is one, and thus from Eq. (5.10), the partial pressure of oxygen in equilibrium with iron and its oxide is

$$\mathrm{RT}\ \ln(P_{\mathrm{O}_2}) = \Delta G^\circ + 2\mathrm{RT}\ \ln(a_{\mathrm{FeO}}) \tag{5.11}$$

If pure iron oxide results from the oxidation process, then the activity of the oxide is one, and the partial pressure of oxygen is

$$\mathrm{RT}\ \ln(P_{\mathrm{O}_2}) = \Delta G^\circ \tag{5.11a}$$

If for some reason not pure iron oxide results from the oxidation reaction, and say its activity takes a value of 0.1, the partial pressure of oxygen under these conditions is

$$\mathrm{RT}\ \ln(P_{\mathrm{O}_2}) = \Delta G^\circ + 2\mathrm{RT}\ \ln(0.1) \tag{5.11b}$$

Since the equilibrium constant is fixed at a given temperature, the effect of decreasing the activity of iron oxide results in a decrease of the partial pressure of oxygen to keep the K value constant. Such decrease is represented by the term RT ln(0.1) in Eq. (5.11b). Physically this means that if the activity of an oxide is less than unity, it becomes more difficult to reduce it to a metal. In an alloy, a metal with low activity becomes more difficult to oxidize and higher oxygen potentials are required. This is illustrated in Fig. 5.4.

Of interest is the reduction of oxides with carbon; two possible reactions can occur between carbon and oxygen, these are

$$\mathrm{C} + \mathrm{O}_2 = \mathrm{CO}_2 \tag{5.12a}$$

$$2\mathrm{C} + \mathrm{O}_2 = 2\mathrm{CO} \tag{5.12b}$$

Also carbon monoxide can be oxidized with oxygen to form carbon dioxide

$$2\mathrm{CO} + \mathrm{O}_2 = 2\mathrm{CO}_2 \tag{5.13}$$

From these reactions, it has been observed

- Temperature has little effect on the thermal stability of CO_2
- Increasing the temperature results in increasing the stability of CO
- At 1000 K CO and CO_2 are formed in equal proportions
- When CO is cooled to low temperatures it decomposes into O_2 and CO_2

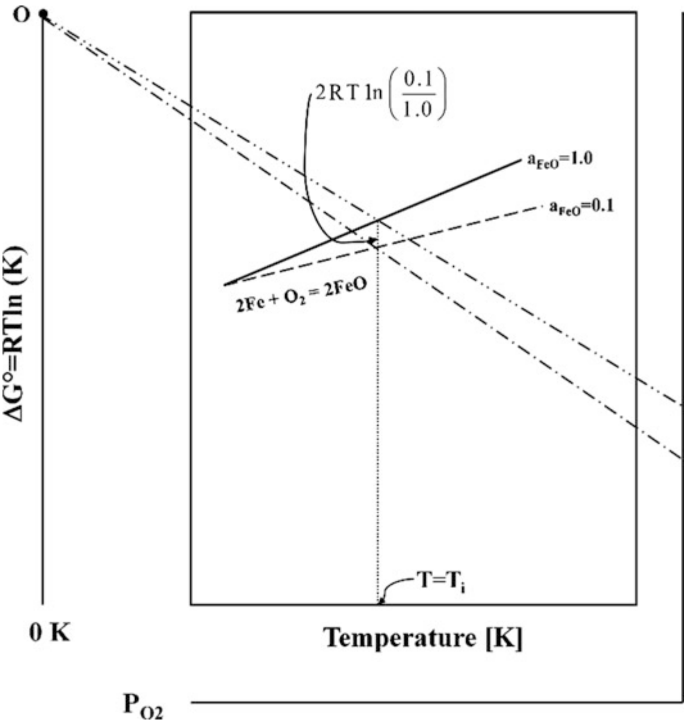

Fig. 5.4 Effect of reducing activities on the equilibrium pressure of oxygen

Effect of Entropy Changes

As indicated in Eq. (1.22), the Gibbs free energy depends on the entropy and this quantity represents the slope in a $\Delta G°$ versus T line. Therefore, at any phase transformation, the Gibbs free energy line exhibits slope changes due to the corresponding entropy change upon the transformation taking place. To illustrate this, Fig. 5.5 shows the Gibbs free energy lines for the oxidation of liquid and gaseous potassium at the boiling point of this metal, the lines coexist below the boiling temperature the liquid is more stable and has lower values for Gibbs free energy, whereas at temperatures above the boiling point, the gaseous phase is the stable one.

The entropy change is largely determined by the number of gas molecules that are consumed or produced. In the solid state, if two solids react to produce another solid, the net entropy change is practically zero, the same goes for a solid–gas reaction in which a single gaseous product is obtained. However, when it comes to gaseous reactions, the net entropy change becomes important; consider reaction (5.13), there are 3 mol (2 mol of CO and 1 mol of O_2) on the left side of the equation; on the right side there are two moles of CO_2. The net molar balance is −1 mol, consequently the entropy change is negative, thus $\frac{d(\Delta G°)}{dT}$ is positive.

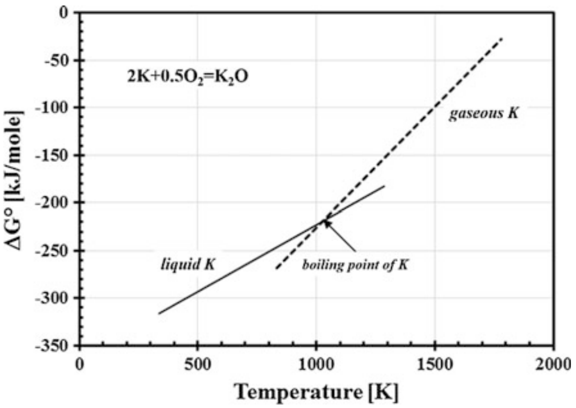

Fig. 5.5 Gibbs free energy lines for the oxidation of liquid and gaseous potassium. At the boiling point there is a sharp change in the slope of the line due to the entropy change

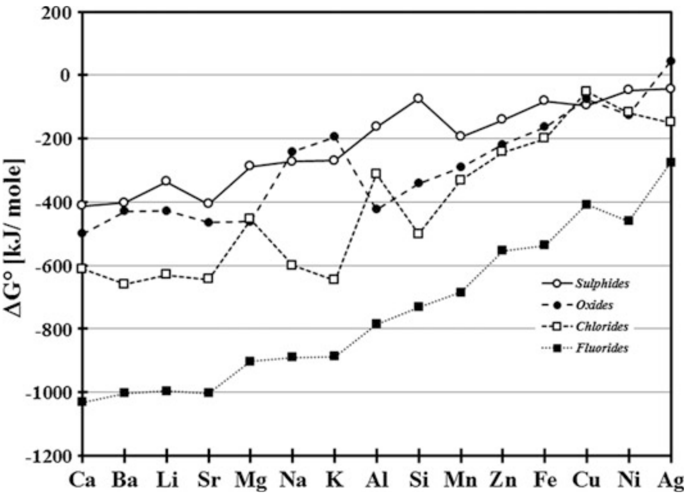

Fig. 5.6 Comparison of the Gibbs free energy of formation of several metal compounds at 1000 K

It is also important to note that Ellingham can be constructed for sulfides, chlorides, fluorides, etc.

Based on this, it is possible to compare the relative stability of metal oxides, sulfides, etc. To do so, the Gibbs free energy is expressed in terms of a mole of S_2, O_2, Cl_2, F_2, etc. This is shown in Fig. 5.6.

As seen in this figure, fluorides are the most stable compounds followed by the chlorides, oxides, and sulfides. These differences in stability allow separating the various metals during their extraction and refining.

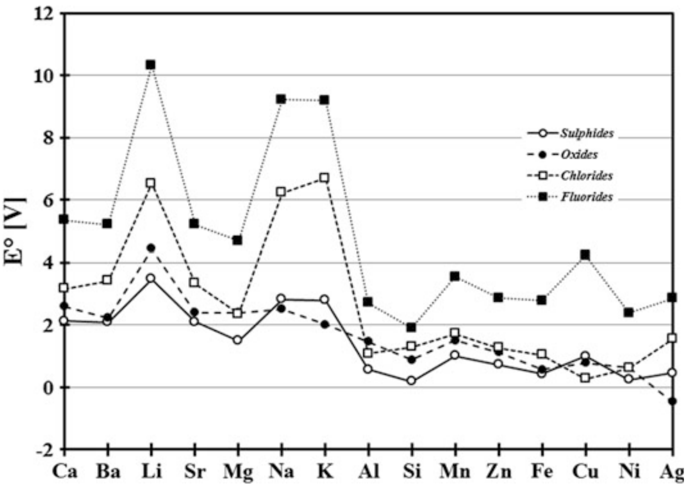

Fig. 5.7 Reversible decomposition voltage of pure metal oxides, sulfides, chlorides, and fluorides at 1000 K

The relative stability of carbon and hydrogen compounds shows that they can only be used to reduce metal oxides. In the case of sulfides, carbon and hydrogen sulfides are less stable than metal sulfides, therefore they cannot be used to reduce metal sulfides to metallic. In the case of fluorides, hydrogen may be used to reduce some metal fluorides (CuF).

Chlorides like $MgCl_2$, cannot be reduced by hydrogen or carbon to produce Mg metal. This also is the case for reducing aluminum oxide to metallic aluminum. Such compounds are typically reduced by applying electrical (direct) current (electrowinning). Similar principles apply to aqueous electro refining, where only fairly noble metals can be deposited on a cathode. More reactive metals cannot be reduced since hydrogen gas will be formed.

In Chap. 3 it was established the relationship between the Gibbs free energy of formation and the voltage needed to obtain a metal, therefore we can compare the voltages needed to decompose the different metal compounds. This is shown in Fig. 5.7:

As expected to decompose the fluorides, more voltage is needed, since as appreciated in Fig. 5.6 these compounds exhibit the highest chemical stability. The opposite is also true for sulfides.

Predominance Area Diagrams

Given the relative stability of compounds, the question that now arises is how these different species interact among them? Furthermore, it is necessary to actually know under which conditions the different equilibria relations will hold so a given chemical species may or may not exist or coexist with different ones.

The chemistry in metallurgical systems is quite complex and therefore it should be explained by putting together (as much as possible) all the thermodynamic data that shows the equilibria in Me–*X*–*Y* systems. Where Me is any metal, *X* is a gaseous species such as O_2, S_2, SO_2, CO, CO_2, Cl_2, F_2, N_2, etc., and *Y* is another gas different from *X*, but that it can also react with Me.

It can be shown thermodynamically that, at a given temperature, the various relationships between the solid and gaseous components at equilibrium are determined by the partial pressures of *X* and *Y* alone. Thus, if *X* and *Y* are chosen as process variables, bivariant equilibria can be represented by reactions such as[1,2]

$$\begin{array}{ll} 2\mathrm{Me} + X_2 = 2\mathrm{Me}X & \text{(a)} \\ \mathrm{Me} + YX_n = \mathrm{Me}Y + X_n & \text{(b)} \\ 2\mathrm{Me}Y + 3X_2 = 2\mathrm{Me}X + 2YX_2 & \text{(c)} \\ 2\mathrm{Me}X + 2YX_2 + X_2 = 2\mathrm{Me}YX_4 & \text{(d)} \\ \mathrm{Me}Y + 2X_2 = \mathrm{Me}YX_4 & \text{(e)} \\ 2\mathrm{Me} + Y_2 = 2\mathrm{Me}Y & \text{(f)} \end{array} \tag{5.14}$$

For the reactions shown in expression (5.14), we should consider the activity of the condensed phases (Me and MeX_n Y_m compounds) as unity and express their equilibrium constants in terms of the partial pressures (equilibrium) of *X*, *Y*, and X_n Y_m species, thus we obtain the following expressions:

$$\begin{array}{ll} K_a = \frac{1}{P_{X_2}} & (\mathrm{a}') \\ K_b = \frac{P_{X_n}}{P_{YX_n}} & (\mathrm{b}') \\ K_c = \frac{P_{YX_2}^2}{P_{X_2}^3} & (\mathrm{c}') \\ K_d = \frac{1}{P_{YX_2}^2 P_{X_2}} & (\mathrm{d}') \\ K_e = \frac{1}{P_{X_2}^2} & (\mathrm{e}') \\ K_f = \frac{1}{P_{Y_2}} & (\mathrm{f}') \end{array} \tag{5.15}$$

If we take the logarithm of the expressions shown in relationships (5.15), we obtain

$$\begin{array}{ll} \log K_a = -\log P_{X_2} & (\mathrm{a}'') \\ \log K_b = \log P_{X_n} - \log P_{YX_n} & (\mathrm{b}'') \\ \log K_c = 2\log P_{YX_2} - 3\log P_{X_2} & (\mathrm{c}'') \\ \log K_d = -(2\log P_{YX_2} + \log P_{X_2}) & (\mathrm{d}'') \\ \log K_e = -2\log P_{X_2} & (\mathrm{e}'') \\ \log K_f = -\log P_{Y_2} & (\mathrm{f}'') \end{array} \tag{5.15a}$$

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[1] Kellog H.H., Basu S.K., Trans AIME, 218, 1960, 70–81.

[2] Rosenqvist T., Principles of extractive metallurgy 2nd Ed., McGraw-Hill, New York, 1983.

from the set of expressions shown in (5.15a) is evident the various relationships between solid and gaseous components at equilibrium are solely determined by the partial pressures of *X* and *Y* alone.

The relevant thermodynamic information associated to the reactions (5.14), can be presented graphically using gas compositions at fixed temperature. This is illustrated in Fig. 5.8

In the diagram presented in Fig. 5.8, the axes are defined by the partial pressure of *Y* and *X* gases. Inside the diagram, different areas are formed; they are known as predominance areas and they are identified by a chemical species made of combinations of Me, *X,* and *Y.*

Diagrams like this, indicate the state of equilibrium between two different gaseous reactants and a solid chemical compound for different gaseous contents at a fixed temperature. For example, consider point 1 in the diagram above. If the partial pressures of *X* and *Y* are those indicated by *x* and *y* respectively, then under such partial pressures, Me*X* (point 1) will be the stable solid phase in equilibrium with the gases.

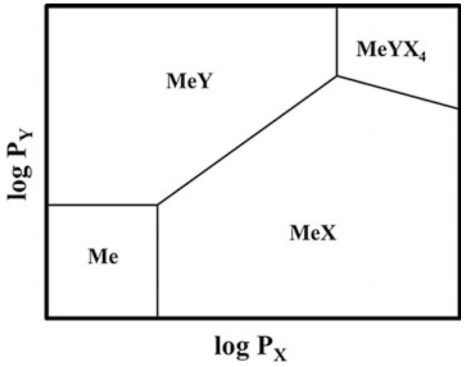
Additionally, the lines in the diagram indicate gas compositions at which two solid phases will be in equilibrium. It also can be seen in Fig. 5.8 that there are points where three lines coincide; this means that at such points three solid phases will be in equilibrium with the gas phase. This only happens at a very specific gas composition.

These kinds of diagrams are known as stability, predominance area or Kellogg diagrams. They are useful in indicating how the gas phase should be controlled at a given temperature to produce a desired metal product.

Kellogg diagrams can be constructed following the Gibbs rule of phases. A system at a fixed temperature and made of three components (Me, *X*, *Y*) and two phases (solid and gaseous) results in three degrees of freedom. Of these three degrees, one is lost since the temperature is constant. The two remaining degrees of freedom are related to the partial pressures of *X* and *Y* components. Thus the axes of these diagrams are related to the *X* and *Y* contents in the system.

Once the axes of the diagrams are determined, it is necessary to decide which chemical species are going to be included in the diagram. These kinds of diagrams are custom made and represent the equilibrium between the selected species. If any

Fig. 5.8 Schematics of a predominance area diagram for the system Me–X–Y



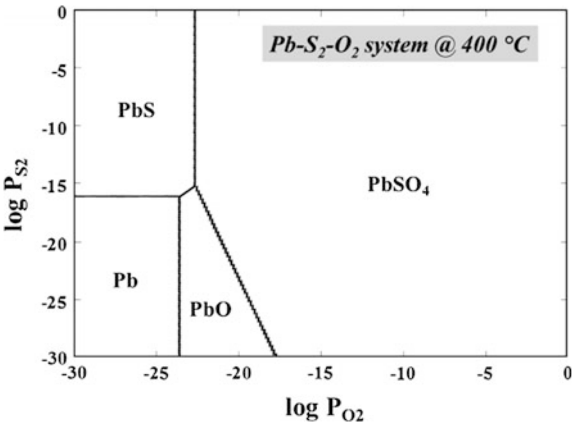


Fig. 5.9 Predominance area diagram for the $Pb–S_2–O_2$ system at 400 °C

major species are not included in the diagram, then an actual situation is not fully represented.

To define the predominance areas within the diagram it is necessary to use the equations shown in (5.15a). That set of equations clearly show that they represent straight lines. Such lines when they intercept each other define phase boundaries and also equilibrium between species. Take for example the $Pb–S_2–O_2$ system at 400 °C, shown in Fig. 5.9.

Form the previous diagram; *X* corresponds to oxygen whereas *Y* corresponds to S_2 gas. Once the partial pressures of these two gases define the axis of the diagram, the different areas can be easily defined by the intersection of the equations shown in (5.15a). For example, the Pb area is defined by the intersection of the lines corresponding to expressions (a") and (f"). Additionally, the phase boundary between lead oxide and metallic lead is also defined by (f"). Similarly, (a") defines the phase boundary between the metal and its sulfide. Lead sulfate field is defined by three different reactions: The oxidation of the sulfide (relation e"), the sulphidation of the oxide (relation analogous to e", not shown in 5.15a); and the reaction between the oxide and the sulfide (relation d").

These diagrams are particularly useful in depicting sulfide roasting operations. As a consequence of this, it is often found predominance area diagrams in terms of SO_2 and O_2 gases.

Thermodynamic data as presented in Ellingham diagrams indicate that by increasing the temperature, the value of the equilibrium constant decreases; consequently the equilibrium lines in Kellogg diagrams move towards the right side in these diagrams. For a given partial pressure of oxygen, the SO_2 pressure sets itself; this results in changing the relative stability of the compounds in the diagram. If a compound is stable at low temperature, it becomes unstable at high temperature and vice versa. This is better illustrated in Fig. 5.10.

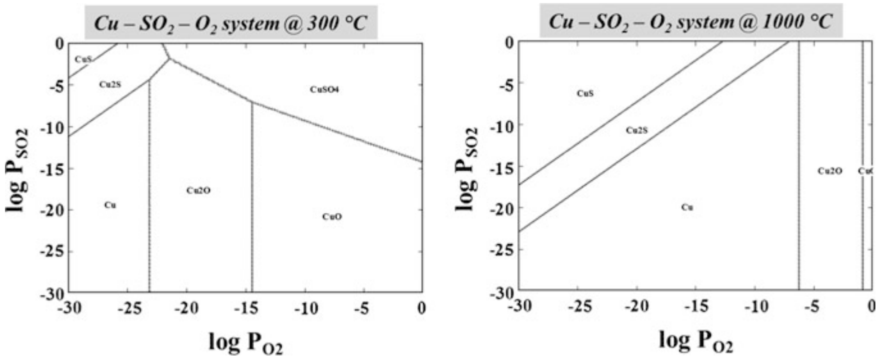


Fig. 5.10 Change in stability in phases present in the Cu–SO_2–O_2 system as a function of temperature

Phase Diagrams

These diagrams are the graphical representation of the collection of phases that are present in a system under a given set of conditions of pressure, temperature, and chemical composition. The phases in the system are under equilibrium conditions (minimum Gibbs free energy). Similar to Kellogg diagrams, these types of diagrams must fulfill Gibb's phase rule.

Phase diagrams are constructed in terms of the number of components present in a system. For example, a system made of two components is known as a binary system. Systems with three components are called ternary, and so on.

To construct one of these diagrams, it is necessary to have information about the system under study, i.e., it is necessary to know if the components exhibit mutual solubility (in the solid and/or liquid states), if so, it should be considered if that solubility is limited or unlimited; also is necessary to know under which compositional range exist miscibility, etc.

If Gibbs free energy is plotted for a solid solution of A in B versus the molar fraction of B at a given temperature, it will result in a curve like the one shown in Fig. 5.11

From the Gibbs free energy curve shown in Fig. 5.11, it is evident that if the solution is formed; at any composition, the solution has lower free energy than either pure A or B, henceforth it will be the stable state of the system at the given temperature. At the composition (x_B) shown by the PQZ line, the free energy of the mixture of pure A and pure B correspond to point P (see Fig. 4.4); whereas that of the solid solution is represented by point Q. The Gibbs free energy of mixing (ΔG_{mix}) is thus represented by the PQ segment (Eq. 4.47). This happens when there is total solubility between A and B at all compositions at a fixed temperature.

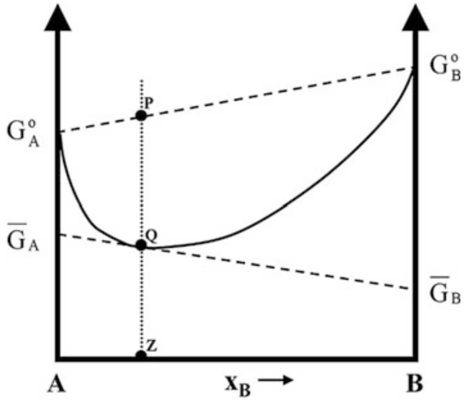


Fig. 5.11 Gibbs free energy in a binary AB system at a fixed temperature

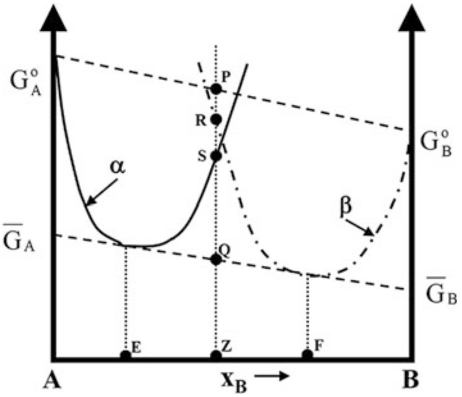


Fig. 5.12 Gibbs free energy composition curves for a binary system with limited solubility in the solid state at a fixed temperature

On the other hand, if there is limited solubility at a given temperature, then it is expected that two solid solutions (α solution rich in A where B dissolves into A and β solution rich in B where A dissolves into B) will be formed. The Gibbs free energy diagram in Fig. 5.11 has to be modified to show the presence of these two solid solutions. This is illustrated in Fig. 5.12:

At equilibrium, any composition of the alloy lying between points E and F would consist of a mixture of the two solid solutions α and β, whereas any alloy of composition to the left of point E would only consist of α, and to the right of point F will only consist of β solution.

If we now add to this analysis the presence of the liquid phase, where there is total solubility in the liquid state and limited solubility in the solid phase, it is necessary to add a third Gibbs free energy curve, that of the liquid solution. As the temperature decreases from T_1 (all system is liquid) to T_5, (all system is solid). As the temperature drops, the liquid fraction constantly decreases until it disappears, consequently, the stability of the liquid decreases in a way that its Gibbs free energy

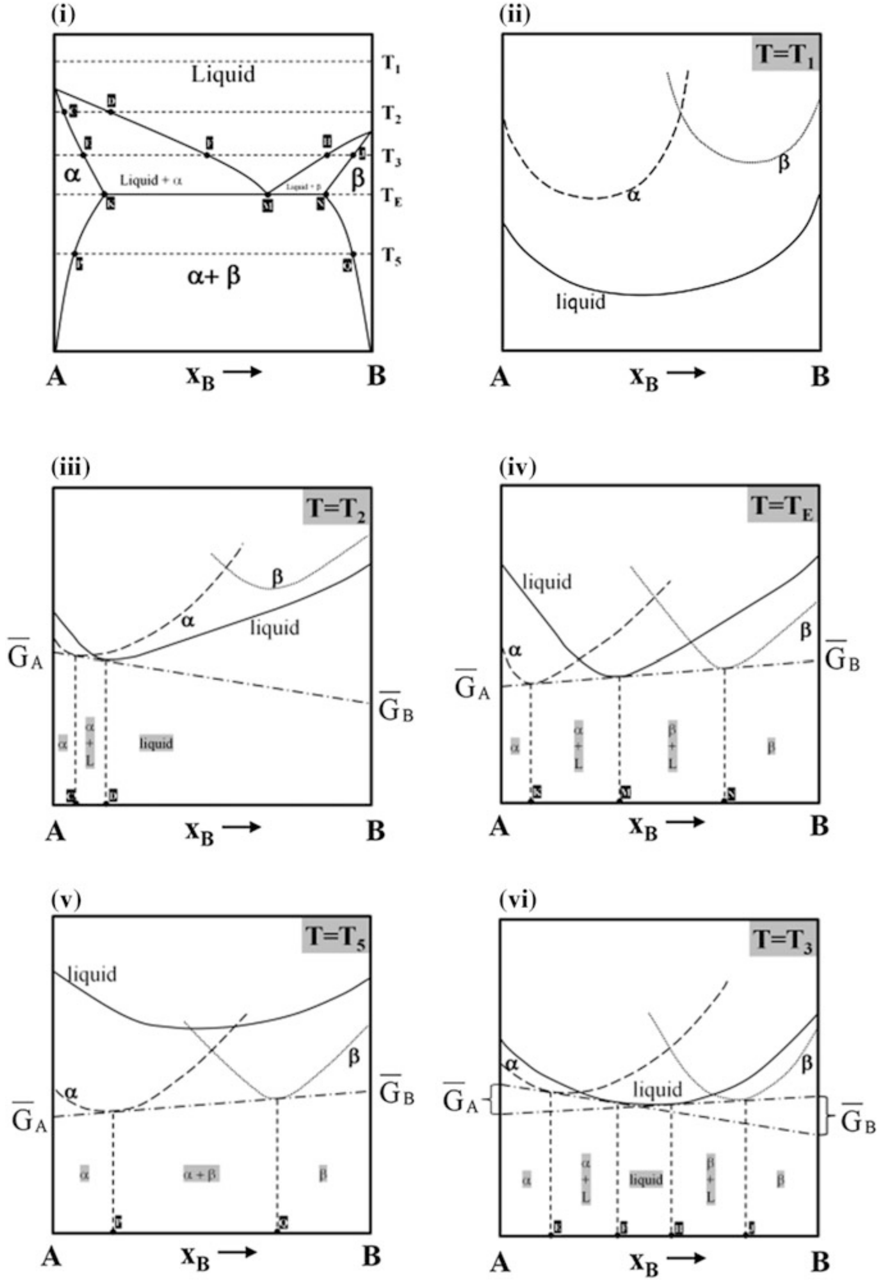


Fig. 5.13 Gibbs free energy curves for the A-B system as it solidifies from T_1 to T_5

curve moves until it is replaced by the curves of the resulting solid solutions. This is illustrated in the sequence shown in Fig. 5.13 below.

Figure 5.13 shows the Gibbs free energy curves for the solid and liquid phases of an eutectic (a liquid solution decomposes into two solid solutions at a fixed temperature and composition) system at different temperatures. The Gibbs free energy curves are also compared with the corresponding phase diagram.

Diagram (i) in Fig. 5.13 represents the phase diagram in which a liquid solution (total solubility) decomposes at T_E (eutectic temperature) into α and β solid solutions.

The minimum freezing temperature in the system is that of T_E. Below such temperature, the entire system is in the solid state. Above that temperature, the liquid fraction increases as temperature does so. From this description, it is clear that at $T = T_1$, only the liquid phase exists at all compositions; therefore, the liquid is the most stable phase; consequently, the Gibbs free energy of the liquid has a lower value than those of the α and β solid phases; thus Gibbs free energy curve of the liquid lies below those of the solid phases (diagram ii).

When the system's temperature reaches T_2 (just below the melting point of A and above that of B), the α phase starts to stabilize at compositions to the left of point C in diagram (iii). Between points C and D, a mixture of the liquid and α phases are in equilibrium so they coexist in this composition interval. To the right of point D, only the liquid phase exists, since it has the lower Gibbs free energy. At this temperature (T_2), α phase is not stable at all.

If the temperature keeps dropping, until reaching T_3, βphase appears (diagram iv). The Gibbs free energy curves for α and β phases pass below that of the liquid at the left of point E and to the right of point J respectively; this means that at such composition intervals α and β are stable and no liquid is present. Between points E and F, a mixture of α and liquid exist. Similarly, between H and J points, only liquid and β mixture exists. Between points F and H, only liquid the liquid solution exists.

As temperature now reaches T_E (eutectic temperature), the Gibbs free energy curves of both α and β phases have the same tangent than that of the liquid free energy curve. At that particular temperature, (unique to this system) point M represents the eutectic point where α, β and the liquid coexist simultaneously. The composition of α in the eutectic mixture is defined by point K (this point also represents the maximum solubility of B in A in the solid state). Point N represents the composition of β in the mixture (maximum solubility of A in B in the solid state). Between points K and M, the alloy consists of primary α and eutectic (α + β) in equilibrium; between M and N points, primary β and eutectic are in equilibrium. To the left of K and to the right of N, only α and β respectively will be the stable phases.

Below T_E, at T_5, no more liquid is present at any composition; this is because the Gibbs free energy curve of the liquid no longer intercepts the α curve or the β one. Also the liquid curve does not have a common tangent with any of the solid phases between points R and S (points of contact). Between points P and Q, there is a mixture of α and β. To the left of point P only α exists; whereas to the right of Q, there is only β.

Calculation of Phase Diagrams

The previous discussion seems to depict phase diagrams as simply an intersections f Gibbs free energy curves; however, this is not the case. Lots of thermodynamic information lies behind what was described.

The key concept in drawing phase diagrams is that of the chemical potential. The resulting Gibbs free energy curves and their corresponding intersections depend on how the chemical potential of the different phases in the system meet at specific points (equilibrium between phases).

Because of this, specific (invariant) reactions are found in multicomponent systems. These reactions are

In considering the different equilibria taking place in a multicomponent system, the Gibbs free energy of the phases in the system depends on the temperature, the pressure and the composition as indicated in Eq. (4.27) (Table 5.3)

$$dG = VdP - SdT + \sum_{i=1}^{n} \mu_i dn_i \tag{4.27}$$

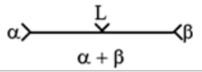
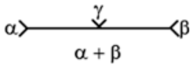
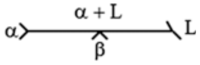
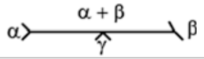
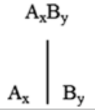
Additionally, for a system under equilibrium at T and P fixed, the chemical potential of the species contained in the different phases contained in the system is derived from Fig. 4.2, thus we obtain

$$d\mu_i^{\alpha} = d\mu_i^{\beta} \tag{5.16}$$

Inserting (5.15) into (4.27) results in

$$V_i^{\alpha}dP - S_i^{\alpha}dT + \sum_{i=1}^{r-1}\left(\frac{\partial \mu_i^{\alpha}}{\partial x_i^{\alpha}}\right)dx_i^{\alpha} = V_i^{\beta}dP - S_i^{\beta}dT + \sum_{i=1}^{r-1}\left(\frac{\partial \mu_i^{\beta}}{\partial x_i^{\beta}}\right)dx_i^{\beta} \tag{5.17}$$

Table 5.3 Invariant reactions found in multicomponent phase diagrams

Reaction	Definition	Graphical representation
Eutectic	A liquid transforms into two solids (L = α + β)	
Eutectoid	A solid transforms into two solids (γ = α + β)	
Peritectic	A liquid and a solid combine to produce another solid (α + L = β)	
Peritectoid	Two solids combine to form a third solid (α + β = γ)	
Compound	Two components react to form a compound of specific stoichiometry. (Ax + By = AxBy)	

Expression (5.17) relates the temperature, the pressure, and the composition in every phase comprising the system. Also by recognizing that when $\Delta G = 0$, then the entropy can be expressed in terms of the enthalpy ($\Delta S = \Delta H/T$) associated to mixing. Such enthalpy term represents the heat involved in transferring a mole of species i from phase α to phase β; if the mixture behaves ideally, this enthalpy term equals the latent heat of transformation from phase α to phase β. After some manipulation[3] of Eq. (5.17) we obtain general expressions for α and β phases to determine the equilibrium lines in phase diagrams. Such equations are, for α phase

$$\sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\alpha} \Delta V_i^{\alpha\to\beta} \right) \mathrm{d}P - \sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\alpha} \frac{\Delta H_i^{\alpha\to\beta}}{T} \right) \mathrm{d}T = - \sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\alpha} \frac{\mathrm{RT}}{x_i^{\beta}} \mathrm{d}x_i^{\beta} \right) \tag{5.18a}$$

Whereas for β phase

$$\sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\beta} \Delta V_i^{\beta\to\alpha} \right) \mathrm{d}P - \sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\beta} \frac{\Delta H_i^{\beta\to\alpha}}{T} \right) \mathrm{d}T = - \sum_{\mathrm{i=1}}^{\mathrm{r}} \left(x_i^{\beta} \frac{\mathrm{RT}}{x_i^{\alpha}} \mathrm{d}x_i^{\alpha} \right) \tag{5.18b}$$

The set of Eqs. (5.18) cannot be directly integrated and is not very useful beyond showing how do temperature, pressure and composition vary simultaneously. However, from these expressions a number of new ones can be deducted depending on the specific type of phase diagram.

Computing phase diagrams relates to calculate phase boundaries among phases in equilibrium. For example, consider a binary solution made of A and B components: these components form liquid and solid solutions that behave ideally, the chemical potential of each component associated to the solidification of the liquid solution becomes:

$$\Delta\mu_i^{\mathrm{o},l\to\mathrm{s}} = \Delta H_i^{\mathrm{o},l\to\mathrm{s}} - T\Delta S_{\mathrm{i}}^{\mathrm{o},l\to\mathrm{s}} \tag{5.19}$$

Recalling that the enthalpy change in ideal solutions is zero, Eq. (5.19) reduces to:

$$\Delta\mu_i^{\mathrm{o,s}\to l} = \Delta S_i^{\mathrm{o,s}\to l}\left(T_i - T_{i,\mathrm{fusion}}\right) \tag{5.20}$$

If component B melts at a higher temperature than A, then its chemical potential is greater than that of A and vice versa.

Then the liquidus[4] and solidus[5] lines for these kinds of diagrams can be calculated using the following expression:

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[3] Rastogi, R.P., Thermodynamics of phase equilibria and phase diagrams. Journal of chemical education, 41 (8), 1964, 443–448.

[4] The temperature above which only liquid exist.

[5] The temperature that separates the solid phase from a solid + liquid region in a phase diagram.

$$\ln\left(\frac{a_i^{\text{liquid}}}{a_i^{\text{solid}}}\right) = -\frac{\Delta\mu_i^{\text{o,s}\rightarrow l}}{\text{RT}} \tag{5.21}$$

Since the enthalpy of mixing is zero and also by assuming that $Cp_{\text{liquid}} \approx Cp_{\text{solid}}$, then the change in chemical potential can be approximated to the latent heat of fusion ($\Delta H^{\circ}_{\text{i,fusion}}$).

Substituting these considerations into (5.21) results in

$$\ln\left(\frac{a_i^{\text{liquid}}}{a_i^{\text{solid}}}\right) = -\frac{\Delta H^{\circ}_{i,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{i,\text{fusion}}}\right) \tag{5.22}$$

Both solutions (liquid and solid) are assumed ideal; then the activity of each component in solution is equal to their respective mole fraction. Thus for component A, we have

$$\frac{x_A^{\text{liquid}}}{x_A^{\text{solid}}} = \exp\left[-\frac{\Delta H^{\circ}_{A,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,\text{fusion}}}\right)\right] \tag{5.23a}$$

Analogously, for component B, we obtain

$$\frac{x_B^{\text{liquid}}}{x_B^{\text{solid}}} = \exp\left[-\frac{\Delta H^{\circ}_{B,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,\text{fusion}}}\right)\right] \tag{5.23b}$$

To determine the solidus line, the mass balance indicates that $x_A^{\text{solid}} + x_B^{\text{solid}} = 1$. Combining equations set (5.23) with the previous conditions results in

$$x_A^{\text{solid}}\exp\left[-\frac{\Delta H^{\circ}_{A,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,\text{fusion}}}\right)\right] + x_B^{\text{solid}}\exp\left[-\frac{\Delta H^{\circ}_{B,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,\text{fusion}}}\right)\right] = 1 \tag{5.24a}$$

For the liquidus line, a similar expression is obtained

$$x_A^{\text{liquid}}\exp\left[-\frac{\Delta H^{\circ}_{A,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,\text{fusion}}}\right)\right] + x_B^{\text{liquid}}\exp\left[-\frac{\Delta H^{\circ}_{B,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,\text{fusion}}}\right)\right] = 1 \tag{5.24b}$$

Equations (5.24) need to be solved for T, to obtain each of the lines. Systems exhibiting this behavior are: Cu–Ni, Si–Ge, NiO–MgO, among others. The Si–Ge phase diagram is shown in Fig. 5.14:

In simple eutectic systems, where the solubility in the solid state is negligible, it is possible to consider the activity of the solid phase as 1, and the liquidus line can be calculated using a variation of Eq. (5.22)

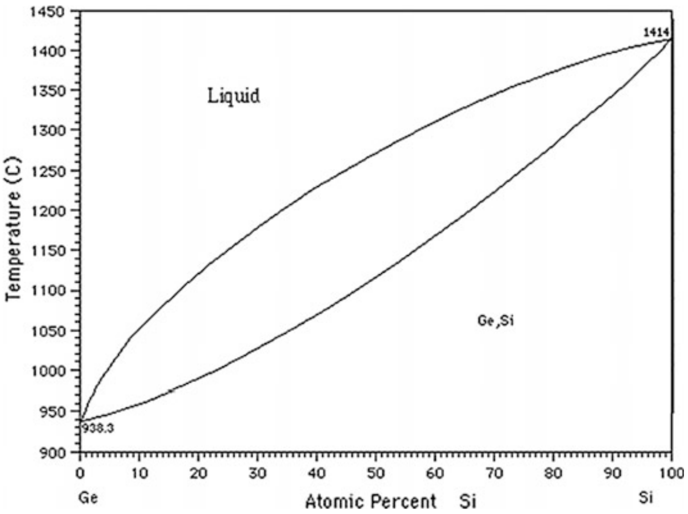

Fig. 5.14 Si–Ge phase diagram. The diagram exhibits total solubility in the liquid and in the solid phases

$$\ln a_i^{\text{liquid}} = -\frac{\Delta H^{\circ}_{i,\text{fusion}}}{R}\left[\frac{1}{T} - \frac{1}{T_{i,\text{fusion}}}\right] = \ln x_i^{\text{liquid}} + \ln \gamma_i^{\text{liquid}} \tag{5.25}$$

In the event that a regular solution forms in the liquid state, the liquidus line for component A is given by the expression

$$\ln\left(1 - x_B^{\text{liquid}}\right) + \frac{\Omega}{\text{RT}}\left(x_B^{\text{liquid}}\right)^2 = -\frac{\Delta H^{\circ}_{A,\text{fusion}}}{\text{R}}\left(\frac{1}{T} - \frac{1}{T_{A,\text{fusion}}}\right) \tag{5.26a}$$

The corresponding liquidus line for component B is

$$\ln\left(x_B^{\text{liquid}}\right) + \frac{\Omega}{\text{RT}}\left(1 - x_B^{\text{liquid}}\right)^2 = -\frac{\Delta H^{\circ}_{B,\text{fusion}}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,\text{fusion}}}\right) \tag{5.26b}$$

These lines (Eqs. 5.25, 5.26a, 5.26b) meet at the eutectic temperature and composition (T_E, x_E).

Figure 5.15 shows the phase diagram of the Cu–Ag system which is representative of this type of systems:

From the previous discussion, it becomes evident that the form of phase diagrams with any number of components is ruled by Gibbs phase rule.

Therefore, as already shown, phase diagrams can be calculated from equations involving Gibbs free energy of a particular between the considered phases. If many equilibria take place in a system, then a set of Gibbs free energy equations must develop; and to determining the corresponding phase diagram, the set of

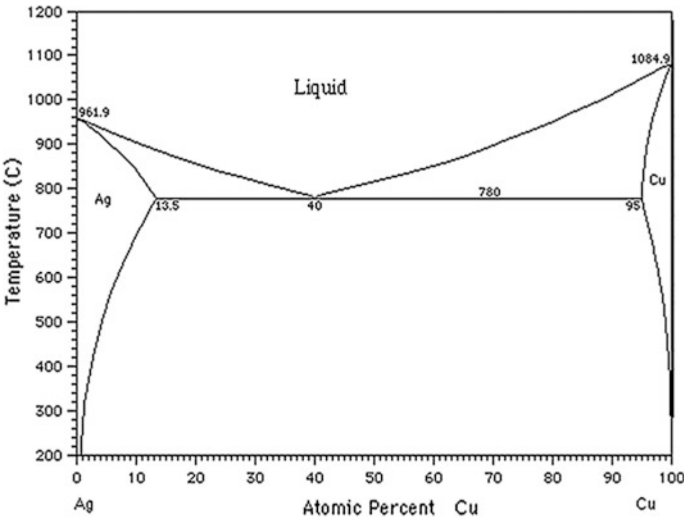

Fig. 5.15 Cu–Ag eutectic system

thermodynamic equations must be solved after careful assessment of all thermodynamic quantities involved in describing the system under study. (Figure 5.16).

The assessment of thermodynamic values can be done after minimizing simultaneously the Gibbs free energy expressions.[6,7] This method is particularly useful in describing systems with three or even more components. (Figure 5.17).

The expressions needed to perform the minimization of Gibbs free energy are constructed by writing down the excess properties of phases in solution in terms of composition and temperature. For example, consider a simple binary system; its excess enthalpy and entropy can be represented as polynomials with the form:

$$H^E = x_A x_B \left(h_0 + h_1 (x_B - x_A) + h_2 (x_B - x_A)^2 + h_3 (x_B - x_A)^3 + \ldots \right) \tag{5.27a}$$

Similarly, for entropy we have

$$S^E = x_A x_B \left(s_0 + h_1 (x_B - x_A) + \mathrm{s}_2 (x_B - x_A)^2 + s_3 (x_B - x_A)^3 + \ldots \right) \tag{5.27b}$$

where h_i and s_i are empirical coefficients that are considered (for better approximation) independent of temperature.

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[6] Pelton, A.D., Thermodynamics and phase diagrams of materials, in Phase Transformations in Materials (ed G. Kostorz), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 1–73. doi: 10.1002/352760264X.ch1.

[7] Sangster, J., Pelton, A.D., J. Physical and Chemical Reference Data, 16 (3), 1987, 509–561.

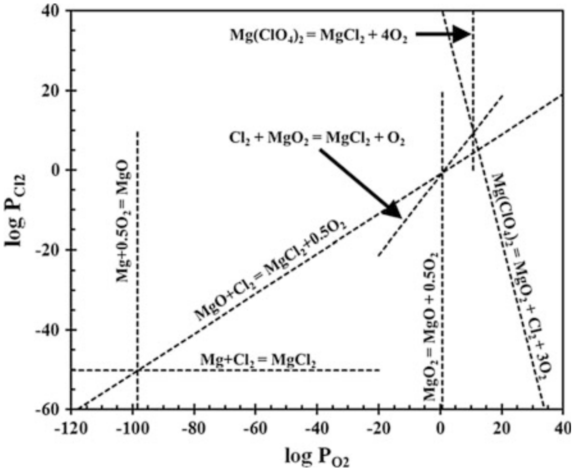

Fig. 5.16 Plotting of the set of logarithmic equations in Table 5.4

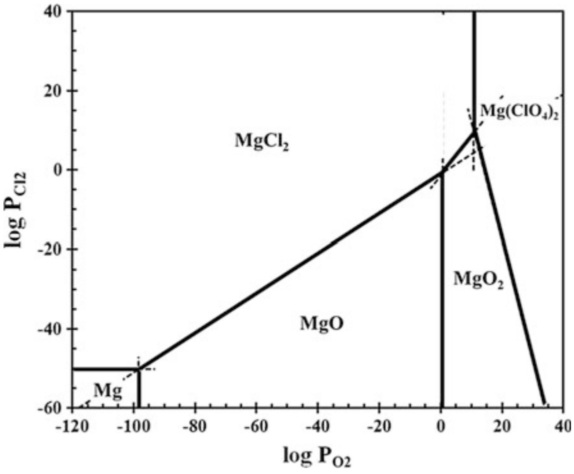

Fig. 5.17 Phase predominance diagram for the Mg–Cl2–O2 system at 300 °C

If the series shown in Eqs. (5.27a, 5.27b) are truncated after the first term, then

$$G^E = H^E - TS^E = x_A x_B (h_0 - Ts_0) \tag{5.28}$$

Since the excess enthalpy of mixing equals the excess Gibbs free energy, then this polynomial technique can be considered an extension of regular solution theory. This approach is very satisfactory for systems exhibiting small deviations from ideal behavior. In more complex systems, more sophisticated models are needed.

For example, oxide mixtures or highly ionic systems are better described by sub-lattice models such as that proposed by Temkin,[8] in which he considered that cations and anions are evenly distributed on their respective sites regardless of their charges; in such case, the Gibbs free energy of mixture is represented nearly identical to that of an ideal solution.

Examples of Calculations

Example 1. Phase predomination diagram Part (a) Using the data below, construct a phase predominance diagram for the Mg–Cl–O system at 300 °C

	Reactions @ $T = 573$ K	ΔG [J]
1	$Mg + 0.5\ O_2(g) = MgO$	−539667
2	$Mg + Cl_2(g) = MgCl_2$	−550524
3	$Cl_2(g) + MgO = MgCl_2 + 0.5O_2(g)$	−10858
4	$Cl_2(g) + MgO_2 = MgCl_2 + O_2(g)$	−15156
5	$MgO_2 = MgO + 0.5\ O_2(g)$	−4298
6	$Mg(ClO_4)_2 = 3O_2(g) + Cl_2(g) + MgO_2$	−459339
7	$Mg(ClO_4)_2 = MgCl_2 + 4O_2(g)$	−474495

Solution

To obtain the phase predominance diagram for the set of given equations, we need to express the respective equilibrium constant in terms of the partial pressures of oxygen and chlorine gas. The other species should be considered as condensed and pure, thus their activity values 1.

After this first step, we need to express the equilibrium constants in terms of a logarithm function; these steps are shown in the table below: (Table 5.4).

The next step in solving this problem is to plot the logarithmic expressions shown in the table. It can be seen that every one of these expressions represents straight lines

Once the different lines are plotted, we should mark the actual phase boundaries. To do so, we have to join the interceptions where three equilibrium lines meet. After this is done, we need to label the respective phase fields:

Part (b)

The Zn–S–O system at 500 °C can be represented by means of the attached predominance area diagrams

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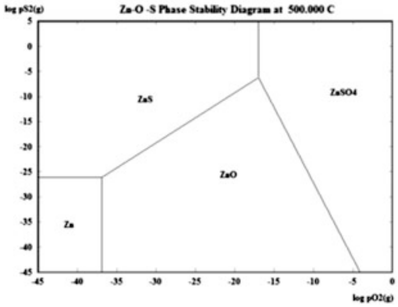
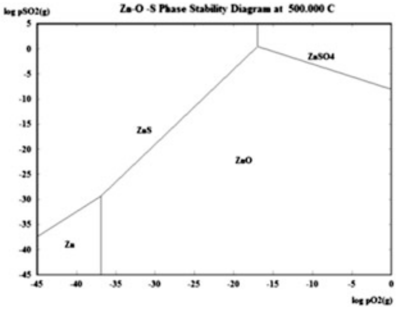
[8] Temkin, M., Acta Physicochimica, 20, 1945, 411.

Table 5.4 Equilibrium constants and its logarithmic form for chemical reactions in the Me–Cl_2–O_2 system

Reaction	Equilibrium constant	Logarithmic function
1	$K_1 = \frac{1}{\sqrt{P_{O_2}}}$	$\log P_{O_2} = -2 \log K_1$
2	$K_2 = \frac{1}{P_{Cl_2}}$	$\log P_{Cl_2} = -\log K_2$
3	$K_3 = \frac{\sqrt{P_{O_2}}}{P_{Cl_2}}$	$\log P_{Cl_2} = \frac{1}{2} \log P_{O_2} - \log K_3$
4	$K_4 = \frac{P_{O_2}}{P_{Cl_2}}$	$\log P_{Cl_2} = \log P_{O_2} - \log K_4$
5	$K_5 = \sqrt{P_{O_2}}$	$\log P_{O_2} = 2 \log K_5$
6	$K_6 = P_{O_2}^3 P_{Cl_2}$	$\log P_{Cl_2} = \log K_6 - 3 \log P_{O_2}$
7	$K_7 = P_{O_2}^4$	$\log P_{O_2} = \frac{1}{4} \log K_7$





These diagrams show the same equilibria, but with different coordinate axis.

Use these diagrams to estimate the equilibrium constant for the following reaction:

½ $S_2 + O_2 = SO_2$.

What is the value of $\Delta G°$ for this reaction at 773 K?

Solution

In the P_{SO2}–P_{O2} diagram you have the equilibrium

$$\begin{aligned} &Zn + SO_2 + O_2 = ZnSO_4 \\ &K_1 = \frac{1}{P_{SO_2} \times P_{O_2}} \end{aligned} \tag{1}$$

For reaction (1), log $P_{SO2} = 0$, log $P_{O2} = -16$

In the P_{S2}–P_{O2} diagram you have the equilibrium

$$\begin{aligned} &Zn + 0.5S_2 + 2O_2 = ZnSO_4 \\ &K_2 = \frac{1}{\sqrt{P_{S_2}} \times P_{O_2}^2} \end{aligned} \tag{2}$$

For reaction (2), log $P_{S2} = -7$, log$P_{O2} = -16$.
Subtracting reaction (1) from (2)

$$\begin{array}{ll} Zn + 0.5S_2 + 2O_2 = ZnSO_4 & \log K_2 = -0.5\log P_{S_2} - 2\log P_{O_2} \\ ZnSO_4 = Hg + SO_2 + O_2 & \log K_1 = \log P_{SO_2} + \log P_{O_2} \end{array}$$

$$0.5S_2 + O_2 = SO_2 \quad \log K_3 = \log P_{SO_2} - \log P_{O_2} - 0.5\log P_{S_2} \tag{3}$$

From reaction (3)

$$\begin{aligned} \log K_3 &= \log P_{SO_2} - (\log P_{O_2} + 0.5\log P_{S_2}) \\ \log K_3 &= 0 - (-16 - 0.5 \times 7) \\ \log K_3 &= 19.5 \end{aligned}$$

$$K_3 = 10^{19.5}$$

$$\begin{aligned} \Delta G^\circ &= -\mathrm{RT}\ \ln K_3 \\ \Delta G^\circ &= -8.314 \times 773 \times \ln 10^{19.5} \\ \Delta G^\circ &= -289\ \mathrm{kJ/mole} \end{aligned}$$

Example 2. Calculation of liquidus and solidus lines in phase diagrams Part (a) When mixtures of silicon and germanium are heated, melting occurs over a range of temperatures:

N	X_{Si}	$T_{start\ melting}$ [°C]	X_{Si}	$T_{finish\ melting}$ [°C]
1	1	1414	1	1414
2	0.95	1408	0.97	1391
3	0.885	1395	0.9325	1366
4	0.85	1388	0.8925	1340
5	0.81	1377	0.875	1329
6	0.785	1369	0.7993	1281
7	0.765	1364	0.7625	1259
8	0.6975	1346	0.6875	1215
9	0.665	1335	0.595	1168
10	0.6275	1320	0.5375	1135
11	0.59	1307	0.43	1083
12	0.5525	1294	0.345	1045
13	0.495	1270	0.29	1027
14	0.4475	1250	0.2375	1005
15	0.385	1221	0.1575	977
16	0.35	1206	0.1075	962

(continued)

(continued)

N	X_{Si}	$T_{start\ melting}$ [°C]	X_{Si}	$T_{finish\ melting}$ [°C]
17	0.32	1188	0.0575	950
18	0.2625	1157	0.015	940
19	0.2325	1142	0	938
20	0.18	1109		
21	0.165	1098		
22	0.1275	1074		
23	0.105	1056		
24	0.08	1038		
25	0.06	1016		
26	0.045	1001		
27	0.03	983		
28	0.0225	972		
29	0.0125	955		
30	0	938		

(i) With the data provided, construct the corresponding phase diagram

(ii) Calculate the solidus and liquidus lines for this system ($\Delta H_{fusion,Si}$ = 50.2 kJ/mole, $\Delta H_{fusion,Ge}$ = 36.9 kJ/mole)

(iii) Compare the calculated diagram with the experimental data, comment on your findings.

Solution

We need to plot the data provided to find the experimentally determined phase diagram. The data reveals that the Ge–Si system exhibits complete solubility in both the

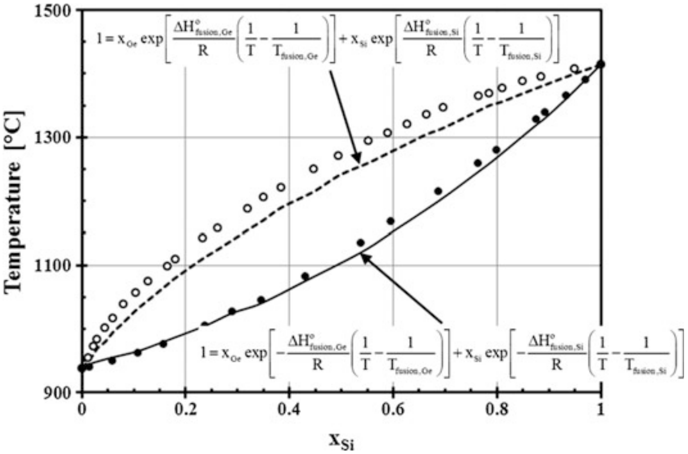


Fig. 5.18 Comparison between experimental data and calculated one on the solidification of Si–Ge alloys

liquid and solid states, therefore ideal solution in each of these phases can be assumed. Further, to calculate the corresponding solidus and liquidus lines, we need to use Eqs. 5.24a and 5.24b, respectively. The resulting diagram is shown in Fig. 5.18.

In the figure it can be noticed the experimental data (full symbols solidus line, empty symbols liquidus line), along with the calculated equilibrium lines. It is clear that the computed solidus line is in better agreement with the provided data than the estimated liquidus line. In both cases there is good agreement between experimental data and the calculated ones. The more pronounced deviation exhibited by the liquid phase can be attributed to the expected higher entropy associated to the liquid state. Such entropy term is not present in the corresponding liquidus line equation.

Part (b). The following data was found on the heating of different Ag–Cu mixtures upon melting:

N	X_{Cu}	T [°C]	N	X_{Cu}	T [°C]	N	X_{Cu}	T [°C]
1	0	962	28	0.425	793	55	0.775	940
2	0.0175	953	29	0.4375	800	56	0.7875	947
3	0.03	947	30	0.4475	803	57	0.795	950
4	0.0575	930	31	0.46	807	58	0.805	957
5	0.07	923	32	0.4675	810	59	0.815	963
6	0.1	907	33	0.475	813	60	0.8225	967
7	0.115	900	34	0.4975	820	61	0.835	977
8	0.1425	887	35	0.51	823	62	0.85	987
9	0.16	877	36	0.5175	827	63	0.865	993
10	0.1875	863	37	0.53	830	64	0.8825	1003
11	0.205	857	38	0.5425	833	65	0.8925	1010
12	0.2275	847	39	0.5525	837	66	0.9025	1017
13	0.235	843	40	0.585	850	67	0.915	1027
14	0.2575	837	41	0.595	853	68	0.9225	1033
15	0.275	830	42	0.6025	857	69	0.9375	1043
16	0.285	827	43	0.6175	860	70	0.9525	1057
17	0.295	823	44	0.63	867	71	0.9675	1063
18	0.3075	817	45	0.6475	873	72	0.97	1067
19	0.3175	813	46	0.66	880	73	0.9775	1072
20	0.33	810	47	0.6775	890	74	0.9825	1077
21	0.35	803	48	0.6925	897	75	0.9875	1080
22	0.36	800	49	0.705	903	76	0.9925	1083
23	0.3725	793	50	0.715	910	77	1	1084
24	0.3825	790	51	0.725	917			
25	0.3925	787	52	0.74	923			
26	0.4	780	53	0.75	927			
27	0.41	790	54	0.7625	933			

Independently, Hultgren et al. published the following activity data for liquid Ag–Cu alloys at 1400 K (1127 °C).

X_{Ag}	A_{Ag}	γ_{Ag}	X_{Cu}	A_{Cu}	γ_{Cu}
1	1.000	1.000	0	0.000	0.000
0.9	0.918	1.020	0.1	0.221	2.210
0.8	0.852	1.065	0.2	0.348	1.740
0.7	0.770	1.100	0.3	0.468	1.560
0.6	0.678	1.130	0.4	0.600	1.500
0.5	0.615	1.230	0.5	0.675	1.350
0.4	0.552	1.380	0.6	0.738	1.230
0.3	0.485	1.617	0.7	0.791	1.130
0.2	0.394	1.970	0.8	0.846	1.058
0.1	0.250	2.500	0.9	0.912	1.013
0	0.000	0.000	1	1.000	1.000

(i) With the data provided, plot the liquidus lines corresponding to the silver and copper components in the system

(ii) Calculate the solidus and liquidus lines for this system ($\Delta H_{\mathrm{fusion,Ag}}$ = 11.3 kJ/mole, $\Delta H_{\mathrm{fusion,Cu}}$ = 13.1 kJ/mole) assuming no terminal solution in the solid state and also by assuming a regular solution in the liquid (Ω= 15 kJ/mole)

(iii) Compare the calculated liquidus lines with the data provided, comment on your findings.

Solution

For part (i), simply we need to plot the data provided (temperature versus x_{Cu}). To determine the liquidus line assuming no solid state solutions in part (ii), we need to use Eq. (5.25). Use the silver and copper activities provided by Hultgren et al. to carry out the computation of the liquidus line. As indicated by (5.25) the liquidus temperature is an implicit function, thus to find its value we need to use a numerical approach to promptly solve the problem. In this case the bisection method with a convergence criterion of 0.001 was used.

Comparison between the data provided and that estimated with Eq. (5.25) is shown in Fig. 5.19. Finally, for part (iii), Eqs. (5.26a, 5.26b) were used to determine the corresponding liquidus lines. Similar to Eq. (5.25), the set of Eqs. (5.26) are implicit functions of *T*, thus they were solved numerically as in part (ii). The resulting lines are also plotted in Fig. 5.19.

As seen in the figure, it is clear that assuming regular solution in the liquid state offers a better fitting in relation to experimental data than the assumption of non-solid solutions. Regarding to the computation in part (ii), the data provided was taken at 1127 °C, which is far higher than the actual liquidus temperature for the different compositions therefore is expected that the activities of either copper or

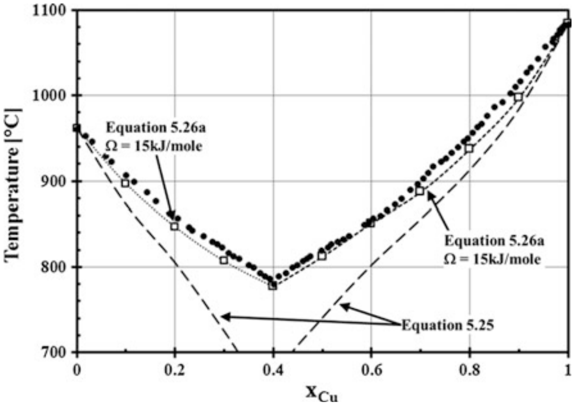


Fig. 5.19 Calculation of liquidus lines in the Ag–Cu system, using different models

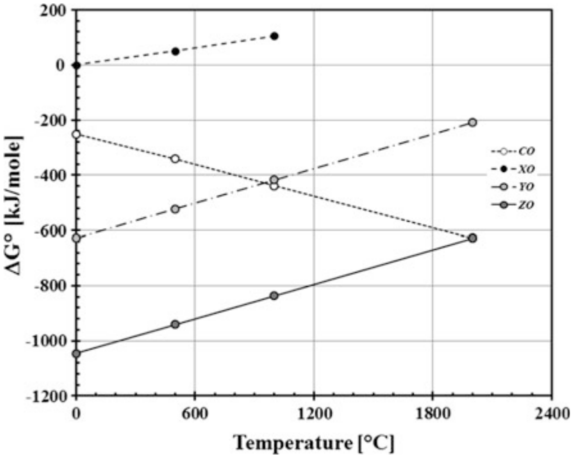


Fig. 5.20 Ellingham diagram for the CO, XO, YO, and ZO species

silver would be different when equilibrium with a minimum portion of solid within the system. Also from the data provided, it was found that the Ω parameter was of 13.5 kJ/mole. When using this value in expressions (5.26) there is considerable departure from the experimental data. The best fitting was found when the interaction parameter (Ω) has a value of 15 kJ/mole. (Figure 5.20) and (Fig. 5.21).

Example 3 Part (a) With the attached Ellingham diagram
Answer

(i) The temperature at which Ni, NiO, and oxygen at 10^{-12} atm are in equilibrium

(ii) The temperature at which Si, SiO_2, CO, and CO_2 (1 atm) are in equilibrium together

(iii) The CO_2 pressure in equilibrium with that of CO in (ii)

(iv) The mean values of $\Delta H°$ and $\Delta S°$ for the reactions

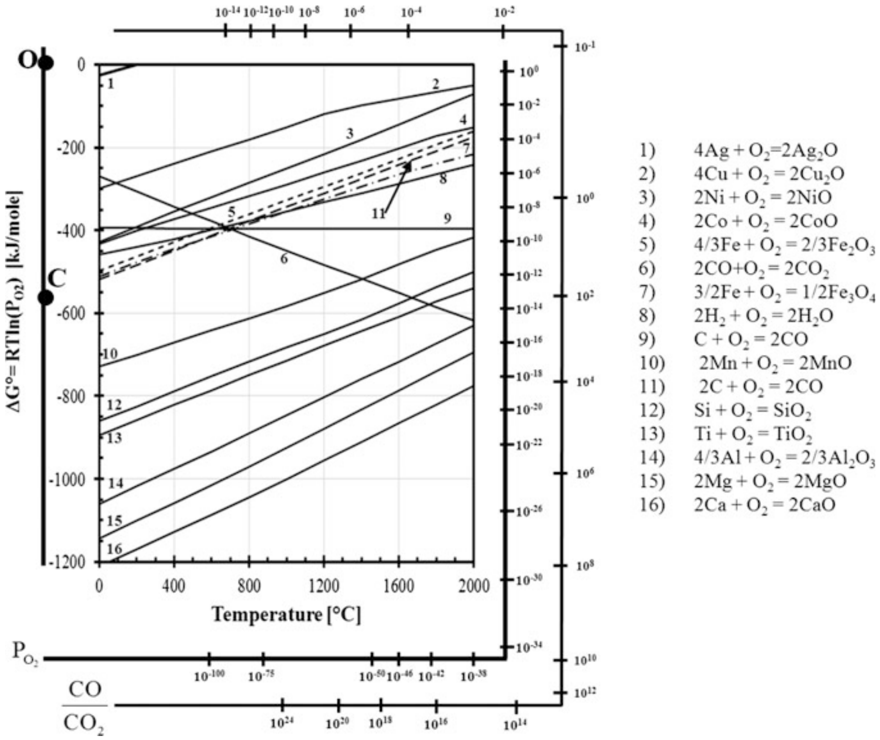


Fig. 5.21 Ellingham diagram for some oxides

a. $2Mn + O_2 = 2MnO$
b. $4/3Al + O_2 = 2/3Al_2O_3$

(v) Determine the $\Delta G°$ for the reaction: $3/2Si + Al_2O_3 = 2Al + 3/2SiO_2$ at 1000 °C
(vi) Will the reaction in (v) proceed to the right or to the left?
(vii) At what temperature, if any, will the reactants and products in part (v) be in equilibrium
(viii) By reference to the Ellingham diagram, comment on the feasibility of
  a. Reducing MnO with CO
  b. Reducing Al_2O_3 with CO
  c. Reducing Al_2O_3 with Ca

Solution Part (i)

We need to draw a line from point O in the scale at the left side of the diagram to $P_{O2} = 10^{-12}$. At the point in which this line intercepts the Ni–NiO equilibrium, we need to draw a second line perpendicular to the temperature axis from that interception to the temperature axis and then directly read form the diagram the temperature. In this case the equilibrium temperature is approximately 1075 °C (1348 K).

Part (ii)

For this part, the temperature can be found at the intersection between lines 6 and 12. At that intersection, we need to draw a straight line from that point to the temperature axis and read directly. In this case, the temperature is roughly 1680 °C.

Part (iii)

From part (ii) the equilibrium we are looking for is Si + $2CO_2$ = SiO_2 + 2CO (line 12–6 in the diagram). The equilibrium constant is $K = (P_{CO}/P_{CO2})^2$. The equilibrium CO/CO_2 ratio in equilibrium with the reaction we are looking for can be read from the diagram; in this case that ratio is 10^{-2} (draw a line from point C in the left side scale that passes through the Si–CO_2–SiO_2–CO intersection and extend it to the CO/CO_2 ratio scale and read directly). Since the total pressure is 1 atm, $P_{CO} + P_{CO2} = 1$. Thus solving the following system:

$$\left(\frac{P_{CO}}{P_{CO_2}}\right)^2 = 10^{-2}$$

$$P_{CO} + P_{CO_2} = 1$$

This results in $P_{CO2} = 0.91$ atm.

Part (iv)

Extending the Mn/MnO and Al/Al_2O_3 (lines 10 and 14 respectively) to the left side scale of the diagram directly yields the mean enthalpy change ($\Delta H°$). On the other hand direct calculation of the slope of these lines gives the mean entropy term ($\Delta S°$). This results in $\Delta H°_{Mn/MnO} = -775$ kJ/mole; $\Delta H°_{Al/Al2O3} = -1140$ kJ/mole; $\Delta S°_{Mn/MnO} = 0.16$ kJ/mole; $\Delta S°_{Al/Al2O3} = 0.22$ kJ/mole.

Parts (v, vi & vii)

The equilibrium we are looking for is: 3/2Si + Al_2O_3 = 2Al + $3/2SiO_2$. To get this reaction we need to combine reactions (12) and (14). The Gibbs free energy changes for these reactions at 1000 °C are −680 kJ/mole and −850 kJ/mole, respectively. To obtain the desired equilibrium we must multiply both reactions by 3/2 and subtract reaction (14) from reaction (12). Consequently the Gibbs free energies values have to be multiplied by the 3/2 factor. This results in $3/2 \times -680 + 3/2 \times 850 = 255$ kJ/mole.

The positive Gibbs free energy change indicates that the reaction would take place to the left, this means that silicon cannot reduce aluminum oxide; however, aluminum can reduce silicon oxide.

By examining lines 12 and 14 in the diagram, they are almost parallel over the entire temperature interval, and also line 14 lies beneath line 12; this means that at any temperature, aluminum is able to reduce silicon oxide; but the silicon never can reduce aluminum oxide. This means that the products and reactants in the proposed reaction never reach the equilibrium condition.

Part (viii)

Manganese oxide can be reduced with CO at least at 1400 °C. Below that temperature that is not possible, since $\Delta G°$ for Mn/MnO is below that of CO/CO_2. Aluminum oxide can only be reduced by CO gas above 2000 °C. Finally, aluminum oxide can be reduced by calcium at any temperature indicated in the diagram since the Gibbs free energy line of formation of CaO is always below that of the aluminum oxide.

Part (b) The following Gibbs free energies of formation are given in kJ/mole of oxygen.

T [°C]	CO	Xo	YO	ZO
0	−251	0	−628	−1046
500	−342	50.2	−523	−941
1000	−439	105	−418	−837
2000	−628		−209	−628

What information can be obtained from this data set regarding to the extraction of metals X, Y, and Z?

Solution

By plotting the data provided (*DG*° versus *T*) for each of the components shown in the table, it results in the following diagram:

From this graph, it is clear that over the entire temperature interval, XO cannot exist since its energy of formation is always positive, furthermore it can be reduced by any of the other oxides. YO can only be reduced by CO above 900 °C, below this temperature that is not possible since the Gibbs free energy line of YO lies below that of CO under 900 °C. The same can be concluded for ZO, but for this species, the equilibrium temperature is reached at 2000 °C.

Exergy

6

Introduction

Up to this point, several thermodynamic functions have been developed to predict the equilibrium position of chemical systems, especially those related to metallurgical processes. The examples developed throughout the manuscript represent classical chemical thermodynamics calculations aimed at predicting the behavior of metallurgical systems.

However, in spite of its usefulness, thermodynamics has some limitations. One of these; relates to the inability to determine how well the energy is used in the different metallurgical operations.

Traditionally, chemical and metallurgical systems are evaluated and/or designed based upon mass and energy balances. This approach has been taught for many years both in academia and in industry.

However, the constant exploitation of natural resources to produce metals (alloys, ceramics, etc.) at the expense of expanding the consumption of natural resources such as fossil fuels and increasingly depleted ore bodies has led to the reexamination of such traditional approach.

In addition to the high energy and natural resources consumption, metallurgical processes produce considerable streams of waste materials with different degrees of toxicity. Therefore, besides looking at maximizing metal production, it has become imperative for engineers to reduce as possible the ecological footprint associated to their processing units.

Recent trends in shifting towards industrial sustainability have led to optimizing the efficiency of extraction and refining processes. However, the estimation of process efficiency is not as simple as considering the ratio of process outputs to process inputs.

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To address this efficiency issue it is necessary to view a little further than the results offered by mass and energy balances. It was commented that such balances present some limitations.[1,2]

1. Enthalpy (energy) balances are based on the First Law of Thermodynamics, which only considers the energy as a constant, thus no energy degradation is accounted for.
2. Heat balances do not provide information about the quality of the sensible heat associated to a reactant stream.
3. Energy balances come in hand with mass balances; both of these balances are solved independently and the former depends on the later. Because of this, they do not reveal any significant information in terms of process optimization.
4. Energy balances are expressed in terms of energy units (J); whereas the mass balances are expressed in terms of the amount of matter (kg, mole); therefore two different dimensions are obtained after conducting these types of calculations resulting impossible to estimate a single process efficiency.

To overcome these limitations, it has been proposed to conduct exergy analysis of metallurgical processes.

The Concept of Exergy

Exergy is a concept that is derived from the First and the Second Laws of Thermodynamics. Exergy overcomes the limitations of the First Law of Thermodynamics which states that energy is conserved. On the other hand, it also uses the concept of thermal efficiency derived from the Second Law of Thermodynamics to indicate at what point during any process energy degrades so the process can be improved. The relationship between energy, exergy, and entropy is illustrated in Fig. 6.1.

A simple yet concise definition of exergy has been provided by Rickert[3]

> Exergy is the shaft work or electrical energy necessary to produce a material in its specified state from materials common in the environment in a reversible way, heat being exchanged only with the environment at temperature T_o.

According to this definition, to calculate the exergy associated to a process it is necessary to define the environment. The environment is set as temperature (T_o) as 298 K or 25 °C and pressure (P_o) of 1.01325×10^5 Pa (1 atm). The exergy (B) of a

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[1] Morris, D.R., Steward, F.R., Exergy analysis of a chemical metallurgical process. Met Trans, 15B (4), 1984, 645–654.

[2] Klaasen, B., Jones, P.T., Durinck, D., Dewulf, J., Wollants, P., Blanpain, B., Exergy-based efficiency analysis of pyrometallurgical processes. Met. Mater. Trans, 41B (6), 2010, 1205–1219.

[3] Rickert, L., The efficiency of energy-utilization in chemical processes, Chemical Engineering Science, 29 (7), 1974, 1213–1620.

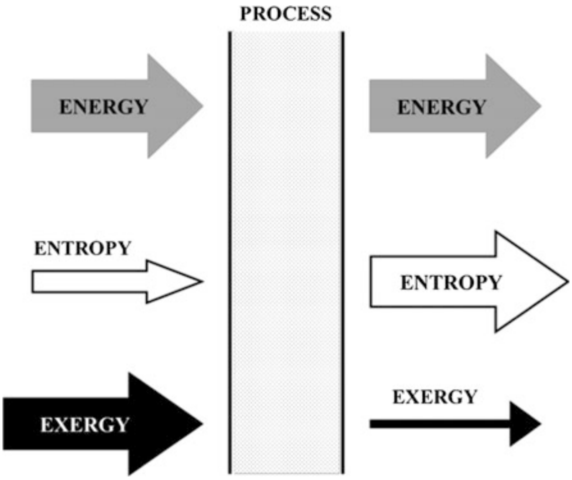

Fig. 6.1 Relationship between energy, entropy and exergy

material stream can be calculated by means of considering four distinctive exergy contributions: kinetic exergy, potential exergy, chemical exergy, and physical exergy. Thus the total exergy can be calculated by

$$B = B_{\mathrm{k}} + B_{\mathrm{p}} + B_{\mathrm{ch}} + B_{\mathrm{ph}} \tag{6.1}$$

The kinetic exergy is referred to the rotation velocity of planet Earth; the potential exergy relates to the elevation with respect of Earth's surface at the process location. The chemical exergy is the maximum work obtainable from the substance at T_{o} and P_{o}. The physical exergy is the maximum work obtainable from the state defined by T and P to the environmental state defined by T_{o} and P_{o}.

For metallurgical processes, the kinetic and potential exergies can be neglected, thus reducing expression (6.1) to

$$B = B_{\mathrm{ch}} + B_{\mathrm{ph}} \tag{6.2}$$

As mentioned before, to successfully use Eq. (6.2), it is necessary to define the reference state.

Reference State

The reference state can be defined in many different ways; however, it is advantageous to do so in terms of the surrounding atmospheric conditions. For physical exergy, the most common environmental (reference state) conditions are 25 °C (298 K) of temperature and 1 atm (101.3 kPa) of pressure. Recalling Chap. 1, the standard state has been defined in the same manner as the reference state.

Conveniently all thermodynamic data for chemical substances like enthalpies and Gibbs free energy of formation are reported at this temperature and pressure.

In terms of chemical exergy, the reference state is more complicated. It has been suggested that the reference state of a chemical substance is that in which the substance occurs naturally in the planet. Because of this, the reference state of each element can be chosen from a compound present either in the atmosphere, the oceans or the Earth's crust.

Once the reference state has been properly defined, it is now possible to calculate both the physical and chemical exergies.

Physical Exergy and Chemical Exergy

The physical exergy of a process or a material stream can be computed by

$$B_{\mathrm{ph}} = \left(H_T^\circ - H_{298}^\circ\right) - T_0\left(S_T^\circ - S_{298}^\circ\right) \tag{6.3}$$

On the other hand, the chemical exergy can be calculated as

$$B_{\mathrm{ch}} = \Delta G_{\mathrm{f}}^\circ + \sum_{i=1} n_i B_{\mathrm{ch,\,i}}^\circ \tag{6.4}$$

From these last equations, H_{T}° is the standard enthalpy of reaction at temperature T; H_{298}° is the standard enthalpy of reaction at 298 K; S_{T}° is the standard entropy of reaction at temperature T; S_{298}° is the standard entropy of reaction at 298 K; T_0 is the ambient temperature (298 K). $\Delta G_{\mathrm{f}}^\circ$ is the standard Gibbs free energy of formation of reaction at 298 K; n_{i} is the *i*th chemical element taking part in a reaction; and $B_{\mathrm{ch,i}}^\circ$ is the chemical exergy of each element taking part in a reaction.

To determine the enthalpy and entropy terms in Eqs. (6.3) and (6.4), we need to use the heat capacities of the different species participating in the reactions under study. It was indicated in Chap. 1, that heat capacities are represented as a function of temperature, with the general form

$$\mathrm{Cp} = A + B \times 10^{-3}T + \frac{C \times 10^{-5}}{T^2} + D \times 10^{-6}T^2 \tag{6.5}$$

Data for B_{ch}° of chemical elements and many inorganic compounds have been gathered and reported by Szargut et al.[4] Some of these values are shown in Table 6.1.

Furthermore, in many metallurgical operations, oxygen enriched air is used to enhance the metal refining processes while decreasing the volume of off gases produced.

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[4] Szargut, J., Morris, D.R., Steward, F.R., Exergy analysis of thermal, chemical, and metallurgical processes. Hemisphere, New York, 1988.

Table 6.1 Chemical exergy of some elements and inorganic compounds

Compound/element	*B*°ch (kJ/mole)	Compound/element	*B*°ch (kJ/mole)	Compound/element	*B*°ch (kJ/mole)
Ag	70.2	CaO	110.2	$Fe_{0.947}O$ (wüstite)	113.3
AgCl	22.2	$CaO.Al_2O_3$	275.4	FeO	127.0
$AgNO_3$	43.1	CaS	844.6	Fe_2O_3	16.5
Ag_2O	57.6	$CaSO_4$	8.2	Fe_3O_4	121.6
Ag_2S	709.5	$CaSiO_3$	23.6	$Fe(OH)_3$	39.6
Al	888.4	Ca_2SiO_4	95.7	FeS	885.6
$AlCl_3$	444.9	Cl_2 (gas)	123.6	FeS_2 (pyrite)	1428.7
Al_2O_3	200.4	Co	265.0	$FeSO_4$	173
$Al_2O_3.3H_2O$	209.5	$CoCl_2$	118.8	FeSi	1157.3
Al_2SiO_5 (sillimanite)	15.4	CoO	52.8	$FeSiO_3$	161.7
$3Al_2O_3.2SiO_2$	618.8	Co_3O_4	38.2	Fe_2SiO_4	236.2
As	494.6	CoS	792.2	$FeTiO_3$	131.4
As_2O_5	216.9	$CoSO_4$	99.8	H_2	236.1
Au	15.4	Cr	544.3	HCl (gas)	84.5
$AuCl_3$	155.5	Cr_2O_3	36.5	HF (gas)	80
Au_2O_3	114.7	$CrCl_2$	311.9	HNO_3 (liq)	43.5
B	628.5	Cr_7C_3	4874.2	H_2O (gas)	9.5
B_2O_3	69.4	Cu	134.2	H_2O (liq)	0.9
Ba	747.7	$CuCO_3$	31.5	H_2S (gas)	812.0
$BaCO_3$	26.3	$CuCl_2$	82.1	H_2SO_4	163.4
$BaSO_4$	3.4	CuO	6.5	He	30.37
Bi	274.5	Cu_2O	124.4	K	366.6
Bi_2O_3	61.4	$Cu(OH)_2$	15.3	KCl	19.6
C (graphite)	410.26	CuS	690.3	KF	62.2

(continued)

Table 6.1 (continued)

Compound/element	*B*°ch (kJ/mole)	Compound/element	*B*°ch (kJ/mole)	Compound/element	*B*°ch (kJ/mole)
CO	275.10	Cu_2S	791.8	KNO_3	−19.4
CO_2	19.87	$CuSO_4$	89.8	K_2O	413.1
Ca	712.4	F_2 (gas)	466.3	KOH	107.6
$CaCO_3$	1.0	Fe	376.4	Li	393.0
$CaCO_3.MgCO_3$ (dolomite)	15.1	Fe_3C	1560.2	LiCl	70.7
CaF_2	11.4	$FeCl_3$	230.2	Li_2O	225.7
LiOH	74.1	NaCl	14.3	$SiCl_4$	481.9
Mg	633.8	NaI	136.1	SiO_2 quartz	1.9
$MgCO_3$	37.9	$NaNO_3$	−22.7	SiO_2 amorphous	7.9
$MgCl_2$	165.9	Na_2O	296.2	Sn white	544.8
MgO	66.8	NaOH	74.9	Sn gray	544.9
$Mg(OH)_2$	40.9	Na_2SO_4	21.4	$SnCl_2$	386.4
MgS	901.6	Ni	232.7	SnO	289.9
$MgSO_4$	80.7	$NiCO_3$	36.4	SnO_2	29.1
$MgSiO_3$	22.0	$NiCl_2$	97.2	SnS_2	1604.6
Mn	482.3	NiO	23.0	Ti	906.9
$MnCO_3$	81.8	NiS	762.8	TiO_2	21.4
MnO	119.4	Ni_3S_2	1720.2	Ti_2O_3	385.5
MnO_2	21.1	$NiSO_4$	90.4	U	1190.7
MnS	873.5	O_2 (gas)	3.97	UO_2	162.9
$MnSO_4$	142.4	O_3 (gas)	169.1	UO_3	43.9
$MnSiO_3$	102.3	Pb	232.8	V	721.1
Mo	730.3	$PbCO_3$	23.5	V_2O_3	299.7
Mo_2C	1824.6	PbO_2	19.4	V_2O_5	32.5

(continued)

Table 6.1 (continued)

Compound/element	$B°$ch (kJ/mole)	Compound/element	$B°$ch (kJ/mole)	Compound/element	$B°$ch (kJ/mole)
MoO_2	201.2	PbS	743.7	W	827.5
MoS_2	1723.1	$PbSO_4$	37.2	WC	1199.5
N_2 (gas)	0.72	$PbSiO_4$	75.5	WO_2	297.5
NH_3 (gas)	337.9	S	609.6	Zn	339.2
NO (gas)	88.9	SO_2 (gas)	313.4	$ZnCO_3$	23.9
NO_2 (gas)	55.6	SO_3 (gas)	249.1	$ZnCl_2$	93.4
N_2O (gas)	106.9	Se	346.5	ZnO	22.9
Na	336.6	Si	854.6	ZnS	747.6
Na_2CO_3	41.5	SiC	1204.6	$ZnSO_4$	82.3

Increasing the relative oxygen content in the blasts used in these processes adds an additional exergy cost, which can be computed with the equation

$$B^{o}_{O_2,enrichment} = \mathrm{RT}_0 \ln\left(\frac{P_{O_2}}{P^{o}_{O_2}}\right) \tag{6.6}$$

In Eq. (6.6), $P^{\circ}_{O_2}$ is the partial pressure of oxygen in ambient air (0.21 atm), whereas P_{O_2} is the partial pressure of oxygen in the enriched blast. If no extra oxygen is added to the air; then P_{O_2} is 0.21 atm, therefore $P^{\circ}_{O_2\,\mathrm{enrichment}}$ is zero.