Chemical Thermodynamics at a Glance

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To my colleagues at universities here and abroad who give their friendship and
to my numerous students, past and present, who are always a source of delight.

To Sheila Anne Jenkins.

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Preface

When Blackwell approached me about writing this book I was pleased to respond. With many decades of experience in teaching thermodynamics and with an understanding of the need to present the underlying mathematics needed in a palatable way, I felt up to the challenge. Armed with the results of Blackwell's own suvey of both UK and American universities' teaching needs in this area the contents seemed pretty self-evident.

Students these days come to university armed with a very varied and often quite novel range of experience and this enforces the need to present difficult subjects like thermodynamics in a logical (but, at the same time, quite thorough) way.

Such is the aim of this text. Thermodynamics and the necessary mathematics are embodied as a series of 54 'Frames' plus an Appendix. These frames are multicrossreferenced which enables the text to be used in a variety of ways:

- as a means of reading up on thermodynamics and using the 'bite-sized' frames as the basis of one hour study periods which develop in a logical and progressive manner and cover the necessary thermodynamics for most undergraduate science courses.
- as an aide memoire to review course material already received. In this mode one can start reading at any Frame and because these are liberally cross-referenced the reader will be directed to different sections of the book according to need;
- as a last minute revision aid for examinations, to review specific parts of the syllabus quickly and easily. The extensive index to the frames provides an immediate location of the relevant Frames needed to highlight a given topic. The division of the material into short sections makes this much easier than ploughing through the standard text. The use of bullet points is intended to further clarify the important points. The overview presented in Frame 54, and the figure printed inside the front cover of the book will also be found useful;
- The book can also be used at the post-graduate level to supplement, refresh and reinforce earlier teaching.

I have tried to contain within the 54 Frames presented, sufficient discussion of the necessary maths, as well as of the relevant thermodynamics suitable for an undergraduate course (such as is provided here at Warwick).

The author has drawn widely on his accumulated knowledge acquired by reading the many texts (too numerous to mention) available in thermodynamics and it is from the authors of such texts that many of the ideas presented have their origins and to whom thanks are due. Also there is a degree of originality built into many of the Frames that attempts to present some of the more difficult material in a new light.

The author, as well as being an acclaimed teacher, is also an active researcher who has recently developed a new approach to thermodynamics (VBT – Volume Based Thermodynamics) published in high impact international journals, which is proving useful as a research tool.

The author has recently reported an entirely new approach for the acquisition of thermochemical data for condensed materials. The author lectures widely in this country and abroad.

I am indebteded to my colleague Dr Joe Lee (University of Manchester) who gave of his time willingly and diligently in order to read the manuscript of this text and make the many useful and improving comments he did. His insightfulness led to many interesting and stimulating phonecalls and I am grateful to him both as a personal friend and as one of my former teachers. Naturally any errors that may remain are totally my responsibility. I also acknowledge the constant help and support given to me by Sheila Anne Jenkins in all of my projects, not least, in the preparation of the manuscript for this book.

I hope that you may find this text useful and I would be glad to hear from students, worldwide, about their experiences with the text in the hope that any future edition can reflect on these and improve presentation whenever necessary.

0. Symbols and Notation

Thermodynamics employs quite complicated notation which, at first sight, may give the impression of great difficulty. This can be totally misleading and should not be allowed to discourage beginners. In actual fact the notation is intended to make things *easier* to understand in most cases.

Thus, in this text, several pre-amble frames are first presented which explain areas where experience of teaching has shown students have uncertainties or difficulties. The key is to read these frames carefully and to become familiar with the meaning, not forgetting to employ the extensive cross-referencing between the various frames to supplement your knowledge.

The purpose of the tables below is:

- To give the IUPAC standard notation for symbols which are commonly abbreviated to rather more simple notation in this text.
- These abbreviations were consciously made in order that the text did not become cluttered with extended symbols and terminology. To have retained the suggested notation, on the grounds of rigour, would have led to a text that might have appeared to be more complicated than it is. So the form presented is to give, in the table below, details of the IUPAC notation and alongside this give a compendium of symbols used in the text. Cross-reference can then be made at will (see also *Quantities, Units and Symbols in Physical Chemistry*, I. Mills, Blackwell Scientific Publications (latest edition), for the definitive word on this issue).

In most cases the properties refer to one mole of material or one mole of reactant.

Table 0.1 Symbols, terminology and units.

Symbol	Quantity	Usual units	Notes	IUPAC symbol
A	Helmholtz energy	kJ mol^{-1}	$A = U - TS$	$\boldsymbol{A}$
A	area of a triangle	m^{2}	$A = {}^{1}\!/_{2}$(base)(perpendicular height)	$\boldsymbol{A}$
a	activity			$\boldsymbol{a}$
$a_{\pm}$	mean ionic activity		$a_{\pm} = m_{\pm} \cdot \gamma_{\pm}/m^{o}$	$a_{\pm}$
C_p	heat capacity at constant pressure	J K^{-1} mol^{-1}	$C_p = (\partial H/\partial T)_P$	$\boldsymbol{C_{p,m}}$
C_v	heat capacity at constant volume	J K^{-1} mol^{-1}	$C_V = (\partial U/\partial T)_V$	$\boldsymbol{C_{v,m}}$
$[\ ] = c$	amount, molar concentration	mol dm^{-3}	used in equilibrium expressions	
$[\ ]_o = c^o$	standard molar concentration	mol dm^{-3}	used in equilibrium expressions	
$[H^+] = 10^{-7}$	biochemical standard state	mol dm^{-3}	denoted by prime on symbol e.g. $\Delta G^{o'}$	$\boldsymbol{\Delta_r G^{o}}$
ρ	density, mass density	g cm^{-3}		$\boldsymbol{\rho}$
e	charge on the proton	C	$e = 1.602 \times 10^{-19}$ C	
EA	electron affinity	kJ mol^{-1}	$X(g) + e^-(g) \rightarrow X^-(g)$	
f	fugacity	Pa	effective pressure of real gases	$\boldsymbol{f}$
F	Faraday constant	C mol^{-1}	$F = eL = 96{,}485.3$ C mol^{-1}	$\boldsymbol{F}$
G	Gibbs energy (Gibbs free energy)	kJ mol^{-1}	$G = H - TS$	$\boldsymbol{G_m}$
γ	activity coefficient		$= a/x = a/m_i$ (species i)	γ
$\gamma_{\pm}$	mean ionic activity coefficient		$\gamma_{\pm}^{(v++v-)} = \gamma_{+}^{v+} \cdot \gamma_{-}^{v-}$	$\gamma_{\pm}$
H	enthalpy	kJ mol^{-1}	$H = U + PV$	
IP	ionisation potential	kJ mol^{-1}	$M(g) \rightarrow M^+(g) + e$	
K_a	equilibrium constant written in terms of activity	dimensionless		$\boldsymbol{K_a}$
$K_{c/co}$	equilibrium constant written in terms of concentration ratios: $[\ ]/[\ ]_o$	dimensionless		$\boldsymbol{K_{c/co}}$
$K_{p/po}$	equilibrium constant written in terms of partial pressure ratios: p/P^{o}	dimensionless	$\Delta G^{o} = -RT \ln K_p$	$\boldsymbol{K_{p/po}}$
$K_{m/mo}$	equilibrium constant written in terms of partial pressure ratios: p/P^{o}	dimensionless		$\boldsymbol{K_{m/mo}}$
subscript m	implies molar quantity (m can be omitted since units can indicate molar quantity (e.g. mol^{-1}))			e.g. $\boldsymbol{\Delta_{vap} H_m}$
subscript r	implies reaction (also implies molar)			e.g. $\boldsymbol{\Delta_r G^{o}}$, $\boldsymbol{\Delta_r H^{o}}$
μ	chemical potential	J mol^{-1}	$(\partial G/\partial n_B)_{T,\,P,\,nj \neq nB}$	$\boldsymbol{\mu}$
m	mass	kg		$\boldsymbol{m}$
$m_{\pm}$	mean ionic molality	mol kg^{-1}	$m_{\pm}^{(v++v-)} = m_{+}^{v+} \cdot m_{-}^{v-}$	$\boldsymbol{m_{\pm}}$
m	molarity	mol kg^{-1}		$\boldsymbol{m}$
L, N_A	Avogadro constant	mol^{-1}	$= 6.023 \times 10^{23}$	$\boldsymbol{L}$, $\boldsymbol{N_A}$
n	amount (of substance)	dimensionless		$\boldsymbol{n}$

(*continued*)

Table 0.1 (*continued*)

Symbol	Quantity	Usual units	Notes	IUPAC symbol
P	total pressure	Pa / bar	$P = \sum p_i = (RT/V)\sum n_i$	$\boldsymbol{P}$
	1 bar = 100 kPa = 10^5 Pa; 1 mmHg = 1 Torr; 1 atm = 760 Torr = 101325 Pa; 1 bar = 10^5 Pa			
p_i	partial pressure of gas i in mixture	Pa / bar / atm		$\boldsymbol{p_i}$
q	heat absorbed by thermodynamic system from surroundings	J (kJ)	acquisitive convention	$\boldsymbol{q}$
q_P	heat absorbed by thermodynamic system at constant pressure from surroundings	J (kJ)		$\boldsymbol{q_P}$
q_V	heat absorbed by thermodynamic system at constant volume from surroundings	J (kJ)		$\boldsymbol{q_V}$
R	gas constant	$J\ K^{-1}\ mol^{-1}$	$= 8.314\ J\ K^{-1}\ mol^{-1}$	$\boldsymbol{R}$
S	entropy	$J\ K^{-1}\ mol^{-1}$		$\boldsymbol{S}$
T	temperature	K		$\boldsymbol{T}$
T_b	boiling point	K		
T_f	fusion temperature	K		
T_m	melting point	K		
T_{sub}	sublimation temperature	K		
$U(= E)$	internal energy	$kJ\ mol^{-1}$	denoted E in some textbooks	$\boldsymbol{U}$
V	volume	m^3		$\boldsymbol{V}$
V_m	molar volume	m^3		$\boldsymbol{V_m}$
w	work done by surroundings on system	J (kJ)	uses acquisitive convention	$\boldsymbol{w}$
w'	work done other than (PV) mechanical work of expansion/compression done by surroundings on system	J (kJ)	uses acquisitive convention e.g. gravitational, electrical work etc.	$\boldsymbol{w'}$
x_i	mole fraction of component i	dimensionless		$\boldsymbol{x_i}$
X_f	final value of property X (state function) following a change	units of X		
X_i	initial value of property X (state function) before a change	units of X		
$\Delta_f G^o$	standard Gibbs energy of formation per mole	$kJ\ mol^{-1}$		$\boldsymbol{\Delta_f G^O}$
ΔH^o	enthalpy change per mole under standard conditions			$\boldsymbol{\Delta_r H}$
$\Delta H^o(X–Y)$	bond enthalpy or bond dissociation enthalpy for X–Y bond sometimes written as E(X–Y) or BE(X–Y) and (wrongly) described as bond *energy*			
$\Delta_{at} H^o$	standard enthalpy of atomisation per mole (compound (s, l, g) → atom(g))			
$\Delta_c H^o$	standard enthalpy of combustion per mole (compound + $O_2(g) \rightarrow CO_2(g) + H_2O(l)$ + etc)			$\boldsymbol{\Delta_c H^O}$
$\Delta_f H^o$	standard enthalpy of formation per mole (elements in standard states →compound)			$\boldsymbol{\Delta_f H^O}$
$\Delta_{fus} H^o$	standard enthalpy of fusion per mole (solid → liquid)			$\boldsymbol{\Delta_{fus} H}$
$\Delta_{hyd} H^o$	standard enthalpy of hydration (ion(g) → ion(aq))			$\boldsymbol{\Delta_{hyd} H^O}$
$\Delta_{mix} H^o$	standard enthalpy of mixing per mole (ion(g) → ion(aq))			$\boldsymbol{\Delta_{mix} H^O}$
$\Delta_r H^o$	standard enthalpy of reaction per mole (reactants → products)			$\boldsymbol{\Delta_r H^O}$
$\Delta_{sub} H^o$	standard enthalpy of sublimation per mole (solid → gas)			$\boldsymbol{\Delta_{sub} H^O}$
$\Delta_{sol} H^o$	standard enthalpy of solution per mole (solute → solution)			$\boldsymbol{\Delta_{sol} H^O}$
$\Delta_{trs} H^o$	standard enthalpy of transition per mole (between phases)			$\boldsymbol{\Delta_{trs} H^O}$
$\Delta_{vap} H^o$	standard enthalpy of vaporisation per mole (liquid → gas)			$\boldsymbol{\Delta_{vap} H^O}$
$\Delta_f S^o$	standard entropy of formation per mole			$\boldsymbol{\Delta_f S^O}$
ΔU	internal energy change per mole sometimes written as ΔE [$\Delta U = w$ (adiabatic process, $q = 0$); $\Delta U = 0$ (*isolated system*); $\Delta U = q + w$ (*open* system); $\Delta U = q$ (closed system, $dV = 0$)]			$\boldsymbol{\Delta_U}$

Table 0.2 Notation used to denote changes in thermodynamic properties.

Notation	Meaning	Notes
δq, δw	infinitesimally small *quantities* of heat added to system or work done by surroundings on system	'delta' q or w only defined for process or path *not* changes in state functions
dX	small *change* in property X (state function)	'dee' X (e.g. dU)
ΔX	measurable *change* in property X (state function)	'Delta' X N.B. changes: $\delta \ll d < \Delta$
d$X \rightarrow 0$	change in X approaches zero	
dy/dx	differential coefficient of y with respect to x	
d$V = 0$	no change in volume	isochoric process
d$P = 0$	no change in pressure	isobaric process
d$T = 0$	no change in temperature	isochoric process
$\delta q = 0$	no heat enters or leaves system	adiabatic process
$\int$y.dx	integral of y with respect to x	
$\sum$	sum of individual values	e.g. $\sum_{i=1}^{3} x_i = x_1 + x_2 + x_3$
$\prod$	product of individual values	e.g. $\prod_{i=1}^{3} x_i = x_1.x_2.x_3$
$\sum \Delta_f X^o$(Products)	sum of individual $\Delta_f X^o$ values ($X = G$ or H) of all products of a reaction	
$\sum \Delta_f X^o$(Reactants)	sum of individual $\Delta_f X^o$ values ($X = G$ or H) of all reactants of a reaction	
$N!$	$= N(N–1)(N–2)(N–3)\ldots.3.2.1$	'factorial N' e.g. $6! = 6.5.4.3.2.1 = 720$
0!	factorial zero	$= 1$
$\vert x \vert$	modulus of x	i.e. positive value of x (ignores any negative sign)
$>$	greater than	e.g. $8 > 6$
$\geq$	greater than or equal to	
$<$	less than	e.g. $4 < 7$
$\leq$	less than or equal to	
$\pm$	plus or minus	
$\neq$	not equal to	e.g. $4 \neq 5$
$\approx$	approximately equal to	
$\int$	integral of	
$a \pm b \pm c$	means $a + b + c$ (upper signs) and $a - b - c$ (lower signs)	used for shorthand form of equations
(s) or (c)	solid or crystalline phase	e.g. $H_2O(s)$ = ice
(l)	liquid phase	e.g. $H_2O(l)$ = water
(g)	gaseous (vapour) phase	e.g. $H_2O(g)$ = steam
^{o}	standard state (superscript)	sometimes written as $^\ominus$
$_o$	standard state (subscript)	e.g. $[\;]_o$ standard state concentration
ΔC_p^o	$= \sum C_p$(Reactants) – $\sum C_p$(Products) for a reaction	
$\Delta_f G^o$	standard Gibbs energy of formation per mole	
ΔH^o	enthalpy change per mole under standard conditions	
$\Delta H^o(X - Y)$	bond enthalpy or bond dissociation enthalpy for X–Y bond sometimes written as E(X – Y) or BE(X – Y) and (wrongly) described as bond *energy*	

1. Thermodynamic Changes, Properties and Types of Function

1.1 Thermodynamic System and Surroundings

A thermodynamic *system* refers to:

the physical process or the chemical reaction at the centre of interest.

The remainder of the universe is designated to be:

the surroundings, although in practice, these can be restricted to those parts of the universe adjacent to the system.

One can define the boundaries of the thermodynamic system in any way one chooses.
Systems can be classified (see Figure 7.3, Frame 7) as follows:

CLOSED SYSTEM – no material is exchanged with the surroundings (e.g. autoclave – a sealed vessel for carrying out high pressure reactions).
OPEN SYSTEM – material is exchanged (e.g. by evaporation) with the surroundings. The system does not have to be OPEN in order to change the amounts of substances present; this can occur by chemical reaction or interphase transfer within a closed system.
ISOLATED SYSTEM – neither material nor energy exchange with the surroundings (e.g. thermos flask).

Processes can be either:

CHEMICAL – involving reaction and chemical change or PHYSICAL – involving physical change (e.g. variation of pressure, P, or phase such as in boiling (liquid → vapour).

Many processes involve one or more of the following situations (d denotes a change in the property specified):

ISOTHERMAL = constant temperature ($\mathrm{d}T = 0$);
ISOCHORIC = constant volume ($\mathrm{d}V = 0$);
ISOBARIC = *Isopiestic* = constant pressure ($\mathrm{d}P = 0$);
ADIABATIC = no flow of heat ($q = 0$) between system and surroundings;
REVERSIBLE = process in which certain parameters (usually pressure, P or temperature, T) are only minutely (i.e. infinitesimally) different from those of the immediate surroundings. The process must also be close to equilibrium;

Energy can be transferred between the surroundings and the system and is subdivided into:

heat, represented by the symbol, q and work, represented by the symbol, w.

Work can be further subdivided into various categories: mechanical or '*PV*' work (Frames 8 and 9), $w = -P\mathrm{d}V$; electrical work, $w_{\mathrm{elec,}}$ (see Equation (8.13), Frame 8); magnetic work, w_{mag}; gravitational work, w_{grav} (see Equation (8.12), Frame 8); surface work, w_{surf} etc.

1.2 Thermodynamic Changes

A property, X, which *alters its value* from an *initial state* (i) (value of the property X_{i}) to a *final state* (f) (value of the property X_{f}) has changed in value by ($X_{\mathrm{f}} - X_{\mathrm{i}}$). If change occurring in X is *small*, we denote this by $\mathrm{d}X$ and for *larger* (measurable) changes, by ΔX. Such notation applies predominantly to *state functions* (see section 1.7 below), examples are H (enthalpy), U (internal energy), G (Gibbs energy), etc.

To talk about a *change*, dq, in *heat added* to a thermodynamic system and to try and equate it to ($q_{\mathrm{f}} - q_{\mathrm{i}}$) does not make any sense since it is impossible to define, or quantify, the *amount of heat possessed* by a body (or contained within it) at any 'snapshot' instant. Therefore q_{i} and q_{f} are simply *not definable* for a process in the same way that we can record the temperature, T, at any instant. Hence q is *not* a property of a system but is defined only *during a change* – we can only measure *quantities* of heat *supplied* or *released* during a process. Addition (or release) of an infinitesmally small *amount* of heat is denoted by δq.

Similarly work done, w, *by* or *on* a system, (Frames 8 and 9), a *quantity of work* is either *attributable to* or *transferred* during a physical change (e.g. during expansion or contraction); but there is no amount of work *possessed* by a system at any instant, it is definable only during a process.

Thus q and w are different from most other functions in thermodynamics.

1.3 Thermodynamic Intensive and Extensive Properties

Thermodynamic properties which depend on the *amount (mass) of material present* (e.g. internal energy: U; enthalpy: H, etc.) are termed EXTENSIVE properties.

For *extensive* quantities, X (in general):

$$X_{\mathrm{m}} = \text{molar } X \overset{\text{definition}}{=} \frac{X}{n} \tag{1.1}$$

where n is the amount of material present. Since X is proportional to n, the above quotient in (1.1) is independent of n and therefore X_{m} is INTENSIVE.

Intensive properties are such that if the material were continuously sub-divided then the property would be *identical for all parts* of the sub-divided material. Such properties are independent of the size (or amount) of sample (e.g. density: ρ; temperature: T and all molar quantities. Frequently in the text we omit the subscript m from the symbol.

Extensive quantities show an *exact* proportionality to n, only when intensive quantities, like T and P, remain constant.

1.4 Molar Quantities and the Concept of the Mole

Molar as an adjective does *not* actually mean ‘of or for 1 mole’. For a pure substance molar means simply ‘divided by amount of substance’. Thus the molar mass of material, M, is the mass of the material, w divided by the amount of material, n:

$$M = \frac{w}{n} \tag{1.2}$$

Since the purpose of this book is presentation of thermodynamics in a form which is easy to assimilate the use of IUPAC (the body recommending chemical notation) notation has *not* been adopted in the text, but *importantly*:

reference to IUPAC notation is provided in the glossary (Frame 0).

Thus use of extended symbols (e.g. $C_{\mathrm{p,m}}\ \Delta_{\mathrm{m}} H$) has usually been avoided. The simpler forms C_{p} and ΔH being adopted.

IUPAC recommend that the *mole* should be replaced by amount of substance. Readers should however be aware of the wide usage of the concept of the mole elsewhere. The term *mole fraction*, x, is a IUPAC acceptable name. The Term *amount fraction* is not recommended.

1.5 Meaning of the Term *Molar* in Relation to Chemical Reactions

Consider the combustion reaction:

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)} \tag{1.3}$$

at 298K and 1 bar (= 100 kPa).

Molar enthalpy of combustion of methane gas, $\Delta_{\mathrm{c}} H^{o}(\mathrm{CH_4, g})$

If the amount of methane gas combusted is $n(\mathrm{CH_4})$ and the enthalpy change on combustion is ΔH, then the molar enthalpy of combustion is given by:

$$\Delta_{\mathrm{m}} H = \Delta_{\mathrm{c}} H^{o}(\mathrm{CH_4, g}) = \frac{\Delta H}{[n(\mathrm{CH_4, g})\ \text{combusted}]} = \frac{\Delta H}{[-\Delta n_{\mathrm{CH4}}]} = \Delta H \tag{1.4}$$

where Δn_{CH4} is the change in the amount of methane (since methane decreases, this quantity will be negative (= -1 mol). Thus $-\Delta n_{\mathrm{CH4}}$ is then positive.

On the other hand where there is no intention to focus on any one particular species we treat things differently:

1.5.1 Molar enthalpy (change) of the reaction (1.3)

The molar enthalpy change of the reaction is calculated using the equation:

$$\Delta_{\mathrm{m}} H = \frac{\Delta H}{\Delta \xi} \tag{1.5}$$

where $\Delta\xi$ (delta xi) is the change in the extent of the reaction.

The reaction (1.3) above is a statement of the stoichiometry, and reports the *stoichiometric* numbers, v, which take values:

$$v_{CH4} = -1; \quad v_{O_2} = -2; \quad v_{CO_2} = +1; \quad v_{H_2O} = +2; \tag{1.6}$$

recorded as: positive (+) for products, and negative (−) for reactants.

Suppose that we undertake combustion of 16 g (i.e. 1 mol) methane gas at a particular temperature, T and pressure, P and determine, calorimetrically, the change in enthalpy, ΔH (in units of J or kJ). We define:

$$\begin{aligned}\Delta n_{CH_4} &= \{[\text{amount of } CH_4 \text{ in products}] - [\text{amount of } CH_4 \text{ in reactants}]\} \\ &= (0-1)\,\text{mol} = -1\,\text{mol}\end{aligned} \tag{1.7}$$

similarly:

$$\Delta n_{O_2} = (0-2) = -2\,\text{mol}; \Delta n_{CO_2} = (1-0) = +1\,\text{mol}; \Delta n_{H_2O} = +2\,\text{mol} \tag{1.8}$$

[In equations (1.7)–(1.8) a negative sign signifies overall *loss* (of reactant); a positive sign signifies an overall *gain* (of product)].

The extent of our experimental reaction, $\Delta\xi$ (the same for all species involved) can be calculated using:

$$\Delta\xi = \Delta n_{CH4}/v_{CH4} = \frac{(-1)}{(-1)} = 1\,\text{mol} \tag{1.9}$$

similarly:

$$\Delta\xi = \Delta n_{O_2}/v_{O_2} = \frac{(-2)}{(-2)} = 1\,\text{mol}; \Delta\xi = \Delta n_{CO_2}/v_{CO_2} = \frac{(+1)}{(+1)} = 1\,\text{mol}; \Delta\xi = \Delta n_{H_2O}/v_{H_2O} = \frac{(+2)}{(+2)} = 1\,\text{mol} \tag{1.10}$$

thus:

if we combust 1 mol of methane this will correspond to 1 *mole of reaction* (or, $\Delta\xi$ is 1 mol).

Now $\Delta_m H$, the *molar* enthalpy change of the combustion reaction, is given as:

$$\Delta_m H = \frac{\Delta H}{\Delta\xi} = \Delta H \tag{1.11}$$

BUT if the chemical equation (1.3) given is multiplied through by a factor of ½ to give:

$$\tfrac{1}{2}CH_4(g) + O_2(g) \rightarrow \tfrac{1}{2}CO_2(g) + H_2O(l) \tag{1.12}$$

then:

$$\Delta\xi = \frac{\Delta n_{CH_4}}{v_{CH_4}} = (-1)/(-\tfrac{1}{2}) = 2\,\text{mol} \tag{1.13}$$

and:

$$\Delta_m H = \frac{\Delta H}{\Delta\xi} = \frac{\Delta H}{(2)} = \tfrac{1}{2}\Delta H \tag{1.14}$$

i.e. $\Delta_m H$ for reaction (1.12) corresponds to *half* $\Delta_m H$ for the reaction (1.3).

From the above it can be seen that a chemical equation gives a connection between $\Delta\xi$ and the various Δn.

These conclusions are used in application of Hess's Law (Frame 11, section 11.8).

The same principles above apply: to a *physical process* when represented as a chemical equation, for example:

$$Br_2(l) \rightarrow Br_2(g); \quad 298\,\text{K}, 100\,\text{kPa} \tag{1.15}$$

and to *any extensive function of state* (e.g. ΔU, ΔH, ΔS, ΔG etc.).

1.6 Types of Thermodynamic Function: Path Dependent Function, *q* and *w*

Path dependent changes result when *heat or work* are involved. Suppose we have a gas having a volume V_i which we heat up from T_i to T_f and then expand it (at a fixed temperature T_f) from the intial volume V_i to a volume, V_f. The heat supplied to the gas, q_1 and the work done, w_1, by the gas in expanding against external pressure *will be different* from the case where the gas is first expanded at fixed T_i from a volume V_i to V_f, doing work of expansion, w_2 and is then heated (q_2) from T_i to T_f ending up in the *same* final state (V_f, T_f) (Figure 1.1). It is easy to see that q_1 and q_2 are different from one another (i.e. they depend on the *precise* path followed). In the first case one is heating *a volume*, V_i, *of gas* whilst in the second case one is heating *a* (*larger*) *volume*, V_f *of gas*, both from T_i to T_f, and heat required (an extensive property) must be such that $q_2 > q_1$. Similarly for the work of expansion: w_1 expands the gas at the higher temperature T_f, and hence $w_2 < w_1$.

We shall discuss adoption of a convention for the *sign* for work of expansion – (Frames 7, 9, 14 and 15) and use it when we discuss in more detail the gas expansion processes (Frame 9). Also (FIRST LAW OF THERMODYNAMICS – see Frames 2, 8) the internal energy change, ΔU for the *overall process* in Figure 1.1 (i.e. gas at V_i and $T_i \rightarrow$ gas at V_f and T_f) (being a state function) is identical for both paths between the SAME initial and final states (and so is *route independent*).

Here *energy is neither created nor destroyed but merely converted from one form to another* (*i.e. heat and work, w → internal energy*). Hence for the *specific* processes in Figure 1.1:

$$q_1+w_1=q_2+w_2=\Delta U_1=\Delta U_2=\Delta U$$
$$\text{although: } q_1 \neq q_2 \text{ and } w_1 \neq w_2 \qquad (1.16)$$

The First Law (equation 1.16) is subject to the constraint that we are not allowed to change the internal energy, ΔU, by adding or removing material. Equation (1.16) applies to a closed (but not necessarily unreactive) system.

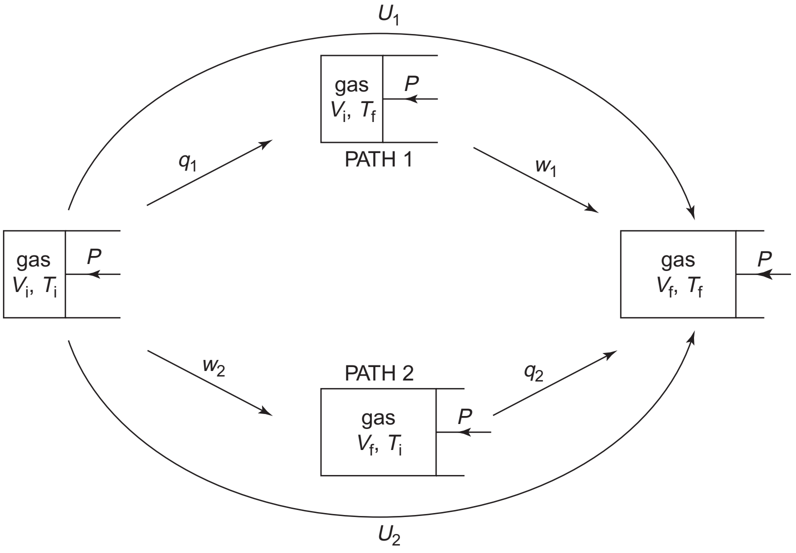


Figure 1.1 Comparison of path dependent functions (q and w) and path independent change (ΔU) during the expansion of a gas from (V_i, T_i) to (V_f, T_f) via two different states (V_i, T_f) (path 1) and (V_f, T_i) (path 2). V and T represent the volume and temperature of the gas. q and w represent the heat absorbed by the gas and the work done by the gas on the surroundings in expanding against the external pressure, P. w_1 and w_2 are both negative (using the convention discussed in Frame 7) since work of expansion is expended by the gas and lost from the (gas) system.

1.7 State Functions, *X*

Properties that are *path independent* depend only on the conditions at the start and at the end stages of the change are referred to as *state functions.*

These are often denoted by *capitalised* (upper case) symbols (examples are:

Gibbs energy, G (Frames 13 and 18); Enthalpy, H (Frames 13, 18 and 19); Entropy, S (Frames 11, 13, 15 and 19); Internal Energy, U (Frames 1, 8 and 10); Volume, V; Pressure, P; Temperature, T ...etc.);

for a state function X, ΔX depends *only* on the *difference between* the *final value*, X_f *and* the *initial value* of the property, X_i for the process:

Since $\int_{X_i}^{X_f} dX$, the integral of the change in $X(= dX)$ can be written (Frame 2) as $[X_f - X_i]$ then ΔX can be equated to an integral:

$$\Delta X = [X_f - X_i] = \int_{X_i}^{X_f} dX \qquad (1.17)$$

ΔX is then the same *whatever* route or path is selected to achieve the change and hence is path independent.

Expanding equation (1.16), in more detail:

$$\Delta U_1 = q_1 + w_1 = q_2 + w_2 = \Delta U_2 = \Delta U = [U_f - U_i] = \int_{U_i}^{U_f} dU \qquad (1.18)$$

In Frame 9 we consider the expansion of an ideal gas along an isotherm (or constant temperature curve for which $dT = 0$) from (P_i, V_i) to (P_f, V_f). Whilst the state functions P and V show *identical* changes in the two expansion processes considered ($dP = P_f - P_i$); $dV = (V_f - V_i)$ the work done in the two cases is entirely different. Two routes (paths) are considered:

expansion proceeds *infinitely slowly* (= *reversibly*), the external pressure never more than dP(i.e. a very small increment) less than the internal gas pressure at any point in time. The work performed by the gas is the maximum possible $w = w_{\max} = -nRT\ln(V_f/V_i)$ (sign convention explained in Frame 7);

expansion proceeds *irreversibly* and *not* as a succession of equilibrium positions. This expansion is akin to a situation where a gas confined inside a cylinder, under pressure, P_i at volume V_i is suddenly exposed to the external (constant) atmospheric pressure, $P_f = P_{atm}$. Gas flows out from the cylinder until the final volume is V_f and pressure is P_f. The work done (Frame 9), $w = -P_f\Delta V = -P_f(V_f - V_i)$ is only a fraction of that performed in the process above yet the initial and final states of the gas are identical. This illustrates, again, that w is a path dependent function.

2. Integration in Thermodynamics

Some of the examples which are related to thermodynamics provided later in this Frame are meant to provide a first exposure to these thermodynamic functions. Such functions will be explained later in greater detail. The intention in introducing them so early is to show how the integration process impinges on the derivation of a number of key equations. The reader should endeavour to follow the logic used although he/she may not appreciate fully, until later, the underlying thermodynamic context.

2.1 Standard Integrals: Integration of Sums of Functions

Four common integrals encountered in thermodynamics (and their results) are shown below:

$$\int_{x_\mathrm{i}}^{x_\mathrm{f}} \mathrm{d}x = [x]_{x_\mathrm{i}}^{x_\mathrm{f}} = [x_\mathrm{f} - x_\mathrm{i}] \tag{2.1}$$

$$\int_{x_\mathrm{i}}^{x_\mathrm{f}} x.\mathrm{d}x = \left[\frac{x^2}{2}\right]_{x_\mathrm{i}}^{x_\mathrm{f}} = {}^1\!/_2[x_\mathrm{f}^2 - x_\mathrm{i}^2] \tag{2.2}$$

$$\int_{x_\mathrm{i}}^{x_\mathrm{f}} x^n\mathrm{d}x = \left[\frac{x^{n+1}}{(n+1)}\right]_{x_\mathrm{i}}^{x_\mathrm{f}} = \frac{\left[x_\mathrm{f}^{n+1} - x_\mathrm{i}^{n+1}\right]}{(n+1)} \qquad (n \neq -1) \tag{2.3}$$

$$\int_{x_\mathrm{i}}^{x_\mathrm{f}} \left(\frac{1}{x}\right)\mathrm{d}x = [\ln x]_{x_\mathrm{i}}^{x_\mathrm{f}} = [\ln x_\mathrm{f} - \ln x_\mathrm{i}] = \ln\left(\frac{x_\mathrm{f}}{x_\mathrm{i}}\right) \tag{2.4}$$

The integrals shown above are called:

- *Definite integrals* – because they have limits imposed. Thus for example:

$$\mathrm{I}_{\text{definite}} = \int_1^4 x.\mathrm{d}x = \left[\frac{x^2}{2}\right]_1^4 = {}^1\!/_2[(4)^2 - (1)^2] = \frac{15}{2} \tag{2.5}$$

as opposed to:

- *Indefinite integrals* – which have no limits specified. On integration of indefinite integrals a constant c has to be included. Thus for example:

$$\mathrm{I}_{\text{indefinite}} = \int x.\mathrm{d}x = \frac{x^2}{2} + \mathrm{c} \tag{2.6}$$

now:

$$\mathrm{I}_{\text{indefinite}}\ (\text{when } x = 4) = (8 + \mathrm{c}) \tag{2.7}$$

and:

$$\mathrm{I}_{\text{indefinite}}\ (\text{when } x = 1) = ({}^1\!/_2 + \mathrm{c}) \tag{2.8}$$

$$\mathrm{I}_{\text{definite}}\ (2.5) = [\mathrm{I}_{\text{indefinite}}\ (\text{when } x = 4) - \mathrm{I}_{\text{indefinite}}\ (\text{when } x = 1)] = [(8 + \mathrm{c}) - ({}^1\!/_2 + \mathrm{c})] = 15/2 \tag{2.9}$$

where we see that the constant, c cancels out when we evaluate the integral as in equation (2.9).

The integral of the sum of two or more functions can be written as the sum of two or more separate integrals, thus:

$$\int [f(x) + g(x)]\mathrm{d}x = \int f(x).\mathrm{d}x + \int g(x).\mathrm{d}x \tag{2.10}$$

(for notation see Frame 3, section 3.1).

Constants (= c) can be taken outside the integral sign as mere multiples and are then unaffected by the subsequent integration taking place, thus:

$$\int \mathrm{c}.f(x).\mathrm{d}x = \mathrm{c}\int f(x).\mathrm{d}x \tag{2.11}$$

2.2 Area Underneath a Curve can be Obtained by Integration

Figure 2.1 displays the function (line): $y = 3x$, underneath which function, (i.e. between the limits $x = 0$ (origin) and $x = 4$) lies the shaded triangle. The base of the triangle, $b = 4$ units. The height, h, of this triangle is 12 units. The area of a triangle is given by $^1\!/_2$ (*base*) (*perpendicular height*) $= {}^1\!/_2 bh = 24$ units^2. This corresponds to the area between the line (curve) $y = 3x$ and the abscissa ($y = 0$), otherwise known as the x-axis. This area, A, can be expressed as an integral:

$$A = \int_0^4 y\mathrm{d}x = \int_0^4 3x.\mathrm{d}x = 3\int_0^4 x.\mathrm{d}x = 3[{}^1\!/_2 x^2]_0^4 = 3[{}^1\!/_2(16) - 0] = {}^1\!/_2(48) = 24\ \text{units}^2 \tag{2.12}$$

In general then the integral: $\int_a^b y.\mathrm{d}x$ becomes synonymous with the area sandwiched between the curve formed when y is plotted versus x and the x-axis over the range of values: $x = a$ and $x = b$. This is also true when the graph is a curve.

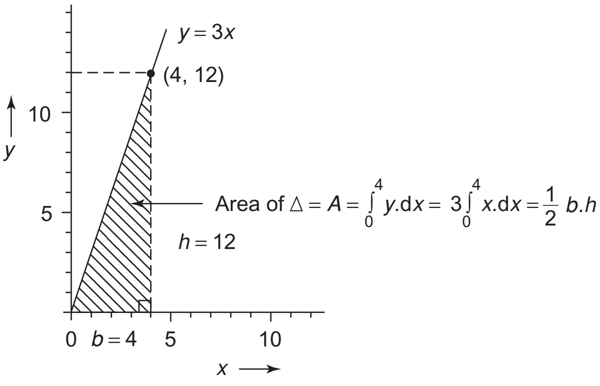


Figure 2.1 Area between the curve (line) $y = 3x$ and the ordinate (x-axis) can be equated to the integral shown.

2.3 Examples of Areas under Curves arising in Thermodynamics

We shall see later (Frames 11, 13, 14, 15, 16, 19) that the standard entropy, S_T^o of a material (assuming it exhibits no phase changes between absolute zero of temperature and T/K and no residual entropy at 0 K) is given by the equation:

$$S_T^o = \int_0^T \frac{C_{\mathrm{p,m}}}{T}.\mathrm{d}T \qquad (2.13)$$

By analogy with the triangle area example above, it will be clear that the value of the absolute entropy, S_T^o at temperature T could be established by measuring the area under the graph of $C_{\mathrm{p,m}}/T$ plotted versus T over the range $T = 0$ K (absolute zero) and the temperature T/K (Figure 2.2(a)). If phase changes *are* involved (e.g. solid converts to liquid) then integrations for each of the individual phases can be separated out and entropy corrections then applied for the (isothermal) entropy change associated with the individual phase changes themselves (at the relevant transition temperature, see Frames 15 and 16).

Integration (2.13) can also be performed analytically if C_{p} is known as a function of temperature, T, for example if:

$$C_{\mathrm{p}} = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2 \qquad (2.14)$$

with constants a, b and c known. Then since:

$$C_{\mathrm{p}}/T = \left(\frac{\mathrm{a}}{T}\right) + \mathrm{b} + (\mathrm{c}T) \qquad (2.15)$$

and:

$$S_T^o = \int_0^T \frac{C_{\mathrm{p}}}{T}\mathrm{d}T = \int_0^T \left(\frac{\mathrm{a}}{T}\right)\mathrm{d}T + \mathrm{b} + \int_0^T (\mathrm{c}T)\mathrm{d}T = \mathrm{a}\int_0^T \left(\frac{1}{T}\right)\mathrm{d}T + \mathrm{b} + \mathrm{c}\int_0^T T\cdot\mathrm{d}T \qquad (2.16)$$

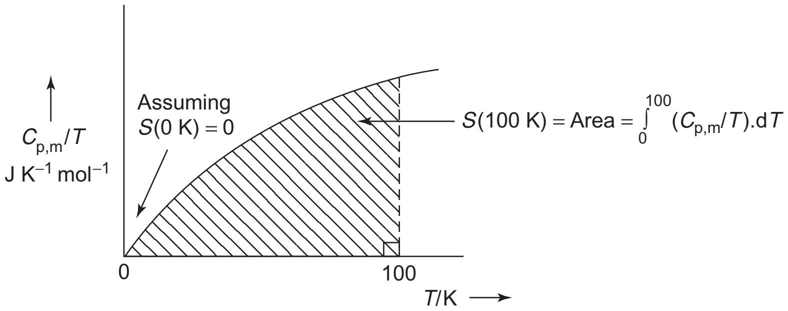


Figure 2.2 Plot of $C_{\mathrm{p,m}}/T$ versus T. The area under the curve gives an estimate of S^o(100 K), the absolute entropy of the material at 100 K. We need to assume that the Third Law (Frame 16) applies and that S^o (0 K) = 0 at T = 0 K.

Areas under curves of interest, can be determined by use of graphical software.

A further discussion of these approaches is made in Frame 15, section 15.4 when we consider in more detail the calculation of entropy, S.

2.4 Functions which can Involve Integration Procedures

2.4.1 Heat capacity integrals

We shall see that (Frame 10):

$$(\partial H/\partial T)_{\mathrm{P}} = C_{\mathrm{p}} \qquad (2.17)$$

Notice that ∂ replaces d in this case because there is a dependence of H on more than one variable (i.e. T and P). This relation gives rise to an important equation for the calculation of the enthalpy change, in heating (or cooling) a material between the two temperatures T_{i} to T_{f}.

Quite often C_{p} varies hardly at all with temperature change so that it can be taken outside the integral and assumed to be a constant (equation (2.11)):

$$\Delta H = \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \mathrm{d}H = \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} C_{\mathrm{p}}.\mathrm{d}T = C_{\mathrm{p}} \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \mathrm{d}T = C_{\mathrm{p}}[T_{\mathrm{f}} - T_{\mathrm{i}}] = C_{\mathrm{p}}\Delta T \qquad (2.18)$$

However if C_p *is* a function of T as in the form of equation (2.14), then the integration involves a sum of terms (using an equation of type (2.10) for its evaluation):

$$\Delta H = \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{d}H = \int_{T_\mathrm{i}}^{T_\mathrm{f}} C_\mathrm{p}\mathrm{d}T = \int_{T_\mathrm{i}}^{T_\mathrm{f}} (\mathrm{a} + \mathrm{b}T + \mathrm{c}T^2)\mathrm{d}T = \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{a}.\mathrm{d}T + \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{b}T.\mathrm{d}T + \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{c}T^2.\mathrm{d}T \tag{2.19}$$

so that (since a, b and c are constants and can thus be taken outside the integral – equations (2.11) and (2.16)):

$$\Delta H = \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{d}H = [H_{T_\mathrm{f}} - H_{T_\mathrm{i}}] = \mathrm{a}\int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{d}T + \mathrm{b}\int_{T_\mathrm{i}}^{T_\mathrm{f}} T.\mathrm{d}T + \mathrm{c}\int_{T_\mathrm{i}}^{T_\mathrm{f}} T^2.\mathrm{d}T \tag{2.20}$$

where the result of the first integration in equation (2.20), leads to $[H_{T_\mathrm{f}} - H_{T_\mathrm{i}}]$, which represents the difference, ΔH, in enthalpy, H, at temperature T_f minus the enthalpy at temperature T_i, in other words, it represents the overall enthalpy change required to raise the temperature of the material from T_i to T_f, which we write as ΔH:

$$\Delta H = \mathrm{a}[T]_{T_\mathrm{i}}^{T_\mathrm{f}} + \left(\frac{\mathrm{b}}{2}\right)[T^2]_{T_\mathrm{i}}^{T_\mathrm{f}} + \left(\frac{\mathrm{c}}{3}\right)[T^3]_{T_\mathrm{i}}^{T_\mathrm{f}} = \mathrm{a}[T_\mathrm{f} - T_\mathrm{i}] + \left(\frac{\mathrm{b}}{2}\right)[T_\mathrm{f}^2 - T_\mathrm{i}^2] + \left(\frac{\mathrm{c}}{3}\right)[T_\mathrm{f}^3 - T_\mathrm{i}^3] \tag{2.21}$$

2.4.2 Kirchhoff's equation

A further equation (Frame 11) involving an integration is Kirchhoff's equation which relates the enthalpy changes, $\Delta H^o_{T_1}$ and $\Delta H^o_{T_2}$ for a chemical reaction taking place at temperatures, T_1 and T_2, to an integral involving the heat capacity difference, ΔC_p, between the products and reactants in the reaction:

$$\Delta C^o_\mathrm{p} = \Sigma C^o_\mathrm{p}(\text{Products}) - \Sigma C^o_\mathrm{p}(\text{Reactants}) \tag{2.22}$$

so that:

$$\Delta H^o_{T_2} - \Delta H^o_{T_1} = \int_{T_\mathrm{i}}^{T_\mathrm{f}} \Delta C^o_\mathrm{p}.\mathrm{d}T = \Delta C^o_\mathrm{p}[T_2 - T_1] \tag{2.23}$$

The second equality in equation (2.23) applies for C_p values of products and reactants which are independent of the temperature change $(T_2 - T_1)$, or if C_p is a function of temperature (as in equation 2.14) then integration has to be involved (equation (2.19)) and the first equality in equation (2.23) is then relevant.

2.5 State and Path Dependent Functions and Integration

If we integrate a state function (Frame 1), the integral represents the overall change and has a definite value governed solely by the initial and final values of the given property. Thus:

$$\Delta U = \int_{U_\mathrm{i}}^{U_\mathrm{f}} \mathrm{d}U = [U]_{U_\mathrm{i}}^{U_\mathrm{f}} = [U_\mathrm{f} - U_\mathrm{i}] \tag{2.24}$$

In order to perform an integration $\int y.\mathrm{d}x$ we must be able to define precisely dx (or the initial and final values for the change) i.e. integration is linked to state function properties.

In some cases this is not possible. Examples are (Frame 1) heat absorbed (or released) by the system, q and work done (on or by the system), w. We cannot specify the *absolute* heat actually present in a material, we cannot therefore define q_i or q_f for a process and this makes q (and also w, for similar reasons) *different mathematically* from properties for which the final and initial values *can* be quantified (i.e. $\int \mathrm{d}w \neq (w_\mathrm{f} - w_\mathrm{i})$ and $\int \mathrm{d}q \neq (q_\mathrm{f} - q_\mathrm{i})$, so instead we write:

$$\int \delta w = w \tag{2.25}$$

and

$$\int \delta q = q \tag{2.26}$$

if integration is required).

More complicated texts define exact and inexact integrals in this context.

Frame 13 shows that dS, an entropy change taking place at a fixed temperature T, can be equated to $\delta q_\mathrm{rev}/T$ or that in a reversible process the increase in entropy is equal to the heat which it absorbs (δq_rev) divided by the absolute temperature, T at which the process takes place. S is a state function (which *can* be integrated) and thus:

$$\mathrm{d}S = \frac{\delta q_\mathrm{rev}}{T} \tag{2.27}$$

and hence:

$$\int_{S_\mathrm{i}}^{S_\mathrm{f}} \mathrm{d}S = \Delta S = \int \frac{\delta q_\mathrm{rev}}{T} = \left(\frac{1}{T}\right) \int \delta q_\mathrm{rev} = \frac{q_\mathrm{rev}}{T} \tag{2.28}$$

for an isothermal change only. This represents one statement of the Second Law of Thermodynamics (Frames 10, 13 and 17). Similarly:

$$\mathrm{d}H = \delta q_\mathrm{P} \tag{2.29}$$

for a process at constant pressure (q_P is the heat absorbed) and hence, once again, since H is a state function integration is meaningful and:

$$\int_{H_\mathrm{i}}^{H_\mathrm{f}} \mathrm{d}H = \Delta H = \int \delta q_\mathrm{P} = q_\mathrm{P} \tag{2.30}$$

A similar situation arises for work, w. Frame 9 discusses expansion work performed by ideal gases. Finally the First Law of Thermodynamics (Frame 8) can be written:

$$\mathrm{d}U = \delta q + \delta w \tag{2.31}$$

integration then leads to:

$$\int \mathrm{d}U = \int \delta q + \int \delta w \tag{2.32}$$

and (since U is a state function but q and w are not) to:

$$\Delta U = (U_\mathrm{f} - U_\mathrm{i}) = q + w \tag{2.33}$$

and thus the integrals are handled differently [i.e. q and w integrals as in equations (2.26) and (2.25)] but:

$$\int_{U_\mathrm{i}}^{U_\mathrm{f}} \mathrm{d}U = [U_\mathrm{f} - U_\mathrm{i}] \tag{2.34}$$

depending on whether the initial and final values of the function being integrated can be uniquely defined or not. Note that if initial and final states i and f are close together then $\Delta U \longrightarrow \mathrm{d}U$ and the change in U becomes infinitesimally small.

Equation (2.33) is an expression of the First Law of Thermodynamics (Frames 1, 2 and 8).

3. Graphical Gradients and Intercepts Differentiation in Thermodynamics Equation of State for an Ideal Gas

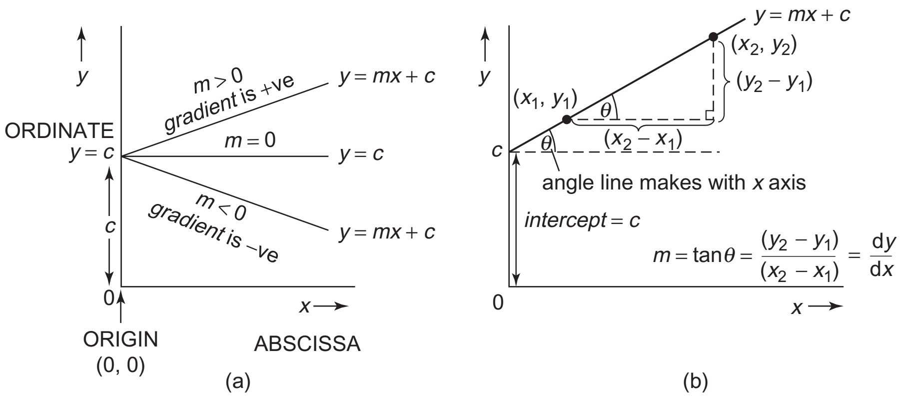
3.1 Staight Line (Linear) Graphs: Gradients and Derivatives

Any equation of first degree (i.e. involving only x (and having no x^2, x^3 etc. terms)) can be represented by a straight line graph. The general equation takes the form:

$$y = mx + c \tag{3.1}$$

The line has a *gradient* or slope equal to m and an *intercept* (i.e. meets the y-axis) at a distance c from the origin (0,0). It should be noted that if a graph is plotted which does not actually include the origin then the value of c is no longer equal to the intercept and adjustment must then be made in its calculation to take account of the shift in origin necessary to include the point (0,0).

In the case where equations of type (3.1) apply we can say that y is a function (f) of x (i.e. write $y = f(x)$) indicating again that y depends on x as the *only* variable. Once the function $f(x)$ is defined by $mx + c$ (where m and c are constants), the graph can be plotted in (Figures 3.1(a) and (b)) by making a table of corresponding x and y values and plotting them (a minimum of two points are needed to define a straight line).



(a) (b)

Figure 3.1 Graphs illustrating: (a) the gradients (slopes) = m of lines having: $m > 0$ (positive), $m = 0$ (parallel to x-axis) and $m < 0$ (negative) and (b) the relationship of the gradient, m, to tan θ, where θ is the angle between the line and the horizontal.

The gradient of the line, m, can also be equated to the differential coefficient (written as $\mathrm{d}y/\mathrm{d}x$)) and can be said in turn to be the result of differentiating y with respect to x. The intercept on the y-axis (the ordinate) when $x = 0$ is c, another constant (subject to the caveat above). m can also be determined from the coordinates, (x_1, y_1) and (x_2, y_2) of two arbitrary points (best separated as far apart as is possible to improve the accuracy of this calculation of gradient) on the straight line.

$$m = \tan\theta = \frac{(y_2 - y_1)}{(x_2 - x_1)} = \mathrm{d}y/\mathrm{d}x \tag{3.2}$$

m can be positive, zero or negative and the direction of the slope of the lines vary accordingly (Figure 3.1(a)).

We can also define a derivative of a derivative (or second derivative) written as $\mathrm{d}^2y/\mathrm{d}x^2$ and equalling the differential of $\mathrm{d}y/\mathrm{d}x$ with respect to x ($= \mathrm{d}/\mathrm{d}x\{\mathrm{d}y/\mathrm{d}x\}$). This represents the change in the gradient ($= \mathrm{d}y/\mathrm{d}x$) as x is increased.

In the case of the straight line the gradient is constant (and is equal to m). Thus the second derivative written as:

$$d^2y/dx^2 = d/dx\{dy/dx\} = 0 \tag{3.3}$$

or as:

$$d\{dy/dx)/dx = 0 \tag{3.4}$$

this arises since:

$$dy/dx = m \tag{3.5}$$

for the straight line and therefore:

$$d\{dy/dx\}/dx = d[m]/dx = 0 \tag{3.6}$$

(i.e. the differential of a constant ($= m$) is zero). These equations tell us that there is no change in gradient as x is increased – which is the main attribute possessed by a straight line.

In the case of non-linear functions, the second derivatives are able to determine the curvature of these functions from the manner in which their gradient changes as the ordinate (x-axis) is increased. If the change in the gradient for increasing x is negative the curve will dip down or if positive the curve will rise upwards. Figure 3.2 explores these relationships which can be informative and useful in qualitative discussions of how thermodynamic functions vary.

Such discussions will be employed later to investigate a number of thermodynamic relationships in Frames 17–22.

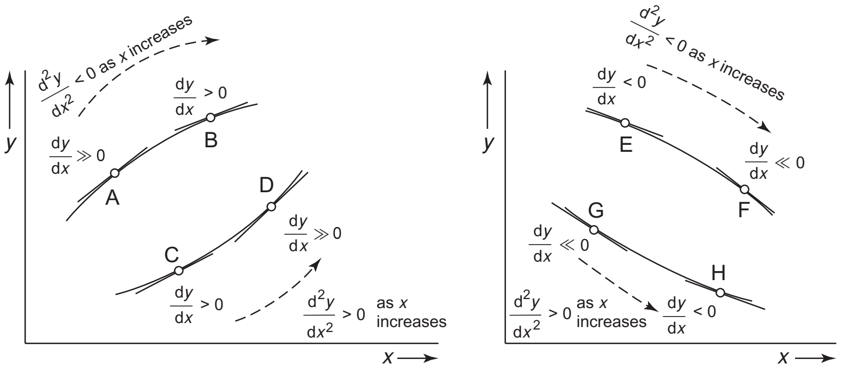


Figure 3.2 Useful procedure for predicting curvature of plots of functions. The symbolism e.g. $dy/dx > 0$; $dy/dx \gg 0$ is employed to signify that both gradients are positive but that the second one is *more* positive than the first. Hence in this case d^2y/dx^2 is then > 0 and represents the change in the gradient as x increases, which allows us to predict the curvature of the function plot.

3.2 Adoption of Linearity to Aid Extrapolation Procedures in Thermodynamics

One example of an experimental problem that can usefully be solved by adjusting theory to yield linear equations is the example of the determination of heat capacities, C_p at low temperatures, especially temperatures where experimental values are simply inaccessible. Because C_p cannot be measured experimentally down to absolute zero then an appropriate extrapolation needs to be made (see Frame 16). This latter possibility arises because the Debye theory of heat capacities at low temperatures predicts that as $T \to 0$:

$$C_p = \alpha T^3 + \beta T \tag{3.7}$$

and so division of equation (3.7) by T leads us to:

$$C_p/T = \alpha T^2 + \beta \tag{3.8}$$

which is linear in form (compare equation (3.8) with equation (3.1) by putting $y = C_p/T$ and $x = T^2$). Since heat capacities can be measured experimentally down to at least 8 K, it is a simple matter then to draw a graph of C_p/T versus T^2 (which has a linear form and therefore is defined by means of only a few points and an absolute minimum of only two) and hence we can obtain values of C_p down to absolute zero by extrapolation of the line to $T^2 = 0$.

3.3 Partial Derivatives

Not all functions are this simple. Consider for example the function $z = \mathrm{f}(x, y)$ where this time a function z depends on the variation of *two* variables, x *and* y. For example if:

$$z = \mathrm{f}(x, y) = 3x^2 + 5xy - 6y^2 \tag{3.9}$$

we need to know values of x and y before we can define z. The functional dependence of the area, A, of a rectangle upon the lengths of its two sides, x and y, is similar in depending on two (independent) variables and takes the form:

$$A = xy \tag{3.10}$$

Thus if A is to be plotted versus x *and* y a three-dimensional plot will be required with three axes corresponding to A, x and y for its representation (and the graph will represent a surface).

This example is used in Frame 5 to illustrate the meaning and interpretation of partial derivatives. A is a function depending on two variables: $A = f(x, y)$ and this has implications for the meaning and interpretation of the differential coefficients corresponding to the various slopes which are represented as *partial* derivatives $(\partial A/\partial x)_y$ and $(\partial A/\partial y)_x$ rather than as *ordinary* derivatives $\mathrm{d}y/\mathrm{d}x$ etc. as were discussed earlier in this Frame and for which only one variable is involved.

The simplest way of (geometrically) defining a partial derivative for $z = f(x,y)$ is to say that this is represented by a 2-D surface in 3-D (xyz) space and that $(\partial A/\partial x)_y$ is simply the slope of a constant y line on the surface. In algebraic terms, one simply treats y as a constant in the $f(x, y)$ expression and then differentiates with respect to x.

3.4 Standard Differentials

The differential (with upright d) $\mathrm{d}y/\mathrm{d}x$ can also be interpreted as representing the rate at which y changes as x is varied (which is what the slope of the line in Figure 3.1 also means). Velocity or speed, v, as it is commonly referred to (= rate of change of distance, s travelled with time, t so that $v = \mathrm{d}s/\mathrm{d}t$) is a typical differential function and is measured in miles travelled per hour.

If we know that the *rate equation* takes the form:

$$\mathrm{d}y/\mathrm{d}x = m \tag{3.11}$$

where m is a constant then we can cross multiply and also write:

$$\mathrm{d}y = m.\mathrm{d}x \tag{3.12}$$

and interpret this to mean that if a change is made in x (= dx) then the corresponding change in y (= dy) is calculated by multiplying the constant m by the change in x(= dx).

We can also integrate both sides of the equation (3.12) to give:

$$\int \mathrm{d}y = \int m.\mathrm{d}x \tag{3.13}$$

which generates back the original function (integral (3.13) being an indefinite integral (section 2.1, Frame 2) we have needed to add a constant c);

$$y = mx + c \tag{3.14}$$

Thus we recover the precise form of the function $y = f(x)$ which generated the rate equation by differentiation. Thus the processes of differentiation and integration have a reciprocal relationship and can be considered to represent the reverse of one another in the sense shown in Figure 3.3.

Figure 3.3 summarises the relationships and discussion above.

The expression $y = mx + c$ denotes a straight line, whose slope (gradient) is measured by tan $\theta = m$ which will be constant (characterising the straight line).

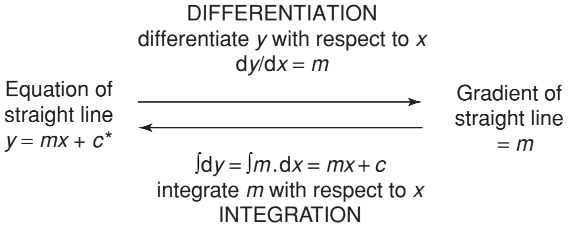


Figure 3.3 Reciprocal relationship between differentiation and integration * this constant c on integration of a constant gradient over x arises from the indefinite nature of the integral.

Table 3.1 Differential coefficients of functions of x commonly encountered in thermodynamics.

Function	Differential coefficient
$y = \mathrm{a}$	$\mathrm{d}y/\mathrm{d}x = 0$
$y = \mathrm{a}x^n$	$\mathrm{d}y/\mathrm{d}x = \mathrm{a}\, nx^{n-1}$
$y = \mathrm{a} \ln x$	$\mathrm{d}y/\mathrm{d}x = \mathrm{a}/x$
$y = \mathrm{a} \ln (\mathrm{b}x)$	$\mathrm{d}y/\mathrm{d}x = \mathrm{a}/x$
$y = \mathrm{e}^{\mathrm{a}x} = \exp(\mathrm{a}x)^*$	$\mathrm{d}y/\mathrm{d}x = \mathrm{a}\mathrm{e}^{\mathrm{a}x} = \mathrm{a}.\exp(\mathrm{a}x)$
Product Rule: $y = uv$	differential coefficient = first factor (u) multiplied by differential of second factor ($\mathrm{d}v/\mathrm{d}x$)+ second factor (v) multiplied by the differential of the first factor ($\mathrm{d}u/\mathrm{d}x$) $\mathrm{d}y/\mathrm{d}x = u.\mathrm{d}v/\mathrm{d}x + v.\mathrm{d}u/\mathrm{d}x$
Quotient Rule: $y = u/v$	differential coefficient = square the denominator (v) and place it in the denominator of the expression for $\mathrm{d}y/\mathrm{d}x$; the numerator of the expression for $\mathrm{d}y/\mathrm{d}x$ is then given by: denominator (v) multiplied by differential of numerator ($\mathrm{d}u/\mathrm{d}x$) – numeraror (u) multiplied by the differential of the denominator ($\mathrm{d}v/\mathrm{d}x$) $\mathrm{d}y/\mathrm{d}x = [v.\mathrm{d}u/\mathrm{d}x - u.\mathrm{d}v/\mathrm{d}x]/v^2$

a and b are constants. *Exponential functions can be written as e raised to the appropriate power or as exp and using brackets to enclose the power.

We need to be familiar with the following simple differentials for our applications in thermodynamics:

3.5 $\mathbf{d}T/\mathbf{d}T = 1$

$\mathrm{d}T/\mathrm{d}T$ is the differential coefficient of temperature with respect to temperature and following our discussion above would be the gradient of the graph of T plotted versus T (Figure 3.4) and accordingly is equal to 1 or tan 45°. Similarly in general:

$$\frac{\mathrm{d}x}{\mathrm{d}x} = 1 \tag{3.11}$$

where x is any variable.

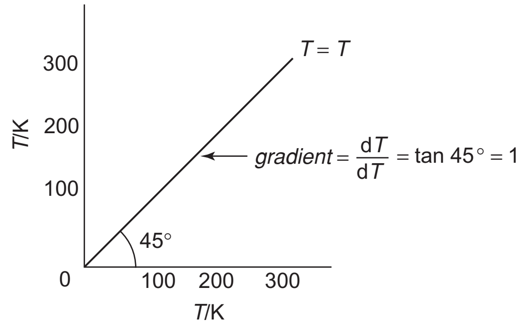


Figure 3.4 Graph to illustrate that $\mathrm{d}T/\mathrm{d}T = 1 = \tan 45°$.

4. The Ideal Gas

4.1 Equation of State for an Ideal Gas: The Rectangular Hyperbola

For an *ideal gas* the general *equation of state* or overall relationship connecting the possible variables P, pressure, T, temperature, V, volume, n, amount of gas is given by:

$$PV = nRT \tag{4.1}$$

where $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$, which is *the gas constant*.

The combined gas law above is compounded from *three individual laws*: those of:

- *Boyle* (P is proportional to V (i.e. $P \propto V$) when T and n are held constant);
- *Charles* (V is proportional to T^{-1} (i.e. $V \propto 1/T$) when P and n are held constant);

and

- *Avogadro* (V is proportional to n (i.e. $V \propto n$) when P and T are constant *with the proportionality constant being identical for all materials*).

4.2 Thermodynamic Definition of an Ideal gas

An ideal gas is one in which:

- interactions between the atoms or molecules are negligibly small. Accordingly no energy (work) is required to expand the gas since there are no forces between the atoms or molecules to overcome, we can express this mathematically in terms of a partial differential:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = 0 \tag{4.2}$$

  There is no change in (internal) energy of the gas as its volume is increased (i.e. gas is expanded) whilst the temperature is kept constant. This provides a convenient mathematical *definition* (in thermodynamic terms) *of an ideal gas*.
- a second molecular requirement of an ideal gas is that the size of the molecules is negligible compared with the container volume.

4.3 Rectangular Hyperbola

The general form of a curve of y plotted versus x for the function is:

$$xy = c \tag{4.3}$$

(where c is a constant) is called the *rectangular hyperbola*. The curve is the *locus* of a point drawn such that the *area enclosed between two lines drawn parallel to the x and y axes from the point always encloses an area whose magnitude is constant and which is equal to c* (provided that the origin is included as one corner of this rectangle).

Two such hyperbolae arising from the individual laws are illustrated in Figure 4.1. for:

- the *Boyle* relationship above for which $\mathrm{d}n = 0$ and $\mathrm{d}T = 0$

and

- the *Charles* relationship for which $\mathrm{d}n = 0$ and $\mathrm{d}P = 0$.

In the graph (Figure 4.1a) of P versus V, the enclosed rectangle has an area $= nRT$ whilst in the graph (Figure 4.1b) of V versus $1/T$ the area of the enclosed rectangle is nR/P. Note also that it is a feature of the curves that in Figure 4.1(a) as $P \to 0$ then $V \to \infty$ and in Figure 4.1(b) as $V \to 0$ then $1/T \to \infty$. When a variable approaches infinity the curve at this limit is often called an asymptote.

Curve 4.1(a) will be used in discussion of the work done when a gas is expanded (Frame 9).

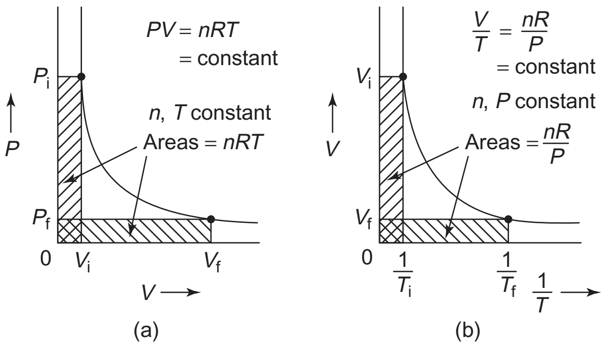


Figure 4.1 Curves having the form of rectangular hyperbolae as encountered in studying ideal gas laws under various conditions.

4.4 Alternative Linear Plots which can be made for Gases

Using the discussion of straight line graphs for which in general:

$$y = mx + c \tag{4.4}$$

rearrangement of equation (4.1)

$$PV = nRT \tag{4.1}$$

can be made such that if P and T are constant and V is plotted versus n (*Avogadro's Law*) we have:

$$V = \left(\frac{RT}{P}\right) n \tag{4.5}$$

and thus a plot (Figure 4.2(a)) of V versus n will be a straight line passing through the origin (since when $n = 0$, $V = 0$) and will have a gradient equal to (RT/P).

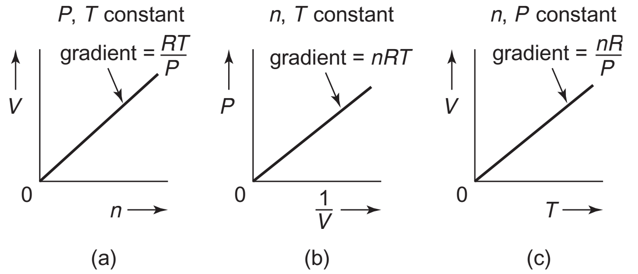


Figure 4.2 Linear Plots derived from Equation of State for an Ideal Gas: $PV = nRT$.

Other plots of P versus $1/T$ (Figure 4.2(b)) and V versus T (Figure 4.2(c)) will also be linear provided that n and T and n and P, respectively, are kept constant.

4.5 Concentration Expressions for Gases

Concentration is the chemical amount of substance, n, present divided by volume. In the case of gases concentration is used in equilibrium constant expressions, labelled $K_{c/co}$ (see Appendix). Frequently concentrations are given in units of mol dm^{-3}. Since concentration is also the amount of gas per unit volume, then concentration, c is given by:

$$c = [\,] = \frac{n}{V} = (P/RT) \tag{4.6}$$

4.6 Other Equations of State for Gases

There are a number of equations of state for gases which attempt to account for the deviations found from the ideal (perfect) gas equation (4.1). These have the following features:

- they take many different forms and include additional parameters whose values are often specific for a particular gas;
- the larger the number of parameters they contain, usually the better they fit to experiment over a wider range of temperature and pressure;
- most of them are empirical, although one, the *van der Waals equation* has theoretical backing and takes the form:

$$\left(\frac{P + a}{V_{\mathrm{m}}^2}\right) \cdot (V_{\mathrm{m}} - b) = RT \tag{4.7}$$

where V_{m} is the molar volume ($= V/n$) (Frame 1). An alternative form is:

$$\left(\frac{P + an^2}{V^2}\right) \cdot \left(\frac{V}{n} - b\right) = RT \tag{4.8}$$

where n is the amount of substance and a (connected with intermolecular forces) and b (connected with finite molecular size) are constants (always > 0) and specific for individual gases.

5. Partial Derivatives $(\partial z/\partial y)_x$ Simplified

5.1 Partial Derivatives and their Interpretation

In thermodynamics we to encounter *partial* derivatives, written with curly ∂ symbols, $\partial y/\partial x$. Partial derivatives are used for functions, which depend on more than one variable, an example being:

$$z = \mathrm{f}(x, y) \tag{5.1}$$

This is in contrast to *ordinary* derivatives, $\mathrm{d}y/\mathrm{d}x$ which apply to functions dependent on a single variable.

$$y = \mathrm{f}(x) \tag{5.2}$$

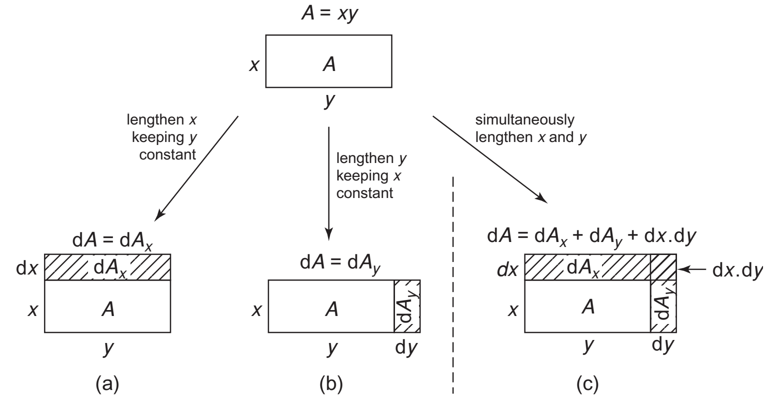


Figure 5.1 Effect on Area A of (a) increasing side x keeping side y at constant length ($= \mathrm{d}A_x$), (b) increasing side y keeping side x at constant length ($= \mathrm{d}A_y$) and (c) increasing sides x and y simultaneously ($= \mathrm{d}A$). Since $(\partial A/\partial x)_y$ is the increase in area per unit increase in x (i.e. for $\mathrm{d}x = 1$) then this actually equals y, since for every unit increase in $\mathrm{d}x$, $\mathrm{d}A_x$ increases by $(y)(\mathrm{d}x) = (y)(1) = y$. Similarly $(\partial A/\partial y)_x = x$.

Numerous examples of partial derivatives arise in thermodynamics; examples include:

- $\left(\dfrac{\partial H}{\partial T}\right)_P$
- $\left(\dfrac{\partial \ln K}{\partial P}\right)_T$

(Frames 10 and 47).

The notation looks complicated but, easy to comprehend using the example below.

Consider the area A of a rectangle having sides of length x and y. A is a function of two variables x and y.

$$A = \mathrm{f}(x, y) = xy \tag{5.3}$$

Suppose now we wish to make this area, A, larger by lengthening the side x by $\mathrm{d}x$ whilst keeping the length of y constant (Figure 5.1(a)). The area increase (written as $\mathrm{d}A_x$) will depend on:

the rate of change of the area *per unit increase* in x, when y is kept constant

multiplied by:

the increase ($= \mathrm{d}x$) which is made in x.

The notation for this rate of change is written as $(\partial A/\partial x)_y$. If now we multiply this rate of change by the actual change in length x ($= \mathrm{d}x$), then this will give the *actual* change in area ($\mathrm{d}A_x$) of the rectangle by increasing the length of side from x to $(x + \mathrm{d}x)$. We can write all of this in standard notation thus:

$$\mathrm{d}A_x = \left(\frac{\partial A}{\partial x}\right)_y .\mathrm{d}x \tag{5.4}$$

or in words, as follows:

(Increase in area) = (Rate at which area increases per unit increase in x) *multiplied by* (actual increase in x)

Alternatively, we can also increase the area of our rectangle by lengthening y by an amount $\mathrm{d}y$ whilst this time keeping the length of the side x at its original value (Figure 5.1(b).

The *actual* change made in the area ($\mathrm{d}A_y$) of the rectangle by increasing the length of side y from y to $(y + \mathrm{d}y)$ is:

$$\mathrm{d}A_y = \left(\frac{\partial A}{\partial y}\right)_x .\mathrm{d}y \tag{5.5}$$

or in words, as follows:

(Increase in area) = (Rate at which area increases per unit increase in y) *multiplied by* (actual increase in y)

We can consider another overall change ($= \mathrm{d}A$) in the area, A of the rectangle time brought about by *simultaneous increase* of both side x and side y. This type of change corresponds, more, to the situation in thermodynamics where two variables which can affect the value of a third tend to vary *simultaneously* rather than one staying constant whilst the other varies.

In the case of our rectangle, Figure 5.1(c) illustrates the fact that simultaneous increase of both x and y at the same time has the effect of: achieving both increases in area ($= \mathrm{d}A_x$ and $\mathrm{d}A_y$) discussed in the two individual processes above; and adding a further, but much smaller, area ($= \mathrm{d}x.\mathrm{d}y$)

We can write:

$$\mathrm{d}A = \mathrm{d}A_x + \mathrm{d}A_y + \mathrm{d}x.\mathrm{d}y = \left(\frac{\partial A}{\partial x}\right)_y .\mathrm{d}x + \left(\frac{\partial A}{\partial y}\right)_x .\mathrm{d}y + \mathrm{d}x.\mathrm{d}y \qquad (5.6)$$

If small changes are made in x (i.e. $\mathrm{d}x \to 0$) and y (i.e. $\mathrm{d}y \to 0$) then the area dx.dy $\to 0$ (Figure 5.1(c)) will vanish and:

$$\mathrm{d}A = \left(\frac{\partial A}{\partial x}\right)_y \cdot \mathrm{d}x + \left(\frac{\partial A}{\partial y}\right)_x \cdot \mathrm{d}y \qquad (5.7)$$

There are two points to be made here. Firstly, since:

$$A = x.y \qquad (5.3)$$

in our example, then:

$$\left(\frac{\partial A}{\partial x}\right)_y = y; \left(\frac{\partial A}{\partial y}\right)_x = x \qquad (5.8)$$

so that equation (5.7) becomes:

$$\mathrm{d}A = y.\mathrm{d}x + x.\mathrm{d}y \qquad (5.9)$$

Equation (5.9) has some parallels with the **Product Rule** (Frame 3, Table 3.1) of ordinary differentiation in which:

$$\frac{\mathrm{d}(uv)}{\mathrm{d}x} = \frac{u.\mathrm{d}v}{\mathrm{d}x} + \frac{v.\mathrm{d}u}{\mathrm{d}x} \qquad (5.10)$$

in the sense that if we ignore the subject of the differentiation (i.e. $\mathrm{d}x$) – and treat it as though it "cancels" throughout:

$$\mathrm{d}(uv) = u.\mathrm{d}v + v.\mathrm{d}u \qquad (5.11)$$

This is precisely the form taken by equation (5.9) when we remember that:

$$\mathrm{d}A_\mathrm{i} = \mathrm{d}(xy) \qquad (5.12)$$

and so from equation (5.11):

$$\mathrm{d}A = \mathrm{d}(xy) = x.\mathrm{d}y + y.\mathrm{d}x \qquad (5.13)$$

5.2 Partial Derivatives in Thermodynamics

Internal energy, U is a function of temperature, T and pressure, P. Thus:

$$U = \mathrm{f}(T, P) \qquad (5.14)$$

and

$$U = \mathrm{f}(T, V) \qquad (5.15)$$

By analogy with equation (5.7) the following relationship (which assumes constant amount of substance present) can be written:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_P \cdot \mathrm{d}T + \left(\frac{\partial U}{\partial P}\right)_T \cdot \mathrm{d}P \qquad (5.16)$$

and such equations can be used to transform variables and equations. Thus since (Frame 10, Equation 10.13):

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad (5.17)$$

then equation (5.16) can be written:

$$\mathrm{d}U = C_V.\mathrm{d}T + \left(\frac{\partial U}{\partial P}\right)_T .\mathrm{d}P \qquad (5.18)$$

For a system at constant T and P in which the Gibbs energy G is a function of temperature, T, pressure P, and the amount of components 1 and 2, n_1 and n_2 we can write:

$$G = \mathrm{f}(n_1, n_2) \qquad (5.19)$$

following equation (5.7) we can, correspondingly write:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} .\mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} .\mathrm{d}n_2 = \mu_1.\mathrm{d}n_1 + \mu_2.\mathrm{d}n_2 \qquad (5.20)$$

In this equation, for each partial derivative, *three* variables are held constant whilst one is varied. Further the partial derivatives: $\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}$ and $\left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1}$ can be replaced by chemical potential, μ_1 and μ_2, which they define (Frames 5, 25, 27, 28, 29, 35, 37, 38 and 39) since:

μ_i = *chemical potential* of component i in a mixture of components *1, 2, 3, . . . i, j . . .*

$$= \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,n_3 \ldots n_j,\ldots} \qquad (5.21)$$

6. Logarithms and Exponentials Adapting Equations in Thermodynamics to Apply to Special Conditions

6.1 Logarithms and Exponentials

A logarithm is the power to which its base must be raised to give the number.

- *Log to base e:* written as ln or as $\log_e$ (and corresponds to the LN key on a calculator);
- The base e has the value, $e = 2.718\ldots$;
- Thus: if $y = e^x$ then $\ln y = x$. e^x is called the *exponential* of x and can also be written as $\exp(x)$.

and

- *Log to base 10:* is written as lg or log or $\log_{10}$ (and corresponds to the LOG key on a calculator);
- Thus: if $y = 10^x$ then $\log_{10} y = x$ and y is called the *argument* of the logarithmic function;
- Also $\lg 100 = \log_{10} 100 = \log_{10} 10^2 = 2$ (the latter result arising from the fact that: $\log x^n = n \log x$ (equation (6.13) below);
- Use of this base (10) is less common these days.

Interconversion between bases of logs:

$$\ln x = 2.303 \log_{10} x = 2.303 \lg x \tag{6.1}$$

and

$$\log_{10} x = \lg x = 0.434 \ln x \tag{6.2}$$

The following relationships are valid:

$$\ln(ab) = \ln a + \ln b \tag{6.3}$$

$$\ln\left(\frac{a}{b}\right) = \ln a - \ln b \tag{6.4}$$

$$e^a.e^b = e^{a+b} \quad \textit{or} \quad \exp(a).\exp(b) = \exp(a+b) \tag{6.5}$$

$$e^a/e^b = e^{a-b} \quad \textit{or} \quad \frac{\exp(a)}{\exp(b)} = \exp(a-b) \tag{6.6}$$

$$(e^a)^b = e^{ab} \quad \textit{or} \quad (\exp(a))^b = \exp(ab) \tag{6.7}$$

$$e^0 = 1 \quad \textit{or} \quad \exp(0) = 1 \tag{6.8}$$

$$\ln(1+x) \approx x \quad \text{as} \quad x \to 0 \tag{6.9}$$

$$\ln(1-x) \approx -x \quad \text{as} \quad x \to 0 \tag{6.10}$$

and two *most important* relationships. Firstly:

$$\ln(e^x) = e^{\ln x} = x \quad \textit{or} \quad \ln(\exp(x)) = x \quad \textit{or} \quad \exp(\ln x) = x \tag{6.11}$$

which arises from the definition of ln. Thus:

$$\exp(\ln K_p) = K_p \tag{6.12}$$

for example and secondly:

$$\ln x^n = n \ln x \tag{6.13}$$

Note also that the specific relationships: (6.3), (6.4) and (6.13) for ln functions also apply to log functions.

6.2 Taking Logarithms (or Exponentials)

This next section is of prime importance in thermodynamics.

The key point here is:

- we can take logarithms (to base e or base 10) *only of positive numbers*.
- this means that we can only take logaithmns of *dimensionless quantities*

If we have log x or ln x, the pure number x is called the *argument* of the logarithmic function. We give here a table of illegal and legal arguments of which we can take the logarithm. The principles set out also apply to taking exponentials. We concentrate our discussion on the extraction of *logarithms* since this is of immediate relevance to thermodynamics.

Table 6.1 Logarthmic (or exponential) arguments.

Illegal arguments for logarithms or exponentials	**Legal arguments for logarithms or exponentials**
P	$\frac{P_1}{P_2}$ or $\frac{P_f}{P_i}$ or $\frac{P}{P^o}$ or $\frac{P}{\text{bar}}$
V, T	$\frac{V_\text{f}}{V_\text{i}}$ or $\frac{V}{\text{cm}^3}$; T/K $a, x, \left(\frac{a_i}{x_i}\right)$
$K_c = \frac{[\text{B}][\text{C}]}{[A]}$	$K_{c/c_o} = \frac{[\text{B}][\text{C}]}{([A]c^\text{o})}$ or $K_a = \frac{a_B a_C}{a_A}$

where P^o and c^o are chosen standard pressure and concentration respectively. In respect of standard state values, if a value is given to something like the equilibrium constant K_a then the appropriate value of standard molality, m^o (or concentration, c^o or standard pressure, p^o or more than one ($p^o c^o$) if both solutions and gases are involved) need to be defined. Also temperature, T and, if appropriate, total pressure, P are given.

In the majority of cases 1 mol kg^{-1}, 1 mol dm^{-3} and 100 kPa = 1 bar are chosen for the standard molality, m^o, standard concentration, c^o and standard pressure, p^o respectively and unless otherwise stated these values should be assumed in this book.

The illegal arguments on the left-hand side of Table 6.1 all have units and are not dimensionless. Thus P is measured in pressure units (Pa, bar, atm, Torr, mm Hg, lb in^{-2} etc.) and only *ratios* of pressures can be dimensionless and then only if their units correspond so cancel to give a dimensionless number. Similarly P/bar is legal since we imply by this that the pressure P is measured in bar and if then divided effectively by 1 bar, yields a dimensionless number (which equals the number factor by which the pressure P is greater than 1 bar).

When it comes to the equilibrium constant, K_c (*or* K_{c/c_o}) first defined in Frame 40 and needed in logarithmic form in key equation (41.12) in Frame 41 (and later applications). K_c involves the quotient of concentration terms which might be measured in typical concentration units of mol dm^{-3} (see section 40.2, Frame 40). In the example given for K_c in Table 6.1, there are more (concentration) terms in the numerator than in the denominator, thus although we have a ratio the units will not cancel completely and the dimensions of K_c will be the unit of concentration (e.g. mol dm^{-3}). To render K_c dimensionless and suitable as a logarithmic argument we can use the strategy of dividing each of the individual concentrations: [A], [B] and [C] by a standard concentration, c^o which is defined (Frame 26, section 26.2). To denote that this procedure has been adopted we relabel K_c as K_{c/c_o} and thus K_{c/c_o} is defined (equation (40.2) of Frame (40) for a more complicated situation) thus:

$$K_{c/c_o} = \left[\frac{([\text{B}]/c^o)\cdot([\text{C}]/c^o)}{([\text{A}]/c^o)}\right] = \frac{[\text{B}]\,[\text{C}]}{([\text{A}]\cdot c^o)}; \quad c^o = \text{standard concentration} \tag{6.14}$$

Thus c^o is then a chosen standard *unit* concentration and usually has identical units to those of the concentrations of A, B and C. Thus if [A], [B] and [C] were measured in mol dm^{-3} then c^o is chosen to be 1 mol dm^{-3}. Then the expression in equation (6.14) becomes dimensionless because the residual c^o in concentration units ensures that the whole ratio is dimensionless (the residual c^o term providing the means of cancelling the remaining unpaired concentration term). We can hence define the logarithmic term: ln K_{c/c_o} meaningfully.

It should also be noted however that, under certain conditions no division by c^o is necessary, for example because the equilibrium constant quotient contains as many concentration terms in its numerator as in its denominator. In such cases we could say that:

- $K_c = K_{c/c_o}$ and *both* are dimensionless;

and that:

- both the terms: ln K_c and ln K_{c/c_o} are valid (legal) logarithmic expressions.

Mole fractions, x (Frames 30, 31 and 40), activities, a (Frames 38, 39, 62 and 68) which we meet later are individually dimensionless quantities and therefore ratios thereof are all valid arguments for the logarithmic function.

Equilibrium constants – since they are always expressed in the form of dimensionless ratios (often employing standard concentrations or pressures to achieve this) – *have no units associated with them*. (see Frame 0). In this text (*and in others*) if for example ln p or ln c is written we should interpret these to correspond to ln (p/P^o) or ln (c/c^o) where P^o or c^o are defined in terms of a unit standard state.

6.3 Adapting Equations for Special Conditions in Thermodynamics

Once special conditions are applied to establish a thermodynamic equation, all subsequently derived equations (and their rearrangements) *are subject to the imposed conditions*.

6.3.1 Absolute Zero of Temperature

We can define the Gibbs energy function, G in thermodynamics by the equation:

$$G = H - TS \tag{6.15}$$

The Gibbs energy (or Gibbs function), G, was formerly referred to as the *Free energy* or *Gibbs free energy*.

If we impose the condition that the temperature is at absolute zero, i.e. $T = 0$ K then the general equation (6.15) becomes the special case where:

$$G = H \tag{6.16}$$

6.3.2 Enthalpy Changes at Constant Pressure

We can define the enthapy function, H in thermodynamics by the equation:

$$H = U + PV \tag{6.17}$$

If we consider a small change in H, dH, we can write:

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(PV) = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \tag{6.18}$$

where d(PV) is considered as a differential which can be treated using the Product Rule in the form given in Frame 5, Equation (5.11).

Thus for a process under conditions of constant pressure (for which d$P = 0$), we have:

$$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V \tag{6.19}$$

6.3.3 Multiple Conditions Imposed

The point being made in this section is that once conditions have been imposed they then apply to all subsequent equations. It is less important here to appreciate the exact significance of the symbols themselves.

Substituting equation (6.17) into equation (6.15):

$$G = U + PV - TS \tag{6.20}$$

For a small change in G, dG (Frame 8):

$$\mathrm{d}G = \mathrm{d}U + \mathrm{d}(PV) - \mathrm{d}(TS) = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T \tag{6.21}$$

Again we have used the Product Rule (Frame 5, Equation (5.11)) to differentiate the two product forms (PV) and (TS) arising. We assume now that *T and P are constant* (*conditions* 1 and 2). This could correspond to that of a system which is open to the atmosphere (hence $P \approx 1$ bar) and at constant temperature ($T = 298$ K). Since now d$T = 0$ and d$P = 0$ equation (6.22) applies:

$$\mathrm{d}G = \mathrm{d}U + P\mathrm{d}V - T\mathrm{d}S \tag{6.22}$$

Next, using the First Law of Thermodynamics (Frame 8) and assuming that *only mechanical (PV) work* (Frames 1, 8 and 9) is involved (*condition* 3) then:

$$\mathrm{d}U = q - P\mathrm{d}V \tag{6.23}$$

If dU in equation (6.22) is now replaced by ($q - P\mathrm{d}V$) then the resulting equation (6.24) will apply when conditions 1–3 hold.

$$\mathrm{d}G = q - P\mathrm{d}V + P\mathrm{d}V - T\mathrm{d}S = q - T\mathrm{d}S \tag{6.24}$$

If we finally assume (*condition* 4) that the system is at equilibrium (for which d$G = 0$) and in which case (Frames 8 and 9) also:

$$q = q_{\mathrm{rev}} \tag{6.25}$$

then equation (6.24) becomes:

$$q_{\mathrm{rev}} - T\mathrm{d}S = 0 \tag{6.26}$$

or rearranging

$$q_{\mathrm{rev}} = T\,\mathrm{d}S \tag{6.27}$$

or dividing through T

$$\mathrm{d}S = \frac{q_{\mathrm{rev}}}{T} \tag{6.28}$$

The latter equation corresponds to one form of the *Second Law of Thermodynamics* (Frames 10, 13 and 14). Because of the logical progression made above, gradually and systematically imposing conditions 1–4, equation (6.28) will apply *only* for processes taking place when the following four conditions are satisfied:

- the process takes place at constant temperature (i.e. is isothermal);
- the process takes place at constant pressure (i.e. is isochoric);
- the process is one in which, if work *is* performed, no work other than mechanical (PV) work is performed (See section 8.1, Frame 8);
- the process is at equilibrium.

An example to which equation (6.28) might be applied is the vaporisation process in which a liquid → gas at ambient temperature and pressure. Here liquid and gas phases are at equilibrium.

An important point to be made is that in cases where we are calculating *state functions* (Frame 1) we can assume (if it makes calculations easier) that the process takes place at equilibrium even though practically the process of interest to us may be being undertaken under conditions far from equilibrium. The only caveat to this is that we have to assume the same initial and final states in our *equilibrium* calculation as exist in the actual process we are trying to mimic. Only then will the calculated change in the state function property correspond to the change we are targeting.

6.4 Interpretation of Changes

One might ask the question: under conditions of constant temperature, pressure what would be the increase in $\mathrm{d}G$ brought about by *increasing* the amount of component 1 by $\mathrm{d}n_1$ whilst keeping n_2, the amount of component 2 constant?

Equation (5.19) Frame 5 took the form:

$$\mathrm{d}G = \mu_1.\mathrm{d}n_1 + \mu_2.\mathrm{d}n_2 \tag{5.20}$$

since $\mathrm{d}n_2 = 0$ (no change to component 2) then:

$$\mathrm{d}G = \mu_1.\mathrm{d}n_1 \tag{6.29}$$

The increase in G, $\mathrm{d}G$, is given by the chemical potential, μ_1 ($= (\partial G/\partial n_1)_{T,P,n_2}$, equation (5.20), Frame 5) of component 1 multiplied by the amount by which this component is increased ($= \mathrm{d}n_1$).

6.5 Quadratic Equations

In the course of solving problems related to equilibria (Frame 47) it is sometimes necessary to solve quadratic equations (i.e. determine their *roots* or solutions). In order to determine x as the solution of an equation in the quadratic form:

$$\mathrm{a}x^2 + \mathrm{b}x + \mathrm{c} = 0 \tag{6.30}$$

(i.e. containing a term in x squared ($= x^2$)).

The solution is given by the equation:

$$x = \frac{[-\mathrm{b} \pm (\mathrm{b}^2 - 4\mathrm{ac})^{1/2}]}{2\mathrm{a}} \tag{6.31}$$

Since there are two alternative signs (±) which may be chosen in calculating x from equation (6.31), this gives rise to two possible solutions: one obtained by taking first the + sign and the second by taking the − sign in equation (6.31). However it is not always the case that both these roots (solutions) are valid as the solution for the specific problem being considered. For example, if we are solving to find a concentration and one of the roots emerges as being negative, this is clearly not a sensible valid solution and is therefore discarded, the positive root then being the only acceptable solution to the problem.

7. Thermodynamic Conventions

7.1 The Nature of Thermodynamics

- Thermodynamics works!
- It is a *practical subject* which is *well-established* and *developed* and whose *predictions* are reliable.
- It has its origins in the study of *macroscopic* (i.e. *bulk, observable*) properties of materials (e.g. temperature, T; pressure, P; volume, V etc.) made *en masse*.

Some of the subject's main features are shown on the inside of the front cover.

7.2 Systems, Surrounding and Conventions

It is standard practice in thermodynamics to divide things up into the *system* and the *surroundings* (Frame 1). Figure 7.1 shows two examples. In defining the system we define a definitive boundary. Once this designation is made, thermodynamics then considers the transfer of energy (defined as the *capacity to do work*, w or *transfer heat*, q) and matter to and from the system. For this we need to adopt a *sign convention*.

The one chosen is the *acquisitive* convention (illustrated in Figure 7.2). If our system *receives* heat *from* the surroundings ($q > 0$) or has work *done on itself by the surroundings* ($w > 0$) then these are regarded as *positive* acquisitions.

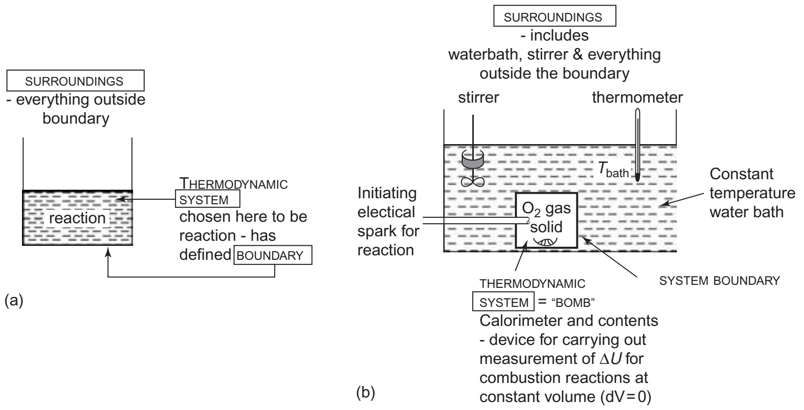


Figure 7.1 Examples of division of thermodynamic studies into *system* and *surroundings*.

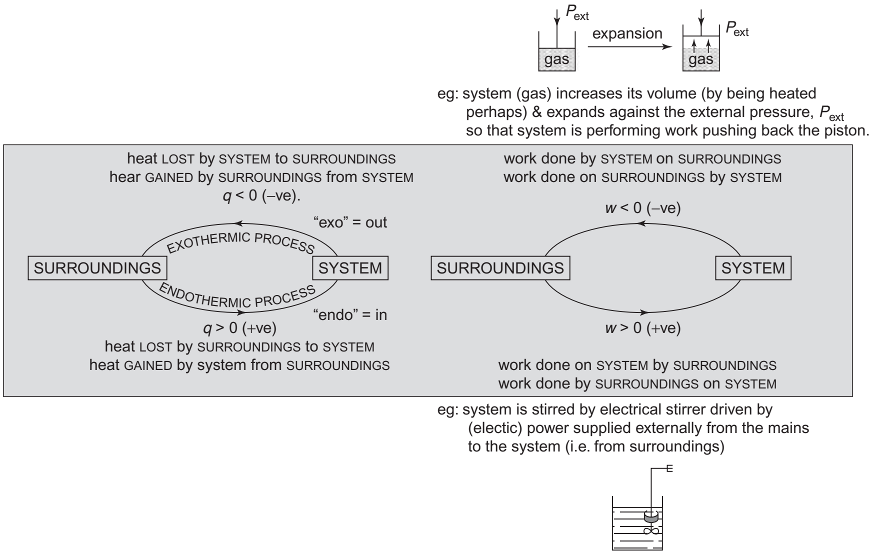


Figure 7.2 ACQUISITIVE convention for heat (a) and work (b) in thermodynamics. The First Law of Thermodynamics written in accordance with this convention takes the form: $\Delta U = q + w$, where ΔU is the change in internal energy of the system, q is the heat absorbed *by* the system *from* the surroundings and w is the work done *on* the system *by* the surroundings.

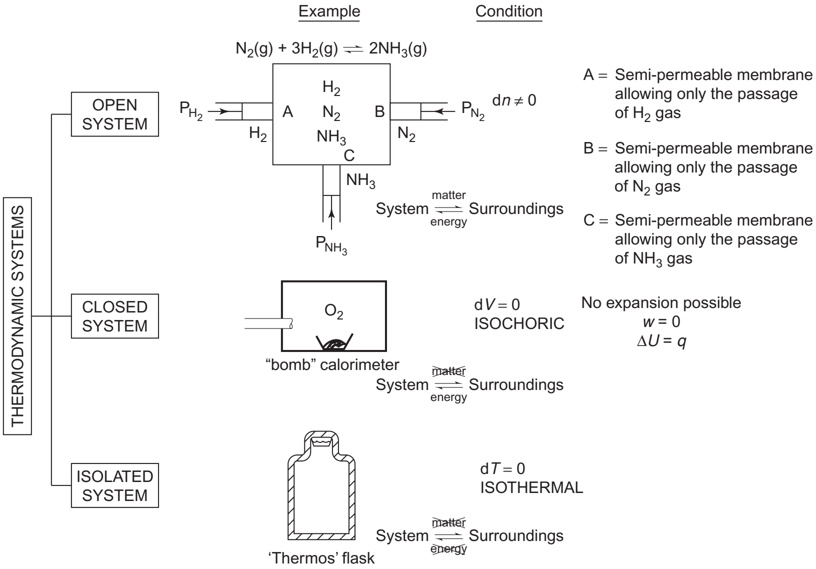


Figure 7.3 Designated types of thermodynamic system. (Symbols like dP, dT, dV denote small changes. For a description of this notation consult Frame 0, section 0.2.)

Conversely if the *system* either *loses heat* ($q < 0$) or it *does work on the surroundings* ($w < 0$) such *loss* is regarded as a *negative* acquisition.

7.3 Heat, *q* and Work, *w*

Heat and work are both *forms of transfer of energy*. Heat is transferred as a flow of energy driven by a difference in temperature. In Figure 7.4, the temperature gradient ($T_2 > T_1$) causes heat to flow from right to left and the material acquires a uniform temperature (T_3) throughout.

This leads us to the *Zeroth Law of Thermodynamics* (which is really a statement of experience) which states that if we have an adiabatically insulated system ($q = 0$) in which a body A is in thermal equilibrium with a body B and B is, in turn, in thermal equilibrium with a third body C then A will be in equilibrium with C even though it may not be in direct contact.

$$\text{if A} \leftrightharpoons \text{B} \quad \textit{and} \quad \text{B} \leftrightharpoons \text{C}, \quad \text{then A} \leftrightharpoons \text{C}$$

Zeroth Law of Thermodynamics

7.4 Spontaneous Processes

Figure 7.4 illustrates the *spontaneous* process in which heat is transferred from a hotter to a colder body. This process proceeds *without outside intervention*. The reverse process is never observed. In thermodynamics we need to establish criteria which enable us to identify spontaneity.

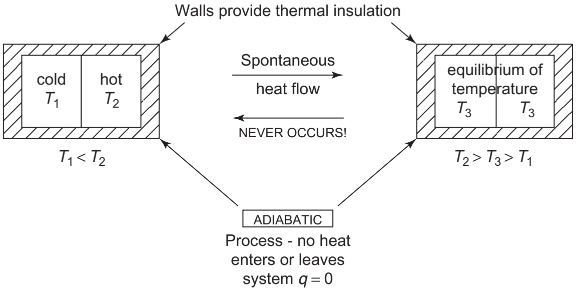


Figure 7.4 Equilibration between hot (T_2) and cold (T_1) materials in thermal contact. Note: Process of heat transfer hot → cold is a *spontaneous* process. The reverse process cold → hot is *never* observed to take place.

8. Heat and Work
First Law of Thermodynamics

8.1 Heat, *q* and Work, *w*

The concept of heat, q, being transferred is a familiar experience. In contrast, the concept of work being done, w, (in the thermodynamic sense!) is relatively unfamiliar.

Work is done when a force, F, moves through a distance, dx. Thus an infinitesimal displacement, δx brought about by a force, F, produces an infinitesimal amount of work, δw such that:

$$\delta w = F.\delta x \tag{8.1}$$

and thus work done by a force, F, which causes a finite displacement, say from x_i to x_f, ($=$ dx), is given by:

$$w = \int \delta w = \int_{x_\mathrm{i}}^{x_\mathrm{f}} F.\mathrm{d}x \tag{8.2}$$

In thermodynamics the sign attributed to w depends on the acquisitive convention already described (Frame 7). If a system is doing work on the surroundings it is losing energy and this is regarded as being *negative* by our convention.

Pressure, P, can be defined as the force, F, exerted per unit area, A, then:

$$P = \frac{F}{A} \tag{8.3}$$

and work, w, (which via the acquisitive convention is negative) can therefore also be calculated in terms P and the associated volume change, dV, thus:

$$w = -\int F.\mathrm{d}x = -\int_{x_\mathrm{i}}^{x_\mathrm{f}} PA.\mathrm{d}x = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} P.\mathrm{d}V \tag{8.4}$$

Thus (Figure 8.1) in the case of a gas expanding against a fixed (i.e. constant) external pressure, P_ext:

$$w = -\int_{V_\mathrm{i}}^{V_\mathrm{f}} P_\mathrm{ext}.\mathrm{d}V = -P_\mathrm{ext}\int_{V_\mathrm{i}}^{V_\mathrm{f}} \mathrm{d}V = -P_\mathrm{ext}(V_\mathrm{f} - V_\mathrm{i}) = -P_\mathrm{ext}\Delta V \tag{8.5}$$

The fact that P_ext is constant enables it to be taken outside the integral sign (Frame 2). Thus, in general for expansion against constant pressure, P:

$$w = -P\Delta V \tag{8.6}$$

or for a smaller volume change dV:

$$w = -P\mathrm{d}V \tag{8.7}$$

This *mechanical* work of expansion is often referred to as "PV" work.

In equations (8.6) and (8.7), important key equations, the appropriate sign convention ($w < 0$, work done by system on surroundings) has been adopted.

Work, w, and heat q, *are modes of energy transfer* between system and surroundings and vice versa. w and q are *transferred during* the processes taking place. It is vital that this distinction is understood by the reader.

At the microscopic (molecular) level, the process of supplying heat, q ($q > 0$) can be associated with an increase in the thermal motions of the constituent atoms / molecules making up the system and giving rise to an increase in internal energy of that system. Addition of heat to a system generally leads to a rise in the temperature, ΔT.

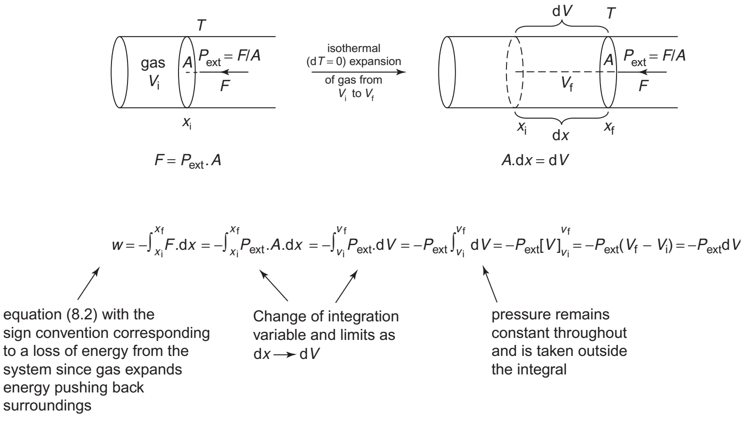


Figure 8.1 Gas (initial volume, V_i) expands a distance, dx, at a fixed temperature, T, against a piston enclosing it with pressure, P_ext (corresponding to a force, F, exerted over a cross-sectional area, A) to a final volume, V_f. x_i and x_f represent the initial and final positional coordinates of the piston and the overall change in volume, d$V = V_\mathrm{f} - V_\mathrm{i}$.

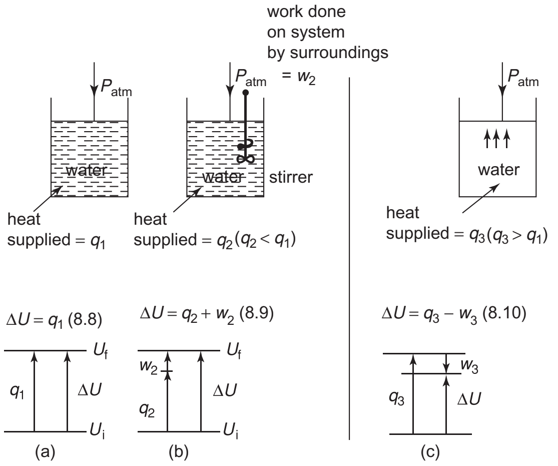
8.2 First Law of Thermodynamics

If heat, q, is supplied ($q > 0$) to a thermodynamic system, then since the *energy must be conserved* (i.e. neither created nor destroyed – a statement which is equivalent to the *First Law of Thermodynamics*), one option is that it can be used solely to increase the internal energy, ΔU, of the system (Figure 8.2a) and hence in that case:

$$\Delta U = q_1 \tag{8.8}$$

If (as in Figure 8.2b), work, ($= w_2$) is done *on* the system *by* the surroundings (i.e. $w_2 > 0$) as well as heat being supplied ($= q_2$; $q_2 < q_1$) then the conservation of energy expressed by the First Law then takes the form:

$$\Delta U = q_2 + w_2 \tag{8.9}$$



Water expands (although is not evoporating i.e. changing its phase) and so pushes external (atmospheric) pressure backwards in order to increase its volume. so doing work on surroundings w_3(< 0, lost from system). The work needed is provided by some of the heat energy, q_3, supplied.

Figure 8.2 Diagram for section 8.2.

Here work is done *by* the surroundings *on* the system. The stirrer is driven by mains electricity (an external source of energy to the system). Work is done by the stirrer in the (microscopic) sense that the atoms of the metal blade all move in a concerted direction as the blade rotates and so they create a force on the molecules of the water forcing these, in turn, to move through a distance and hence work is done.

In other cases (Figure 8.2c) heat q_3 ($q_3 > q_1 > q_2$) can be supplied, part of which can be used to increase the internal energy of the system but some of which can be used by the water to increase its volume (by expanding). In this expansion process energy is needed to force back the external pressure imposed on its surface by the atmosphere thus doing work of expansion *against* the surroundings ($= -w_3$). For this case:

$$\Delta U = q_2 - w_3 \tag{8.10}$$

We must not, however, allow the water to evaporate (change phase) since then;

- the system becomes an open system (Frame 1);

and

- once it becomes an open system and evaporation takes place this would affect the internal energy, ΔU (e.g. if the water volume were halved the internal energy would be halved).

Accordingly, equations (8.8), (8.9) and (8.10) all represent statements of the First Law of Thermodynamics as it applies to the different scenarios above. Because of the sign convention needed (Frame 7) the equation adopts its varying forms depending on the energy balances which are taking place.

8.3 Other Forms of Work

Work can take forms other than that of mechanical (PV) work of expansion and contraction. We can experience electrical, gravitational, magnetic, surface and other forms of work ($= w'$). Most generally then, we can state the First Law of Thermodynamics by means of the following equation:

$$\Delta U = q + w + w' \tag{8.11}$$

where q is the heat absorbed *by* the system *from* its surroundings, w and w' are respectively, mechanical and other forms of work done *by* the surroundings *on* the system. Gravitational work could take the form:

$$w'_{\mathrm{grav}} = \int_{H_i}^{H_f} m\mathrm{g}.\mathrm{d}H \tag{8.12}$$

where m is the mass of a falling weight under gravity g through a height dH. If work, w' takes the form of charge, q flowing through an electrical potential difference, E

$$w'_{\mathrm{elec}} = \int E.\mathrm{d}q \tag{8.13}$$

then the electrical work is given by equation (8.13). This is related to work obtainable from electrical cells.

9. Work of Expansion

In this frame we bring together the properties of ideal gases (See Sections 4.1 and 4.2; Frame 4) and the specific calculation of work done when a gas is expanded (Frame 7).

9.1 Irreversible Expansion

If one suddenly opens the tap (valve) on a cylinder containing a gas confined under a pressure P_i (much greater than atmospheric pressure, P_{atm} (i.e. $P_i \gg P_{\mathrm{atm}}$)) and allows it to escape by into the atmosphere this process will continue until the pressures are equalised and the final pressure $P_f = P_{\mathrm{atm}}$. The expansion (leaving aside all discussion of *throttle effects* at the valve, gas/air mixing, friction effects etc.) takes place rapidly – and under non-equilibrium conditions – usually at constant temperature, T (= ambient) and is a *spontaneous process*. Since this process is not at equilibrium and hence is not reversible, we refer to it as being an *irreversible* process.

The work done on expansion of the gas from initial volume, V_i, pressure, P_i to a final volume V_f, pressure, P_f is calculated using equation (8.5), Frame 8, recognising that P is a constant throughout (i.e. the process is isobaric). P_i (at the instant the tap is opened and the expansion begins) is equal to $P_f = P_{\mathrm{ext}} = P_{\mathrm{atm}}$ (on opening the tap the gas experiences atmospheric pressure). Accordingly:

$$w_{\mathrm{irr}} = -\int_{V_i}^{V_f} P_{\mathrm{ext}}.\mathrm{d}V = -P_f \int_{V_i}^{V_f} \mathrm{d}V = -P_f(V_f - V_i) = -P_{f.}\Delta V = -P_{\mathrm{atm}} \cdot \Delta V \tag{9.1}$$

and w_{irr} will correspond to the area of the shaded rectangle (= $P_{f.}\Delta V$) in Figure 9.1a representing this expansion process.

9.2 Work of Irreversible Adiabatic Expansion

If the above expansion is carried out adiabatically (i.e. so rapidly that no heat can enter or leave the system, thus $q = 0$) then since:

$$\Delta U = q + w \tag{9.2}$$

(equation 8.11, Frame 8, $w' = 0$) and:

$$q = 0 \tag{9.3}$$

then:

$$\Delta U = w_{\mathrm{irr}} \tag{9.4}$$

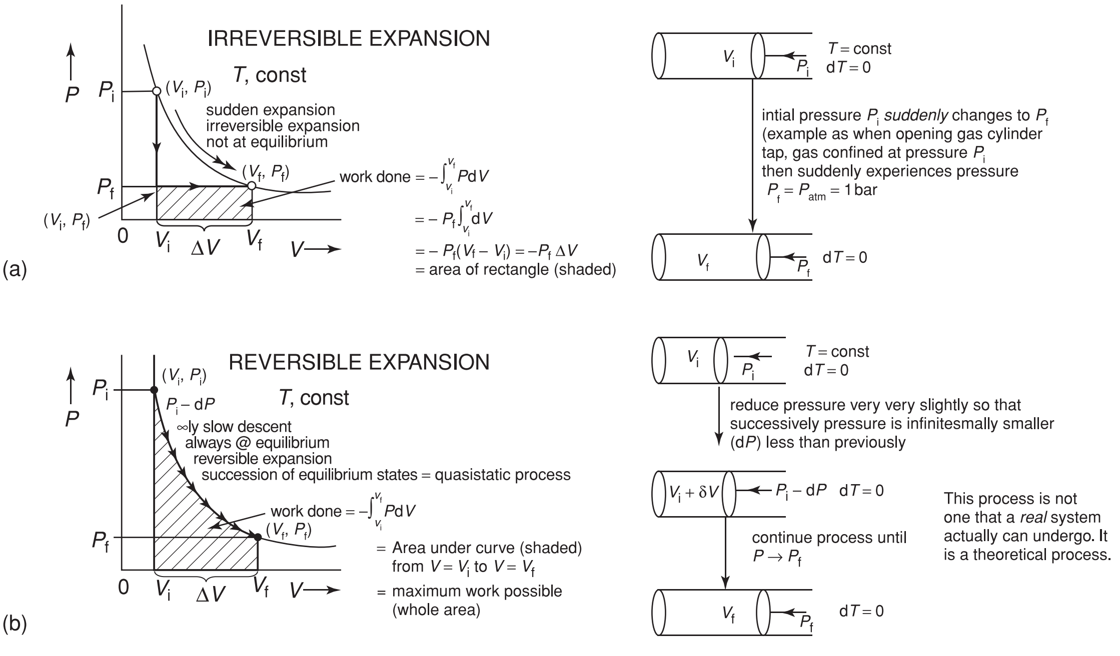


Figure 9.1 Work of (a) reversible expansion and (b) irreversible expansion of an ideal gas from (V_i, P_i) to (V_f, P_f).

and the work to perform the expansion is *provided solely by the gas giving up its internal energy*, ΔU, correspondingly the gas will cool.

A practical example of this is the coldness at the nozzle of a rapidly deflating balloon. The internal energy, U, possessed by the gas is being used to provide work to push back the atmospheric pressure to allow the air contained within the balloon to be released from the balloon envelope. Loss by the air of this internal energy, ΔU, causes the temperature of the emerging air to fall.

9.3 Work of Reversible Expansion

If an amount n of gas, at pressure, P_i, having volume, V_i, at constant temperature, T, is expanded in such a way that the opposing pressure is always made just infinitesimally smaller than P_i at any snapshot instant (i.e. $= P_i - dP$) and this process is continued (always maintaining the current pressure to be only marginally less than that of the gas) until the *same final state* as in the irreversible expansion discussed in the section above (that of P_f and V_f) is reached, then this expansion is termed an expansion under *reversible conditions*. It is the case that if, at any moment, the opposing pressure to the gas pressure, P were made equal to $P + dP$ then the expansion would be *reversed* and become a contraction. Thus during the course of this particular mode of (reversible) expansion we *proceed through a succession of equilibrium states*.

- One way of imagining this process would be to think of a vertical piston arrangement where at the start the pressure exerted by the gas of volume V_i, namely P_i, is exactly balanced by placing an appropriate weight of sand so as to cause an equalising downward pressure of P_i onto the gas confined by the piston. A *reversible expansion* process could then be started by successively removing the sand one grain at a time. As the removal of a grain actually makes the sand very slightly lighter (and so it exerts an infinitely smaller downward pressure on the gas) the gas will expand very slightly so as to equalise the new pressure. This process is then repeated ad infinitum until the final volume V_f is achieved at a pressure P_f.
- The thermodynamic behaviour of the gas, now experiencing not a constant but a slowly decreasing pressure, is itself governed by the $PV = nRT$ isotherm and the pressure of the gas will change and adjust itself so as to follow the rectangular hyperbola shown in Figure 9.1b. The gas during this reversible expansion mode takes up *every intermediate value* of V and P between the two limits: V_i and V_f and P_i and P_f. Each state (V, P) at any snapshot in time is such that if it were an isolated system it would remain in that state indefinitely without any tendency to change.
- The *sand* analogy made above makes one appreciate that this reversible process cannot feasibly be carried out in practice – it would be infinitely slow since in order to truly achieve a smooth transition between the individual snapshot equilibrium states it would be necessary to make the sand grains infinitesimally small in size and so their number would approach infinity and the whole process would take an infinite amount of time to achieve! The concept of reversibility is therefore a *theoretical concept rather than a practical one*. Despite this the concept of reversibility is extremely useful in thermodynamics and will arise in later discussions.

In contrast to the case of the irreversible expansion, P is *not constant* during the reversible expansion but varies along the isotherm (equation (4.1), Frame 4):

$$P = n\frac{RT}{V} \tag{9.5}$$

Thus P cannot be taken outside the integral in equation (9.1) and so we write:

$$w_{\text{rev}} = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \left(\frac{nRT}{V}\right) dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right) \tag{9.6}$$

The varying P is substituted by *nRT/V* and the integration then performed over the changing volume. w_{rev} is the work done by the gas in expanding reversibly from (V_i, P_i) to (V_f, P_f). It can be equated to the *area enclosed between the curve of P plotted versus V and the V axis* (i.e. the abscissa) (see Frame 2). w_{rev} is larger than the work done, w_{irr}, during the irreversible process of expansion and it also represents the *maximum work obtainable from any expansion process* which takes the gas from the state (V_i, P_i) to the state (V_f, P_f).

Since:

$$|w_{\text{rev}}| \neq |w_{\text{irr}}| \tag{9.7}$$

and

$$|w_{\text{rev}}| > |w_{\text{irr}}| \tag{9.8}$$

In equations (9.7) and (9.8) we write moduli to describe the *magnitude* of the work done in the two cases so avoiding the sign convention issues here. We again see that:

- w is a path independent function (compare equations (9.1) and (9.4)) whose values differ depending on the route or path taken (an irreversible path contrasted with a reversible path) between the initial and final states

and

- w_{rev} represents the maximum work obtainable from a reversible process.

10. Internal Energy, *U* and Enthalpy, *H*

10.1 Internal Energy, *U* and the Enthalpy Function, *H*; q_P & q_V

Application then of the *First Law of Thermodynamics* (Frames 1, 2 and 8) leads to the relationship:

$$\Delta U = q + w = q - P\Delta V \tag{10.1}$$

Where a thermodynamic system has to a fixed volume, $\Delta V = 0$ (e.g. in a bomb calorimeter or autoclave) and not permitted to expand ($w = 0$) and then:

$$\Delta U = q_V \tag{10.2}$$

where q_V represents the heat absorbed (if $q_V > 0$) or released (if $q_V < 0$) at constant volume by or from the system. Hence ΔU, *the change in internal energy* will be the result obtained from thermochemical measurements made on closed systems which are held at constant volume.

We note here, as was found in the example of the calculation of the work done during the irreversible adiabatic of expansion of a gas (equation 9.4 Frame 9), that *under specific conditions* a *path dependent function* can become identically equal to the change in a state function.

In the two cases we have met the conditions are quite stringent:

- in the first case (the adiabatic expansion) q has to be equal to zero

and

- in this second case volume must remain constant throughout.

In order to describe the heat changes, q_P which take place in a system (where the external pressure P is constant – most usually being equal to P_{atm} ($= 1$ bar)) we need to rearrange equation (10.1), since in this system work of expansion (leading to a change of volume) may now be permitted, so that:

$$q = \Delta U + P\Delta V = q_P \tag{10.3}$$

where q_P represents the heat absorbed (if $q_P > 0$) or released (if $q_P < 0$) at constant pressure by or from the system.

Recalling (Frame 1) that U and V are both state functions

$$\Delta U = U_f - U_i \tag{10.4}$$

$$\Delta V = V_f - V_i \tag{10.5}$$

where i and f signify initial and final values of these respective properties.

Substitution of equation (10.4) and (10.5) into (10.3) and grouping terms, leads us to:

$$q_P = \Delta U + P\Delta V = (U_f - U_i) + P(V_f - V_i) = (U_f + PV_f) - (U_i + PV_i) \tag{10.6}$$

The term $[(U_f + PV_f) - (U_i + PV_i)]$, represents the difference between two functions having the form $(U + PV)$. These can be separately identified with the final and initial states of the system and therefore have, themselves, the attributes of a state function (Frame 1). We define the term $(U + PV)$ as a new state function, H, the *enthalpy*, so that:

$$\Delta H = H_f - H_i \tag{10.7}$$

where:

$$H = (U + PV) \tag{10.8}$$

so that equation (10.6) becomes:

$$q_P = \Delta H = (H_f - H_i) = (U_f + PV_f) - (U_i + PV_i) \tag{10.9}$$

and also we are provided with yet another path dependent function which can – under specific conditions (constant pressure in this case) – be equated directly to a change in a state function (i.e. enthalpy, ΔH) (Frame 1).

Since so many *chemical processes* are conducted under *constant pressure* (for example in open beakers onto which the atmosphere exerts a constant pressure) rather than under constant volume conditions (in which systems need to be confined inside a closed vessel) we encounter *changes in enthalpy*, ΔH, more frequently than we do changes in internal energy, ΔU.

At constant pressure, $\Delta P = 0$:

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P = \Delta U + P\Delta V \tag{10.10}$$

using the Product Rule (Frame 6) for the differentiation of the term PV (as in section 6.5.3). Now since work of expansion can be equated to $-P\Delta V$ then in equation (10.10) ΔH is equal to the change in internal energy minus the energy needed to perform expansion.

10.2 General Heat Capacity, *C* and Heat Capacity at Constant Pressure C_p and at Constant Volume, C_v

The rate of change of temperature, $\mathrm{d}T$ caused by the supply of heat, q, to a substance is termed the heat capacity, C, thus:

$$C = \frac{\mathrm{d}q}{\mathrm{d}T} = \frac{\delta q}{\mathrm{d}T} \tag{10.11}$$

When C is an extensive variable the dimension is [energy (temperature)$^{-1}$], unless molar quantities are involved, in which case C_m becomes an intensive variable with the units [energy (temperature)$^{-1}$ (mol)$^{-1}$].

At constant pressure the heat absorbed by the substance δq can be replaced by δq_P and hence (by virtue of equation 10.9) by $\mathrm{d}H$.

This enthalpy change is used both to raise the temperature and to provide work of expansion of the material as its temperature increases, and so the heat capacity can be defined as:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{10.12}$$

where, because either the pressure, P (i.e. open to the atmosphere and hence exposed to atmospheric pressure, but note, *not* an *open* system in the *thermodynamic sense* (Frame 1), since the latter term defines a system/process which exchanges material with the surroundings), or the volume, V (i.e. in a closed system) can be held constant, the ordinary derivatives ($\mathrm{d}/\mathrm{d}T$) in the general definition (10.11) are now replaced by partial derivatives ($\partial/\partial T$) (the function C depends on two variables, V and P).

At constant volume, q_V, the heat absorbed which raises the temperature of the material (equation 10.2) equates to $\mathrm{d}U$ and hence:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \tag{10.13}$$

Changing partial derivatives to ordinary derivatives – which we can do if we are keeping P constant – and rearranging equation (10.12)

$$\mathrm{d}H = C_p.\mathrm{d}T \tag{10.14}$$

and then integrating between limits of i and f we have:

$$\Delta H = \int_{H_i}^{H_f} \mathrm{d}H = \int_{T_i}^{T_f} C_P.\mathrm{d}T \tag{10.15}$$

where ΔH is the enthalpy change when the temperature of a substance (a heat capacity, C_p) is raised from T_i to T_f.

10.3 Methods of Calculating ΔH

There are several possible approaches which can be used to calculate ΔH and these are given in Figure (10.1).

Calculation of ΔH, the enthalpy change involved when the temperature of a substance with heat capacity, C_p, is raised from T_i to T_f.

It should be noted that these calculations (equations (10.18) and (10.19) in the figure) lead to a value of ΔH ($= \Delta_m H$) in units of J mol^{-1} and that this must then be divided by 10^3 (i.e. multiplied by kJ/(1000 J)) in order to give $\Delta H (= \Delta_m H)$ in its more usual units of kJ mol^{-1} (10^3 J = 1 kJ). This fact is important and should be remembered in respect of heat capacity calculations.

10.4 Use of Heat Capacity for the Calculation of Enthalpy Change, ΔH

Suppose we wish to calculate the enthalpy change, ΔH, to raise the temperature of the products (ΔH_{prod}) and reactants (ΔH_{react}) of a chemical reaction from T_1 to T_2.

Considering the two reactions, at temperatures, T_1 and T_2:

$$\begin{array}{ccl} & \mathrm{aAB + bCD \rightarrow cEF} & \quad \text{at temperature } T_2 \\ \Delta H_{react}\uparrow & \qquad\qquad \uparrow \Delta H_{prod} & \\ & \mathrm{aAB + bCD \rightarrow cEF} & \quad \text{at temperature } T_1 \end{array}$$

then using equation (10.18) (assuming that $C_{p,m}(\mathrm{AB})$, $C_{p,m}(\mathrm{CD})$ and $C_{p,m}(\mathrm{EF})$, the molar heat capacities of the reactants AB and CD and the products, EF, are *independent* of temperature change between T_1 and T_2), then:

$$\Delta H_{react} = [\mathrm{a}C_{p,m}(\mathrm{AB}) + \mathrm{b}C_{p,m}(\mathrm{CD})](T_2 - T_1) \tag{10.16}$$

and

$$\Delta H_{prod} = [\mathrm{c}C_{p,m}(\mathrm{EF})](T_2 - T_1) \tag{10.17}$$

$$\Delta H = \int_{T_i}^{T_f} C_p.\mathrm{d}T \longrightarrow$$

1. Assume that C_P does not vary over the temperature range involved: $\Delta T = T_f - T_i$. Thisisusually true for modest temperature changes.

$$\Delta H = C_P \int_{T_i}^{T_f} \mathrm{d}T = C_P(T_f - T_i) = C_p.\Delta T \quad (10{:}18)$$

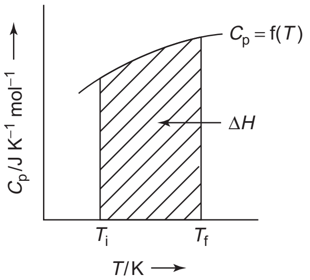
2. Assume that $C_P = \mathrm{f}(T)$ and that it takes the analytical form: $C_P = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2$, where a, b and c are known constants.

$$\Delta H = \int_{T_i}^{T_f} C_P.\mathrm{d}T = \int_{T_i}^{T_f} (\mathrm{a} + \mathrm{b}T + \mathrm{c}T^2).\mathrm{d}T = \mathrm{a}\int_{T_i}^{T_f} \mathrm{d}T + \mathrm{b}\int_{T_i}^{T_f} T.\mathrm{d}T + \mathrm{c}\int_{T_i}^{T_f} T^2.\mathrm{d}T$$

so that:

$$\Delta H = \mathrm{a}(T_f - T_i) + \tfrac{1}{2}\mathrm{b}(T_f^2 - T_i^2) + (\mathrm{c}/3)(T_f^3 - T_i^3) \quad (10{:}19)$$

3. Since:



$$\Delta H = \int_{T_i}^{T_f} C_P.\mathrm{d}T = \text{Area between curve of } C_P \text{ plotted versus } T \text{ and } T \text{ axis between the limits } T_i \text{ to } T_f.$$

ΔH can be obtained by plotting the graph and using graphical software. The area found is then related to ΔH (in J mol^{-1}) .

Figure 10.1 Methods of calculating ΔH using equation (10.15)

If either T_1 or T_2 happen to be equal to 298.15 K then the $C_{p,m}$ values required will be those tabulated in thermochemical databases. Frame 11 discusses further the use of heat capacity.

10.5 Use of Heat Capacity for Entropy Change, ΔS Calculations

As will be seen later (in Frame 14) the equation (6.28), constitutes one half of the *Second Law of Thermodynamics*:

$$\mathrm{d}S = \frac{\delta q_{\mathrm{rev}}}{T} \qquad (10.20)$$

where dS is the change in entropy, S, and δq_{rev} is the heat added to the system during a reversible process (i.e. a process taking place as a succession of equilibrium states) and T is the (constant) temperature at which this process takes place. The other part of the Second Law is that:

$$\mathrm{d}S \geq \frac{\delta q}{T} \qquad (10.21)$$

or

$$\Delta S_{\mathrm{universe}} \geq 0 \qquad (10.22)$$

which appears later as equation (13.18), Frame 13 and used again in Frame 14.

Again under *specific conditions* a path dependent function, q equates to the change in a state function, namely the change in entropy, dS multiplied by T, i.e.

$$q_{\mathrm{rev}} = T\cdot\mathrm{dS} \qquad (10.23)$$

By virtue of equations (10.8) and (10.12):

$$\mathrm{d}q_P = C_{p,m}\cdot\mathrm{d}T = \mathrm{d}H \qquad (10.24)$$

and hence:

$$\mathrm{d}S = C_{p,m}\cdot\mathrm{d}T/T = \left(\frac{C_{p,m}}{T}\right)\cdot\mathrm{d}T \qquad (10.25)$$

so that:

$$\Delta S = \int_{S_i}^{S_f} \mathrm{d}S = \int_{T_i}^{T_f} \left[\frac{C_{p,m}}{T}\right].\mathrm{d}T \qquad (10.26)$$

Thus a plot of C_p/T versus T gives the entropy change, ΔS as the area under the curve and the T axis (Frame 2, section 2.3, Figure 2.2a), between the limits T_i and T_f, or:

$$\Delta S = S_f - S_i = C_{p,m} \int_{T_i}^{T_f} \left[\frac{1}{T}\right].dT = \int_{T_i}^{T_f} \frac{dT}{T} \tag{10.27}$$

and hence:

$$\Delta S = C_{p,m}\left[\ln\left(\frac{T}{K}\right)\right]_{T_i}^{T_f} = C_{p,m}\left[\ln\left(\frac{T_f}{K}\right) - \ln\left(\frac{T_i}{K}\right)\right] = C_{p,m}\ln\left(\frac{T_f}{T_i}\right) \tag{10.28}$$

if $C_{p,m}$ is assumed to be constant over the temperature range considered (Figure 10.1). K = Kelvin.

Similarly by analogy:

$$\Delta S = C_{v,m}.\ln\left(\frac{T_f}{T_i}\right) \tag{10.29}$$

for a process taking place at constant volume.

Such calculations as these are usually only made for gases when the change in entropy, ΔS tends to be significant (and not for solids and liquids).

Entropy, S and entropy changes, ΔS will be discussed further in Frames (13–17) etc.

11. Reference States

11.1 Tabulated Thermodynamic Data. Definition of $\Delta_f H^o$, $\Delta_f G^o$ and $\Delta_f S^o$

Thermochemical tables list values of: the standard enthalpy of formation, $\Delta_f H^o$ (formerly called heats of formation); the standard Gibbs energy of formation, $\Delta_f G^o$; the standard entropy, S^o; the heat capacity at constant pressure, $C^o_{p,m}$ for substances in defined physical states (e.g. solid (s) or crystalline (c), liquid (l), aqueous (aq) or gas (g)). In much of this frame we shall be assuming that the heat capacities, $C^o_{p,m}$, are temperature independent.

Experimental conditions (and chemical formulae) are *not* written as subscripts but as on-line values in parentheses, e.g. $\Delta_f H(T, P^o)$ or $\Delta_f H(300\text{ K}, 1\text{ bar})$. We shall not overcomplicate our notation (referring the reader to the Glossary (Frame 0). In this text we might refer to $\Delta_f H(T, P^o)$ or $\Delta_f H(300\text{ K}, 1\text{ bar})$ simply as $\Delta_f H(T)$ and $\Delta_f H(300\text{ K})$. The subscripts Δ_f, Δ_r and Δ_c by convention imply molar quantities (i.e. in full notation: $\Delta_{f,m}$ $\Delta_{r,m}$ and $\Delta_{c,m}$) but these additional symbols are omitted in this text.

11.2 Reference States (rs) and Standard Enthalpy of Formation, $\Delta_f H^o$

For a general compound, $C_aH_bO_cN_d$ then the *standard enthalpy of formation* for the compound, $\Delta_f H^o(C_aH_bO_cN_d, s)$, is the enthalpy change taking place when **1 mole** of the compound $C_aH_bO_cN_d$ is formed from its *elements all in their standard reference states* (i.e. defined as the *form* these elements take at the temperature of interest† (see Note 11.1) (usually 25 °C = 298 K) and (curiously) *at a pressure of* 101.325 Pa (*i.e.* 1 atm)* (see Note 11.1). The superscript ^{o} refers to the standard pressure (1 bar).

Thus:

$$aC(\text{s, graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) + \frac{d}{2}N_2(g) \xrightarrow{\Delta_f H^o(C_aH_bO_cN_d,s)} C_aH_bO_cN_d(s) \tag{11.1}$$

$\Delta_f G^o$ ($\Delta_f S^o$) are analogously defined.

Typical elemental reference states (rs) are: C(s, graphite), $H_2(g)$, $O_2(g)$, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, $I_2(s)$, Sn(s, white), P(s, α, white)‡ (see Note 11.1), As(s, grey, metallic) etc.

Also:

$$\Delta_f X(\text{element, rs}) = 0 \ (X = G, H) \tag{11.2}$$

In *solution* (rs) corresponds to a *concentration* of 1 mol dm^{-3} *except* in biochemistry applications (see section 11.3).

In contrast to $\Delta_f G^o$ and $\Delta_f H^o$ which are *relative values* (representing *differences* between values for the compound and the elemental reference states, *arbitrarily* assigned to be zero), standard entropy values, S^o (Frame 16, section 16.2) are *absolute values*. This arises because the entropy of a perfectly crystalline solid *at the absolute zero of temperature* has a value of zero (Frames 16 and 17), i.e.:

$$S^o(\text{crystalline solid, 0 K}) = 0\text{ J K}^{-1}\text{ mol}^{-1} \tag{11.3}$$

and so provides a zero (an origin) for absolute scale of entropy, S^o. Values of $\Delta_f H^o$ for 25 °C are tabulated ($P^o = 1$ bar).

11.3 Biochemical Reference State

The normal reference state [H$^+$] concentration of 1 mol dm^{-3} and for which $\Delta_f G^o(H^+, aq)$ (corresponding to: $\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-) = 0$ kJ mol^{-1}, corresponds to a pH ($= -\log_{10}[H^+]$) of zero is inappropriate when working in biochemical media (normally at pH ≈ 7). A *biochemical reference state* corresponding to **$[H^+] = 10^{-7}$ mol dm^{-3}** is adopted, but reference concentrations *for all other species* in solution *remain* at 1 mol dm^{-3}.

- For this biochemical reference state we employ a prime $'$ on the appropriate symbol.
- Thus $\Delta G^{o\prime}$ indicates a change for a reaction in which [H$^+$] is standardised at 10^{-7} mol dm^{-3} to distinguish it from the case of ΔG^o under normal standard state convention (when $[H^+] = 1$ mol dm^{-3}).

11.4 Calculation of ΔH for reactions at temperature 298 K

Sometimes reactions needed for the determination of some $\Delta_f H^o$ values are *thermodynamically* feasible but the reactions are, *kinetically*, extremely slow. An example is the reaction:

$$S(\text{s, rhombic}) + O_2(g) \rightarrow SO_2(g) \tag{11.4}$$

ΔH^o is given by:

$$\Delta H^o = \Delta_f H^o(\mathrm{SO_2, g}) - \Delta_f H^o(\mathrm{S, rhombic, s}) - \Delta_f H^o(\mathrm{O_2, g}) = \Delta_f H^o(\mathrm{SO_2, g}) \tag{11.5}$$

by virtue of equation (11.2): Reaction (11.5) is a direct measure of $\Delta_f H^o(\mathrm{SO_2, g})$.

$\Delta H^o(T)$, for reaction (11.4) could be measured at a higher temperature, say T_2 (when it speeds up) and we then need a method of converting the enthalpy change $\Delta H^o(T_2)$, at T_2, to a corresponding value, $\Delta H^o(T_1)$, at $T_1 = 298\,\mathrm{K}$ which would then equate to $\Delta_f H^o(\mathrm{SO_2, g})$. We consider this problem in section 11.6 below.

More generally, for a reaction:

$$\mathrm{aA + bB \rightarrow cC + dD} \tag{11.6}$$

we can establish that the enthalpy of the reaction, $\Delta_r H^o$, to be given by the equation:

$$\Delta_r H^o = \sum \Delta_f H^o(\text{Products}) - \sum \Delta_f H^o(\text{Reactants}) = \mathrm{c}\Delta_f H^o(\mathrm{C}) + \mathrm{d}\Delta_f H^o(\mathrm{D}) - \mathrm{a}\Delta_f H^o(\mathrm{A}) - \mathrm{b}\Delta_f H^o(\mathrm{B}) \tag{11.7}$$

where $\Delta_f H^o(\mathrm{i})$ (i = A, B, C and D) represents the standard enthalpy of formation (section 11.2) of the compound i.
Equation (11.7) can be used:

- for the calculation of $\Delta_f H^o$ for an individual compound (say D) at 298 K when $\Delta_r H^o$ for a reaction involving that compound is known together with the $\Delta_f H^o$ values of all the other materials involved (i.e. A, B and C);
- for the calculation of $\Delta_r H^o$ when the $\Delta_f H^o$ values of all the compounds involved in the reaction are known.

11.5 Gibbs Energy of Formation, $\Delta_f G^o$

Later in this text (Frame 13) we shall encounter the *Gibbs energy of a reaction,* $\Delta_r G^o$ which combines the effects of both enthalpy change, $\Delta_r H^o$ and the entropy change, $\Delta_r S^o$ (equation (13.10), Frame 13, see also section 13.2).

Analogous equations to equation (11.7) for $\Delta_r G^o$ and $\Delta_r S^o$ have the specific forms:

$$\Delta_r G^o = \sum \Delta_f G^o(\text{Products}) - \sum \Delta_f G^o(\text{Reactants}) = \mathrm{c}\Delta_f G^o(\mathrm{C}) + \mathrm{d}\Delta_f G^o(\mathrm{D}) - \mathrm{a}\Delta_f G^o(\mathrm{A}) - \mathrm{b}\Delta_f G^o(\mathrm{B}) \tag{11.8}$$

and

$$\Delta_r S^o = \sum \Delta_f S^o(\text{Products}) - \sum \Delta_f S^o(\text{Reactants}) = \mathrm{c}\Delta_f S^o(\mathrm{C}) + \mathrm{d}\Delta_f S^o(\mathrm{D}) - \mathrm{a}\Delta_f S^o(\mathrm{A}) - \mathrm{b}\Delta_f S^o(\mathrm{B}) \tag{11.9}$$

$$\Delta_r S^o = \mathrm{c}S^o(\mathrm{C}) + \mathrm{d}S^o(\mathrm{D}) - \mathrm{a}S^o(\mathrm{A}) - \mathrm{b}S^o(\mathrm{B}) \tag{11.10}$$

where $\Delta_f S^o(\mathrm{i})$ and $S^o(\mathrm{i})$ (i = A, B, C and D) represent the standard enthalpy of formation and the standard entropies of the species i. Note that $\Delta_f S^o$ as well as (more usually) standard entropies, S^o can both be used to calculate $\Delta_r S^o$. $\Delta_f S^o$ is not tabulated in thermochemical tables.

We shall not discuss the entropy-based terms $\Delta_f S^o(\mathrm{i})$ and $S^o(\mathrm{i})$ until Frame 15, section 15.7.

11.6 Calculation of ΔH for reactions at temperatures other than 298 K

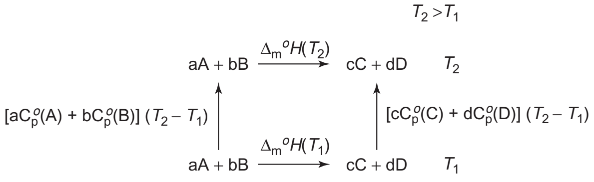


Figure 11.1 Relationship between $\Delta_m H^o(T_2)$ and $\Delta_m H^o(T_1)$ for reaction (11.10) taking place at two temperatures : T_1 and T_2 ($T_2 > T_1$). (11.6)

Enthalpy is a state function, for two temperatures T_1 and T_2 we can draw the cycle in Figure 11.1.

Using the heat capacities, C_p^o for A, B, C and D to calculate the enthalpy required to raise their temperatures from T_1 to T_2 ($T_1 < T_2$) we can establish, directly from the cycle

$$\begin{aligned}\Delta_m H(T_2) = \Delta_m H(T_1) + [&\textstyle\sum C_p^o(\text{Products})(T_2 - T_1) \\ &- \textstyle\sum C_p^o(\text{Reactants})(T_2 - T_1)]\end{aligned} \tag{11.11}$$

simplifying to:

$$\Delta_m H^o(T_2) = \Delta_m H^o(T_1) + \{\sum C_p^o(\text{Products}) - \sum C_p^o(\text{Reactants})\}(T_2 - T_1) = \Delta_m H^o(T_1) + \Delta C_p^o.\Delta T \tag{11.12}$$

where $\Delta_m H^o(T_2)$ and $\Delta_m H^o(T_1)$ are the molar enthalpy changes for reaction (11.6) at temperatures T_2 and T_1 respectively. Equation (11.12) is known as *Kirchhoff's equation.*

Alternatively

$$\Delta_m H^o(T_2) = \Delta_m H^o(T_1) + \int_{T_1}^{T_2} \Delta C_p^o \cdot \mathrm{d}T \tag{11.13}$$

This form is utilised when C_p^o ($= C_{p,m}^o$) values are temperature dependent (Frame 10).

If each $C_{p,m,i}^o$ is known as a function of T, e.g. $\mathrm{a} + \mathrm{b}T + \mathrm{c}T^2$ one can express $\Delta_m C_p^o$ in this format and perform the integral in equation (11.13) analytically.

Kirchhoff's Equation in the form of equations (11.11), (11.12) or (11.13) can be used:

- for the calculation of $\Delta_m H^o(T_2)$ from data for ΔH^o for the reaction at temperature T_1, provided that the heat capacities of reactants and products are all known. It could thus be used, in the example in section 11.4, to calculate $\Delta_f H^o(SO_2,g)$ at 298 K (taken to be $\Delta_m H^o(T_1)$) from the ΔH^o data established at another (higher) temperature, $\Delta_m H^o(T_2)$
- for the calculation of ΔH^o for reactions at temperatures ($= T \neq 298$ K) by employing thermochemical tables to estimate ΔH^o_{298} at 298 K in order to provide $\Delta_m H^o(T)$ at the other temperature, T (provided that the heat capacities of reactants and products are all known) in which case the equations below could be used:

From equation (11.12) we have:

$$\Delta_m H^o(T_2) = \Delta_m H^o(298\,\text{K}) + \left\{\sum C^o_p(\text{Products}) - \sum C^o_p(\text{Reactants})\right\}(\text{T}_2 - 298) \tag{11.14}$$

or specifically for the reaction (11.6)

$$\begin{aligned}\Delta_m H^o(T) = {} & [\text{c}\Delta_f H^o(\text{C}) + \text{d}\Delta_f H^o(\text{D}) - \text{a}\Delta_f H^o(\text{A}) - \text{b}\Delta_f H^o(\text{B})] \\ & + \{\text{c}C^o_p(\text{C}) + \text{d}C^o_p(\text{D}) - \text{a}C^o_p(\text{A}) - \text{b}C^o_p(\text{B})\}(\text{T} - 298)\end{aligned} \tag{11.15}$$

11.7 Standard Enthalpies of Combustion, $\Delta_c H^o$

The *standard enthalpy of combustion* of benzoic acid ($C_6H_5.COOH$) is the *IUPAC standard* used for calorimetry calibration.

The *standard enthalpy of combustion* of a compound, $C_aH_bO_cN_d$, $\Delta_c H^o(C_aH_bO_cN_d, s)$, containing the elements C, H, O and N, is ΔH^o for the reaction:

$$C_aH_bO_cN_d(s) + \left\{a + \left(\frac{b}{4}\right) - 2c\right\} O_2(g) \rightarrow aCO_2(g) + \left(\frac{b}{2}\right) H_2O(l) + \left(\frac{d}{2}\right) N_2(g) \tag{11.16}$$

and thus for benzoic acid the *combustion reaction* is:

$$C_6H_5.COOH(s) + 15/2\ O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l) \tag{11.17}$$

Much like enthalpies of formation, enthalpies of combustion can also be used to determine enthalpy changes for reactions otherwise difficult to measure. Thus for a reaction between a solid and a gas, for example:

$$C(s, graphite) + 2\ H_2(g) \overset{\Delta_r H^o}{\rightarrow} CH_4(g) \tag{11.18}$$

to determine $\Delta_r H^o$ for this reaction we could opt to measure (by flame calorimetry), the enthalpies of combustion, $\Delta_c H^o$ for each of the reactants (C and H_2) and the product (CH_4), thus:

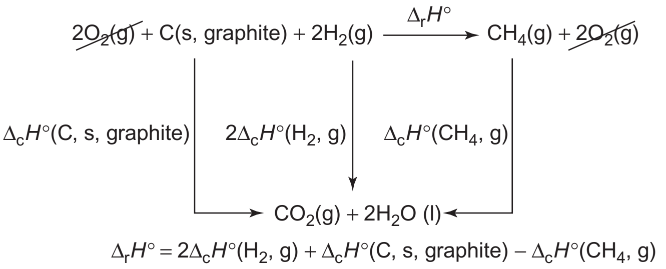


Figure 11.2 Thermochemical cycle showing the incorporation of combustion reactions to determine the enthalpy of reaction (11.18) giving rise to equation (11.24).

$$C(s, graphite) + O_2(g) \xrightarrow{\Delta_c H^o(C,s,graphite)} CO_2(g) \tag{11.19}$$

$$2H_2(g) + O_2(g) \xrightarrow{\Delta_c H^o(H_2,g)} 2H_2O(l) \tag{11.20}$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta_c H^o(CH_4,g)} CO_2(g) + 2H_2O(l) \tag{11.21}$$

There are two ways of deducing how the data obtained for reactions (11.19)–(11.21) could be used to provide $\Delta_r H^o$ for the elusive reaction (11.18). These are:

- by drawing a thermochemical cycle (as in Figure 11.2);

or

- by addition and subtraction of appropriate combinations of equations (11.19)–(11.21) such that superfluous compounds cancel one another and are then eliminated.

To illustrate this, if reaction (11.21) is reversed, the enthalpy change is now the negative of $\Delta_c H^o(CH_4, g)$ (i.e. – $\Delta_c H^o(CH_4, g)$)

$$CO_2(g) + 2H_2O(l) \overset{-\Delta_c H^o(CH_4,g)}{\rightarrow} CH_4(g) + 2O_2(g) \tag{11.22}$$

If then reactions (11.19) and (11.20) are added to reaction (11.22) to give:

$$C(s, graphite) + O_2(g) + 2H_2(g) + O_2(g) + CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) + 2H_2O(l) + CO_2(g) \tag{11.23}$$

If molecules appearing on both sides of the equations are cancelled out the resultant species left correspond to those of the target reaction (11.18) and the associated thermochemistry then leads to the result that:

$$\Delta_r H^o = 2\Delta_c H^o(\mathrm{H_2, g}) + \Delta_c H^o(\mathrm{C, s, graphite}) - \Delta_c H^o(\mathrm{CH_4, g}) \qquad (11.24)$$

See Note 11.2.

11.8 Hess's Law of Enthalpy Summation

State functions (Frame 1, section 1.5) are amenable to the construction of thermochemical cycles since provided that we can devise alternative routes between the same initial and final states, then the changes in state functions via these two alternative routes will be identical.

A cycle of enthalpy changes is shown in Figure 11.3 for the reaction of compounds A and B, with compounds C, D, E, F, G and H formed as intermediates or products. The cycle could equally well be written for ΔU, ΔG and ΔS changes.

The cycle (Figure 11.3) applies even if the intermediate reactions are hypothetical and cannot be carried out experimentally.

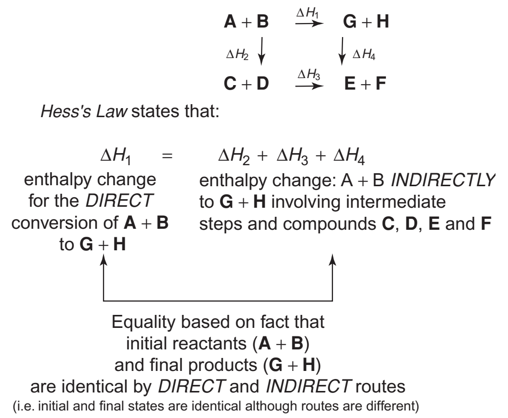
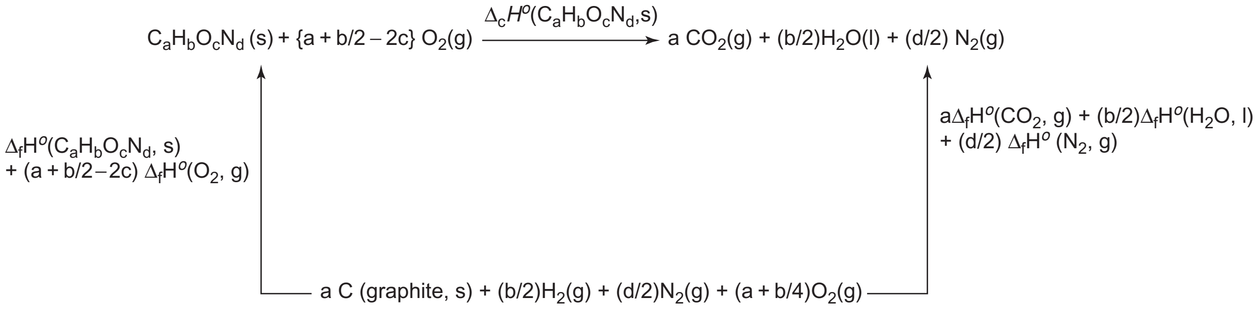


Figure 11.3 Thermochemical cycle showing the application of **Hess's Law**.

11.9 Determination of Standard Enthalpy of Formation of a Compound from Combustion Calorimetry

Combustion experiments on a material, $C_aH_bO_cN_d$ can be used, with standard data for $\Delta_f H^o(\mathrm{CO_2, g})$ and $\Delta_f H^o$ $(\mathrm{H_2O, l})$ to provide an experimental value for the standard enthalpy of formation of the compound, $\Delta_f H^o(C_aH_bO_cN_d, s)$ (Figure 11.4).



$$\Delta_f H^o(C_aH_bO_cN_d, s) = a\Delta_f H^o(\mathrm{CO_2, g}) + (b/2)\Delta_f H^o(\mathrm{H_2O, l}) - \Delta_c H^o(C_aH_bO_cN_d, s)$$

Figure 11.4 Thermochemical cycle for determination of $\Delta_f H^o(C_aH_bO_cN_d, s)$ from combustion experiments.
Note: $\Delta_f H^o\ (O_{2,g}) = \Delta_f H^o\ (N_{2,g}) = 0$ by virtue of equation (11.2).

12. Bond Enthalpy (Energy)

Thermodynamic stability can be related to the *enthalpy of the individual bonds* formed by pairs of constituent atoms which make up a compound. Distinction needs to be made between this and *chemical stability* concerned with the activation required to make the reaction proceed (kinetically).

12.1 Definition of Bond Enthalpy (Energy), ΔH^o(X–Y)

The bond enthalpy, ΔH^o(X–Y), of the X–Y bond (sometimes called, bond dissociation enthalpy or, loosely, bond energy and sometimes given the alternative symbols E(X–Y) or $BE_{\mathrm{X-Y}}$) is a quantitative (thermochemical based) description of the *average* enthalpy required to break an X–Y bond.

Decomposition of $NH_3(g)$ into its gaseous atoms breaks 3 N–H bonds and the enthalpy change of the reaction, $\Delta_r H$ can be equated to three (supposedly equal) bond enthalpy terms, thus:

$$\mathrm{NH_3(g)} \overset{\Delta_r H^o}{\rightarrow} \mathrm{N(g) + 3H(g)} \tag{12.1}$$

$$\Delta_r H \approx 3\Delta H(\mathrm{N-H}) \tag{12.2}$$

However the stepwise decomposition of the NH_3 molecule at 298 K proceeds as follows:

$$\mathrm{NH_3(g)} \overset{\Delta_r H_2^o}{\rightarrow} \mathrm{NH_2(g) + H(g)} \quad \Delta_r H_1^o = 435.1\ \mathrm{kJ\ mol^{-1}} \tag{12.3}$$

$$\mathrm{NH_2(g)} \overset{\Delta_r H_2^o}{\rightarrow} \mathrm{NH(g) + H(g)} \quad \Delta_r H_2^o = 376.6\ \mathrm{kJ\ mol^{-1}} \tag{12.4}$$

$$\mathrm{NH(g)} \overset{\Delta_r H_3^o}{\rightarrow} \mathrm{N(g) + H(g)} \quad \Delta_r H_3^o = 355.6\ \mathrm{kJ\ mol^{-1}} \tag{12.5}$$

from which we see that the individual $\Delta_r H^o$ values differ somewhat from one another, but average to 389 kJ mol^{-1} taken ΔH^o(N–H), of the N–H bond.

$NH_3(g)$ is formed by sp^3 hybrid bonds whereas $NH_2(g)$ is formed by sp^2 hybrids and thus the enthalpy in breaking the N–H bond in these two situations will not be the same. Accordingly an average is taken.

12.2 Typical Magnitudes for Bond Enthalpies, ΔH^o(X–Y)

Bond enthalpies range from of 146 kJ mol^{-1} for ΔH^o(O–O), one of the *weakest* bonds, through 628 kJ mol^{-1} for ΔH^o(B–F) which is one of the *strongest single* bonds, through 749 kJ mol^{-1} for a C=O bond to 1079 kJ mol^{-1} for ΔH^o(C≡O), one of the strongest bonds known. Table 12.1 cites other values.

Table 12.1 Typical bond enthalpies, ΔH^o(X–Y)/kJ mol^{-1}.

Bond, X–Y	**ΔH^o(X–Y)/ kJ mol^{-1}**	**Bond, X–Y**	**ΔH^o(X–Y)/ kJ mol^{-1}**
C–H	414	C–N	292
O–H	464	C–O	351
H–H	436	C=C, C=N	611
C–C, C–Si	347	N=N	456
N–N	161	O=O	498
F–F	153	P=P	351
Cl–Cl	243	N≡N	946
Br–Br	192	C≡C	837
H–Cl	431	P≡P	490

12.3 Use of Bond Enthalpy Data

This rather approximate bond enthalpy data has a number of important uses:

- to provide a scale of relative strengths of chemical bonds.

- in a similar way to standard enthalpy, $\Delta_f H^o$ and combustion, $\Delta_c H^o$ data, bond enthalpies can be used to estimate the enthalpy change, $\Delta_r H^o$ for reactions which exclusively involve *gaseous species*. In such cases:

$$\begin{aligned}\Delta_r H^o &\approx \Sigma\Delta H^o(\text{X–Y})_{\text{bonds broken}} - \Sigma\Delta H^o(\text{X–Y})_{\text{bonds formed}}\\ &\approx \Sigma\Delta H^o(\text{X–Y})_{\text{reactants}} - \Sigma\Delta H^o(\text{X–Y})_{\text{products}}\end{aligned} \tag{12.6}$$

Consider the gaseous hydrogenation reaction:

$$H_2(g) + C_2H_4(g) \overset{\Delta_r H^o}{\rightarrow} C_2H_6(g) \tag{12.7}$$

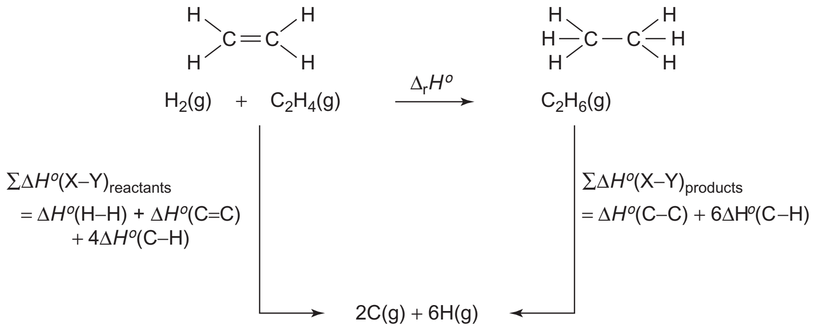
Experimentally:

$$\Delta_r H^o = \Delta_f H^o(C_2H_6, g) - \Delta_f H^o(C_2H_4, g) - \Delta_f H^o(H_2, g) = -137 \text{ kJ mol}^{-1} \tag{12.8}$$

Using bond enthalpies (Table 12.1), and equation (12.6)

$$\begin{aligned}\Delta_r H^o &\approx \Sigma\Delta H^o(\text{X–Y})_{\text{reactants}} - \Sigma\Delta H^o(\text{X–Y})_{\text{products}}\\ &\approx \Delta H^o(\text{H–H}) + \Delta H^o(\text{C=C}) - 2\Delta H^o(\text{C–H}) - \Delta H^o(\text{C–C}) \approx -118 \text{ kJ mol}^{-1}\end{aligned} \tag{12.9}$$

The error in the estimate is approximately 14%.



$$\begin{aligned}\Delta_r H^o &= \Sigma\Delta H^o(\text{X – Y})_{\text{reactants}} - \Sigma\Delta H^o(\text{X – Y})_{\text{products}}\\ &= \Delta H^o(\text{H–H}) + \Delta H^o(\text{C=C}) + 4\Delta H^o(\text{C–H}) - \Delta H^o(\text{C–C}) - 6\Delta H^o(\text{C–H})\\ &= \Delta H^o(\text{H–H}) + \Delta H^o(\text{C=C}) - \Delta H^o(\text{C–C}) - 2\Delta H^o(\text{C–H})\end{aligned}$$

Figure 12.1 Consideration of bond broken and bonds formed in reaction (12.7)

- If the reactions involve states other than gaseous ones then ancillary thermodynamic data has to be introduced in addition to the bond enthalpies.

  Consider the estimation of the standard enthalpy of formation of gaseous ethane, $\Delta_f H^o(C_2H_6, g)$ (known to be -84.667 kJ mol^{-1}). The target reaction is:

$$2C(\text{s, graphite}) + 3H_2(g) \xrightarrow{\Delta_f H^o(C_2H_6,g)} C_2H_6(g) \tag{12.10}$$

  which since it involves solid graphite means that equation (12.6) cannot be used directly and so needs some modification. The cycle given in Figure (12.2) can be employed, from which we see that:

$$\Delta_f H^o(C_2H_6, g) \approx 2\Delta_{\text{vap}} H^o(\text{C, s, graphite}) + 3\Delta H^o(\text{H–H}) - 6\Delta H^o(\text{C–H}) - \Delta H^o(\text{C–C}) \approx -89 \text{ kJ mol}^{-1} \tag{12.11}$$

returning an error of approximately 6%.

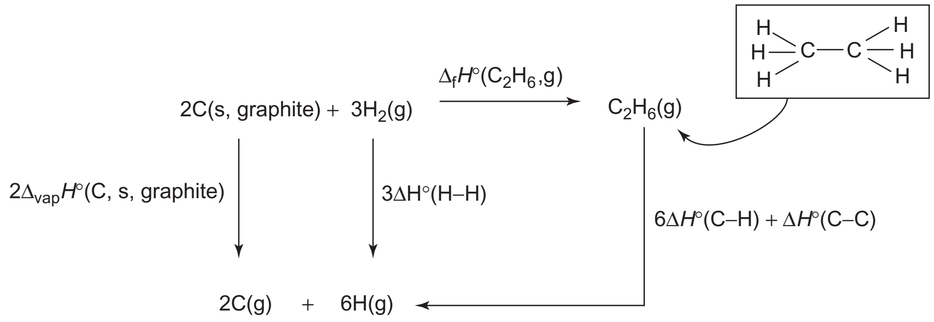


Figure 12.2 Thermochemical cycle used for reaction (12.10)

13. Spontaneity, Entropy and Gibbs Energy

13.1 Spontaneity revisited

When a volatile liquid (taken as the thermodynamic *system*) (Frames 1, 7) (say ether or alcohol) is applied to the skin (taken to be the *surroundings*) it rapidly and *spontaneously evaporates* (evidenced by a cooling sensation). Heat, $q_P = \Delta_{\text{vap}} H^o$ is *absorbed* from the skin by the ether during the evaporation process of the ether molecules:

$$\text{Et}_2\text{O(l)} \overset{\Delta_{\text{vap}} H^o}{\rightarrow} \text{Et}_2\text{O(g)} \tag{13.1}$$

(i.e. the system) which renders $\Delta_{\text{vap}} H^o > 0$ for the process since heat is added to the system.

Whilst, as we have seen (Equation (10.10), Frame 10), the enthalpy change, $\Delta_{\text{vap}} H^o$, which takes account of the need for the ether to evaporate and also to expand ($P\Delta V$) against the external atmospheric pressure, also involves an (internal) energy, ΔU, component and in this case it appears that, for this particular spontaneous process, this energy is *increasing*. At first sight this is counterintuitive since we might expect spontaneous processes to be only those that *lose* energy and end up with the energy curve reaching a minimum at equilibrium.

Certainly this should be true if *energy were the only driving force* determining whether reactions take place (i.e. are spontaneous) and the energy curve reached a minimum at equilibrium.

However, pursuing this idea further, this situation would further mean that only *exothermic* reactions (for which $\Delta H^o < 0$ and enthalpy is *lost* from the system) would be expected to proceed naturally (i.e. be spontaneous).

When we glance at the *evidence* below it appears that *energy change – in the form of enthalpy change – is not always the only driving force contributing towards a spontaneous process or reaction*.

- Although the *majority* of spontaneous reactions *are* exothermic and do lead to a decrease in the enthalpy there are a *minority* of *endothermic reactions* which are spontaneous* (see Note 13.1).
- A good example is the suite of thermal decomposition reactions. Heat is needed to begin the decomposition process (so that: $\Delta H > 0$) which accelerates as *temperature is raised*. A gas is often released during this process. A specific example might be a metal carbonate:

  $$\text{MCO}_3\text{(s)} \rightarrow \text{MO(s)} + \text{CO}_2\text{(g)} \tag{13.2}$$

  where M might be Ca or Mg, for example.
- Ammonium chloride crystals *spontaneously* dissolve in water and yet $\Delta H = +15.1$ kJ mol^{-1}:

  $$\text{NH}_4\text{Cl(s)} \overset{\text{H}_2\text{O(l)}}{\rightarrow} \text{NH}_4\text{Cl(aq)} \tag{13.3}$$

  The word *spontaneous* in this context is meant to convey the sense of the dissolution of the crystals in water proceeding without further intervention.
- We also find that some reactions *reverse their direction of spontaneity* under certain (changed) conditions, thus the reaction:

  $$2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)} \tag{13.4}$$

  takes place at *moderate temperatures* and is *enthalpy* driven by a *negative* (i.e. reducing) $\Delta H^o = -198.4$ kJ mol^{-1} where:

  $$\Delta H^o = 2[\Delta_f H^o(\text{SO}_3, \text{g}) - \Delta_f H^o(\text{SO}_2, \text{g})] \tag{13.5}$$

  recall (Frame 11) that:

  $$\Delta_f H^o(\text{O}_2, \text{g}) = 0\,\text{kJ}\,\text{mol}^{-1} \tag{13.6}$$

  whilst at very high temperatures the gaseous SO_3 *spontaneously* decomposes in the reverse direction:

  $$2\text{SO}_3\text{(g)} \rightarrow 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \tag{13.7}$$

  Reaction (13.4) is now reversed and ΔH (now reversed in sign) will no longer be exothermic but is now *endothermic* and hence positive (= +198.4 kJ mol^{-1}) and *so one concludes that other factors must be invoked and moreover, such factors could be influenced by the higher temperature T.*

Summarising then, these three examples suggest that whatever the driving force for spontaneity is, it must:

- involve factors *other than merely the sign of the enthalpy change*

and

- it is influenced by temperature

and

- there appear to be *at least two factors* involved which may, at least at times, *operate against each other*.

We now investigate a case where the driving force of enthalpy change is negligible. If we search the literature to find a compound whose standard enthalpy of formation, $\Delta_f H^o$ is close to zero, one example is silver (I) chlorite, $AgClO_2(s)$. If we examine its decomposition reaction in which it forms its elements in their standard states ($\Delta_f H^o$ for each of which is also zero), then the decomposition:

$$AgClO_2(s) \rightarrow Ag(s) + {}^1\!/_2Cl_2(g) + O_2(g) \tag{13.8}$$

will, by virtue of the above facts, have an overall ΔH^o given by:

$$\Delta H^o = [\Delta_f H^o(\text{Ag, s}) + {}^1\!/_2\Delta_f H^o(\text{Cl}_2, \text{g}) + \Delta_f H^o(\text{O}_2, \text{g}) - \Delta_f H^o(\text{AgClO}_2, \text{s})] \tag{13.9}$$

which is virtually zero, yet the decomposition of the material proceeds spontaneously (gently warming is all that is needed to start the kinetics of the decomposition off). The driving force here is no longer enthalpy change (since $\Delta H^o \approx 0$).

If we consider the series of endothermic reactions discussed above:

- in the case of the evaporating liquid ether or alcohol (reaction 13.1): *1 mole of gas is produced from 1 mole of liquid* during this spontaneous evaporation process;
- in the decomposition processes represented by reaction (13.2), *1 mole of gas* (*and 1 mole of solid – MO*) *is produced from 1 mole of* MCO_3;
- note that an aqueous solution of NH_4Cl does *not* spontaneously separate into solid NH_4Cl + pure water, even though $\Delta H = -15$ kJ mol^{-1} for the process and the enthalpy would accordingly be lowered;
- oxidation process (13.5) is *enthalpy* driven at lower temperatures since $\Delta H = -198.4$ kJ mol^{-1} although in the reverse reaction (which becomes spontaneous when the temperature T is high) *2 moles of gas are converted to 3 moles of gas* (i.e. an increase in 1 mole of gas);
- in process (13.9) *1 mole of solid decomposes to give* $2^1\!/_2$ *moles of gas* in a reaction which has no enthalpy change to drive it.

The conclusion here is clear:

- *firstly* in endothermic situations spontaneity appears to be favoured by the production of either gaseous molecules from condensed state (i.e. solid or liquid) molecules *or* else by production of a solution (in this case $NH_4Cl(aq)$, equating to NH_4^+ and Cl^- ions moving in solution) from the *more ordered* solid NH_4Cl. Thus in the endothermic reactions:

  (13.2): 1 mole of solid → 1 mole of solid + 1 mole of gas.
  (13.4): 1 mole of solid + ∞ moles of liquid → 1 mole of aqueous ions (NH_4^+ and Cl^-).
  (13.8): 2 moles of gas → 3 moles of gas.
  (13.9): 1 mole of solid → 1 mole of solid + $1^1\!/_2$ mole of gas.

  Recognising that solids – having defined crystal structures defining the ordered atomic arrays present – are more ordered than either aqueous solutions (or liquids) or gases (in which the molecules or ions rapidly move around), we can therefore equate one driving force for spontaneity to be *associated with* an *increase* in the *degree of disorder* which can be brought about during the given process. These factors will be supplementary to and in addition to enthalpy/energy factors.
- *secondly*, in the example reactions discussed (13.4) and (13.7), when the spontaneity of a reaction is *reversed*; temperature is observed to play a part. Reaction (13.4) is *enthalpy* driven by $\Delta H = -198.4$ kJ mol^{-1}, whereas reaction (13.8) (for which $\Delta H > 0$) occurs because temperature increase enhances the importance of this second factor associated with increased disorder – *entropy* – and leads to an increase in the number of molecules of gas produced.

13.2 Entropy, *S* and Gibbs (free) energy, *G*, functions

Suppose now that we decide to combine a *second factor*, in addition to the enthalpy change, ΔH^o in the search for an *overall parameter (G)* the change in which (ΔG^o) will indicate to us whether a given reaction or process *is likely to take place spontaneously*. Suppose we call this second factor, the *entropy* change (ΔS^o) which will be based on the change in a function defined as entropy (S). Then, from the evidence above, it seems likely that:

- ΔS must be related to an increase in randomness or molecular disorder since in all the cases discussed where $\Delta H \geq 0$ the molecular state of the reaction products was more disordered than the reactants from which they were spontaneously formed;
- enthalpy and entropy factors (ΔH^o and ΔS^o) will work against one another and therefore *should have opposite signs*;
- entropy change (ΔS) will be linked to the *production of less ordered* gaseous molecules from more ordered condensed state *molecules and will favour spontaneity* more when the former are produced as product;
- at higher temperatures, the importance of ΔS *as a second factor* is more likely to be enhanced and thus it should be *introduced in the form* $T\,\Delta S$.

It emerges from thermodynamics that the *overall thermodynamic criterion for spontaneity* is vested in a quantity defined as the *Gibbs (free) energy* change, ΔG which, for an isothermal (Frame 1) process, is defined by the equation:

$$\Delta G = \Delta H - T\Delta S \tag{13.10}$$

or, more fundamentally:

$$G = H - TS \tag{13.11}$$

Equations (13.10) and (13.11) are able to rationalise all of the observations made above, provided that we associate a decrease in ΔG (i.e. $\Delta G < 0$) for a reaction with spontaneity. This driving force will *cease* once:

$$\Delta G = 0 \tag{13.12}$$

and gives rise to a state of equilibrium for the process when no further reaction (process) will then take place.

In the reaction (13.2) above the solid metal carbonate decomposes *spontaneously* into solid calcium oxide and gaseous carbon dioxide, the Gibbs energy change, ΔG, for the reaction will be negative and in this case – *because the products are separated from themselves and from the starting material* – this decomposition reaction will proceed *to completion*.

However in contrast to this, in a case where reactants and products are all together *in one single phase* (say, in the gaseous phase or in aqueous solution) no equivalent separation of reactants and products is possible. Talking about this reaction *going to completion* would be misleading since an equilibrium with reactant(s) and product(s) present is almost always the result, even though ΔG might, in this case, be negative also.

All ΔG can actually tell us is (via equations like (41.12), Frame 41), what the equilibrium constant, $K_{\mathrm{p/p_o}}$ (see Frame 0) is for the reaction and this in turn enables us to specify the amounts of the individual species present at equilibrium.

In equation (13.10) when $\Delta G = 0$ then:

$$\Delta H - T\Delta S = 0 \tag{13.13}$$

which rearranges to give:

$$\Delta S = \frac{\Delta H}{T} \tag{13.14}$$

In situations where ΔH *can* be equated to q (e.g. at constant pressure (Frame 10, Equation (10.9)) then we can write:

$$\Delta S = \frac{q_{\mathrm{rev}}}{T} \tag{13.15}$$

where q is specified to be q_{rev} in recognition of the fact that equation (13.15), from which equation (13.16) is derived, applies only to a state in equilibrium.

Equation (13.15) is analogous to our earlier equation (2.27), Frame 2, relating to the Second Law of Thermodynamics. The argument above should not, however, be regarded as a *proof* of the Second Law equation but rather regarded as a convienient further introduction of the same idea.

We have seen earlier (Section 6.3, Frame 6) that conditions once they are imposed carry forward and apply to the final equations of a derivation. We will investigate the nature of this relationship further in the next frame.

13.3 Equation for the Calculation of Entropy, *S*. Second Law of Thermodynamics

From above we see that a change in entropy, ΔS is related (for $\Delta S > 0$) to the heat ($= q_{\mathrm{rev}}$) added to a thermodynamic system under equilibrium (i.e. $\Delta G = 0$) conditions (i.e. reversibly – since the conditions for a reversible change are the same as those for a state of equilibrium) divided by the absolute temperature, T (measured in Kelvin). Thus for smaller changes in entropy, $\mathrm{d}S$ we can write:

$$\mathrm{d}S = \frac{q_{\mathrm{rev}}}{T} \tag{13.16}$$

This equation can be regarded as a quantitative form of the *Second Law of Thermodynamics*. Note: Should we need to integrate this expression, since $\int \delta q = q$ (Frame 2, equation (2.26)) then equation (13.16) can be written:

$$\int_{S_{\mathrm{i}}}^{S_{\mathrm{f}}} \mathrm{d}S = [S]_{S_{\mathrm{i}}}^{S_{\mathrm{f}}} = [S_{\mathrm{f}} - S_{\mathrm{i}}] = \Delta S = \int \frac{\Delta q_{\mathrm{rev}}}{T} = q_{\mathrm{rev}}/T \tag{13.17}$$

which is equivalent to equation (13.15).

Entropy and the Second Law of Thermodynamics (Frame 2) provide us with a way of deciding whether a given process or reaction is spontaneous.

Clausius' statement of the Second Law took the form: "*Die Entropie der welt strebt einem maximum zu*" = *The entropy of the universe tends towards a maximum* and applies to an *isolated* system.

Thus, when considering entropy changes we have to consider changes in *both* the system (ΔS_{system}) and the surroundings ($\Delta S_{\text{surroundings}}$), the sum of these being equal to the entropy change of the universe ($\Delta S_{\text{universe}}$).

Another (alternative) statement of the Second Law is that for an isolated system:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} \geq 0 \qquad (13.18)$$

where the $>$ sign applies to a spontaneous or natural process for which ΔS_{total} is positive and the $=$ sign applies to a process at equilibrium (i.e. one which is reversible).

Unlike energy (First Law) (Frame 1, 2, 8) which cannot be created nor destroyed (i.e. is conserved) in contrast, entropy is *constantly increasing* as a result of the occurrence of the natural spontaneous processes which are continually taking place.

14. Entropy and Second Law The Equivalence of the Criteria, $\Delta G_{\text{system}} < 0$ and $\Delta S_{\text{universe}} > 0$ to Judge the Spontaneity of Processes

14.1 Entropy Changes – Further Matters

Before we go on to calculate entropy changes for specific processes there are three matters which have been raised that we need to further expand upon.

These are:

- the question as to what extent (if at all) we need to consider the entropy change of the *surroundings* during routine calculations of the overall entropy change for thermodynamic systems;
- why the $\Delta G < 0$ condition (which only requires us to consider the thermodynamic system and not the surroundings) is equivalent to the condition $\Delta S_{\text{universe}} > 0$ (which requires (Frame 13, equation (13.18)) one to consider the entropy change of both the system *and* its surroundings) for spontaneity of reactions and processes

and

- to investigate further the requirement to use q_{rev} in equations (13.15), (13.16) and (13.17), Frame 13 when calculating the change in entropy of a system.

14.2 Entropy Changes in Surroundings and the System

We saw in Frame 13, section 13.3 that:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} \geq 0 \qquad (13.18)$$

This condition indicates that *spontaneous processes* are accompanied by an overall increase in the total entropy, $\Delta S_{\text{universe}}$.

Also from Frame 13 we have an equation for calculating entropy change in the form:

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad (13.15)$$

We can also use this equation to calculate $\Delta S_{\text{surroundings}}$ of the surroundings if we use the subterfuge of regarding the surroundings as our thermodynamic system. We can do this for the cases of both an endothermic and an exothermic reaction. Since these *surroundings* are defined (Frame 1, 7) as being the rest of the universe (i.e. *outside the thermodynamic system*) and since they are vast we can regard them as having a constant temperature, T^* (usually ambient) and as acting as a heat sink. The surroundings (for the moment now being regarded as the system) can also be regarded as being at a constant pressure (usually atmospheric), P at any given instant* (see Note 14.1). Thus any heat transfer, q_P either to or from the surroundings takes place at constant pressure and (Frame 10) can equally well be regarded as being related to the corresponding enthalpy change, ΔH, taking place, which being a state function can be regarded as a heat transfer under reversible conditions (since the change will be the same either for a reversible or an irreversible process).

14.3 Exothermic and Endothermic Reactions

Consider first an *exothermic* reaction for which $\Delta H_{\text{system}} < 0$ (i.e. negative), the heat absorbed by the surroundings, $q_{\text{surroundings}}$, treated now as our *system* (and using the Acquisitive Convention as previously described, Frame 7) will be regarded as being positive and will be equal to $-\Delta H_{\text{system}}$ (which is then a positive quantity). Thus:

$$q_{\text{surroundings}} = -\Delta H_{\text{system}} > 0 \qquad (14.1)$$

and since this heat, which is supplied to the surroundings, will increase the degree of disorder in the molecules of the surroundings then:

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} = -\Delta H_{\text{system}}/T > 0 \qquad (14.2)$$

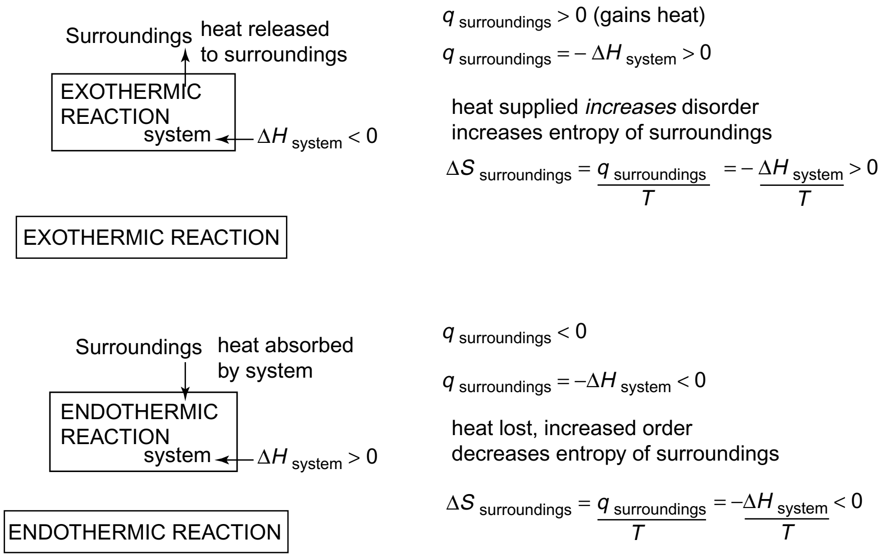


Figure 14.1 Exothermic and endothermic reactions and the estimation of $\Delta S_{\text{surroundings}}$.

at temperature, T and hence rearranging the equalities in equation (14.2) we have:

$$\Delta H_{\text{system}} = -T\Delta S_{\text{surroundings}} \tag{14.3}$$

Alternatively, consider now an *endothermic* reaction for which $\Delta H_{\text{system}} > 0$ (i.e. positive), the heat *now lost* from the surroundings, $q_{\text{surroundings}}$, which will be treated as being negative (since we are treating the surroundings as our system, for the moment) and will be equal to $-\Delta H_{\text{system}}$ (which is a negative quantity), thus we have:

$$q_{\text{surroundings}} = -\Delta H_{\text{system}} < 0 \tag{14.4}$$

and since this heat lost from surroundings will now *decrease* the degree of disorder in the molecules of the surroundings then:

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}}{T} = \frac{q_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} < 0 \tag{14.5}$$

and hence again rearranging, we can write an equation which is equivalent to equation (14.3):

$$\Delta H_{\text{system}} = -T\Delta S_{\text{surroundings}} \tag{14.3}$$

Since for a thermodynamic *system*, q_{rev} is the heat added reversibly, then:

$$\Delta S_{\text{surroundings}} = \frac{-q_{\text{rev}}}{T} \tag{14.6}$$

Substituting equation (14.6) into equation (13.18) we have:

$$\Delta S_{\text{system}} - \frac{q_{\text{rev}}}{T} \geq 0 \tag{14.7}$$

and hence, rearranging the inequality, that:

$$\Delta S_{\text{system}} \geq \frac{q_{\text{rev}}}{T} \tag{14.8}$$

where q_{rev} is the heat absorbed by the system at temperature T and the *inequality* in (14.8) applies to irreversible (i.e. naturally occurring) processes whilst the *equality* in (14.8) applies to reversible processes and the latter can then be written as in equations (13.15) or (13.16), Frame 13.

Reversible processes do not occur in nature and, in any case, as we have seen (Frame 9) they would take an infinite amount of time for completion. They rather represent the limit of irreversible changes much as in the case of the gas expansion discussion (Frame 9) when maximum work was involved at this limit of reversibility.

14.4 Criteria of Spontaneity Revisited

For a system at equilibrium then (from equation 13.15, Frame 13):

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} \tag{13.15}$$

and as equation (13.15) shows we can calculate entropy changes for systems *without reference to the entropy change of the surroundings.* Frame 15 shows examples where such a procedure is used.

Further, since (from Frame 13, equation (13.10)):

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} \tag{14.9}$$

Then using equation (14.3) derived for both exo- and endothermic cases and substituting for ΔH_{system} in equation (14.9), leads to:

$$\begin{aligned}\Delta G_{\text{system}} &= -T\Delta S_{\text{surroundings}} - T\Delta S_{\text{system}} \\ &= -T[\Delta S_{\text{surroundings}} - \Delta S_{\text{system}}] \\ &= -T[\Delta S_{\text{universe}}] \qquad (14.10)\end{aligned}$$

Thus the latter equation: $\Delta G_{\text{system}} = -T[\Delta S_{\text{universe}}]$ shows how the two criteria which can be used to assess the thermodynamic spontaneity of reactions or processes are *basically identical* since if:

$$\Delta G_{\text{system}} < 0 \qquad (14.11)$$

then automatically:

$$\Delta S_{\text{universe}} > 0 \quad \text{since } T > 0 \qquad (14.12)$$

This addresses the question raised in section 14.1 as the second bullet point.

The former condition being easier to use than the latter since it only involves calculating the thermodynamic parameters just for the chosen system alone is generally adopted and is used for the thermodynamic study of most systems we shall encounter here. The latter approach, involving condition (14.12), requires evaluation of ΔS_{system} for the system *and* $\Delta S_{\text{surroundings}}$ for the surroundings.

We look at the two formats further below.

14.5 Equilibrium Conditions

It is also true, from equation (14.10) that the equilibrium condition:

$$\Delta G_{\text{system}} = 0 \qquad (14.13)$$

corresponds to:

$$\Delta S_{\text{universe}} = 0 \qquad (14.14)$$

14.6 Endothermic and Exothermic Reactions Evaluated using the $\Delta G_{\text{system}} < 0$ (Equation (14.11)) Criterion

An *endothermic* reaction has $\Delta H_{\text{system}} > 0$ so that since (Frame 13):

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} \qquad (14.15)$$

- if $\Delta S_{\text{system}} < 0$ then the reaction will not be spontaneous, since $\Delta G_{\text{system}} > 0$;
- if $\Delta S_{\text{system}} > 0$ then the reaction can be spontaneous if the $T\Delta S_{\text{system}}$ term (which is negative) is greater than the ΔH_{system} (positive) term

An *exothermic* reaction has $\Delta H_{\text{system}} < 0$ so that:

- if $\Delta S_{\text{system}} < 0$ then the reaction will not be spontaneous if the ΔH_{system} (negative) term is greater than the (positive) $T\Delta S_{\text{system}}$ term.
- if $\Delta S_{\text{system}} > 0$ then the reaction will always be spontaneous since both the ΔH_{system} and the $T\Delta S_{\text{system}}$ term will be negative.

14.7 Endothermic and Exothermic Reactions Evaluated using $\Delta S_{\text{universe}} > 0$ (Equation (14.12)) Criterion

An *endothermic* reaction has $\Delta S_{\text{surroundings}} < 0$ (see above) so that since (Frame 13, equation (13.18)):

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \qquad (14.16)$$

- if $\Delta S_{\text{system}} < 0$ the reaction will not be spontaneous, since $\Delta S_{\text{universe}}$ can never be positive;
- if $\Delta S_{\text{system}} > 0$ then provided that ΔS_{system} can overcome the decrease in $\Delta S_{\text{surroundings}}$ the reaction will be spontaneous, otherwise it will not be spontaneous.

An *exothermic* reaction has $\Delta S_{\text{surroundings}} > 0$ (see above) so that:

- if $\Delta S_{\text{system}} < 0$ then the reaction will be spontaneous provided that $\Delta S_{\text{surroundings}}$ can overcome the decrease in ΔS_{system}, otherwise it will not be spontaneous.
- if $\Delta S_{\text{system}} > 0$ then the reaction will always be spontaneous since both $\Delta S_{\text{surroundings}}$ and ΔS_{system} are positive quantities.

It should be noted that *both sets of criteria lead to the same conclusions* and that those given in section 14.6 which are more convienient – since surroundings do not have to be considered at all – should normally be used.

Later on, in section 18.4, Frame 18, we shall return to the above considerations albeit briefly in order to show that similar conclusions to those in this Frame can be reached using an alternative approach which shows that once we have established equation (14.8) above we can further establish that:

- the change in free energy needs to be less than zero for a spontaneous process

and

- $\Delta S_{\text{surroundings}} > 0$

from an alternative standpoint (i.e. that of equation (18.5), Frame 18).

15. Calculation of Entropy

In the previous Frames 13 and 14, we have established that:

- In order to calculate the entropy change for a process we only usually need consider the ΔS for the system (for a processes near equilibrium) and use the equation:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{13.15}$$

for reversible processess taking place at constant temperature and the equation:

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T} \tag{15.1}$$

for reversible processes in which the entropy change is much smaller.

- The above measure of the entropy change for a process calculates ΔS from the heat, q_{rev} that *would be* absorbed *if* the process *had been carried out under reversible conditions* divided by the absolute temperature, T at which that change takes place.

We now proceed to illustrate the practical calculation of ΔS in a number of specific cases.

15.1 Calculation of Entropy Change, ΔS, for Reversible Expansion Process

Suppose we consider now the process of *reversible* expansion of an ideal gas at constant temperature, T (Figure 15.1) for which (Equation (4.2), Frame 4):

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = 0^{*} \text{ (see Note 15.1)} \tag{15.2}$$

where the internal energy, U, is unaltered (i.e. $\Delta U = 0$) by an expansion process and for which (First Law) then:

$$q_{\text{rev}} = -w_{\text{rev}} \tag{15.3}$$

and thus any heat supplied to the system is used in its entirety to perform the work of expansion and force the frictionless piston (Figure 15.1) to move outwards. Thus:

$$q_{\text{rev}} = -w_{\text{rev}} = nRT\ln\frac{V_{\text{f}}}{V_{\text{i}}} \tag{15.4}$$

where V_{i} is the initial volume and V_{f} , the final volume (Equation (9.6), Frame 9). Equation (15.2) has been established here only from consideration of molecular forces and the properties of an ideal gas but it can be obtained directly from classical thermodynamic arguments (see more advanced texts).

Suppose that in a second experiment the piston is no longer frictionless, again the temperature is constant, now to achieve the same expansion *more* heat will be needed to overcome the frictional forces which oppose the expansion. So here $q > q_{\text{rev}}(q = q_{\text{rev}} + q')$ but the work performed *will be the same for the expansion process*. q_{rev} is a particular value of the heat absorbed by the gas and it is only this value which defines the entropy change, ΔS. This shows, as was seen in Frame 1, that q and w depend on the specific parameters of the *experiment* or *path* and are not state functions in contrast to the entropy change, ΔS.

In a third experiment, the initial conditions of V_{i}, P_{i} for the ideal gas and its temperature, T are identical to those in the first two experiments. This time no heat is supplied (corresponding to an adiabatic process, $q = 0$) and a shutter is lowered in front of the moveable (frictionless) piston, after which the pressure on the piston is adjusted to, P_{f}, the same pressure that was experienced at the end of the two previous experiments. The air in the voidage between shutter and piston is now evacuated creating a vacuum, after which the shutter is withdrawn and the gas expands irreversibly. The work done is now:

$$w_{\text{irr}} = -P(V_{\text{f}} - V_{\text{i}}) = -P\Delta V \tag{15.5}$$

However the change in entropy, ΔS, will be independent of whether the gas is expanded reversibly or irreversibly since the initial (V_{i}, P_{i}, T) and final (V_{f}, P_{f}, T) states of the system are *identical* in all three experiments (reversible *and* irreversible expansions) and the entropy is given, in each case, by:

$$\Delta S = \frac{q_{\text{rev}}}{T} = \left[\frac{nRT\ln V_{\text{f}}}{V_{\text{i}}}\right]\Big/ T = nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right) \tag{15.6}$$

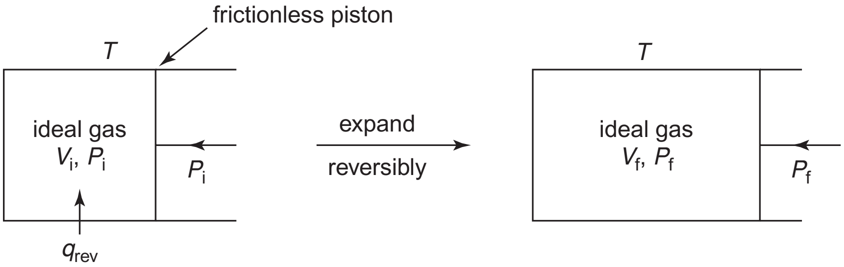


Figure 15.1 Reversible expansion process for an ideal gas.

Reiterated, any measure of the entropy change for a process is the heat that *would be* absorbed *if* the process *had been carried out under reversible conditions* divided by the absolute temperature at which that change takes place.

Entropy change, being identical for both reversible and irreversible changes, means that it cannot usefully be employed in most cases to investigate equilibria and the reliance on ΔG (Frame 13, 39, 40, 41, 43, 45, 46, 47, 49) is a much more satisfactory strategy.

15.2 Calculation of the Entropy Change, ΔS, on Isothermal (i.e. d$T = 0$) Expansion of a Gas

We have already considered this calculation in section 15.1 above since equation (15.6) applies and:

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{-w_{\text{rev}}}{T} = \left[nRT\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)\right]\Big/T = nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)^{\dagger} \quad \text{(see Note 15.2)} \tag{15.6}$$

This relationship is correct for both reversible and irreversible expansion processes. Also since for an amount n of an ideal gas (Frame 9):

$$P = \frac{nRT}{V} \tag{15.7}$$

and therefore at constant temperature; P is proportional to $1/V$ then equation (15.6) can also take the form:

$$\Delta S = nR\ln\left(\frac{P_{\text{i}}}{P_{\text{f}}}\right) = -nR\ln\left(\frac{P_{\text{f}}}{P_{\text{i}}}\right) \tag{15.8}$$

15.3 Calculation of the Entropy Change ΔS, for Phase Transitions at Constant Temperature, T and Pressure, P

A phase transition occurs (Frames 17–26) when for example: a solid melts to form a liquid: (s) → (l) at its melting point, T_{m}, or a liquid is vaporised to a gas: (l) → (g) at its boiling point, T_{b}, or a solid sublimes to a vapour: (s) → (g) at its sublimation temperature, T_{sub}.

The entropy of the phase transition, $\Delta_{\text{trans}}S$, taking place *at a fixed temperature*, can be calculated using equation (13.14), Frame 13 and since pressure is constant $q_{\text{rev,P}} = \Delta H$ for the process (Frame 10). ΔH being a state function, the enthalpy of transition, $\Delta_{\text{trans}}H$ will be identical both for reversible and irreversible changes, so that:

$$q_{\text{rev}} = q_{\text{rev,P}} = \Delta H = \Delta_{\text{trans}}H \tag{15.9}$$

and the corresponding entropy of transition will be given by:

$$\Delta_{\text{trans}}S = \frac{\Delta_{\text{trans}}H}{T_{\text{trans}}} \tag{15.10}$$

More specifically for the three transitions mentioned above:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{m}}};\ \Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_{\text{b}}};\ \Delta_{\text{sub}}S = \frac{\Delta_{\text{sub}}H}{T_{\text{sub}}} \tag{15.11}$$

15.4 Calculation of the Entropy Change ΔS, during a Temperature Change from T_{i} to T_{f} at Constant Pressure (d$P = 0$)

In this case the temperature is *not* held constant but changes from T_{i} to T_{f} during a process. A practical example here might be the entropy increase caused by boiling water at constant pressure. The equation (15.1) is now used since integration is necessary in order to take account of the gradual change taking place in the temperature. The *entropy* change, ΔS, required to raise the temperature of 1 mole of water from T_i to T_f at constant pressure is given (using equation (13.16), Frame 13) by:

$$\Delta S = \int_{S_i}^{S_f} dS = \int_{S_i}^{S_f} \frac{\delta q_{rev}}{T} \tag{15.12}$$

and since (Frame 10, equation (10.14)):

$$dq = \delta q = dH = C_p.dT \tag{15.13}$$

then

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{15.14}$$

Since the heat supplied, dq at constant pressure, P is equal to the change in enthalpy, dH, which is itself a state function – and is therefore identical for both reversible *and* irreversible processes – hence we can write:

$$dq_{rev} = \delta q_{rev} = dH = C_p.dT \tag{15.15}$$

and, substituting in equation (15.12) we have:

$$\Delta S = \int_{S_i}^{S_f} dS = \int_{S_i}^{S_f} \frac{\delta q_{rev}}{T} = \int_{T_i}^{T_f} \left[\frac{C_p}{T}\right].dT \tag{15.16}$$

which can take two forms, depending on whether we are able to assume C_p to be constant over the temperature range T_i to T_f, in which case either:

- $$\Delta S = \int_{T_i}^{T_f} \left[\frac{C_p}{T}\right] \cdot dT = C_{p.} \int_{T_i}^{T_f} \frac{dT}{T} = C_p \cdot [\ln T]_{T_i}^{T_f} = C_p \cdot \ln\left(\frac{T_f}{T_i}\right) \tag{15.17}$$

when C_p is constant, or

- $$\Delta S = \int_{T_i}^{T_f} \left[\frac{C_p}{T}\right].dT \tag{15.18}$$

The latter equation means that the entropy change, ΔS, is equal to the area under the curve when C_p/T is plotted versus T (Frame 2, section 2.3).

15.5 Calculation of the Entropy Change ΔS, during a Temperature Change from T_i to T_f at Constant Volume (d$V = 0$)

Similar expressions are applicable to processes in which the temperature change from T_i to T_f is made under conditions of constant volume, (d$V = 0$), in which case (Frame 10, equation (10.13)) since:

$$C_v = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{15.19}$$

then C_v simply replaces C_p in the expressions above, leading to:

$$\Delta S = \int_{T_i}^{T_f} \left[\frac{C_v}{T}\right].dT = C_{v.} \int_{T_i}^{T_f} \frac{dT}{T} = C_v.[\ln T]_{T_i}^{T_f} = C_v.\ln\left(\frac{T_f}{T_i}\right) \tag{15.20}$$

when C_v is constant over the temperature range T_i to T_f, or

$$\Delta S = \int_{T_i}^{T_f} \left[\frac{C_v}{T}\right].dT \tag{15.21}$$

15.6 Calculation of the Entropy Change ΔS, for More Complicated Processes

For processes more complicated than those described above the usual procedure is to break down these processes into a series of steps corresponding to the individual processes of the type discussed in sections 15.1 to 15.5 above.

Thus if we need to consider the entropy change involved in heating a substance from a temperature T_1 to another temperature T_2, and at an intermediate temperature T – lying between T_1 and T_2 (i.e. $T_1 < T < T_2$) – the substance changes its phase, then we can invoke two of the steps above (i.e. those described in sections 15.3 and 15.4) to write the expression for the overall change in entropy, ΔS, thus:

$$\Delta S = \int_{T_i}^{T} \left[\frac{C_p}{T}\right].\mathrm{d}T + \left[\frac{\Delta H_{trs}}{T}\right] +. \int_{T}^{T_2} \left[\frac{C_p}{T}\right]\mathrm{d}T \tag{15.22}$$

15.7 Calculation of the Entropy Change, ΔS, for Individual Reactions

In the case of reactions, as opposed to processes, in order to calculate ΔS we can use standard absolute entropies or standard entropies of formation derived from thermochemical tables.

- **Using standard absolute molar entropy data, S^o**: Equation (11.10) applies.
- **Using standard entropy of formation data, $\Delta_f S^o$**: Equation (11.9) applies.

16. The Third Law of Thermodynamics

16.1 The Third Law of Thermodynamics

Entropy, S, for a compound is, increased as the physical state of the substance becomes more disordered. Conversely, when matter becomes more organised, entropy will be reduced.

In the limit the *Third Law of Thermodynamics* comes into play which states that:

- if *at the absolute zero of temperature*, $T = 0$ K we have a *truly 'perfect' crystal* in which all atoms are identical and reside on their lattice points,

and

- there are no imperfections present within the crystal lattice
- then the absolute entropy of the crystalline solid will be zero, i.e.

$$S^o(0\,\mathrm{K}) = 0 \tag{16.1}$$

From Frame 15 and equation (15.18) the *entropy difference*, $\Delta S (= S_{T_2} - S_{T_1})$, *for 1 mole of substance* undergoing a temperature change between, T_1 and T_2, and under constant pressure, then, assuming that no phase change(s) take place, will be given by:

$$\Delta S = \int_{S_{T_1}}^{S_{T_2}} \mathrm{d}S = [\mathrm{S}]_{S_{T_1}}^{S_{T_2}} = S^o(T_2) - S^o(T_1) = \int_{T_1}^{T_2} \left[\frac{C_\mathrm{p}}{T}\right].\mathrm{d}T \tag{16.2}$$

16.2 Absolute Scale of Entropies. Absolute Standard Entropy, $S^o_{298\mathrm{K}}$

In equation (16.2) if we now:

- make the *lower* of these temperatures equal to the absolute zero of temperature (i.e. $T_1 = 0$ K);
- assume a *constant pressure* corresponding to $P = P^o = 1$ bar;
- assume the *Third Law of Thermodynamics* (equation (16.1)) applies

then equation (16.2) takes in the form:

$$S^o(T_2) - S^o(0\,\mathrm{K}) = S^o(T_2) = \int_0^{T_2} \left[\frac{C_\mathrm{p}}{T}\right].\mathrm{d}T \tag{16.3}$$

Further, if:

- T_2 is now put equal to 298.15 K;
- $S^o(T_2)$ then becomes equal to the *standard entropy*, $S^o (= S^o(298\ \mathrm{K}))$ at a $T = 298$ K and $P^o = 1$ bar.

from which we see that entropy absolute values are always going to be positive.

We have therefore used the Third Law of Thermodynamics to define *absolute zero* for a scale of standard entropy, thus:

$$S^o_\mathrm{m}(298\ \mathrm{K}) = \int_0^{298} \left[\frac{C_\mathrm{p}}{T}\right].\mathrm{d}T \tag{16.4}$$

Absolute standard molar entropy values, $S^o_\mathrm{m}(298\ \mathrm{K})$ can be provided. They are tabulated at 25 °C and for $P^o = 1$ bar pressure. It should be noted from equation (16.4) that the values are *absolute* entropy values (in contrast to values of $\Delta_\mathrm{f}H^o$ and $\Delta_\mathrm{f}G^o$ values which are quoted as differences (i.e. relative values) in thermochemical tables (Frame 11, section 11.2)).

A typical profile of a curve of C_p/T plotted versus T for a substance remaining solid and undergoing no phase transitions (changes in crystalline form) or phase changes (to a liquid, for example) is shown in Figure 16.1 and the area under this curve will be equal to the standard entropy, S^o_{298} at 298 K. (Frame 2, section 2.3 and Frame 10, section 10.4).

In many (and probably most) cases, phase changes may occur between $T = 0$ K and 298 K, as for example in the case of a gas at 298 K and having therefore undergone at least one or more solid → liquid and liquid → gas phase transitions between 0 K and 298 K. In such a case the absolute standard entropy of the gas will be given (adapting equation (15.22), Frame 15) by:

$$\Delta S = \int_0^{T_m} \left[\frac{C_p(s)}{T}\right].dT + \left[\frac{\Delta H_{fus}}{T_m}\right] +. \int_{T_m}^{T_b} \left[\frac{C_p(l)}{T}\right] dT + \left[\frac{\Delta H_{vap}}{T_b}\right] +. \int_{T_b}^{298.15} \left[\frac{C_p(g)}{T}\right] dT \tag{16.5}$$

where $C_p(s)$, $C_p(l)$ and $C_p(g)$ are the heat capacities of the solid, liquid and gaseous phases and T_m and T_b are the melting and boiling points. Phase changes *within* the solid state can also be experienced but are not considered above. The general nature of phase changes, how they arise and how they are predictable, using thermodynamics, will be considered in the later Frames 18–24.

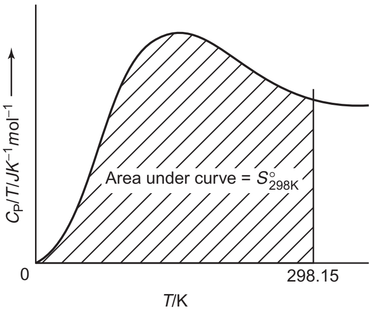


Figure 16.1 Plot of C_p/T versus T for a solid stable up to 298 K with no change of phase.

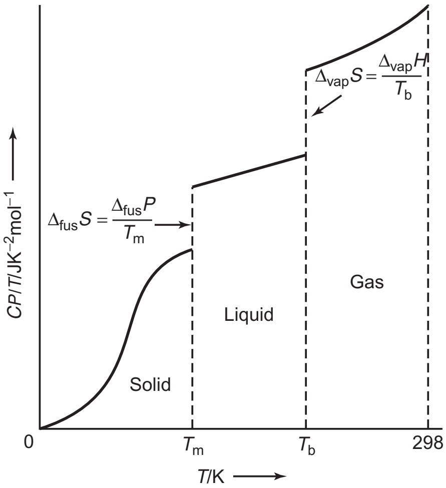


Figure 16.2 Plot of C_p/T versus T for substances undergoing phase changes at T_m (melting) and T_b (boiling) between 0 K and 298 K. Area under the plot $+\Delta_{fus}S + \Delta_{vap}S = S^o_{298}$ (substance, g).

16.3 Practicalities of Determining Entropy Values, S^o_T

The absolute zero of temperature *cannot* be reached experimentally (although C_p for a few solids have – exceptionally – been measured as low as 0.05 K). Crystalline solids are sometimes *not entirely* devoid of lattice imperfections.

Even though the Third Law of Thermodynamics, as expressed in equation (16.1) may not hold *precisely*, the entropy of solid materials close to $T = 0$ K becomes *extremely small* and the use of clever extrapolation techniques, (Frame 3, section 3.2) ensures that reasonably accurate values of S^o_T can usually be obtained.

These '*Third Law Entropies*' can, in any case, be checked and tested using alternative measurements of entropy. Examples are:

- equilibrium constants, K_{p/p_o} measured over temperature ranges yield values of ΔS^o (and ΔH^o) (see Frames 46, 48 and 49)
- electrochemical cells where the cell potential is measured over a range of temperature

and

- spectroscopic techniques

16.4 Exceptions to the Third Law of Thermodynamics

S^o(298 K) for N_2O, as experimentally determined from C_p/T measurements is some 6 J K^{-1} mol^{-1}smaller than the spectroscopically derived result. This *residual* entropy arises from the fact that the true crystal lattice contains units arranged both as NNO as well as ONN close to the absolute zero of temperature. This *residual disorder* therefore contrasts with the perfectly ordered arrangement of either NNO NNO or ONN ONN which would satisfy requirements of perfect order at 0 K.

A smaller but entirely similar effect is found in the carbon monoxide, CO, lattice at 0 K and this material displays a residual entropy of 4.5 J K^{-1} mol^{-1}. This case is discussed in Frame 17, section 17.1.

The hydrogen bonding present in solid ice, $H_2O(s)$ near the absolute zero of temperature leads to the existence of two kinds of bonding of the hydrogen atom to the oxygen atom. These covalently and hydrogen bonded atoms find themselves randomly arranged in the low temperature lattice and therefore again a degree of disorder is manifested.

Isotopic disorders (e.g. in solid chlorine atoms ^{35}Cl and ^{37}Cl isotopes can arise) and nuclear spin degeneracy (*ortho* and *para* hydrogen) are two rather less important factors which can also give rise to residual disorder in solids at 0 K.

Such effects, being at the electronic or nuclear level, will often arise both in reactant and product within the particular reactions being studied and therefore to a large extent may cancel out in practical calculational usage.

The Third Law of Thermodynamics:

- is rather less general than the other laws of thermodynamics

and

- applies to a specific class of material (that of perfectly crystalline solids).

17. The Statistical Definition of Entropy

17.1 Boltzmann and Entropy

Imagine a large trough of clean water at a fixed temperature located in an area free of draughts and other spurious effects. Into this water, using a dropper (or pipette) *into one corner of the trough*, we carefully place a few drops of *intensely coloured* dye, taking care not to cause ripples or disturbance of the water. Experience dictates that on returning several hours later, we find that, despite there being no aquatic currents present, the dye will have begun to disperse into the larger volume of the water.

This represents a manifestation of the second driving tendency described in Frame 13, section 13.2 and observed in nature – namely, the tendency to achieve increased disorder during any natural (spontaneous) process with the result that the entropy, S is increased in accordance with the Second Law of Thermodynamics (equation (13.16), Frame 13).

The occurrence of the reverse effect – namely one in which a previously uniformly coloured volume of water clears itself and reverts to just having a small region (of volume) in which is contained a high concentration of the colorant molecules, whilst the main volume of the water has become completely clear – is *never* observed in our experience of natural phenomena!

This kind of paradox was pointed out by Boltzmann. Its rationalisation is based on the fact that:

- any conceived molecular motion of the molecules in the water (consistent with usual behaviour) has an equal probability of occurring as any other molecular motion
- of all the prescribed motions of molecules possible, a *vastly greater number* of these motions will favour the tendency for the molecules of dye to disperse from their original location.

The driving force (which we have called entropy (Frame 13) and labelled, S is then linked to the achieving of a more probable (i.e. more likely) molecular distribution.

Boltzmann proposed the general relationship for solids whereby:

$$S = k \ln W = \left(\frac{R}{L}\right) \ln W \tag{17.1}$$

where k is the Boltzmann constant ($= 1.381 \times 10^{-23}$ J K^{-1}), R is the gas constant ($= 8.314$ J K^{-1} mol^{-1}) and L (sometimes denoted as N_A) is Avogadro's constant ($= 6.022 \times 10^{23}$ mol^{-1}):

$$k = \frac{R}{L} \tag{17.2}$$

and W is the number of individual arrangements possible within the crystal structure of the solid (see Note 17.1)

If we attempt to interpret the observations with regard to residual entropy in Frame 16, section 16.4 and those features that are not entirely in accord with the Third Law, we see that equation (17.1) represents a statistical interpretation of entropy which gives a reasonable account of these departures from the Third Law as well as giving an entirely consistent account of the Third Law itself.

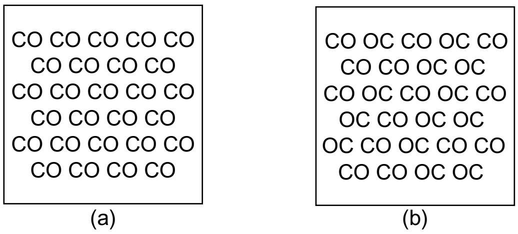


Figure 17.1 Schematic representation of (a) a hypothetical, completely ordered CO crystal; (b) a randomly disordered crystal of CO in which half the dipoles are aligned one way and half aligned the other way.

Returning to the example (Frame 16, section 16.4) of the solid CO crystal. If we consider firstly the (*hypothetical*) *perfectly ordered* crystal (shown schematically in Figure 17.1(a)) then since there can be only *one* arrangement in which the dipoles C → O are always completely aligned and in which perfect symmetry is found, then $W = 1$ in equation (17.1) and in this case:

$$S = k \ln W = \left(\frac{R}{N}\right) \ln W = k \ln (1) = 0 \tag{17.3}$$

which accords with the Third Law prediction that a perfectly ordered crystalline material will exhibit zero entropy at the absolute zero of temperature.

In the actual CO crystal, represented in Figure 17.1(b) as a randomly oriented (and therefore disordered) mixture of molecules in which, although aligned, both possible dipole directions are presented so that approximately half point one way and the other half point in the opposite direction. In this (real) case each individual CO molecule therefore, can acquire one, of the two dipole orientations and for 1 mole of CO – which contains L molecules, where L is Avogadro's constant – the number of possible arrangements (see Note 17.2) will then be 2^L so that the entropy at 0 K is predicted, by Boltzmann's equation to be:

$$S = k \ln W = \left(\frac{R}{L}\right) \ln(2^L) = \left(\frac{R}{L}\right). L \ln 2 = R \ln 2 = 0.693R = 5.8\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{17.4}$$

This value is reasonably close to the experimental 'residual' entropy value of $S^o(0\ \mathrm{K})$ for CO at 0 K (reported in Frame 16, section 16.4) which is recorded to be 4.5 J K^{-1} mol^{-1}.

As a yet further indication that the Boltzmann equation (17.1) is valid we can refer to the entropy change, ΔS, undergone by expanding 1 mole of a gas at constant temperature (isothermally, as in Frame 15, section 15.2) by doubling its volume from V_i to $V_f = 2V_i$ (Figure 17.2). Prior to the expansion, if the actual number (which will be large) of possible molecular arrangements, $W_i = n$ ($n \gg 1$) then, in twice the volume at the end of the expansion the number of molecular arrangements will be equal to $W_f = 2^L.n$ (see note 17.2) and hence:

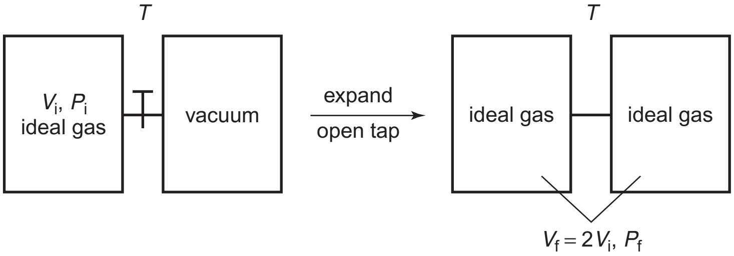


Figure 17.2 1 mole of an ideal gas having volume, V_i at pressure, P_i and temperature, T is expanded into an evacuated space of equal volume. The result is that the gas occupies twice its original volume and so the final volume, $V_f = 2V_i$ at pressure, P_f and temperature, T.

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln\left(\frac{W_f}{W_i}\right) = k \ln(2^L.n/n) \tag{17.5}$$

then, by virtue of equation (17.2) and the fact (Frame 6, equation (6.13)):

$$\ln 2^L = L \ln 2 = 0.693L \tag{17.6}$$

then:

$$\Delta S = \left(\frac{R}{L}\right).L \ln 2 = R \ln 2 = 0.693R \tag{17.7}$$

which is similar in form to equation (17.4) above.

We can now compare the Boltzmann equation value (17.4) above with the value of this same entropy change, ΔS, calculated using equation (15.5) of Frame 15, whereupon, since $V_f = 2V_i$:

$$\Delta S = \frac{q_{\mathrm{rev}}}{T} = R \ln\left(\frac{V_f}{V_i}\right) = R \ln\left(\frac{2V_i}{V_i}\right) = R \ln 2 \tag{17.8}$$

The latter result is identical to the Boltzmann result.

18. $dG = VdP - SdT$: Variation of G with Temperature ($dP = 0$) for Pure Substance

We shall now consolidate the thermodynamics discussed in the foregoing frames. We use it to examine how thermodynamics can be used, first, to predict and explain the behaviour of *a pure substance* in *various single phases* (solid, liquid and gas). We shall try to infer the properties of pure substances and compare our predictions with actual properties observed experimentally. We shall find that our predictions are broadly consistent with the latter illustrating the power of thermodynamics as a practical and useful tool.

A pure material represents an example of a *one-component system*, which can exist in more than one phase.

18.1 The Equation: $dG = VdP - SdT$: a Key Equation in Thermodynamics

In Frame 13, section 13.2 we established the Gibbs function, G, as the index of spontaneous change. Equation (13.10) Frame 13 gave the relationship between G and the enthalpy, H and entropy, S namely:

$$G = H - TS \tag{18.1}$$

Accordingly, a change in G, $\mathrm{d}G$, can then be written as:

$$\mathrm{d}G = \mathrm{d}(H - TS) = \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T \tag{18.2}$$

using the principles discussed earlier.

The enthalpy function, H, was defined in Frame 10 (equation (10.8)) as:

$$H = U + PV \tag{18.3}$$

and hence:

$$\mathrm{d}H = \mathrm{d}(U + PV) = \mathrm{d}U + \mathrm{d}(PV) = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \tag{18.4}$$

Substitution of $\mathrm{d}H$ as given by equation (18.4) into equation (18.2) leads us to:

$$\mathrm{d}G = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T \tag{18.5}$$

and since (First Law of Thermodynamics, Frame 10, equation (10.1)) when only mechanical (PV) work is involved:

$$\mathrm{d}U = q + w = q - P\mathrm{d}V \tag{18.6}$$

Combining equations (18.5) and (18.6) we have:

$$\mathrm{d}G = q - P\mathrm{d}V + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T = q + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T \tag{18.7}$$

where the $P\mathrm{d}V$ terms have cancelled out.

If we are considering a process (or material) at equilibrium (then in equation (18.7): $q = q_{\mathrm{rev}}$), then we can employ the Second Law of Thermodynamics in the form of equation (13.16), Frame 13 so that:

$$q_{\mathrm{rev}} = T\mathrm{d}S \tag{18.8}$$

Substitution for the $T\mathrm{d}S$ term in equation (18.7) and replacement of q by q_{rev} leads to:

$$\mathrm{d}G = q_{\mathrm{rev}} + V\mathrm{d}P - q_{\mathrm{rev}} - S\mathrm{d}T = T\mathrm{d}S + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T = V\mathrm{d}P - S\mathrm{d}T \tag{18.9}$$

Equation (18.9) now represents one of the most important equations (see Note 18.1) in thermodynamics since it governs the stability and thermodynamic behaviour of the various phases of pure materials, as we will demonstrate.

First of all, we explore the nature of the variation of, G, H and S with temperature, T and pressure P – we are now at the very heart of thermodynamics!

18.2 The Equation: d$G = V$dP −SdT (18.9); Derivation from Functional Dependence of $G = \text{f}(P, T)$

From Frame 5, section 5.2 we learned that if:

$$G = \text{f}(P, T) \tag{18.10}$$

we can write for a change in the function, G:

$$\text{d}G = \left(\frac{\partial G}{\partial P}\right)_T .\text{d}P + \left(\frac{\partial G}{\partial T}\right)_P .\text{d}T \tag{18.11}$$

There is only one (pure) substance present so its composition need not be specified.

It will emerge that equation (18.11) is identical to (18.9) by virtue of relationship (18.14) below and equation (20.3) of Frame 20.

18.3 Variation of Gibbs Energy, G with Temperature, T at Constant Pressure (d$P = 0$)

For one mole of substance for a *one-component phase* (equation (18.9)):

$$\text{d}G = V\text{d}P - S\text{d}T \tag{18.12}$$

Under conditions where the pressure is held constant (i.e. d$P = 0$) then equation (18.12) becomes:

$$\text{d}G = -S\text{d}T \tag{18.13}$$

so that rearranging whilst keeping the pressure constant, leads to:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{18.14}$$

or, qualitatively expressed (using the interpretation of partial derivatives introduced in Frame 5, sections 5.1 and 5.2) the gradient of the graph of G plotted versus T (at constant pressure) is equal to the value of – S, the negative of the entropy.

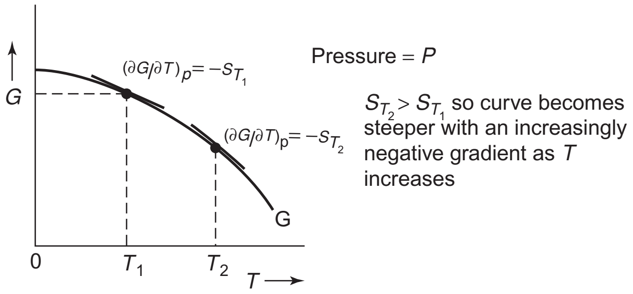


Figure 18.1 Graph of G versus T at constant pressure, P, for 1 mole of a normal substance (in any phase) solid, liquid or gas. The extent of curvature will depend on the values of $-S_g$, $-S_l$ and $-S_s$ for the individual phases. (Frames 21–23). Amount of substance, n, also constant.

Since for solid, liquid or gaseous phases of a substance, S *is greater than 0 (positive)* (Frame 16, section 16.2). This therefore means:

- a curve of G versus T at constant pressure, at any temperature selected, will always have a negative gradient (equal to – S). The change in this gradient as temperature is increased corresponds to the second derivative (see Frame 3, section 3.1 and Figure 3.2) furthermore expressed by:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = \frac{-C_P}{T} \tag{18.15}$$

- Now since C_p/T, at all temperatures, will always be greater than zero (i.e. a positive quantity) since $C_p > 0$ and $T > 0$ and this will also be true *for all phases* (i.e. solid, liquid or gas) then – C_p/T, at all temperatures, will always be less than zero. This can be interpreted to signify that the curve of G versus T will be convex upwards (Figure 18.1).
- The curve will have an increasingly negative gradient as the temperature increases. Also as T increases, then S increases – the system becomes more disordered with rise in temperature – and hence $(\partial G/\partial T)_P$, the actual gradient of the graph of the curve at a specific temperature will become progressively steeper. The curve will increasingly dip downwards as the temperature increases.
- Also, since at $T = 0$ K, S for most solids is zero (Third Law of Thermodynamics), the graph of G versus T will start off (at $T = 0$) having a zero gradient (i.e. being parallel to the T axis) (see Figure 18.1).

19. Variation of Enthalpy and Entropy Functions, *H* and *S*, with Temperature (d$P = 0$) Pure for Substance

19.1 Variation of Enthalpy, *H* with Temperature, *T* at Constant Pressure (d$P = 0$)

From equation (10.12) of Frame 10, for one mole of substance:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_\mathrm{p} \tag{19.1}$$

and often (Frame 10, Figure 10.1) we can assume that:

$$\left(\frac{\partial C_\mathrm{p}}{\partial T}\right)_P \approx 0 \tag{19.2}$$

This latter relationship is an expression of the fact (as previously noted, Frame 11) that C_p does not usually vary significantly over modest ranges of temperature. Since $(\partial H/\partial T)_P$ represents the gradient of the plot of H versus T under conditions of consant pressure, this means that the curve of enthalpy, H, versus T will be approximately linear albeit with a slightly positive (but almost constant) gradient $= C_\mathrm{p}$ (Figure 19.1).

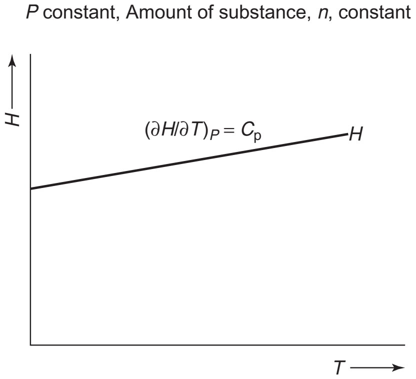


Figure 19.1 Graph of H versus T at constant pressure, P, for 1 mole of a normal substance (in any phase) solid, liquid or gas.

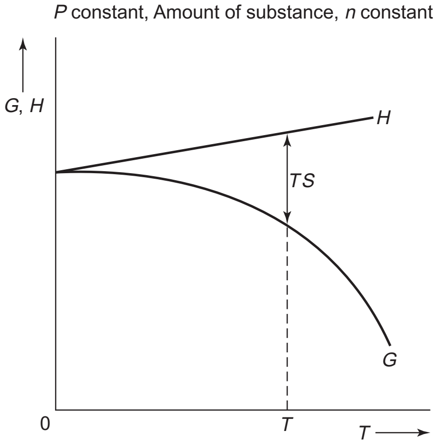


Figure 19.2 Graph of G and H versus T at constant pressure, P, for 1 mole of a normal substance (in any phase) solid, liquid or gas.

Since:

$$G = H - TS \tag{18.1}$$

Then if G and H are plotted as a function of temperature, T, on the same graph at constant pressure, P, we have (Figure 19.2):

- that the two curves (i.e. of G versus T and of Hversus T) diverge as temperature increases;
- that at any given temperature, T the gap between the two curves as measured by $(H - G)$ is given (equation 18.1) by:

$$H - G = TS \tag{19.3}$$

and

- that at $T = 0$ K we have:

$$G = H \tag{19.4}$$

so that these curves for G and H approach one another *asymptotically* as $T \to 0$ (as opposed to merely *intersecting* at $T = 0$) (Figure 19.2).

19.2 Variation of Entropy, *S* with Temperature, *T* at Constant Pressure (dP = 0)

- The Third Law of Thermodynamics (Frame 16, equation (16.1)) states that, for a perfectly crystalline substance:

$$S^o{}_{0\,\mathrm{K}} = 0 \tag{16.1}$$

where $S^o_{0\,\mathrm{K}}$ is the standard entropy for *one mole* at absolute zero of temperature ($T = 0\,\mathrm{K}$) and since, also arising from equation (10.25), Frame 10, we have that:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_\mathrm{P}}{T} \tag{19.5}$$

- Using the fact that:

$$\frac{C_\mathrm{p}}{T} > 0 \tag{19.6}$$

then the curve of S versus T (at constant pressure) – in the absence of phase changes – from the ordinate at $T = 0$ K to some temperature T_m, which represents the limit of stability of the solid phase (i.e. T_m corresponds to the melting point) will be as is shown in Figure 19.3

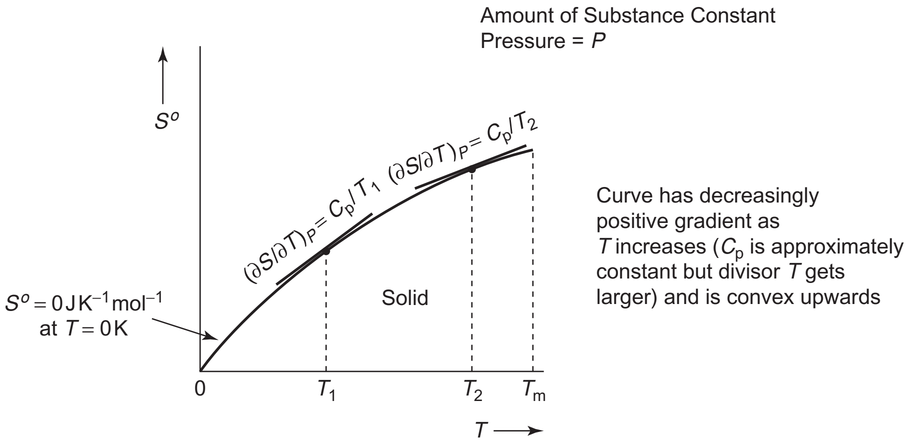


Figure 19.3 Graph of S versus T at constant pressure, P, for a solid for the temperature range: $0 \le T \le T_\mathrm{m}$. $(\partial^2 S/\partial T^2)_P = \partial[C_\mathrm{P}/T]/\partial T$ which can be differentiated by the quotient rule, (Frame 3) leading to $[T(\partial C_\mathrm{p}/\partial T)_P - C_\mathrm{p}]/T^2 = -C_\mathrm{p}/T^2 < 0$ since $(\partial C_\mathrm{p}/\partial T)_P \approx 0$ equation (19.2).

- Since, the change in the gradient as the temperature increases is expressed as $(\partial^2 S/\partial T^2)_P$ then differentiation of equation (19.5) with respect to T at constant pressure P gives:

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_P = \partial\left[\frac{C_\mathrm{P}}{T}\right]/\partial T = \frac{-C_\mathrm{p}}{T^2} < 0 \tag{19.7}$$

the curve of S versus T starts at the origin (for a perfectly crystalline solid) and has a convex upwards curvature with decreasingly positive gradient ($= C_\mathrm{P}/T$) as temperature increases.

20. Variation of Gibbs Energy, *G* With Pressure, *P* at Constant Temperature (d*T* = 0) and Variation of Entropy, *S* With Pressure, *P* at Constant Temperature (d*T* = 0) for an Ideal Gas

20.1 Variation of Gibbs Energy, *G* with Pressure, *P* at Constant Temperature (d*T* = 0)

For one mole of substance (Frame 18, equation (18.9)):

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{20.1}$$

which is valid for:

- a constant amount of substance present;

or

- for a closed system capable of only mechanical work and changing reversibly (and this could include a chemical change)

The equation also applies for:

- a pure substance in a single phase (the application in which it is used here) and corresponds to the Gibbs–Duhem equation (Frame 50) for a pure phase.

Under conditions where *temperature* is held constant (i.e. $\mathrm{d}T = 0$) and *pressure is varied* then:

$$\mathrm{d}G = V\mathrm{d}P \tag{20.2}$$

so that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{20.3}$$

- Qualitatively expressed this means that the gradient of the graph of G plotted versus P (at constant temperature) is equal to the value of V, the *molar* volume.
- Consider now that the molar volume, V_g of any gas at 273 K and 1 bar pressure is 22 400 cm^3 (= 22.4 dm^3). This is much larger than the molar volume of a liquid. Take for example liquid water for which, since 1 mole weighs 18 g and has a density of 1 g cm^{-3} then $V_\mathrm{l} = 18\ \mathrm{cm}^3$. The volume of ice is slightly higher than that of liquid water but of very similar magnitude especially when compared to 22 400 cm^3 for the gas (steam). Thus, since in general the (molar) volume of a gas, V_g is *very much greater* than the corresponding (molar) volume of either the liquid or solid phases (V_l or V_s):

$$V_\mathrm{g} \gg (V_\mathrm{l} \text{ or } V_\mathrm{s}) \tag{20.4}$$

- This means that the graph of G versus P (at constant temperature) for solids and liquids will show relatively small variation with pressure variation. This is consistent with the fact that liquids and solids are virtually incompressible when compared to gases and therefore, for the present purposes, we need not consider them any further.
- However for *gases*, since:

$$\left(\frac{\partial G_\mathrm{g}}{\partial P}\right)_T = V_\mathrm{g} \tag{20.5}$$

and V_g is relatively large we *do* need to consider variation of G with P for an ideal gas (at constant temperature).

The change in the gradient as pressure is increased is expressed by:

$$\left(\frac{\partial^2 G_\mathrm{g}}{\partial P^2}\right)_T = \left(\frac{\partial V_\mathrm{g}}{\partial P}\right)_T \tag{20.6}$$

Since for an ideal gas (Frame 4, equation 4.1): $PV_g = nRT$, then:

$$V_g = \frac{nRT}{P} \tag{20.7}$$

- Hence from equations (20.5) and (20.7) then:

$$\left(\frac{\partial V_g}{\partial P}\right)_T = \frac{-nRT}{P^2} \tag{20.8}$$

The negative term: $-nRT/P^2$ will always be less than zero (negative). This is because: $P > 0$ and T, n and R are all positive and constant (at all temperatures) and hence $-nRT/P^2 < 0$.
Another way of rationalising this change in gradient with increase of pressure is to recognise that (for gases) as pressure is increased the volume will tend to decrease.

- Hence the curve of G versus P should be convex upwards (Figure 20.1) and have a decreasingly positive gradient as pressure increases.

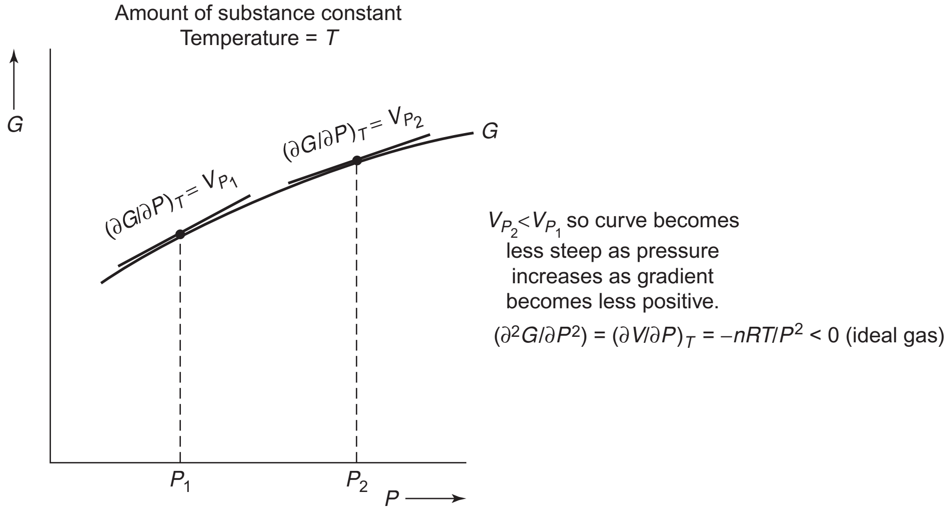


Figure 20.1 Graph of G versus P at constant temperature, T, for an ideal gas.

- Further, since from equation (20.2), for n moles of an ideal gas undergoing a change of pressure from a state having Gibbs energy, G_i, at pressure P_i to one having Gibbs energy, G_f, at pressure P_f we have (using equation (20.7)):

$$\int_{G_i}^{G_f} dG = \int_{P_i}^{P_f} V_g.dP = nRT \int_{P_i}^{P_f} dP/P \tag{20.9}$$

so that:

$$\Delta G = [G]_{G_i}^{G_f} = G_{m,f} - G_{m,i} = nRT[\ln P]_{P_i}^{P_f} = nRT \ln (P_f/P_i) \tag{20.10}$$

or

$$G_f = G_i + nRT \ln\left(\frac{P_f}{P_i}\right) \tag{20.11}$$

Suppose we wish to compare the value of the free energy of a gas, G at pressure P to its value when the pressure is 1 bar. This is denoted as G^0 (Frame 11, section 11.2). We can do this by making the substitutions: $G_i = G^0$; $P_i = P^0 = 1$ bar; $G_f = G$; $P_f = P$ in equation (20.11), giving:

$$G = G^o + nRT \ln(P/P^o) = G^0 + nRT \ln(P/\text{bar}) \tag{20.12}$$

Note in equation (20.12) when $P = 1$ bar, $\ln(P/\text{bar}) = \ln(1) = 0$ and $G = G^0$

$$G = G^o + RT \ln\left(\frac{P}{P^o}\right); \quad P^o = \text{standard pressure} \tag{20.13}$$

[Frame 6, section 6.2 and the Appendix should be consulted for more details about the treatment of logarithmic expressions].

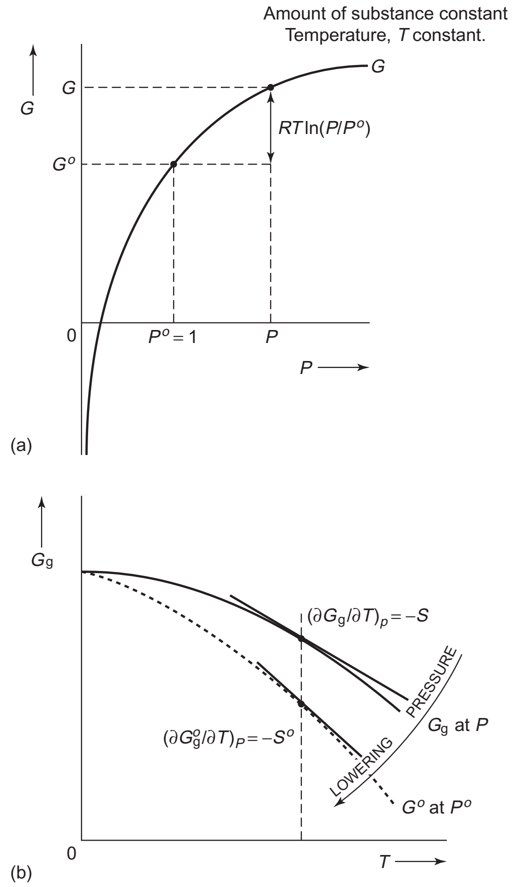


Figure 20.2 Graph of (a) G versus P at constant temperature, T, for 1 mole of an ideal gas and (b) G versus T at two pressures P/bar and $P^o = 1$ bar where $P > 1$ bar, showing the effect of lowering the pressure on the Gibbs energy, G, of 1 mole of gas. Note that the difference $(G - G^o)$ at any temperature, T is given by $RT\ \ln(P/P^o)$ in accordance with equation (20.13).

We shall see later (Frames 35, 37, 38, 39) that G and G^o can, under certain circumstances, be replaced by chemical potentials, μ and μ^o and that these relationships and that of (20.12) are really key equations when considering the thermodynamics of equilibria between phases (Frame 35).

20.2 Variation of Entropy *S* with Pressure, *P* for a Gas at Constant Temperature, (d*T* = 0)

- Also since for 1 mole of an ideal gas:

$$G = G^o + RT\ln\left(\frac{P}{P^o}\right); \quad P^o = \text{ standard pressure} \tag{20.13}$$

Differentiating equation (20.13) term by term with respect to temperature, T, (whilst maintaining the pressure, P, to be constant), we have:

$$\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial G^o}{\partial T}\right)_P + \left\{\partial/\partial T\left[RT\ln\left(\frac{P}{P^o}\right)\right]\right\}_P; \quad P^o = \text{ standard pressure} \tag{20.14}$$

and by virtue of equation (18.14, Frame 18):

$$-S = -S^o + R\ln\left(\frac{P}{P^o}\right); \quad P^o = \text{ standard pressure} \tag{20.15}$$

where S^o is the standard entropy of the gas at the standard pressure P^o.

Thus:

$$S = S^o - R\ln\left(\frac{P}{P^o}\right); \quad P^o = \text{ standard pressure} \tag{20.16}$$

and since:

$$\Delta S = S - S^o \tag{20.17}$$

we have that:

$$\Delta S = -R \ln\left(\frac{P}{P^o}\right); \quad P^o = \text{ standard pressure} \tag{20.18}$$

where ΔS is the entropy change of a gas as its pressure is changed from the standard pressure, P^o to a pressure P. More generally therefore we can write that:

$$\Delta S = -R \ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{20.19}$$

where, now, ΔS represents the entropy change for a gas when its pressure is changed from P_i to P_f.

21. Variation of Gibbs Energy Function, *G* Versus Temperature, *T* for Solid, Liquid and Gaseous Phases

21.1 Variation of Gibbs Energy Function, *G* with Temperature, *T* for the Solid, Liquid and Gaseous Phases of a Pure Substance, at Constant Pressure (d$P = 0$)

In Frames 18, 19 and 20 we demonstrated the behaviour of G, H and S *for 1 mole of substance* under various conditions. In this frame we examine how the behaviour of the G curves forces substances to exist in solid, liquid and gaseous phases and ultimately gives rise to the transformations which take place between these phases (e.g. melting, boiling, sublimation etc.). The more detailed graphs (Figure 21.1) emerge by consideration of the following key steps. Suppose we consider the superposition of three curves for G versus T for specific solid (G_s), liquid (G_l) and gaseous (G_g) phases upon one another. Each curve will have characteristics as demonstrated in Frame 18, Figure 18.1. We consider, in each case, *1 mole* of material. We can reason as follows to arrive at Figure 21.1:

- Close to $T = 0\,\mathrm{K}$ the most stable phase to exist is the solid state, a point discussed further in Frame 22, section 22.1. Thus at $T = 0\,\mathrm{K}$, G_s, the Gibbs energy of the solid phase, would be expected to be *lower* than that for any (hypothetical) liquid phase, G_l, which in turn would be anticipated to be lower than that for any (hypothetical) gaseous phase, G_g at this temperature.

$$G_s < G_l < G_g \quad \text{at} \quad T = 0\,\mathrm{K} \tag{21.1}$$

- As the temperature increases each separate G versus T curve shows the characteristics displayed in Figure 18.1, Frame 18 where the individual gradients are given by:

$$\left(\frac{\partial G_s}{\partial T}\right)_P = -S_s; \left(\frac{\partial G_l}{\partial T}\right)_P = -S_l; \left(\frac{\partial G_g}{\partial T}\right)_P = -S_g \tag{21.2}$$

- Since we also know that a crystalline solid is more ordered than the corresponding liquid which, in turn, is more ordered than the corresponding vapour phase, then since entropy is related to degree of disorder (Boltzmann equation (17.1), Frame 17) then:

$$S_g \gg S_l > S_s \tag{21.3}$$

- The consequence of the relationship (21.3) is that the curve of G_s versus T will vary in curvature least of all (with the gradient of the tangent to the solid curve $= -S_s$, which is smaller than either – S_g or $-S_l$); the curve of G_l versus T will have an increased curvature (with the gradient of the tangent to the liquid curve $= -S_l$) when compared to that of the solid curve and this causes the solid and liquid curve to eventually cross (at T_m), the melting point where the solid transforms to form a liquid. This corresponds to point A in Figure 21.1.
- This therefore is interpreted to mean that there is a phase transition as the Gibbs energy of the liquid, G_l becomes less than that for the solid, G_s and hence the liquid (now having the lower Gibbs energy) becomes the more stable phase. The principle that the most stable of two phases is the one possessing the lowest Gibbs energy is taken up Frame 29, section 29.1 and examined further in Frame 22, section 22.2.
- The much greater disorder displayed by gases means that: $S_g \gg S_l$ and consequently the curve of G_g versus T exhibits the greatest curvature of all the curves (with the gradient of the tangent to the gas curve $= -S_g$). Thus the curve shows much greater change with temperature than either that for the liquid or the solid. The consequence is that the gaseous curve (G_g versus T) will dip *below* that of the *currently stable* liquid phase as the temperature continues to increase until the boiling temperature is reached (at point B, Figure 21.1, where the gas and liquid phases have identical Gibbs energies). Hence G_g becomes lower than G_l and the gas then becomes the stable phase thereafter. The point B corresponds to the boiling temperature, T_b at the (constant) pressure P involved.

  From the above rationale (and without having made any prior or additional assumptions) we see that our analysis leads – via thermodynamic argument – to a prediction that pure materials existing in their normal phases exhibit melting and boiling phenomena, as is observed experimentally.

As a caveat to the considerations involving the solid phase it should be mentioned that some solids undergo mesomorphic changes before melting (although these have been assumed not to occur in the solids so far discussed).

21.2 Variation of Entropy, *S* with Temperature, *T* for the Solid, Liquid and Gaseous Phases of a Pure Substance, at Constant Pressure ($dP = 0$)

In Figure 21.1, placed directly below the graph of G_g, G_l and G_s versus T, we sketch a graph of the corresponding entropy functions: S_g, S_l and S_s versus temperature, T whilst mapping from the upper to the lower graph the phase stabilities as predicted at the various values of temperature, T, in the upper graph.

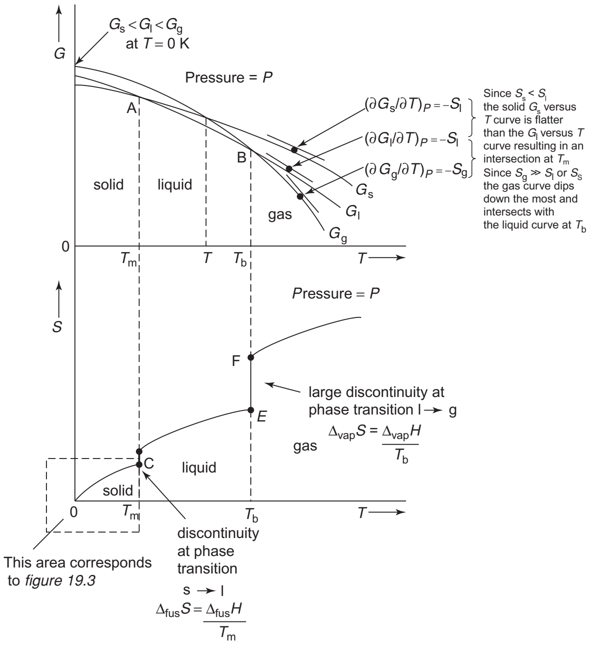


Figure 21.1 Graph of G_g, G_l and G_s and of S_g, S_l and S_s versus temperature, T, at constant pressure, P ($dP = 0$) for a normal substance existing in three simple phases (solid, liquid and gas (vapour)).

- The *solid* portion of the S versus T graph between $0 \leq T \leq T_m$ corresponds exactly to that reproduced in Figure 19.3 (Frame 19, section 19.2) already discussed.
- At a temperature, T_m there is a phase transition in which the solid melts:
$$(s) \rightarrow (l) \tag{21.4}$$
and also, since we know that the entropy of a liquid is greater than that of a solid (inequality 21.3) then in the region of the graph marked DE in which the *liquid* is now the more stable phase (i.e in the temperature range $T_m \leq T \leq T_b$) the curve for S_l versus T will be elevated above that for the solid phase and hence a discontinuity (marked CD) *automatically* appears on our graph. This predicts therefore that the entropy of the solid at T_m exhibits a discontinuity and 'jumps' (along CD) up to the liquid curve. The curvature of the graph portion S_l versus T will have similar features to that shown by the S_s versus T curve (i.e. is upwardly convex).
- The entropy change, $\Delta_{fus}S$, for the process (s) → (l) at T_m and hence the magnitude of the entropy rise at temperature brought about by the phase change (CD) can be calculated using equation (15.10) (Frame 15), applying to the fusion process:
- At point E, the gaseous (vapour) phase suddenly becomes the more stable than the liquid phase (at the boiling temperature T_b) and moreover, since $S_g \gg S_l$, a similar (but larger) discontinuity (EF) will appear naturally in our curves (Note also that we predict that: EF > CD).

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m} \tag{21.5}$$

- Similarly at EF, the entropy change, $\Delta_{vap}S$, for the process (l) → (g) at T_b and hence the magnitude of the entropy rise at temperature brought about by the phase change (EF) can be calculated using equation (15.10) (Frame 15), suitably adapted in order to apply to the vaporisation process, and hence:

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b} \tag{21.6}$$

Hence we predict, from our simple thermodynamic arguments, there is a sharp rise in the entropy at phase transitions undergone by pure substances and that:

$$\Delta_{vap}S > \Delta_{fus}S \tag{21.7}$$

For normal substances, this is borne out experimentally.

22. Variation of Enthalpy Function, *H* with Temperature for Solid, Liquid and Gaseous Phases

22.1 Relative Values of the Enthalpy Function, *H* for Solid, Liquid and Gas

- The enthalpy function, H, was first introduced in Frame 10, equation (10.8). In Figure 18.1, Frame 18 was shown the general variation of the Gibbs energy G as a function of temperature, T and using the equation:

$$G = H - TS \tag{18.1}$$

  it is clear that the intercept of the curve on the G axis at $T = 0\,\mathrm{K}$ will be equal to H, the enthalpy function. Later (Frame 21) we extended the scope of Figure 18.1 (Frame 18) by considering *individual* phases solid, liquid and gas and plotted G versus T curves for each of these phases on the *same* axes. We can therefore see that the intercepts of the solid, liquid and gaseous phase curves on the G axis at $T = 0\,\mathrm{K}$ will correspond then to H_s, H_l and H_g.
- Also we see that:

$$H_g > H_l > H_s > 0 \tag{22.1}$$

This can be accounted for qualitatively by employing a simple model which permits the prediction of H (and S and G) for the above phases. Schematically we can think of our respective solid, liquid and gas as shown in Figure 22.1. The structure of a *liquid*, unlike that of a solid, cannot be specified in terms of an array of identical cells in a so called ‘crystal structure’ specified by atomic coordinates, it has only a *limited* degree of short-range order and radial distribution (probability) functions are employed in its description. In the case of an (ideal) gas the molecules are *unconstrained* by attractive forces between them and here the gas (as also does a liquid) assumes the shape of its containing envelope. The enthalpy term, H, is related to the degree of attraction between the molecules in the respective phases and this is indicated by the fact (as we shall see below) that enthalpy has to be expended (Frame 21, section 21.2) in order to convert one phase into another in the sequence: solid → liquid → gas.

In the case of the solid → liquid process (melting) $\Delta_{\mathrm{fus}}H$ is required in order to overcome the tightly bound molecules of the solid and create the increased separation found between the molecules of the liquid. Thus:

$$H_l > H_s \tag{22.2}$$

Similarly for the liquid → gas transformation (vaporisation) $\Delta_{\mathrm{vap}}H$ is required to break the forces present in the liquid and achieve the free movement found within gas molecules. Thus:

$$H_g > H_l \tag{22.3}$$

in this case. This model, when coupled with the consideration of the relative *entropy* values – which are: $S_g \gg S_l > S_s$, on the grounds of increasing molecular order – further predicts that the solid will be the most stable phase at low temperatures and that the gas will be the most stable phase at high temperatures.

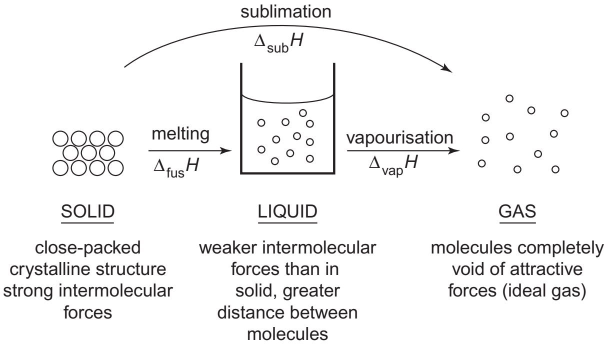
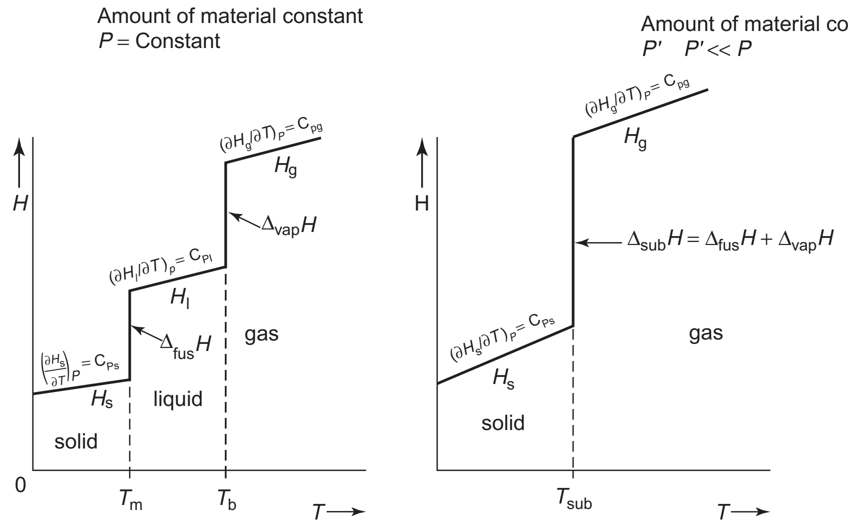


Figure 22.1 Schematic diagram of molecular packing in solid (a), liquid (b) and gas (c).

22.2 Variation of Enthalpy Function, *H* with Temperature, *T* for the Solid, Liquid and Gaseous Phases of a Pure Substance at Constant Pressure, *P*

In this Frame we examine the variation of H_s, H_l and H_g with temperature at constant pressure, P as shown in Figure 22.2(a). It takes account of a number of facts:

- $H_g > H_l > H_s > 0$ from equation (22.1) above;



(a) (b)

Figure 22.2 Graph of the variation of H with temperature, T at constant pressure, P (a) for normal situations, involving melting and boiling processes (b) for the case where sublimation takes place (at very low pressures = P', where $P' \ll P$).

- The existence of melting point, T_m and boiling point, T_b and the stability of the various phases over the respective temperature ranges;
- The positive gradients ($= (\partial H/\partial T)_P = C_P$) of the curves of H versus T and the almost constancy of the gradients (i.e. near linearity) of H versus T as temperature increases ($= (\partial^2 H/\partial T^2)_P = (\partial C_P/\partial T) \approx 0$).

Figure 22.2(b) sketches the situation when sublimation takes place at temperature T_{sub} and pressure P' ($P' \ll P$).

The following features are predicted from these graphs:

- The existence of various *enthalpies of transition* (which have to be invoked in order to explain the perceived 'jump' (Frame 21, section 21.2) from one curve to another at the discontinuities caused by the differing magnitudes of H_g, H_l and H_s.
- Thus enthalpy changes of $\Delta_{fus}H$, $\Delta_{vap}H$ and $\Delta_{sub}H$ which are all greater than zero (i.e. positive) are necessary and occur at the fixed temperatures of T_m, T_b and T_{sub}, as was discussed also in Frame 21. We also see that:

$$\Delta_{fus}H < \Delta_{vap}H \tag{22.4}$$

$$\Delta_{sub}H > \Delta_{fus}H \tag{22.5}$$

and

$$\Delta_{sub}H > \Delta_{vap}H \tag{22.6}$$

23. Effect of Pressure on Melting Point, T_m and Boiling Point, T_b Case (i): (Normal) Substances for Which: $V_\mathrm{g} \gg V_\mathrm{l} > V_\mathrm{s}$

The change in Gibbs energy, G for *one mole*, with pressure, P at constant temperature T is dependant on volume, V (equation (20.3) Frame 20):

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{20.3}$$

For most substances, labelled as case (i):

$$V_\mathrm{g} \gg V_\mathrm{l} > V_\mathrm{s} \tag{23.1}$$

for gaseous, liquid and solid phases, respectively (see earlier brief discussion in Frame 20, condition (20.4), section 20.1). However for the:

ice (s)–water (l)–steam (g) (H_2O) system

a reversal to the liquid/solid volume order given in inequality (23.1) is exhibited so that, in this case labelled as (ii) specifically for water, we have:

$$V_\mathrm{g} \gg V_\mathrm{l} < V_\mathrm{s} \tag{23.2}$$

We can anticipate that this change will have a marked effect on the properties of H_2O when these are compared with other substances (for example, it clearly will change the relative behaviour of the curves discussed in Figure 21.1 Frame 21) and we later show that our predictions are borne out experimentally by the, so called, ‘anomalous’ properties of pure water, which are, in turn, largely brought about by the existence of hydrogen bonding in water molecules.

We consider the two cases separately:

- Case (i): normal substances, for which: $V_\mathrm{g} \gg V_\mathrm{l} > V_\mathrm{s}$ (this Frame)

and

- Case (ii): water, for which: $V_\mathrm{g} \gg V_\mathrm{l} < V_\mathrm{s}$ (Frame 24)

by discussing the variation of G versus T for varying pressures, P and mapping the effect of pressure on the melting and boiling temperatures onto a *phase diagram*. Such a diagram shows which phase exists as being the most stable at a selected value of both temperature, T and pressure, P.

23.1 Case (i): Phase Behaviour of Normal Substances, for which: $V_\mathrm{g} \gg V_\mathrm{l} > V_\mathrm{s}$

Consider two pressures, P_u (being the higher (upper) pressure and P_l, a lower pressure (i.e. $P_\mathrm{u} > P_\mathrm{l}$). At pressure, P_u, the behaviour of the G versus T curve can be likened to that at general pressure P as shown in Figure 18.1, Frame 18 and this is transcribed as the solid curve in Figure 23.1. The phase transition points for melting (T_m, P_u) and boiling (T, P_u) (labelled A and B) are now projected down onto the lower P versus T, phase diagram in Figure 23.1.

When the pressure is lowered (say to P_l) this will affect the Gibbs energy in accordance with the value of V (equation 20.3, Frame 20). Since:

$$V_\mathrm{g} \gg V_\mathrm{l} > V_\mathrm{s} \tag{23.1}$$

the curve for the gaseous phase will therefore be lowered to a much greater extent ($= V_\mathrm{g}$) than is the liquid curve ($= V_\mathrm{l}$), which is, in turn, lowered by only slightly more than the solid curve ($= V_\mathrm{s}$). The effect of this lowering of pressure on

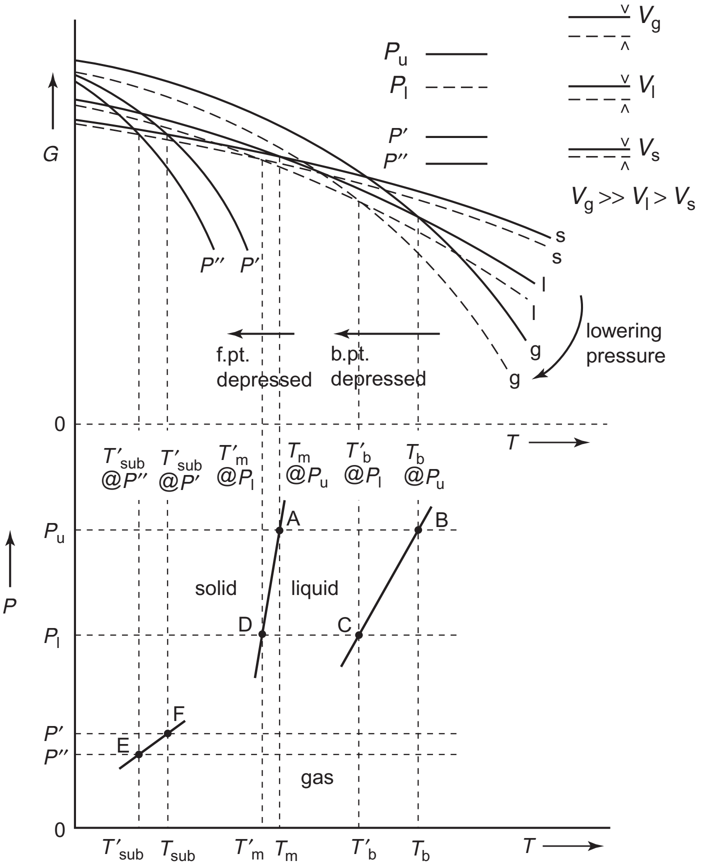


Figure 23.1 Effect of lowering pressure $P_u \rightarrow P_l \rightarrow P' \rightarrow P''$ on boiling point (T_b), melting point (T_m) and sublimation temperatures (T_{sub}) for normal substances.

Figure 21.1 is shown in Figure 23.1 by sketching the new curves: --- (P_l) beneath the — (P_u) curves in accordance with the relative magnitudes shown in equation (23.1). Considering the intersection points on the revised curve — corresponding to (T_m, P_l) and (T_b, P_l), we see that the boiling temperature, T_b, has been *lowered* and so the substance now boils at a *lower* temperature at pressure, P_l than it did at pressure, P_u. Similarly this qualitative treatment also shows that the melting (freezing) point will also be *depressed* at the pressure, P_l (at T'_m) as compared to the situation at pressure P_u (at T_m) (although to a lesser extent than the lowering effect on the boiling point).

Projecting the new phase transition points (T'_m, P_l) and (T'_b, P_l) onto the phase (P versus T) diagram leads to points D and C and hence the line AD represents the variation of melting point (i.e. solid–liquid equilibria) with pressure for the substance whilst the line CB represents the variation in the boiling point with pressure for the liquid/gas equilibrium. We can now inscribe the areas of the phase diagram with labels 'solid', 'liquid' and 'gas' indicating the stability of the phases within these areas. The line BC maps the points (T_b, P) at which the equilibrium between liquid and gas exists whilst the line AD maps the points (T_m, P) where the solid/liquid equilibrium exists and therefore correspond to temperatures and pressures at which the two phases will co-exist together with one another.

Since $(\partial G_g/\partial T)_P = V_g$ and $V_g \gg V_l$ and $V_g \gg V_s$ then the effect of pressure reduction will affect the gaseous curve much more markedly that the solid or liquid curves. At very low pressures, (P' and P'' where $P'' < P' \ll P_l$) the effect will be to cause the G_g versus T curve to be down below the G_l versus T curve, so causing it to intersect *only* with the solid G_s versus T curve (and thus altering the overall form of the graph from that shown in Figure 21.1, Frame 21). Since now as temperature rises at both

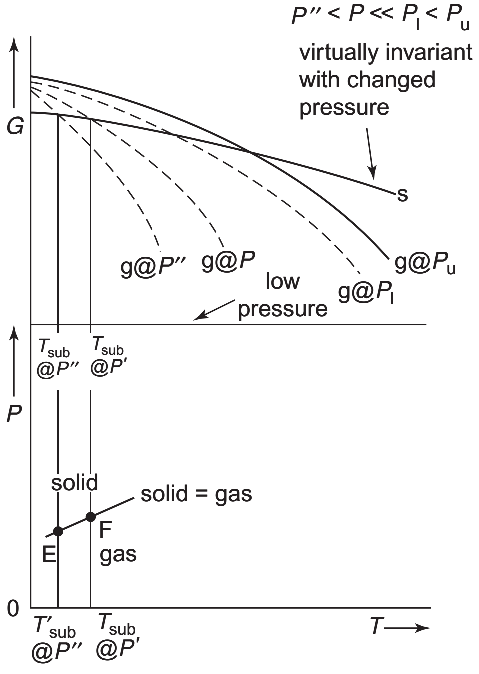


Figure 23.2 Sublimation plot in Figure 23.1 in more detail.

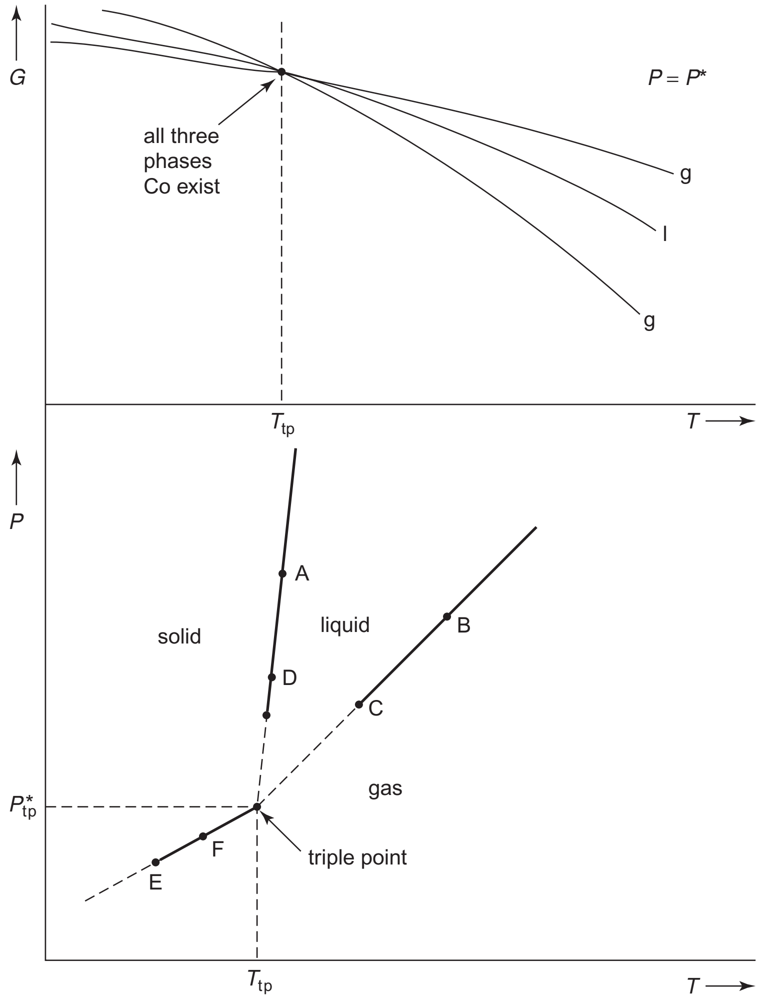


Figure 23.3 Detail of predicted form of the phase diagram for normal substances showing the existence of the triple point arising from the intersection of all three G versus T plots at the given pressure P^*_{tp}.

pressures P' and P'' we go from the solid phase having the lowest Gibbs energy, G_s directly to a situation where the *gas* is the most stable phase, without the intervention of a liquid phase at all – in other words sublimation (*solid → gas*) has been induced at temperatures T_{sub} and T'_{sub} at pressures P' and P'' respectively. The variation of T_{sub} with varying pressure then maps down onto the phase (P versus T) diagram as the line EF in Figures 23.1 and 23.2.

On the phase diagram (Figure 23.3) the lines AD, BC and EF when extrapolated meet at a point labelled as the '*triple' point*, corresponding to one single specific temperature and one single specific pressure at which *all three phases* (solid, liquid and gas) will coexist and be equally stable (see Frame 50, section 50.4). This corresponds to the situation (at a specific pressure which we have labelled P^*) where the curves of G_g, G_l and G_s versus temperature mutually intersect with one another.

23.2 Prediction of General Form of Phase Diagram for Normal Substances: (Case (i))

The lower portion of Figure 23.3 displays the form predicted for a typical phase diagram for normal substances (case (i)) by application of the thermodynamic principles developed thus far.

23.3 Comparison with Experimental Phase Diagrams

If we compare the *experimentally established* phase diagrams, for the substances iodine (I_2) and carbon dioxide (CO_2), with the form we have predicted by logical use and development of the thermodynamics discussed so far we see that our conjectures

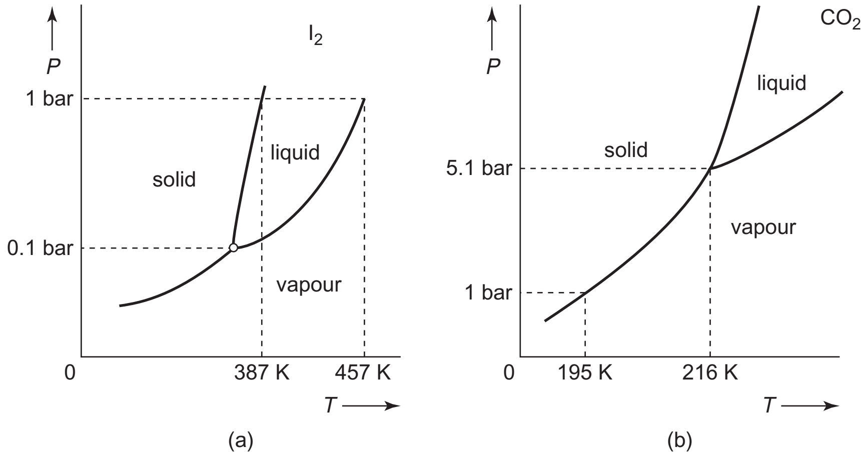


Figure 23.4 Form of the experimental phase diagram for two normal substances: (a) iodine (I_2) and (b) carbon dioxide (CO_2).

are broadly correct. In Figure 23.4 the diagram (a) for I_2 and (b) for CO_2 accord well with the phase diagram shown in the lower halves of Figures 23.3 and 23.1.

24. Effect of Pressure on Melting Point, T_m and Boiling Point, T_b

Case (ii): Water

The change in Gibbs energy, G, with pressure, P at constant temperature T is dependant on volume, V (equation (20.3) Frame 20):

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{20.3}$$

For *water* (case (ii)) (Frame 23):

$$V_g \gg V_l < V_s \tag{23.1}$$

in other words the volume of *1 mole* of the liquid phase (i.e. liquid water) *is less than* that of *1 mole* of the solid phase (i.e. ice). Water is thus regarded as exhibiting anomalous behaviour in this respect when compared to normal substances. The fact that: $V_l < V_s$ means that the respective densities of these phases (since $V \alpha 1/\rho$) are such that: $\rho_l > \rho_s$ so that the density of liquid water is below that of ice (hence ice 'floats' on top of the pond and since $V_l < V_s$ pipes can burst during a 'thaw' as frozen ice melts and expansion to form the corresponding liquid water ensues). We consider the effect of this relative volume variation as it affects our G versus T diagrams and hence how the properties of water (case (ii)) are likely to differ from those of normal substances (case(i)).

24.1 Case (ii): Phase Behaviour of Water, for which: $V_g \gg V_l < V_s$

Beginning with the general curve of G versus T at constant pressure as shown in Figure 18.1 (Frame 18) we can speculate how this diagram must be changed in the case of H_2O when the pressure is lowered. As before (Figure 23.1, Frame 23) we start with a curve — showing the variation of G_g, G_l and G_s versus T at constant pressure (say P_u). If we sketch in the change brought about by reducing the pressure to P_l (where $P_l < P_u$) on the basis of the relationship (23.1) we predict that whilst the pressure–temperature variation of the boiling point, T_b will be affected similarly to case (i) (Frame 23) for normal substances (i.e. depressed by lowering of the pressure), in the case of the melting temperature, T_m, lowering of the pressure will actually *elevate* T_m (i.e. so affecting this property in *the opposite* way to that found in the case of normal substances (case (i))!).

We can, further, consider the case of sublimation for the process ice → vapour. Once again such a phase change will only be induced at really low pressures, i.e. at P_l' and P_l'' for example (Figure 24.2), where $P_l' < P_l'' \ll P_l < P_u$. In this case the G_g versus T curve is, once again, seen to be pulled downwards so as to intersect with the G_s versus T curve and eliminating any possibility of its intersection with the G_l versus T curve as the temperature (at the extremely low pressures, in most cases) rises.

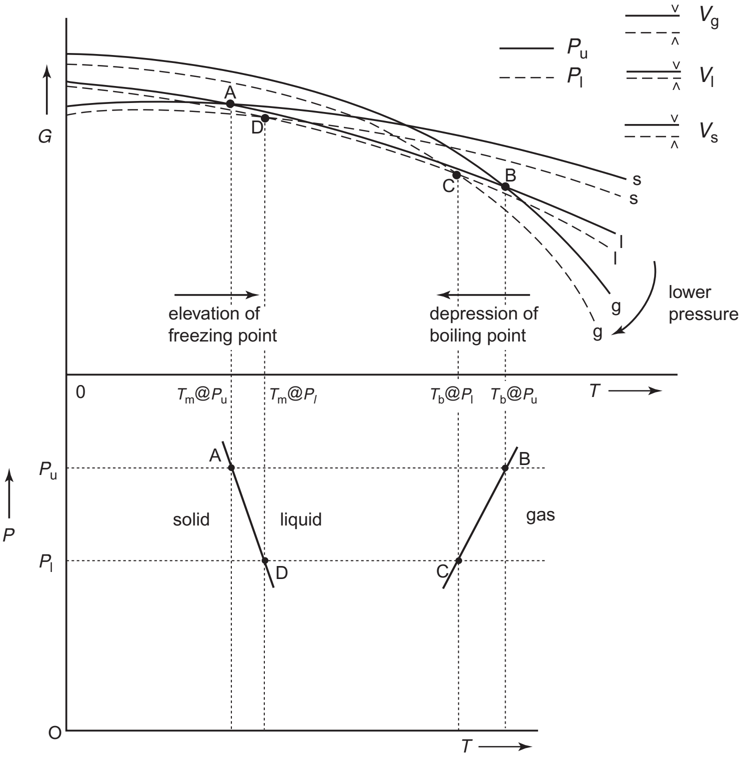


Figure 24.1 Graph of G_i, G_l and G_s and of S_g, S_l and S_s versus temperature, T, at constant pressure, P ($dP = 0$) for water existing in three simple phases (solid, liquid and gas (vapour)).

24.2 Prediction of General Form of Phase Diagram for Water

Combining Figures 24.1 and 24.2 for H_2O and mapping the curves AD, BC and EF onto a phase diagram, we predict that, for H_2O the phase diagram should have the general features shown in Figure 24.3.

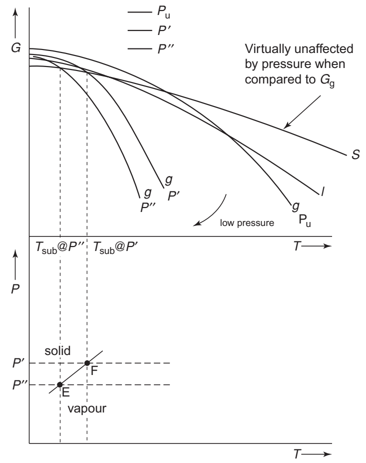


Figure 24.2 Effect of lowering pressure $P_u \rightarrow P_l \rightarrow P' \rightarrow P''$ on boiling point (T_b), melting point (T_m) and sublimation temperatures (T_{sub}) for water.

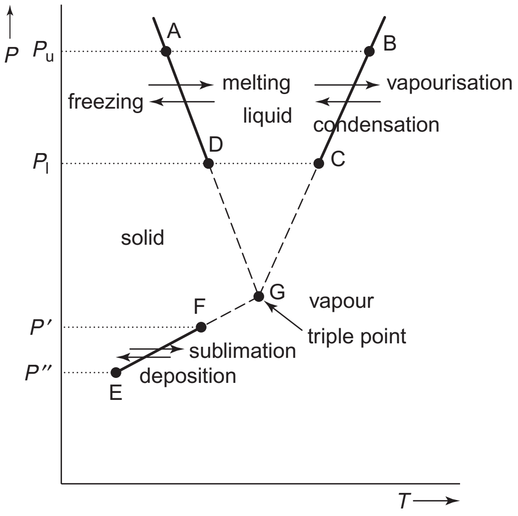


Figure 24.3 Predicted form of the phase diagram for water.

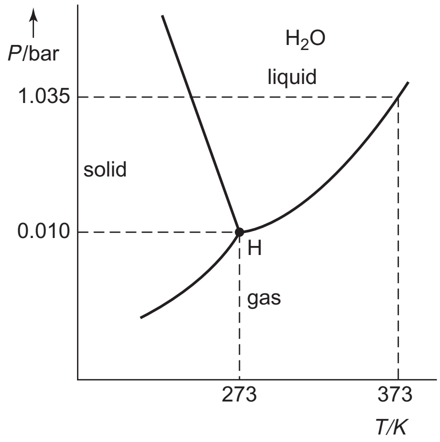


Figure 24.4 Experimental form of the phase diagram for water close to the triple point (at modest pressures).

24.3 Comparison with Experimental Phase Diagram for H_2O

The phase diagram for water, shown close to the triple point H, at which ice is in equilibrium with liquid water and water vapour (steam) is sketched in Figure 24.4.

At high pressures, this phase diagram becomes much more complicated than is shown in Figure 24.4. It then features many different forms of solid ice etc. However our basic predictions above are upheld well at modest pressures. The predominant feature of the phase diagram for water (case (ii)) which differs from those displayed by normal substances (case (i)) is that the gradient of the solid / liquid line (AD) ($dP/dT < 0$) whilst normally (case (i)) it is positive ($dP/dT > 0$).

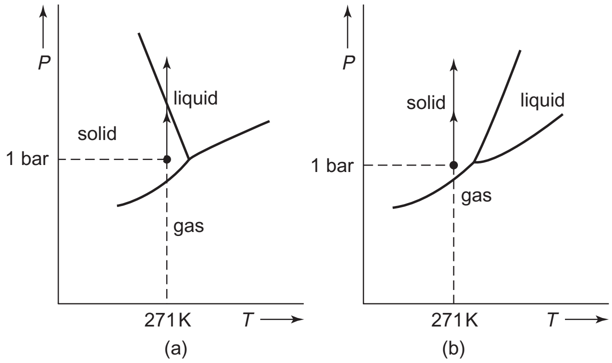


Figure 24.5 Sketch showing how pressure on the solid phase in the case of the phase diagram for water (a) will cause melting whilst normally (b) it will have no effect whatsoever. This is a feature of the gradient dP/dT of the solid/liquid line which differs in the two cases. Note that 271K corresponds to −2° C.

25. Phase Equilibria. Clapeyron Equation

We can now develop *quantitative* relationships. The basic equations governing equilibrium are (Frame 18):

$$G = H - TS \tag{18.1}$$

and

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{18.9}$$

H can be related to (Frame 22, section 22.1) the molecular interactions while S is related to the volume available for the molecules to move in. For gases S is large because of the high degree of randomness present. The stability of gases is thus dominated by their entropy, S.

25.1 Clapeyron Equation. Solid/Liquid Equilibrium at Temperature, *T* and Pressure, *P*

In Figure 23.1, Frame 23 (normal substances, case (i)) or Figure 24.1, Frame 24 (for water, case (ii)) we can move along the line AD which joins points of pressure/temperature values at which *1 mole* of solid and liquid phases co-exist and are in equilibrium. Suppose we move (in Figure 25.1) from an arbitrary point **a** on the line AD to another point **b.** Note that although the slope of AD as shown in the figure is for case (i) 'normal' substances, the slope could equally be the other way (i.e. as for case (ii) water) and the broad discussion below will still apply.

Suppose at point **a** (T'_m, P) the *molar* Gibbs energies of the liquid and solid are G_l and G_s respectively, then because liquid and solid are in equilibrium (at this melting point, T'_m) then:

$$G_\mathrm{l} = G_\mathrm{s} \tag{25.1}$$

Note that these quantities G_l and G_s refer to Gibbs energies of *1 mole* of substance (i.e. are Gibbs energies per mole) as has been assumed throughout Frames 18–24.

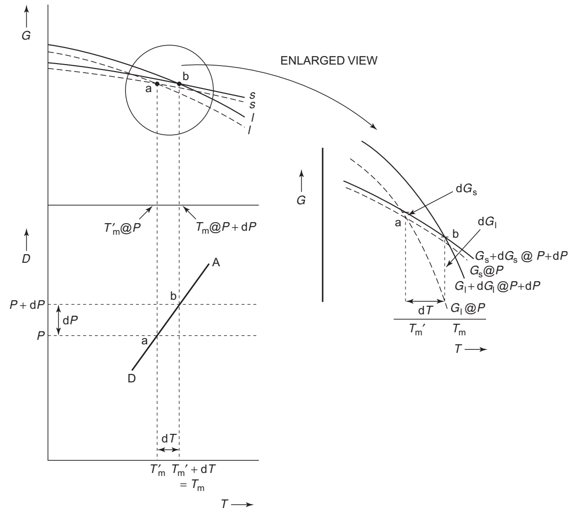


Figure 25.1 Solid/liquid equilibrium at two temperatures and pressures; $(T,\ P) = (T'_\mathrm{m},\ P)$ and $(T + \mathrm{d}T,\ P + \mathrm{d}P) = (T_\mathrm{m},\ P + \mathrm{d}P)$ denoted by points **a** and **b.** At both points **a** and **b** (and indeed at any point along AD) solid and liquid are in equilibrium and their Gibbs energies are therefore equal along AD.

Suppose also, that when we move along AD to point **b** at $(T'_\mathrm{m} + \mathrm{d}T,\ P + \mathrm{d}P) = (T_\mathrm{m},\ P + \mathrm{d}P)$ the Gibbs energy of the liquid is altered to $(G_\mathrm{l} + \mathrm{d}G_\mathrm{l})$ and that for the solid is altered to $(G_\mathrm{s} + \mathrm{d}G_\mathrm{s})$. Since at this point also liquid and solid are in equilibrium the Gibbs energies will once again be equal then:

$$(G_\mathrm{l} + \mathrm{d}G_\mathrm{l}) = (G_\mathrm{s} + \mathrm{d}G_\mathrm{s}) \tag{25.2}$$

Subtracting equation (25.1) from (25.2) leads to:

$$\mathrm{d}G_\mathrm{l} = \mathrm{d}G_\mathrm{s} \tag{25.3}$$

From equation (18.9), Frame 18 and equation (25.3) we can now write, for the liquid and solid phases respectively, that:

$$V_\mathrm{l}\mathrm{d}P - S_\mathrm{l}\mathrm{d}T = V_\mathrm{s}\mathrm{d}P - S_\mathrm{s}\mathrm{d}T \tag{25.4}$$

where V and S are once again *molar* properties ($= V_\mathrm{m}$ and S_m (Frame 0)).

Rearranging equation (25.4) we have:

$$V_\mathrm{l}\mathrm{d}P - V_\mathrm{s}\mathrm{d}P = S_\mathrm{l}\mathrm{d}T - S_\mathrm{s}\mathrm{d}T \tag{25.5}$$

and hence:

$$(V_\mathrm{l} - V_\mathrm{s})\mathrm{d}P = (S_\mathrm{l} - S_\mathrm{s})\mathrm{d}T \tag{25.6}$$

and:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{(S_\mathrm{l} - S_\mathrm{s})}{(V_\mathrm{l} - V_\mathrm{s})} \tag{25.7}$$

Equation (25.7) now gives an expression for the rate of change of pressure with temperature ($= \mathrm{d}P/\mathrm{d}T$) which corresponds to the gradient of the line representing the solid–liquid equilibrium in the phase diagram (gradient of AD Figure 25.1). This quantitative equation (25.7) now enables us to rationalise that since:

$$S_l > S_s \tag{25.8}$$

holds (for normal substances (case (i)) and for water (case (ii)) then the numerator of the equation (25.8) will *always* be positive. Thus the sign of $\mathrm{d}P/\mathrm{d}T$ the gradient of the line AD for the solid–liquid equilibrium will be determined by the sign of the demoninator in equation (25.7). For normal substances:

$$V_l > V_s \tag{25.9}$$

the denominator of will be positive (> 0) making $\mathrm{d}P/\mathrm{d}T$, the gradient of the solid–liquid phase diagram line (AD) positive (as is shown in Figures 23.1 and 23.4, Frame 23).

In the (anomalous) case (ii) of water, however, the inequality in (25.9) is reversed, and the denominator in equation (25.7), $(V_l - V_s) < 0$. Hence $\mathrm{d}P/\mathrm{d}T$, in this case, will be negative (as shown in Figures 24.1 and 24.4, Frame 24). This rationalises the nature of the solid–liquid equilibrium lines which have been discussed in Frames 23 and 24.

In equation (25.7), we can equate:

$$(S_l - S_s) = \Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T} \tag{25.10}$$

using the entropy relationship of equation (13.14) discussed in Frame 13. We can also write:

$$(V_l - V_s) = \Delta_{\text{fus}} V \tag{25.11}$$

hence combining equations (25.7), (25.10) and (25.11) we can write that:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V} \tag{25.12}$$

This is one form of the *Clapeyron Equation* which gives the slope of the P, T line (AD) for the solid–liquid equilibrium in the phase diagram (Figure 25.1, Frame 25).

25.2 Clapeyron Equation. Liquid/Gas Equilibrium at Temperature, *T* and Pressure, *P*

Using similar types of argument applied to the liquid–gas equilibrium line (BC in Figures 23.1, 23.3 and 24.1 in Frames 23 and 24):

$$\mathrm{d}G_g = \mathrm{d}G_l \tag{25.13}$$

and therefore that (equation 18.9, Frame 18 and equation (25.13)):

$$V_g \mathrm{d}P - S_g \mathrm{d}T = V_l \mathrm{d}P - S_l \mathrm{d}T \tag{25.14}$$

and hence $\mathrm{d}P/\mathrm{d}T$, the slope of line CD will be given by:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{(S_g - S_l)}{(V_g - V_l)} \tag{25.15}$$

and since for both normal substances (case (i)) and for water (case (ii)):

$$S_g \gg S_l; \quad V_g \gg V_l \tag{25.16}$$

and hence both $(S_g - S_l)$ and $(V_g - V_l)$ will be positive and hence the line BC has a positive slope in both the Figures 23.1, 23.3 and 24.1 of Frames 23 and 24.

Furthermore since (equation (21.6), Frame 21):

$$(S_g - S_l) = \Delta_{\text{vap}} S = \Delta_{\text{vap}} H / T_b \tag{25.17}$$

and:

$$(V_g - V_l) = \Delta_{\text{vap}} V \tag{25.18}$$

so that:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\text{vap}} S}{\Delta_{\text{vap}} V} = \frac{\Delta_{\text{vap}} H}{(T_b \Delta_{\text{vap}} V)} \tag{25.19}$$

This is a further form of the *Clapeyron Equation* which gives the slope of the P versus T line (BC) for the liquid–vapour equilibrium in the phase diagram.

26. Clausius–Clapeyron Equation Trouton's Rule

26.1 The Clausius–Clapeyron Equation

Continuing to consider *pure* substances, the molar volume of a gas, $V_{\mathrm{m,g}}$:

$$V_{\mathrm{m,g}} = 22\,400\ \mathrm{cm^3\ mol^{-1}} \quad \textit{for all gases} \tag{26.1}$$

(strictly for an ideal gas 0 °C and 1 atm but in any case the correct order of magnitude. Taking water (case (ii)) as an example, its molar mass, M (= molecular weight × g mol^{-1}) = about 18 g mol^{-1} and its density, $\rho = 1$ g cm^{-3} then:

$$V_{\mathrm{m,1}} = \frac{M}{\rho} \approx 18\ \mathrm{cm^3\ \ mol^{-1}} \tag{26.2}$$

whilst, more normal liquids (case (i)) are likely to have $V_{\mathrm{m,l}}$ approximately 10 times this volume. In either case:

$$V_{\mathrm{m,g}} \gg V_{\mathrm{m,l}} \tag{26.3}$$

and so $V_{\mathrm{m,l}}$ can be neglected when compared to $V_{\mathrm{m,g}}$, hence:

$$\Delta_{\mathrm{vap}} V \approx V_{\mathrm{m,g}} \tag{26.4}$$

so that (equation 25.19, Frame 25):

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} S}{V_{\mathrm{m,g}}} = \frac{\Delta_{\mathrm{vap}} H}{T V_{\mathrm{m,g}}} \tag{26.5}$$

Further, if the gas (vapour) is assumed to be ideal (Frames 4, 9, 14, 15, and 31), then:

$$V_{\mathrm{m,g}} = \frac{RT}{P} \tag{26.6}$$

where R is the gas constant (= 8.314 J K^{-1} mol^{-1}), and substituting equation (26.6) into equation (26.5):

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H}{\left\{T\left(\frac{RT}{P}\right)\right\}} = \frac{\Delta_{\mathrm{vap}} H.P}{RT^2} \tag{26.7}$$

Rearranging the above equation:

$$\frac{\mathrm{d}P}{P} = \left[\frac{\Delta_{\mathrm{vap}} H}{RT^2}\right]\mathrm{d}T \tag{26.8}$$

Integration of both sides, assuming that $\Delta_{\mathrm{vap}} H$ is independent of temperature and pressure:

$$\int_{P_1}^{P_2} \frac{\mathrm{d}P}{P} = \left[\frac{\Delta_{\mathrm{vap}} H^o}{R}\right] \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T^2} \tag{26.9}$$

this leads to:

$$[\ln P]_{P_1}^{P_2} = \left[\frac{\Delta_{\mathrm{vap}} H^o}{R}\right] \left[\frac{-1}{T}\right]_{T_1}^{T_2} \tag{26.10}$$

(See Note 26.1) so that:

$$\ln\left(\frac{P_2}{P_1}\right) = -\left(\frac{\Delta_{\mathrm{vap}} H^o}{R}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{26.11}$$

(See Note 26.2).

If we now take exponentials (Frame 6) of both sides of equation (26.11) we have:

$$\left(\frac{P_2}{P_1}\right) = \exp\left\{-\left(\frac{\Delta_{\mathrm{vap}} H^o}{R}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]\right\} \tag{26.12}$$

Equation (26.11) can be transformed to produce yet another form of the Clausius–Clapeyron equation.

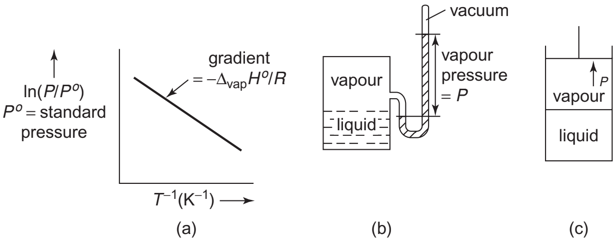


Figure 26.1 (a) Plot of ln (P/P^o) (P^o = standard pressure) versus $1/T$. (b) The measurement of the vapour pressure over a liquid. (c) Representation of vapour pressure, P, over a liquid as used in this text.

A liquid boils, at T_b (= T_2, say) when its vapour pressure (say P_2) equals that of the surrounding atmosphere, (= P^o = 1 atm), so that we can write (using equation (26.11)) that:

$$\ln\left(\frac{P^o}{P_1}\right) = -\left(\frac{\Delta_{vap}H^o}{R}\right)\left[\frac{1}{T_b} - \frac{1}{T_1}\right]; \quad P^o = \text{standard pressure} = 1\text{ atm} \tag{26.13}$$

(See Note 26.3). Multiplying out:

$$\ln\left(\frac{P^o}{P_1}\right) = -\left[\frac{\Delta_{vap}H^o}{RT_b}\right] + \left[\frac{\Delta_{vap}H^o}{RT_1}\right]; \quad P^o = \text{standard pressure} \tag{26.14}$$

but (equation (21.6), Frame 21):

$$\frac{\Delta_{vap}H^o}{T_b} = \Delta_{vap}S^o \tag{26.15}$$

so that:

$$\ln\left(\frac{P^o}{P_1}\right) = -\left[\frac{\Delta_{vap}S^o}{R}\right] + \left[\frac{\Delta_{vap}H^o}{RT_1}\right]; \quad P^o = \text{standard pressure} \tag{26.16}$$

or, for any temperature, T and pressure, P:

$$\ln\left(\frac{P^o}{P}\right) = -\left[\frac{\Delta_{vap}S^o}{R}\right] + \left[\frac{\Delta_{vap}H^o}{RT}\right]; \quad P^o = \text{standard pressure} \tag{26.17}$$

The above equations are variously labelled as *Clausius–Clapeyron equations*. Subject to the satisfactory nature of the assumptions made, a plot (Figure 26.1(a)) of the variation of the natural logarithm of the vapour pressure, $\ln(P/P^o)$, over a liquid measured at various temperatures against the reciprocal of temperature $(1/T)$ should be linear and have a gradient equal to $-\Delta_{vap}H^o/R$ so provides a means of measuring $\Delta_{vap}H^o$ for a variety of liquids (Figure 26.1(b)). Also from vapour pressure data for solids at two or more different temperatures one can measure $\Delta_{sub}H^o$.

In this text we shall use the notation shown in Figure 26.1(c) to represent vapour pressure over a liquid.

An alternative proof of the Clausius–Clapeyron Equation emerges (Frame 50) using the Gibbs Duhem Equation.

26.2 Trouton's Rule

A rule of thumb, called *Trouton's Rule*, approximates the enthalpy of vaporisation, $\Delta_{vap}H^o$ by:

$$\Delta_{vap}H^o \approx 88\left(\frac{T_b}{\text{K}}\right) \quad \text{J mol}^{-1} \tag{26.18}$$

Accordingly, the entropy of vaporisation, $\Delta_{vap}S^o$:

$$\Delta_{vap}S^o = \frac{\Delta_{vap}H^o}{T_b} \approx 88\,\text{J K}^{-1}\text{ mol}^{-1} \tag{26.19}$$

where T_b is the boiling point of the liquid at 1 atmosphere pressure (= 1.0325 bar) or 1 bar. Substances like water and ammonia pose *exceptions*. Hydrogen bonding in these liquids gives a greater degree of ordering and thus:

$$\Delta_{vap}H^o > 88\ T_b\,\text{J K}^{-1}\text{ mol}^{-1} \tag{26.20}$$

Most non-polar liquids have an entropy of vaporisation approximating to 85 J K^{-1} mol^{-1}.

27. Open Systems. Chemical Potential. Chemical Reactions

Up to now the applications we have considered have involved *one component* systems involving only *pure substances* and representing a *fixed amount of matter* (usually 1 mole).

We need now to explore how thermodynamics can be used to study chemical reactions in which one substance is converted into another during a chemical reaction or as part of a physical process (Frame 29).

Such processes can give rise to variation in the amount of the various species present and accordingly to a corresponding transfer or conversion of matter. We confine our immediate attention to simpler reactions in which there is no change of phase (homogeneous systems).

In what we consider below, we have regarded chemical potential as being an 'add-on' when we go from a closed system (Frame 1) with no material transfer occurring, to an open system, where material is added to or taken away from the system. This approach is adopted in the interests of simplicity and to inspire a logical development of the material. Some notes on an alternative approach are provided (see Note 27.1).

27.1 Chemical Potential

We have made mention earlier (Frame 5, section 5.4) albeit very briefly, of the definition of the chemical potential, μ_{i}, of a substance i. For a two component system having components labelled as 1 and 2, this intensive quantity (Frame 1, section 1.3) is defined as the rate of change of Gibbs energy per mole of substance present:

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \mu(1) \tag{27.1}$$

This definition is very similar in form to the partial derivative, $(\partial A/\partial x)_y$ (> 0) discussed (Frame 5, section 5.1) in relation to the area change $\mathrm{d}A_x$ brought about by increasing the length of the side x of a rectangle whilst retaining the other side y at a fixed (i.e. constant) value. By knowing the rate at which A is affected by unit change in x (i.e. knowing $(\partial A/\partial x)_y$) we could then easily calculate the effect on area which will be caused by lengthening side x by a specific amount ($= \mathrm{d}x$). Thus if side x is increased by $\mathrm{d}x$, then the increase in area $\mathrm{d}A_x$ is given by:

$$\mathrm{d}A_x = \left(\frac{\partial A}{\partial x}\right)_y .\mathrm{d}x \tag{27.2}$$

Similarly with the chemical potential, μ_{i}, under conditions of constant temperature and pressure, if we know the chemical potential or the rate of change of free energy, $\mathrm{d}G$, brought about for each unit increase in the amount of the compound 1 ($= (\partial G/\partial n_1)_{T,P,n_2}$) whilst the amount of the other component material (i.e. n_2) remains fixed, then we can easily establish the change, $\mathrm{d}G$, brought about by an increase, $\mathrm{d}n_1$ in the substance 1.

$$\mathrm{d}G = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} .\mathrm{d}n_1 = \mu(1).\mathrm{d}n_1 \tag{27.3}$$

If we rearrange and then integrate equation (27.3) for the addition of 1 mole of material, we have:

$$\int \mathrm{d}G = \int \mu(1).\mathrm{d}n_1 = \mu(1) \int \mathrm{d}n_1 \tag{27.4}$$

leading to:

$$G = \mu(1).n_1 \tag{27.5}$$

So that the chemical potential multiplied by the amount of the substance present gives the free energy of a pure material, conversely, dividing equation (27.5) through by n_1:

$$\mu(1) = \frac{G}{n_1} \tag{27.6}$$

showing that the chemical potential, μ, represents the free energy per mole, G, of a pure substance.

Chemical potentials can apply to phase transformations and equilibria both for pure substances and in mixtures.

In the case of the one-component, closed systems, discussed earlier (Frames 18–25) there were *no changes* in the total amount of material involved (so that: $\mathrm{d}n = 0$). In these latter cases the situation was simply that G was a function of temperature, T and pressure, P:

$$G = \mathrm{f}(T, P) \tag{27.7}$$

and hence (see Frame 5, section 5.1, compare equations (5.3) with equation (27.7) and equation (5.7) with equation (27.8)) we can write:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_T.\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_P.\mathrm{d}T \tag{27.8}$$

and, by virtue of equations (20.3), Frame 20 and (18.14), Frame 18, then equation (27.8) becomes:

$$\mathrm{d}G = V{\cdot}\mathrm{d}P - S{\cdot}\mathrm{d}T \tag{27.9}$$

In systems where the amounts of substances present change – either because we are discussing a chemical reaction or where the amount of material present in each phase varies – then for a two-component system (i.e. having a component 1 + a component 2), G is now dependant also on the amounts of substance, n_1 and n_2 present as well as on pressure, P and temperature, T. So that now, in place of equation (27.7) we have:

$$G = \mathrm{f}(P, T, n_1, n_2) \tag{27.10}$$

and hence we can write:

$$\begin{aligned}\mathrm{d}G &= \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}.\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2}.\mathrm{d}T + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}.\mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1}.\mathrm{d}n_2 \\ &= \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}.\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2}.\mathrm{d}T + \mu(1).\mathrm{d}n_1 + \mu(2).\mathrm{d}n_2 \end{aligned} \tag{27.11}$$

In this equation *three* of the four possible variables are held constant in each partial derivative with only one being varied. The partial derivatives: $(\partial G/\partial n_1)_{T,P,n_2}$ and $(\partial G/\partial n_2)_{T,P,n_1}$ are replaced (in the second line) by the symbols for chemical potential, $\mu(1)$ and $\mu(2)$ (which they define). Further, since from Frame 18, equation (18.14) and Frame 20, equation (20.3), $(\partial G/\partial T)_{P,n_1,n_2}$ and $(\partial G/\partial P)_{T,n_1,n_2}$ equate to – S and V respectively, then:

$$\mathrm{d}G = V.\mathrm{d}P - S.\mathrm{d}T + \mu(1).\mathrm{d}n_1 + \mu(2).\mathrm{d}n_2 \tag{27.12}$$

and now, if the temperature, T and pressure, P are then constant (i.e. $\mathrm{d}T = 0$; $\mathrm{d}P = 0$) for the system under study, then equation (27.12) reduces to:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}.\mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1}.\mathrm{d}n_2 = \mu(1).\mathrm{d}n_1 + \mu(2).\mathrm{d}n_2 \tag{27.13}$$

Because of the close link between G and μ it will be clear that the chemical potential, just like free energy, can be regarded as the driving force which determines whether material can either transfer within the system, move outside it or undergo chemical reaction. It is the latter question which we explore next.

27.2 Multicomponent Systems

For *multicomponent* systems **(**say comprising *n* components**)** we can expand equation (27.11) to take the form:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}.\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2}.\mathrm{d}T + \sum_{i=1}^{n}\mu(i).\mathrm{d}n_\mathrm{i} = V.\mathrm{d}P - S.\mathrm{d}T + \sum_{i=1}^{n}\mu(i).\mathrm{d}n_\mathrm{i} \tag{27.14}$$

27.3 Chemical Reactions and Equilibrium

Suppose we consider a chemical reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{27.15}$$

where a, b, c and d represent the amount of A, B, C and D involved in the reaction. Since G is a state function (Frame 1, section 1.5), we can already anticipate that ΔG will equal the difference between the sum of the free energies of the final state minus those of the initial state (i.e. the sum of the free energies of the products minus the sum of the free energies of the reactants):

$$\begin{aligned}\Delta G = (G_\mathrm{f} - G_\mathrm{i}) &= \sum_{\text{Products}} G(\text{Products}) - \sum_{\text{Reactants}} G(\text{Reactants}) \\ &= [cG(\mathrm{C}) + dG(\mathrm{D})] - [aG(\mathrm{A}) + bG(\mathrm{B})]\end{aligned} \tag{27.16}$$

where $G(\mathrm{A}),\ G(\mathrm{B}),\ G(\mathrm{C})$ and $G(\mathrm{D})$ are the molar free energies of A, B, C and D respectively.

Initially (at time, $t = 0$, at the commencement of the reaction) A and B are mixed together and are the *only* substances present. As the reaction proceeds the amount of the reactants A and B initially present will decrease giving rise to an increasing amount of the products, C and D. This corresponds to a transfer of matter and hence the changes in chemical potentials can usefully be employed to track this reaction thermodynamically. The Gibbs energy of the reaction, *at any point in time*, will depend on its temperature, T and the pressure, P as well as the amount of A, B, C and D present. Suppose we assume that the reaction proceeds to an extent, $\mathrm{d}\varepsilon$. $\mathrm{d}\varepsilon$ is then an extensive variable (Frame 1, section 1.3) (and is expressed in moles) which is equal to zero at the start of the reaction. Once the reaction proceeds this will result in the following changes in the amounts of matter present:

- the change in the amount of A = $\mathrm{d}n_\mathrm{A}$ will correspond to a *decrease* to the extent of: $-a.\mathrm{d}\varepsilon$ moles;
- the change in the amount of B = $\mathrm{d}n_\mathrm{B}$ will correspond to a *decrease* to the extent of: $-b.\mathrm{d}\varepsilon$ moles;
- the change in the amount of C = $\mathrm{d}n_\mathrm{C}$ will correspond to an *increase* to the extent of: $+c.\mathrm{d}\varepsilon$ moles;
- the change in the amount of D = $\mathrm{d}n_\mathrm{D}$ will correspond to an *increase* to the extent of: $+d.\mathrm{d}\varepsilon$ moles

Here

$$G = \mathrm{f}(T, P, n_\mathrm{A}, n_\mathrm{B}, n_\mathrm{C}, n_\mathrm{D}) \tag{27.17}$$

we can write equation (27.11):

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_{T,n_\mathrm{A},n_\mathrm{B},n_\mathrm{C},n_\mathrm{D}}.\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_\mathrm{A},n_\mathrm{B},n_\mathrm{C},n_\mathrm{D}}.\mathrm{d}T + \mu(\mathrm{A}).\mathrm{d}n_\mathrm{A} + \mu(\mathrm{B}).\mathrm{d}n_\mathrm{B} + \mu(\mathrm{C}).\mathrm{d}n_\mathrm{C} + \mu(\mathrm{D}).\mathrm{d}n_\mathrm{D} \tag{27.18}$$

which, for a reaction at constant temperature, T and pressure, P, will reduce to:

$$\mathrm{d}G = \mu(\mathrm{A}).\mathrm{d}n_\mathrm{A} + \mu(\mathrm{B}).\mathrm{d}n_\mathrm{B} + \mu(\mathrm{C}).\mathrm{d}n_\mathrm{C} + \mu(\mathrm{D}).\mathrm{d}n_\mathrm{D} \tag{27.19}$$

By substitution into equation (27.19) for $\mathrm{d}n_\mathrm{A}$, $\mathrm{d}n_\mathrm{B}$, $\mathrm{d}n_\mathrm{C}$ and $\mathrm{d}n_\mathrm{D}$ we have:

$$\begin{aligned}\mathrm{d}G &= \mu(\mathrm{A}).(-a.\mathrm{d}\varepsilon) + \mu(\mathrm{B}).(-b.\mathrm{d}\varepsilon) + \mu(\mathrm{C}).(+c.\mathrm{d}\varepsilon) + \mu(\mathrm{D})(+d.\mathrm{d}\varepsilon)\\ &= [c.\mu(\mathrm{C}) + d.\mu(\mathrm{D}) - a.\mu(\mathrm{A}) - b.\mu(\mathrm{B})].\mathrm{d}\varepsilon\end{aligned} \tag{27.20}$$

when the rate of change of free energy with respect to the extent of reaction (i.e. equal to the differential coefficient: $\mathrm{d}G/\mathrm{d}\varepsilon$) reaches a *minimum* we will have reached *equilibrium* since then, the chemical potentials will have driven the reaction to its fullest possible extent.

If we have a function:

$$y = \mathrm{f}(x) \tag{27.21}$$

the conditions (Frame 3) that y is a minimum are that:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 0 \tag{27.22}$$

and also that:

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} > 0 \tag{27.23}$$

Hence, for the function (27.20) it will reach a minimum value as the reaction proceeds (Figure 27.1). We can calculate this minimum by first evaluating:

$$\frac{\mathrm{d}G}{\mathrm{d}\varepsilon} = [c.\mu(\mathrm{C}) + d.\mu(\mathrm{D}) - a.\mu(\mathrm{A}) - b.\mu(\mathrm{B})] \tag{27.24}$$

from equation (27.20) and hence this will be at its minimum value when $\mathrm{d}G/\mathrm{d}\varepsilon = 0$ or when:

$$[c.\mu(\mathrm{C}) + d.\mu(\mathrm{D})] = [a.\mu(\mathrm{A}) + b.\mu(\mathrm{B})] \tag{27.25}$$

or, described in words:

- when the *total chemical potential for the products is equal to that for the reactants* this corresponds to the reaction's *equilibrium position.*

Translating equation (27.25) back in terms of molar free energies, $G(\mathrm{A})$, $G(\mathrm{B})$, $G(\mathrm{C})$ and $G(\mathrm{D})$ we can write that:

$$[c.G(\mathrm{C}) + d.G(\mathrm{D})] = [a.G(\mathrm{A}) + b.G(\mathrm{B})] \tag{27.26}$$

or that:

$$[c.G(\mathrm{C}) + d.G(\mathrm{D})) - (a.G(\mathrm{A}) + b.G(\mathrm{B})] = 0 \tag{27.27}$$

so, alternatively stated:

- when *the sum of the difference between the free energies of the products and those of the reactants* (weighted by the appropriate stoichiometric coefficients a, b, c and d) *are equal to zero* then this will correspond to the condition of *equilibrium* for the reaction (27.15).

- The situation then corresponds to the case where:

$$\Delta G = 0 \tag{27.28}$$

in equation (27.16) and also signifies that equilibrium has been attained (and is in accord with the discussion in Frame 13, section 13.2 and equation (13.12)).

The situation showing how $G = \mathrm{f}(T, P, n_\mathrm{A}, n_\mathrm{B}, n_\mathrm{C}, n_\mathrm{D})$ varies with the extent of reaction, ε is shown in Figure 27.1.

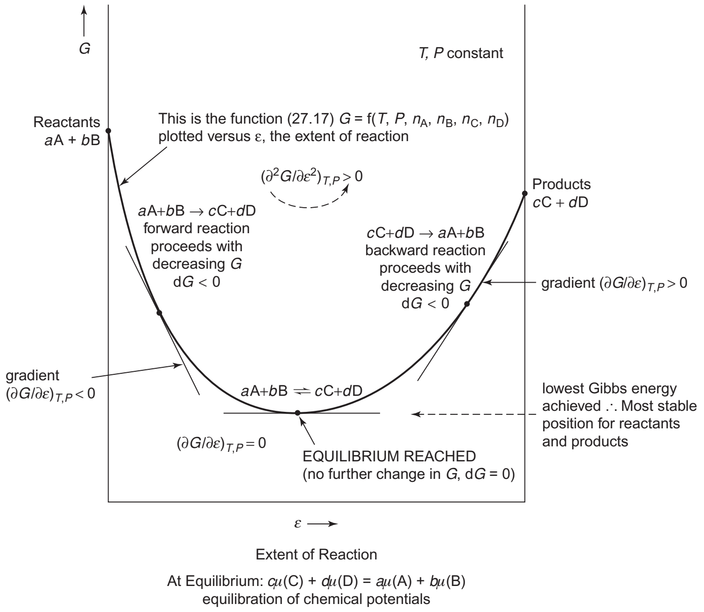


Figure 27.1 Variation of free energy, G for the reaction: $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$ as a function of the extent of reaction, ε. Note: The driving force towards the equilibrium position, starting from either *extreme* of the reaction (i.e. $a\mathrm{A} + b\mathrm{B}$ or $c\mathrm{C} + d\mathrm{D}$) is a *decrease in the overall Gibbs energy*, $\mathrm{d}G < 0$ or an (equivalent) *equilibration* of the sum of the chemical potentials for the reactants and products: $(c.\mu(\mathrm{C}) + d.\mu(\mathrm{D})) = (a.\mu(\mathrm{A}) + b.\mu(\mathrm{B}))$.

28. Coupled Reactions

We now use the thermodynamics so far discussed to study a situation where we have two consecutive reactions.

28.1 Thermodynamics of Coupled Reactions

Consider two masses, M and m (where $M > m$) having a tendency to fall under gravity. If we connect them together with a string (i.e. 'couple' them) passing over a pulley system, we will observe that establishment of equilibrium will lead to the situation where one mass can actually *raise* the other mass. Once the connecting link is removed both will again tend to fall under gravity. Once the masses have been 'coupled' this tendency for each of them to fall can, in favourable circumstances, be halted and reversed.

Analogously, with well chosen pairs of reactions, one thermodynamically unfavourable, i.e. $\Delta G_1 > 0$, can be driven by another thermodynamically *favourable*, reaction where $\Delta G_2 \ll 0$ and hence $\Delta G_2 \ll \Delta G_1$. We consider TWO multiphase (i.e. contaning more than one phase) reactions:

$$\mathrm{AB_2(s)} + 2\ \mathrm{C_2(g)} \overset{\Delta G_1>0}{\rightarrow} \mathrm{AC_4(l)} + \mathrm{B_2(g)} \tag{28.1}$$

and

$$\mathrm{D(s)} + \mathrm{B_2(g)} \overset{\Delta G_2\ll 0}{\rightarrow} \mathrm{DB_2(g)} \tag{28.2}$$

We illustrate this phenomenon of 'coupling' reactions for the case where we require to synthesise $\mathrm{AC_4(l)}$. Assume that $\mathrm{AC_4(l)}$ cannot be produced by the multiphase reaction (28.1) because $\Delta G_1 > 0$ and the reaction is thermodynamically unfavourable. If a second reaction, such as (28.2), is chosen, which:

- *consumes* any *unwanted product(s)* in the reaction (28.1), so leaving the target product;
- is a reaction for which $\Delta G_2 \ll 0$;
- is chosen such that it proceeds well to the right. The extent of reaction ($\mathrm{d}\xi$) is *as large as possible*.

then this second reaction can 'drive' the first one towards completion, since the combined reaction:

$$\mathrm{AB_2(s)} + 2\mathrm{C_2(g)} + \mathrm{D(s)} \overset{\Delta G_3}{\rightarrow} \mathrm{AC_4(l)} + \mathrm{DB_2(g)} \tag{28.3}$$

has a ΔG value ($= \Delta G_3$) such that:

$$\Delta G_3 < 0 \tag{28.4}$$

because addition of the Gibbs energies, whilst taking into account their relative magnitudes, leads to:

$$\begin{array}{c} \Delta G_1 + \Delta G_2 = \Delta G_3 \\ [> 0] \quad [\ll 0] \quad [< 0] \end{array} \tag{28.5}$$

$\mathrm{B_2(g)}$ is involved in *both* reactions being the product necessary to remove from the first reaction.

Suppose we assume that the reaction (28.1) proceeds to an extent, $\mathrm{d}\varepsilon_1$ whilst the reaction (28.2) proceeds to an extent, $\mathrm{d}\varepsilon_2$. Once the reactions begin this will result in the following changes in the amounts of matter present in each

- the change in the amount of $\mathrm{AB_2(s)} = \mathrm{d}n_{\mathrm{AB_2}} = (-\mathrm{d}\varepsilon_1)$;
- the change in the amount of $\mathrm{C_2(g)} = \mathrm{d}n_{\mathrm{C_2}} = (-2\mathrm{d}\varepsilon_1)$;
- the change in the amount of $\mathrm{AC_4(l)} = \mathrm{d}n_{\mathrm{AC_4}} = (+\mathrm{d}\varepsilon_1)$;
- the change in the amount of $\mathrm{B_2(g)} = \mathrm{d}n_{\mathrm{B_2}} = (\mathrm{d}\varepsilon_1 - \mathrm{d}\varepsilon_2)$;
- the change in the amount of $\mathrm{D(s)} = \mathrm{d}n_{\mathrm{D}} = (-\mathrm{d}\varepsilon_2)$;
- the change in the amount of $\mathrm{DB_2(g)} = \mathrm{d}n_{\mathrm{DB_2}} = (+\mathrm{d}\varepsilon_2)$.

At constant temperature, T and pressure, P for this reaction (see equation (27.3), Frame 27)

$$\begin{aligned} \mathrm{d}G = {} & \mu(\mathrm{AB_2, s}) \cdot \mathrm{d}n_{\mathrm{AB_2}} + \mu(\mathrm{C_2, g}) \cdot \mathrm{d}n_{\mathrm{C_2}} + \mu(\mathrm{AC_4, l}) \cdot \mathrm{d}n_{\mathrm{AC_4}} + \mu(\mathrm{B_2, g}) \cdot \mathrm{d}n_{\mathrm{B_2}} \\ & + \mu(\mathrm{D, s}) \cdot \mathrm{d}n_{\mathrm{D}} + \mu(\mathrm{DB_2, g}) \cdot \mathrm{d}n_{\mathrm{DB}} \end{aligned} \tag{28.6}$$

substituting for the change in the amount of reactants and products in relation to the extent of the reaction, we have:

$$\begin{aligned} \mathrm{d}G = {} & \mu(\mathrm{AB_2, s}) \cdot (-\mathrm{d}\varepsilon_1) + \mu(\mathrm{C_2, g}) \cdot (-2\mathrm{d}\varepsilon_1) + \mu(\mathrm{AC_4, l}) \cdot (\mathrm{d}\varepsilon_1) \\ & + \mu(\mathrm{B_2, g}) \cdot (\mathrm{d}\varepsilon_1 - \mathrm{d}\varepsilon_2) + \mu(\mathrm{D, s}) \cdot (-\mathrm{d}\varepsilon_2) + \mu(\mathrm{DB_2, s}) \cdot (\mathrm{d}\varepsilon_2) \end{aligned} \tag{28.7}$$

Collecting terms:

$$\begin{aligned} \mathrm{d}G = {} & [\mu(\mathrm{AC_4, l}) + \mu(\mathrm{B_2, g}) - 2\mu(\mathrm{C_2, g}) - \mu(\mathrm{AB_2, s})] \cdot \mathrm{d}\varepsilon_1 \\ & + [\mu(\mathrm{DB_2, g}) - \mu(\mathrm{B_2, g}) - \mu(\mathrm{D, s})] \cdot \mathrm{d}\varepsilon_2 \end{aligned} \tag{28.8}$$

The above equation (28.8) gives the *overall change* in free energy, $\mathrm{d}G$, of the *two* reactions (28.1) and (28.2) when coupled together. It can be regarded also as representing the sum of the Gibbs energy changes taking place in the separate reactions, $\mathrm{d}G_1 + \mathrm{d}G_2$, i.e.:

$$\mathrm{d}G_3 = \mathrm{d}G_1 + \mathrm{d}G_2 \tag{28.9}$$

where:

$$\mathrm{d}G_1 = [\mu(\mathrm{AC_4, l}) + \mu(\mathrm{B_2, g}) - 2\mu(\mathrm{C_2, g}) - \mu(\mathrm{AB_2, s})] \cdot \mathrm{d}\varepsilon_1 \tag{28.10}$$

and

$$\mathrm{d}G_2 = [\mu(\mathrm{DB_2, g}) - \mu(\mathrm{B_{2,} g}) - \mu(\mathrm{D, s})] \cdot \mathrm{d}\varepsilon_2 \tag{28.11}$$

28.2 Interpretation of the Theory of Coupled Reactions

To reiterate the situation, from these results we can see that if a proposed multiphase reaction (28.1) is selected in order to prepare a given target material (say $\mathrm{AC_4}$, l) but its free energy change: $\Delta G_1 > 0$ it is such that it makes it a *thermodynamically unfavourable* reaction, since (effectively):

$$[\mu(\mathrm{AC_4, l}) + \mu(\mathrm{B_2, g})] > [2\mu(\mathrm{C_2, g}) - \mu(\mathrm{AB_2, s})] \tag{28.12}$$

then it is possible that we could 'drive' it by 'coupling' it with reaction (28.2) for which:

$$\mu(\mathrm{DB_2,\ g}) \ll [\mu(\mathrm{B_{2,}\ g}) + \mu(\mathrm{D, s})] \tag{28.13}$$

Since the second reaction (28.2) is thermodynamically *favourable* and: $\Delta G_2 \ll 0$ therefore reaction (28.1) will now be 'driven' simply because:

$$\Delta G_1 + \Delta G_2 < 0 \tag{28.14}$$

and hence, from equation (28.3), $\mathrm{d}G$ for the overall reaction:

$$\mathrm{D(s)} + \mathrm{AB_2(s)} + 2\mathrm{C_2(g)} \rightarrow \mathrm{AC_4(l)} + \mathrm{DB_2(g)} \tag{28.15}$$

is such that: $\Delta G_3 < 0$ and so the reaction will be thermodynamically favourable and the equilibrium will now lie to the right-hand side (Frame 42, section 42.1).

From equation (28.8) above it will further be seen that if reaction (28.2) is also chosen so as to be one in which the equilibrium lies well to the right, i.e. the extent of this reaction, $\mathrm{d}\varepsilon_2$ is quite large and so:

$$\mathrm{d}\varepsilon_2 \gg 0 \tag{28.16}$$

then this will also contribute further to making ΔG_3 as negative as possible.

It should be noted, of course:

- that there usually are only a handful of possible combinations which can be conceived for coupled reactions
- that we can also couple reactions where the single product of the first reaction is then made the reactant in the second, and an unwanted reactant in the first is removed by making it a reactant in the second reaction
- coupled reactions can be extremely important in biochemistry.

There is an alternative (involving a simpler analysis) way to view these reactions proceeding from equations related to the van't Hoff Equation (Frames 46 and 47) in the form:

$$\ln K_{\mathrm{p/p_o}} = \exp(-\Delta G^{\mathrm{o}}/RT) \tag{28.17}$$

introduced later in this text. The conclusions drawn are identical (section 47.2, Frame 47).

29. Chemical Potentials Applied to Physical Processes in Multiphase Closed Systems

Consider the role of chemical potential in examining the transition of material between different phases. Our earlier premise (Frame 21, section 21.1 – fifth bullet point) – that if we have two phases present then the phase having the *lowest* free energy, G (and hence the *lowest* chemical potential, μ) will represent the more stable of the two phases – can now be further examined.

In reactions we have seen (Frame 27, section 27.3 and Figure 27.1) these are driven by a tendency for the sum of the chemical potentials of the products to become equal to the sum of those for the reactants. Reaching equality corresponds to the attainment of the equilibrium.

We consider below processes in which equality of chemical potentials illustrates the determination of equilibrium.

29.1 Equalisation of Chemical Potentials

Consider a multicomponent system containing n different substances (or *components*) numbered $1,2,\ldots,i,\ldots,n$ where we use i to represent any general component. Suppose, T and pressure, P are held constant and that *all* the components *except i* have a constant composition throughout the system. Consider two separate regions of the system, labelled A and B (Figure 29.1) in which the chemical potential of i is $\mu_{\mathrm{i}}^{(\mathrm{A})}$ in region A and $\mu_i^{(\mathrm{B})}$ in region B. The fact that the chemical potentials $\mu_i^{(\mathrm{A})}$ and $\mu_i^{(\mathrm{B})}$ are different hinges on the fact that equilibrium has not yet been established for the component i in the system.

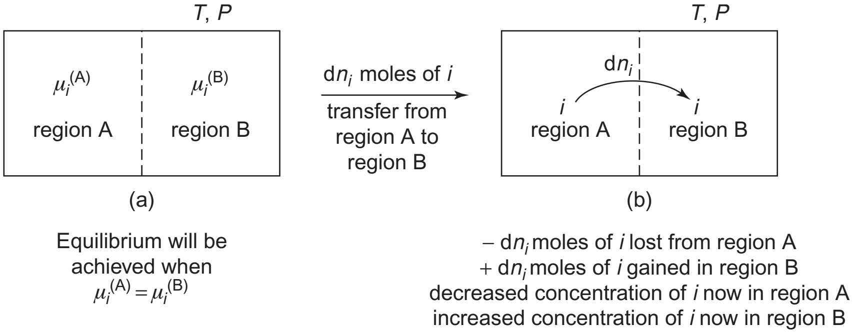


Figure 29.1 Consideration of transfer of an amount dn_i of substance i from region A to region B when all other components remain at constant composition and temperature and pressure remain constant (and are therefore not considered).

An equation of the form of (27.3), Frame 27 can be used to calculate changes, $\mathrm{d}G_{(\mathrm{A})}$ and $\mathrm{d}G_{(\mathrm{B})}$ brought about in the regions A and B when an amount $\mathrm{d}n_i$ of component i is transferred across from region A to region B.

Accordingly, in this transfer:

$$\mathrm{d}G_{(\mathrm{A})} = \mu_i^{(\mathrm{A})}(-\mathrm{d}n_i) \tag{29.1}$$

$$\mathrm{d}G_{(\mathrm{B})} = \mu_i^{(\mathrm{B})}(+\mathrm{d}n_i) \tag{29.2}$$

and hence the total free energy change, $\mathrm{d}G$, caused by the transfer of an amount $\mathrm{d}n_i$ of material:

$$\mathrm{d}G = \mathrm{d}G_{(\mathrm{A})} + \mathrm{d}G_{(\mathrm{B})} = \mu_i^{(\mathrm{A})} \cdot (-\mathrm{d}n_i) + \mu_i^{(\mathrm{B})} \cdot (+\mathrm{d}n_i) = [\mu_i^{(\mathrm{B})} - \mu_i^{(\mathrm{A})}] \cdot \mathrm{d}n_i \tag{29.3}$$

In order that this movement of an amount $\mathrm{d}n_i$ of component i from region A to region B occurs spontaneously (Frame 14, section 14.4) then $\mathrm{d}G$ would negative. This, in turn, would require (comparing equation (29.3) with equation (27.13), Frame 27) that:

$$\mu_i^{(\mathrm{B})} < \mu_i^{(\mathrm{A})} \tag{29.4}$$

This means, in turn, that to achieve an equilibrium position a substance will always migrate to a region *where its chemical potential can be lowest*.

This principal can be automatically extended to apply to phases of substances and confirms our earlier conjecture (Frame 21, section 21.1) that the phase with the lower free energy will always correspond to the more stable phase.

The system in Figure 29.1(b) in achieving equilibrium adjusts the amount of material present in each region A and B, therefore, to give an overall value of d$G = 0$, which requires that:

$$\mu_i^{(\mathrm{A})} = \mu_i^{(\mathrm{B})} \tag{29.5}$$

chemical potentials for each component i are equalised between the regions (phases) A and B.

29.2 Generalisations

Often we are interested in phase transitions and how various components might distribute themselves between the various possible phases of a system. From equation (27.14), Frame 27 we see that at constant temperature, T and pressure, P for a *multicomponent* system containing n components (1,2, ... i, ... , n) that:

$$\mathrm{d}G = \mu_1.\mathrm{d}n_1 + \mu_2.\mathrm{d}n_2 + \cdots + \mu_\mathrm{i}.\mathrm{d}n_\mathrm{i} + \cdots = \sum_{i=1}^{n} \mu_\mathrm{i}.\mathrm{d}n_\mathrm{i} \tag{29.6}$$

This equation permits us to examine, within a multicomponent system:

- the amount of substance that will be present in each individual phase;
- the chemical potential of the components that are present in each of the phases

always provided that the phases are susceptible to transfer of material between themselves (i.e. they are *open* phases).

Figure 29.2 displays three situations at constant temperature, T and pressure, P. In diagram (a) we have a single 'closed' phase (labelled α) which contains two components labelled 1 and 2 whose chemical potentials are $\mu_1^{(\alpha)}$ and $\mu_2^{(\alpha)}$ but the thermodynamic system is such that no matter can be transferred across the boundaries of the system. Hence adapting equation (29.6) to apply to this case, the change in free energy, d$G^{(\alpha)}$ for the system is given by:

$$\mathrm{d}G^{(\alpha)} = \mu_1^{(\alpha)}.\mathrm{d}n_1^{(\alpha)} + \mu_2^{(\alpha)}.\mathrm{d}n_2^{(\alpha)} \tag{29.7}$$

Since no material transfer takes place, then:

$$\mathrm{d}n_1^{(\alpha)} = \mathrm{d}n_2^{(\alpha)} = 0 \tag{29.8}$$

and hence d$G^{(\alpha)} = 0$, the system is in equilibrium and also then:

$$\mu_1^{(\alpha)}.\mathrm{d}n_1^{(\alpha)} + \mu_2^{(\alpha)}.\mathrm{d}n_2^{(\alpha)} = 0 \tag{29.9}$$

This is one form of the Gibbs–Duhem equation discussed in more detail in Frame 68.

In the diagram in Figure 29.2(b) we display a three-phase system (with phases labelled α, β and γ) each phase containing two components (labelled 1 and 2). Since the phases are 'open' then transfer of material is possible between some of the phases present. Thus d$n_i^{(\beta)}$ signifies the amount of material i which is removed from phase β phase to γ, as is shown. The following transfers occur in Figure 29.2(b):

- for component 1:

d$n_1^{(\alpha)}$ from phase α to phase β;
d$n_1^{(\beta)}$ from phase β to phase γ;

- for component 2:

d$n_2^{(\alpha)}$ from phase α to phase β;
d$n_2^{(\beta)}$ from phase β to phase γ;

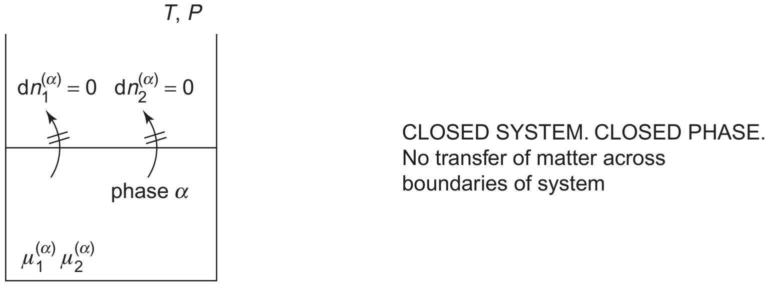
Various conditions can be written which correspond to the system being at equilibrium:

$$\mathrm{d}G = \mathrm{d}G^{(\alpha)} + \mathrm{d}G^{(\beta)} + \mathrm{d}G^{(\gamma)} = 0 \tag{29.10}$$

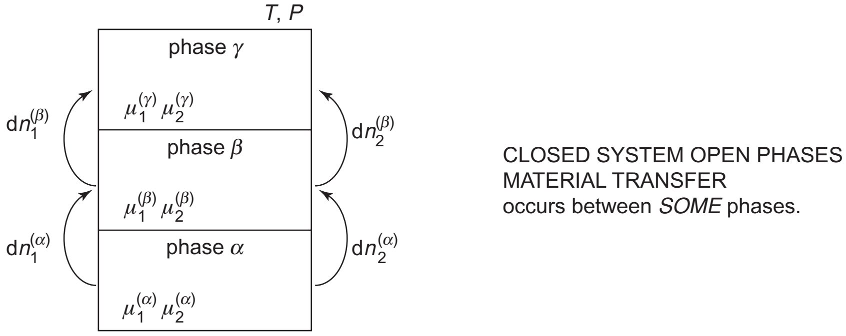
$$\mathrm{d}G^{(\alpha)} = \mu_1^{(\alpha)}.\mathrm{d}n_1^{(\alpha)} + \mu_2^{(\alpha)}.\mathrm{d}n_2^{(\alpha)} \tag{29.11}$$

$$\mathrm{d}G^{(\beta)} = \mu_1^{(\beta)}.\mathrm{d}n_1^{(\beta)} + \mu_2^{(\beta)}.\mathrm{d}n_2^{(\beta)} \tag{29.12}$$

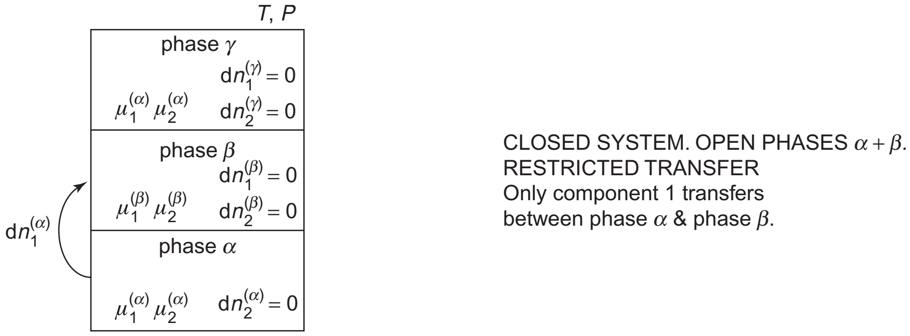
$$\mathrm{d}G^{(\gamma)} = \mu_1^{(\gamma)}.\mathrm{d}n_1^{(\gamma)} + \mu_2^{(\gamma)}.\mathrm{d}n_2^{(\gamma)} \tag{29.13}$$



(a) Single phase (α), 2 components (1 & 2)



(b) three phase system (α, β, γ), 2 components (1 & 2)



(c) three phase system (α, β, γ), 2 components (1 & 2)

Figure 29.2 Three scenarios

so that, adding equations (29.11), (29.12) and (29.13):

$$\begin{aligned}\mathrm{d}G &= \mu_1^{(\alpha)}.\mathrm{d}n_1^{(\alpha)} + \mu_2^{(\alpha)}.\mathrm{d}n_2^{(\alpha)} + \mu_1^{(\beta)}.\mathrm{d}n_1^{(\beta)} + \mu_2^{(\beta)}.\mathrm{d}n_2^{(\beta)} + \mu_1^{(\gamma)}.\mathrm{d}n_1^{(\gamma)} + \mu_2^{(\gamma)}.\mathrm{d}n_2^{(\gamma)} \\ &= \mathrm{d}G^{(\alpha)} + \mathrm{d}G^{(\beta)} + \mathrm{d}G^{(\gamma)} = 0 \end{aligned} \tag{29.14}$$

Suppose we now limit the possible transfer occurring (Figure 29.2(c)) such that:

- an amount $\mathrm{d}n_1$ ($= \mathrm{d}n_1^{(\alpha)}$) of component 1 is transferred from phase α to phase β. This means that:

$$\mathrm{d}n_2^{(\alpha)} = \mathrm{d}n_2^{(\beta)} = \mathrm{d}n_2^{(\gamma)} = 0 \tag{29.15}$$

  and

$$\mathrm{d}n_3^{(\alpha)} = \mathrm{d}n_3^{(\beta)} = \mathrm{d}n_3^{(\gamma)} = 0 \tag{29.16}$$

- there is no corresponding transfer of substance 2 between phases and therefore the composition of substance 2 remains unchanged in all phases.

$$\mathrm{d}n_2^{(\alpha)} = \mathrm{d}n_2^{(\beta)} = \mathrm{d}n_2^{(\gamma)} = 0 \tag{29.15}$$

- there is no alteration to the composition of phase γ:

$$\mathrm{d}n_1^{(\gamma)} = \mathrm{d}n_2^{(\gamma)} = 0 \tag{29.17}$$

$$\mathrm{d}G^{(\gamma)} = 0 \tag{29.18}$$

We can then write for this situation, that the overall free energy of the system, dG:

$$\mathrm{d}G = \mathrm{d}G^{(\alpha)} + \mathrm{d}G^{(\beta)} + \mathrm{d}G^{(\gamma)} = \mu_1^{(\alpha)} \cdot (-\mathrm{d}n_1) + \mu_1^{(\beta)} \cdot (+\mathrm{d}n_1) + \mathrm{d}G^{(\gamma)} \tag{29.19}$$

where we have used the appropriate forms of equations (29.11) and (29.12) and – since there are no compositional changes taking place in phase γ – then this phase must, itself, already be in equilibrium (equation (29.18)) and hence, from equation (29.19) then:

$$\mathrm{d}G = \mathrm{d}G^{(\alpha)} + \mathrm{d}G^{(\beta)} = [\mu_1^{(\beta)} - \mu_1^{(\alpha)}]\mathrm{d}n_1 \tag{29.20}$$

To establish total equilibrium the overall dG *must equal* 0 and to achieve this (already established for phase γ, then equilibrium needs to be established between phases α and β and since in equation (29.20):

$$\mathrm{d}n_1 \neq 0 \tag{29.21}$$

and transfer of component 1 does take place, then:

$$[\mu_1^{(\beta)} - \mu_1^{(\alpha)}] = 0 \tag{29.22}$$

or material 1 will transfer between phases α and β until the chemical potentials of substance 1 in the two phases become equal, i.e.:

$$\mu_1^{(\alpha)} = \mu_1^{(\beta)} \tag{29.23}$$

In order that equilibrium exists between phases α and γ and between β and γ, it must also be the case that, for substance 1:

$$\mu_1^{(\alpha)} = \mu_1^{(\gamma)} \tag{29.24}$$

and

$$\mu_1^{(\beta)} = \mu_1^{(\gamma)} \tag{29.25}$$

leading to the overall conditions for equilibrium for the system for *both* components 1 and 2 that:

$$\mu_1^{(\alpha)} = \mu_1^{(\beta)} = \mu_1^{(\gamma)} \tag{29.26}$$

and

$$\mu_2^{(\alpha)} = \mu_2^{(\beta)} = \mu_2^{(\gamma)} \tag{29.27}$$

29.3 Summary

Generalising for any system containing n components in p phases the conditions governing the transfer of matter between phases are:

- that chemical equilibrium between the phases should be established such that:

$$\mathrm{d}G = \mathrm{d}G^{(\alpha)} + \mathrm{d}G^{(\beta)} + \mathrm{d}G^{(\gamma)} + \cdots + \mathrm{d}G^{(p)} = 0 \tag{29.28}$$

and

- that the chemical potential for *each* component, i, present should be *the same in every phase* at constant temperature, T and pressure, P.

$$\mu_\mathrm{i}^{(\alpha)} = \mu_\mathrm{i}^{(\beta)} = \mu_\mathrm{i}^{(\gamma)} = \cdots = \mu_\mathrm{i}^{(p)} \text{ for all components } \mathrm{i} = 1, 2, \ldots, \mathrm{i} \ldots \mathrm{n} \tag{29.29}$$

For an alternative approach see Note 29.1.

30. The Phase Rule

In each of the phase diagrams (Figures 23.3 and 23.4 in Frame 23), we can observe the following features:

- a *point* (the *triple point*) at a particular, P and T where all three phases (p = number of phases present in the system = 3) are present (i.e. corresponding to the co-existence of solid, liquid and gas phases);
- *lines* occur which connect the values of P, T, at which equilibria between solid and liquid (e.g. line AD) (melting), liquid and gas (e.g. line BC) (vaporisation), and solid and gas (e.g. line EF) (sublimation) occur;
- *areas* in which only *one phase* (solid, liquid or gas) exists at the relevant temperatures and pressures corresponding to these regions in the phase diagram.

A phase is that portion of a system which is homogeneous. A complicated system can have more than one solid phase corresponding to different crystal structure variations (e.g. pleomorphic forms of $CaCO_3$: calcite, aragonite and vaterite). Sometimes it can also have more than one liquid phase but usually contains only one gaseous phase. We can have a system having a total of p phases with c components (i.e. substances) present. Thus many of the important phase systems are more complicated than the simple one-component systems so far discussed.

We first discuss what is meant by *degree of freedom* and how we can specify the *composition* of a given mulitcomponent phase. We define independent and dependent variables and the *Phase Rule* itself. The latter, which is quite general, applies to *multicomponent* systems and links the number of components (c), the number of phases (p) and the number of degrees of freedom (f) required for complete specification of a system in terms of temperature, pressure and composition.

30.1 Degrees of Freedom or Variance of a Thermodynamic System (*F*)

The number of degrees of freedom (= f) of a thermodynamic or other system is the *minimum* number of variables needed completely define the system at equilibrium. Knowledge of these variables enable the system to reproduced in all details.

- To specify the triple point (tp) in Figure 23.3, Frame 23 we need to specify only 2 variables, the pressure P^*_{tp} and the temperature T_{tp}.

  Here there are *no degrees of freedom* ($f = 0$) since there is only *one* unique value of temperature (T_{tp}) and pressure (P^*_{tp}), corresponding to a single (triple) point at which solid, liquid and gas (i.e. three phases hence $p = 3$) co-exist together. Thus at the triple point:

$$\mu_1^{(\mathrm{solid})}(T_{\mathrm{tp}}, P^*_{\mathrm{tp}}) = \mu_1^{(\mathrm{liquid})}(T_{\mathrm{tp}}, P^*_{\mathrm{tp}}) = \mu_1^{(\mathrm{gas})}(T_{\mathrm{tp}}, P^*_{\mathrm{tp}}) \tag{30.1}$$

Here we can see an example of a quite general principle that:

$$\begin{aligned}&[\textit{number of degrees of freedom, } f] \\ &\quad = [\textit{number of variables, } v] - [\textit{number of independent equations linking the variables, } e]\end{aligned} \tag{30.2}$$

since there are:

- two variables (T and P), $v = 2$

and

- two related equations within the relationship (30.1) (i.e. two = signs) and therefore $e = 2$

thus:

- from equation (30.2):

$$f = v - e = 2 - 2 = 0 \tag{30.3}$$

- In contrast if two separate phases co-exist ($p = 2$) at a given temperature and pressure, then we can have any one of the following situations:

$$\mu_1^{(\mathrm{solid})}(T_{\mathrm{m}}, P) = \mu_1^{(\mathrm{liquid})}(T_{\mathrm{m}}, P) \tag{30.4}$$

$$\mu_1^{(\mathrm{liquid})}(T_{\mathrm{b}}, P) = \mu_1^{(\mathrm{gas})}(T_{\mathrm{b}}, P) \tag{30.5}$$

$$\mu_1^{(\mathrm{solid})}(T_{\mathrm{sub}}, P) = \mu_1^{(\mathrm{gas})}(T_{\mathrm{sub}}, P) \tag{30.6}$$

where T_m, T_b and T_{sub} are the melting, boiling and sublimation temperatures at the pressure, P. These values of T and P ($v = 2$) have to define (i.e. fall on) the lines AB, CD and EF respectively, T and P are no longer independent because once one of these variables, say temperature, T is specified, then the *corresponding pressure, P* is automatically fixed (since it must lie also on the line) and therefore can only take *one precise* value. Conversely specifying a pressure, P, on the line, fixes the corresponding temperature, T. We thus *one choice* (i.e. either to specify a temperature or a pressure) and hence we have *one degree of freedom* (of choice) (so that $f = 1$). It should also be noted that because there is one equation representing the particular line AB, CD or EF then $e = 1$ in equation (30.2), so satisfying the relationship between, f, v and e.

Here again there are two variables (T and P) but now only one equation (i.e. represented by either equation (30.4), (30.5) or (30.6) depending on which equilibrium is being discussed), hence from equation (30.2):

$$f = v - e = 2 - 1 = 1 \tag{30.7}$$

This is called a *univariant* system.

- Finally in Figure 23.3, Frame 23 there are regions (areas) where both T and $P(v = 2)$ can freely vary over quite wide ranges and, these two variables are completely independent of one another. If we choose a selected temperature, T then in the areas of the phase diagram where only one phase ($p = 1$) exits there are a plethora of choices of a corresponding P value for which the point with coordinates (T, P) lies within the single-phase stability area of the diagram. In such areas we thus have *a choice* of both temperature and pressure (i.e. as variables which we can arbitrarily select) and hence we have *two degrees of freedom* (so $f = 2$). There are no defining equations for the areas, hence $e = 0$.

  In this case:

$$f = v - e = 2 - 0 = 2 \tag{30.8}$$

This is called a *bivariant* system.

In more complicated phase diagrams composition also features as a variable or variables and so in order to broaden this discussion we need to discuss how we can quantify the composition of components within a mixture of these components.

30.2 Specification of Composition in a Mixture of Substances. Mole Fraction, *x*

To completely specify a mixture we need to define a minimum level of specification using the least number of variables – just sufficient so as to exactly define our system in such a way as to make it completely reproducible from a knowledge of these variables.

This is best achieved by using *mole fraction*, x, to define the composition of the phases.

Suppose we have a system containing c components labelled 1, 2, …, c within any given phase. If there are $n_1, n_2, \ldots, n_c$ moles of each individual component present in the mixture we can define the composition by specifying the *mole fractions*, $x_1, x_2, \ldots, x_c$ of the components (Figure 30.1) where x_i for, component i is defined as:

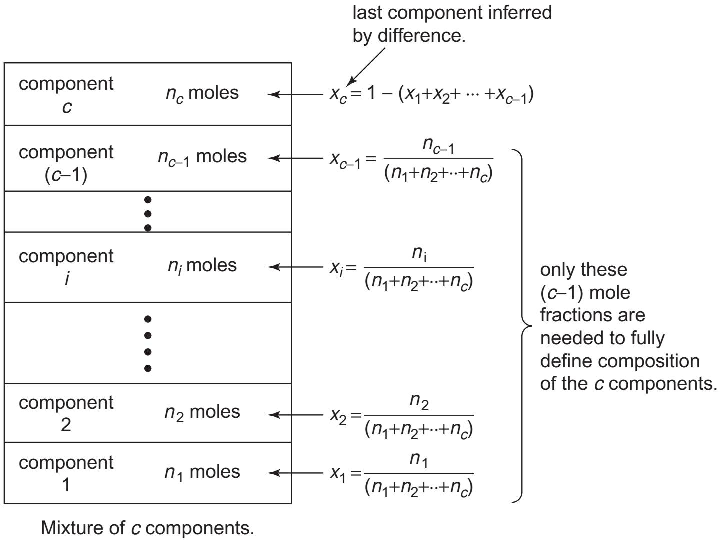


Figure 30.1 Schematic diagram. Mole fraction, x, is used to completely define the composition of the c components present. Only $(c - 1)$ mole fractions need be stated since the final composition, x_c can be inferred from the other $(c - 1)$ because the total mole fraction sum $= (x_1 + x_2 + \cdots + x_c) = 1$.

$$\begin{aligned} x_i &= [\text{amount of component } i \text{ present}]/[\text{total amount of all substances present}] \\ &= \frac{n_i}{(n_1 + n_2 + \cdots + n_i + \cdots + n_c)} \end{aligned} \tag{30.9}$$

As a general principle if one divides up *any quantity* using fractions the total sum of the individual fractions *will always add up to unity*. Beacause of this rule, we need only specify *one less than the total* of fractions actually involved since the final one is such as to make the total up to a whole (= 1).

Mole fractions are no exception (see Note 30.1):

$$\{x_1 + x_2 + \cdots + x_c\} = \sum_{i=1}^{c} n_i/(n_1 + n_2 + \cdots + n_i + \cdots + n_c)] = \sum_{i=1}^{c} n_i \Big/ \sum_{i=1}^{c} n_i = 1 \tag{30.10}$$

The consequences of the use of this fractional definition is that we only need to specify the mole fractions, $x_1, x_2, \ldots x_{(c-1)}$ of $(c-1)$ out of total of c components, since the final cth mole fraction (i.e. x_c) can be *inferred* by subtracting the sum $(c-1)$ others from 1.

30.3 Independent and Dependent Variables

For any thermodynamic system:

$$\begin{aligned}&[\text{number of independent components (or chemical species) required to specify the system}]\\ &\quad = [\text{total } \textit{number} \text{ of components (or chemical species)}]\\ &\qquad - [\text{number of chemical equilibria linking these components (or chemical species)}]\end{aligned} \tag{30.11}$$

This equation can be illustrated easily with reference to the equilibrium between nitrogen, hydrogen and ammonia in the gaseous phase:

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) \tag{30.12}$$

For this equilibrium, the equilibrium constant, K_x, (see Appendix and Frames 43 section 43.3), which is, in this example, conveniently written in terms of the mole fractions: x_{N_2}, x_{H_2} and x_{NH_3} of nitrogen, hydrogen and ammonia present, is given by:

$$K_x = \frac{(x_{NH_3})^2}{(x_{N_2}).(x_{H_2})^3} \tag{30.13}$$

As we shall see later the K_x, is a *constant* related to the mole fractions present when the system is at equilibrium. If the amount of one of these species present is now varied, then the equilibrium reestablishes itself so that the amounts of the other chemical species adjust themselves in such a way that their new values when substituted into equation (30.13) give the equilibrium constant, K_x.

Furthermore,

$$x_{H_2} + x_{N_2} + x_{NH_3} = 1 \tag{30.14}$$

In this reaction we cannot alter any one of the mole fractions (x_{N_2}, x_{H_2} or x_{NH_3}) without automatically altering the other two, thus of the three variables each one of them is dependent on the other two, so that we have one dependent variable. Put another way only two of the variables are independent. Thus in this example:

$$[\text{number of independent components (or chemical species) required to specify the system}] = 2$$

$$[\text{total } \textit{number} \text{ of components (or chemical species)}] = 3$$

$$[\text{number of chemical equilibria linking these components (or chemical species)}] = 1$$

so that equation (30.11) holds

30.4 The Phase Rule

Figure 30.2 illustrates schematically system at equilibrium consisting of p phases in which each of the c components (numbered $1, 2, \ldots, c$) exist in each phase. The equilibrium condition requires (Frame 29; section 29.3, equation (29.9)) equality of the chemical potential for each of the c components across each of the p phases $(1, 2, \ldots, p)$ and is specified by the following set of equations :

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} = \cdots = \mu_1^{(p)} \tag{30.15}$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} = \cdots = \mu_2^{(p)} \tag{30.16}$$

$$\bullet$$

$$\mu_c^{(1)} = \mu_c^{(2)} = \mu_c^{(3)} = \cdots = \mu_c^{(p)} \tag{30.17}$$

The total number of equations above is $c(p-1)$ (i.e. there are $(p-1)$ = signs for each of the c components) hence in equation (30.2) the term:

$$[\textit{number of independent equations linking the variables}] = e = [c(p-1)] \tag{30.18}$$

The number of variables needed to specify the T, P, and composition of the system will be equal to 2 (i.e. for temperature

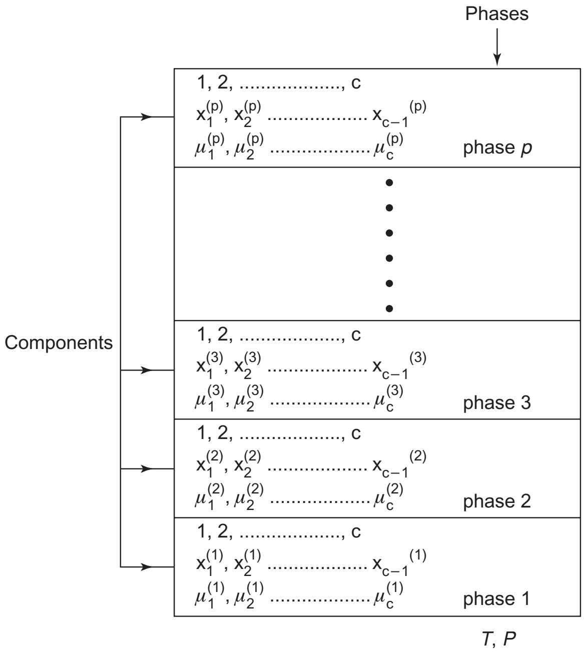


Figure 30.2 Schematic diagram. Complicated system comprising c components present in each of the p phases. In each phase (Frame 29, section 29.2) the chemical potential of each of the components must be equal at equilibrium.

and pressure) + the number of variables required to specify the composition (i.e. number of mole fraction variables required). The latter will be for c components and is equal to $(c-1)$ and thus, in each of p phases, this will be $p(c-1)$ hence in equation (30.2) the term:

$$[\textit{number of variables}] = v = [2 + p(c-1)] \tag{30.19}$$

and hence, for the *general case of any phase system*:

$$\begin{aligned} f &= [\textit{number of degrees of freedom}] \\ &= v - e = [2 + p(c-1)] - [c(p-1)] = [2 + pc - p - cp + c] \end{aligned} \tag{30.20}$$

and thus since the terms pc and cp cancel then:

$$f = c - p + 2 \tag{30.21}$$

which is the *Phase Rule* whose purpose is to define the number of degrees of freedom, f, needed to completely define a phase system when at equilibrium.

In words the Phase Rule states:

$$\begin{aligned} &[\textit{number of degrees of freedom needed in order to completely define a phase system at equilibrium}] \\ &\quad = [\text{number of components present}] - [\text{number of phases present}] + 2 \end{aligned} \tag{30.22}$$

An alternative, and equally satisfactory, proof of the Phase Rule emerges in Frame 50, section 50.3 using the Gibbs–Duham Equation as the starting point.

30.5 Application of the Phase Rule: $f = c - p + 2$

Returning now to the beginning of this Frame we can see that using the Phase Rule (equation (30.21)) where three phases solid, liquid and gas co-exist (then $p = 3$) and the number of components ($c = 1$) because a pure material is being considered, then:

$$f = c - p + 2 = 1 - 3 + 2 = 0 \tag{30.23}$$

so there are no degrees of freedom and the phase is defined completely using a (triple) point on the phase diagram.

If, on the other hand we have either solid–liquid, liquid–gas or solid–gas equilibria involving just two phases (then $p = 2$), then for a single (pure) component ($c = 1$) and here:

$$f = c - p + 2 = 1 - 2 + 2 = 1 \tag{30.24}$$

and so we have one degree of freedom in order to specify the phase completely. Examples here are the lines in the phase diagrams already discussed (examples being the lines AD for the solid–liquid equilibrium and CD for the liquid–gas equilibrium in Figure 24.1 in Frame 24 and the line EF for the solid–gas equilibrium in Figure 24.2 in Frame 24.

If we have a single degree of freedom ($f = 1$) the situation is represented by a connecting line (of the general form: $y = \mathrm{m}x + \mathrm{c}$, or more usually $P = \mathrm{a}T + \mathrm{b}$ where a and b are constants) through all the points (T, P) which represent an equilibrium. Hence if either T or P is specified the value of the other variable is then fixed by the equation.

Finally if only one phase is present (then $p = 1$) as either a pure solid, pure liquid or a pure gas (hence $c = 1$) then:

$$f = c - p + 2 = 1 - 1 + 2 = 2 \tag{30.25}$$

we now have 2 degrees of freedom (represented say by P and T which are no longer constrained to obey a fixed linear equation), hence the phase can, in this case, be represented by an area on the phase diagram.

31. Ideal and Real Gases
Dalton's Law of Partial Pressures

31.1 Ideal (Perfect) Gases

Ideal (perfect) gases have been discussed earlier (in Frames 4 & 9) and are defined as those gases which obey the relationship:

$$PV = nRT \tag{31.1}$$

where P is the total pressure of the gas, V is the volume of the gas, n, the amount of substance (so that V/n defines the molar volume of ideal gas $= V_m$), T is the absolute (or thermodynamic) temperature and R is the gas constant ($= 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$).

Gases tend to obey the *Ideal Gas Law* (31.1) well, especially at low pressures where no intermolecular forces are present. In *ideal solutions* whether solutions of gases in gases (this Frame), solids in liquids (Frame 32) or liquids in liquids (Frame 33) it is not so much interactions which are *absent* but rather that none are preferential and so dominate the behaviour. Solute–solute, solute–solvent and solvent–solvent interactions are often broadly similar and so there are few preferential molecular orientations favoured above others. Such a situation arises, usually, due to the high state of dilution of the system.

31.2 Dalton's Law of Partial Pressures for Gas Mixtures (Solutions). Mole Fractions and Partial Pressures

Consider a 'solution' of gases. The total pressure, P, of m gases $(1, 2, \ldots, i, \ldots, m)$ is given by the ideal gas law (Frame 9) equation (31.1):

$$P = \frac{nRT}{V} \tag{31.2}$$

where n is the total amount of gas of the m gases present in the mixture:

$$n = n_1 + n_2 + \cdots + n_i + \cdots + n_m \tag{31.3}$$

and therefore we can write, substituting n in equation (31.2) by equation (31.3):

$$\begin{aligned} P &= \{n_1 + n_2 + \cdots + n_i + \cdots + n_m\}\frac{RT}{V} \\ &= \left\{n_1\frac{RT}{V}\right\} + \left\{n_2\frac{RT}{V}\right\} + \cdots + \left\{n_i\frac{RT}{V}\right\} + \cdots + \left\{n_m\frac{RT}{V}\right\} \\ &= [p_1 + p_2 + \cdots + p_i + \cdots + p_m] \end{aligned} \tag{31.4}$$

Each separate term here can be defined generally (where i is any value in the range $1, 2, \ldots, i, \ldots m$):

$$p_i = \left\{n_i\frac{RT}{V}\right\} \tag{31.5}$$

Here the individual pressure, p_i is defined as the *partial pressure* of the ith gas in the mixture and is the pressure a mixture component gas would exert if it occupied the *same volume* alone and:

- the total sum of the partial pressures of the m gases in the mixture is equal to the total pressure, P, exerted by the gas mixture. This is known as *Dalton's Law of Partial Pressures.*
- the partial pressure of the gas $p_i = x_i P$ where x_i is the mole fraction of the gas i present and P is the total pressure.
- this definition is true whether the gas mixture is ideal or not.
- optionally, the gas law can be applied *separately* to each individual gas in the mixture.
- properties ultimately depend on the *number* of gas molecules present but not on the *nature* of these gas molecules.

Using the definition of *mole fraction*, x, introduced in Frame 30, section 30.2, equation (30.9) we can relate the partial pressure of the individual component, i, to the total pressure of the gas since, for this i th gaseous component, the ratio:

$$\frac{p_i}{P} = \left(\frac{n_i RT}{V}\right) \Big/ \left(\frac{nRT}{V}\right) = \frac{n_i}{n} = x_i = \textit{mole fraction} \text{ of gas } i \text{ in the mixture} \tag{31.6}$$

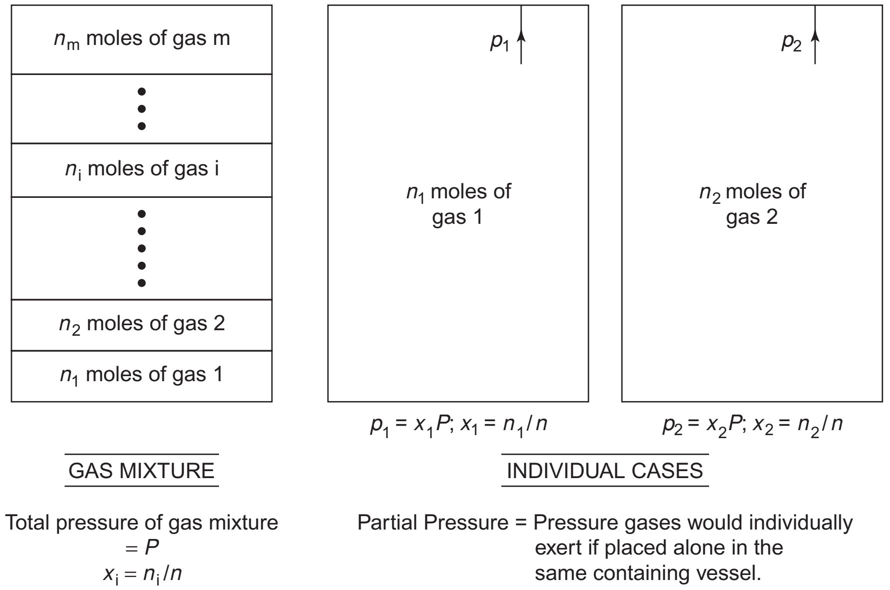


Figure 31.1 Schematic diagram illustrating Dalton's Law of Partial Pressures.

and hence:

$$p_i = x_i \cdot P \tag{31.7}$$

Thus the individual partial pressure, p_i exerted by a gas within a mixture can be calculated from the total pressure, P simply by multiplying this by the mole fraction of gas, x_i present. This definition is true whether the gas mixture is ideal or not.

When convienient we shall use the symbol y_i to indicate the mole fraction of vapour phase components in order to distinguish them from the mole fractions (x_i) of liquid components. Examples of this convention can be seen in Frame 33 in Figure 33.1(a), in the extended treatment of binary liquid ideal solutions discussed in Frame 34 and also seen in Frame 36, Figure 36.2. The mole fractions will, however, have to be redefined at these various points in the context of the text.

31.3 Ideal Gas Mixtures

Discussion of this topic is deferred until Frame 37, section 37.3.

31.4 Real (Non-ideal) Gases

In gases at moderate to high pressure departures from the Ideal Gas Law in the form of equation (31.1) become evident. The internal forces now become more significant as the atoms/molecules are forced into closer contact as the pressure, P increases. Eventually the atoms/molecules of a gas can be so tightly compressed together that repulsive forces (at very high pressures) can actually predominate. Clearly, in such cases, the Ideal Gas Law is no longer sufficient and equation (31.1) needs modification to a more sophisticated form. A number of *equations of state* for *real gases* are in evidence, two examples, not discussed further, are represented by:

- the *Virial Equation*: $= RT[1 + (\mathrm{B}/V_m) + (\mathrm{C}/V_m^2) + (\mathrm{D}/V_m^3) + \cdots]$

where B, C and D are independent of the amount of substance, n and are the virial coefficients defined for each specific gas.

- the *van der Waals Equation*: $(P + \mathrm{a}(n/V)^2)(V - n\mathrm{b}) = nRT$

where a and b are constants for a specific gas.

Thus *real gases* are those whose behaviour no longer fits the Ideal Gas Equation (31.1) and in this sense they are defined as non-ideal (imperfect) gases. The Ideal Gas Law is thus a limiting law in the sense that it serves to provide the demarcation between ideal gas and non-ideal (real) gas behaviour.

32. Ideal Liquid Mixtures Vapour Pressure and Raoult's Law

Figure 32.1 shows the extent to which 'mixtures' of various phases can be formed. There are examples of all types of '(single-phase) mixtures' formed between the various different possible binary phases, although no one single example is shown by the *same* substance. Those binary combinations bearing an asterisk are the more common of the types found.

In the *special case* where some of the components are in comparatively very low abundance, we call:

- the liquid mixture a *solution*;
- the components present in the *major* proportion the *solvent*;

and

- those in the *minor* proportion *solutes* (Figure 32.2).

For a solution containing just solvent and one solute, where x_{solute} is the mole fraction of solute and x_{solvent} is the mole fraction of solvent then (Frame 30, section 30.2, equation (30.6)):

$$x_{\text{solute}} + x_{\text{solvent}} = 1 \tag{32.1}$$

In this case, the solvent and solute species are treated differently in a thermodynamic sense and this will be considered later.

For the time being, we will treat all components *equivalently* and refer to mixed liquid phases simply as 'liquid mixtures'.

We shall discuss first the concept of the *ideal liquid mixture* (section 32.2) [i.e. one whose vapour pressure characteristics are such that they follow Raoult's Law (see below)] and contrast this with a *real liquid mixture* [i.e. one where non-ideal behaviour is exhibited and for which Raoult's Law is no longer obeyed]. We can then compare this concept of an ideal and real *liquid mixture* with that of ideal and real gases (Frame 31) showing that the ideas are fairly similar in nature and that parallels can be drawn and applied to their distinction and also that their definitions refer to limiting laws which apply.

Solutions	gas	liquid	solid
gas	√*	√	√
liquid		√*	√*
solid			√

Figure 32.1 Pairs of phases which can form examples of mixtures. (*indicates the more common combinations found).

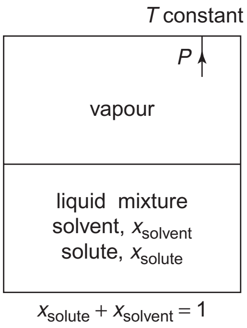


Figure 32.2 Solution made up of solvent + solute comprises a solution whose composition can be defined using mole fractions, x_{solvent} and x_{solute} (which sum to 1). Above any solution exists a vapour (gas) usually composed almost exclusively of (volatile) solvent molecules, since the solute(s) are normally involatile and therefore do not, themselves, exert or contribute to the vapour pressure over the solution. Temperature T is constant. P is the vapour pressure.

32.1 Vapour Pressure Over Liquid Mixtures

Suppose we have an evacuated vessel (Figure 32.3(a)) into which we introduce a liquid which is to form a volatile component A (Figure 32.3(b)) as part of a liquid mixture. It will be observed that the pure A exerts a *vapour pressure*, P^*, when confined *alone* in the containing vessel. This can also be referred to as the 'saturated vapour pressure', P^{sat} in the sense that it equates to the *saturation* of the vapour space with *only* the pure liquid. The vapour pressure itself can be recorded by means of a manometer attached to the vapour space. This vapour pressure emerges because solvent molecules are volatile and leave the surface of the liquid, so creating a pressure in the vapour (or gas) above the liquid (which is the solvent).

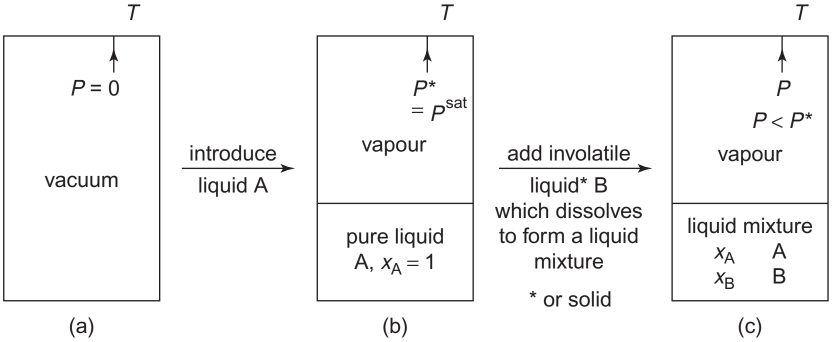


Figure 32.3 Vapour pressure, P^*, for pure A ($x_A = 1$, no B present: $x_B = 0$) and vapour pressure, P, for a liquid mixture ($x_A + x_B = 1$, $x_{\text{solute}} < x_{\text{solvent}}$).

It is observed that if now a second *involatile* component B (often in the form of a solid) is added to the liquid solvent so as to dissolve and form a liquid mixture (Figure 32.3(c)) then the new vapour pressure, P, is observed to be *lower* than the vapour pressure, $P^* = P^{\text{sat}}$ experienced over the pure liquid A (i.e. $P < P^*$) (Figure 32.4(b)). It should be noted also that this new vapour pressure, although over the mixture, results entirely from the volatility exhibited by the solvent molecules (since the second involatile component exerts no vapour pressure itself (i.e. $P_B = 0$) and so makes no contribution whatsoever to the total vapour pressure over the mixture.

This lowering of the vapour pressure can be rationalised quite simply. Since (Figure 32.4(b) and (c)) when B molecules are present at the surface (as well as in the body of the solution), in addition to solvent molecules, the effect of their presence will be to reduce the total number of A molecules which can actually contribute to the vapour pressure, P now measured, as compared to the situation (Figure 32.4(b)) where there are only A molecules present (B molecules being absent). In the pure A the positions of these *involatile* B molecules are all occupied by *volatile* molecules and hence *maximum* vapour pressure is then exerted and observed. There are no involatile (non-contributory) molecules. Hence: $P < P^*$. On the basis of this molecular model it is not surprising to find that the vapour pressure, P, over the solution (which is, as we have seen, exerted by A molecules only), is directly proportional to the mole fraction of A molecules, x_A, actually present within a given liquid mixture.

$$P \propto x_A \tag{32.2}$$

Obviously the more B molecules that are added to the mixture, the smaller will be $x_A (= 1 - x_B)$ (see equation (32.1)).

32.2 Ideal Liquid Mixtures. Raoult's Law. Ideal Liquid Mixture of Involatile B and Volatile A

For the line AB showing the linear variation of vapour pressure, P, over a mixture plotted versus x_A (or x_B) in Figure 32.4(a) we can see that:

$$P = 0 \quad \text{when} \quad x_A = 0 \tag{32.3}$$

which is interpreted to mean that since $x_A = 0$, we have only B molecules present, these, being involatile, contribute no vapour pressure to the mixture and so $P = 0$ and

$$P = P^* = P^{\text{sat}} \quad \text{when} \quad x_A = 1 \tag{32.4}$$

which records that when we have pure liquid A present, the vapour pressure over the pure liquid is $P^* (= P^{\text{sat}})$. Considering the analytical form (Frame 3) (i.e. $y = mx + c$) of the straight line (AB) in Figure 32.4(a) when $y = P$ and $x = x_A$ then:

$$P = m \cdot x_A + c \tag{32.5}$$

and since (condition (32.3)): $P = 0$ when $x_A = 0$ then:

$$c = 0 \tag{32.6}$$

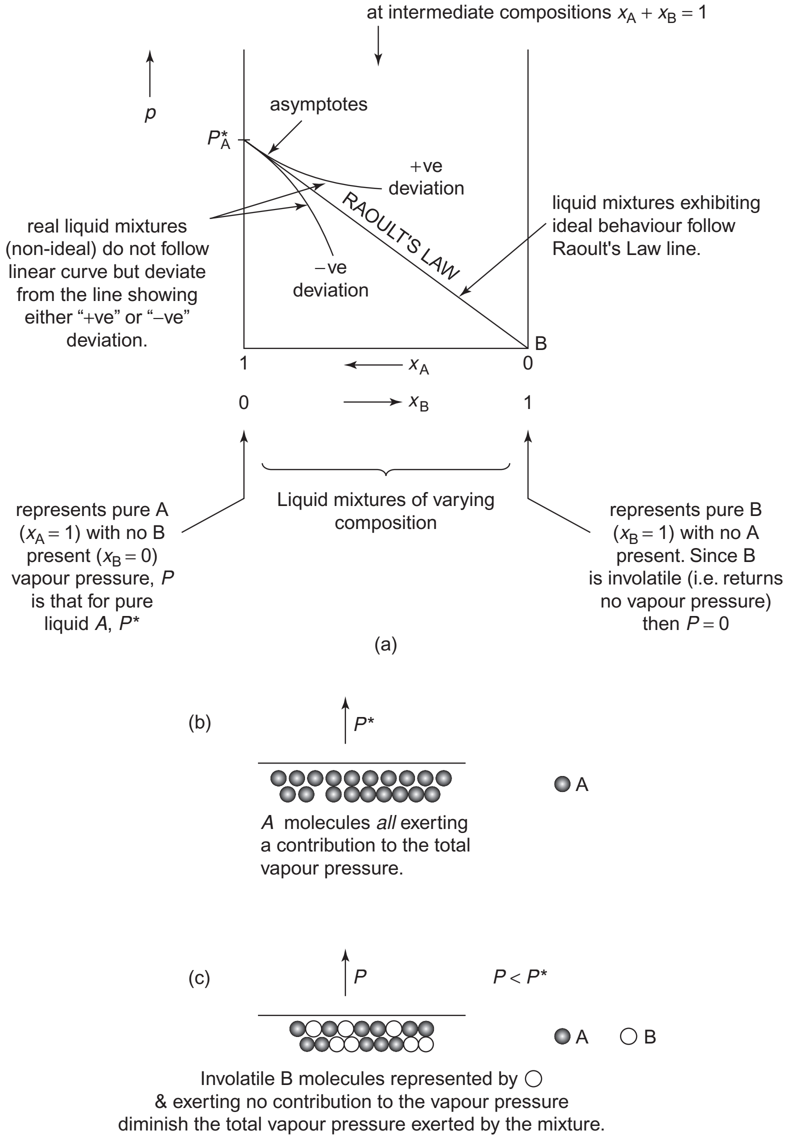


Figure 32.4 (a) Vapour pressure, P, versus composition, x_A, for the A + B liquid mixture. Note extremes where we have just pure A ($x_A = 1$) when pressure is equal to P^* and just pure B which is involatile and for which $P = 0$. Schematic drawing of surface of (b) pure A and (c) liquid mixture respectively showing that the full effect of the volatile pure solvent molecules in creating a vapour pressure is reduced in the presence of involatile B molecules which are present in the liquid mixture.

Since also (condition (32.4)): $P = P^* = P^{\text{sat}}$ when $x_A = 1$, then:

$$P^* = m + c = m \text{ (since } c = 0) \tag{32.7}$$

so that the equation of the line AB (Figure 32.4(a)) takes the form:

$$P = x_A . P^* \tag{32.8}$$

Equation (32.8) is known as *Raoult's Law* which simply states that the total vapour pressure, P, over a binary liquid mixture containing an *involatile* component B is equal to the vapour pressure, P^*, exerted by the *pure* volatile component A multiplied by its mole fraction, x_A, present in the solution.

This serves to *define* an *ideal liquid mixture* of such a system, stated simply:

- if the liquid mixture obeys Raoult's law over the entire range of composition ($0 \leq x_A \leq 1$) then it is classified as an ideal liquid mixture.

Here Raoult's law acts as the limiting demarcation criterion between ideal and real or non-ideal liquid mixtures. As Figure 32.4(a) indicates, in practice, non-ideal (real) liquid mixtures do not show linear behaviour but their vapour pressure deviates from (i.e. above or below) the line AB.

The vapour pressure lowering $(P^* - P)$ observed by the addition of B to pure A and caused by adding an involatile component B (mole fraction $= x_{\mathrm{B}}$) is given by:

$$(P^* - P) = P^* - x_{\mathrm{A}}.P^* = P^*(1 - x_{\mathrm{A}}) = P^*.x_{\mathrm{B}} \tag{32.9}$$

and is directly proportional to the amount of B present. Equation (32.9) is obtained by substituting P as given by equation (32.8) in $(P^* - P)$ and then factoring P^* outside the bracket.

32.3 Colligative Properties

The lowering of the vapour pressure of a pure liquid A by the addition of B (as above) is one example of a colligative property (defined in Frame 51) where such properties are further discussed and include:

- depression of the freezing point by addition of solute to pure liquid (Frame 51);
- elevation of the boiling point by addition of solute to pure liquid (Frame 52);
- creation of osmotic pressure (Frame 53).

33. Ideal Liquid Mixtures Real Liquid Mixtures

33.1 Ideal Binary Liquid Mixtures

Raoult's Law applies to certain liquid mixtures which are discussed in fuller detail in Frame 34. Two liquids, referred to as binary liquids, can, in some cases (e.g. ethanol and water), be miscible in all proportions. Figure 33.1 shows two liquids A and B at constant temperature, T, which are present in a binary mixture. Both A and B are assumed, in this case, to be volatile and thus now each liquid will contribute to the overall vapour pressure P.

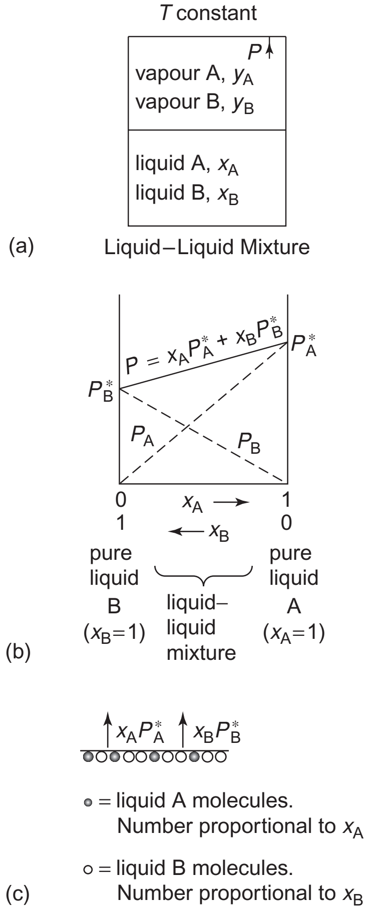


Figure 33.1 (a) Liquid–liquid mixture exerting vapour pressure, P and for which: $x_A + x_B = 1$. (b) Vapour pressure, P, versus composition, x, for a liquid liquid mixture (solution) which is miscible in all proportions (i.e. mutually soluble over the entire composition range). (c) Schematic drawing to represent the surface of the liquid which contains mole fractions: x_A of A and x_B of B and showing competition between the two volatile molecules A and B to exert individual vapour pressure.

The following parameters are used to define the composition of the system (Figure 33.1(a)):

- x_A = mole fraction of liquid A present in the mixture of liquids A and B;
- x_B = mole fraction of liquid B present in the mixture of liquids A and B;
- y_A = mole fraction of vapour A present in the vapour above the liquid mixture formed by liquids A and B;
- y_B = mole fraction of vapour B present in the vapour above the liquid mixture formed by liquids A and B.

The mole fractions (by definition) Frames (30, 31, 40), sum to unity, so that in the liquid phase:

$$x_A + x_B = 1 \tag{33.1}$$

where x_A and x_B denote the mole fractions of the liquids A and B present whilst y_A and y_B denote the mole fraction contributions made by the liquids A and B to the vapour phase:

$$y_A + y_B = 1 \tag{33.2}$$

The condition (compare Frame 32, section 32.2) that the liquids form an *ideal liquid mixture* is that their vapour pressure P (Figure 33.1(b)) must be such that Raoult's Law (Frame 32, equation (32.8) for solvent and involatile solute) is obeyed. In its extended form, for the present case of two volatile liquids A and B, this latter Law takes the extended form:

$$P = x_A.P_A^* + x_B.P_B^* \tag{33.3}$$

over the entire composition range ($0 \leq x_A \leq 1$; $1 \geq x_B \geq 0$). P_A^* and P_B^* are the vapour pressures which would be measured over the pure liquids A and B, respectively, when placed alone in the containing vessel. x_A and x_B are the mole fractions of liquids A and B present in the liquid mixture which together exert the vapour pressure, P.

Figure 33.1(c) sketches a model of the surface of the liquid mixture of liquids A and B. The relative numbers of each type of liquid molecule (A or B) on the surface will be proportional to x_A and x_B respectively. Since the vapour pressure exerted when there are no B molecules present (i.e. *in pure liquid A*) is P_A^* then having B molecules present reduces the ability of A molecules to return the full vapour pressure P_A^*. Since the proportion of liquid A is x_A then the partial vapour pressure returned will be reduced to $x_A.P_A^*$. For B molecules a similar argument leads to the conclusion that a partial vapour pressure $x_B.P_B^*$ should arise from x_B molecules of B when co-existent with x_A molecules of A within the liquid phase. The total vapour pressure, P, is given by equation (33.3). Thus, Raoult's Law, in the form of the latter equation, is rationalised for this system of two liquids.

For a *multicomponent* (see Frame 29) *ideal system* of liquids, for which c, the number of components present is greater than 2, ($c > 2$), the vapour pressure contribution from each liquid, P_i, should be such that:

$$P_i = x_i.P_i^* \tag{33.4}$$

where P_i^* is the vapour pressure exerted by liquid i when alone in the container, x_i represents the mole fraction of liquid i in the liquid mixture and P_i is the partial vapour pressure (Frames 31 and 32) exerted in the vapour phase by liquid i when present in the mixture. This equation should hold:

- for all components;
- over the entire composition range

in order for the system to be classified as ideal.

33.2 Positive and Negative Deviations from Raoult's Law

Few liquid mixtures are actually ideal over their entire composition range. Figure 33.2 illustrates two cases where the vapour pressure of liquid mixtures (solutions) deviate from Raoult's Law (Frame 32 and this frame, equations (33.3) and (33.4)) (positively A/B or negatively C/D) over the composition range but shows (see caption to figure) the end composition members (both representing cases of dilute solutions) do follow Raoult's Law for a limited, small, composition range.

In addition (in Figure 33.3) if tangents are drawn (i.e. lines CK and DL and lines GI and HJ) to the partial pressure vapour curve for the *low abundance species* at the two ends of the composition range then we can represent such lines by linear relationships (which again hold over a small range of composition). These take the general form:

$$x_i = K_i.P_i \tag{33.5}$$

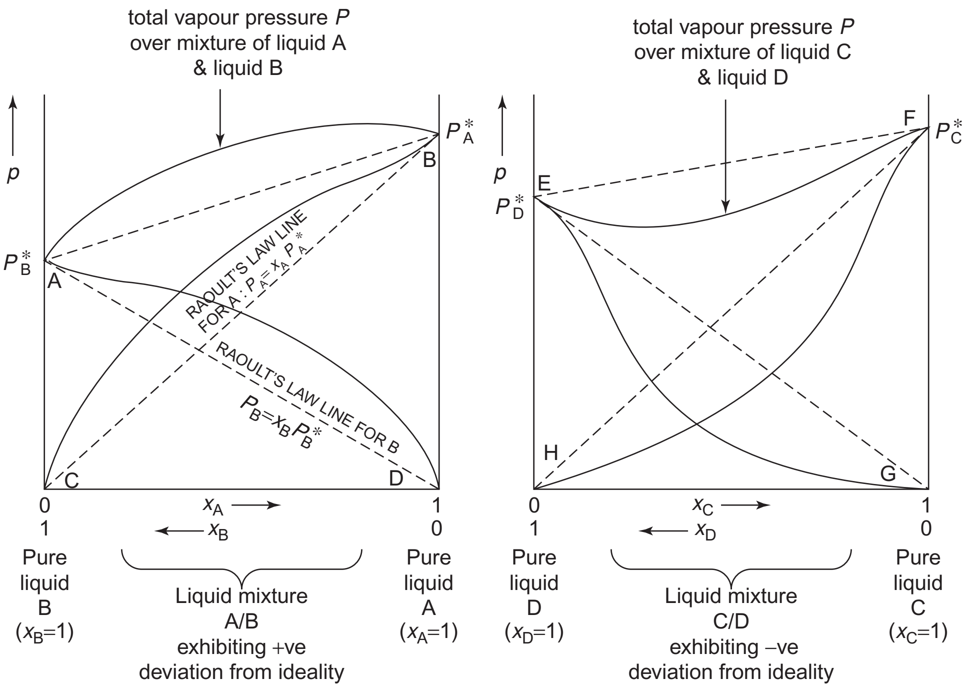
where i represents the end component that is acting as the so-called solute (i.e. having the lower mole fraction) in the so-called ideal dilute solution so that P_i is the partial vapour pressure exerted by the solute component i, K_i (= Henry's law constant, having units of (pressure)$^{-1}$) is the proportionality constant for the linear relationship between x_i and P_i, or the gradient of the tangential lines drawn as shown. This relationship (33.5) is termed *Henry's Law*. The specific linear forms are referred to and are shown in Figures 33.3(a) and (b).

The intercepts of these tangents with the ordinate axes (Frame 3) representing P have no chemical or other significance whatsoever, the purpose of drawing the tangents is merely a means of providing a simple *linear relationship* between x_{solute} ($= x_i$) and the partial vapour pressure exerted by the (volatile) solute, P_i, which will be applicable only to a small range of composition.

Thus we can define an *ideal dilute solution* as one for which:

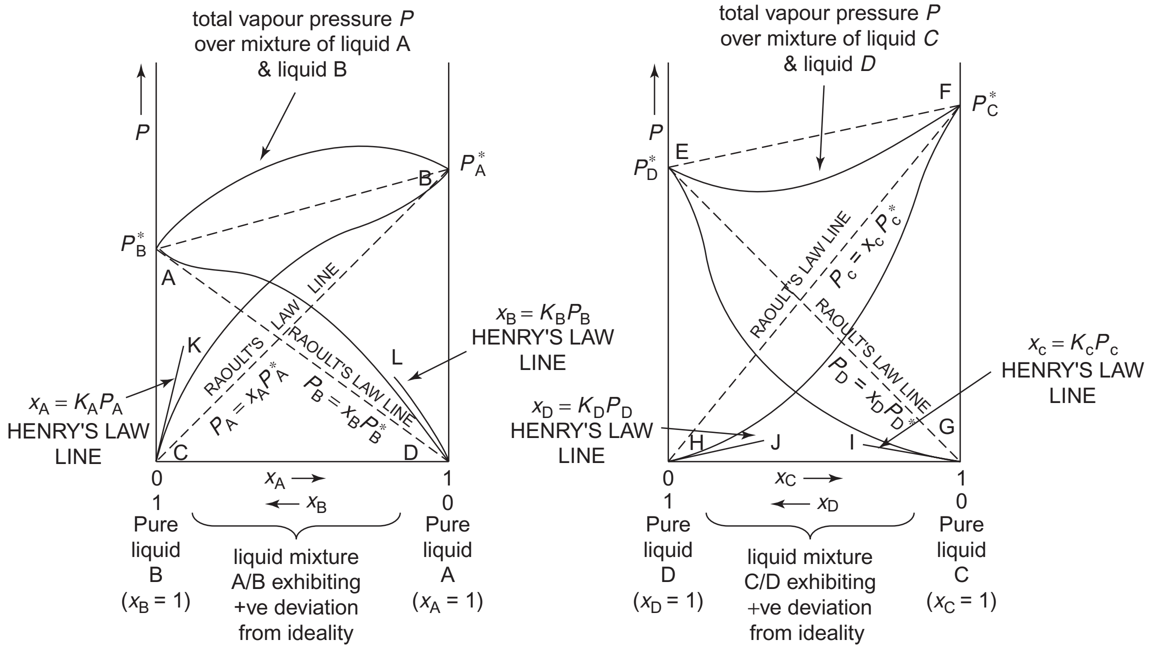
- the solvent, j, present at mole fraction, x_j, and having a saturated vapour pressure (Frame 32, Figure 32.3 and section 32.1), P_j^* obeys Raoult's Law:

$$P_j = x_j.P_j^* \tag{33.6}$$



(a) (b)

Figure 33.2 (a) Positive (liquid A + liquid B) and (b) negative (liquid C + liquid D) deviations from Raoult's Law. In (a) graph of P versus x shows that at the two dilute solution extremities of the graph (i.e. as $x_A \rightarrow 0$, $x_B \rightarrow 1$ (point A) or $x_B \rightarrow 0$, $x_A \rightarrow 1$ (point B)) the vapour pressure P, when solutions are nearly pure solvents (B at point A and A at point B) and therefore very dilute then the linear Raoult's Law curve (dotted) is (briefly) tangential to the experimental curve and is followed quite closely. In graph (b) we have the same features. In the extremity where $x_D \rightarrow 0$, $x_C \rightarrow 1$ (point F) the vapour pressure curve for solvent C approaches the Raoult's Law line FH. In the other extremity where $x_C \rightarrow 0$, $x_D \rightarrow 1$ (point E), vapour pressure curve of P for solvent D approaches the Raoult's Law line EG.



(a) (b)

Figure 33.3 Henry's Law behaviour for solutes in ideal dilute solutions. Reproduction of Figure 33.2 but with tangents (CK, DL, HJ and GI) appropriately drawn to the partial vapour pressure curves at the ends where they are acting as 'solute'.

Further discussion of Raoult's Law is made in Frame 36, section 36.3.

- the solute, i, obeys Henry's Law:

$$x_{\mathrm{i}} = K_{\mathrm{i}}.P_{\mathrm{i}} \tag{33.7}$$

Further discussion of Henry's Law is made in Frame 36, section 36.3 also.

33.3 Real (Non-Ideal) Liquid Mixtures

Intermediate compositions shown in Figures 33.2 and 33.3 provide examples of non-ideal behaviour as exhibited by a mixture of two liquids A and B and C and D in the sense that they deviate from Raoult's Law. We need to consider further the question of how departures from ideality can be handled thermodynamically. This is addressed in Frames 38 and 39 and elsewhere in this text.

34. Binary Liquid Mixtures

In this frame we consider, in some further detail the pressure–composition properties of a binary ideal liquid mixture at constant temperature, T, as defined in Figure 34.1. Here we assume that both components are in the liquid phase and that they are volatile and miscible (dissolve in each other (Frame 33)). Whilst the treatment here is not exhaustive it is intended to give the reader some insight into how to apply the principles developed so far to the ideal vapour and ideal liquid phases of a system.

34.1 Binary Ideal Liquid Mixture. Dependence of Vapour Pressure, P on Liquid Composition, x_A, x_B

In the liquid (where mole fractions are represented by x) and vapour (where mole fractions are represented by y) phases, the mole fractions x_A and x_B for the liquids A and B are such that, for the liquid phase:

$$x_A + x_B = 1 \tag{34.1}$$

and for the vapour phase (consisting of a vapour having mole fraction, y_A of vapour A and y_B of vapour B):

$$y_A + y_B = 1 \tag{34.2}$$

Since the individual vapour pressures exerted by liquids A and B (p_A and p_B) of an ideal liquid mixture must follow Raoult's Law (Frame 32, equation (32.8)), then we have:

$$p_A = x_A.P_A^* \tag{34.3}$$

$$p_B = x_B.P_B^* \tag{34.4}$$

where P_A^* and P_B^* are the saturated vapour pressures exerted by liquids A and B when present alone (Frame 32, section 32.1) and since the mole fractions of the liquids A and B present must add up to 1, then:

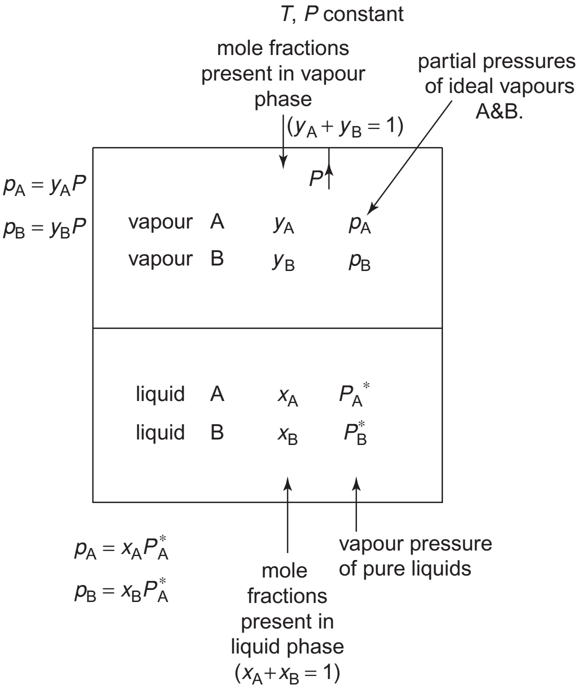


Figure 34.1 Binary Ideal liquid–liquid mixture in which the vapour behaves ideally and the liquid–liquid mixture obeys Raoult's Law.

$$x_B = (1 - x_A) \tag{34.5}$$

so that (substituting equation (34.5) for x_B in equation (34.4)), then:

$$p_B = (1 - x_A)P_B^* \tag{34.6}$$

Now because (Dalton's Law of Partial Pressures (Frame 31, section 31.2) applies to the vapour phase, combining this law with equations (34.3) and (34.6) we have:

$$P = p_A + p_B = x_A.P_A^* + (1 - x_A)P_B^* \tag{34.7}$$

so that (multiplying out the right-hand side of equation (34.7) and collecting terms involving x_A:

$$P = P_B^* + x_A(P_A^* - P_B^*) \tag{34.8}$$

and we see that total vapour pressure of the binary liquid mixture, P, is then a linear function of x_A, giving rise to Figure 34.2 where we can see that the linear (Frame 3) equation (34.8) fits at both extremes where $x_A = 0$ and $x_A = 1$, since when $x_A = 0$ in equation (34.8) then $P = P_B^*$ and when $x_A = 1$ in equation (34.8) then $P = P_B^* + (P_A^* - P_B^*) = P_A^*$.

Figure 34.2 (showing P as a function of x_A – and hence also x_B, since $x_A + x_B = 1$) also shows that if we add B ($x_B \to 0$) – also a liquid – to pure liquid A ($x_A \to 1$) then the vapour pressure over the liquid mixture, P, will rise (i.e. moving right to left, increasing x_B, the curve represented by equation (34.8) rises and P increases). This is in contrast to adding A ($x_A \to 0$) to pure liquid B as solvent ($x_B \to 1$) since then the vapour pressure over the liquid mixture, P, falls (i.e. moving left to right, increasing x_A, the curve represented by equation (34.8) falls and P decreases).

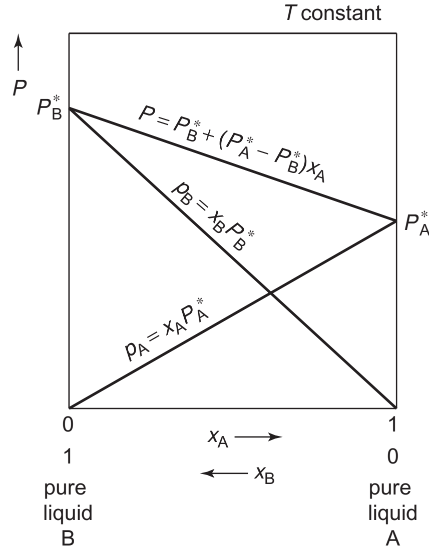


Figure 34.2 Pressure–composition diagram for binary ideal liquid mixture. Dependence of P on mole fraction (x_A, x_B) of liquid present. Note. Liquid B is more volatile than liquid A since $P_B^* > P_A^*$ – it exerts a higher (saturated) vapour pressure.

34.2 Binary Ideal Liquid Mixture. Dependence of Vapour Pressure, *P*, on Vapour Composition: y_A, y_B

We can also investigate how P is affected by changes in the mole fractions of A and B present in the *vapour phase* (and represented by y_A and y_B) (Figure 34.1). From Dalton's Law (Frame 31, equation (31.7)) we have:

$$p_A = y_A.P \tag{34.9}$$

$$p_B = y_B.P \tag{34.10}$$

[N.B. The symbolism used for the gas component has changed from that used in Frame 31 (being x_i in equation (31.7), Frame 31) to becoming y_A and y_B in this application. This was referred to earlier in Frame 31, section 31.2)].

Concentrating now on the vapour A (mole fraction = y_A) and using firstly equation (34.9), followed by equation (34.3) and finally equation (34.8):

$$y_A = \frac{p_A}{P} = \frac{x_A P_A^*}{[P_B^* + x_A(P_A^* - P_B^*)]} \tag{34.11}$$

so that (see Note 34.1):

$$x_A = \frac{y_A P_B^*}{[P_A^* + y_A(P_A^* - P_B^*)]} \tag{34.12}$$

and substituting for x_A (as given in equation (34.12)) into equation (34.8) leads to:

$$P = P_B^* + x_A(P_A^* - P_B^*) = P_B^* + \frac{y_A P_B^*(P_A^* - P_B^*)}{[P_A^* - y_A(P_A^* - P_B^*)]} \tag{34.13}$$

leading to (see Note 34.2):

$$P = \frac{P_B^* P_A^*}{[P_A^* - y_A(P_A^* - P_B^*)]} \tag{34.14}$$

Figure 34.3 shows a plot of P versus y_A (for the vapour phase) which is *not linear* like equation (34.8), but curved. At the two extremities of this latter graph when $y_A = 0$ then (equation (34.14)):

$$P = \frac{P_B^* P_A^*}{P_A^*} = P_B^* \tag{34.15}$$

and when $y_A = 1$ then (equation (34.14)):

$$P = \frac{P_B^* P_A^*}{[P_A^* - P_A^* + P_B^*]} = P_A^* \tag{34.16}$$

and for the intermediate compositions: $0 < y_A < 1$ the curve dips downwards to lower values of P.

[It is important to note however that the extremities of Figure (34.2) and (34.3) are the same (i.e. at: $x_A = 1$, $P = P_A^*$; $x_B = 1$, $P = P_B^*$ (Figure 34.2) and at: $y_A = 1$, $P = P_A^*$; $y_B = 1$, $P = P_B^*$ (Figure 34.3)].

A typical experimental phase diagram for the system toluene–benzene is sketched in Figure 34.4 from which it can be seen that this diagram corresponds exactly in form to a superposition of the liquid and vapour curves derived in Figures 34.2 and

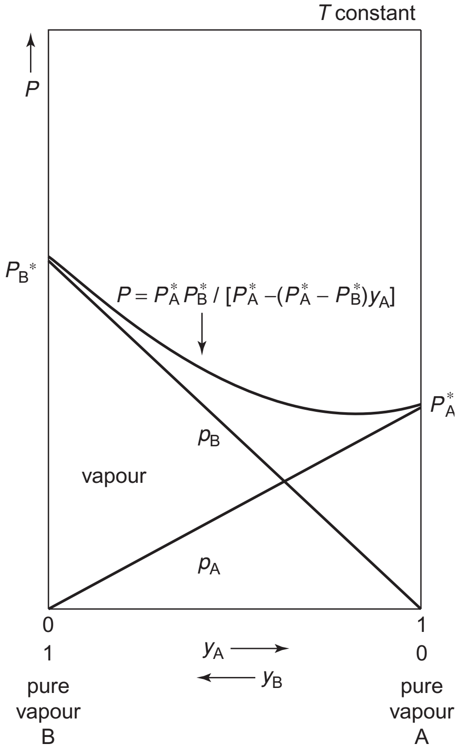


Figure 34.3 Pressure–composition diagram for Binary Ideal Liquid Mixture. Dependence of P on mole fraction (y_A, y_B) of vapour present.

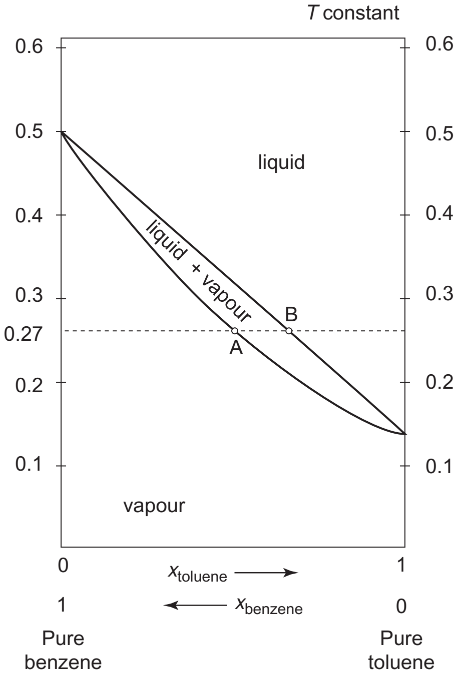


Figure 34.4 Pressure–composition diagram for Ideal Liquid Mixture of toluene and benzene showing liquid and vapour compositions. The region of the plot enclosed and labelled 'liquid + vapour' corresponds to the area of stability of both liquid and vapour.

34.3 upon each other. There is, however, a slight adjustment of the two scales that one would have to make in order that the superimposed figures match the experimental one and are compatible with it. Figure 34.2 has a composition scale based on (x_A, x_B) values for the liquid phase whilst Figure 34.3 has a composition scale based on (y_A, y_B) values for the vapour phase. Figure 34.4, on the other hand, has a composition scale based on the *overall* composition of liquid *and* vapour and the total applied pressure.

In the (dilute) region of interest the liquid phase obeys Raoult's Law and therefore it is in this region, that we can write, using Raoult's Law in the form of equations (34.3) and (34.4) and Dalton's Law of Partial Pressures in the form of equations (34.9) and (34.10) that:

$$p_{\mathrm{A}} = x_{\mathrm{A}}.P_{\mathrm{A}}^{*} = y_{\mathrm{A}}.P \tag{34.17}$$

and

$$p_{\mathrm{B}} = x_{\mathrm{B}}.P_{\mathrm{B}}^{*} = y_{\mathrm{B}}.P \tag{34.18}$$

or (following cross-multiplication of the two right-hand most equalities in equations (34.17) and (34.18), that:

$$\frac{x_{\mathrm{A}}}{y_{\mathrm{A}}} = \frac{P}{P_{\mathrm{A}}^{*}} \tag{34.19}$$

and

$$\frac{x_{\mathrm{B}}}{y_{\mathrm{B}}} = \frac{P}{P_{\mathrm{B}}^{*}} \tag{34.20}$$

or

$$P = \left(\frac{x_{\mathrm{A}}}{y_{\mathrm{A}}}\right) \cdot P_{\mathrm{A}}^{*} \tag{34.21}$$

and

$$P = \left(\frac{x_{\mathrm{B}}}{y_{\mathrm{B}}}\right) \cdot P_{\mathrm{B}}^{*} \tag{34.22}$$

so that, in other words, the total vapour pressure of the liquid mixture, P, *in the dilute region only*, is equal to the ratio of the mole fractions of the liquid and vapour for a given component, i, $(x_{\mathrm{i}}/y_{\mathrm{i}})$ multiplied by the saturated vapour pressure (Frame 32, section 32.1) that the pure component P_{i}^{*} exerts when alone in the container.

35. Chemical Potentials and Equilibrium Relationships

In these next frames we return to two topics mentioned earlier, those of chemical potential (Frames 5, 27, 28 and 29) and equilibria (Frame 14).

35.1 Equalisation of Chemical Potentials for Components in Multiple Phases at Equilibrium

In Frame 29 we established two principles which form the basis of how we describe the stability of phases in equilibrium with each other.

- In a multicomponent system *at equilibrium*, the chemical potential of a given component, i, present in more than one phase (labelled α, β, γ... etc.) will be such that:

$$\mu(\mathrm{i})^{(\alpha)} = \mu(\mathrm{i})^{(\beta)} = \mu(\mathrm{i})^{(\gamma)} = \cdots \tag{35.1}$$

- The above applies to *all* components present in a thermodynamic system

35.2 General Principles of Equating Chemical Potentials for Components in Different Phases at Equilibrium: the Simplest Case

We consider first a simple equilibrium (Figure 35.1) – that between a pure liquid and its (pure) vapour, assumed to be ideal:

$$\text{liquid} = \text{vapour (gas)} \tag{35.2}$$

In this system only one component is present (no need to specify i) and according to equation (35.1) and the principle in section 35.1 above, at equilibrium:

$$\mu^{(\text{liquid})} = \mu^{(\text{vapour})} \tag{35.3}$$

From Frame 20 for the free energy, G, for n moles of an ideal gas:

$$G = G^o + nRT\ln(P/P^o) \quad P^o = \text{standard pressure} \tag{20.12}$$

where G^o is the free energy of the gas under conditions of standard pressure, P^o and G is the free energy of the gas under pressure P.

Examining equation (20.12):

- the term: $nRT\ln(P/P^o)$ is equal to the Gibbs energy difference: $(G - G^o)$;
- the term: $nRT\ln(P/P^o)$ can be considered as a 'correction term' which gives the change in Gibbs energy, G, when P is modified to P^o, the standard pressure.
- P^o can be chosen to be any standard pressure, e.g. 1 bar, 1 atm etc. and needs to be specified in relation to equation (20.12).

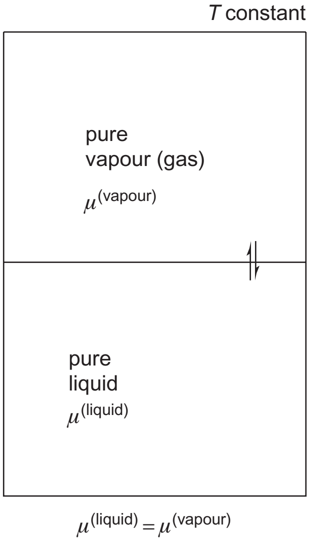


Figure 35.1 Conditions corresponding to equation (35.3).

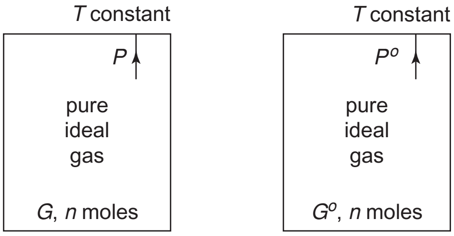


Figure 35.2 Conditions corresponding to equation (20.12).

For the component, i, of a gas in a mixture:

$$G(\mathrm{i}) = G^o(\mathrm{i}) + nRT\ln(p_\mathrm{i}/P^o) \quad P^o = 1 \text{ bar} \qquad (35.4)$$

where p_i is the partial pressure exerted by the component gas labelled i in the gas mixture (Figure 35.2) and the standard pressure has been (arbitrarily) fixed at 1 bar.

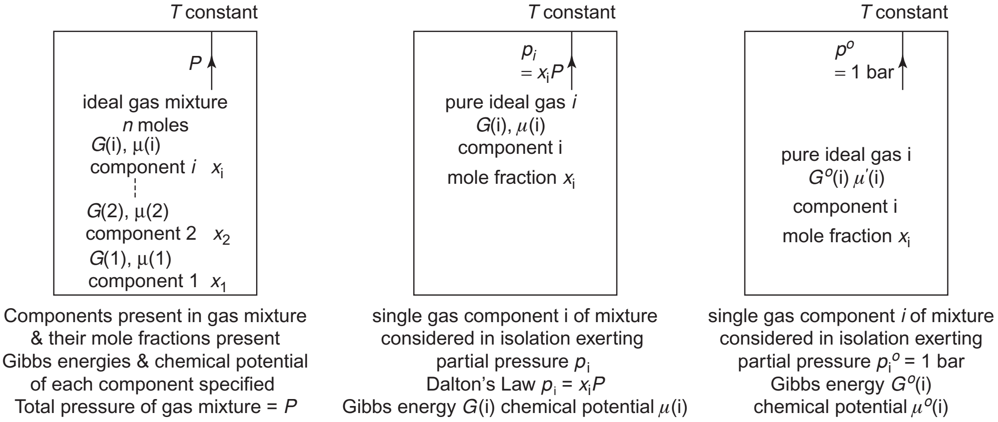


Figure 35.3 Conditions corresponding to equation (35.4).

Dividing equation (35.4) through by n:

$$\frac{G(\mathrm{i})}{n} = \frac{G^o(\mathrm{i})}{n} + RT\ln\left(\frac{p_i}{P^o}\right) \quad P^o = 1 \text{ bar} \qquad (35.5)$$

and thus, since chemical potential is defined for a pure substance as: $\mu(\mathrm{i}) = G(\mathrm{i})/n$ (Frame 27) then for 1 mole of a pure gaseous component, i:

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \mu^o(\mathrm{i})^{(\mathrm{gas})} + RT\ln\left(\frac{p_i}{P^o}\right) \quad P^o = 1 \text{ bar} \qquad (35.6)$$

where $\mu^o(\mathrm{i})^{(\mathrm{gas})}$ is the chemical potential of the vapour i under the condition where the pressure is standard at P^o (= 1 bar).

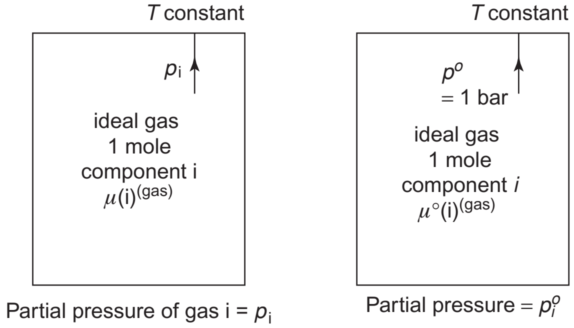


Figure 35.4 Conditions corresponding to equation (35.6).

Examining equation (35.6):

- the logarithmic term: $\ln(p_i/P^o) = 0$ when $p_i = P^o$ so that $p_i/P^o = 1$ and $\ln(1) = 0$. This will be true for any chosen standard state;
- this means that when $p_i = P^o$, $\mu(\mathrm{i})^{(\mathrm{gas})}$ for the case where the ith component exerts a partial pressure of P^o:

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \mu^o(\mathrm{i})^{(\mathrm{gas})} \qquad (35.7)$$

- when equation (35.6) is being evaluated (i.e. when quantities are being substituted) if the chosen standard pressure, $P^o = 1$ bar, for example, then this needs to be stated since it defines the meaning of the term $\mu^o(\mathrm{i})^{(\mathrm{gas})}$ unequivocally.

The above approach to interpreting the significance of *non-logarithmic* terms will be used again throughout this text (For example, Frame 36, section 36.1).

In the case of a liquid in equilibrium with its vapour Figure 35.1 we have *only one component* (i) to consider and since 'gas' can be considered to be synonymous with 'vapour', hence equation (35.3) can be rewritten in the form:

$$\mu^{(\mathrm{liquid})} = \mu^{(\mathrm{vapour})} = \mu^{(\mathrm{gas})} = \mu^{o(\mathrm{gas})} + RT\ln\left(\frac{P}{P^o}\right) \quad P^o = 1 \text{ bar} \qquad (35.8)$$

by combining it with equation (35.6) as shown. More succinctly:

$$\mu^{(\text{liquid})} = \mu^{o(\text{gas})} + RT\ln\left(\frac{P}{P^o}\right) \qquad P^o = 1\text{ bar} \tag{35.9}$$

where P is the total pressure of our system as shown in Figure 35.5.

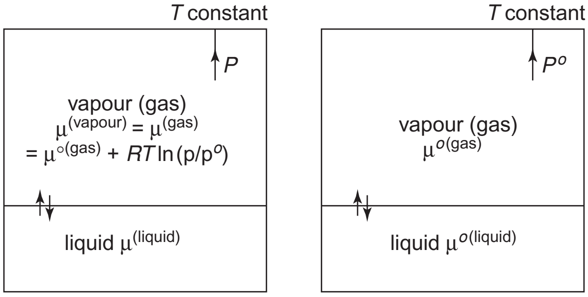


Figure 35.5 Conditions corresponding to equations (35.8) and (35.9).

Equation (35.9) can be rearranged to the form:

$$\mu^{(\text{liquid})} - \mu^{o(\text{gas})} = RT\ln\left(\frac{P}{P^o}\right) \qquad P^o = \text{standard pressure} \tag{35.10}$$

where the equation (35.10) expresses the difference between $\mu^{(\text{liquid})}$, at pressure, P and $\mu^{o(\text{gas})}$, in the form of a logarithmic term.

35.3 General Principles of Equating Chemical Potentials for Components in Different Phases at Equilibrium: the Ideal Liquid Mixture Consisting of Liquid Phases

Whenever we have a liquid or liquid mixture we will always have a vapour phase in equilibrium with it. Consequently equation (35.6) is an extremely important equation which we shall apply numerous times in this text. It offers a starting point for discussing the majority of systems, since these invariably have a *vapour phase* present.

Consider now a more complicated system, as is shown in Figure 35.6. Here the mixture of liquids present obey Raoult's Law (Frames 32, equation (32.8) and 33, equation (33.6)) and hence they constitute an *ideal liquid mixture.* On the basis of this law, for each component, i:

$$p_\text{i} = x_\text{i}.P_\text{i}^* \tag{35.11}$$

or, dividing through by the standard pressure, P^o:

$$\frac{p_\text{i}}{P^o} = \frac{x_\text{i}.P_\text{i}^*}{P^o} \tag{35.12}$$

where x_i is the mole fraction of the liquid component i in the liquid phase. We can then define the vapour phase present by the equation:

$$\mu(\text{i})^{(\text{liquid mixture})} = \mu(\text{i})^{(\text{gas})} \tag{35.13}$$

which simply equates the chemical potentials. Also for the vapour phase (equation (35.6)) adapted to incorporate Raoult's Law in the form of equation (35.12) takes the form:

$$\begin{aligned}\mu(\text{i})^{(\text{gas})} &= \mu^o(\text{i})^{(\text{gas})} + RT\ln\left(\frac{p_\text{i}}{P^o}\right)\\ &= \mu^o(\text{i})^{(\text{gas})} + RT\ln\left(\frac{x_\text{i}\cdot P_\text{i}^*}{P^o}\right)\\ &= \mu^o(\text{i})^{(\text{gas})} + RT\ln\left(\frac{P_\text{i}^*}{P^o}\right) + RT\ln x_\text{i}; \quad P^o = \text{standard pressure}\end{aligned} \tag{35.14}$$

Two things should be noted here:

- we have used a property of logarithms (Frame 6) that: ln (ab) = ln a + ln b to split the P_i^*/P^o and x_i product term in the logarithm into two separate logarithmic terms.
- a split into *three* logarithmic terms on the basis that: ln (ab/c) = ln a + ln b− ln c and so writing: RT ln (x_i) + RT ln (P_i^*) – RT ln (P^o) would be invalid for the following reason. Whilst we can take the logarithm of the dimensionless mole fraction in the term: RT ln x_i we cannot define ln (P_i^*) because P_i^* represents a pressure and therefore is not dimensionless and amenable to being the argument of a logarithmic function (see Frame 6, section 6.3; Appendix). However dividing P_i^* by P^o where the latter is the standard pressure renders the ratio (P_i^*/P^o) dimensionless and hence ln (P_i^*/P^o) is then a legitimate logarithmic expression for equation (35.14) which is perfectly valid when partitioned into only two logarithmic terms.

Combining equations (35.13) and (35.14) leads to:

$$\mu(\mathrm{i})^{(\text{liquid mixture})} = \mu^o(\mathrm{i})^{(\text{gas})} + RT\ \ln\left(\frac{P_\mathrm{i}^*}{P^o}\right) + RT\ \ln x_\mathrm{i} \quad P^o = \text{standard pressure} \tag{35.15}$$

a complicated equation for which we need to define clearly what each of the various terms means. We can do this by considering the definition of $\mu(\mathrm{i})^{(\text{liquid mixture})}$ in equation (35.15) under the conditions where the term: $RT \ln x_\mathrm{i}$ will vanish (so becoming equal to zero). In that case $\mu(\mathrm{i})^{(\text{liquid mixture})}$ will be equal to $[\mu^o(\mathrm{i})^{(\text{gas})} + RT \ln (P_\mathrm{i}^*/P^o)]$. The term $RT \ln x_\mathrm{i}$ vanishes when $\ln x_\mathrm{i} = 0$ or when $x_\mathrm{i} = 1$, a condition that corresponds to component i being the only (sole) liquid present in the 'mixture'. Figure 35.6(b) shows the condition when $x_\mathrm{i} = 1$. In this case $\mu(\mathrm{i})^{(\text{liquid mixture})}$ (the chemical potential of liquid component i in the liquid mixture) corresponds to $\mu^*(\mathrm{i})^{(\text{pure liquid})}$ – the chemical potential of pure liquid i. Hence we can write:

$$\mu(\mathrm{i})^{(\text{liquid mixture})} = \mu^*(\mathrm{i})^{(\text{pure liquid})} + RT\ \ln x_\mathrm{i} \tag{35.16}$$

which is the *key equation* of this section. The asterisk on the term $\mu^*(\mathrm{i})^{(\text{pure liquid})}$ refers to the fact that the pressure is not at the standard pressure since the pure liquid will be in equilibrium with its own vapour at a vapour pressure equal to P_i^*.

It also follows from the above arguments that:

$$\mu^*(\mathrm{i})^{(\text{pure liquid})} = \left[\mu^o(\mathrm{i})^{(\text{gas})} + RT\ln\left(\frac{P_\mathrm{i}^*}{P^o}\right)\right] \quad P^o = \text{standard pressure} \tag{35.17}$$

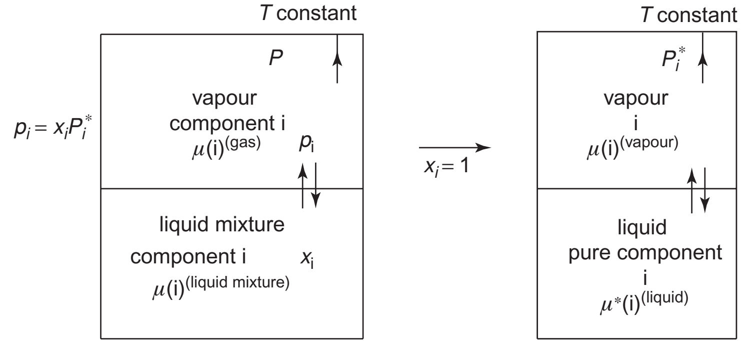


Figure 35.6 (a) Ideal liquid mixture, at equilibrium at temperature, T, containing a component, i, which exerts a partial pressure, p_i, in the vapour phase and which, in the liquid phase behaves ideally, so that Raoult's law holds: $p_\mathrm{i} = x_\mathrm{i}.P_\mathrm{i}^*$. (b) Shows the system (a) under conditions where $x_\mathrm{i} = 1$ (i.e. i is the sole component). The vapour pressure is then equal to P_i^*.

but then this relationship could have been inferred directly from consideration of the system shown in Figure 35.6(b) using the principle (35.1) above with the equilibrium condition: $\mu^*(\mathrm{i})^{(\text{pure liquid})} = \mu(\mathrm{i})^{(\text{vapour})}$ and then employing equation (35.6) for $\mu(\mathrm{i})^{(\text{vapour})}(= \mu(\mathrm{i})^{(\text{gas})})$, which is equal to the term in square brackets in equation (35.17).

Two of the main principles used when applying thermodynamics to phase equilibria are:

- defining the equilibrium by equating the chemical potentials of each component within the different phases in which it is present;

and

- interpreting and defining the meaning of the *non-logarithmic* terms in the chemical potential equations by examining the conditions imposed when the logarithmic term vanishes, the non-logarithmic term then corresponds to the original subject (i.e. the left-hand side quantity) of the equation under the conditions for which the logarithmic term is zero.

The next frame (Frame 36) gives some further examples of such applications.

36. Interpretation of the Logarithmic Term. Molality

36.1 The Nature of Logarithmic Terms in Chemical Potential Equations

In equation (35.16), Frame 35 we saw that for a multicomponent ideal liquid mixture (Frame 35, Figure 35.6(b) containing a number of components, then for each component i:

$$\mu(\mathrm{i})^{(\text{liquid mixture})} = \mu^*(\mathrm{i})^{(\text{pure liquid})} + RT\ln x_\mathrm{i} \tag{35.16}$$

where x_i is the mole fraction of component i in the liquid mixture. Rearranging:

$$RT\ln x_\mathrm{i} = [\mu(\mathrm{i})^{(\text{liquid mixture})} - \mu^*(\mathrm{i})^{(\text{pure liquid})}] \tag{36.1}$$

and we could interpret this logarithmic term: $RT\ln x_i$ as providing the correction needing to be added to the chemical potential of the pure liquid component i, $\mu(\mathrm{i})^{(\text{pure liquid})}$, to establish its chemical potential (at mole fraction x_i) in an ideal liquid mixture of chemical potential, $\mu(\mathrm{i})^{(\text{liquid mixture})}$. In other words the logarithmic term is a kind of *correction term* to the chemical potential when *conditions are altered* (or are *no longer valid*).

In this connection we might recall Frame 20, equation (20.13), Figure 20.2 where the Gibbs energy, G (equivalent to chemical potential, μ, for 1 mole) at pressure P was given by:

$$G = G^o + RT\ln\left(\frac{P}{P^o}\right) \quad P^o = \text{standard pressure} \tag{20.13}$$

where G^o is the molar Gibbs energy under conditions where the pressure is P^o. The role of the logarithmic term: $RT\ \ln(P/P^o)$ is to act as a 'correction' term to convert G^o which applies at standard pressure, P^o to G which applies at pressure P. This can be seen graphically in Figure 20.2(b) in Frame 20, where the term $RT\ \ln(P/P^o)$ is shown to be the difference between the two curves at different pressures at a particular temperature, T.

This interpretation gives the first clue that we might be able to use such terms to convert our equations for the chemical potential of *ideal liquid mixtures* into ones which can apply to *non-ideal* (*real*) *liquid mixtures*. In Frame 38 we shall return to this idea, when a term such as: $RT\ln a$ (where a is defined as an 'activity') is used for treating liquid mixtures and a term $RT\ \ln(f/P^o)$ (where f/P^o is defined as a 'fugacity' ratio, f being the fugacity) used in treating gases, can be employed, in just such a way, to convert our ideal models into tools to begin the study of non-ideal situations.

36.2 Molality, *m*

It is necessary here to digress briefly in order to introduce the term molality which is required for the definition of an ideal dilute solution (section 36.3 below). The *molality* of a component, i, in a solution, m_i, is defined as the amount of the solute, i, in 1 kg (= 1000 g) of solvent.

Thus for a solute, labelled A, in a solvent, labelled B, the molality, m_A is given by:

$$m_\mathrm{A} = \frac{n_\mathrm{A}}{W_\mathrm{B}} = [\text{amount of solute}]/[\text{mass of solvent}] \tag{36.2}$$

Since water as a solvent has a density of 1 g cm^{-3} then 1000 g of water has a volume of exactly 1 dm^{-3} and hence the concentration, c_i (Frame 40, section 40.3) of a substance, i, in water (in mol dm^{-3}) will be identical to its molality (in mol kg^{-1}) at a temperature of 298 K. This will not be true, of course:

- for solvents other than water;
- at temperatures other than 298 K.

36.3 Chemical Potentials for Ideal Dilute Solutions at Equilibrium

We have seen earlier (in Frames 32 and 33) that in order to be classified as an ideal solution then Raoult's Law (Frame 32, 33) must be obeyed over the entire concentration range. In the case of ideal dilute solutions Raoult's Law (Frame 32, equation (32.8) and Frame 33, equation (33.6)) must apply to the solvent and Henry's Law (Frame 33, equation (33.7)) must apply to the solute, albeit over a very small (dilute) and *limited* concentration range (see Figure 36.1).

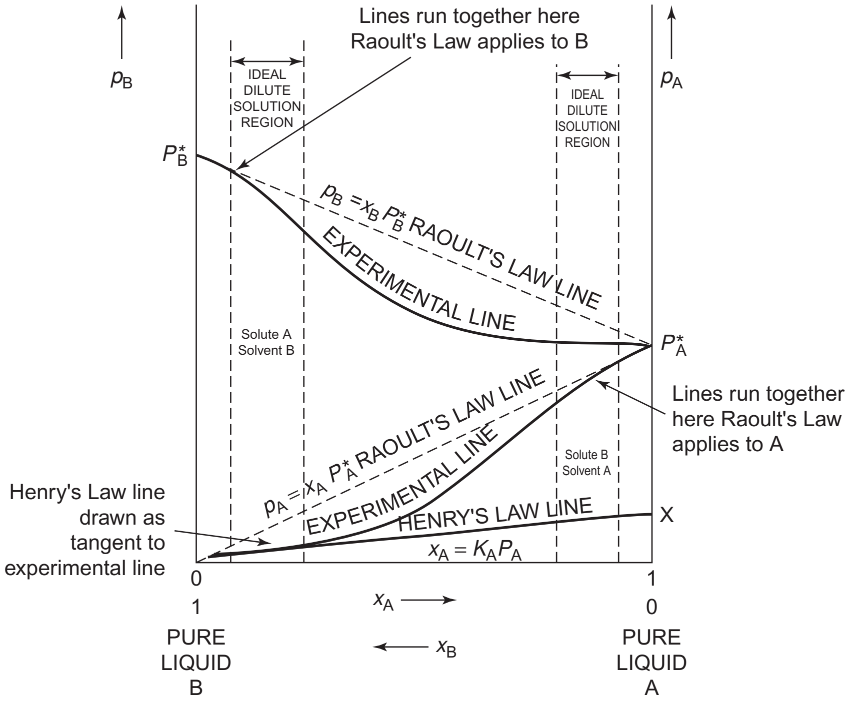


Figure 36.1 Ideal dilute solution regions for liquid–liquid mixture (solution) A/B.

The treatment which was developed in Frame 35, section 35.3 for an ideal liquid mixture is also equally valid and applicable to the ideal dilute solution region shown in Figure 36.1 of course. At the left-hand side of the diagram (which is the region to which we shall, at present, confine our discussion) B is acting as the solvent and A acting as the solute, so that, adapting equation (35.16) Frame 35 (i.e. putting component i equal to component B):

$$\mu(\mathrm{B})^{(\text{solution})} = \mu^*(\mathrm{B})^{(\text{solvent})} + RT \ln x_\mathrm{B} \tag{36.3}$$

where $\mu(\mathrm{B})^{(\text{solution})}$ is the chemical potential of B in the solution, $\mu^*(\mathrm{B})^{(\text{solvent})}$ is the chemical potential of the pure liquid B in equilibrium with its vapour at P_B^* and x_B is the mole fraction of the solvent present in the solution phase of the mixture (Figure 36.2).

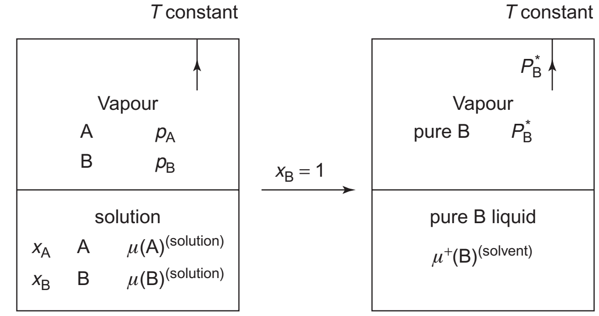


Figure 36.2 Conditions corresponding to equation (36.3).

The factor that makes an ideal dilute solution different from an ideal liquid mixture is the fact that the *solute* (in this case A) follows Henry's Law (Frame 33, section 33.2) which takes the form:

$$x_\mathrm{A} = K_\mathrm{A} \cdot p_\mathrm{A} \tag{36.4}$$

which can be written also as:

$$\left(\frac{p_\mathrm{A}}{P^o}\right) = \left(\frac{x_\mathrm{A}}{K_\mathrm{A} \cdot P^o}\right); \quad P^o = \text{standard pressure} \tag{36.5}$$

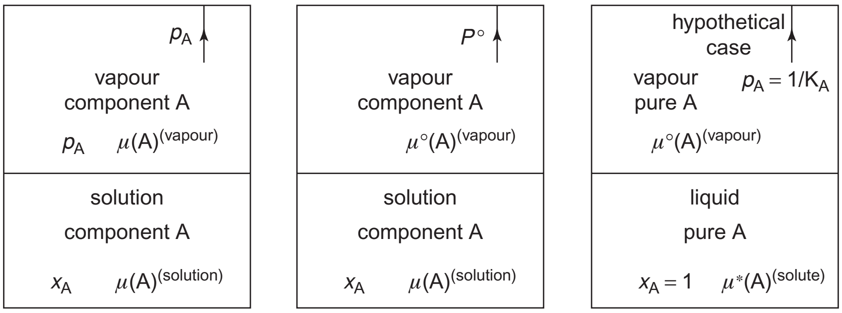
so that now both bracketed terms are dimensionless. Since K_A has units of $(\text{pressure})^{-1}$ (see discussion of equation (33.5) Frame 33) then multiplying it by a standard pressure, P^o makes it dimensionless like x_A and p_A/P^o. This facititates handling the logarithmic terms below (Frame 6, section 6.3; Appendix).

Since solute A present in the solution is in equilibrium with its own vapour, we can write:

$$\mu(\mathrm{A})^{(\text{solution})} = \mu(\mathrm{A})^{(\text{vapour})} = \mu^o(\mathrm{A})^{(\text{vapour})} + RT \ln\left(\frac{p_\mathrm{A}}{P^o}\right) \quad P^o = 1\ \text{bar} \tag{36.6}$$

where standard pressure has been arbitarily chosen to be $P^o = 1$ bar and because the solute A also obeys Henry's Law we can combine equations (36.5) and (36.6) to give:

$$\mu(\mathrm{A})^{(\text{solution})} = \mu^o(\mathrm{A})^{(\text{vapour})} + RT \ln\left[\left(\frac{x_\mathrm{A}}{K_\mathrm{A} \cdot P^o}\right)\right]; \quad P^o = \text{standard pressure} \tag{36.7}$$



Ideal dilute solution containing liquids A & B
Component A only considered

Ideal dilute solution containing liquids A & B
Component A only considered
Vapour of A at standard pressure $P^0 = 1$ bar

Hypothetical case corresponding to point X in Figure 36.1

Figure 36.3 Conditions corresponding to equations (36.6), (36.7), (36.8) and (36.10).

Proceeding as before we can split the logarithmic term:

$$\mu(A)^{(solution)} = \left[\mu^o(A)^{(vapour)} + RT\ln\left(\frac{1}{K_AP^o}\right)\right] + RT\ln x_A$$

$$= [\mu^o(A)^{(vapour)} - RT\ln(K_AP^o)] + RTlnx_A; \qquad (36.8)$$

where x_A is the mole fraction of solute present. The log term will vanish when: $x_A = 1$, that is when the system corresponds to a (*hypothetical*) state where the 'ideal dilute solution' has become entirely made up of pure solute! This corresponds to the point X in Figure 36.1 and as such is corresponds to a non-realisable pressure and is in this sense hypothetical. The state corresponds to the (hypothetical) chemical potential the pure solute would have if Henry's Law applied over the entire composition range (to include $x_A = 1$). This is not the case, of course, and we designate the chemical potential of this hypothetical state as $\mu^*(A)^{(solute)}$. Hence (Figure 36.3):

$$\mu^*(A)^{(solute)} = [\mu^o(A)^{(vapour)} - RT\ln(K_AP^o)] \qquad (36.9)$$

and

$$\mu(A)^{(\text{ideal dilute solution})} = \mu^*(A)^{(solute)} + RT\ln x_A \qquad (36.10)$$

The definition of mole fraction, x,is given in equation (30.9) Frame 30 and since in the present case the total amount of substance present is $(n_A + n_B)$ then:

$$x_A = \frac{n_A}{(n_A + n_B)} \qquad (36.11)$$

and hence in equation (36.10):

$$\mu(A)^{(\text{ideal dilute solution})} = \mu^*(A)^{(solute)} + RT\ln\left[\frac{n_A}{(n_A + n_B)}\right] \qquad (36.12)$$

since $n_A \to 0$ in the region of our interest, then:

$$\frac{n_A}{(n_A + n_B)} \to \frac{n_A}{n_B} \qquad (36.13)$$

and so equation (36.12) reduces to:

$$\mu(A)^{(\text{ideal dilute solution})} = \mu^*(A)^{(solute)} + RT\ln\left(\frac{n_A}{n_B}\right) \qquad (36.14)$$

if we now define, w_B as the mass of component B present (where B has a molar mass $= M_B$) then (Frame 1, section 1.4, rearranging equation (1.2)):

$$n_B = \frac{w_B}{M_B} \qquad (36.15)$$

and so equation (36.14) becomes:

$$\mu(A)^{(\text{ideal dilute solution})} = \mu^*(A)^{(solute)} + RT\ln\left(\frac{n_AM_B}{w_B}\right) \qquad (36.16)$$

Multiplying the logarithmic argument (n_AM_B/w_B) by m^o/m^o $(= 1)$ where m^o is the standard molality does not change the argument's value and so an equivalent form to equation (36.16) is the equation (36.17):

$$\mu(A)^{(\text{ideal dilute solution})} = \mu^*(A)^{(solute)} + RT\ln\left(\frac{n_AM_Bm^o}{W_Bm^o}\right); \quad m^o = \text{standard molality} \qquad (36.17)$$

The molality of A, defined by m_A is the amount of A divided by the mass of the solvent (B) (equation (36.2)):

$$m_A = \frac{n_A}{W_B} \tag{36.2}$$

and so the ratio n_A/W_B appearing as part of the argument of the log term in equation (36.17) can be substituted by m_A and then the resulting logarithmic term can be split into two separate logarithmic terms thus:

$$\begin{aligned}\mu(\mathrm{A})^{(\text{ideal dilute solution})} &= \mu^*(\mathrm{A})^{(\text{solute})} + RT\ln\left(\frac{m_A M_B m^o}{m^o}\right)\\ &= \mu^*(\mathrm{A})^{(\text{solute})} + RT\ln\left(\frac{m_A}{m^o}\right) + RT\ln(M_B m^o);\\ &\qquad m^o = \text{standard molality};\quad P^o = \text{standard pressure}\end{aligned} \tag{36.18}$$

Substituting now for $\mu^*(\mathrm{A})^{(\text{solute})}$ in equation (36.18) using equation (36.9) we have:

$$\mu(\mathrm{A})^{(\text{ideal dilute solution})} = [\mu^o(\mathrm{A})^{(\text{vapour})} - RT\ln(K_A P^o)] + RT\ln\left(\frac{m_A}{m^o}\right) + RT\ln(M_B m^o); \tag{36.19}$$

and defining a new chemical potential, $\mu^{**}(\mathrm{A})$ defined by:

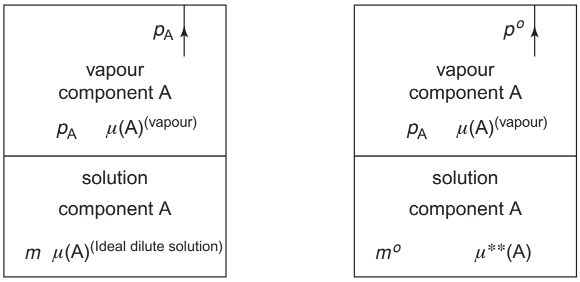
$$\mu^{**}(\mathrm{A}) = \mu^o(\mathrm{A})^{(\text{vapour})} - RT\ln(K_A P^o) + RT\ln(M_B m^o) \tag{36.20}$$

then equation (36.19) becomes:

$$\mu(\mathrm{A})^{(\text{ideal dilute solution})} = \mu^{**}(\mathrm{A}) + RT\ln\left(\frac{m_A}{m^o}\right); \tag{36.21}$$

or generally for a solution of molality, m:

$$\mu(\mathrm{A})^{(\text{ideal dilute solution})} = \mu^{**}(\mathrm{A}) + RT\ln\left(\frac{m}{m^o}\right);\quad m^o = \text{standard molality};\quad P^o = \text{standard pressure} \tag{36.22}$$



Ideal dilute solution
containing liquids A+B
component A only considered

Figure 36.4 Conditions corresponding to equations (36.21 and 36.22).

which defines the chemical potential of an ideal dilute solution in terms of the molality, m of the solution in terms of the standard molality, m_o (usually 1 mol kg^{-1}) and at the appropriate standard pressure, P^o (usually 1 bar). $\mu^{**}(\mathrm{A})$ represents the chemical potential of an ideal dilute solution having a molality equal to that of the standard molality, m^o and this final expression is the definition (for the solute) in an *ideal dilute solution* (M_B is its molar mass = molecular weight × g mol^{-1}).

The following relationships (partly utilised in the derivation above) could be utilised to convert x_A (in equation (36.10)) into an equation, of similar form to equation (36.22), in terms of concentration, c (= amount of solute/volume of solution):

$$\begin{aligned}x_A &= \frac{n_A}{(n_A + n_B)} \approx \frac{n_A}{n_B} = \frac{n_A M_B}{W_B} = \frac{n_A M_B}{(V_B \cdot \rho_B)} \approx \frac{n_A M_B}{(V_{\text{solution}} \cdot \rho_B)}\\ &= M_B \cdot \frac{c_A}{\rho_B} = \left(\frac{M_B \cdot c^o}{\rho_B}\right) \cdot \left(\frac{c_A}{c^o}\right)\quad c^o = \text{standard concentration}\end{aligned} \tag{36.23}$$

where n = amount of substance, W = mass, M = molar mass, ρ = *density* and V = *volume.*

A similar derivation of the above relationship could have been achieved by proceeding via liquid expressions rather than the gas expressions used above. We are able to proceed via the latter, because at the Henry's Law end of the diagram:

- the gas will be dilute in component A

and

- the use of partial pressures is appropriate.

Equations (36.21) and (36.22) are always true where the molality approaches the limit:

$$m_{\mathrm{A}}\ (= m) \rightarrow 0 \tag{36.24}$$

but will also often be a good approximation when the molality, $m_{\mathrm{A}}\ (= m)$, is finite but small.

In Frame 39, section 39.3 we consider the question of deviations from ideal dilute solution behaviour at higher molalities.

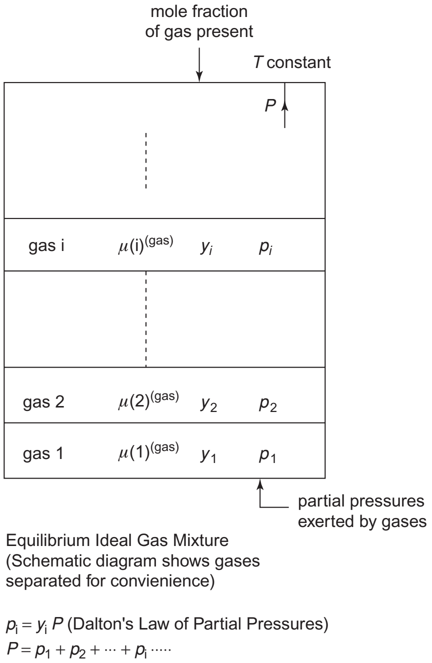


Figure 36.5 Equilibrium ideal gas mixture.

36.4 Chemical Potentials for a Mixture of Ideal Gases at Equilibrium

An ideal gas mixture conforms to the gas equation and $PV = nRT$ but there is an additional aspect to the definition, namely that the chemical potential of a component, i, of the mixture at a partial pressure, p_{i} is equal to the chemical potential of the pure material, i, at the same total pressure.

Similar principles to those used in section 36.3 above may be used to calculate $\mu(\mathrm{i})^{(\mathrm{gas})}$ for each component, i, for a mixture of ideal gases having mole fraction, $y_{\mathrm{i}}\ (= n_{\mathrm{i}}/n)$ where n_{i} is the amount of i present and n is the total amount of gas in the entire mixture (Figure 36.2).

Using equation (35.6) (Frame 35, Figure 35.4) we have:

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \mu^{o}(\mathrm{i})^{(\mathrm{gas})} + RT\ln\left(\frac{p_{\mathrm{i}}}{P^{o}}\right) \tag{36.25}$$

where $\mu^{o}(\mathrm{i})^{(\mathrm{gas})}$ is the chemical potential of the pure gas i at standard pressure, P^{o} (i.e. when the log term vanishes) and since the partial pressure, p_{i} of any component i of the ideal gas mixture is related to the total pressure P of the gas mixture by Dalton's Law of Partial Pressures (Frames 31, equation (31.7) and 34) then:

$$p_{\mathrm{i}} = y_{\mathrm{i}} \cdot P \tag{36.26}$$

where y_{i} is the mole fraction of the component gas, i, and so substituting equation (36.26) into equation (36.25) :

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \mu^{o}(\mathrm{i})^{(\mathrm{gas})} + RT\ln\left(\frac{y_{\mathrm{i}} \cdot P}{P^{o}}\right); \tag{36.27}$$

Equation (36.27) can then be written as:

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \left[\mu^{o}(\mathrm{i})^{(\mathrm{gas})} + RT\ln\left(\frac{P}{P^{o}}\right)\right] + RT\ln y_{\mathrm{i}} \tag{36.28}$$

and when the mole fraction, $y_{\mathrm{i}} = 1, RT\ln y_{\mathrm{i}} = 0$ and *only* gas i is then present, so that $\mu(\mathrm{i})^{(\mathrm{gas})}$ then corresponds with $\mu^{*}(\mathrm{i})^{(\mathrm{gas})}$

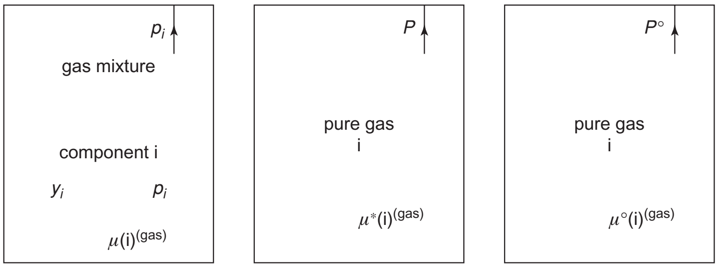


Figure 36.6 Conditions corresponding to equation (36.25), (36.28) and (36.30).

which is the chemical potential for the pure gas i under pressure P. The asterisk on $\mu^{*}(\mathrm{i})^{(\mathrm{gas})}$ is used to record the fact that the standard pressure P^{o} *does not* apply to this term. We can now write that:

$$\mu^{*}(\mathrm{i})^{(\mathrm{gas})} = \left[\mu^{o}(\mathrm{i})^{(\mathrm{gas})} + RT\ln\left(\frac{P}{P^{o}}\right)\right] \quad P^{o} = \text{standard pressure} \tag{36.29}$$

If we now subtract equation (36.27) from equation (36.28), for each component of the gas mixture we can write that:

$$\mu(\mathrm{i})^{(\mathrm{gas})} = \mu^{*}(\mathrm{i})^{(\mathrm{gas})} + RT\ln y_{\mathrm{i}} \tag{36.30}$$

Again we see that the logarithmic term, $RT \ln y_i$, corrects the chemical potential of the *pure* gas, i, at pressure P so that it applies to a mixture at pressure, P in which i is one of many components when i is present at a composition level corresponding to mole fraction, y_{i}.

Equation (36.30) therefore defines an *ideal mixture* of gases the 'ideality' this time stemming from the fact that Dalton's Law of Partial Pressures (Frame 31 and 34) is obeyed by the gas mixture.

We will consider further the mixing of ideal gases in Frame 37, section 37.3.

Although we have derived a number of chemical potential expressions for ideal situations we have not shown how we can use such equations in a practical sense. We have hinted at, but not considered the treatment of real (non-ideal) solutions. The question will be: can we adapt these ideal models of mixtures and solutions to apply to non-ideal cases? These two issues will be considered in the frames that follow.

37. Thermodynamics of Ideal Mixing

37.1 Chemical Potentials and Thermodynamic Equilibrium

Chemical potentials find their main use in the interpretation of the equilibria existing when chemical reactions take place. Thus when a substance A reacts with another substance B to produce products, say C and D, chemical potentials (with their ability to handle different phases of material) are especially useful in developing the underlying theory (Frames 5, 27, 28, 29, 35 and 36) and this leads on to supplying answers to a number of key questions, which include:

- once 'equilibrium' is reached and the reaction effectively stops, how much of the products C and D will have been produced (and how much of the original reactants A and B will remain)?
- if a reaction is not spontaneous under standard conditions can these be adjusted so as to obtain a yield of the products C and D?
- if so, which conditions can usefully be altered?
- how will temperature and pressure affect the position of equilibrium of the reaction?

Before we begin to study reactions in detail we discuss the concept of 'mixing' *without* a reaction taking place. We now give an example of the use of chemical potentials to study the thermodynamics of mixing for two ideal solutions designated A and B which can be either solid, liquid or gaseous:

$$\text{A (s, l or g)} + \text{B (s, l or g)} \overset{\text{mixing}}{\rightarrow} \text{ideal solution (s, l or g)} \tag{37.1}$$

and the calculation of:

- the free energy change on mixing, $\Delta_{\text{mix}} G^o$
- the corresponding, enthalpy, $\Delta_{\text{mix}} H^o$
- the entropy of mixing $\Delta_{\text{mix}} S$

and

- the volume change on mixing, $\Delta_{\text{mix}} V$.

In our model, A and B can be solids forming a solid solution, liquids forming a solution or gases forming a mixture.

The results obtained are general but apply only in cases where the mutual interactions between A and A, B and B and between A and B are virtually identical, meaning that the molecules can mix *without* showing a preference.

In real solutions we can anticipate departures from this situation and therefore the thermodynamics presented here needs to have the above caveat imposed.

If we adapt equation (27.5) presented in Frame 27, the standard free energy of an ideal solution, G^o(solution) at 1 bar pressure and made up from an amount n_A of A and an amount n_B of B is given by the equation:

$$G\,(\text{ideal solution}) = n_A\mu(\text{A}) + n_B\mu(\text{B}) \tag{37.2}$$

As Figure 37.1 illustrates, for substances which behave ideally adding n_A moles of A to n_B moles of B gives us $(n_A + n_B)$ moles of solution. The molar Gibbs energy of a solution, G_m is (Frame 27, Section 27.1) defined by:

$$G_m = \frac{G\,(\text{solution})}{(n_A + n_B)} \tag{37.3}$$

Thus for *one mole of solution*, for which the free energy per mole is equal to $\mu^{(\text{solution})}$, combining equations (37.2) and (37.3) we have:

$$\mu^{(\text{ideal solution})} = \frac{G\,(\text{ideal solution})}{(n_A + n_B)} = \frac{[n_A\mu(\text{A}) + n_B\mu(\text{B})]}{(n_A + n_B)} \tag{37.4}$$

where μ(A) and μ(B) are the chemical potentials of A and B *in the solution*. Equation (37.4) can be rearranged to give:

$$\mu^{(\text{ideal solution})} = \left[\frac{(n_A)}{(n_A + n_B)}\right]\mu(\text{A}) + \left[\frac{(n_B)}{(n_A + n_B)}\right]\mu(\text{B}) \tag{37.5}$$

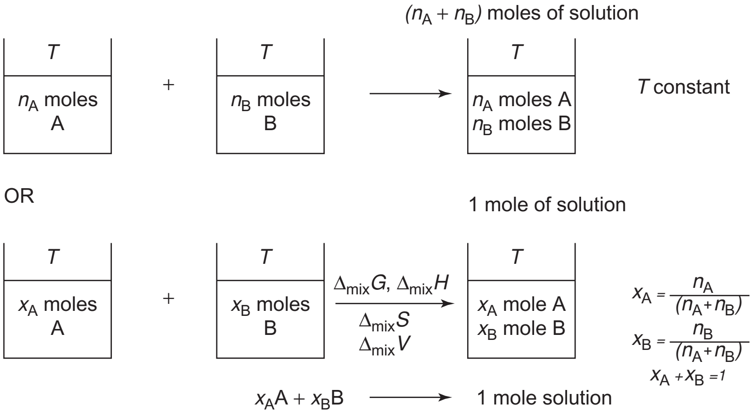


Figure 37.1 Ideal mixing of A and B (solid, liquid or gaseous).

which – since mole fractions x_A and x_B (Frames 30, 31 and 40) are defined:

$$x_A = \left[\frac{(n_A)}{(n_A + n_B)}\right] \tag{37.6}$$

$$x_B = \left[\frac{(n_B)}{(n_A + n_B)}\right] \tag{37.7}$$

such that:

$$x_A + x_B = 1 \tag{37.8}$$

– then equation (37.4) takes the simpler form:

$$\mu^{(\text{ideal solution})} = x_A\mu(\text{A}) + x_B\mu(\text{B}) \tag{37.9}$$

This nicely illustrates why mole fractions are such a useful and convenient representation of relative composition. As seen in Figure 37.1 if we consider our process as being:

$$\begin{aligned} x_A\text{A} + x_B\text{B} &\rightarrow (x_A + x_B) \text{ ideal solution of A and B} \\ &= 1 \text{ mole of ideal solution of A and B} \end{aligned} \tag{37.10}$$

then this process leads to the formation of 1 mole of the solution whose chemical potential is given by $\mu^{(\text{solution})}$. Note the amount of A + the amount of B add up to give the same amount of mixture ONLY in the case of *ideal* mixing (For non-ideal mixing cases see more advanced texts).

37.2 Ideal Mixing

If we consider the chemical potential of *pure* A and *pure* B, these will be respectively denoted by $\mu^o(\text{A})$ and $\mu^o(\text{B})$ at standard pressure (say 1 bar). For *1 mole* of mixture the change in Gibbs energy is given by:

$$\begin{aligned} \Delta_{\text{mix}}G &= \sum G(\text{after mixing}) - \sum G\,(\text{before mixing}) \\ &= \Delta_{\text{mix}}\mu = \sum \mu(\text{after}) - \sum \mu(\text{before}) \end{aligned} \tag{37.11}$$

and hence:

$$\begin{aligned} \Delta_{\text{mix}}G &= \mu^{(\text{ideal solution})} - [x_A\mu^o\,(\text{A}) + x_B\mu^o\,(\text{B})] \\ &= x_A\,\mu(\text{A}) + x_B\,\mu(\text{B}) - [x_A\,\mu^o(\text{A}) + x_B\mu^o(\text{B})] \end{aligned} \tag{37.12}$$

Since for a component A in an ideal solution, the chemical potential, $\mu(\text{A})$ can be written (using equations of the type (35.16), Frame 35 (liquids) and equation (36.30), Frame 36 (gases):

$$\mu(\text{A}) = \mu^*(\text{A}) + RT\ln x_A \tag{37.13}$$

and likewise for a component B:

$$\mu\,(\text{B}) = \mu^*(\text{B}) + RT\ln x_B \tag{37.14}$$

so that (Figure 37.1):

$$\begin{aligned} \Delta_{\text{mix}}\,G &= x_A[\mu^o(\text{A}) + RT\ln x_A] + x_B[\mu^o(\text{B}) + RT\ln x_B] - [x_A\mu^o(\text{A}) + x_B\mu^o(\text{B})] \\ &= x_A\mu^o(\text{A}) + x_ART\ln x_A + x_B\mu^o(\text{B}) + x_BRT\ln x_B - x_A\mu^o(\text{A}) - x_B\mu^o(\text{B}) \\ &= x_ART\ln x_A + x_BRT\ln x_B \\ &= RT\{x_A\ln x_A + x_B\ln x_B\} \end{aligned} \tag{37.15}$$

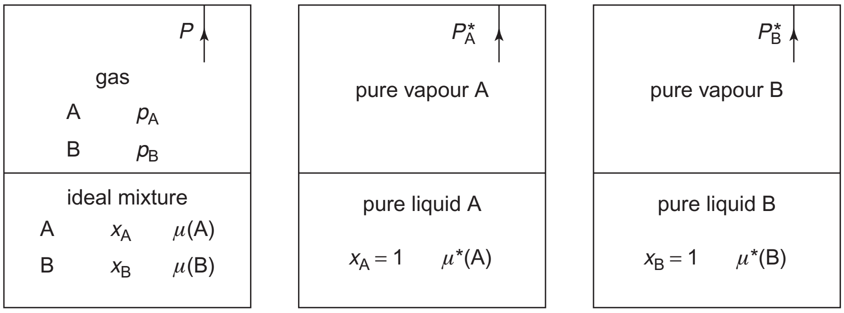


Figure 37.2 Conditions corresponding to equations (37.13), (37.14) and (37.15).

It should be noted here that since:

$$\ln(\text{mole fraction}) < 0 \tag{37.16}$$

then

$$\Delta_{\text{mix}}G < 0 \tag{37.17}$$

so that mixing of liquids is a spontaneous process.

Since we know that equation (18.14), Frame 18:

$$\left(\frac{\partial \text{G}}{\partial T}\right)_P = -S \tag{37.18}$$

then:

$$\begin{aligned}\Delta_{\text{mix}}S &= -\left(\frac{\partial \Delta_{\text{mix}}G}{\partial \text{T}}\right)_P = -\left(\frac{\partial[x_A RT \ln x_A + x_B RT \ln x_B]}{\partial \text{T}}\right)_P \\ &= -x_A R \ln x_A - x_B R \ln x_B \\ &= -R\{x_A \ln x_A + x_B \ln x_B\}\end{aligned} \tag{37.19}$$

It is important to note that if mixing takes place one would expect the entropy to increase (since mixing increases the degree of randomness of the system). Thus we would anticipate that: $\Delta_{\text{mix}}S > 0$, yet equation (37.19), at first sight, appears to give a negative entropy of mixing!

Equation (37.19) does give a positive result for $\Delta_{\text{mix}}S$ because:

- the mole fraction terms, x_A and x_B are (by definition (Frame 30)) *always* less than 1;

and

- the logarithm of a quantity which is less than 1 is itself negative.

Also since, from equation (13.10), Frame 13:

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S \tag{37.20}$$

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S \tag{37.21}$$

and so from equations (37.15) and (37.19):

$$\Delta_{\text{mix}}H = RT\{x_A \ln x_A + x_B \ln x_B\} - RT\{x_A \ln x_A + x_B \ln x_B\} = 0 \tag{37.22}$$

and so for mixing the components of ideal liquid mixtures together there is no enthalpy of mixing. We can also calculate the volume change, since (Frame 20, equation (20.3)):

$$\left(\frac{\partial \text{G}}{\partial P}\right)_T = V \tag{37.23}$$

so that:

$$\Delta_{\text{mix}}V = \left(\frac{\partial \Delta_{\text{mix}}G}{\partial P}\right)_T = \left(\frac{\partial[RT\{x_A \ln x_A + x_B \ln x_B\}]}{\partial P}\right)_T = 0 \tag{37.24}$$

since the term $[RT\ \{x_A \ln x_A + x_B \ln x_B\}]$ is not a function of pressure, the differential vanishes and therefore there is no volume change on mixing.

Thermodynamic mixing functions for non-ideal systems are discussed later in Frame 39, sections 39.4 and 39.5.

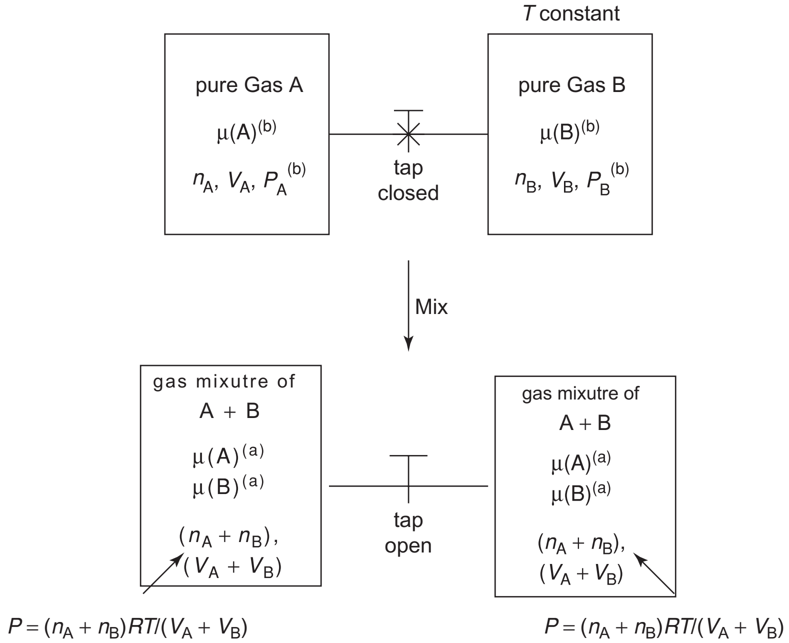


Figure 37.3 Isothermal mixing of pure gas, A with pure gas, B.

37.3 Mixing of Ideal Gases

Figure 37.3. shows the isothermal mixing process for two pure gases A and B. Employing:

- expressions for an ideal gas in the form of equation (35.6), Frame 35;
- the ideal gas law in the form of equation (4.1), Frame 4;
- an extension of equation (27.5) frame 27:

we can write the following equations to define the system before and after isothermal ($\Delta T = 0$) mixing:

- *Before Mixing*:
  For pure gas A:

$$\mu_{\mathrm{A}}^{(\mathrm{b})} = \mu_{\mathrm{A}}^{o} + RT \ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{b})}}{P^{o}}\right); \quad P^{o} = \text{standard pressure} \tag{37.25}$$

$$p_{\mathrm{A}}^{(\mathrm{b})} = \frac{n_{\mathrm{A}}RT}{V_{\mathrm{A}}} \tag{37.26}$$

  For pure gas B:

$$\mu_{\mathrm{B}}^{(\mathrm{b})} = \mu_{\mathrm{B}}^{o} + RT \ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{b})}}{P^{o}}\right); \quad P^{o} = \text{standard pressure} \tag{37.27}$$

$$p_{\mathrm{B}}^{(\mathrm{b})} = \frac{n_{\mathrm{B}}RT}{V_{\mathrm{B}}} \tag{37.28}$$

$$G^{(\mathrm{b})} = G_{\mathrm{A}}^{(\mathrm{b})} + G_{\mathrm{B}}^{(\mathrm{b})} = n_{\mathrm{A}}\mu_{\mathrm{A}}^{(\mathrm{b})} + n_{\mathrm{B}}\mu_{\mathrm{B}}^{(\mathrm{b})} \tag{37.29}$$

- *After Mixing Isothermally* ($\Delta T = 0$) *at standard pressure, P^{o}*:
  Total pressure, $P^{(\mathrm{a})}$

$$P^{(\mathrm{a})} = \frac{(n_{\mathrm{A}} + n_{\mathrm{B}}).RT}{(V_{\mathrm{A}} + V_{\mathrm{B}})} \tag{37.30}$$

  For mixed gas A:

$$\mu_{\mathrm{A}}^{(\mathrm{a})} = \mu_{\mathrm{A}}^{o} + RT \ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{a})}}{P^{o}}\right); \quad P^{o} = \text{standard pressure} \tag{37.31}$$

$$p_{\mathrm{A}}^{(\mathrm{a})} = \frac{n_{\mathrm{A}}RT}{(V_{\mathrm{A}} + V_{\mathrm{B}})} \tag{37.32}$$

For mixed gas B:

$$\mu_{\mathrm{B}}^{(\mathrm{a})} = \mu_{\mathrm{B}}^{o} + RT\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{a})}}{P^{o}}\right); \quad P^{o} = \text{standard pressure} \tag{37.33}$$

$$p_{\mathrm{B}}^{(\mathrm{a})} = \frac{n_{\mathrm{B}}RT}{(V_{\mathrm{A}} + V_{\mathrm{B}})} \tag{37.34}$$

$$G^{(\mathrm{a})} = G_{\mathrm{A}}^{(\mathrm{a})} + G_{\mathrm{B}}^{(\mathrm{a})} = n_{\mathrm{A}}\mu_{\mathrm{A}}^{(\mathrm{a})} + n_{\mathrm{B}}\mu_{\mathrm{B}}^{(\mathrm{a})} \tag{37.35}$$

where $P^{(\mathrm{a})}$ is the total pressure of the gas mixture after mixing and p_{A} and p_{B} are the partial pressures of the two gases A and B, present in the amounts n_{A} and n_{B} before mixing.

The Gibbs energy of mixing, ΔG_{mix} will be given by:

$$\begin{aligned}
\Delta G_{\mathrm{mix}} &= G^{(\mathrm{a})} - G^{(\mathrm{b})} \\
&= n_{\mathrm{A}}(\mu_{\mathrm{A}}^{(\mathrm{a})} - \mu_{\mathrm{A}}^{(\mathrm{b})}) + n_{\mathrm{B}}(\mu_{\mathrm{B}}^{(\mathrm{a})} - \mu_{\mathrm{B}}^{(\mathrm{b})}) \\
&= n_{\mathrm{A}}\left[\left\{\mu_{\mathrm{A}}^{o} + RT\ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{a})}}{P^{o}}\right)\right\} - \left\{\mu_{\mathrm{A}}^{o} + RT\ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{b})}}{P^{o}}\right)\right\}\right] \\
&\quad + n_{\mathrm{B}}\left[\left\{\mu_{\mathrm{B}}^{o} + RT\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{a})}}{P^{o}}\right)\right\} - \left\{\mu_{\mathrm{B}}^{o} + RT\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{b})}}{P^{o}}\right)\right\}\right] \\
&= n_{\mathrm{A}}\left[RT\ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{a})}}{P^{o}}\right) - RT\ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{b})}}{P^{o}}\right)\right] \\
&\quad + n_{\mathrm{B}}\left[RT\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{a})}}{P^{o}}\right)\Bigg\} - RT\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{b})}}{P^{o}}\right)\Bigg\}\right]\Bigg] \\
&= RT\left[n_{\mathrm{A}}\ln\left(\frac{p_{\mathrm{A}}^{(\mathrm{a})}}{p_{\mathrm{A}}^{(\mathrm{b})}}\right) + n_{\mathrm{B}}\ln\left(\frac{p_{\mathrm{B}}^{(\mathrm{a})}}{p_{\mathrm{B}}^{(\mathrm{b})}}\right)\right]
\end{aligned} \tag{37.36}$$

By virtue of equations (37.32) and (37.26):

$$\frac{p_{\mathrm{A}}^{(\mathrm{a})}}{p_{\mathrm{A}}^{(\mathrm{b})}} = \left[\frac{n_{\mathrm{A}}RT}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right]\Bigg/\left[\frac{n_{\mathrm{A}}RT}{V_{\mathrm{A}}}\right] = \left[\frac{V_{\mathrm{A}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right] \tag{37.37}$$

and by virtue of equations (37.34) and (37.28):

$$\frac{p_{\mathrm{B}}^{(\mathrm{a})}}{p_{\mathrm{B}}^{(\mathrm{b})}} = \left[\frac{n_{\mathrm{B}}RT}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right]\Bigg/\left[\frac{n_{\mathrm{B}}RT}{V_{\mathrm{B}}}\right] = \left[\frac{V_{\mathrm{B}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right] \tag{37.38}$$

substitution of (37.37) and (37.38) into equation (37.36) leads to:

$$\Delta G_{\mathrm{mix}} = RT\left[n_{\mathrm{A}}\ln\left[\frac{V_{\mathrm{A}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right] + n_{\mathrm{B}}\ln\left[\frac{V_{\mathrm{B}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right]\right] \tag{37.39}$$

and since:

$$\left[\frac{V_{\mathrm{A}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right] < 0 \tag{37.40}$$

and

$$\left[\frac{V_{\mathrm{B}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})}\right] < 0 \tag{37.41}$$

then their logarithms in equation (37.39), since fractional and less than zero, will be negative and so:

$$\Delta G_{\mathrm{mix}} < 0 \tag{37.42}$$

and therefore turning the tap and mixing the gases corresponds to a spontaneous process as might have been anticipated.

The entropy of mixing ΔS_{mix} can be derived, using the relationship (18.14), Frame 18 and accordingly writing:

$$\Delta S_{\mathrm{mix}} = S^{(\mathrm{a})} - S^{(\mathrm{b})} = \left\{-\left(\frac{\partial G^{(\mathrm{a})}}{\partial T}\right)_{P(\mathrm{a})}\right\} - \left\{-\left(\frac{\partial G^{(\mathrm{b})}}{\partial T}\right)_{pA,pB}\right\} = -\left(\frac{\partial G^{(\mathrm{a})}}{\partial T}\right)_{P(\mathrm{a})} + \left(\frac{\partial G^{(\mathrm{b})}}{\partial T}\right)_{p\mathrm{A},p\mathrm{B}} \tag{37.43}$$

where, we recall that, $P^{(a)}$ is the total pressure of the gas mixture after mixing and p_A and p_B are the partial pressures of the two gases A and B before mixing. Since n_A and n_B are constant and ΔG_{mix} is not a function of $P^{(a)}$ (equation (37.36) or the (constant) temperature T, then equation (37.43) can be written as an ordinary differential (Frame 3):

$$\Delta S_{\text{mix}} = \frac{-\mathrm{d}(\Delta G_{\text{mix}})}{\mathrm{d}T} \tag{37.44}$$

and so that:

$$\begin{aligned}\Delta S_{\text{mix}} &= -\mathrm{d}\left(RT\left[n_A \ln\left[\frac{V_A}{(V_A+V_B)}\right] + n_B \ln\left[\frac{V_B}{(V_A+V_B)}\right]\right]\right)\Big/\mathrm{d}T \\ &= -R\left[n_A \ln\left[\frac{V_A}{(V_A+V_B)}\right] + n_B \ln\left[\frac{V_B}{(V_A+V_B)}\right]\right]\end{aligned} \tag{37.45}$$

now since:

$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}} \tag{37.46}$$

then:

$$\begin{aligned}\Delta H_{\text{mix}} = &\left\{RT\left[n_A \ln\left[\frac{V_A}{(V_A+V_B)}\right] + n_B \ln\left[\frac{V_B}{(V_A+V_B)}\right]\right]\right\} \\ &+ T\left\{-R\left[n_A \ln\left[\frac{V_A}{(V_A+V_B)}\right] + n_B \ln\left[\frac{V_B}{(V_A+V_B)}\right]\right]\right\} \\ = &\ 0\end{aligned} \tag{37.47}$$

38. Chemical Potentials of Real Gases Fugacity, *f*, Activity, *a* and Activity Coefficient, ϕ

38.1 Chemical Potential, $\mu^{(\text{real gas})}$ for a Real (Non-Ideal) Gas. Fugacity, *f*

Lewis, recognising that the chemical potentials for most situations invariably take the general form:

$$\mu = \mu^o + RT \ln [\;] \tag{38.1}$$

proposed that the chemical potential for a non-ideal gas (i.e. a gas that does not behave according to the ideal gas law, equation 4.1, Frame 4) should take a similar format, both for the gas as a whole (Figure 38.1):

$$\mu^{(\text{real gas})} = \mu^{o(\text{real gas})} + RT \ln\left(\frac{f}{P^o}\right); \quad P^o = \text{standard pressure} \tag{38.2}$$

and, for a gaseous system of many components (Figure 38.2), for each of the components, i, present in the gas, so that:

$$\mu(\text{i})^{(\text{real gas})} = \mu^o(\text{i})^{(\text{real gas})} + RT \ln\left(\frac{f_\text{i}}{P^o}\right); \tag{38.3}$$

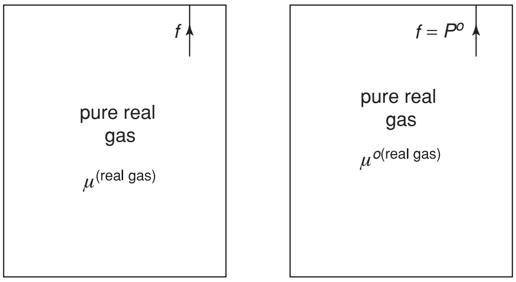


Figure 38.1 Conditions corresponding to equation (38.2).

In the above equations:

- f is called the fugacity, has the dimensions of pressure, and is a function of temperature, T, pressure, P, and composition, whilst f_i is called the fugacity of the component i in the gas and also is a unit of pressure.
- $\mu^{o(\text{real gas})}$ is the chemical potential of a gas when the overall fugacity is equal to the arbitrarily chosen standard pressure, P^o whilst $\mu^o(\text{i})^{(\text{real gas})}$, which is a function of temperature, T, is the chemical potential of the gaseous component, i, when the fugacity of this component is equal to the standard pressure, P^o.
- $\mu^{(\text{real gas})}$ and $\mu(\text{i})^{(\text{real gas})}$ are the chemical potentials of the real gas and for the component gas, i, within the mixture of real gases.

Fugacity, f, corresponds to a pressure, P whilst f_i, the fugacity of a component, i, behaves in a similar way to partial pressure, both adjusted to represent the departure from ideality. f therefore plays the same role for a real gas as pressure, P does for an ideal gas (Figures 38.1 and 38.2).

Real gases are represented by equation (38.2) above. As these approach behaviour as exhibited by ideal gases which can be represented by equation (20.13), Frame 20, (which when written in terms of chemical potentials takes the form):

$$\mu^{(\text{ideal gas})} = \mu^{o(\text{ideal gas})} + RT \ln\left(\frac{P}{P^o}\right)$$

$$P^o = \text{standard pressure} \tag{38.4}$$

then the fugacity term, $f \to P$. This will be particularly true at low pressure so that, as $P \to 0$ then $f = P$ and the gas is then said to be ideal (Figure 38.3(a)). Fugacity, f, can then be interpreted to represent the effective pressure which an ideal gas would have to have in order to have the same value of the chemical potential as the real gas (Figure 38.3(b)).

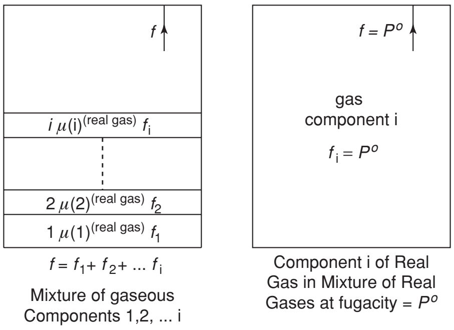


Figure 38.2 Conditions corresponding to equation (38.3).

38.2 Fugacity, *f*, Activity, *a* and Activity Coefficient, γ

We can write the following relationship between f and P:

$$f = \phi \cdot P \tag{38.5}$$

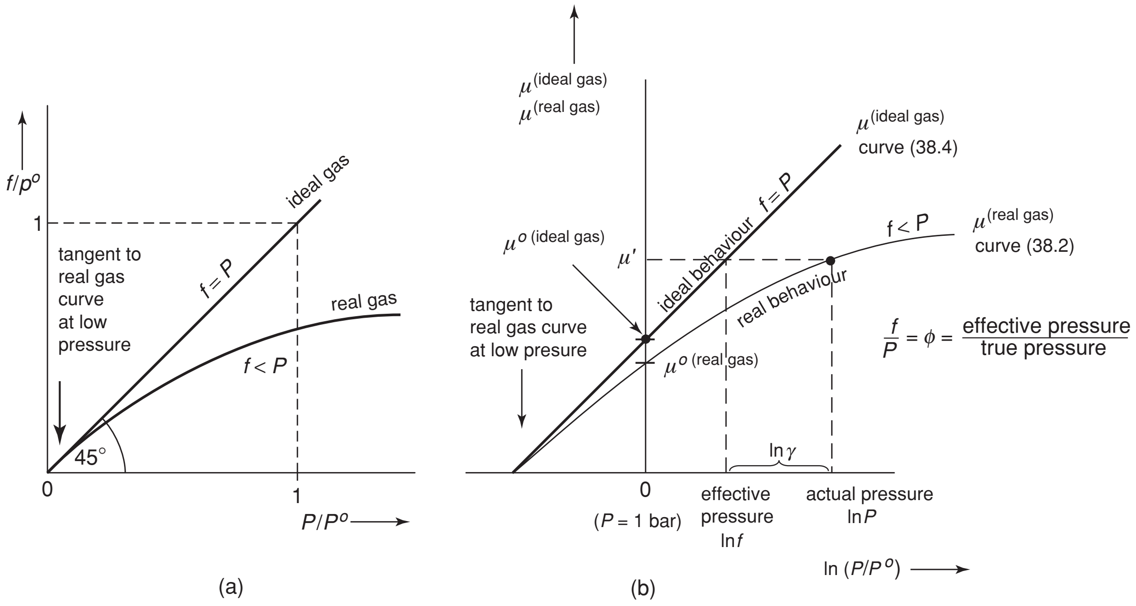


Figure 38.3 (a) Plot of fugacity, f/P^o versus P/P^o. For a real gas generally $f < P$, although at higher pressures (i.e. for $P > 2$ bar) f can then sometimes become larger than P (not shown). (b) Plots of equation (38.2) for real gases and equation (38.4) for ideal gases showing that fugacity, f, can be interpreted as the *effective* pressure which an ideal gas would have to have in order to have the same chemical potential ($= \mu'$) as the real gas at its true pressure, P.

where ϕ is called the *fugacity coefficient* and on the basis of Figure 38.3(b) and equation (38.5):

$$\phi = \frac{f}{P} = \text{[effective pressure on ideal model to give same chemical potential]/[true pressure]} \tag{38.6}$$

Similarly we can write for any component, i, in a mixture of real gases:

$$f_\text{i} = \phi_\text{i} \cdot p_\text{i} \tag{38.7}$$

for the individual components.

f (and f_i) are sometimes called the *activity* and given the symbols a (and a_i) in some texts, each having the unit of pressure, so that:

$$a = \phi \cdot P \tag{38.8}$$

and

$$a_\text{i} = \phi \cdot p_\text{i} \tag{38.9}$$

and we can then also write:

$$\mu^{\text{(real gas)}} = \mu^{o\text{(real gas)}} + RT\ln\left(\frac{a}{P^o}\right) \quad P^o = \text{standard pressure} \tag{38.10}$$

in place of equation (38.2).

38.3 Model for a Real Gas by Correction of the Ideal Model

Replacing (f/P^o) in equation (38.2) with the activity coefficient ϕ correcting the usual pressure term (P/P^o) using equation (38.5), we have:

$$\begin{aligned}\mu^{\text{(real gas)}} &= \mu^{o\text{(real gas)}} + RT\ln\left[\phi\cdot\left(\frac{P}{P^o}\right)\right]\\ &= \mu^{o\text{(real gas)}} + RT\ln\left(\frac{P}{P^o}\right) + RT\ln\phi \quad P^o = \text{standard pressure}\end{aligned} \tag{38.11}$$

In equation (38.11) we have split the logarithmic term into two log terms. This we can do because:

- ϕ is dimensionless (section 6.2, Frame 6);
- (P/P^o) is dimensionless (section 6.2, Frame 6);
- $\ln(ab) = \ln a + \ln b$ (section 6.11, Frame 6);

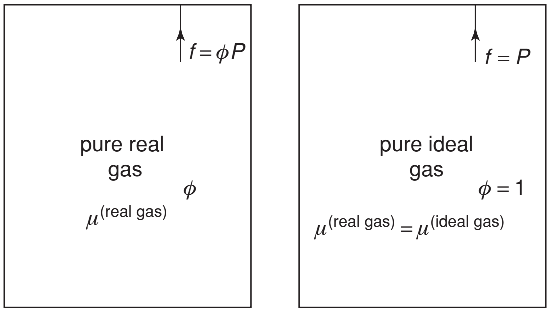


Figure 38.4 Conditions corresponding to equation (38.11) and (38.12).

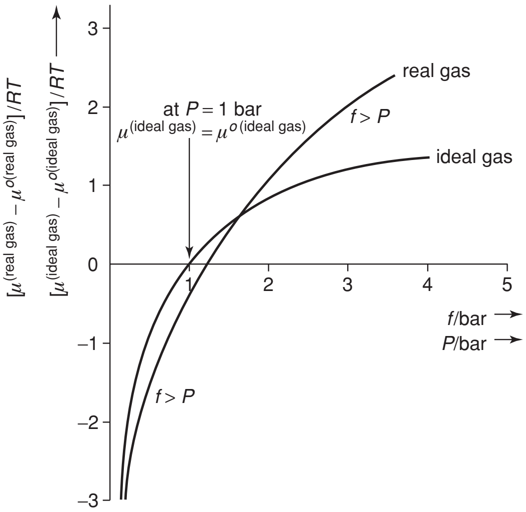


Figure 38.5 Graphs of $[(\mu^{\text{(real gas)}}-\mu^{o\text{(real gas)}})]$ versus f for real gases and of $[(\mu^{\text{(ideal gas)}}-\mu^{o\text{(ideal gas)}}]$ versus P for ideal gases superimposed.

Also when $\phi = 1$, $\ln\phi = 0$ and $f = P$ (Figure 38.4):

$$\mu^{\text{(real gas)}} = \left[\mu^{o\text{(real gas)}} + RT\ln\left(\frac{P}{P^o}\right)\right] = \mu^{\text{(ideal gas)}} \quad P^o = \text{standard pressure} \tag{38.12}$$

which is identical to the equation for an ideal gas so that:

$$\mu^{\text{(real gas)}} = \mu^{\text{(ideal gas)}} + RT\ln\phi \tag{38.13}$$

and we see that the RT ln ϕ term acts as a *correction factor* for a model for an ideal gas as represented by $\mu^{\text{(ideal gas)}}$ in equation (38.4). Thus if we know the value of ϕ then we can treat the thermodynamics of a real gas as though it were an ideal gas and then correct the chemical potential by the $RT\ln\phi$ term.

f/P^o and P/P^o can be written (by rearranging equations (38.2) and (38.4) in the forms:

$$\left(\frac{f}{P^o}\right) = \exp\left[\frac{(\mu^{\text{(real gas)}} - \mu^{o\text{(real gas)}})}{RT}\right] \tag{38.14}$$

and:

$$\left(\frac{P}{P^o}\right) = \exp\left[\frac{(\mu^{\text{(ideal gas)}} - \mu^{o\text{(ideal gas)}}}{RT}\right] \tag{38.15}$$

and Figure 38.5 shows the appropriate graphs of $[\mu - \mu^o]$ versus f and P which illustrates how f departs from P.

38.4 Calculation of Fugacity, *f*, using the Virial Equation for a Gas at Moderate Pressures

For gases that do not deviate excessively from ideal behaviour the approximate relationship:

$$f \approx \frac{P^2_{\text{(real gas)}}}{P_{\text{(ideal gas)}}} \tag{38.16}$$

has been found to hold, where $P_{\text{(real gas)}}$ is the pressure of the real (i.e. non-ideal) gas and $P_{\text{(ideal gas)}}$ is the pressure of an ideal gas having *the same volume* as the real gas. If we suppose that a real gas has a molar volume V, given by the Virial Equation (briefly mentioned previously in Frame 31), then:

$$P_{\text{(real gas)}} = RT\left[1 + \left(\frac{\mathrm{B}}{V}\right) + \left(\frac{\mathrm{C}}{V^2}\right) + \left(\frac{\mathrm{D}}{V^3}\right) + \ldots..\right]\Big/V \tag{38.17}$$

and for an ideal gas having the same volume:

$$P_{\text{(ideal gas)}} = \frac{RT}{V} \tag{38.18}$$

Hence a real gas at temperature T:

$$f \approx \frac{{P_{\text{(real gas)}}}^2}{P_{\text{(ideal gas)}}} = RT\left[1 + \left(\frac{\mathrm{B}}{V}\right) + \left(\frac{\mathrm{C}}{V^2}\right) + \left(\frac{\mathrm{D}}{V^3}\right) + \ldots\right]^2\Big/V \tag{38.19}$$

39. Chemical Potentials of Real Solutions. Activity, *a* and Activity Coefficients, $\underline{f}$

In this frame we shall discuss solutions of liquids although what is said applies equally well also to solid solutions.

39.1 Chemical Potential, $\mu^{\text{(real liquid mixture)}}$ for a Real (Non-Ideal) Liquid Mixture. Activity, *a*

We begin by restating the equation (35.16), Frame 35 that we established to hold for the pure liquid *solvent* in an ideal liquid mixture, this time writing $\mu(\text{i})^{\text{(liquid mixture)}}$ as $\mu(\text{i})^{\text{(ideal liquid mixture)}}$. The chemical potential, $\mu(\text{i})^{\text{(ideal liquid mixture)}}$, for an ideal liquid mixture is then:

$$\mu(\text{i})^{\text{(ideal liquid mixture)}} = \mu^*(\text{i}) + RT\ln x_i \tag{39.1}$$

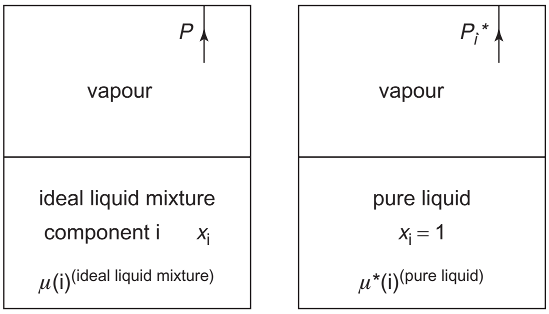


Figure 39.1 Conditions corresponding to equation (39.1).

where x_i is the mole fraction of the 'solvent' present and $\mu^*(\text{i})$ is the chemical potential of the pure liquid solvent. This equation has a linear form when $\mu(\text{i})^{\text{(ideal liquid mixture)}}$ is plotted versus $\ln x_\text{i}$, having a positive gradient (= RT) and an intecept corresponding to $\mu^*(\text{i})^{\text{ (pure liquid)}}$ as seen (Figure 39.2a).

In real (non-ideal) liquid mixtures quite often equation (39.1) is simply not valid. Nor is the one (i.e. equation (36.8), Frame 36) holding for the *solute* in ideal dilute solution, which took the form:

$$\mu(\text{j})^{\text{(ideal dilute solution)}} = \mu^*(\text{j})^{\text{(pure solute)}} + RT\ln x_\text{j} \tag{39.2}$$

where x_j was the mole fraction of the solute present. Conditions corresponding to Equation (39.2) are given in Figure 36.3, Frame 36 and are discussed there.

Following the ideas of Frame 38 (for gases) we can again define an alternative equation to cover departures from ideality and hence formulate one which will apply to real solutions, this takes the form:

$$\mu(\text{i})^{\text{(real liquid mixture)}} = \mu^*(\text{i})^{\text{(pure liquid)}} + RT\ln a_\text{i} \tag{39.3}$$

where a_i is called the activity (which is the liquid mixture equivalent, in concept, to the fugacity term, used as the argument (Frame 6) of a logarithmic term, to take account of non-ideal behaviour of gases) and refers to the solvent and $\mu(\text{i})^{\text{(real liquid mixture)}}$ defines the chemical potential of component, i, in a real solution and $\mu^*(\text{i})^{\text{(pure liquid)}}$ is the chemical potential of the pure liquid solvent when the activity, $a_\text{i} = 1$ and thus the logarithmic term vanishes (since $\ln 1 = 0$). Figure 39.2(b) shows a plot of equation (39.3) of $\mu(\text{i})^{\text{(real liquid mixture)}}$ versus $\ln a_\text{i}$.

What we would like to be able to do is to determine for a real (i.e. non-ideal) liquid mixture what effective concentration we need to use in order to adapt the ideal equation (39.1) to give the same chemical potential as the real liquid mixture. Now, for gases, we have established (Frame 38) that:

$$\frac{f}{P} = \phi = \textit{fugacity coefficient} = \frac{\text{(effective pressure)}}{\text{(true pressure)}} \tag{38.6}$$

so, adopting a similar procedure for liquid mixtures the activity, a_i can be defined as:

$$a_\text{i} = \gamma_\text{i} x_\text{i} \tag{39.4}$$

so that:

$$\frac{a_\text{i}}{x_\text{i}} = \gamma_\text{i} = \textit{activity coefficient} = \text{(effective mole fraction)/(true mole fraction)} \tag{39.5}$$

Now as $x_\text{i} \rightarrow 1$ and the liquid mixture becomes that of a pure liquid then in equation (39.1) (see right-hand diagram in Figure 39.1), component i becomes the sole liquid present, taking on the role of the pure liquid solvent and thus: $\mu(\text{i})^{\text{(ideal liquid mixture)}} \rightarrow \mu^*(\text{i})^{\text{(pure liquid)}}$ and at $x_\text{i} = 1$:

$$\mu(\text{i})^{\text{(ideal liquid mixture)}} = \mu^*(\text{i})^{\text{(pure liquid)}} = \mu^{\text{(solvent)}} \tag{39.6}$$

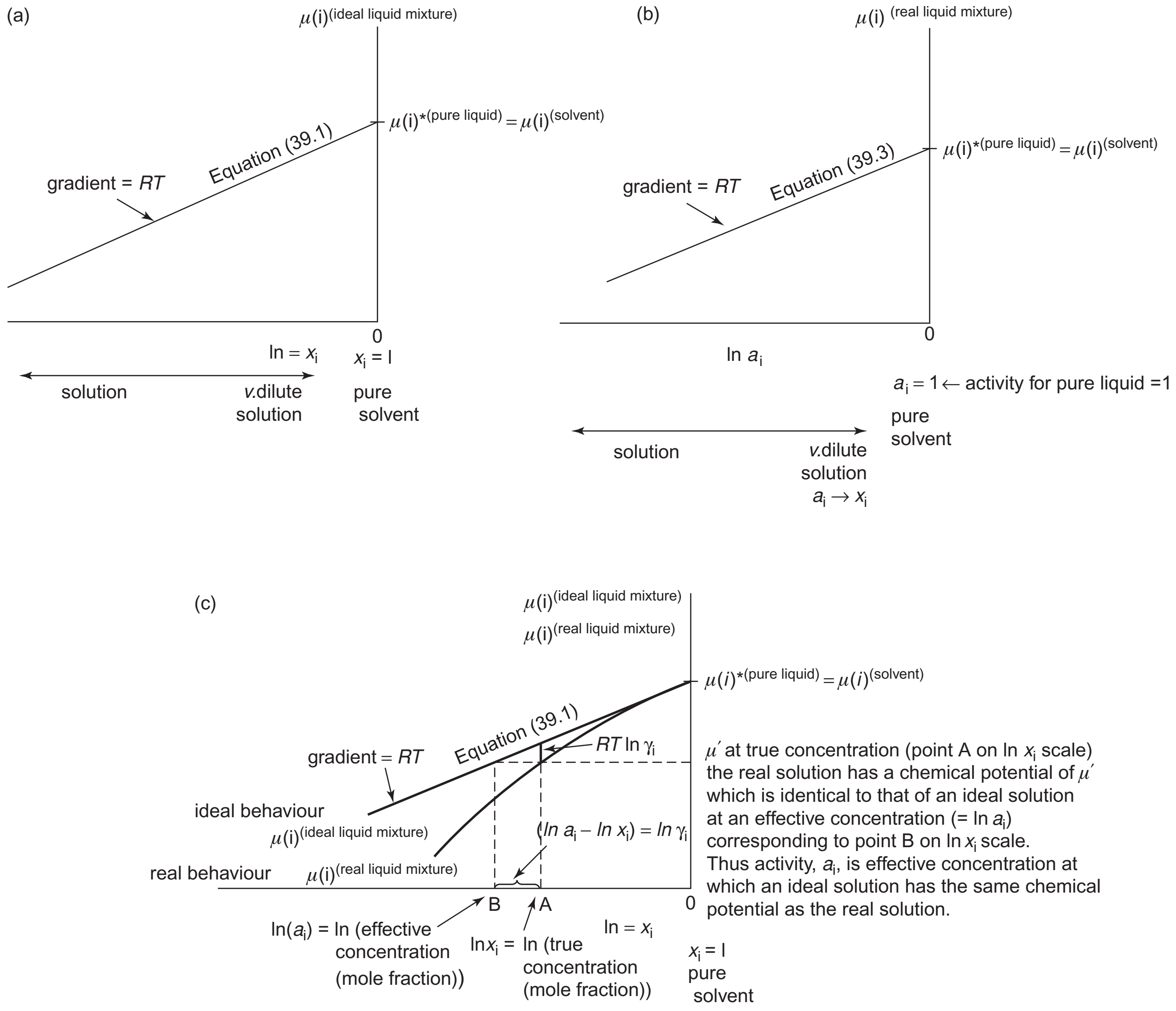


Figure 39.2 The graphs show plots of (a) $\mu(\mathrm{i})^{(\text{ideal liquid mixture})}$ versus ln x_i, (b) $\mu(\mathrm{i})^{(\text{real liquid mixture})}$ versus ln a_i and (c) $\mu(\mathrm{i})^{(\text{ideal liquid mixture})}$ and $\mu(\mathrm{i})^{(\text{real liquid mixture})}$ versus ln x_i. It should be noted that the values of ln x_i and ln a_i are negative for values of $x_i < 0$ and $a_i < 0$ and hence the origin appears on the right-hand side of the graphs. The graph (c) illustrates one interpretation of activity as being the value of x_i which needs to be substituted into equation (39.1) in order to give the identical chemical potential value for the real solution but on the ideal curve.

In a real liquid mixture also if one component predominates (as $x_i \rightarrow 1$) then: $\mu\,(\mathrm{i})^{(\text{real solution})} \rightarrow \mu^*(\mathrm{i})^{(\text{pure liquid})}$ and at $x_i = 1$:

$$\mu(\mathrm{i})^{(\text{real liquid mixture})} = \mu^*(\mathrm{i})^{(\text{pure liquid})} = \mu^{(\text{solvent})} \tag{39.7}$$

According to equation (39.3) which defines $\mu(\mathrm{i})^{(\text{real liquid mixture})}$ then if condition (39.7) is met then:

$$\ln \mathrm{a_i} = 0 \quad \text{or} \quad \mathrm{a_i} = 1 \quad \text{as} \quad x_{\text{solvent}} = 1 \tag{39.8}$$

which in turn implies that the *activity of a pure liquid* is equal to unity (= 1). Thus, in defining the equilibrium constant, K_a (Frames 43 and 46) and in particular evaluating the activities of the constituents of K_a as part of the expression for ΔG in equation (43.8), Frame 43), as well as in other expressions involving activities of pure liquids, these can be set equal to 1 (see equations (43.2) and discussion in Frame 43).

If we now subtract equation (39.1) from equation (39.3):

$$\begin{aligned}\mu\,(\mathrm{i})^{(\text{real liquid mixture})} - \mu\,(\mathrm{i})^{(\text{ideal liquid mixture})} &= [\mu^*\,(\mathrm{i})^{(\text{pure liquid})} + RT \ln a_i] - [\mu^*\,(\mathrm{i})^{(\text{pure liquid})} + RT \ln x_i] \\ &= RT \ln a_i - RT \ln x_i \\ &= RT \ln\left(\frac{a_i}{x_i}\right) \end{aligned} \tag{39.9}$$

which by virtue of equation (39.5) leads us to:

$$\mu\,(\mathrm{i})^{(\text{real liquid mixture})} - \mu\,(\mathrm{i})^{(\text{ideal liquid mixture})} = RT\ln\gamma_{\mathrm{i}} \tag{39.10}$$

and we see that, again (see Frame 38), a logarithmic term, this time in the form: $RT\ln\ \gamma_{\mathrm{i}}$ in its role as a correction term modifying the chemical potential for component, i, in an ideal solution to inform about the chemical potential the same component would have in a real (non-ideal) solution.

It is the term:

$$\log_{10}\gamma = 2.303\ln\gamma \tag{39.11}$$

which is evaluated, as the aim of the Debye–Hückel Theory. This theory was specifically developed to study real ionic solutions.

Figure 39.2(c) shows a plot of both $\mu(\mathrm{i})^{(\text{real liquid mixture})}$ and $\mu(\mathrm{i})^{(\text{ideal liquid mixture})}$ versus ln x_{i}. Equation (39.3) is no longer linear (as it was in Figure 39.2(b)) in this plot since the ordinate scale has now been changed, instead the curve for $\mu(\mathrm{i})^{(\text{real liquid mixture})}$ forms a tangent to the ideal curve in the region where the liquid mixture is extremely dilute (i.e. where $x_{\mathrm{i}} \rightarrow 1$). As the non-ideal liquid mixture becomes more concentrated the curves diverge. The figure shows the role of activity, a_{i}, in defining an effective concentration (or mole fraction) at which the chemical potential of an ideal liquid mixture would be identical to that of the real liquid mixture at a particular concentration (mole fraction) corresponding to point A.

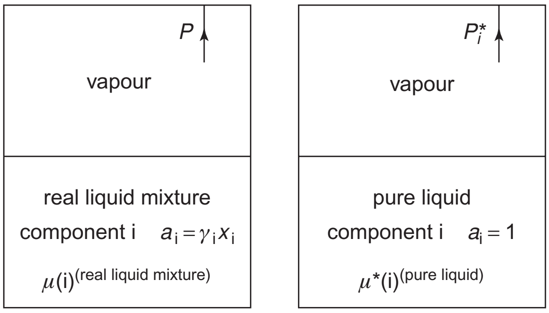


Figure 39.3 Conditions corresponding to Equation (39.3).

Figure 39.4 shows that if $\gamma_{\mathrm{i}} = 1$ then $a_{\mathrm{i}} = x_{\mathrm{i}}$ (i.e. the effective mole fraction corresponds to the actual mole fraction as made up) then we have ideal behaviour. As discussed before (Frame 33, Figure 33.2) both positive and negative deviations from ideality can occur in real liquid mixtures.

For a system conforming to Raoult's Law:

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{o} + RT\ln \mathrm{x}_{\mathrm{A}} = \mu_{\mathrm{A}}^{o} + RT\ln\left(\frac{p_{\mathrm{A}}}{P^{o}}\right) \quad \text{with } p_{\mathrm{A}} = x_{\mathrm{A}}\cdot P_{\mathrm{A}}^{*} \tag{39.12}$$

for a positive deviation (say) at a particular x_{A}:

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{o} + RT\ln a_{\mathrm{A}} = \mu_{\mathrm{A}}^{o} + RT\ln\left(\frac{p_{\mathrm{A}}(+)}{P^{o}}\right) \quad \text{with } p_{\mathrm{A}}(+) > x_{\mathrm{A}}\cdot P_{\mathrm{A}}^{*} \tag{39.13}$$

Comparing equations (39.12) and (39.13):

$$a_{\mathrm{A}} > x_{\mathrm{A}} \tag{39.14}$$

so that positive (negative) deviations from Raoult's Law correspond to γ being greater than (less than) 1 (Figure 39.4)

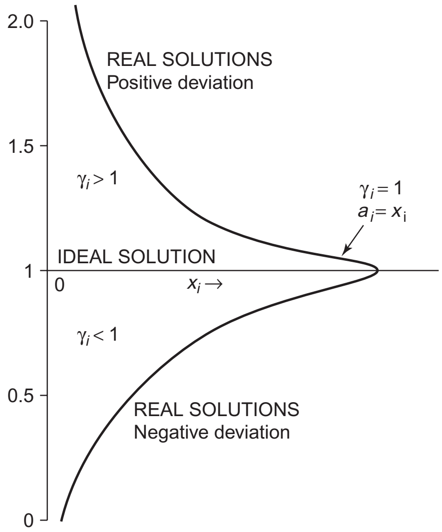


Figure 39.4 Deviation from ideal behaviour as a function of concentration is measured by the value of γ_{i}.

39.2 Use of Concentration, c and Molality, *m* and the Definition of Activity

When the amount of material present is measured by either concentration, c_{i} or molality (= amount of solute/mass of solvent) m_{i} the definition of activity differs slightly from the case (equation (39.4)) where a dimensionless measure (like mole fraction, x) is used. Equations for chemical potential, μ, involving mole fractions, x_{i} apply quite well when one is examining equilibria in solution. However in other cases concentration, c_{i} or molalities, m_{i} are often used. Activity will then be defined in relation to a standard concentration, c^{o}:

$$a_{\mathrm{i}} = \gamma_{\mathrm{i}}\cdot\left(\frac{c_{\mathrm{i}}}{c^{o}}\right); \quad c^{o} = \text{standard concentration} \tag{39.15}$$

where the standard concentration, c^{o} is defined for a particular application (often as 1 mol dm^{-3} for example). In this case:

$$\left(\frac{a_{\mathrm{i}}\cdot \mathrm{c}^{o}}{c_{\mathrm{i}}}\right) = \gamma_{\mathrm{i}} = \textit{activity coefficient} = (\text{effective concentration})/(\text{true concentration}) \tag{39.16}$$

In the case of molalities, m_{i}, activity is defined as:

$$a_{\mathrm{i}} = \gamma_{\mathrm{i}}\cdot\left(\frac{m_{\mathrm{i}}}{m^{o}}\right); \quad m^{o} = \text{standard molality} \tag{39.17}$$

where the standard molality, m^o is defined for a particular application (often as 1 mol kg^{-1}). Accordingly:

$$\left(\frac{a_i \cdot m^o}{m_i}\right) = \gamma_i = \textit{activity coefficient} = (\text{effective molality})/(\text{true molality}) \tag{39.18}$$

the principles remaining much the same as have been described above. In dilute solution, of course, γ_i, becomes equal to 1.

In the case of *aqueous solutions*, at 'ordinary' temperatures, molality/mol kg^{-1} and concentration/mol dm^{-3} are nearly equivalent. Hence apart from their units molality and concentration are interchangeable in the case of *aqueous* solutions.

39.3 Chemical Potential Representing Deviation from an Ideal Dilute Solution

In Frame 36, section 36.3 we studied the ideal dilute solution, consisting of solvent, B and solute, A, for which we found:

- for the *Solute, A*: Equations (36.21) and (36.22), Frame 36 gave an expression for the chemical potential of the solute, A, in an ideal dilute solution, $\mu(\mathrm{A})^{(\text{ideal dilute solution})}$ which took the form:

$$\mu(\mathrm{A})^{(\text{ideal dilute solution})} = \mu^{**}(\mathrm{A}) + RT\ln(m/m^o); \quad m^o = \text{standard molality}; \quad P^o = \text{standard pressure} \tag{36.21}$$

  and which defined the chemical potential of the solute in an ideal dilute solution in terms of the molality, m of the solution and of the standard molality, m^o (usually 1 mol kg^{-1}) at the standard pressure, P^o (usually 1 bar). $\mu^{**}(\mathrm{A})$ represents the chemical potential of an ideal dilute solution having a molality equal to that of the standard molality, m^o.
- for the *Solvent*, B: The corresponding ideal dilute solution, obeyed equation (36.3), Frame 36 in the case of the solvent, B and:

$$\mu(\mathrm{B})^{(\text{ideal dilute solution})} = \mu(\mathrm{B})^{(\text{solution})} = \mu^*(\mathrm{B})^{(\text{solvent})} + RT\ln x_\mathrm{B} \tag{36.3}$$

  where $\mu(\mathrm{B})^{(\text{solution})}(= \mu(\mathrm{B})^{(\text{ideal dilute solution})})$ is the chemical potential of the solvent B in the solution, $\mu^*(\mathrm{B})^{(\text{solvent})}$ is the chemical potential of the pure liquid B in equilibrium with its vapour at P_B^* and x_B is the mole fraction of the solvent present in the solution phase of the mixture.

It was pointed out, in Frame 36, that equation (36.21), always held where the molality approached the limit:

$$m \to 0 \tag{39.19}$$

and will often act as a good approximation even when the molality, m, is finite, although it needs to be small in magnitude.

At higher molalities, m, non-ideal liquid mixture behaviour:

- deviates from equation (36.21);

and

- for a single component solvent, also from equation (36.3)

In these (higher molality) cases, equation (39.20) applies to the solvent (B):

$$\mu(\mathrm{B})^{(\text{non-ideal liquid mixture})} = \mu^*(\mathrm{B})^{(\text{solvent})} + RT\ln a_\mathrm{B} \tag{39.20}$$

where x_B (from equation (36.3)) has been replaced by the activity a_B, which is effectively defined by equation (39.18).

Also the activity coefficient, $\underline{f}_\mathrm{B}$, (underlined to avoid its confusion with fugacity) is defined by the equation:

$$\underline{f}_\mathrm{B} = \frac{a_\mathrm{B}}{x_\mathrm{B}} \tag{39.21}$$

and hence, substituting equation (39.21) into equation (39.20) we have:

$$\mu(\mathrm{B})^{(\text{non-ideal liquid mixture})} = \mu^*(\mathrm{B})^{(\text{solvent})} + RT\ln x_\mathrm{B} + RT\ln \underline{f}_\mathrm{B} \tag{39.22}$$

or:

$$\mu(\mathrm{B})^{(\text{non-ideal liquid mixture})} = \mu(\mathrm{B})^{(\text{ideal liquid mixture})} + RT\ln \underline{f}_\mathrm{B} \tag{39.23}$$

and the logarithmic term: $RT\ln \underline{f}_\mathrm{B}$ once again emerges as the factor which corrects the chemical potential for the solute in the the ideal liquid mixture to give the chemical potential for the non-ideal liquid mixture, $\mu(\mathrm{B})^{(\text{non-ideal liquid mixture})}$.

39.4 Mixing Functions for Non-Ideal Liquid Mixtures

Frame 37 considered the thermodynamics of mixing. The total molar Gibbs energy, G_m of a binary liquid mixture, is given (in terms of the amounts, n_A and n_B, of the two components) by equation (37.9), Frame 37:

$$\mu^{(\text{ideal solution})} = G(\text{ideal solution})/(n_\mathrm{A} + n_\mathrm{B}) = G_\mathrm{m} = x_\mathrm{A}\mu(\mathrm{A}) + x_\mathrm{B}\mu(\mathrm{B}) \tag{37.9}$$

where $\mu(\mathrm{A})$ and $\mu(\mathrm{B})$ are the chemical potentials of A and B *in the liquid mixture*. For a non-ideal liquid mixture then we have:

$$\begin{aligned}\Delta G_{\mathrm{m,mix}} = G_{\mathrm{m}}^{(\mathrm{after})} - G_{\mathrm{m}}^{(\mathrm{before})} &= x_{\mathrm{A}} \cdot (\mu\,(\mathrm{A})^{*} + RT \ln a_{\mathrm{A}}) + x_{\mathrm{B}} \cdot (\mu\,(\mathrm{B})^{*} + RT \ln a_{\mathrm{B}}) - x_{\mathrm{A}} \cdot \mu\,(\mathrm{A})^{*} - x_{\mathrm{B}} \cdot \mu\,(\mathrm{B})^{*} \\ &= RT \cdot \{x_{\mathrm{A}} \cdot \ln a_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln a_{\mathrm{B}}\} \\ &= RT \cdot \{x_{\mathrm{A}} \cdot \ln x_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln x_{\mathrm{B}} + x_{\mathrm{A}} \cdot \ln \underline{f}_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln \underline{f}_{\mathrm{B}}\} \qquad (39.24)\end{aligned}$$

derived from substituting a generalised form of equation (39.20) and using the relationship (39.21) we derive the equation (39.25) for which we note the following points:

- the first terms: $[x_{\mathrm{A}} \cdot \ln x_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln x_{\mathrm{B}}]$ since $x_{\mathrm{A}} < 1$ and $x_{\mathrm{B}} < 1$ will give rise to a series of negative terms which will sum overall to a negative term;
- the sign of the terms: $[x_{\mathrm{A}} \cdot \ln \underline{f}_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln \underline{f}_{\mathrm{B}}]$ will depend on the values of the individual activity coefficients, $\underline{f}_{\mathrm{A}}$ and $\underline{f}_{\mathrm{B}}$ and since $\underline{f}_{\mathrm{A}}$ and $\underline{f}_{\mathrm{B}}$ can each be either < 1 or > 1 these terms can be either negative or positive;
- the activity coefficients, $\underline{f}_{\mathrm{A}}$ and $\underline{f}_{\mathrm{B}}$, also depend on composition.

39.5 Graphical Representations of $G_{\mathrm{m,\,mix}}$ for Non-Ideal Liquid Binary Mixtures

Figure 39.5. shows the behaviour of $\Delta G_{\mathrm{m,mix}}$ for an ideal binary liquid mixture as a function of the mole fraction of component A, x_{A} ($= 1 - x_{\mathrm{B}}$). Since the liquid mixture is ideal then the activity coefficients are both equal to unity:

$$\underline{f}_{\mathrm{A}} = \underline{f}_{\mathrm{B}} = 1 \qquad (39.25)$$

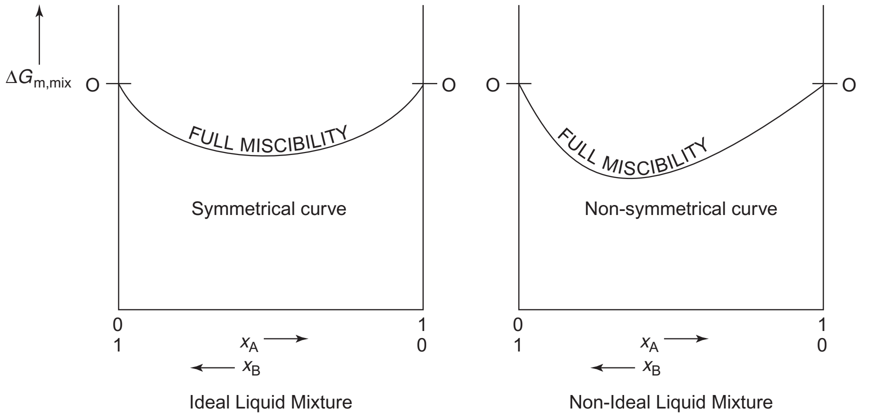


Figure 39.5 Full Miscibility at fixed temperature and pressure for an Ideal Liquid Mixture (for which activity coefficients are equal to unity $\underline{f}_1 = \underline{f}_2 = 1$) and Non-Ideal Liquid mixture exhibiting full miscibility (dotted line).

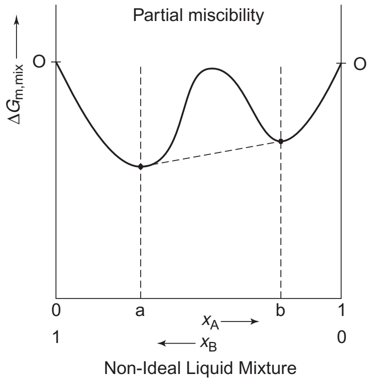


Figure 39.6 Non-ideal liquid mixture exhibiting partial miscibility.

and for a binary liquid mixture equation (39.24):

$$\Delta G_{\mathrm{m,mix}} = RT \cdot \{x_{\mathrm{A}} \cdot \ln x_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln x_{\mathrm{B}} + x_{\mathrm{A}} \cdot \ln \underline{f}_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln \underline{f}_{\mathrm{B}}\} \qquad (39.26)$$

and by virtue of equation (39.25) then the logarithmic terms vanish and:

$$x_{\mathrm{A}} \cdot \ln \underline{f}_{\mathrm{A}} = 0 \qquad (39.27)$$

and

$$x_{\mathrm{B}} \cdot \ln \underline{f}_{\mathrm{B}} = 0 \qquad (39.28)$$

hence, substituting equations (39.27) and (39.28) into equation (39.26) leads to:

$$\Delta G_{\mathrm{m,mix}} = RT\{x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\} \qquad (39.29)$$

in agreement with the result derived earlier as equation (37.15), Frame 37 for an ideal binary liquid mixture.

In the case of equation (39.24) in the form:

$$\Delta G_{\mathrm{m,mix}} = RT \cdot \{x_{\mathrm{A}} \cdot \ln a_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln a_{\mathrm{B}}\} \qquad (39.30)$$

we can consider two further possibilities both relating to non-ideal liquid mixtures:

- the case where: $[x_{\mathrm{A}} \cdot \ln a_{\mathrm{A}} + x_{\mathrm{B}} \cdot \ln a_{\mathrm{B}}]$ has only one extremum (Figure 39.5) with:

$$\underline{f}_{\mathrm{A}}, \underline{f}_{\mathrm{B}} < 1 \qquad (39.31)$$

where the liquid mixture exhibits full miscibility.

and

- the case where: $[x_A \cdot \ln a_A + x_B \cdot \ln a_B]$ has three extrema (Figure 39.6) with:

  $$\underline{f}_A \gg 1, \quad \underline{f}_B < 1 \tag{39.32}$$

  or

  $$\underline{f}_A < 1, \quad \underline{f}_B \gg 1 \tag{39.33}$$

  or

  $$\underline{f}_A \gg 1, \quad \underline{f}_B \gg 1 \tag{39.34}$$

  where the liquid mixture exhibits partial miscibility.

In Figure 39.6, ——- represents $\Delta G_{m,mix}$ for a two phase system (where phase 1: $x_A = a$; phase 2: $x_A = b$). Between the two phases in the region where $a \le x_A \le b$, a mixture of the two phases is more stable than the single phase, represented by ——-.

40. Measurements of Equilibrium Constant, *K*

Chemical reactions are frequently found to be at equilibrium. The concentrations of reactants and products present once equilibrium has been reached are defined by an equilibrium constant, K. Because equilibrium constants must be formulated in such a way that they are dimensionless and represent pure numbers (in order that we can take their logarithms) we need to discuss this issue separately and we do so in Appendix A.

40.1 The Equilibrium Constant, *K*. Measures of Concentration of Reactants and Products in Equilibrium Expressions

K, the equilibrium constant was first mentioned in Section 6.3 of Frame 6 where we discussed its use as a logarithmic argument. The relevance of discussing the logarithm of equilibrium constant is readily seen by reference to the key equation (41.13) derived in Frame 41.

There are a number of alternative ways in which the equilibrium constant for a given reaction, K can be expressed and these are studied in this frame. The following Frames 41–49 further discuss the equilibrium constant and its representation. The equilibrium position for a reaction can be approached from either direction (i.e. from the products or (more usually) from the reactants). This was illustrated earlier in this text in Figure 27.1 of Frame 27.

The equilibrium constant, $K_{c/co}$ (the subscript 'c/c^o' implying that *concentrations* are used in the expression) for the reaction:

$$\mathrm{aA} + \mathrm{bB} = \mathrm{cC} + \mathrm{dD} \tag{40.1}$$

is defined by:

$$K_{c/co} = \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\}\Big/\left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\}; \quad c^o = \text{standard concentration} \tag{40.2}$$

and similarly, the reaction quotient, Q_c – appropriate for non-equilibrium situations (Frame 41) – is defined by:

$$Q_{c/co} = \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\}\Big/\left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\}; \quad c^o = \text{standard concentration} \tag{40.3}$$

where [A], [B], [C] and [D] represent concentrations measured in units of c^o (usually 1 mol dm^{-3}) the standard concentration and thus division of the concentration terms by c^o leaves us with a series of dimensionless ratios e.g. ([C]/c^o) is a pure number and hence to an equilibrium constant, $K_{c/co}$ which will also be a dimensionless quantity (see Note 40.1). Depending on the physical states of A, B, C and D and the nature of the reaction being studied, concentration units other than 1 mol dm^{-3} can sometimes be more appropriate or convienient to use in which case c^o would then be redefined. Hence in those of our equations that introduce c^o we indicate this arbitary choice by writing 'c^o = standard concentration' to the right of the equation.

(See Note 40.2).

40.2 Concentration, *c* or [ ] or Molarity

The terms concentration and molarity are synonymous terms. Concentration of a reactant or product, c, often represented with square brackets [ ], is measured by the amount of substance, n divided by the volume of the solution. mol dm^{-3} are the usual units used for molarity or concentration:

$$c = [\quad] = \frac{n}{V} = \frac{[\text{amount of solute}]}{[\text{volume of solution}]} \tag{40.4}$$

40.3 Partial Pressure, *p*ᵢ

Since for any gaseous component, i, its partial pressure, p_i is given (Frame 31, equation (31.5)) by:

$$p_\mathrm{i} = \left\{\frac{n_\mathrm{i}RT}{V}\right\} \tag{40.5}$$

and thus, combining equations (40.4) and (40.5) for a component, i, we can write that:

$$c_{\mathrm{i}} = [\quad] = \left\{\frac{n_{\mathrm{i}}}{V}\right\} = \frac{p_{\mathrm{i}}}{RT} \tag{40.6}$$

so that, also, the standard concentration, c^o, is given in terms of the standard pressure, p^o by the equation:

$$\frac{c_{\mathrm{i}}}{c^o} = \frac{(p_{\mathrm{i}}/p^o)}{RT} = \frac{p_{\mathrm{i}}}{p^o}RT \tag{40.7}$$

Relationships (40.6) and (40.7) recognise the proportionality between concentration, c_{i} and partial pressure, p_{i} (atm) at constant temperature, T (having the proportionality constant $= 1/RT$). The former measure (concentration, c_{i}) can be used when dealing with solutions which are present in reactions (see notes about solids in equilibrium expressions later – Frame 43).

40.4 Mole fraction, x_{i}

The mole fraction, x_{i}, has previously been defined in Frames 30 and 31 and has been used frequently (in Frames 34, 35, 36 and 37) for a component in a mixture containing m components as:

$$x = \frac{n_{\mathrm{i}}}{(n_1 + n_2 + \cdots + n_{\mathrm{i}} + \cdots n_{\mathrm{m}})} = \frac{n_{\mathrm{i}}}{\sum_{\mathrm{i}=1}^{\mathrm{m}} n_{\mathrm{i}}} \tag{40.8}$$

where n_{i} is the amount of i present and $(n_1 + n_2 + \cdots + n_{\mathrm{i}} + \cdots n_{\mathrm{m}}) = n$ represents the total amount, n, present in the mixture. Hence x_{i} is a fraction and the sum of the individual mole fractions of all the m components adds up to 1.

$$\sum_{\mathrm{i}=1}^{\mathrm{m}} x_{\mathrm{i}} = (x_1 + x_2 + \cdots + x_{\mathrm{i}} + \cdots x_{\mathrm{m}}) = 1 \tag{40.9}$$

In Frame 37 mole fractions were used in the discussion of the thermodynamics of ideal mixtures. In expressing the equilibrium constant, K_x, in terms of mole fractions, no division of the individual terms by standard states is required (Appendix; Frame 6, section 6.3) since mole fractions are already, themselves, dimensionless. Thus equation (40.10) defines K_x:

$$K_x = \frac{\{(x_{\mathrm{C}})^{\mathrm{c}}(x_{\mathrm{D}})^{\mathrm{d}}\}}{\{(x_{\mathrm{A}})^{\mathrm{a}}(x_{\mathrm{B}})^{\mathrm{b}}\}} \tag{40.10}$$

40.5 Molality, m_{i}

It is appropriate here to discuss molality, m_{i} but this topic (of necessity) was introduced in Frame 36, section 36.2 to which the reader is now referred. The *molality* of a solute in a solution is defined as the amount of the solute divided by the mass of solvent.

40.6 Equilibrium Constant in Terms of Molalities, $K_{m/mo}$

In expressing equilibrium constants, $K_{m/mo}$, in terms of molality:

- each molality concentration term is written so as to be dimensionless, by defining a standard molality, m^o:
- i.e. we effectively divide the individual molalities, represented in equation (40.11) as m_{A}, m_{B}, m_{C} and m_{D} and usually measured in mol kg^{-1} by a standard molality, m^o, in this case equal to 1 mol kg^{-1} so making the quantities represented by (m_{A}/m^o), (m_{B}/m^o), (m_{C}/m^o) or (m_{D}/m^o) pure number ratios which are needed so that $K_{m/mo}$ can be properly defined and in order to take the logarithm of $K_{m/mo}$ in order to find ΔG^o (Frame 41).
- hence we write:

$$K_{m/mo} = \left\{\left(\frac{m_{\mathrm{C}}}{m^o}\right)^{\mathrm{c}}\left(\frac{m_{\mathrm{D}}}{m^o}\right)^{\mathrm{d}}\right\} \Big/ \left\{\left(\frac{m_{\mathrm{A}}}{m^o}\right)^{\mathrm{a}}\left(\frac{m_{\mathrm{B}}}{m^o}\right)^{\mathrm{b}}\right\} \qquad m^o = \text{standard molality} \tag{40.11}$$

In aqueous solutions at temperature 298 K, the *numerical values* of the molalities m_{A}, m_{B}, m_{C} and m_{D} measured in mol kg^{-1} are such that they are equal to the concentrations: [A], [B], [C] and [D] measured in mol dm^{-3} and hence we can write that:

$$K_{m/mo} = K_{c/co} \tag{40.12}$$

so that:

$$\left\{\left(\frac{m_{\mathrm{C}}}{m^o}\right)^{\mathrm{c}}\left(\frac{m_{\mathrm{D}}}{m^o}\right)^{\mathrm{d}}\right\} \Big/ \left\{\left(\frac{m_{\mathrm{A}}}{m^o}\right)^{\mathrm{a}}\left(\frac{m_{\mathrm{B}}}{m^o}\right)^{\mathrm{b}}\right\} = \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\} \Big/ \left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\};$$

$$m^o = 1\ \text{mol kg}^{-1} \quad c^o = 1\ \text{mol dm}^{-3} \tag{40.13}$$

Thus, in this specific case, the equilibrium constant written in terms of molalities is identical in value to that written in terms of concentration.

41. Reaction Quotient, Q and Equilibrium Constant, K Relationship Between ΔG^o and K_{p/p^o}

41.1 Thermodynamics of Reactions. Reaction Quotient, Q

Consider a reaction in which *only gaseous materials* are involved.

$$a\mathrm{A(g)} + b\mathrm{B(g)} = c\mathrm{C(g)} + d\mathrm{D(g)} \tag{41.1}$$

for which K_X would take the form:

$$K_X = \frac{\{X_\mathrm{C}^\mathrm{c} \cdot X_\mathrm{D}^\mathrm{d}\}}{\{X_\mathrm{A}^\mathrm{a} \cdot X_\mathrm{B}^\mathrm{b}\}} \tag{41.2}$$

where X can be variously $x, p, p/P^o, f, f/P^o, c, c/c^o. m, m/m^o, a$ and P^o and c^o are the standard pressure and concentration appropriately defined.

The free energy change of the overall reaction (Frame 27, reaction (27.15) ΔG, can be written:

$$\Delta_\mathrm{r} G = dG(\mathrm{D}) + cG(\mathrm{C}) - aG(\mathrm{A}) - bG(\mathrm{B}) \tag{41.3}$$

in terms of free energies or, alternatively, we can discuss the reaction in terms of chemical potentials so that:

$$\Delta_\mathrm{r} G = d\mu(\mathrm{D}) + c\mu(\mathrm{C}) - a\mu(\mathrm{A}) - b\mu(\mathrm{B}) \tag{41.4}$$

Since one cannot talk about a Gibbs energy for a particular component of a mixture then equation (41.3) could, strictly speaking, only apply when the reactants and the products are individually separated, whereas equation (41.4) uses chemical potentials, which *can* be used for both a mixture and for an individual component. Equation (41.4) thus covers all cases.

Substituting equations of the form of equation (35.6) of Frame 35 for $\mu(\mathrm{A})$, $\mu(\mathrm{B})$, $\mu(\mathrm{C})$ and $\mu(\mathrm{D})$ we have:

$$\begin{aligned}\Delta_\mathrm{r} G = {}& d\left[\mu^o(\mathrm{D}) + RT\ln\left(\frac{p_\mathrm{D}}{P^o}\right)\right] + c\left[\mu^o(\mathrm{C}) + RT\ln\left(\frac{p_\mathrm{C}}{P^o}\right)\right]\\ & - a\left[\mu^o(\mathrm{A}) + RT\ln\left(\frac{p_\mathrm{A}}{P^o}\right)\right] - b\left[\mu^o(\mathrm{B}) + RT\ln\left(\frac{p_\mathrm{B}}{P^o}\right)\right] \quad P^o = \text{standard pressure}\end{aligned} \tag{41.5}$$

(See Note 41.1) collecting similar terms together we have:

$$\begin{aligned}\Delta_\mathrm{r} G = {}& [d\mu^o(\mathrm{D}) + c\mu^o(\mathrm{C}) - a\mu^o(\mathrm{A}) - b\mu^o(\mathrm{B})]\\ & + RT\left[d\ln\left(\frac{p_\mathrm{D}}{P^o}\right) + c\ln\left(\frac{p_\mathrm{C}}{P^o}\right) - a\ln\left(\frac{p_\mathrm{A}}{P^o}\right) - b\ln\left(\frac{p_\mathrm{B}}{P^o}\right)\right] \quad P^o = \text{standard pressure}\end{aligned} \tag{41.6}$$

where $p_{\mathrm{A},} p_{\mathrm{B},} p_\mathrm{C}$ and p_D are the partial pressures exerted by A, B, C and D during the reaction.

Since the difference in the chemical potentials of the products and reactants multiplied by the amount of each present will, under standard conditions (i.e. $P = P^o =$ standard pressure), be equal to $\Delta_\mathrm{r}\, G^o$ then equation (41.6) takes the form:

$$\begin{aligned}\Delta_\mathrm{r} G &= \Delta G^o + RT\left[d\ln\left(\frac{p_\mathrm{D}}{P^o}\right) + c\ln\left(\frac{p_\mathrm{C}}{P^o}\right) - a\ln\left(\frac{p_\mathrm{A}}{P^o}\right) - b\ln\left(\frac{p_\mathrm{B}}{P^o}\right)\right]\\ &= \Delta G^o + RT\ln\left[\left\{\left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d}\left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c}\right\}\Big/\left\{\left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a}\left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b}\right\}\right] \quad P^o = \text{standard pressure}\end{aligned} \tag{41.7}$$

using the fact that (Frame 6, equation (6.13):

$$n\ln \mathrm{x} = \ln(x^n) \tag{41.8}$$

Equation (41.7) can now be written:

$$\Delta_\mathrm{r} G = \Delta_\mathrm{r} G^o + RT\ln Q_{p/p^o} \tag{41.9}$$

where $Q_{p/po}$ defined by:

$$Q_{p/po} = \left[\left\{\left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d}\left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c}\right\}\Big/\left\{\left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a}\left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b}\right\}\right] \quad P^o = \text{standard pressure} \tag{41.10}$$

41.2 Thermodynamics of Reactions. Equilibrium Constant, K_p

Suppose now that *equilibrium* (which will correspond to $\Delta_\mathrm{r} G = 0$) is reached, under standard conditions, then $Q_{p/po}$ will then correspond to the equilibrium concentrations found ($= (Q_{p/po})_\mathrm{e} = K_{p/po}$), so that equation (41.10) would take the form:

$$0 = \Delta_\mathrm{r} G^o + RT\ln(Q_{p/po})_\mathrm{e} = \Delta_\mathrm{r} G^o + RT\ln K_{p/po} \quad P^o = \text{standard pressure} \tag{41.11}$$

or, rearranging:

$$\Delta G^o = -RT \ln K_{p/po} \quad P^o = \text{standard pressure} \tag{41.12}$$

where $K_{p/po}$ is the equilibrium constant (in terms of partial pressures – hence subscript p/p^o representing p/P^o in equation (41.13)) which is defined as:

$$K_{p/po} = (Q_{p/po})_\text{e} = \left[\left\{\left(\frac{p_\text{D}}{P^o}\right)_\text{e}^\text{d}\left(\frac{p_\text{C}}{P^o}\right)_\text{e}^\text{c}\right\} \Big/ \left\{\left(\frac{p_\text{A}}{P^o}\right)_\text{e}^\text{a}\left(\frac{p_\text{B}}{P^o}\right)_\text{e}^\text{b}\right\}\right] \quad P^o = \text{standard pressure} \tag{41.13}$$

where (p_A/P^o), (p_B/P^o), (p_C/P^o) and (p_D/P^o) are the partial pressures of the gases in reaction (41.1) (Frames 31 and 40) which are found at equilibrium (See Note 41.2).

Equation (41.12) is a key equation in thermodynamics, related to the van't Hoff Equation (Frames 46 and 47) considered later, which can be used to interpret the thermodynamics of reactions (see Frame 47, section 47.2). Once rearranged to equation (41.16) it enables us to take $\Delta_\text{f}G^o$ data direct from thermochemical tables for example and calculate K_p of the reaction (41.1) under the standard conditions. (i.e. $T = 298.15$ K and $P^o = 1$ bar). This can be done for reactions involving *any chemical species* for which standard data is available. Concentrations may well be employed in place of partial pressures.

A corollary of equation (41.12) is that $K_{p/po}$ for a reaction ΔG^o under standard pressure conditions defined by P^o can then be worked out. Rearranging equation (41.12) and then taking exponentials (Frame 6, section 6.17) we have:

$$\frac{-\Delta G^o}{RT} = \ln K_{p/po} \tag{41.14}$$

$$\exp[\ln K_{p/po}] = \exp\left[\frac{-\Delta G^o}{RT}\right] \tag{41.15}$$

or

$$K_{p/po} = \exp\left[\frac{-\Delta G^o}{RT}\right] \quad P^o = \text{standard pressure} \tag{41.16}$$

Equation (41.16) is another *key equation in thermodynamics, R* (gas constant) (= 8.314 J K^{-1} mol^{-1}). $K_{p/po}$ is a function of T.

41.3 Equilibrium Constants for Non-ideal gases

If we have a gas reaction:

$$\text{A(g)} = \text{B(g)} \tag{41.17}$$

in which real gases (Frame 31) are involved then, Frame 38, fugacities, f, replace partial pressures and $\Delta_r G$, is given by:

$$\Delta_r G = \Delta G^o + RT \ln\left[\left(\frac{f_\text{B}}{P^o}\right) \Big/ \left(\frac{f_\text{A}}{P^o}\right)\right] \quad P^o = \text{standard pressure} \tag{41.18}$$

and if $\Delta_r G = 0$ then:

$$\Delta G^o = -RT \ln\left[\left(\frac{f_\text{B}}{P^o}\right) \Big/ \left(\frac{f_\text{A}}{P^o}\right)\right] \quad P^o = \text{standard pressure} \tag{41.19}$$

or:

$$\Delta G^o = -RT \ln K_{f/po} \quad P^o = \text{standard pressure} \tag{41.20}$$

where $K_{f/po}$ is the equilibrium constant written in terms of the fugacities, f_A and f_B of the gases A and B respectively and which replace the partial pressure terms of $K_{p/po}$. $K_{f/po}$ is rarely encountered in everyday thermodynamics however.

In equation (41.19) since in the ratio $[(f_\text{B}/P^o)/(f_\text{A}/P^o)]$ the P^o terms cancel and we could write

$$\Delta G^o = -RT \ln\left(\frac{f_\text{B}}{f_\text{A}}\right) \tag{41.21}$$

However this is only the case because (see Appendix) in the case of reaction (41.17):

[*stoichiometric numbers of* reactant(s)] = [*stoichiometric numbers of moles of* product(s)] (41.22)

both – in this case – being = 1. For reactions in which equation (41.22) is true then the P^o terms will always cancel out. In cases where equation (41.22) does not hold however, $K_{f/po}$, once defined will depend on P^o terms also.

42. Chemical Equilibrium

42.1 Relationship between Equilibrium Constant, K_{p/p^o} and Gibbs Energy Change, ΔG^o

Key equation (41.10) in Frame 41:

$$\Delta G^o = -RT \ln K_{p/po} = -RT \ln K_p \tag{41.10}$$

relates ΔG^o to the value of $K_{p/po}$.

Table 42.1 shows the corresponding values of K and ΔG^o which can be easily worked out from equation (41.10).

Table 42.1 Corresponding values of K and ΔG^o/kJ mol^{-1} at $P^o = 1$ bar and $T = 298$ K

Equilibrium constant, $K_{p/po}$	**Standard free energy change, ΔG^o/kJ mol^{-1}. (at $p^o = 1$ bar and $T = 298$ K)**	**Equilibrium constant, $K_{p/po}$**	**Standard free energy change, ΔG^o/kJ mol^{-1}. (at $p^o = 1$ bar and $T = 298$ K)**
10^{-36}	148.4	$10^1 = 10$	– 5.7
•	•	$10^2 = 100$	– 11.4
•	•	10^3	– 17.1
10^{-6}	34.2	10^4	– 22.8
10^{-5}	28.5	10^5	– 28.5
10^{-4}	22.8	10^6	– 34.2
10^{-3}	17.1	•	•
$10^{-2} = 0.01$	11.4	•	•
$10^{-1} = 0.1$	5.7	10^{36}	– 148.4
$10^0 = 1$	0		

From the table we observe the following:

- Table 42.1 is independent of the standard states chosen (i.e. c^o, p^o, m^o etc.);
- $K = 10^{-36}$ or 10^{36} do not represent any kind of limit;
- At the *upper left end* of the table *K is very small in magnitude*;
- At the *upper left end* of the table the concentration of the *products is small* compared with the concentration of the reactants;
- At the *upper left end* of the table ΔG^o/kJ mol^{-1} is large and positive;
- At the *upper left end* of the table the equilibrium lies well over to the left-hand side;
- As we descend the table K increases by factors of 10;
- As we descend the table the equilibrium shifts such that the concentrations of the *products become larger and* the concentrations of the reactants *become smaller*;
- As we descend the table ΔG^o/kJ mol^{-1} decreases;
- At the *lower right end* of the table *K is very large in magnitude*;
- At the *lower right end* of the table the concentration of the *products is large* compared with the concentration of the reactants;
- At the *lower right end* of the table ΔG^o/kJ mol^{-1} is large and negative;
- At the lower right *end* of the table the equilibrium lies well over to the right-hand side of the reaction (products predominate);
- At the mid-point of the table, when $K = 1$, concentration of products equals concentration of reactants and ΔG^o/kJ mol^{-1} = 0;

In general: If $K > 1$ products dominate and reaction moves towards completion; If $K < 1$ reactants dominate and reaction tends not to occur

42.2 Reaction Criteria

If ΔG^o/kJ mol$^{-1} > 0$ this does not mean that the reaction cannot occur because

- it can be driven by providing an *external source of energy* e.g. by an electric current in a suitable cell.
- it can be *coupled to* another reaction (Frame 28);

Many industrial processes actually have ΔG^o/kJ mol^{-1} values which are positive. ΔG^o has the following attributes:

- an indicator of the value of the equilibrium constant;
- it represents the value of ΔG (see equation (41.9), Frame 41) when the reaction quotient, Q, is equal to 1;
- according to its sign it will govern how the reaction moves from there (i.e. $Q = 1$) towards equilibrium;
- it represents the value of ΔG for the reaction when the reactants and products are *separated* and are thus *individually* at pressure P^o (and–hypothetically–ideal). In this guise all that matters is the sign of ΔG^o as to whether the reaction will proceed to completion or not even start.

The more negative ΔG^o, the more likelihood there is that the reaction will occur of its own accord. However, reactions may be too slow (in the absence of a catalyst) despite having a large negative free energy change. For example:

$$H_2(g) + {}^1\!/_2O_2(g) \rightarrow H_2O(l) \tag{42.1}$$

has a free energy change of $\Delta G^o/\text{kJ mol}^{-1} = -238$ kJ mol^{-1} but it is kinetically too slow to occur at any appreciable rate.

Even a reaction for which $\Delta G^o/\text{kJ mol}^{-1} < 0$ may require warming to provide activation energy (and so start the kinetics).

42.3 The Effect on Equilibrium Constants of Changing the Stoichiometric Coefficients of a Reaction

Suppose that for a reaction:

$$\mathrm{aA + bB = cC + dD} \tag{42.2}$$

the equilibrium constant, $K_{c(42.2)}$ is given by:

$$K_{c/co(42.2)} = \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\}\Big/\left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\}; \quad c^o = \text{standard concnetration} \tag{42.3}$$

then for the reverse reaction:

$$\mathrm{cC + dD = aA + bB} \tag{42.4}$$

the equilibrium constant, $K_{c(42.4)}$ will be given by:

$$K_{c/co(42.4)} = \left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\}\Big/\left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\}; \quad c^o = \text{standard concnetration} \tag{42.5}$$

or

$$K_{c/co(42.2)} = 1/[K_{c/co(42.4)}] \tag{42.6}$$

If the stochiometric coefficients are changed in reaction (42.2) by a factor n, such that:

$$\mathrm{naA + nbB = ncC + ndD} \tag{42.7}$$

then the equilibrium constant, $K_{c/co(42.7)}$ is then given by:

$$\begin{aligned} K_{c/co(42.7)} &= \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{nc}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{nd}}\right\}\Big/\left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{na}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{nb}}\right\} \\ &= \left\{\left(\frac{[\mathrm{C}]}{c^o}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{c^o}\right)^{\mathrm{d}}\right\}^{\mathrm{n}}\Big/\left\{\left(\frac{[\mathrm{A}]}{c^o}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{c^o}\right)^{\mathrm{b}}\right\}^{\mathrm{n}}; \quad c^o = \text{standard concnetration} \end{aligned} \tag{42.8}$$

and therefore:

$$K_{c/co(42.7)} = [K_{c/co(42.2)}]^{\mathrm{n}} \tag{42.9}$$

Thus if we multiply a chemical equation such as equation (42.2) by a factor n, $\Delta G_{(42.2)}$ will be multiplied by n:

$$\Delta G_{(42.7)} = \mathrm{n}\Delta G_{(42.2)} \tag{42.10}$$

and equation (42.10) will apply.

If three reactions with equilibrium constants, K_1, K_2 and K_3 are summed to given an overall reaction, then the new equilibrium constant for the combined reaction, K_{combined} is given by:

$$K_{\text{combined}} = K_1.K_2.K_3 \tag{42.11}$$

42.4 Generality of Relationships

Relationships (42.6), (42.9) and (42.10) are general and apply for $K_{p/po}$, $K_{m/mo}$, $K_{f/po}$, K_x and not just for $K_{c/co}$.

43. *K* for a Multiphase Reaction

43.1 Writing Equilibrium Constant Expressions

Concentration expressions *are never included* in equilibrium constants for the following materials in the reactions being studied: pure solids; pure liquids; and solvents in dilute solutions.

A molecular pure solid contains a *fixed number of molecules within a given volume* and hence the molecular concentration within the solid is constant and does not vary. Provided there is always some solid present, the overall concentration (Frame 40) or activity (Frame 39) remains unchanged during reactions in which the solid is either reacted (and hence removed) or formed (and hence increased) or when further solid is added. A similar situation applies in the case of pure liquids.

Similarly, the concentration (activity) of solvents in dilute solutions is (virtually) unchanged during reactions and thus their concentration (activity) can be regarded as being constant. The *constant* concentrations of solids, liquids or solvents are therefore, effectively absorbed (i.e. are included) within the equilibrium *constant* itself.

Thus consider the reaction of the liquid drying agent thionyl chloride, $SOCl_2$ and liquid water it seeks to 'dry' (the two liquids are immiscible):

$$\mathrm{SOCl_2(l) + H_2O(l) \rightarrow SO_2(g) + 2HCl(g)} \tag{43.1}$$

We can write an equilibrium constant expression ($= K'_{p/po}$) as:

$$K'_{p/po} = \left(\frac{p_{SO2}}{P^o}\right)\cdot\left(\frac{p_{HCl}}{P^o}\right)^2 \Big/ (a_{SOCl2}).(a_{H2O}); \quad P^o = \text{standard pressure} \tag{43.2}$$

but the *true* equilibrium constant ($= K_{p/po}$) takes account of the constancy (Frame 39) of $a_{SOCl2} = 1$ and $a_{H2O} = 1$, in view of their immiscibilty by absorbing the constant terms and hence:

$$\begin{aligned} K_{p/po} = K'_{p/po}(a_{SOCl2}).(a_{H2O}) &= \left(\frac{p_{SO2}}{P^o}\right)\cdot\left(\frac{p_{HCl}}{P^o}\right)^2 \\ &= (p_{SO2}\cdot p_{HC^2})\cdot(P^o)^{-3}; \quad P^o = \text{standard pressure} \end{aligned} \tag{43.3}$$

and so since the activities of these pure liquids are equal to unity (section 39.1, Frame 39) then the equilibrium constant, $K_{p/po}$ involves inclusion of only the gaseous species involved in the reaction (43.1).

43.2 Multiphase Reactions and Equilibrium Constant, *K*

Consider a (specific) *multiphase* reaction:

$$\mathrm{MgCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Mg^{2+}(aq) + 2HCO_3^-(aq)} \tag{43.4}$$

Equilibrium constant, K is written in terms of activities (and partial pressure).

In view of the earlier discussion we need to explain why this is *not* written as: $K_{a/ao}$. The fact is that activity is a dimensionless quantity and so standard activity, a^o is not needed in an equilibrium constant expression (i.e. to divide out the *units* of activity, since there are none!) and so it is never defined. Thus insertion of activities (rather than activity ratios, a/a^o) leads to:

$$\begin{aligned} \Delta G &= \mu(\mathrm{Mg^{2+}, aq}) + 2\mu(\mathrm{HCO_3^-, aq}) - \mu(\mathrm{MgCO_3, s}) - \mu(\mathrm{H_2O, l}) - \mu(\mathrm{CO_2, g}) \\ &= [\mu^o(\mathrm{Mg^{2+}, aq}) + RT\ln\, a^{2+}_{Mg}] + 2[\mu^o(\mathrm{HCO_3^-, aq}) + RT\ln\, a^-_{\mathrm{HCO3}}] \\ &\quad - \mu^o(\mathrm{MgCO_3, s}) - [\mu^o(\mathrm{H_2O, l}) + RT\ln\, a_{\mathrm{H2O}}] - \Big[\mu^o(\mathrm{CO_2, g}) \\ &\quad + RT\ln\left(\frac{p_{CO2}}{P^o}\right)\Big]; \quad P^o = \text{standard pressure} \end{aligned} \tag{43.5}$$

then since:

$$\Delta G^o = [\mu^o(\mathrm{Mg^{2+}, aq}) + 2\mu^o(\mathrm{HCO_3^-, aq}) - \mu^o(\mathrm{MgCO_3, s}) - \mu^o(\mathrm{H_2O, l}) - \mu^o(\mathrm{CO_2, g})]; \quad P^o = \text{standard pressure} \tag{43.6}$$

where ΔG^o is the free energy change for reaction (43.4) when all the reactants and products are in their standard states (i.e. at unit activity for Mg^{2+}, HCO_3^- and H_2O and at standard pressure, P^o, in the case of the CO_2 gas) and hence:

$$\Delta G = \Delta G^o + RT \ln\ a^{2+}_{Mg} + 2RT\ \ln a^-_{\mathrm{HCO3}} - RT \ln\ a_{\mathrm{H2O}} - RT \ln\ \left(\frac{p_{CO2}}{P^o}\right)\Big]$$

$$= \Delta G^o + RT \ln \left[\frac{(a^{2+}_{Mg}).(a^-_{\mathrm{HCO3}})^2}{(a_{\mathrm{H2O}})} \Big/ \left(\frac{p_{CO2}}{P^o}\right)\right]; \quad P^o = \text{standard pressure} \qquad (43.7)$$

If the reaction (43.4) is at equilibrium and hence: $\Delta G = 0$ then:

$$\Delta G^o = -RT \ln\ K_a = -RT \ln \left[\frac{(a^{2+}_{Mg}).(a^-_{\mathrm{HCO3}})^2}{(a_{\mathrm{H2O}})} \Big/ \left(\frac{p_{CO2}}{P^o}\right)\right]; \quad P^o = \text{standard pressure} \qquad (43.8)$$

(See Note 43.1)

Further, since the activity of a pure liquid is equal to 1 (Frame 39, section 39.1) then: $a_{H2O} = 1$. The activity, a_i, of an ion, i, in aqueous solution can be defined as follows (Frame 39, equations (39.15 and 17)

$$a_\mathrm{i} = \gamma_\mathrm{c}(c_\mathrm{i}/c^o) = \gamma_\mathrm{m}\,(m_\mathrm{i}/m^o); \quad c^o = 1\,\mathrm{mol\,dm^{-3}}; \quad m^o = 1\,\mathrm{mol\,kg^{-1}} \qquad (43.9)$$

where the two activity coefficients, γ_c and γ_m are generally different (see Note 43.2); although both become zero for ideal dilute solutions. For aqueous solutions at common ambient temperatures they will be similar. We are using the fact that numerically, c and m are almost identical (see Note 43.2) (provided that $c^o = 1$ mol dm^{-3} and $m^o = 1$ mol kg^{-1}) for aqueous solutions at 298 K (although their units are different)(see Frame 40, section 40.5 and footnote below this frame) and when in dilute solution: $\gamma_\mathrm{i} = 1$ thus, using molalities, m^{2+}_{Mg} and m^-_{HCO3} (Frame 40, section 40.5), to express the ionic concentrations, a^{2+}_{Mg} and a^-_{HCO3}:

$$a_{\mathrm{Mg2+}} = \left(\frac{m^{2+}_{\mathrm{Mg}}}{m^o}\right); a^-_{HCO3} = \left(\frac{m^-_{\mathrm{HCO3}}}{m^o}\right) \qquad (43.10)$$

then:

$$\Delta G^o = -RT \ln K_{m/mo} = -RT \ln \left[\left(\frac{m^{2+}_{\mathrm{Mg}}}{m^o}\right)\cdot\left(\frac{m^-_{\mathrm{HCO3}}}{m^o}\right)^2 \Big/ \left(\frac{p_{CO2}}{P^o}\right)\right]$$

$$= -RT \ln \left[\frac{(m^{2+}_{\mathrm{Mg}})\cdot(m^-_{\mathrm{HCO3}})^2}{(p_{CO2})}\right]\cdot\left[\frac{P^o}{(m^o)^3}\right]$$

$$p^o = \text{standard pressure}; \ m^o = 1\,\mathrm{mol\,kg^{-1}} \qquad (43.11)$$

is the explicit form used for the standard Gibbs energy change of reaction (43.4). There are a number of points to note:

- the standard state m^o is explicitly defined in equation (43.11) as 1 mol kg^{-1} as a result of the transformations made in equations (43.10) where activities were transformed into molalities;
- the standard pressure can be chosen at will and depending on the choice made (i.e. $P^o = 1$ bar, 1 torr, 1 atm etc.) will influence the value of ΔG^o, which depends on the standard state chosen.

43.3 Interrelationships between K_x and $K_{p/po}$

For the reaction (41.1) considered in Frame 41:

$$\mathrm{aA(g) + bB(g) \rightarrow cC(g) + dD(g)} \qquad (41.1)$$

$K_{p/po}$, the equilibrium constant in terms of partial pressures, p_i of this can be written:

$$K_{p/po} = \left[\left\{\left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d}\left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c}\right\} \Big/ \left\{\left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a}\left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b}\right\}\right]; \quad P^o = \text{standard pressure} \qquad (43.12)$$

and since (Frame 31, equation (31.7)) using Dalton's Law of Partial Pressures:

$$p_\mathrm{i} = x_\mathrm{i}P \qquad (31.17)$$

then, dividing by P^o we have:

$$\left(\frac{p_\mathrm{i}}{P^o}\right) = x_\mathrm{i}\cdot\left(\frac{P}{P^o}\right) \qquad (43.13)$$

and hence:

$$K_{p/po} = \left[\left\{\left(\frac{x_D P}{P^o}\right)^{\mathrm{d}}\left(\frac{x_{\mathrm{C}} P}{P^o}\right)^{\mathrm{c}}\right\} \Big/ \left\{\left(\frac{x_{\mathrm{A}} P}{P^o}\right)^{\mathrm{a}}\left(\frac{x_{\mathrm{B}} P}{P^o}\right)^{\mathrm{b}}\right\}\right]$$

$$= \left[\frac{\{(x_{\mathrm{D}})^{\mathrm{d}}(x_{\mathrm{C}})^{\mathrm{c}}\}}{\{(x_{\mathrm{A}})^{\mathrm{a}}(x_{\mathrm{B}})^{\mathrm{b}}\}}\right]\left(\frac{P}{P^o}\right)^{(\mathrm{d+c-a-b})} \qquad P^o = \text{standard pressure} \tag{43.14}$$

The power (d + c − a − b) is defined by:

$$(\mathrm{d} + \mathrm{c}) - (\mathrm{a} + \mathrm{b}) = [\text{amount of gaseous products}] - [\text{amount of gaseous reactants}] \tag{43.15}$$

and if we define the equilibrium constant to be written in terms of mole fractions as, K_x at a specific total pressure, P as:

$$K_x = \left[\frac{\{(x_{\mathrm{D}})^{\mathrm{d}}(x_{\mathrm{C}})^{\mathrm{c}}\}}{\{(x_{\mathrm{A}})^{\mathrm{a}}(x_{\mathrm{B}})^{\mathrm{b}}\}}\right] \tag{43.16}$$

then:

$$K_{p/po} = K_x.\left(\frac{P}{P^o}\right)^{(\mathrm{d+c-a-b})} \qquad P^o = \text{standard pressure} \tag{43.17}$$

Hence:

$$K_x = K_{p/po}.\left(\frac{P}{P^o}\right)^{-(\mathrm{d+c-a-b})} = K_{p/po}.\left(\frac{P}{P^o}\right)^{(\mathrm{a+b-c-d})} \qquad P^o = \text{ standard pressure} \tag{43.18}$$

We also see from equation (43.17):

- that since $K_{p/po} = f(T)$, then $K_x = f(T, P)$ is a function of temperature, T and pressure, P.
- if for a given reaction: (a + b) = (c + d) (i.e. the number of molecules of gaseous reactants = number of molecules of gaseous products) then: $K_x = K_{p/po}$ (= K_p, see Appendix) since (d + c − a − b) = 0.

43.4 Varying Expressions for Equilibrium Constants

Suppose that we have a gaseous reaction:

$$\mathrm{X_2(g)} \rightarrow \mathrm{2X(g)} \tag{43.19}$$

and we wish to determine at what value the equilibrium constant, K, will correspond to the system containing equal numbers of X atoms and X_2 molecules.

Equal numbers of atoms and molecules is the same thing as having equal chemical amounts (Frame 1) of atoms and molecules, so that we are looking for the condition where the mole fractions of X and X_2 are equal, i.e.:

$$x_{\mathrm{X2}} = x_{\mathrm{X}} \tag{43.20}$$

and since the total mole fractions of the components of a system total 1 (Frame 40, equation (40.10)) then the above condition can be written:

$$x_{\mathrm{X2}} = x_{\mathrm{X}} = 0.5 \tag{43.21}$$

Writing the equilibrium constant firstly in terms of activities, we have:

$$K_a = \frac{\{a_{\mathrm{X}}\}^2}{a_{\mathrm{X2}}} \tag{43.22}$$

If we now assume the gases behave ideally (i.e. their fugacity coefficients, ϕ_{X} and ϕ_{X2} are equal to 1, and hence (Frame 38, equation (38.9)):

$$a_{\mathrm{i}} = f_{\mathrm{i}} = p_{\mathrm{i}} \tag{43.23}$$

so that (Appendix A):

$$K_a = K_{p/po} = \frac{\{p_{\mathrm{X}}/(\mathrm{bar})\}^2}{\{p_{\mathrm{X2}}/(\mathrm{bar})\}} = \left[\frac{\{p_{\mathrm{X}}\}^2}{\{p_{\mathrm{X2}}\}}\right] \Big/ (\mathrm{bar}) \tag{43.24}$$

Using Dalton's Law of Partial Pressures (Frame 31, section 31.2, equation (31.7)) we can also write:

$$p_i = x_i.P \tag{43.25}$$

where P is the total gas pressure, so that:

$$p_{\mathrm{X}} = x_{\mathrm{X}}.P;\ p_{\mathrm{X2}} = x_{\mathrm{X2}}.P \tag{43.26}$$

and hence:

$$\begin{aligned} K_{p/po} &= \frac{\{p_{\mathrm{X}}/(\mathrm{bar})\}^2}{\{p_{\mathrm{X2}}/(\mathrm{bar})\}} = \left[\frac{\{x_{\mathrm{X}}.P\}^2}{\{x_{\mathrm{X2}}.P\}}\right] \Big/ (\mathrm{bar}) \\ &= \frac{[\{0.5.P\}^2/\{0.5.P\}]}{(\mathrm{bar})} = \frac{0.5.P}{(\mathrm{bar})} \end{aligned} \tag{43.27}$$

where if total gas pressure $P = 1$ bar, then $K_{p/po} = 0.5$. If the temperature at which this condition is reached is determined then ΔG^o can be found.

44. Reactions *Not* at Equilibrium. Concentration – Concentration Plots to Represent Simple Equilibria Effect on Equilibria of Changing Concentrations

44.1 Reactions Not at Equilibrium

For the reaction (41.1), first considered in Frame 41:

$$aA(g) + bB(g) = cC(g) + dD(g) \tag{41.1}$$

If the reaction (41.1) is at a stage where it is not yet at equilibrium, then (equation (41.9)):

$$\begin{aligned}\Delta G &= \Delta G^o + RT \ln Q_{p/po} \\ &= -RT \ln K_{p/po} + RT \ln Q_{p/po} \\ &= -RT \ln \left(\frac{K_{p/po}}{Q_{p/po}}\right)\end{aligned} \tag{44.1}$$

ΔG^o is the free energy difference between products and reactants (each in their standard states at pressure, P^o and 298.15 K). This equation does not refer to the actual reaction (41.2) (Frame 41) *at equilibrium* (except where $K_{p/po} = 1$ and $\Delta G^o = 0$). ΔG refers to the difference in Gibbs energy between products and reactants at other concentrations/pressures not corresponding to equilibrium.

When $\Delta G = 0$ the reaction is then at equilibrium and the concentrations (or partial pressures) of reactants and products are then those that appear in the equilibrium constant expression.

From equation (44.1) we see that:

- If $Q_{p/po} < K_{p/po}$ then $\frac{K_{p/po}}{Q_{p/po}} > 1$ and $\ln\left(\frac{K_{p/po}}{Q_{p/po}}\right) > 0$ (positive) and so $\Delta G < 0$ and reaction (41.1) proceeds towards the formation of more C and D (i.e. products)
- If $Q_{p/po} > K_{p/po}$ then $\frac{K_{p/po}}{Q_{p/po}} < 1$ and $\ln\left(\frac{K_{p/po}}{Q_{p/po}}\right) < 0$ (negative) and so $\Delta G > 0$ and reaction (41.1) proceeds towards the formation of more A and B (i.e. original reactants)
- If $Q_{p/po} = K_{p/po}$ then $\frac{K_{p/po}}{Q_{p/po}} = 1$ and $\ln\left(\frac{K_{p/po}}{Q_{p/po}}\right) = 0 =$ and so $\Delta G = 0$ and reaction (41.1) is at equilibrium.

44.2 Concentration – Concentration Plots for Simple Reactions

In Frames 23 and 24 we introduced phase diagrams which comprised of a series of lines on a pressure, P, temperature, T, grid, which related to the conditions in which either solid was in equilibrium with liquid, liquid in equilibrium with gas or solid in equilibrium with gas. At any point with coordinates (T, P) which was situated on these lines, the two relevant phases then co-existed at equilibrium.

In the case of simple equilibria we can draw similarly informative concentration versus concentration diagrams. Consider a simple reaction:

$$A(g) \rightarrow B(g) \tag{44.2}$$

which might correspond to a simple isomerisation (rearrangement of the atoms within a molecule A to form a different molecule B). A more specific example might be the rearrangement of a straight-chain gaseous hydrocarbon into a branched-chain isomer.

Although the reaction represented here is a gas reaction we do not need to use partial pressures, p_i, to represent the equilibrium constant, $(= K)$ we can equally well use gaseous concentrations, c_i (see for example: Frame 40, equation (40.6)).

We note that $K_{p/po}$ and $K_{c/co}$ can be interconverted using an equation analogous to equation (43.17), Frame 43 and relationship (40.6), Frame 40 (see equation (45.27), Frame 45):

$$K_{p/po} = K_{c/co}.(RT)^{(c + d - a - b)} \tag{44.3}$$

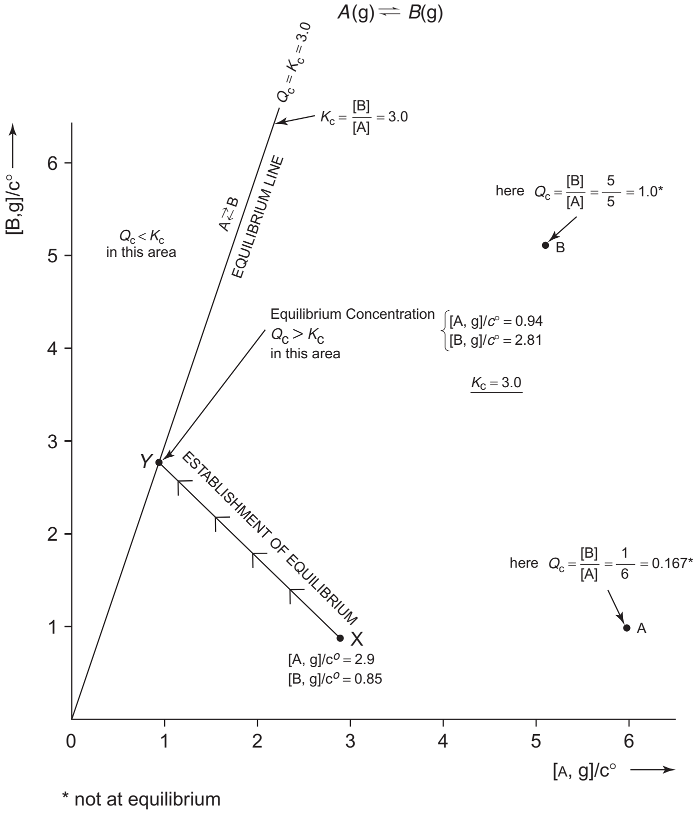


Figure 44.1 Plot of concentration [B, g]/c^o versus [A, g]/c^o for the reaction for which $K_{c/co} = 3.0$.

In reaction (41.1), Frame 41 the power index: (c + d − a − b) represents the *difference* between the amounts of products and the amounts of reactants for a gaseous reaction (equation (43.15) Frame 43). The change in the number of gas molecules in reaction (44.2), (= Δn) is equal to zero. This therefore corresponds to a value of (c + d − a − b) = 0

$$K_{p/po} = K_{c/co}.\left(\frac{P}{P^o}\right)^{(\text{c + d − a − b})} = K_{c/co}.\left(\frac{P}{P^o}\right)^{(\Delta n)} = K_{c/co}.\left(\frac{P}{P^o}\right)^{0} = K_{c/co} \tag{44.4}$$

Hence $K_{p/po}$ and $K_{c/co}$ are identical, in the case of reaction (44.2).

Suppose now that we define, $K_{c/co}$, an equilibrium constant for the isomerisation, in terms of concentration to be:

$$K_{c/co} = \frac{([\text{B, g}]_e)}{([\text{A, g}]_e)} \tag{44.5}$$

where $[\text{A, g}]_e$ and $[\text{B, g}]_e$ are the concentrations of A(g) and B(g) at equilibrium. We also define a reaction quotient, $Q_{c/co}$ in which [A, g] and [B, g] are the concentrations of A(g) and B(g), although not necessarily at equilibrium.

$$Q_{c/co} = \frac{([\text{B, g}])}{([\text{A, g}])} \tag{44.6}$$

At equilibrium (= e) we have:

$$[\text{A, g}]_e = [\text{A, g}] \tag{44.7}$$

and

$$[\text{B, g}]_e = [\text{B, g}] \tag{44.8}$$

and

$$K_{c/co} = Q_{c/co} \tag{44.9}$$

For the purposes of illustration of the concentration–concentration plot let us suppose that the equilibrium constant (= $K_{c/co}$) for this isomerisation reaction (44.2) was equal to 3.0. Figure 44.1 shows a plot of the concentration ratio of B(g)/c^o(= [B, g]/c^o) versus the concentration of A(g)/c^o (= [A, g]/c^o) and has the following features:

- The line:

$$Q_{c/co} = K_{c/co} = 3.0 \tag{44.10}$$

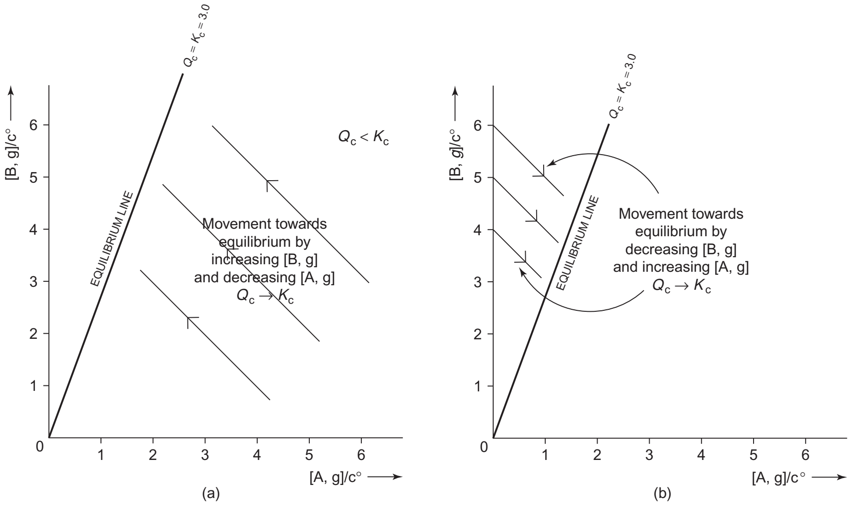


Figure 44.2 Direction of change of reaction quotients, $Q_{c/co}$, necessary to establish equilibrium for the reaction: A(g) → B(g) when $K_{c/co} = 3.0$. (a) for the case when $Q_{c/co} > K_{c/co}$ and (b) for the case when $Q_{c/co} < K_{c/co}$.
Note that Figure 44.2 refers to the two halves of Figure 44.1

(the *equilibrium line*) represents the equilibrium position for the reactant (A) and product (B) under the particular (constant) temperature, T, at which K_c was measured. Thus, any point with coordinates ($[A, g]/c^o$, $[B, g]/c^o$) sited on the line represents an equilibrium situation corresponding to the numbers (= concentration ratios) indicated on the axes.

- In the area to the *right* of the equilibrium line in Figure 44.1 then:

$$Q_{c/co} > K_{c/co} \tag{44.11}$$

and pairs of concentration ratios, $[A, g]/c^o$ and $[B, g]/c^o$ *anywhere in this area do not* represent equilibrium conditions (example points where A(g) and B(g) are not in equilibrium are A and B);

- In the area to the *left* of the equilibrium line in Figure 44.1 then:

$$Q_{c/co} < K_{c/co} \tag{44.12}$$

and pairs of concentrations [A, g] and [B, g] *anywhere in this area do not* represent equilibrium conditions.

We consider below what adjustments in concentration need to be made in order that non-equilibrium concentrations approach, and then become, equilibrium concentrations, driven by the need to minimise ΔG or the change in chemical potentials (Frame 5, 27, 28, 29, 35, 37, 38 and 39).

In the reaction (44.2) if x moles of A(g) isomerise, where x can be fractional (i.e. $x < 1$), then x moles of A(g) are lost and, at the same time, x moles of B(g) are then consequently formed. This means that – because in Figure 44.1 the scales for $[A, g]/c^o$ and $[B, g]/c^o$ are drawn to be identical and because the stoichiometry of the reaction is 1:1 – consequently, any changes in concentration (brought about by interconversion of A into B or B into A) must be such as to proceed *along* or parallel to the *lines drawn at 45^o to the axes of the graph*. (e.g. parallel to or along line XY).

This means that we can use the graphs to predict the shifts in concentration that will occur as the system adjusts itself to equilibrium. Thus if one starts at a particular point (say X) which corresponds to a non-equilibrium concentration ratio of $A(g)/c^o$ and $B(g)/c^o$ then by drawing a line at 45° to the axes (assuming the scale divisions on both axes are identical) from the point until the line intersects the equilibrium line (i.e. $Q_{c/co} = K_{c/co} = 3.0$) (at point Y) then the *coordinates of the intersection point,* Y, will correspond to the final concentration ratios of $A(g)/c^o$ and $B(g)/c^o$ to be found once equilibrium has been established.

Figure 44.2(a) and (b) illustrate this procedure for (a) the region where $Q_{c/co} > K_{c/co}$ and (b) where $Q_{c/co} < K_{c/co}$ respectively.

44.3 Specific Example

Finally, we illustrate the procedure using a definite example: suppose that the starting concentration ratios were: $[A, g]/c^o = 2.90$ and $[B, g]/c^o = 0.85$. This is equivalent, if the standard concentration, c^o was taken to be 1 mol dm^{-3}, to the situation where the concentration of $[A, g] = 2.90$ mol dm^{-3} and that for $[B, g] = 0.85$ mol dm^{-3}.

This mixture is not at equilibrium since $Q_{c/co} \neq K_{c/co}$ (= 3.0) because:

$$Q_{c/co} = \frac{\{[B, g]/c^o\}}{\{[A, g]/c^o\}} = \frac{[B, g]}{[A, g]} = \frac{0.85}{2.90} = 0.29; \quad c^o = 1\,\text{mol dm}^{-3} \tag{44.13}$$

and:

$$Q_{c/co} \ll K_{c/co}(= 3.0) \tag{44.14}$$

and is represented on the right-hand side of Figure 44.1 by the point **X** (2.90, 0.85). If we now construct a line from point X such that for a shift in [A, g] concentration we have the same shift in [B, g] concentration then the stoichiometry demanded by the reaction A(g) = B(g) is satisfied and we move towards the equilibrium line until we intersect it at point **Y** (0.94, 2.81) at which point:

$$Q_{c/co} = \frac{[\mathrm{B, g}]}{[\mathrm{A, g}]} = \frac{2.81}{0.94} = 3.0 = K_{c/co} \quad c^o = 1\,\mathrm{mol\,dm^{-3}} \tag{44.15}$$

and the equilibrium condition has now been established, A and B are now at equilibrium at these concentrations.

45. Equilibrium Calculations for Reactions *Not* Initially at Equilibrium

45.1 Equivalent Calculations to those made in Frame 44, section 44.3, in place of the graphical approach

In the case of the simple equilibrium considered in Frame 44, section 44.3, we can perform *calculations* as an alternative to drawing concentration versus concentration diagrams. Consider the same simple reaction:

$$\mathrm{A(g)} \rightarrow \mathrm{B(g)} \tag{44.2}$$

Suppose (as in section 44.3, Frame 44) initially the starting (non-equilibrium) concentrations are:

$$\begin{array}{ll} \mathrm{A(g)} \rightarrow & \mathrm{B(g)} \\ 2.90 & 0.85\ \mathrm{mol\ dm^{-3}} \end{array} \tag{45.1}$$

so that:

$$Q_{c/co} = \left\{\frac{[\mathrm{B,g}]}{c^o}\right\} \Big/ \left\{\frac{[\mathrm{A,g}]}{c^o}\right\} = \frac{[\mathrm{B,g}]}{[\mathrm{A,g}]} = \frac{0.85}{2.90} = 0.29 \tag{45.2}$$

and here c^o cancels out. Also we see from equation (45.2) that:

$$Q_{c/co} \ll K_{c/co} = 3.0 \tag{45.3}$$

$Q_{c/co}$ needs to be *increased* to attain the value $K_{c/co}$ $Q_{c/co}$ can be increased by increasing concentration of B(g) and therefore decreasing the concentration of A(g) so that equilibrium must be brought about by conversion of some A(g) to B(g).

Assume that $c^o = 1$ mol dm^{-3} and that these concentrations adjust themselves such that [A, g] is reduced by x mol dm^{-3} and (stoichiometry) then [B, g] will be increased by x mol dm^{-3}. Thus:

$$\begin{array}{ll} \mathrm{A(g)} \rightarrow & \mathrm{B(g)} \\ (2.90 - x) & (0.85 + x)\ \mathrm{mol\ dm^{-3}} \end{array} \tag{45.4}$$

so that following this change:

$$Q_{c/co} = \left\{\frac{[\mathrm{B,g}]}{c^o}\right\} \Big/ \left\{\frac{[\mathrm{A,g}]}{c^o}\right\} = \frac{[\mathrm{B,g}]}{[\mathrm{A,g}]} = \frac{(0.85 + x)}{(2.90 - x)} \tag{45.5}$$

and equilibrium will be reached once:

$$Q_{c/co} = K_{c/co} = 3.0 \tag{45.6}$$

So that substituting in equation (45.6) for $Q_{c/co}$ from equation (45.5) and solving for x will tell us just how much A(g) we need to convert to B(g) in order to achieve equilibrium. This exercise leads to the equation:

$$Q_{c/co} = \frac{(0.85 + x)}{(2.90 - x)} = 3.0 \tag{45.7}$$

where upon:

$$(0.85 + x) = 3.0(2.90 - x) \tag{45.8}$$

$$0.85 + x = 8.70 - 3x \tag{45.9}$$

$$4x = 7.85 \tag{45.10}$$

$$x = \frac{7.85}{4} = 1.96 \tag{45.11}$$

Equilibrium concentrations can be calculated by substitution into the expressions below reaction (45.4), thus:

$$[\mathrm{A,g}] = (2.90 - x) = (2.90 - 1.96)\,\mathrm{mol\,dm^{-3}} = 0.94\,\mathrm{mol\,dm^{-3}} \tag{45.12}$$

$$[\mathrm{B,g}] = (0.85 + x) = (0.85 + 1.96)\,\mathrm{mol\,dm^{-3}} = 2.81\,\mathrm{mol\,dm^{-3}} \tag{45.13}$$

and hence, imposing a check on the result, we have:

$$K_{c/co} = Q_{c/co} = \frac{[\mathrm{B,g}]}{[\mathrm{A,g}]} = \frac{2.81}{0.94} = 3.00 \tag{45.14}$$

so that the reaction is now at equilibrium.

This solution also corresponds to the concentration ratios corresponding to point Y in Figure 43.1 of the graphical approach to this problem.

45.2 Calculation of Equilibrium Constant, *K* knowing Initial and Final Reactant (and therefore Product) Concentrations

Suppose we have a reaction with a stochiometry:

$$2\text{A(g)} \rightarrow 2\text{B(g)} + \text{C(g)} \tag{45.15}$$

where A, B and C can represent *molecular* species and we know that:

- initially x moles of A(g) are placed in a 1 dm^3 (litre) flask (i.e. $[\text{A, g}] = x \text{ mol dm}^{-3}$);
- At equilibrium there are y moles of B(g) formed during the reaction in the 1 dm^3 (litre) flask (i.e. $[\text{B, g}] = y \text{ mol dm}^{-3}$);
- since we have adopted units of mol dm^{-3} to represent our concentrations the standard concentration $c^o = 1 \text{ mol dm}^{-3}$.

We can represent the progression of the reaction by the varying concentrations shown below:

$$2\text{A(g)} \rightarrow 2\text{B(g)} + \text{C(g)} \tag{45.16}$$

$$\begin{array}{lcccl} \text{initially at time zero (t = 0 s)} & x & 0 & 0 & \text{mol dm}^{-3} \\ \text{at equilibrium} & (x-y) & y & {}^{1}\!/_{2}y & \text{mol dm}^{-3} \end{array}$$

The concentrations are determined as follows:

- we know from the equation (45.16) that half as many moles of C(g) (i.e. $^{1}\!/_{2}y$ moles) than B(g) must be formed;
- during the reaction the amount of A(g) will have reduced from x to $(x - y)$ of A(g).

Now the equilibrium constant $K_{c/co}$ for this reaction can be written:

$$K_{c/co} = \left\{\left(\frac{[\text{B, g}]}{c^o}\right)^2\left(\frac{[\text{C, g}]}{c^o}\right)\right\} \Big/ \left\{\left(\frac{[\text{A, g}]}{c^o}\right)^2\right\} = \frac{\{[\text{B, g}]^2[\text{C, g}]\}}{\{[\text{A, g}]\}^2}\cdot\left\{\frac{(c^o)^2}{(c^o)^2(c^o)}\right\} = \frac{\{[\text{B, g}]^2[\text{C, g}]\}}{\{[\text{A, g}]\}^2}\cdot\left\{\frac{1}{(c^o)}\right\}$$
$$c^o = 1 \text{ mol dm}^{-3} \tag{45.17}$$

and thus:

$$\begin{aligned} K_{c/co} &= \frac{\{(y)^2(^{1}\!/_{2}y)\}}{\{(x-y)^2\}}\cdot\{1/(c^o)\} \\ &= \frac{(y)^3}{\{2(x-y)^2\cdot c^o\}} \\ c^o &= 1 \text{ mol dm}^{-3} \end{aligned} \tag{45.18}$$

If, on the other hand, alternatively (and equivalently) for the identical reaction (45.15), we assumed that:

- initially an amount x of A(g) are placed in a 1 dm^3 (litre) flask (i.e. $[\text{A, g}] = x \text{ mol dm}^{-3}$);
- once equilibrium has been attained there is an amount z of C(g) present in the 1 dm^3 (litre) flask (i.e. $[\text{C, g}] = z \text{ mol dm}^{-3}$);
- c^o, the standard concentration was again equal to 1 mol dm^{-3}, then we can represent the progression of the reaction concentrations as follows:

$$2\text{A(g)} \rightarrow 2\text{B(g)} + \text{C(g)} \tag{45.19}$$

$$\begin{array}{lcccl} \text{initially at time zero(t = 0s)} & x & 0 & 0 & \text{mol dm}^{-3} \\ \text{at equilibrium} & (x-2z) & 2z & z & \text{mol dm}^{-3} \end{array}$$

The concentrations are determined as follows:

- we know from the equation (45.15) that twice as much B(g) is formed than C(g), so that the amount of C(g) is $2z$;
- during the reaction the amount of A(g) will have reduced from x to $(x - 2z)$ of A(g).

Now another version of the equilibrium constant $K_{c/c}$ for reaction (45.15) can be written as:

$$K_{c^0} = \frac{\{[\mathrm{B, g}]^2 \cdot [\mathrm{C, g}]\}}{\{[\mathrm{A, g}]^2\}} \cdot \left\{\frac{1}{c^o}\right\} \quad c^o = \text{standard concentration} \tag{45.20}$$

and thus:

$$\begin{aligned} K_c &= \frac{\{(2z)^2(z)\}}{\{(x-2z)^2\}} \cdot \left\{\frac{1}{c^o}\right\} \\ &= \frac{4z^3}{(x-2z)^2} \cdot \left\{\frac{1}{c^o}\right\} \quad c^o = \text{standard concentration} \end{aligned} \tag{45.21}$$

If we now equate the two individual concentrations assumed for B(g) in the two models, (45.16) and (45.19), assumed above

$$\frac{[\mathrm{B, g}]}{c^o} = 2z = y \tag{45.22}$$

then equilibrium constants in equations (45.18) and (45.21) are identical.

In general, for a reaction:

$$\mathrm{aA(g) + bB(g) \rightarrow cC(g) + dD(g)} \tag{45.23}$$

$$K_{p/po} = \left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c} \cdot \left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d} \Big/ \left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a} \cdot \left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b}; \quad P^o = \text{standard pressure} \tag{45.24}$$

and

$$K_{c/co} = \left(\frac{[\mathrm{C}]}{c^o}\right)^\mathrm{c} \cdot \left(\frac{[\mathrm{D}]}{c^o}\right)^\mathrm{d} \Big/ \left(\frac{[\mathrm{A}]}{c^o}\right)^\mathrm{a} \cdot \left(\frac{[\mathrm{B}]}{c^o}\right)^\mathrm{b}; \quad c^o = \text{standard concentration} \tag{45.25}$$

and from equation (40.7) Frame 40 we see that since:

$$\left(\frac{p_i}{P^o}\right) \cdot \left(\frac{c_i}{c^o}\right) = RT \quad P^o = \text{standard pressure; } c^o = \text{standard concentration} \tag{45.26}$$

then, dividing equation (45.24) by (45.25):

$$\begin{aligned} K_{p/po}/K_{c/co} &= \left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c} \cdot \left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d} \Big/ \left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a} \cdot \left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b} \Big/ \left[\left(\frac{[\mathrm{C}]}{c^o}\right)^\mathrm{c} \cdot \left(\frac{[\mathrm{D}]}{c^o}\right)^\mathrm{d} \Big/ \left(\frac{[\mathrm{A}]}{c^o}\right)^\mathrm{a} \cdot \left(\frac{[\mathrm{B}]}{c^o}\right)^\mathrm{b}\right] \\ &= \left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c} \cdot \left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d} \cdot \left(\frac{[\mathrm{C}]}{c^o}\right)^\mathrm{c} \cdot \left(\frac{[\mathrm{D}]}{c^o}\right)^\mathrm{d} \Big/ \left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a} \cdot \left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b} \cdot \left(\frac{[\mathrm{A}]}{c^o}\right)^\mathrm{a} \cdot \left(\frac{[\mathrm{B}]}{c^o}\right)^\mathrm{b} \\ &= \left(\frac{p_\mathrm{C}}{P^o}\right)^\mathrm{c} \cdot \left(\frac{[\mathrm{C}]}{c^o}\right)^\mathrm{c} \left(\frac{p_\mathrm{D}}{P^o}\right)^\mathrm{d} \cdot \left(\frac{[\mathrm{D}]}{c^o}\right)^\mathrm{d} \Big/ \left(\frac{p_\mathrm{A}}{P^o}\right)^\mathrm{a} \cdot \left(\frac{[\mathrm{A}]}{c^o}\right)^\mathrm{a} \cdot \left(\frac{p_\mathrm{B}}{P^o}\right)^\mathrm{b} \cdot \left(\frac{[\mathrm{B}]}{c^o}\right)^\mathrm{b} \\ &= (RT)^{\mathrm{c+d-a-b}} = (RT)^{\Delta n} \end{aligned} \tag{45.27}$$

where $\Delta n = \mathrm{c + d - a - b}$ where Δn represents the change in the number of molecules of *gas* in going from reactants to products, for the reaction (45.15):

$$\Delta n = (\textit{number of molecules of products}) - (\textit{number of molecules of reactants}) = (3-2) = 1 \tag{45.28}$$

and hence:

$$K_{p/po} = K_{c/co} \tag{45.29}$$

45.3 Calculation of Equilibrium Constant, *K* for Dissociation Reactions. Extent or Degree of Dissociation, α

Reactions is which a diatomic gaseous molecule, X_2(g) dissociates into two X(g) molecules can be expressed in the form:

$$X_2(g) \rightarrow 2X(g) \tag{45.30}$$

where:

$$K_{c/co} = \frac{([\mathrm{X, g}]/c^o)^2}{([\mathrm{X_2, g}]/c^o)} \quad c^o = \text{standard concentration} \tag{45.31}$$

and it is frequently the case that the 'degree of dissociation' of X_2(g), $(=\alpha)$ is referred to. Usually α is expressed as a percentage. Suppose that we start with x moles of X_2(g) contained in a 1 dm^3 (= 1 litre) flask and we know the degree of dissociation, α at a particular temperature, T/K is α %. We can now proceed with the calculation of the equilibrium constant for the reaction, K_c (which also equals K_p, by virtue of equation (45.28) since Δn is 1) at this temperature, T.

At the start (time $t = 0$) we have x moles of X_2(g) present [X, g] $= x$ mol dm^{-3} and no X(g) molecules ([X, g] = 0 mol dm^{-3}).

Once the temperature is raised to T/K, then α % of the X_2(g) molecules are converted into X(g) molecules *and there are two X molecules produced for every X_2 molecule dissociated also.* Thus $(x\alpha/100) = 0.01x\alpha$ molecules of X_2 are converted to produce: $2(x\alpha/100) = 0.02x\alpha$, X molecules. The concentration of X_2 therefore falls from the original concentration [X_2, g] $= x$ mol dm^{-3}

to $[\mathrm{X}_2, \mathrm{g}] = (x - 0.01x\alpha)\,\mathrm{mol\,dm^{-3}}$ whilst at the same time the concentration of X(g) has risen from zero at the start of the dissociation reaction to the value:

$$[\mathrm{X, g}] = 0.02x\alpha\,\mathrm{mol\,dm^{-3}} \tag{45.32}$$

Substituting the equilibrium concentrations of $[\mathrm{X}_2, \mathrm{g}]$ and [X, g] into the equilibrium constant expression (45.31) we have:

$$\begin{aligned} K_{c/co} &= \left\{ \left(\frac{[\mathrm{X, g}]}{c^o}\right)^2 \Big/ \left(\frac{[\mathrm{X}_2, \mathrm{g}]}{c^o}\right) \right. \\ &= \left(\frac{0.02x\alpha}{c^o}\right)^2 \Big/ \left(\frac{x - 0.01x\alpha}{c^o}\right) = 4 \times 10^{-4} \frac{(\alpha^2 x/c^o)}{(1 - 0.01\alpha)} \quad c^o = 1\,\mathrm{mol\,dm^{-3}} \end{aligned} \tag{45.33}$$

so that if for example the degree of dissociation, α was known to be 1% (so that: $\alpha = 1$) then:

$$\begin{aligned} K_{c/co} &= 4 \times 10^{-4} \left(\frac{\alpha^2 x}{c^o}\right) \Big/ (1 - 0.01\alpha) \\ &= 4 \times 10^{-4} \frac{(x/c^o)}{(0.99)} = 4.04 \times 10^{-4} \left(\frac{x}{c^o}\right) \quad c^o = 1\,\mathrm{mol\,dm^{-3}} \end{aligned} \tag{45.34}$$

and if the initial concentration of X_2 was 2 mol dm^{-3} (so that $x = 2$ mol dm^{-3}), then:

$$K_{c/co} = K_{p/po} = 4.04 \times 10^{-4} \left(\frac{x}{\mathrm{mol\,dm^{-3}}}\right) = 4.04 \times 10^{-4}(2) = 8.08 \times 10^{-4} \tag{45.35}$$

for the dissociation reaction represented by this data.

46. Gibbs–Helmholtz Equation Variation of Equilibrium Constant, $K_{p/po}$, With Temperature, T Van't Hoff Equation

46.1 The Gibbs–Helmholtz Equation

Using two basic equations (18.1) and (18.14) encountered earlier in Frame 18:

- $G = H - TS \qquad (46.1)$
- $\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad (46.2)$

these can be combined, by substituting the expression for – S in equation (46.2) into equation (46.1) to give:

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_{P,n} \tag{46.3}$$

If we divide equation (46.3) on both sides by T^2 it becomes:

$$\frac{G}{T^2} = \frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{P,n} \tag{46.4}$$

Rearranging the G/T^2 and H/T^2 terms onto opposite sides we have:

$$\left[\frac{-G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{P,n}\right] = \frac{-H}{T^2} \tag{46.5}$$

Consider now the differential coefficient of G/T with respect to temperature T at constant pressure, P. G/T if considered as a quotient can be differentiated according to the Quotient Rule (Frame 3, Table 3.1) so that:

$$\left(\partial\left[\frac{G}{T}\right]\Big/\partial T\right)_{P,n} = \left[T\left(\frac{\partial G}{\partial T}\right)_{P,n} - G\left(\frac{\partial T}{\partial T}\right)_{P,n}\right]\Big/T^2 \tag{46.6}$$

and since $(\partial T/\partial T)_{P,n} = 1$ (Frame 3, section 3.5) then:

$$\left(\partial\left[\frac{G}{T}\right]\Big/\partial T\right)_{P,n} = \left[T\left(\frac{\partial G}{\partial T}\right)_{P,n} - G\right]\Big/T^2 = \left[\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{P,n} - \frac{G}{T^2}\right] \tag{46.7}$$

where we have taken $1/T^2$ inside the square bracket and we see that the right-hand side of equation (46.7) is identical (except for the actual *order* of the terms) to the left-hand side of equation (46.5) and hence:

$$\left(\partial\left[\frac{G}{T}\right]\Big/\partial T\right)_{P,n} = -\frac{H}{T^2} \tag{46.8}$$

or, where *changes* in Gibbs energy and enthalpy are involved then:

$$\left(\partial\left[\frac{\Delta G}{T}\right]\Big/\partial T\right)_{P,n} = \frac{-\Delta H}{T^2} \tag{46.9}$$

this is the *Gibbs–Helmholtz Equation.*

46.2 Variation of the Natural Logarithm of the Equilibrium Constant, K, with Temperature, T. The van't Hoff Equation

Whilst a calculation of $(\partial K_{p/po}/\partial T)_P$ would show us directly how the equilibrium constant, $K_{p/po}$ of a reaction was directly affected by changes in temperature, T, and how the equilibrium shifts, it actually proves much more convenient to derive an expression for the variation of the natural *logarithm of the equilibrium constant*, ln $K_{p/po}$ of a reaction with temperature, T, in the form of the derivative: $(\partial \ln K_{p/po}/\partial T)_P$.This arises because we have already established the equation (41.12) (Frame 41):

$$\Delta G^o = -RT \ln K_{p/po} \tag{41.12}$$

which rearranges (dividing through by – RT) to give:

$$\ln K_{p/po} = \frac{-\Delta G^o}{RT} \tag{46.10}$$

and this form is then easily differentiated (Frame 3) with respect to temperature, T,on both sides:

- the left-hand side leads immediately to: $(\partial \ln K_{p/po}/\partial T)_{P,n}$
- the right-hand side (after taking the constant term – $1/R$ outside the bracket) is equivalent to: $(\partial/\partial T[\Delta G/T])_P$ or $(\partial[\Delta G/T]/\partial T)_P$ which is evaluated using the Gibbs–Helmholtz equation (46.9) as – $\Delta H/T^2$.

so that:

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_{P,n} = -\left(\frac{1}{R}\right)\cdot\left(\partial\left[\frac{\Delta G^o}{T}\right]\Big/\partial T\right)_{P,n} = -\left(\frac{1}{R}\right)\cdot\left\{\frac{-\Delta H^o}{T^2}\right\} = \frac{\Delta H^o}{RT^2} \tag{46.11}$$

This last equation (46.11):

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_{P,n} = \frac{\Delta H^o}{RT^2} \tag{46.12}$$

gives us the details of how ln $K_{p/po}$ varies with T when the pressure, P is held constant and is referred to as the *van't Hoff Isochore* (which is a misnomer – see Note 46.1) or the *van't Hoff Equation* (see Note 46.2).

Since logarithms to base 10 (as in $\log_{10} K_{p/po}$) are sometimes quoted we give the alternative (old fashioned) form of the equation:

$$\left(\frac{\partial \log_{10} K_{p/po}}{\partial T}\right)_P = \frac{\Delta H^o}{(2.303RT^2)} \tag{46.13}$$

46.3 Integrated form of van't Hoff Equation

The van't Hoff Equation gives the rate at which (the logarithm of) K_p changes with temperature. The integrated form of this equation enables us to calculate *specific values* of the equilibrium constant, K_p at various temperatures (and enables the determination of the enthalpy change of the equilibrium reaction, ΔH^o*, assuming that this does not vary greatly with temperature* over the temperature range considered).

Collecting the terms involving temperature, T, on the right-hand side of equation (46.12) we have:

$$\mathrm{d}(\ln K_{p/po}) = \frac{\Delta H^o}{RT^2}.\mathrm{d}T \tag{46.14}$$

Here we have modified partial differentials to become ordinary differentials since we are about to integrate. Continuing to use the natural logarithmic form, we now integrate both sides of the equation, thus:

$$\int \mathrm{d}(\ln K_{p/po}) = \int \frac{\Delta H^o}{RT^2}.\mathrm{d}T = \left(\frac{\Delta H^o}{R}\right).\int T^{-2}.\mathrm{d}T \tag{46.15}$$

R, is the gas constant and ΔH^o is assumed here not to vary with temperature and therefore both terms can then be taken outside the integral (see Note 46.3).

Choosing integration limits, in order to perform definite integration, when the temperature is equal to T_2 we assume that $K_{p/po}$ is equal to $K_{p/po2}$ and when the temperature is equal to T_1 we assume that $K_{p/po}$ is equal to $K_{p/po1}$ and these are used as the limits for integration. Thus:

$$\int_{K_{p/po1}}^{K_{p/po2}} \mathrm{d}(\ln K_{p/po}) = \left(\frac{\Delta H^o}{R}\right).\int_{T_1}^{T_2} T^{-2}.\mathrm{d}T \tag{46.16}$$

and we note that the left-hand side is the integral of a differential (and thus one negates the other) giving us simply ln $K_{p/po}$, whilst the right-hand side is a standard integral (Frame 2) form of T^{-2}, hence:

$$[\ln K_{p/po}]_{K_{p/po1}}^{K_{p/po2}} = \left(\frac{\Delta H^o}{R}\right).\int_{T_1}^{T_2} T^{-2}.\mathrm{d}T = \left(\frac{\Delta H^o}{R}\right).\left[\frac{-1}{T}\right]_{T_1}^{T_2} \tag{46.17}$$

so that:

$$[\ln K_{p/po2} - \ln K_{p/po1}] = \left(\frac{\Delta H^o}{R}\right).\left[-\frac{1}{T_2} - \left(\frac{-1}{T_1}\right)\right] \tag{46.18}$$

which can be written as:

$$\ln\left(\frac{K_{p/po2}}{K_{p/po1}}\right) = -\left(\frac{\Delta H^o}{R}\right).\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{46.19}$$

Thus if we know ΔH^o and the equilibrium constant at one temperature (say $K_{p/po1}$ at temperature T_1) then the equilibrium constant *at any other temperature* (for which the equation (46.19) is valid) can be determined.

46.4 Measurement of the Equilibrium Constant, $K_{p/po}$ at Various Temperatures, T

If we combine equations (46.10) and (46.1) we can write:

$$\ln K_{p/po} = \frac{-\Delta G^o}{RT} = \frac{-[\Delta H^o - T\Delta S^o]}{RT} \tag{46.20}$$

and hence that:

$$\ln K_{p/po} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{46.21}$$

From equation (46.21) it is clear that if we measure $K_{p/po}$ for the reaction over a range of varying temperature, T then plot ln $K_{p/po}$ versus the reciprocal of temperature, $1/T$, we should generate a linear graph (Frame 3) whose form is: $y = mx + c$ and (Figure 46.1) whose gradient can be equated to $-(\Delta H^o/R)$ and whose intercept is equal to $\Delta S^o/R$. From such a graph both ΔH^o and ΔS^o for the reaction can be determined.

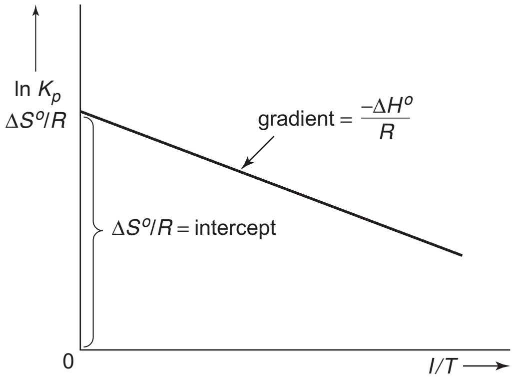


Figure 46.1 Plot of ln $K_{p/po}$ versus $1/T$ (in units of K^{-1}) has gradient of $-(\Delta H^o/R)$ where $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

46.5 Equilibrium Constants in terms of activities, K_a or molalities, $K_{m/mo}$

ΔG^o can also, of course, be defined in terms of K_a, the equilibrium constant written in terms of activities, a. [Note: This symbol should not be confused with that for the acid ionisation constant, also K_a]. In this present case the standard state defined for ΔG^o is that associated with unit activities ($a = 1$) rather than with unit pressure ($P^o = 1$ bar), or in the case where gases are involved, with unit fugacities ($f = 1$). We can then write that:

$$\Delta G^o = -RT\ln K_a \tag{46.22}$$

The equation:

$$\Delta G^o (= \Delta H^o - T\Delta S^o) = -RT\ln K_a \tag{46.23}$$

is called the *van’t Hoff Isotherm*.

It now follows that:

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} \tag{46.24}$$

Since there is a relationship (Frame 39, equation (39.17)) between activities, a_i, activity coefficients, γ_i and molalities, m_i:

$$a_\mathrm{i} = \gamma_\mathrm{i} \cdot \left(\frac{m_\mathrm{i}}{m^o}\right) \tag{46.25}$$

then also:

$$K_a = K_\gamma \cdot K_{m/mo} \tag{46.26}$$

where K_γ is the appropriate quotient of activity coefficients and $K_{m/mo}$ that of molalities. In dilute solution, $\gamma \to 1$ so that:

$$K_\gamma \to 1 \tag{46.27}$$

and hence in dilute solution then:

$$K_a \to K_{m/mo} \tag{46.28}$$

47. Qualitative Interpretation of Van't Hoff Equation. Coupled Reaction

47.1 Simple Model Relating to van't Hoff Equation

$K_{p/po}$ is a measure of the equilibrium composition of a reaction and as was seen in the previous Frame 46:

$$\ln K_{p/po} = \frac{-\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} = \frac{-\Delta G^{o}}{RT} \qquad (46.20)$$

The logarithm of the equilibrium constant, ln K_p depends upon the *difference* of an entropy term, and an enthalpy term which becomes relatively less important as temperature, T is increased.

The additional equality on the right-hand side of equation (46.20) above is added by virtue of equation (46.10), Frame 46 and is used below to provide a neat analysis of the thermodynamics of coupled reactions first discussed in Frame 28.

We can interpret this equation in a qualitatively useful way in order to illustrate the principles:

- Suppose we have a large closed tiered box (Figure 47.1(a)) into which are placed some light plastic balls (Figure 47.1(b)).

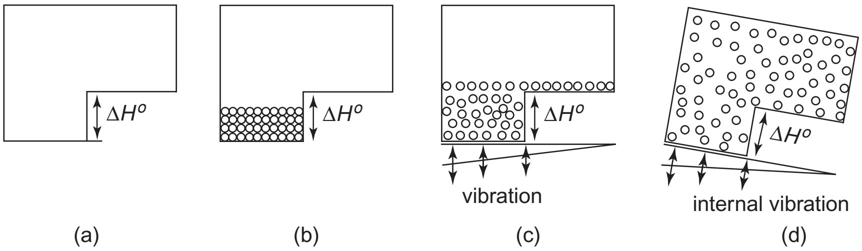


Figure 47.1 Box analogy.

- These balls will initially come to rest in the lowest region of the box (Figure 47.1(b)).
- Next suppose that the box is vibrated gently, oscillations will inevitably cause some of the balls to overcome the enthalpy step and locate themselves into the upper section of the box (Figure 47.1(c)).
- As the vibrations become more violent we will reach a stage where the balls show no preference for occupation of front (higher) or back (lower) sections and there are almost equal concentrations of balls in the two halves (Figure 47.1(d)).
- The above model might be taken as an analogy for a simple reaction A = B for which the left-hand side of the box represents A and the right-hand side of the box, B.

Interpretation:

- the difference in height of the floor of the box can be likened to the enthalpy change, ΔH^o of the process of interest.
- the increasing extent of the vibration is analogous to the effect of increasing temperature T during the process.
- we can represent the equilibrium constant, $K_{p/po}$ by the ratio:

$$K_{p/p^o} = [\text{number of balls in higher section}]/[\text{number of balls in lower section}] \qquad (47.1)$$

- at little or no vibration (corresponding to low temperature, T small) (Figure 47.1(b)), then:

$$[\text{number of balls in higher section}] \to 0 \qquad (47.2)$$

$$[\text{number of balls in lower section}] \to \text{maximum} \qquad (47.3)$$

so that:

$$K_{p/p^o} \to 0 \quad \text{when } T \to 0 \qquad (47.4)$$

- the 'tendency' for a system to become more random is analogous to a corresponding increase in entropy, ΔS^o.
- for the balls to execute a more random motion and occupy the whole volume, this will be proportional to log {[total volume of box available to the balls]/[volume of higher section]}
- the above term represents the entropy term, ΔS^o.

- as T and the vibration increase, the original barrier ΔH^o increasingly becomes less effective in preventing the equal spread of balls also becoming smaller relative to the ΔS^o term and therefore of less importance.
- ΔH^o, assumed to be positive means that at temperature $T = 0\,\mathrm{K}$, we will have all A.
- ΔS^o, also positive means that at temperature $T = \infty\,\mathrm{K}$ then $[\mathrm{B}]/[\mathrm{A}] = \exp(\Delta S^o/R)$ and if the balls are then uniformly distributed, the volume ratio of the two box sections will be equal to this value.

47.2 Thermodynamics of Coupled Reactions Revisited

In an earlier frame (Frame 28) we considered the 'coupling' of the two reactions (28.1) and (28.2):

- reaction (28.1) where solid, liquid and gas phases are present

$$\mathrm{AB_2(s)} + 2\,\mathrm{C_2(g)} \overset{\Delta G_{28.1}>0}{\rightarrow} \mathrm{AC_4(l)} + \mathrm{B_2(g)} \tag{28.1}$$

and

- reaction (28.2) where solid and gaseous phases are present

$$\mathrm{D(s)} + \mathrm{B_2(g)} \overset{\Delta G_{28.2}\ll 0}{\rightarrow} \mathrm{DB_2(g)} \tag{28.2}$$

Reaction (28.1) was a thermodynamically unfavourable reaction, i.e. $\Delta G_{28.1} > 0$, which could be driven towards completion by a second (reaction where $\Delta G_{28.2} \ll 0$ and hence $\Delta G_{28.2} \ll \Delta G_{28.1}$. The second reaction (28.2):

- *consumes* any *unwanted product(s)* in the unfavourable reaction (28.1) (i.e. $\mathrm{B_2(g)}$), so leaving the product $\mathrm{AC_4(l)}$;

then this second reaction can 'drive' the first towards completion, since the combined reaction:

$$\mathrm{AB_2(s)} + 2\,\mathrm{C_2(g)} + \mathrm{D(s)} \overset{\Delta G_{28.3}}{\rightarrow} \mathrm{AC_4(l)} + \mathrm{DB_2(g)} \tag{28.3}$$

has a ΔG value ($= \Delta G_{28.3}$) such that:

$$\Delta G_{28.3} < 0 \tag{47.5}$$

We can write expressions for the equilibrium constants, (see Frame 43, section 43.1), $K_{p/po(28.1)}$ and $K_{p/po(28.2)}$:

$$\begin{aligned} K_{p/po(28.1)} &= \left[\left(\frac{p_{\mathrm{B2}}}{P^{\mathrm{o}}}\right).(a_{\mathrm{AC4}})\right] \Big/ \left[\left(\frac{p_{\mathrm{C2}}}{P^{\mathrm{o}}}\right)^2.(a_{\mathrm{AB2}})\right] \\ &= \left[\left(\frac{p_{\mathrm{B2}}}{P^{\mathrm{o}}}\right)\right] \Big/ \left[\left(\frac{p_{\mathrm{C2}}}{P^{\mathrm{o}}}\right)^2\right] = \left\{\frac{(p_{\mathrm{B2}})}{(p_{\mathrm{C2}})^2}\right\} \cdot P^{\mathrm{o}} \quad P^{\mathrm{o}} = \text{standard pressure} \end{aligned} \tag{47.6}$$

where p_{B2} and p_{C2} are the partial pressures of the gases, $\mathrm{B_2}$ and $\mathrm{C_2}$ and a_{AC4} and a_{AB2} are the activities of the pure liquid $\mathrm{AC_4}$ and the pure solid $\mathrm{AB_2}$ and P^{o} is the standard pressure. Both activities (Frame 39, section 39.1) are equal to unity: $a_{\mathrm{AC4}} = 1$; and $a_{\mathrm{AB2}} = 1$. Also:

$$\begin{aligned} K_{p/po(28.2)} &= \left[\left(\frac{p_{\mathrm{DB2}}}{P^{\mathrm{o}}}\right)\right] \Big/ \left[\left(\frac{p_{\mathrm{B2}}}{P^{\mathrm{o}}}\right).(a_{\mathrm{D}})\right] = \left[\left(\frac{p_{\mathrm{DB2}}}{P^{\mathrm{o}}}\right)\right] \Big/ \left[\left(\frac{p_{\mathrm{B2}}}{P^{\mathrm{o}}}\right)\right] \\ &= \left\{\frac{(p_{\mathrm{DB2}})}{(p_{\mathrm{B2}})}\right\} \quad P^{\mathrm{o}} = \text{standard pressure} \end{aligned} \tag{47.7}$$

where p_{DB2} and p_{B2} are the partial pressures of the gases, $\mathrm{DB_2}$ and $\mathrm{B_2}$ and a_{D} is the activity of the pure solid D and P^{o} is the standard pressure. $a_{\mathrm{D}} = 1$, hence equation (47.7).

By taking exponentials of both sides of equation (46.10) frame 46:

$$K_{p/po} = \exp\left[\frac{-\Delta G^{\mathrm{o}}}{RT}\right] \tag{47.8}$$

and thus if we analyse the case of reaction (28.1) we have:

$$K_{p/po(28.1)} = \left\{\frac{(p_{\mathrm{B2}})}{(p_{\mathrm{C2}})^2}\right\} \cdot P^{\mathrm{o}} = \exp\left[\frac{-\Delta G^{\mathrm{o}}_{(28.1)}}{RT}\right] \tag{47.9}$$

or in rearranged form:

$$\frac{(p_{\mathrm{B2}})}{(p_{\mathrm{C2}})^2} = \left(\frac{1}{P^{\mathrm{o}}}\right) \cdot \exp\left[\frac{-\Delta G^{\mathrm{o}}_{(28.1)}}{RT}\right] \tag{47.10}$$

where $\Delta G^{\mathrm{o}}_{(28.1)} > 0$, this means then that the argument $[-\,\Delta G^{\mathrm{o}}_{(28.1)}/\mathrm{RT}]$ of the exponential term is therefore less than 0 and thus:

$$\exp\left[\frac{-\Delta G^{\mathrm{o}}_{(28.1)}}{RT}\right] \ll 1 \tag{47.11}$$

and therefore:

$$(1/P^{o}) \cdot \exp\left[\frac{-\Delta G^{o}_{(28.1)}}{RT}\right] \ll 1 \tag{47.12}$$

and hence that:

$$\frac{(p_{B2})}{(p_{C2})^{2}} \ll 1 \tag{47.13}$$

or that:

$$p_{B2} \ll (p_{C2})^{2} \tag{47.14}$$

or that in the reaction (28.1) there is very little $B_2(g)$ present and the equilibrium is predominantly on the left-hand side.

Alternatively, we can take the *limiting case* where $\Delta G^{o}_{(28.1)} = 0$, this means that the argument $[-\Delta G^{o}_{(28.1)}/RT]$ of the exponential term is therefore equal to 0 and since: $e^{o} = \exp(0) = 1$ then, from equation (47.10):

$$\frac{(p_{B2})}{(p_{C2})^{2}} = \frac{1}{P^{o}} \tag{47.15}$$

Now since (Dalton's Law of Partial Pressures, Frames 31 and 34):

$$p_{B2} + p_{C2} = P^{o} \tag{47.16}$$

where P^{o} is the total pressure of the gas mixture, then:

$$p_{B2} = P^{o} - p_{C2} \tag{47.17}$$

and substituting into equation (47.15) we have:

$$\frac{(p_{B2})}{(p_{C2})^{2}} = \frac{(P^{o} - p_{C2})}{(p_{C2})^{2}} = \frac{1}{P^{o}} \tag{47.18}$$

Cross-multiplying the last equality in equation (47.18) leads to:

$$P^{o}(P^{o} - p_{C2}) = (p_{C2})^{2} \tag{47.19}$$

and so:

$$(p_{C2})^{2} + P^{o} \cdot p_{C2} - (P^{o})^{2} = 0 \tag{47.20}$$

and thus equation (6.31), Frame 6:

$$\begin{aligned} p_{C2} &= {}^{1}\!/_{2}\{-P^{o} \pm [(P^{o})^{2} + 4(P^{o})^{2}]^{1/2}\} \\ &= {}^{1}\!/_{2}\{-P^{o} \pm [5(P^{o})^{2}]^{1/2}\} = {}^{1}\!/_{2}\{\sqrt{5} - 1\} \cdot P^{o} = 0.618 \cdot P \end{aligned} \tag{47.21}$$

which means that if $\Delta G^{o}_{(28.1)} > 0$ then the partial pressure of C_2, p_{C2},would be even greater than in the (limiting) case where $\Delta G^{o}_{(28.1)} = 0$ when it is already (from equation (47.21)) a substantial fraction (nearly $^{2}/_{3}$ of the total pressure, P^{o}).
If now we examine the case of reactions (28.1) and (28.2), as a pair we have:

- $K_{p/po(28.2)} = \left[\left(\frac{p_{DB2}}{P^{o}}\right)\right] \Big/ \left[\left(\frac{p_{B2}}{P^{o}}\right).(a_D)\right] = \left[\left(\frac{p_{DB2}}{P^{o}}\right)\right] \Big/ \left[\left(\frac{p_{B2}}{P^{o}}\right)\right] = \frac{p_{DB2}}{p_{B2}}$

  P^{o} = standard pressure (47.22)

  or

  $$\frac{p_{DB2}}{p_{B2}} = \exp\left[\frac{-\Delta G^{o}_{(28.2)}}{RT}\right] \tag{47.23}$$

  for the sum of reactions (28.1) and (28.2) (i.e. reaction (28.3)) for which:

  $$\Delta G^{o}_{(28.3)} = \Delta G^{o}_{(28.1)} + \Delta G^{o}_{(28.2)} \tag{47.24}$$

  and

  $$\begin{aligned} K_{p/po(28.3)} &= \left[\left(\frac{p_{DB2}}{P^{o}}\right) \cdot a_{AC4}\right] \Big/ \left[\left(\frac{p_{C2}}{P^{o}}\right)^{2} \cdot (a_D) \cdot (a_{AB2})\right] \\ &= \left[\left(\frac{p_{DB2}}{P^{o}}\right)\right] \Big/ \left[\left(\frac{p_{C2}}{P^{o}}\right)^{2}\right] = \left\{\frac{p_{DB2}}{(p_{C2})^{2}}\right\} \cdot P^{o} \end{aligned}$$

  P^{o} = standard pressure (47.25)

  so that:

  $$\begin{aligned} \left\{\frac{p_{DB2}}{(p_{C2})^{2}}\right\} &= \left(\frac{1}{P^{o}}\right) \cdot \exp\left[\frac{-\Delta G^{o}_{(28.3)}}{RT}\right] \\ &= \left(\frac{1}{P^{o}}\right) \cdot \exp\left[\frac{-\{\Delta G^{o}_{(28.1)} + \Delta G^{o}_{(28.2)}\}}{RT}\right] \end{aligned} \tag{47.26}$$

Also (Dalton's Law of Partial Pressures, Frames 31 and 34):

$$p_{B2} + p_{C2} + p_{DB2} = P^{o} \tag{47.27}$$

Equation (47.26) shows that if $\Delta G^{o}_{(28.2)} \ll 0$ (see section 28.1, Frame 28) then:

- $p_{DB2} \gg p_{B2}$; $p_{DB2} \gg p_{C2}$;
- ensuring that $p_{C2} \approx 0$ and hence that the overall reaction (28.3) is driven towards completion.

The outcomes studied in this section reach identical conclusions to those made in Frame 28.

48. Variation of Equilibrium Constant, *K*, With Overall Total Pressure, *P*

So far we have seen how to assess, within reaction, the effect on the Equilibrium Constant, K, of: (1) changing concentrations of reagents (2) by addition and removal of reagents (3) changing the overall temperature.

We now consider the effect of overall changes in pressure, P on the value of K and hence the position of the equilibrium.

48.1 Variation of the Equilibrium Constant, *K*, with Pressure, *P*

If we take exponentials on both sides of equation (46.1) of Frame 46 we have:

$$\exp(\ln K_{p/po}) = \exp\left(\frac{-\Delta G^o}{RT}\right) \tag{48.1}$$

taking an exponential followed by a natural logarithm negate each other (Frame 6, equation (6.11)):

$$K_{p/po} = \exp\left(\frac{-\Delta G^o}{RT}\right) \tag{48.2}$$

$K_{p/po}$ at any given T, is linked to ΔG^o (Frame 46) and once the standard state is established ($P^o = 1$ bar; $T = 298.15$ K) individual G^o values are then independent of the overall pressure. Hence ΔG^o is *independent* of pressure, P and so is $K_{p/po}$. This means that:

$$\left(\frac{\partial \ln K_{p/po}}{\partial P}\right)_T = 0 \tag{48.3}$$

To consider the effect of change of pressure, P on reaction (see Note 48.1) we need to consider further the example provided in Frame 45, section 45.3 where for the dissociation reaction:

$$X_2(g) \rightarrow 2X(g) \tag{45.24}$$

The equilibrium constant, $K_{p/po}$, written in terms of the partial pressures of $X_2(= p_{X2})$ and $X(= p_X)$ takes the form:

$$K_{p/po} = \left(\frac{p_X}{P^o}\right)^2 \Big/ \left(\frac{p_{X2}}{P^o}\right) = \left(\frac{(p_X)^2}{p_{X2} \cdot P^o}\right) \tag{48.4}$$

Using Dalton's Law of Partial Pressures, p_i (Frames 31 and 34):

$$p_i = x_i . P \tag{48.5}$$

and the same parameters: x and α as in section 45.3, Frame 45. The standard pressure ($= P^o$) being defined as 1 bar. We can write p_{X2} and p_X in terms of mole fractions (x_{X2} and x_X). At equilibrium the concentrations of X_2 and X present are:

$$\underset{(x-0.01\alpha x)}{X_2(g)} \rightarrow \underset{0.02\alpha x \text{ mol dm}^{-3}}{2X(g)} \tag{45.24}$$

then the total amount of gas present in the flask equals:

$$\textit{Total amount of } X_2(g) \textit{ and } X(g) \textit{ present per dm}^3 = (x - 0.01\alpha x) + 0.02\alpha x = (x + 0.01\alpha x) \text{ moles} \tag{48.6}$$

so that the mole fractions present at equilibrium are:

$$x_{X2} = \frac{(x - 0.01\alpha x)}{(x + 0.01\alpha x)} = \frac{(1 - 0.01\alpha)}{(1 + 0.01\alpha)} \tag{48.7}$$

and:

$$x_X = \frac{0.02\alpha x}{(x + 0.01\alpha x)} = \frac{0.02\alpha}{(1 + 0.01\alpha)} \tag{48.8}$$

so that:

$$p_{X2} = x_{X2} \cdot P = \frac{(1 - 0.01\alpha) \cdot P}{(1 + 0.01\alpha)} \tag{48.9}$$

and:

$$p_X = x_X \cdot P = \frac{0.02\alpha \cdot P}{(1 + 0.01\alpha)} \tag{48.10}$$

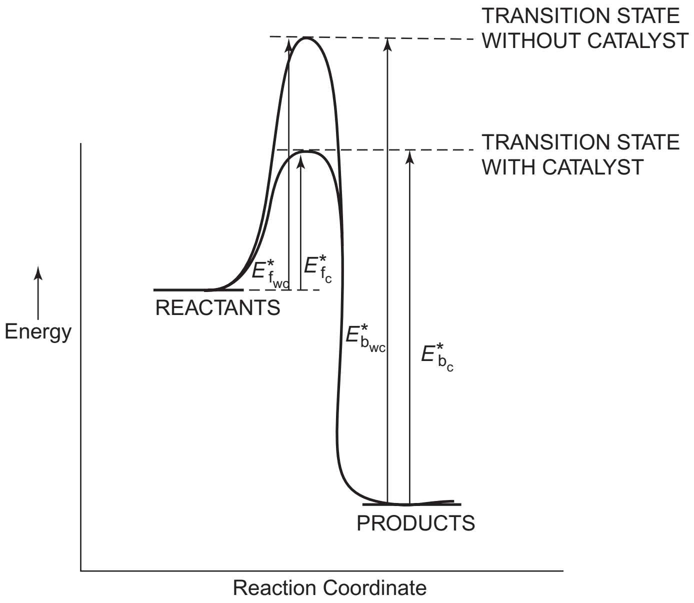


Figure 48.1 Activation energies in the presence and absence of a catalyst. ΔE, the overall energy change (related to ΔG^o) in going from reactants to products is unaffected by the catalyst addition which speeds up the reaction by lowering the activation barrier to the forward and backward routes. The equilibrium position and the thermodynamics are unaffected.

so that:

$$\begin{aligned}
K_{p/po} &= (p_{\mathrm{X}})^2/(p_{\mathrm{X2}}\cdot P^o) = \left[\frac{0.02\alpha\cdot P}{(1+0.01\alpha)}\right]^2 \Big/ \left[\frac{(1-0.01\alpha)\cdot P}{(1+0.01\alpha)}\right]\cdot P^o \\
&= [0.02\alpha]^2\cdot\frac{P}{[(1+0.01\alpha)(1-0.01\alpha)]}\cdot P^o = [0.02\alpha]^2\cdot\frac{P}{[(1-\{0.01\alpha\}^2)]}\cdot P^o \\
&= 0.0004\alpha^2\cdot\frac{P}{[(1-\{0.0001\alpha^2\}]}\cdot P^o \quad P^o = 1\,\mathrm{bar} \qquad (48.11)
\end{aligned}$$

In equation (48.11) the term: $\{0.0001\alpha^2\}$ is very small when compared to 1 so that it can be neglected:

$K_{p/po}$ is proportional to $\alpha^2\cdot(P/P^o)$

$K_{p/po}$ is independent of the total pressure, P, as we reasoned above so therefore:

- if P increases then α must *simultaneously* reduce to keep the term $\alpha^2\cdot(P/P^o)$ constant and independent of change in P;
- if P decreases then α must *simultaneously* increase to keep the term $\alpha^2\cdot(P/P^o)$ constant and independent of change in P.

Since α^2. (P/P^o) must remain constant then α changes very approximately in proportion to the inverse square root of the pressure (i.e. α is proportional to $1/\sqrt{(P/P^o)}$ for this to be the case). Discussion continues in Frame 49.

48.2 Effect of Addition of a Catalyst on the Position of Equilibrium as Measured by the Equilibrium Constant, *K*

Addition of catalysts does not affect the position of equilibrium (and therefore the value of the equilibrium constant, K) only the *rate at which equilibrium is approached.* All a catalyst does is:

- to change the kinetic mechanism or route taken by the reaction;
- lower the activation energy, E^* of both the forward ($= E^*_{\mathrm{f}}$) and backward ($= E^*_{\mathrm{b}}$) reaction (Figure 48.1).

ΔG^o (related to ΔE) does not change and neither, of course, does K_{p/p^o} and so the equilibrium concentrations of the reactants and products in a reaction are totally unchanged by the addition of a catalyst.

49. Le Chatelier's Principle

49.1 Qualitative Interpretation of the Reaction Quotient, *Q* and the Equilibrium Constant, *K*

An equilibrium constant, K, and the reaction quotient, Q (Frames 40, 44 and 45), can both usefully be thought of *qualitatively* in terms of the following representation:

$$K = \prod \textit{(Product concentrations)}^{\mathrm{i}} / \prod \textit{(Reactant concentrations)}^{\mathrm{j}} \tag{49.1}$$

where $\prod$ signifies that mathematical products are taken of the specified concentrations, products or reactants, raised to the appropriate (stoichiometrically related) powers (i and j).

In a reaction proceeding in the *forward* direction, reactant concentrations will be falling at the same time that the product concentrations are rising, hence Q, the reaction quotient, will be *increasing* until it reaches a value $= K$ when the reaction will be at equilibrium. Conversely, in a reaction proceeding in the *backward* direction, reactant concentrations will be rising at the same time that the product concentrations are falling, and hence Q, the reaction quotient, will be *decreasing* until it again reaches the appropriate value of K, when the reaction will be at equilibrium and will then cease, under the current conditions of temperature and pressure.

49.2 Le Chatelier's Principle

Using the equilibrium constant and v'ant Hoff equations (Frames 46 and 47) it is possible to determine *quantitatively* the effect of pressure and temperature on the position of equilibrium taken up by a reversible reaction (see Section 49.4, this frame). Similar conclusions can be reached *qualitatively* using the principle of "mobile equilibrium" originally developed independently by Le Chatelier and by Braun, but now referred to simply as Le Chatelier's principle.

Le Chatelier proposed a principle that is useful in predicting *qualitatively* the likely effect that a '*constraint*' placed on a reaction, at equilibrium, will have on the concentrations of the products and reactants. The *constraint* could be brought about by a change in the overall temperature, T, at which the reaction is being carried out or by alteration of the external pressure, P, for the process.

According to *Le Chatelier's Principle*:

- If a *constraint* is applied to a system at equilibrium then the system will *tend to* adjust the position of equilibrium so as to oppose (or tend to nullify) the effects of this constraint.

The Le Chatelier principle itself can also be derived from the Second Law of Thermodynamics (Frame 14) is of much wider applicability than just to chemical reactions. It applies to all systems which are in equilibrium. Other examples might be: solid – liquid (see Frame 26 where conclusions regarding the effect of pressure on melting point are in agreement with the application of the Le Chatelier principle), solid – solid equilibria or equilibria in solution (see Section 49.7 below).

49.3 Effect on an Equilibrium Reaction of Change in Temperature – Qualitative Interpretation

To see how this works suppose we have an *exothermic* reaction, for which $\boldsymbol{\Delta H < 0}$ (*negative*) then for the forward reaction we have:

$$\text{Reactants} \overset{\Delta H<0}{\rightarrow} \text{Products} + \underset{\textbf{(HEAT)}}{\textbf{ENTHALPY}} \tag{49.2}$$

and so as the reaction proceeds and more products are being formed (and hence Q is increasing in magnitude) and enthalpy in the form of heat is also released. For the corresponding reverse reaction, (which will be *endothermic*) the reverse will be true, i.e.

$$\text{Products} + \underset{\textbf{(HEAT)}}{\textbf{ENTHALPY}} \overset{\Delta H>0}{\rightarrow} \text{Reactants} \tag{49.3}$$

and as *this* reaction proceeds and the *original* reactants are now being reformed (and Q is being correspondingly reduced in size) then enthalpy (in the form of heat) will be absorbed during the process. So we see that according to whether a given reaction 'wishes' to generate or absorb heat (enthalpy), in order to respond to external stimuli (or constraints), it can proceed in the appropriate direction away from its current equilibrium position.

Suppose now that the *temperature, T*, of the original exothermic reaction (49.2) is increased. This will supply *additional* heat energy to a reaction which is already *producing heat* when advancing in a forward direction! In order to '*oppose*' this additional constraint in the form of this further heat supply, the reaction, according to Le Chatelier's principle, will move in a direction so as to tend to absorb this additional heat. Hence reaction (49.2) will reverse itself and proceed in the direction as shown in reaction (49.3), so reducing the product concentrations and increasing the reactant concentrations, the equilibrium constant, K, is accordingly reduced in size (since the *denominator* of K in equation (49.1) will be *increased* as the reactant concentrations increase and the product concentrations (*numerator*) decrease). The reaction now also absorbs some of the heat supplied in raising the temperature and accordingly adjusts its position of equilibrium.

In the case of *endothermic* reactions, the reverse is true, if the temperature is raised then we achieve greater product concentrations and K *increases* its value as T is raised. Here the reaction absorbs heat since $\Delta H > 0$, so if T is increased the reaction moves in the direction in which it can absorb the additional heat supplied from the rise in temperature, i.e. in the forward direction.

Correspondingly inducing a fall in temperature produces the reverse effects to that caused by rise in temperature in each case.

The position of equilibrium (and therefore K) in a reaction where $\Delta H \approx 0$ will be relatively little affected by temperature change.

49.4 Quantitative Thermodynamic Interpretation of Le Chatelier's Principle. Temperature Change

The van't Hoff Isochore or van't Hoff Equation (Equation (46.11), Frame 46) expressed the variation of the ln $K_{p/po}$ term with change in temperature, T in the form:

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} \tag{46.11}$$

For an *exothermic reaction* in which $\Delta H < 0$ (negative) then the term: $\Delta H^o/RT^2$ is also < 0. Since R is constant and positive and T^2 is also positive, the sign of this term will be determined *solely* by *the magnitude of* ΔH^o. Hence for an *exothermic reaction*:

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} < 0 \tag{49.4}$$

so that, from the sign of the derivative, we know that:

- ln $K_{p/po}$ will *decrease* as temperature, T, increases;
- $K_{p/po}$ therefore *decreases* with increasing temperature, T;
- *Fewer products* will therefore be formed as temperature, T, increases.

For an *endothermic reaction,* $\Delta H > 0$ (positive) so that the term: $\Delta H^o/RT^2$ is also positive. Hence for an *endothermic reaction*:

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} > 0 \tag{49.5}$$

so that, from the sign of the derivative, we know that:

- ln $K_{p/po}$ will *increase* as temperature, T, increases;
- $K_{p/po}$ therefore *increases* with increasing temperature, T;
- *More products* will therefore be formed as temperature, T, increases.

For a reaction in which $\Delta H \approx 0$:

$$\left(\frac{\partial \ln K_{p/po}}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2} \approx 0 \tag{49.6}$$

and there will be relatively small changes (if any) in $K_{p/po}$ for such reactions as temperature is varied upwards or downwards.

These three *quantitatively* based conclusions, coming as they do directly from the *van't Hoff Equation,* are exactly as predicted by the Le Chatelier *qualitative* argument used above, as would be anticipated.

49.5 Effect on an Equilibrium Reaction of Change in Pressure – Qualitative Interpretation

The effect of pressure change is a complicated issue. If we have a reaction like a dissociation reaction, for example (Frame 45, reaction (45.24)):

$$X_2(g) \rightarrow 2X(g) \tag{45.24}$$

where the amount of substance present changes in the course of the reaction, then the reaction will be affected by pressure changes *although the overall* K_p*, and hence the position of equilibrium is unchanged as a result of pressure changes* (as has already been discussed in Frame 48). In the reaction above 1 mole of X_2 gas molecules dissociate to produce 2 moles of X atoms.

Avogadro's Law, states that equal numbers of moles of all gases occupy identical volumes – the molar volume being 22.4 dm^3. Thus two moles of gas will occupy 44.8 dm^3 whilst one mole occupies only 22.4 dm^3. Thus if we compare the situation where there is *no dissociation* taking place at all and we have *only* X_2 gas molecules in the flask, then their relatively smaller volume (when compared to X atoms) will give rise to the exertion of a *lower pressure* within their container than is the case where we have *total dissociation*, with *only* X gaseous atoms present, and a much higher volume of gas within the same containing space and accordingly exerting a *larger pressure* within the containing vessel. Thus *as the* X_2 *molecules dissociate* the effect is, therefore, for the internal *pressure to increase*.

Suppose externally we *increase* the pressure, P, on the containing vessel, then according to Le Chatelier's Principle the equilibrium between X_2 (g) and X(g) species will shift in order to try to mitigate the impact of this pressure increase and the equilibrium will shift in the direction of the undissociated molecules, so reducing the degree of dissociation, α. Immediately one might be tempted to say therefore that $K_{p/po}$ for the reaction is thereby decreased. There is need for caution here and the extent of the *qualitative* argument is limited to comment only on the variation of P and of α but *not on* $K_{p/po}$ *variation*. The reason is the *complexity of the issue* and, as seen earlier (Frame 48) – and also in the next section – this complexity arises from the fact that $K_{p/po}$ is a complicated function of both α^2 and of (P/P^o) where P^o is the standard pressure.

If the overall pressure, P, is lowered then α will be increased, there will be more X atoms formed and therefore trying to offset the effect of the pressure reduction the amount of product is increased in turn exerting a greater internal pressure.

Thus we see that as P is increased α is reduced and vice versa.

49.6 Quantitative Thermodynamic Interpretation of Le Chatelier's Principle. Pressure Change

We have actually discussed this already in Frame 48 where we concluded that for a generalised study of dissociation reactions of the type, as illustrated by reaction (45.24), that:

- $$K_{p/po} = A\alpha^2\left(\frac{P}{P^o}\right)\Big/(1 - B\alpha^2); \quad P^o = 1 \text{ bar} \tag{49.7}$$

  where A and B are constants (A = 0.0004; B = 0.0001);
- since $B\alpha^2$ is usually $\ll 1$, then we can regard $K_{p/po}$ as being proportional to the square of the degree of dissociation, α^2 *multiplied by* the ratio of the external to the standard pressure (P/P^o);
- since when (P/P^o) rises, α falls and when (P/P^o) falls, α rises, it transpires that the term $\alpha^2(P/P^o)$ remains pretty constant as pressure, (P/P^o) is varied;
- since apart from the $\alpha^2(P/P^o)$ term in equation (49.7), all the other terms are constants so that consequently, $K_{p/po}$ will *not* vary as pressure changes and the position of equilibrium will be unaltered by changes in (P/P^o).

Considering the reaction:

$$X_2(g) \rightarrow 2X(g) \tag{45.24}$$

at two arbitary pressures P_1 and P_2 at which the respective degrees of dissociation are α_1 and α_2 then the situation is that:

$$\alpha_1^2\left(\frac{P_1}{P^o}\right) = \alpha_2^2\left(\frac{P_2}{P^o}\right) \tag{49.8}$$

and in accordance with equation (49.7), changing the pressure, P, from P_1 to P_2 will leave $K_{p/po}$, the equilibrium constant of reaction (45.24) *unchanged*, by virtue of equation (49.8).

49.7 Solubility of Sparingly Soluble Salts, the "Common Ion" Effect and Le Chatelier's Principle

Observation tells us that if we try to dissolve solid silver (I) chloride, AgCl in pure water then its solubility is extremely small and is found experimentally to be 1.33×10^{-5} mol dm^{-3}.

We could also calculate the solubility from the solubility product, K_{sp}. Suppose the solubility of solid AgCl in water is taken to be s mol dm^{-3}, then on dissolution to form a saturated solution, then equal concentrations of s mol dm^{-3} of Ag$^+$ ions and s mol dm^{-3} of Cl$^-$ ions enter the solution:

$$\begin{array}{ccccc} \mathrm{AgCl(s)} & \rightarrow & \mathrm{Ag^+(aq)} & + & \mathrm{Cl^-(aq)} \\ s & & s & & s \end{array} \tag{49.9}$$

and therefore the solubility, s:

$$s = [\text{solubility of AgCl solid in water}] = [\mathrm{Ag^+, aq}] = [\mathrm{Cl^-, aq}]\,\mathrm{mol\,dm^{-3}} \tag{49.10}$$

and the solubility product, K_{sp} is given by:

$$K_{sp} = \frac{[\mathrm{Ag^+, aq}]}{\mathrm{mol\,dm^{-3}})}\frac{[\mathrm{Cl^-}]}{\mathrm{mol\,dm^{-3}})} = \mathrm{s}^2 = 1.77 \times 10^{-10} \tag{49.11}$$

[since the solution of AgCl is very dilute we anticipate that activity, a, and the concentration, c, were identical and that the activity coefficient, $\gamma = 1$ for this system (see Frame 35 for the relationship between a and c)]. Thus the solubility of AgCl (a 1:1 salt) is just the square root of the solubility product, K_{sp}.

If we now add a $10^{-5}M$ NaCl solution (containing 1×10^{-5} mol dm^{-3}of NaCl) to the saturated solution of AgCl, *the addition of a 'common ion'* (in this case the Cl$^-$ ion) reduces the amount of AgCl which can now be held in the solution and has the effect of causing AgCl to precipitate out – the extent to which can be calculated.

Addition of a 'common ion' (i.e. either Ag$^+$ or Cl$^-$ in the case of AgCl) to a saturated solution will increase the product of the concentration terms: [Ag$^+$,aq][Cl$^-$,aq] well beyond K_{sp}, so disturbing the equilibrium and rendering the solution oversaturated, or supersaturated, to use the more usual term. **Le Chatelier's Principle** dictates that if the additional constraint of Cl$^-$ (or for that matter Ag$^+$) ion addition is made to the solution – then since this is a factor that affects the equilibrium position – it will cause the system to react in such a way as to tend to oppose the effects of the addition and so remove some of the added Cl$^-$ ion. Since AgCl is less soluble than NaCl, then the system can do this by precipitating out of solution some solid AgCl. In this way, removing both Cl$^-$ *and* Ag$^+$ ions, so rapidly reducing the product [Ag$^+$,aq][Cl$^-$,aq] enabling it to reach the value corresponding to K_{sp} and hence restore equilibrium once again.

50. Gibbs–Duhem Equation Gibbs–Duhem–Margules Equation

The Gibbs–Duhem equation (50.6), derived below, proves to be a useful starting point for an alternative derivation of the Clausius Claperyron equation to that offered in Frame 26) and offers an alternative proof of the Phase Rule to that given in Frame 30.

50.1 Gibbs–Duhem Equation

A generalisation of equation (27.5) in Frame 27 leads to:

$$G = \sum_{\mathrm{i}} n_{\mathrm{i}} \cdot \mu_{\mathrm{i}} \tag{50.1}$$

where G is the total free energy of a system containing an amount, n_{i}, of component i having chemical potential, μ_{i}. Differentiation of equation (50.1) treating the right-hand side as a product (using Product Rule: Frame 3, Table 3.1) leads to:

$$\mathrm{d}G = \sum_{\mathrm{i}} \mathrm{d}(n_{\mathrm{i}} \cdot \mu_{\mathrm{i}}) = \sum_{\mathrm{i}} n_{\mathrm{i}} \cdot \mathrm{d}\mu_{\mathrm{i}} + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \cdot \mathrm{d}n_{\mathrm{i}} \tag{50.2}$$

but also (Frame 27) generalising equation (27.12) we have:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \cdot \mathrm{d}n_{\mathrm{i}} \tag{50.3}$$

Subtracting equation (50.3) from equation (50.2) gives

$$0 = V\mathrm{d}P - S\mathrm{d}T - \sum_{\mathrm{i}} n_{\mathrm{i}} \cdot \mathrm{d}\mu_{\mathrm{i}} \tag{50.4}$$

Therefore also:

$$\sum_{\mathrm{i}} n_{\mathrm{i}} \cdot \mathrm{d}\mu_{\mathrm{i}} = V\mathrm{d}P - S\mathrm{d}T \tag{50.5}$$

if (temperature, T and pressure P are constant: $\mathrm{d}T = 0$ and $\mathrm{d}P = 0$):

$$\sum_{\mathrm{i}} n_{\mathrm{i}} \cdot \mathrm{d}\mu_{\mathrm{i}} = 0 \tag{50.6}$$

which is the *Gibbs–Duhem Equation*.

Two further points can be made about the above equations:

- Equation (50.6) shows that if we have a system containing two component substances labelled 1 and 2 at constant temperature and pressure, then:

  $$n_1\mathrm{d}\mu_1 + n_2\mathrm{d}\mu_2 = 0 \tag{50.7}$$

  or that:

  $$\mathrm{d}\mu_2 = -\left(\frac{n_1}{n_2}\right) \cdot \mathrm{d}\mu_1 \tag{50.8}$$

  if a variation in the composition of component 1 ($= \mathrm{d}\mu_1$) is made this will produce a corresponding change in the composition of component 2 ($= \mathrm{d}\mu_2$) as given by equation (50.8).
- If we divide equation (50.5) through by the total amount of substance present ($= n$) this leads to:

  $$\sum_{\mathrm{i}} \left(\frac{n_i}{\mathrm{n}}\right) \cdot \mathrm{d}\mu_i = \left(\frac{V}{n}\right) \cdot \mathrm{d}P - \left(\frac{S}{n}\right) \cdot \mathrm{d}T \tag{50.9}$$

  which can be written in terms of molar volume (V_{m}) and molar entropy (S_{m}) (see Frame 1, section 1.4) as:

  $$\sum_{\mathrm{i}} \left(\frac{n_{\mathrm{i}}}{\mathrm{n}}\right) \cdot \mathrm{d}\mu_{\mathrm{i}} = V_{\mathrm{m}} \cdot \mathrm{d}P - S_{\mathrm{m}} \cdot \mathrm{d}T \tag{50.10}$$

and since we can convert the left-hand side of equation (50.10) into a term involving the sum of mole fractions, x_i, by using equation (30.9), Frame 30:

$$\sum_i x_i = \frac{\{\sum_i n_i\}}{n} = \sum_i (n_i/n) \tag{50.11}$$

then equation (50.10) becomes:

$$\sum_i x_i \cdot d\mu_i = V_m \cdot dP - S_m \cdot dT \tag{50.12}$$

which is another form of the *Gibbs–Duhem equation*.

50.2 Derivation of Clausius–Clapeyron Equation* using the Gibbs–Duhem Equation. [*In the form of Equation (26.5), Frame 26]

Equation (68.5) takes the form:

$$\sum_i n_i d\mu_i = V dP - S dT \tag{50.5}$$

so that for a one-component system at equilibrium ($dG = 0$):

$$n d\mu = V dP - S dT \tag{50.13}$$

Consider now two phases labelled 1 and 2 in this one-component system, for which:

$$n_1 d\mu_1 = V_1 dP - S_1 dT \tag{50.14}$$

where n_1 is the chemical amount of material in phase 1 at temperature T and pressure, P and V_1 is the volume of material in phase 1 whose entropy is S_1. Dividing through by n_1:

$$d\mu_1 = \left(\frac{V_1}{n_1}\right) dP - \left(\frac{S_1}{n_1}\right) dT \tag{50.15}$$

leading to molar quantities (denoted by subscript m), $V_{m,1}$ ($= V_1/n_1$) and $S_{m,1} = S_1/n_1$ and equation (50.11) which then rearranged with these substitutions made, becomes:

$$V_{m,1} dP - S_{m,1} dT + d\mu_1 = 0 \tag{50.16}$$

and similarly for phase 2 we have:

$$n_2 d\mu_2 = V_2 dP - S_2 dT \tag{50.17}$$

where n_2 is the chemical amount of material in phase 2 at temperature T and pressure, P and V_2 is the volume of material in phase 2 whose entropy is S_2. Dividing through by n_2:

$$d\mu_2 = \left(\frac{V_2}{n_2}\right) dP - \left(\frac{S_2}{n_2}\right) dT \tag{50.18}$$

leading to molar quantities (denoted by subscript m), $V_{m,2}$ ($= V_2/n_2$) and $S_{m,2} = S_2/n_2$ and equation (50.14) which then rearranged with these substitutions made, becomes:

$$V_{m,2} dP - S_{m,2} dT + d\mu_2 = 0 \tag{50.19}$$

At equilibrium between phases 1 and 2 at the same temperature and pressure:

$$d\mu_1 = d\mu_2 \tag{50.20}$$

so that subtracting equation (50.16) from equation (50.19) we have:

$$(V_{m,2} - V_{m,1}) \cdot dP - (S_{m,2} - S_{m,1}) \cdot dT + (d\mu_2 - d\mu_1) = 0 \tag{50.21}$$

and by virtue of equation (50.20):

$$(V_{m,2} - V_{m,1}) \cdot dP - (S_{m,2} - S_{m,1}) \cdot dT = 0 \tag{50.22}$$

Rearranging equation (50.22) leads to:

$$\frac{dP}{dT} = \frac{(S_{m,2} - S_{m,1})}{(V_{m,2} - V_{m,1})} \tag{50.23}$$

or that:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \tag{50.24}$$

which if phase 2 were gaseous and phase 1 were liquid, then:

$$\frac{dP}{dT} = \frac{\Delta_{vap} S}{\Delta_{vap} V} \approx \frac{\Delta_{vap} S}{V_g} \tag{50.25}$$

where $\Delta_{\text{vap}} S$ is the entropy of vaporisation, $\Delta_{\text{vap}} V$ is the change in volume of vaporisation and V_{g} is the volume of the vapour in the gas phase (following the arguments made in section 26.1, Frame 26).

Equation (50.25) is one form of the Clausius–Clapeyron Equation as is given in Frame 26, Equation (26.5).

We see here an example of how a given thermodynamic equation can be derived from more than one source as the starting point, thus demonstrating the consistency of the subject, as one would expect.

50.3 Derivation of the Phase Rule using the Gibbs–Duhem Equation

Starting with one Gibbs–Duhem equation in the form of equation (50.12) adapted for a system having c components across each of the p phases (*1,2,... p*) (Figure 30.2):

$$SdT - VdP + \sum_{i=1}^{C} x_i d\mu_i = 0 \tag{50.26}$$

for each phase in an equilibrium system having the 'variables' dT, dP and $d\mu_{\text{i}}$ the same for each phase but with the $S_{\text{m}}, V_{\text{m}}$ and x_{i} different for each of the p phases present we can write a total of p simultaneous equations which will have a total of $c + 2$ unknowns with:

$$p \le c + 2 \tag{50.27}$$

By successive variable elimination we can reduce these p simultaneous equations down to just 1 equation (still with a right-hand side equal to zero) so having eliminated (p – 1) equations during this process leaving us with: $c + 2 - (p - 1) = c - p + 3$ unknowns *and these can be chosen to be any set from the* $c + 2$ unknowns.

This means that one can choose any values for any $(c - p + 3) - 1 = c - p + 2$ of the dT, dp, $d\mu_i$ and the remainder will automatically be determined, so that the number of degrees of freedom, f, is given by:

$$f = c - p + 2 \tag{50.28}$$

This is the Phase Rule (as given in Frame 30, equation (30.21).

Finally, since (change of) chemical potentials are functions of (change of) temperature, pressure and mole fractions, the 'variables' can be changed from dT, dp, $d\mu_i$ to dT, dp, dx_i.

This approach to proving the Phase Rule is an alternative to that in Frame 30.

50.4 Three-phase Equilibria and the Gibbs–Duhem Equation

Yet a further application of this important Gibbs–Duhem equation is in the discussion of the triple-phase equilibrium:

$$\text{solid} \rightleftharpoons \text{liquid} \rightleftharpoons \text{gas} \tag{50.29}$$

for which the only solution of the triple Gibbs–Duhem equation:

$$d\mu = V_{\text{s}} \cdot dT - S_{\text{s}} \cdot dP = V_{\text{l}} \cdot dT - S_{\text{l}} \cdot dP = V_{\text{g}} \cdot dT - S_{\text{g}} \cdot dP \tag{50.30}$$

or:

$$(V_{\text{l}} - V_{\text{s}}) \cdot dT - (S_{\text{l}} - S_{\text{s}}) \cdot dP = (V_{\text{l}} - V_{\text{g}}) \cdot dT - (S_{\text{l}} - S_{\text{g}}) \cdot dP = 0 \tag{50.31}$$

is the trivial one of;

$$dT = dP = d\mu = 0 \tag{50.32}$$

indicating that there are no degrees of freedom associated with the triple point of the phase diagram where solid, liquid and gas phases co-exist (see Frame 23, Figure 23.3 and section 23.1 and also Frame 30, section 30.5).

50.5 Application to Activities

Suppose we have a solvent into which is dissolved an (involatile) solute. If the solutions are real solutions we can write, for the solvent in the solution:

$$\mu^{(\text{solvent})} = \mu^* + RT \ln a_{\text{solvent}} \tag{50.33}$$

and for the solute in the solution:

$$\mu^{(\text{solute})} = \mu^o + RT \ln a_{\text{solute}} \tag{50.34}$$

where μ^* and μ^o are constants and hence, differentiating both sides of each equation:

$$d\mu^{(\text{solvent})} = d(RT \ln a_{\text{solvent}}) \tag{50.35}$$

and

$$d\mu^{(\text{solute})} = \mathrm{d}(RT \ln a_{\text{solute}}) \tag{50.36}$$

[It can be noted at this point that if we use equations (50.19) for either solvent or solute, then we can write, using equations (50.35) and (50.36), that either:

$$V_{m,\text{solvent}1}\mathrm{d}P - S_{m,\text{solvent}}\mathrm{d}T + \mathrm{d}(RT \ln a_{\text{solvent}}) = 0 \tag{50.37}$$

or

$$V_{m,\text{solute}1}\mathrm{d}P - S_{m,\text{solute}}\mathrm{d}T + \mathrm{d}(RT \ln a_{\text{solute}}) = 0 \tag{50.38}$$

which are referred to as the *Gibbs–Duhem–Margules* equations.

Continuing then using the Gibbs–Duhem Equation in the form of equation (50.8), that:

$$\mathrm{d}\mu^{(\text{solvent})} = -\left(\frac{n_{\text{solute}}}{n_{\text{solvent}}}\right)\mathrm{d}\mu^{(\text{solute})} \tag{50.39}$$

then:

$$\mathrm{d}(RT \ln a_{\text{solvent}}) = -\left(\frac{n_{\text{solute}}}{n_{\text{solvent}}}\right)\mathrm{d}(RT \ln a_{\text{solute}}) \tag{50.40}$$

and hence, cancelling the *RT* terms:

$$\mathrm{d}(\ln a_{\text{solvent}}) = -\left(\frac{n_{\text{solute}}}{n_{\text{solvent}}}\right)\mathrm{d}(\ln a_{\text{solute}}) \tag{50.41}$$

Supposing the solution has a solute present at molality, m_{solute} and that the solvent has a molar mass, M then:

$$\left(\frac{n_{\text{solute}}}{n_{\text{solvent}}}\right) = \frac{m_{\text{solute}}}{(1/M_m)} = m_{\text{solute}}M_m \tag{50.42}$$

so that:

$$\mathrm{d}(\ln a_{\text{solvent}}) = -m_{\text{solute}}M_m\,\mathrm{d}(\ln a_{\text{solute}}) \tag{50.43}$$

which gives us a rather complicated relationship between the change in the logarithm of the activity of solute or solvent, as the molality of the solute, m_{solute} is varied. It also tells us that the change in the activity of the solvent is not independent and is affected by the activity of the solute.

51. Colligative Properties: Freezing Point

The fact that the chemical potential of a solvent in a solution (composed of solute + solvent) is less than that of the chemical potential of the pure solvent gives rise to a number of properties:

- vapour pressure lowering on addition of solute to a pure liquid (as discussed in Frame 32). Coverage of this could be made using Raoult's Law treatment at the low x_{A} end ($x_{\mathrm{A}} \approx (\mathrm{m_A} + \mathrm{m_B})$;
- freezing point (T_{m}) depression on addition of solute to a pure liquid;
- boiling point (T_{b}) elevation on addition of solute to a pure liquid;
- the origin of osmotic pressure.

Such properties are termed *colligative properties* (colligative = binding together) and they depend not so much on the nature of the solute particles present but rather on their number, which is expressed by the molality, m_{solute}, in the final form of the equations involved.

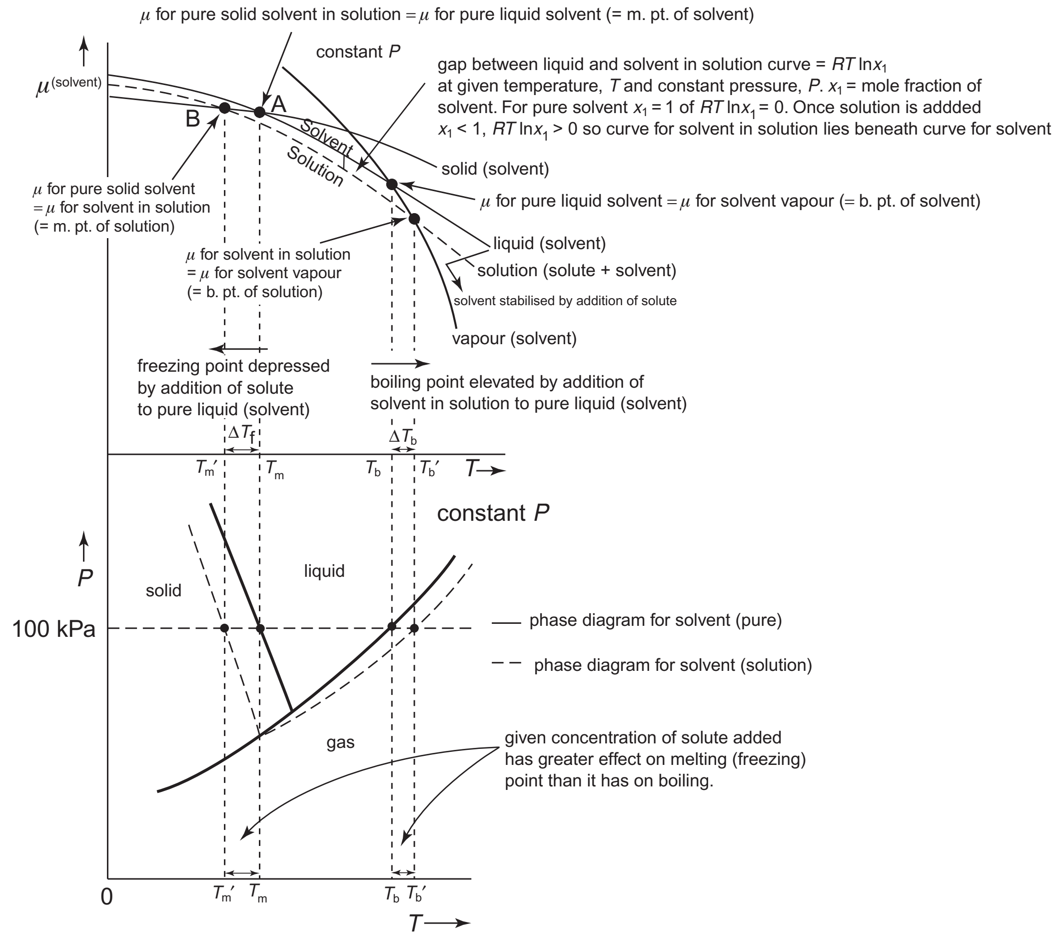


Figure 51.1 Colligative properties: Effect on melting temperature, T_{m} and boiling temperature, T_{b} of the addition of solute to a pure liquid (solvent).

51.1 Freezing Point Depression, ΔT_{f}

Consider the effect on the freezing (melting) point, T_{m} of a liquid of adding some solid (solute) to it. As a practical application we can think of the road gritting protocol in winter. The addition of solids (usually sand/salt mixtures) to road surface water depresses the freezing point to below the lowest temperature likely to be reached and hence inhibits the creation of ice surfaces on the road.

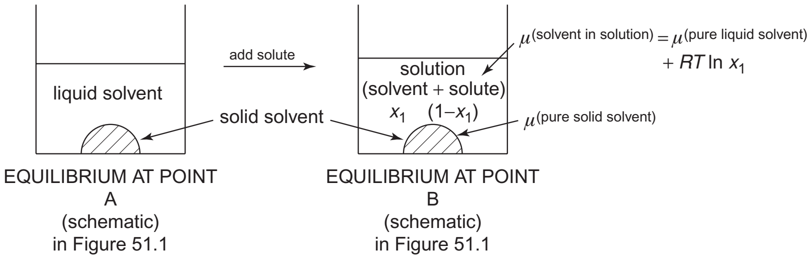


Figure 51.2 Equilibria formed at points A and B in Figure 51.1.

Figure 51.1 illustrates some of the relevant thermodynamic features relating to the addition of solute to a pure solvent to form a solution and its corresponding effect on the melting point, T_m and boiling point, T_b.

A pure liquid (say water), once solute is added acts as the solvent and *provided only relatively small amounts of solute are added* we create a so called ideal solution (Frames 32 and 33). The entropy is increased (i.e. $S_{\text{ideal solution}} > S_{\text{pure solvent}}$) by the addition of solute (more randomness in molecular arrangement is created compared with the pure solvent). The chemical potential is lowered:

$$\mu^{(\text{solvent in solution})} < \mu^{(\text{pure solvent})} \tag{51.1}$$

and so the solvent is made more stable by the addition of a solute. Hence, the curve of μ versus T for the 'solution' in Figure 51.1 is *lower* than that for the pure solvent. We are here considering the case where the pure solvent freezes out of the solution (Figure 51.2(b)).

The process of *fusion* is defined as the phase change taking place when a *liquid is converted into a solid.* The reverse process (liquid → solid) is called melting.

$$\text{liquid} \underset{\text{MELTING}}{\overset{\text{FUSION}}{\longrightarrow}} \text{solid} \tag{51.2}$$

Rather confusingly though, when a solid melts the enthalpy change taking place is called (historically) the enthalpy of *fusion*, $\Delta_{\text{fus}}H^o$! When a liquid solidifies to a solid, an enthalpy equal to $-\Delta_{\text{fus}}H^o$ is exothermically released. Note here that the superscript 'o' is strictly valid only under the standard condition that ($P = P^o$) but that it does not change much with change of pressure (or temperature). Thus the corresponding changes are:

$$\text{solvent (pure liquid)} \overset{-\Delta_{\text{fus}}G^o}{\rightarrow} \text{solvent (pure solid)} \tag{51.3}$$

The equilibrium (51.3) (Figure 51.2(b)) which exists after addition of the solute (Figure 51.2(a)) to the pure solvent is between the aqueous solution formed on the dissolution and the solid (solvent) deposited on freezing:

$$\text{solution (in liquid solution)} \rightarrow \text{solvent (solid)} \tag{51.4}$$

At equilibrium, of course, the chemical potentials are equal (Frame 35):

$$\mu^{(\text{solvent in solution})} = \mu^{(\text{pure solid solvent})} \tag{51.5}$$

From the above definition, the free energy and enthalpy of fusion, $\Delta_{\text{fus}}G^o$ and $\Delta_{\text{fus}}H^o$ respectively of the solvent at constant pressure are such that (for process 51.3):

$$-\Delta_{\text{fus}}G^o = \mu^{(\text{pure solid solvent})} - \mu^{(\text{pure liquid solvent})} \tag{51.6}$$

Also in the case of an ideal dilute solution (Frame 36, section 36.3) we can write that:

$$\mu^{(\text{solvent in solution})} = \mu^{(\text{pure liquid solvent})} + RT \ln x_1 \tag{51.7}$$

where x_1 is the mole fraction of the solvent. Combining equations (51.5) and (51.7) we can write that:

$$\mu^{(\text{solvent in solution})} = \mu^{(\text{pure liquid solvent})} + RT \ln x_1 = \mu^{(\text{pure solid solvent})} \tag{51.8}$$

and taking account of equation (51.6) then:

$$-\Delta_{\text{fus}}G^o = [\mu^{(\text{pure solid solvent})} - \mu^{(\text{pure liquid solvent})}] = RT \ln x_1 \tag{51.9}$$

by virtue of equations (51.7) and (51.8). Rearranging we have:

$$\ln x_1 = \frac{[\mu^{(\text{pure solid solvent})} - \mu^{(\text{pure liquid solvent})}]}{RT} = \frac{-\Delta_{\text{fus}} G^o}{RT} \tag{51.10}$$

As is very often the case in thermodynamics, we can proceed from this point using two different approaches which, ultimately, lead to the same result. So taking the equation (51.10) in the form:

$$\ln x_1 = \frac{-\Delta_{\text{fus}} G^o}{RT} \tag{51.11}$$

- EITHER:

Taking account of the fact that at the melting point, T_m (corresponding to point A in Figure 51.1) solid and liquid solvent are in equilibrium and hence: $\Delta_{\text{fus}} G^o = 0 \quad \text{at} \quad T = T_\text{m}$ and since (Frame 13, equation (13.9)):

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

then it is appropriate at the melting temperature, T_m, to write that:

$$\Delta_{\text{fus}} G^o = \Delta_{\text{fus}} H^o - T_\text{m} \Delta_{\text{fus}} S^o = 0 \tag{51.12}$$

so that, re arranging the right-hand equation in (51.12) we have:

$$\Delta_{\text{fus}} S^o = \frac{\Delta_{\text{fus}} H^o}{T_\text{m}} \tag{51.13}$$

Assuming now that $\Delta_{\text{fus}} H^o$ is independent of temperature change we can write for a general temperature T:

$$\Delta_{\text{fus}} G^o(T) = \Delta_{\text{fus}} H^o - T \left\{ \frac{\Delta_{\text{fus}} H^o}{T_\text{m}} \right\} = \Delta_{\text{fus}} H^o \left[1 - \left(\frac{T}{T_\text{m}} \right) \right] \tag{51.14}$$

where $\Delta_{\text{fus}} G^o(T)$ refers to the value of $\Delta_{\text{fus}} G^o$ at temperature T. Substituting now into equation (51.11):

$$\ln x_1 = \frac{-\Delta_{\text{fus}} G^o}{RT} = -\left(\frac{\Delta_{\text{fus}} H^o}{RT} \right) \left[1 - \left(\frac{T}{T_\text{m}} \right) \right] \tag{51.15}$$

Differentiating both sides of equation (51.11) with respect to x_1 keeping the pressure constant as in Figure 51.1:

$$\left(\frac{\partial [\ln x_1]}{\partial x_1} \right)_P = -\left\{ \partial \left[\frac{\Delta_{\text{fus}} G^o}{RT} \right] \Big/ \partial x_1 \right\}_P \tag{51.16}$$

where P is the constant pressure. Equation (51.16) can also be written:

$$\left(\frac{\partial [\ln x_1]}{\partial x_1} \right)_P = -\left(\frac{1}{R} \right) \left\{ \partial \left[\frac{\Delta_{\text{fus}} G^o}{T} \right] \Big/ \partial x_1 \right\}_P \tag{51.17}$$

changing the differential on the right-hand side to one involving temperature:

$$\left(\frac{\partial [\ln x_1]}{\partial x_1} \right)_P = -\left(\frac{1}{R} \right) \left\{ \partial \left[\frac{\Delta_{\text{fus}} G^o}{T} \right] \Big/ \partial T \right\}_P \left(\frac{\partial T}{\partial x_1} \right)_P \tag{51.18}$$

Using the results in Frame 3, Table 3.1, since: $\mathrm{d}[\ln(ax)]/\mathrm{d}x = 1/x$ then:

$$\left(\frac{\partial [\ln x_1]}{\partial x_1} \right)_P = \frac{1}{x_1} \tag{51.19}$$

and equation (51.8) becomes (using the Gibbs–Helmholtz Equation (46.9) Frame 46):

$$\frac{1}{x_1} = -\left(\frac{1}{R} \right) \left\{ \frac{-\Delta_{\text{fus}} H^o}{T^2} \right\} \left(\frac{\partial T}{\partial x_1} \right)_P \tag{51.20}$$

which becomes, after rearrangement:

$$\frac{1}{x_1} = \left\{ \frac{\Delta_{\text{fus}} H^o}{RT^2} \right\} \left(\frac{\partial T}{\partial x_1} \right)_P \tag{51.21}$$

so that, cross multiplying:

$$\frac{dx_1}{x_1} = \left\{\frac{\Delta_{\text{fus}}H^o}{R}\right\}\frac{dT}{T^2} \tag{51.22}$$

Indefinitely integrating both sides we have:

$$\int \frac{dx_1}{x_1} = \left\{\frac{\Delta_{\text{fus}}H^o}{R}\right\}\int \frac{dT}{T^2} \tag{51.23}$$

and converting to a definite integral since when $x_1 = 1$ we have pure solvent and the freezing point is then T_{m}. When solute is added x_1 changes say to x and the freezing point then becomes (say T) so integrating between these limits we have:

$$\int_1^x \frac{dx_1}{x_1} = \left\{\frac{\Delta_{\text{fus}}H^o}{R}\right\}\int_{T_m}^{T} \frac{dT}{T^2} \tag{51.24}$$

$$[\ln x_1]_1^x = [\ln x - \ln 1] = [\ln x - 0] = \ln x = \left\{\frac{\Delta_{\text{fus}}H^o}{R}\right\}\left[\frac{-1}{T}\right]_{T_m}^{T} \tag{51.25}$$

so that:

$$\ln x = -\left\{\frac{\Delta_{\text{fus}}H^o}{R}\right\}\left[\left(\frac{1}{T}\right) - \left(\frac{1}{T_{\text{m}}}\right)\right] \tag{51.26}$$

Equation (51.26) can be written as follows:

$$\ln x = \frac{-\Delta_{\text{fus}}H^o}{RT} + \frac{\Delta_{\text{fus}}H^o}{RT_{\text{m}}} \tag{51.27}$$

$$\frac{\Delta_{\text{fus}}H^o}{RT} = \frac{\Delta_{\text{fus}}H^o}{RT_{\text{m}}} - \ln x \tag{51.28}$$

$$\left(\frac{1}{T}\right) = \left(\frac{1}{T_{\text{m}}}\right) - \left\{\frac{R\ln x}{\Delta_{\text{fus}}H^o}\right\} \tag{51.29}$$

This equation relates the freezing point of the ideal solution, T'_{m}, to the freezing point of the pure solvent, T_{m}, the enthalpy of fusion of the pure solvent, $\Delta_{\text{fus}}H^o$, the mole fraction, x ($x < 1$), of solvent present and R, the gas constant.

The *freezing point depression* is given (Figure 51.1) by:

$$\Delta T_{\text{f}} = (T_{\text{m}} - T) = (T_{\text{m}} - T'_{\text{m}}) \tag{51.30}$$

Then ($T = T'_{\text{m}}$) :

$$\left(\frac{1}{T}\right) - \left(\frac{1}{T_{\text{m}}}\right) = \left(\frac{1}{T'_{\text{m}}}\right) - \left(\frac{1}{T_{\text{m}}}\right) = -\left\{\frac{R\ln x}{\Delta_{\text{fus}}H^o}\right\} \tag{51.31}$$

if the freezing point depression is small (i.e. $T'_{\text{m}} \approx T_{\text{m}}$), then: $(T_{\text{m}} - T'_{\text{m}})/T_{\text{m}}T'_{\text{m}} \approx \Delta T_{\text{f}}/T^2_{\text{m}}$ and:

$$\ln x = \frac{-(\Delta_{\text{fus}}H^o \cdot \Delta T_{\text{f}})}{RT^2_{\text{m}}} \tag{51.32}$$

Since the sum of the mole fractions of solute and solvent adds up to 1 then:

$$x = x_{\text{solvent}} = (1 - x_{\text{solute}}) \tag{51.33}$$

so that:

$$\ln(1 - x_{\text{solute}}) = \frac{-(\Delta_{\text{fus}}H^o \cdot \Delta T_{\text{f}})}{RT^2_{\text{m}}} \tag{51.34}$$

The left-hand side can be expanded (see frame 6, equation (6.16)) and since when x is small:

$$\ln(1 - x) \approx -x \tag{51.35}$$

so that since our solute addition is small (to preserve the ideal solution condition) then:

$$-x_{\text{solute}} \approx \frac{-(\Delta_{\text{fus}}H^o \cdot \Delta T_{\text{f}})}{RT^2_{\text{m}}} \tag{51.36}$$

and:

$$\Delta T_{\text{f}} \approx \left(\frac{x_{\text{solute}} \cdot RT^2_{\text{m}}}{\Delta_{\text{fus}}H^o}\right) \tag{51.37}$$

If the molality of the solute is m_{solute} and the molar mass of the solvent is M_{m} then:

$$x_{\text{solute}} = \frac{m_{\text{solute}}}{\left[\left(\frac{1}{M_{\text{m}}}\right) + m_{\text{solute}}\right]} \approx m_{\text{solute}} \cdot M_{\text{m}} \tag{51.38}$$

so that:

$$\Delta T_{\mathrm{f}} \approx \left(\frac{m_{\mathrm{solute}} \cdot M_{\mathrm{m}} \cdot RT_{\mathrm{m}}^2}{\Delta_{\mathrm{fus}} H^o}\right) \tag{51.39}$$

or:

$$\Delta T_{\mathrm{f}} \approx K_{\mathrm{f}} \cdot m_{\mathrm{solute}} \tag{51.40}$$

where K_{f}, the cryoscopic constant is given by:

$$K_{\mathrm{f}} = \frac{M_{\mathrm{m}} \cdot RT_{\mathrm{m}}^2}{\Delta_{\mathrm{fus}} H^o} \tag{51.41}$$

Thus the depression of the freezing point, ΔT_{f}, of a liquid (molar mass, M_{m}, melting point, T_{m} and enthalpy of fusion, $\Delta_{\mathrm{fus}} H^o$ at 1 bar pressure) caused by addition of m_{solute} can be calculated using equation (51.37).

- OR, ALTERNATIVELY

Using the Gibbs–Helmholtz Equation (equation (46.8), Frame 46) denoting molar by '$_{\mathrm{m}}$' and pure substance by '*' strictly we should write:

$$\left(\partial\left[\frac{G_{\mathrm{m}}^*}{T}\right]\Big/\partial T\right)_{P,n} = \frac{-H_{\mathrm{m}}^*}{T^2} \tag{51.42}$$

For a small temperature difference, H_{m}^* can be assumed to be constant, and integration gives:

$$\frac{G_{\mathrm{m}}^*(T_1)}{T_1} - \frac{G_{\mathrm{m}}^*(T_2)}{T_2} = H_{\mathrm{m}}^*\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{51.43}$$

Consider now the equilibrium at temperature, T between solid solvent and solvent in a liquid solution

$$\begin{array}{ccc} \text{solvent (pure liquid)} & \overset{-\Delta_{\mathrm{fus}} H^o}{\rightarrow} & \text{solvent (pure solid)} \\ \mu_l(T) & & \mu_{\mathrm{s}}(T) \end{array} \tag{51.3}$$

Only the solvent will be considered, initially at least, so only the physical state (s or l) will be indicated.

$$\mu_{\mathrm{s}}(T) = \mu_{\mathrm{s}}^*(T) \tag{51.44}$$

using equation (39.3) Frame 39:

$$\mu_l(T) = \mu_l^*(T) + RT \ln a \tag{51.45}$$

and since $\mu_l(T) = \mu_{\mathrm{s}}(T)$ then:

$$R \ln a = \left(\frac{\mu_{\mathrm{s}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'} - \frac{\mu_{\mathrm{l}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'}\right) = \left(\frac{G_{\mathrm{s}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'}\right) - \left(\frac{G_{\mathrm{l}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'}\right) \tag{51.46}$$

For the special case of pure solvent equilibrium then $a = 1$, $\ln a = 0$ and $T = T_{\mathrm{m}}$:

$$0 = \left(\frac{G_{\mathrm{s}}^*(T_{\mathrm{m}})}{T_{\mathrm{m}}}\right) - \left(\frac{G_{\mathrm{l}}^*(T_{\mathrm{m}})}{T_{\mathrm{m}}}\right) \tag{51.47}$$

Subtracting equation (51.46) from (51.47) we have:

$$R \ln a = \left\{\left(\frac{G_{\mathrm{s}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'}\right) - \left(\frac{G_{\mathrm{s}}^*(T_{\mathrm{m}})}{T_{\mathrm{m}}}\right)\right\} - \left\{\left(\frac{G_{\mathrm{l}}^*(T_{\mathrm{m}}')}{T_{\mathrm{m}}'}\right) - \left(\frac{G_{\mathrm{l}}^*(T_{\mathrm{m}})}{T_{\mathrm{m}}}\right)\right\} \tag{51.48}$$

and using forms of equation (51.43) for both solid and liquid phases and since (compare equation (51.30)):

$$\left(\frac{1}{T_{\mathrm{m}}'} - \frac{1}{T_{\mathrm{m}}}\right) = (T_{\mathrm{m}} - T_{\mathrm{m}}')\big/T_{\mathrm{m}}T_{\mathrm{m}}' \approx \frac{\Delta T_{\mathrm{f}}}{T_{\mathrm{m}}^2} \tag{51.49}$$

then:

$$R \ln a = (H_{\mathrm{s}}^* - H_{\mathrm{l}}^*)\left(\frac{1}{T_{\mathrm{m}}'} - \frac{1}{T_{\mathrm{m}}}\right) = \frac{-\Delta_{\mathrm{fus}} H \cdot \Delta T_{\mathrm{f}}}{T_{\mathrm{m}}^2} \tag{51.50}$$

and since, adapting equation (51.33): $a \approx x_{\text{solvent}} = (1 - x_{\text{solute}})$:

$$x_{\text{solute}} = \frac{m_{\text{solute}}}{\left[\left(\frac{1}{M_{\text{m}}}\right) + m_{\text{solute}}\right]} \approx m_{\text{solute}} \cdot M_{\text{m}} \tag{51.51}$$

then: or

$$\Delta T_{\text{f}} \approx \left(\frac{m_{\text{solute}} \cdot M_{\text{m}} \cdot RT_{\text{m}}^2}{\Delta_{\text{fus}} H^o}\right) \tag{51.52}$$

which is identical to equation (51.39) above.

52. Colligative Properties: Elevation of the Boiling Point, by Addition of Solute to a Pure Liquid

52.1 Boiling Point Elevation, ΔT_b

We consider here the effect on the boiling point, T_b of a liquid of adding some solid (solute) to it. Figure 51.1 illustrates some relevant thermodynamic features relating to the addition of a solute to a pure liquid (solvent) to form a solution and the corresponding effect on the melting temperature, T_m and boiling temperature, T_b.

The process of *boiling* is defined as the phase change taking place when a *liquid is converted into a vapour* (*or gaseous state*).

$$\text{liquid} \overset{\text{BOILING}}{\rightarrow} \text{gas} \tag{52.1}$$

When a liquid the enthalpy change taking place is called the enthalpy of *vaporisation,* $\Delta_\mathrm{vap}H^o$. Thus the corresponding change is:

$$\text{solvent (liquid)} \underset{-\Delta_\mathrm{vap}G^o}{\overset{-\Delta_\mathrm{vap}H^o}{\rightarrow}} \text{solvent (vapour)} \tag{52.2}$$

The equilibrium (52.2) which exists after addition of the solute to the pure solvent is between the aqueous solution formed on dissolution and the solvent vapour produced on boiling:

$$\text{solution (liquid)} \rightarrow \text{solvent (vapour)} \tag{52.3}$$

is such that the chemical potentials are equal (Frame 35):

$$\mu^{(\text{solution})} = \mu^{(\text{solvent vapour})} \tag{52.4}$$

Also for an ideal solution we can write that:

$$\mu^{(\text{solution})} = \mu^{(\text{liquid solvent})} + RT \ln x_1 \tag{52.5}$$

where x_1 is the mole fraction of the solvent. Combining equations (52.4) and (52.5) we can write that:

$$\mu^{(\text{solvent vapour})} = \mu^{(\text{liquid solvent})} + RT \ln x_1 \tag{52.6}$$

From the above definition, the Gibbs energy and enthalpy of vaporisation, $\Delta_\mathrm{vap}G^o$ and $\Delta_\mathrm{vap}H^o$ respectively of the solvent at constant pressure are such that (for process 52.2):

$$-\Delta_\mathrm{vap}G^o = \mu^{(\text{solvent vapour})} - \mu^{(\text{liquid solvent})} \tag{52.7}$$

Also for an ideal vapour (Frame 34, equation (34.6)) we can write that:

$$\mu^{(\text{solvent vapour})} = \mu^o(\mathrm{g}) + RT \ln\left(\frac{P}{P^o}\right); \quad P^o = 1 \text{ bar} \tag{52.8}$$

where μ^o(g) is the chemical potential of the gas when the pressure is 1 bar, *which is the situation at the boiling point, T_b* (see Note 52.1) of course (Note: A liquid boils when its vapour pressure equals that of the surrounding atmosphere). Hence at the boiling point:

$$\mu^{(\text{solvent vapour})} = \mu^o(\mathrm{g}) \tag{52.9}$$

the second term in equation (52.8) becoming zero because:

$$P = P^o \tag{52.10}$$

Accordingly then, taking account of equation (52.7) that:

$$-\Delta_\mathrm{vap}G^o = [\mu^o(\mathrm{g}) - \mu^{(\text{liquid solvent})}] = RT \ln x_1 \tag{52.11}$$

Proceeding in an analogous fashion to that shown in detail (by two alternative approaches) in Frame 51, we can eventually arrive at the result that:

$$\Delta T_\mathrm{b} \approx \left(\frac{m_\text{solute} \cdot M_\mathrm{m} \cdot RT_\mathrm{b}^2}{\Delta_\mathrm{vap}H^o}\right) \tag{52.12}$$

or:

$$\Delta T_{\mathrm{b}} \approx K_{\mathrm{vap}} \cdot m_{\mathrm{solute}} \tag{52.13}$$

where K_{b}, the ebullioscopic constant is given by:

$$K_{\mathrm{b}}/\mathrm{K\,mol\ kg}^{-1} = \frac{M_{\mathrm{m}} \cdot RT_{\mathrm{m}}^{2}}{\Delta_{\mathrm{vap}} H^{o}} \tag{52.14}$$

Thus the elevation of the boiling point, ΔT_{b}, of a liquid (molar mass, M_{m}, boiling point, T_{b} and enthalpy of vaporisation, $\Delta_{\mathrm{vap}} H^{o}$ at 1 bar pressure) caused by addition of m_{solute} can be calculated using equation (52.12).

53. Colligative Properties: Osmotic Pressure, Π

53.1 Nature of Osmotic Pressure, Π

The nature of osmotic pressure is clearly indicated by Figure 53.1. Suppose:

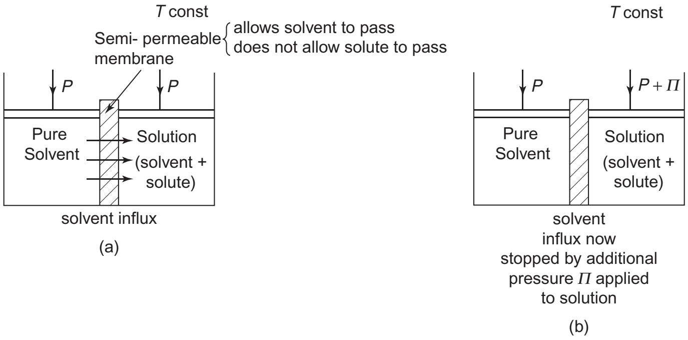


Figure 53.1 Osmotic Pressure.

- we separate a solution (solvent + solute) by means of a membrane from its own pure solvent;
- that the membrane is such that it allows solvent molecules to pass through itself but NOT solute molecules;
- if Figure 53.1(a) the pressure, P, exerted by a piston is the same on both solution and its solvent then (experimentally) solvent molecules will pass through the membrane (left to right) – a corresponding dilution thus results;

If in Figure 53.1(b) an additional pressure is exerted ($= \Pi$) on the solution (right-hand side) of the diagram then the influx of pure solvent into the solution (and the dilution process) is halted. This additional pressure is called *the osmotic pressure*.

53.2 Thermodynamic Treatment

Whilst on the left-hand side of the membrane the pressure on the solvent molecules is $= P$ on the right hand side (Figure 53.1) the pressure on the solvent molecules will be $(P + \Pi)$. This pressure is of course also applied to the solute molecules but thermodynamically this is not important. Since on exertion of the osmotic pressure, Π flow is halted and solvent molecules experience equilibrium their chemical potential in the two compartments must be equal, and hence:

$$\mu^{(\text{solvent})}\ (\text{LHS}) = \mu^{(\text{solvent})}\ (\text{RHS}) \tag{53.1}$$

In this example two factors are affecting the chemical potential of the solvent on the right-hand side, $\mu^{(\text{solvent})}$ (RHS):

- the pressure has been increased ;
- solute is also present

We already know how the presence of solute lowers the chemical potential of the solvent (by $RT \ln x$ in dilute solution) from the previous Frames 51 and 52 (e.g. equation (51.7)):

$$\mu^{(\text{solvent in solution})} = \mu^{(\text{solvent})} + RT \ln a \approx \mu^{(\text{solvent})} + RT \ln x \tag{53.2}$$

where x is the mole fraction of the solvent present and a is the activity.

Regarding the effect of pressure on a pure phase since (Frame 18, section 18.3 where in a detailed note the applicability of equation (53.3) is discussed at length (see Note 18.1)):

$$\mathrm{d}G_\mathrm{m} = V_\mathrm{m}\mathrm{d}P - S_\mathrm{m}\mathrm{d}T \tag{53.3}$$

where V_m is the molar volume of the solvent.

The change in molar Gibbs energy, $\mathrm{d}G_\mathrm{m}$ (and hence in chemical potential, $\mathrm{d}\mu$) when the temperature, T is held constant (so that: $\mathrm{d}T = 0$) and the pressure is changed from $P_\mathrm{i} = P$ to $P_\mathrm{f} = P + \Pi$ can be found by integration of equation (53.3)

$$\int \mathrm{d}G_\mathrm{m} = \int V_\mathrm{m}\mathrm{d}P = V_\mathrm{m} \int \mathrm{d}P \tag{53.4}$$

We can assume that the molar volume of the solvent will be essentially unaffected by the osmotic pressure difference since liquids are virtually incompressible then equation (53.4) leads to:

$$\Delta G_\mathrm{m} = \mu^{(\mathrm{solvent})} - \mu^{(\mathrm{solvent\ in\ solution})} = V_\mathrm{m} \int_{P}^{P+\Pi} \mathrm{d}P = V_\mathrm{m}[(P+\Pi)-(P)] = V_\mathrm{m} \cdot \Pi \tag{53.5}$$

but also from equation (53.2)

$$\mu^{(\mathrm{solvent})} - \mu^{(\mathrm{solvent\ in\ solution})} = -RT\ln a \tag{53.6}$$

so that:

$$V_\mathrm{m} \cdot \Pi = -RT\ln a \tag{53.7}$$

when the solution is dilute we can make a series of similar approximations to those made in Frames 51 and 52

$$a = x \tag{53.8}$$

$$\ln x = \ln x_\mathrm{solvent} = \ln(1 - x_\mathrm{solute}) \approx -x_\mathrm{solute} \tag{53.9}$$

$$x_\mathrm{solute} = \frac{n_\mathrm{solute}}{(n_\mathrm{solvent} + n_\mathrm{solute})} \tag{53.10}$$

so that (since n_solute is very small compared to n_solvent):

$$x_\mathrm{solute} \approx \frac{n_\mathrm{solute}}{n_\mathrm{solvent}} \tag{53.11}$$

$$n_\mathrm{solvent} \cdot V_\mathrm{m} = V = \text{total volume of solvent} \tag{53.12}$$

so that substituting into equation (53.7) the various forms above we have:

$$\left(\frac{V}{n_\mathrm{solvent}}\right) \cdot \Pi = -RT\left\{\frac{-n_\mathrm{solute}}{n_\mathrm{solvent}}\right\} \tag{53.13}$$

whereupon, cancelling the n_solvent terms in the denominator:

$$V \cdot \Pi = RT\{n_\mathrm{solute}\} \tag{53.14}$$

or osmotic pressure is given by:

$$\Pi = n_\mathrm{solute}\,\frac{RT}{V} \tag{53.15}$$

We can proceed from this point in two possible ways:

- Appoximating $V \approx V_\mathrm{solution}$ (in equation (53.12)) then:

$$\Pi = \frac{RT \cdot n_\mathrm{solute}}{V_\mathrm{solution}} = RT \cdot c = \frac{RT \cdot \mathrm{w}_\mathrm{solute}}{(\mathrm{M}_\mathrm{solute} \cdot V_\mathrm{solution})} \tag{53.16}$$

  where $c =$ concentration. Since $\mathrm{w}_\mathrm{solute}$, the mass of the solute is known then $\mathrm{M}_\mathrm{solute}$ is the only unknown.

- $$\Pi = \frac{RT \cdot n_\mathrm{solute} \cdot \rho_\mathrm{solvent}}{\mathrm{w}_\mathrm{solvent}} \tag{53.17}$$

  where ρ_solvent is the density of the solvent and

$$\frac{\mathrm{n}_\mathrm{solute}}{\mathrm{w}_\mathrm{solvent}} = m = \text{molality} \tag{53.18}$$

  so that:

$$\Pi = \frac{RT \cdot \mathrm{w}_\mathrm{solute} \cdot \rho_\mathrm{solvent}}{\mathrm{w}_\mathrm{solvent} \cdot \mathrm{M}_\mathrm{solute}} = RT \cdot \rho_\mathrm{solvent} \cdot m \tag{53.19}$$

These equations can be used for the measurement of the molar masses of proteins and of polymeric materials although strictly speaking equations (53.15) and (53.19) need to be expanded in order to apply to non-ideal situations.

54. Core Thermodynamic Relationships

It is timely, now, to summarise the many important thermodynamic links that exist between the key thermodynamic quantities we have discussed. This is done in Figure 54.1 which appears on the back cover.

54.1 Thermodynamic Links

Figure 54.1 (inside back cover) draws together these various interrelationships. From such a diagram one can, for example, identify *five* routes by which ΔG^o, the standard free energy change, for a reaction can be determined:

- from ΔH^o and ΔS^o by combination (Frames 10 and 13):

  $$\Delta G^o = \Delta H^o - T\Delta S^o \tag{13.10}$$

  where T is the absolute temperature of the reaction
- from equilibrium constant, K_a, data (Frames 40, 41, 45, 46):

  $$\Delta_r G^o = -RT \ln K_a \tag{41.12}$$

- from thermochemical tables (Frame 11):

  $$\Delta_r G^o = \sum \Delta_f G^o(\text{Products}) - \sum \Delta_f G^o(\text{Reactants}) \tag{41.13}$$

  in terms of stochiometric numbers, ν_i.
- by deriving coupled reactions (Frame 28), whose individual ΔG^o values, when added or subtracted, sum up to the target reaction for which ΔG^o is sought.
- from a study of electrochemical cells using:

  $$\Delta G^o = -nFE^o \tag{54.1}$$

  but paying careful attention to the influence of both n and E^o on the value of ΔG^o.

Appendix A: The Logarithmic Function in Thermodynamics

There is often considerable confusion about the use of equilibrium constants, K (Frames 39, 41, 42, 43, 45, 46, 47, 49) (and whether they have units or not) and indeed about the use of formulae (like that for chemical potential, μ, Frames 5, 27, 28, 29, 35, 37, 38 and 39) which contain logarithmic (Frames 6 and 36) terms. The importance of logarithmic terms as corrections for non-ideal behaviour has been referred to earlier (see section 39.3, Frame 39).

The purpose of this appendix is to explore and explain these misconceptions that students frequently exhibit by consideration of the following:

- should equilibrium constants, K, have units associated with them?
- what are the alternative ways of writing expressions for K?
- what notation should be used?
- what are the choices commonly made of standard states?
- when do we need to define standard states?
- how are the equations handled if the units of measurement (of say the pressure) do not correspond to the units chosen for standard state pressure?

A.1 Equilibrium Constants, *K*, Units and Notation

It is common, in textbooks (indeed in this one too (Frames 42, 46 and 49)) to see the equation:

$$\Delta G^o = -RT \ln K_{p/po} \tag{A.1}$$

where K_{p/p^o} represents the equilibrium constant written in terms of the partial pressures (indicated by subscript $_p$ placed on the K symbol) of the reactants and products of the relevant reaction.

However this is only one form of a similar suite of equations and another would be:

$$\Delta G^o = -RT \ln K_a \tag{A.2}$$

where K_a represents the equilibrium constant written this time in terms of activities (indicated by subscript $_a$ placed on the K symbol) of the reactants and products of the relevant reaction.

Let us consider first the question of units. As explained in Frame 6, section 6.3:

- we can only take logarithms (of any base – i.e. either natural ($\ln x$) or to base 10 ($\lg x$ or $\log_{10} x$)) of *dimensionless* quantities;
- thus if we have a pressure, P, measured in pascals (Pa) say, then it would be *incorrect* (indeed *meaningless*) to write: '$\ln P$'. This is because we are attempting to take the logarithm of a quantity, P, which has units (Pa) and is therefore *not* dimensionless.
- if, however, we have a ratio of two pressures: (P/P^o), where these pressures P and P^o are measured in *identical units* (say both in Pa, atm, bar, kPa, Torr, mmHg etc) then, whatever units are used, they cancel, leaving a pure number. Here the term: $\ln (P/P^o)$ is now meaningful and can be evaluated.

It follows from the above discussion then that equilibrium constants, K, being quantities of which we anticipate taking logarithms (as demanded by equations A1 and A2) must:

- be constructed such that they are *dimensionless*;

and

- have *no units* associated with them *in any circumstances*.

This means that if we have a reaction:

$$\mathrm{A(g) + B(g) \rightarrow C(g)} \tag{A.3}$$

and we know the partial pressures, p_A, p_B and p_C (Frames 31 and 40) of the gases A, B and C then writing the equilibrium constant in the form:

$$K_p = \frac{p_C}{p_A} \cdot p_B \tag{A.4}$$

will be an *unsatisfactory expression* for the equilibrium constant because whatever the units measurements of p_{A}, p_{B} and p_{C} are made in, the expression for K_p in equation (A.4) will have overall units of (pressure)$^{-1}$. Thus K_p is not dimensionless and is meaningless.

The problem is that we have to:

- maintain the same numerical magnitude for the equilibrium constant with respect to, say, pressure;

whilst at the same time

- ensuring that the quantity is a pure number so that logarithms can then be taken.

The solution to the problem lies in the following:

- define for this purpose an (arbitary) standard pressure, p^o equal to 1 pressure unit (e.g. $p^o = 1$ bar);
- in order to create a K value which is dimensionless, define the individual partial pressures p_{A}, p_{B} and p_{C} as ratios of this arbitrarily defined standard unit pressure, p^o for both reactants and products and so:
- write the equilibrium constant as:

$$K_{p/po} = \left[\left(\frac{p_{\mathrm{C}}}{p^o}\right)\Big/\left(\frac{p_{\mathrm{A}}}{p^o}\right)\cdot\left(\frac{p_{\mathrm{B}}}{p^o}\right)\right]; \quad p^o = \text{standard pressure} \tag{A.5}$$

In the expression (A.5):

- each of the ratio terms: (p_{A}/p^o), (p_{B}/p^o) and (p_{C}/p^o) is now (individually) dimensionless;
- the corresponding $\Delta_{\mathrm{r}}G^o$ – obtained via equation (41.12), Frame 41 – appertains to this standard pressure, p^o;
- the value does not differ numerically from the original terms: p_{A}, p_{B} and p_{C} making up K_p (because all that has happened is that we have divided each by 1 pressure unit and the units have cancelled provided, of course, that the partial pressures are expressed in the same unit as p^o. If this is not the case unit conversion may be necessary.

and also

- the entire expression for $K_{p/po}$ is numerically (although not dimensionally) equivalent to K_p;
- the expression $K_{p/po}$ is actually dimensionally equivalent to $K_p{\cdot}p^o$, since from equation (A5):

$$K_{p/po} = \left[\frac{(p_{\mathrm{C}})}{(p_{\mathrm{A}})\cdot(p_{\mathrm{B}})}\right]\cdot\left[\frac{(p^o)^2}{p^o)}\right] = \left[\frac{(p_{\mathrm{C}})}{(p_{\mathrm{A}})\cdot(p_{\mathrm{B}})}\right]\cdot[p^o]; \quad p^o = \text{standard pressure}; \tag{A.6}$$

then:

$$K_{p/po} = K_p \cdot p^o; \quad p^o = \text{standard pressure} \tag{A.7}$$

- however now we *are* able to take the logarithm of $K_{p/po}$ and it represents the true form necessary for this equilibrium constant.

We should also note that there is no call to define exactly what the standard pressure to be used is (i.e. $p^o = 1$ bar, 1 Pa, 1kPa, 1 torr, 1 mmHg, 1 atm etc) until we know what units the partial pressures to be used in our $K_{p/po}$ expression have been measured in.

We should further note (see Section 6.3, Frame 6):

- we can evaluate the dimensionless term, ln $(K_{p/po})$ and also evaluate the term: ln $(K_p{\cdot}p^o)$;
- we cannot however – despite the fact that: ln $(ab) = \ln a + \ln b$ (Frame 6, equation (6.10)) – split the term ln $(K_p{\cdot}p^o)$ into two as the sum of two logarithms and write:

$$\ln(K_p{\cdot}p^o) = \ln K_p + \ln p^o \tag{A.8}$$

because, as is seen from Table 6.1., both K_p and p^o are ‘illegal’ arguments for these two logarithmic expressions since when written singly, both have units.

A.2 Alternative Ways of Expressing Equilibrium Constants, K_p, K_c, K_m, and K_f

An alternative form of expressing $K_{p/po}$ could be the following. Once we know the units in which p_{A}, p_{B} and p_{C} are measured (say units of bar) then we could, equivalently to the above, write that:

$$K_{p/bar} = \left[\left(\frac{p_{\mathrm{C}}}{\mathrm{bar}}\right)\Big/\left(\frac{p_{\mathrm{A}}}{\mathrm{bar}}\right)\cdot\left(\frac{p_{\mathrm{B}}}{\mathrm{bar}}\right)\right]; \quad p^o = 1\ \text{bar} \tag{A.9}$$

where we have labelled the equilibrium constant as $K_{p/bar}$ instead of $K_{p/po}$. Here we have used the *unit* of p^o in equation (A.5) in place of p^o. In the equation (A.9) above, (p_{C}/bar) means ‘substitute for p_{C}, a pressure measured in bar’, say

$p_C = 0.8$ bar, then:

$$(p_C/\text{bar})^c = \left(\frac{0.8\text{ bar}}{\text{bar}}\right)^c = (0.8)^c \tag{A.10}$$

and thus once p_C is defined this leads to a pure number. This is repeated for the $(p_A/\text{bar})^a$, $(p_B/\text{bar})^b$ and $(p_D/\text{bar})^d$ terms, all of which also reduce to pure numbers and so, overall, $K_{p/bar}$ is also dimensionless and its logarithm can be taken. Its value will be the same as that forK_{p/p^o} defined by the formula (left-hand side) Figure A.1. and also defined in equation (A6)

Equivalently to equation (A7) we could write:

$$K_{p/bar} = \left[\frac{(p_C)}{(p_A)\cdot(p_B)}\right]\cdot(\text{bar}) = K_p\cdot(\text{bar}) \tag{A.11}$$

Figure A.1. displays the various forms of writing equilibrium constants involving pressure, concentration, molality, mole fractions and fugacity etc – for a general reaction of the form:

$$\text{aA(g)} + \text{bB(g)} \rightarrow \text{cC(g)} + \text{dD(g)} \tag{A.12}$$

Alternative forms could also be the following (not listed in Figure A.1):

$$K_{p/bar} = \left[\left(\frac{p_C}{\text{bar}}\right)^c\cdot\left(\frac{p_D}{\text{bar}}\right)^d \Big/ \left(\frac{p_A}{\text{bar}}\right)^a\cdot\left(\frac{p_B}{\text{bar}}\right)^b\right] = K_{p/po}; \quad p^o = 1\text{ bar} \tag{A.13}$$

or, if the units of p_A, p_B and p_C were atmospheres:

$$K_{p/atm} = \left[\left(\frac{p_C}{\text{atm}}\right)^c\cdot\left(\frac{p_D}{\text{atm}}\right)^d \Big/ \left(\frac{p_A}{\text{atm}}\right)^a\cdot\left(\frac{p_B}{\text{atm}}\right)^b\right] = K_{p/po}; \quad p^o = 1\text{ atm} \tag{A.14}$$

If instead of being measured in partial pressures the gaseous reactants, A and B and the products C and D were measured as concentrations, represented either as c or [ ] (the two measurements being related by equation (40.7), Frame 40, and typical units of concentration being mol dm^{-3}) we can then write the equilibrium constant either as $K_{c/co}$ or $K_{c/moldm-3}$ in any of the following forms, with c^o representing the standard concentration (which could for example be 1 mol dm^{-3}):

- $$\begin{aligned} K_{c/co} &= \left[\left(\frac{c_C}{c^o}\right)^c\cdot\left(\frac{c_D}{c^o}\right)^d \Big/ \left(\frac{c_A}{c^o}\right)^a\cdot\left(\frac{c_B}{c^o}\right)^b\right] \\ &= \left[\frac{(c_C)^c\cdot(c_D)^d}{(c_A)^a\cdot(c_B)^b}\right]\cdot(c^o)^{a+b-c-d} \\ &= K_c.(c^o)^{a+b-c-d} \quad c^o = \text{standard concentration} \end{aligned} \tag{A.15}$$

and the term K_c, (which would be an invalid form for the equilibrium constant) is given by:

$$K_{c/co} = \frac{[C]^c\cdot[D]^d}{[A]^a\cdot[B]^b} \tag{A.16}$$

By virtue of equation (40.7) for an ideal gas, Frame 40:

$$[i] = \frac{p_i}{RT} \tag{40.7}$$

where [i] represents the concentration of species i. Substitution in equation (A.15) for the concentrations, [A], [B], [C] and [D] and for standard concentration, c^o

$$c^o = \frac{p^o}{RT} \tag{A.17}$$

leads to:

$$\begin{aligned} K_{c/co} &= \left[\left(\frac{p_C}{p^o}\right)^c\cdot\left(\frac{p_D}{p^o}\right)^d \Big/ \left(\frac{p_A}{p^o}\right)^a\cdot\left(\frac{p_B}{p^o}\right)^b\right] \\ &= \left[\frac{(p_C)^c\cdot(p_D)^d}{(p_A)^a\cdot(p_B)^b}\right]\cdot\frac{(p^o)^{a+b-c-d}}{(RT)^{a+b-c-d}} \\ &= K_{p/po}\cdot(RT)^{c+d-a-b} \quad p^o = \text{any standard pressure} \end{aligned} \tag{A.18}$$

which gives the relationship between $K_{c/co}$ and $K_{p/po}$ at temperature T.

- $$\begin{aligned} K_{c/moldm-3} &= \left[\left(\frac{c_C}{\text{mol dm}^{-3}}\right)^c\cdot\left(\frac{c_D}{\text{mol dm}^{-3}}\right)^d \Big/ \left(\frac{c_A}{\text{mol dm}^{-3}}\right)^a\cdot\left(\frac{c_B}{\text{mol dm}^{-3}}\right)^b\right] \\ &= \left[\left(\frac{[C]}{\text{mol dm}^{-3}}\right)^c\cdot\left(\frac{[D]}{\text{mol dm}^{-3}}\right)^d \Big/ \left(\frac{[A]}{\text{mol dm}^{-3}}\right)^a\cdot\left(\frac{[B]}{\text{mol dm}^{-3}}\right)^b\right] \\ &= K_{c/c^o} \qquad c^\circ = 1\,\text{mol dm}^{-3} \end{aligned} \tag{A.19}$$

In the case where the gases in reaction (A.12) were non-ideal and fugacities, f_i (Frame 38) were used to represent their partial pressures then, typically the following forms could be written for the equilibrium constant, K_{f/p^o}:

- $$K_{f/bar} = \left[\left(\frac{f_C}{\text{bar}}\right)^c \cdot \left(\frac{f_D}{\text{bar}}\right)^d \Big/ \left(\frac{f_A}{\text{bar}}\right)^a \cdot \left(\frac{f_B}{\text{bar}}\right)^b\right] = K_{f/p^o}; \quad p^o = 1 \text{ bar} \tag{A.20}$$

or

- $$K_{f/p} = \left[\left(\frac{f_C}{p^o}\right)^c \cdot \left(\frac{f_D}{p^o}\right)^d \Big/ \left(\frac{f_A}{p^o}\right)^a \cdot \left(\frac{f_B}{p^o}\right)^b\right]; \quad p^o = \text{any standard pressure} \tag{A.21}$$

Here the standard state is defined as a pressure, p^o (equation (38.5) Frame 38) and not as a fugacity, f^o, since the latter corresponds to a correcting term for pressure.

If the reaction (A.12) took place in solution:

$$\text{aA (aq)} + \text{bB (aq)} \rightarrow \text{cC (aq)} + \text{dD (aq)} \tag{A.22}$$

and the individual molalities were represented by m_i, whilst defining a standard molality, m^o then typically the following forms could be written for the equilibrium constant, $K_{m/mo}$:

- $$K_{m/molkg-1} = \left[\left(\frac{m_C}{\text{mol kg}^{-1}}\right)^c \cdot \left(\frac{m_D}{\text{mol kg}^{-1}}\right)^d \Big/ \left(\frac{m_A}{\text{mol kg}^{-1}}\right)^a \cdot \left(\frac{m_B}{\text{mol kg}^{-1}}\right)^b\right] = K_{m/mo} \quad m^o = 1 \text{ mol kg}^{-1} \tag{A.23}$$

or

- $$K_{m/mo} = \left[\left(\frac{m_C}{m^o}\right)^c \cdot \left(\frac{m_D}{m^o}\right)^d \Big/ \left(\frac{m_A}{m^o}\right)^a \cdot \left(\frac{m_B}{m^o}\right)^b\right] \quad m^o = \text{standard molality} \tag{A.24}$$

or

- one can also use concentration-based K (i.e. $K_{c/co}$) in solutions.

A.3 Further Considerations

- **Reactions where the amounts of reactants equal those of the products**

  If we consider a reaction:

  $$\text{A(g)} + \text{B(g)} \rightarrow \text{C(g)} + \text{D(g)} \tag{A.25}$$

  for which:

  $$[\text{number of molecules of reactant}] = [\text{number of molecules of product}] \tag{A.26}$$

  in contrast to the reaction of the type of (A.3), where the condition (A.26) does *not* hold true. K_p for the above reaction takes the form:

  $$K_p = \left[\frac{p_C \cdot p_D}{p_A \cdot p_B}\right] \tag{A.27}$$

  and, irrespective of what pressure units are used to measure: p_A, p_B, p_C and p_D, the whole ratio in square brackets will be *dimensionless* and so ln K_p can be immediately evaluated and is meaningful ('legal' to write (Frame 6)). Therefore there is no need, in this specific case (and in the case of other reactions which obey condition (A.26)) to specify a standard pressure, p^o but one would probably retain the '^{o}' symbol for the associated $\Delta_r G^o$ for ideal gases or dilute solutions, $\Delta_r G^o$ does not then depend on the choice of p^o (c^o or m^o).

  Further we can also write $K_{p/po}$ for this reaction, if we prefer. Although, at first sight, this appears to involve a standard pressure, p^o, its actual value does not need to be specified – since it actually cancels out, so that:

  $$K_{p/po} = \left[\left(\frac{p_C}{p^o}\right) \cdot \left(\frac{p_D}{p^o}\right) \Big/ \left(\frac{p_A}{p^o}\right) \cdot \left(\frac{p_B}{p^o}\right)\right] = K_p \tag{A.28}$$

  This is true for the corresponding forms of $K_{c/co}$ and $K_{m/mo}$.
- **Equilibrium constant in terms of mole fractions, K_x**

  Since mole fraction, x, is a pure number (fraction) and has no units, the equilibrium constant, K_x is straightforwardly written as:

  $$K_x = \left[\frac{(x_C)^c \cdot (x_D)^d}{(x_A)^a \cdot (x_B)^b}\right] \tag{A.29}$$

  with no standard states involved.

Figure A.1. summarises the various forms of writing various equilibrium constant expressions: $K_{p/po}$, $K_{c/co}$, $K_{m/mo}$, $K_{f/po}$ and K_x for a general reaction of the form of (A.12) in the cases:

- where condition (A.26) holds (left-hand side of figure);

and

- where condition (A.26) does not hold (right-hand side of figure).

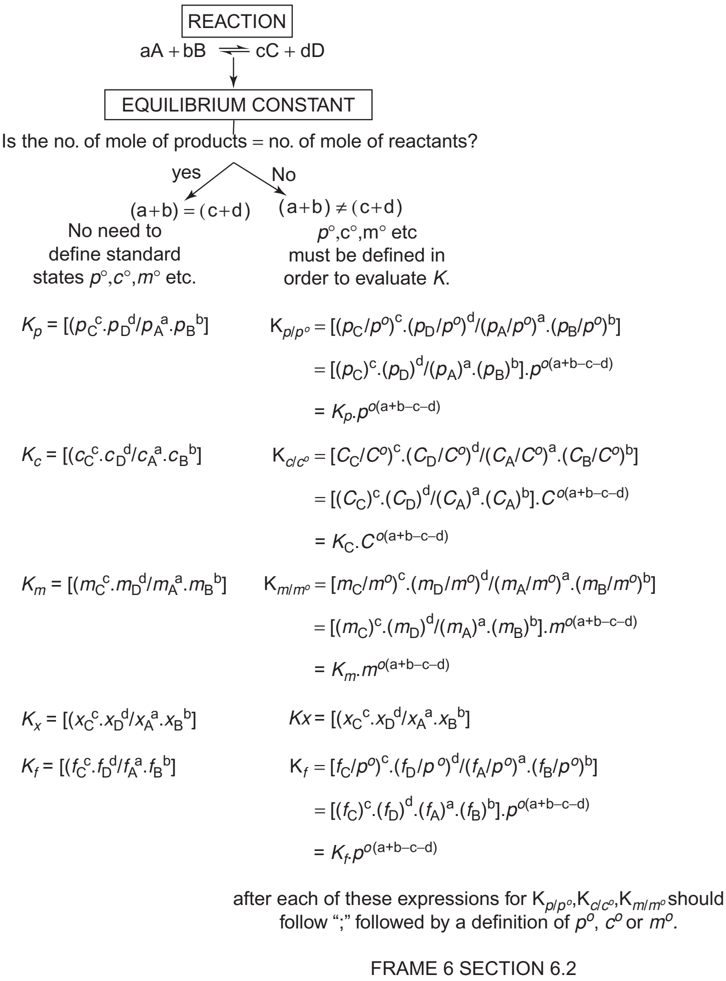


Figure A.1 Forms of writing Equilibrium Constants, *K*.

A.4 Standard Gibbs Energies, $\Delta_r G^o$

In respect of the standard Gibbs energies, $\Delta_r\ G^o$, as defined in equations (A.1) and (A.2), in the latter case K_a refers to an equilibrium constant written in terms of (dimensionless) activities, a, (Frame 39) such that:

$$K_a = \left(\frac{a_C}{a_A \cdot a_B}\right) \tag{A.30}$$

We should note that the value of a depends on the standard state (e.g. a_m (a in terms of molality),:

$$\mu = \mu^o + RT \ln a \tag{A.31}$$

with:

$$\mu^o = \lim_{m \to 0} \left[\mu - RT \ln\left(\frac{m}{m^o}\right)\right] \tag{A.32}$$

m^o as specified.

There is clearly no issue here (even though condition (A.26) does not apply):

- K_a is dimensionless;
- $\ln K_a$ is therefore defined (i.e. 'legal' as in Frame 6, Table 6.1);

In cases where activity is associated with concentration (equation 39.15) or molality (equation (39.17) Frame 39) measurements, the definition of the standard state is required before activity is truly defined. In the case of concentration this is usually 1 mol dm^{-3}, or in the case of molality, 1 mol kg^{-1} and so accordingly the corresponding ΔG^o values given in equation (A.2) will be defined with respect to these standard states.

Analogously, ΔG^o (equation A.1) needs p^o to be defined before $K_{p/po}$ can be evaluated and once this is done then ΔG^o corresponds to conditions where the standard pressure is equal to p^o.

A.5 The Effect of Changes in Standard State on K and ΔG^o

Suppose now that we have measured pressure experimentally in units of atmospheres but wish to calculate ΔG^o with reference to the more modern standard state of 1 bar. Let us suppose the reaction under consideration is (A.3). We can calculate that:

$$K_{p/po} = \left[\left(\frac{p_{\mathrm{C}}}{p^o}\right) \Big/ \left(\frac{p_{\mathrm{A}}}{p^o}\right) \cdot \left(\frac{p_{\mathrm{B}}}{p^o}\right)\right]; \quad p^o = 1 \text{ atm} \tag{A.33}$$

and this will be identical to the equilibrium constant written in the form:

$$K_{p/atm} = \left[\left(\frac{p_{\mathrm{C}}}{\mathrm{atm}}\right) \Big/ \left(\frac{p_{\mathrm{A}}}{\mathrm{atm}}\right) \cdot \left(\frac{p_{\mathrm{B}}}{\mathrm{atm}}\right)\right] = K_{p/po}; \quad p^o = 1 \text{ atm} \tag{A.34}$$

but, in order that ΔG^o is referred to 1 bar (and not 1 atm) we need to calculate:

$$\Delta G^o = -RT \ln K_{p/bar}; \quad p^{o'} = 1 \text{ bar} \tag{A.35}$$

where:

$$K_{p/bar} = \left[\left(\frac{p_{\mathrm{C}}}{p^{o'}}\right) \Big/ \left(\frac{p_{\mathrm{A}}}{p^{o'}}\right) \cdot \left(\frac{p_{\mathrm{B}}}{p^{o'}}\right)\right] = \left[\left(\frac{p_{\mathrm{C}}}{\mathrm{bar}}\right) \Big/ \left(\frac{p_{\mathrm{A}}}{\mathrm{bar}}\right) \cdot \left(\frac{p_{\mathrm{B}}}{\mathrm{bar}}\right)\right]; \quad p^{o'} = 1 \text{ bar} \tag{A.36}$$

In order to convert p (in atm) to p (in bar) we can write (employing dimensional calculus) that:

$$\left(\frac{p}{\mathrm{atm}}\right) = \left(\frac{p}{\mathrm{bar}}\right) \cdot \left(\frac{\mathrm{bar}}{\mathrm{atm}}\right) \tag{A.37}$$

Now:

$$1 \text{ atm} = 1.0325 \text{ bar} \tag{A.38}$$

so that:

$$\left(\frac{\mathrm{atm}}{\mathrm{bar}}\right) = 1.0325 \tag{A.39}$$

so that, taking reciprocals:

$$\left(\frac{\mathrm{bar}}{\mathrm{atm}}\right) = \frac{1}{1.0325} = 0.9685 \tag{A.40}$$

so that, substituting equation (A.40) into equation (A.37):

$$\left(\frac{p}{\mathrm{atm}}\right) = \left(\frac{\mathrm{bar}}{\mathrm{atm}}\right) \cdot \left(\frac{p}{\mathrm{bar}}\right) = 0.9685 \cdot \left(\frac{p}{\mathrm{bar}}\right) \tag{A.41}$$

and hence from equation (A.35):

$$\begin{aligned} K_{p/\mathrm{atm}} &= \left[\left(\frac{p_{\mathrm{C}}}{\mathrm{atm}}\right) \Big/ \left(\frac{p_{\mathrm{A}}}{\mathrm{atm}}\right) \cdot \left(\frac{p_{\mathrm{B}}}{\mathrm{atm}}\right)\right] \\ &= \left[0.9685 \cdot \left(\frac{p_{\mathrm{C}}}{\mathrm{bar}}\right) \Big/ 0.9685 \cdot \left(\frac{p_{\mathrm{A}}}{\mathrm{bar}}\right) \cdot 0.9685 \left(\frac{p_{\mathrm{B}}}{\mathrm{bar}}\right)\right] \\ &= \left[\left(\frac{p_{\mathrm{C}}}{\mathrm{bar}}\right) \Big/ 0.9685 \cdot \left(\frac{p_{\mathrm{A}}}{\mathrm{bar}}\right) \cdot \left(\frac{p_{\mathrm{B}}}{\mathrm{bar}}\right)\right] = 1.0325\, K_{p/bar} \end{aligned} \tag{A.42}$$

so that the equilibrium constant, $K_{p/atm}$ for the standard state appropriate to $p^o = 1$ atm is 1.0325 times larger than the equilibrium constant, $K_{p/bar}$ for the standard state appropriate to $p^o = 1$ bar. This is a minor difference of course.

We can now compare the difference of $[\Delta G^{o\prime} - \Delta G^o]$ or the difference of the Gibbs energy referred to the standard state of 1 bar ($\Delta G^{o'}$) and that for the standard state of 1 atm. (ΔG^o). Thus:

$$\begin{aligned} [\Delta G^{o'} - \Delta G^o] &= [(-RT \ln K_{p/bar}) - (-RT \ln K_{p/atm})] \\ &= [(-RT \ln K_{p/bar}) - (-RT \ln(1.0325 K_{p/bar})] \\ &= [(-RT \ln K_{p/bar}) - (-RT \ln(1.0325) - RT \ln K_{p/bar})] \\ &= [RT \ln(1.0325)] \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})(0.032) \\ &= 79.2 \text{ J mol}^{-1} = 0.08 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K} \end{aligned} \tag{A.43}$$

which illustrates the very minor difference that the change of state of p^o from 1 atmosphere to 1 bar actually makes in practice.

The approach above serves to illustrate how conversions could be made between other pairs of standard states.

A.6 Summary of Main Points in Appendix

- When ratios: p/p^o or $c/c^o (= [\,]/c^o)$ are used in equilibrium constants, strictly speaking K_p and K_c should be designated as $K_{p/po}$ and $K_{c/co}$ etc. Such convention is rarely used in text books but should be adopted in the author's view. The important point here is that whenever logarithmic expressions ($\log_{10}$ or ln) are employed they are only meaningful when the argument is dimensionless (Frame 6, Table 6.1);
- Textbooks give various versions of notation. This Appendix gives more precise coverage of the issue in relation to Equilibrium Constants (Frame 40 and beyond) and should be studied to aid the student's understanding and thus enable interpretation of the differing presentations made in the different textbook sources;
- Thus the notation $K_{p/po}$, $K_{c/co}$, and $K_{m/mo}$ discussed above would normally appear as merely K_p, K_c, and K_m and as regards formulae, forms such as:

$$\Delta G^o = -RT \ln K_p \tag{A.44}$$

$$\Delta G^o = -RT \ln K_{p/po} \tag{A.45}$$

$$\Delta G^o = -RT \ln K_{p/bar} \tag{A.46}$$

  are equivalent (if $p^o = 1$ bar in the case of equations (A.45) and (A.46)).

NOTES

Note 7.1 (inside front cover of book)

[a] Although thermodynamics does not rely on the nature of matter for its predictions, nevertheless it is sometimes helpful conceptually to think at the microscopic level in terms of individual particles of matter (e.g. atoms, molecules etc) in order to aid understanding of some features of the subject.

[b] Although thermodynamic prediction may declare a reaction to be "thermodynamically favourable" to proceed spontaneously (i.e. without external intervention) the reaction may not do so for kinetic reasons (e.g. it may just be too SLOW to proceed).

Note 11.1

[*] Data is traditionally provided at 1 atm pressure and tabulated numerical values can be assumed to apply at 1 bar pressure (the more recent standard adopted) also (see Frame 0).

[†] Temperature is not part of the definition of standard state, we can have standard states at any temperature

[‡] Note red phosphorus P is **not** selected as standard state.

Note 11.2

Alternatively, we can also use stoichiometric numbers (Frame 1, section 1.5) for complete chemical equations. If we label reactions (11.19), (11.20) and (11.21) as (a), (b) and (c) and denote their enthalpy changes as $\Delta_m H_a$ (= Δ_c^o(C, s, graphite)), $\Delta_m H_b$ (= $\Delta_c^o(H_2, g)$ and $\Delta_m H_b$ (= $\Delta_c H^o$ (CH_4, g)), respectively, then we can write equation (11.24) in the alternative form:

$$\Delta_r H^o = \upsilon_a \Delta_m H_a + \upsilon_b \Delta_m H_b + \upsilon_c \Delta_m H_c \qquad (11.25)$$

with:

$$\upsilon_a = +1; \quad \upsilon_b = +1 \quad \text{and} \quad \upsilon_c = -1 \qquad (11.26)$$

Note 13.1

The concept of a 'spontaneous reaction' may be a misnomer in general, although a 'spontaneous *process*' is a more appropriate concept. For (say) a kinetically feasible (closed system) isothermal (Frame 1) gas reaction:

$$A(g) \rightarrow B(g) \qquad (13.9)$$

we know that:

- A (g) will convert to some B(g) until the Gibbs energies (see Frames 1, 18, 20 and 21) or chemical potentials (see Frames 5, 26, 27, 28, 29 38, etc) become equal;
- Pure A(g) will not change completely to pure B(g);
- Pure B(g) will not stay as such, some will change back to A(g);

The progression to equilibrium could be regarded as a series of oscillatory reactions and in this sense it is not correct to say that reaction (13.10) is 'spontaneous'.

Note 14.1

Alternatively the surroundings being so vast could also be regarded as being at constant volume, so that any heat added q_v could be equated to the state function ΔU, the internal energy change taking place at constant volume. The important point here is that being equitable to a *state function change* (i.e. either ΔH or ΔU) must mean that the change is the *same* independently of whether the heat transfer from the surroundings is taking place *reversibly* or *irreversibly*. It also implies that the entropy change, as expected, is a state function also. Thus equation (13.15) applies equally well to irreversible changes also. In the latter case one merely 'imagines' that the irreversible process takes place reversibly.

Note 15.1

In Frame 4, as equation (4.2), equation (15.2) was established as a 'definition' of an ideal gas on the basis of the simplest qualitative argument and not by classical thermodynamic arguments. Just for the record we note here that the relationship can be established by the following route (which involves introduction of the Helmholtz free energy, A and use of the Maxwell

Relationships which are beyond the scope of this text):

$$P = \left(\frac{\partial A}{\partial V}\right)_{T,n} = \left(\frac{\partial U}{\partial V}\right)_{T,n} - T\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial U}{\partial V}\right)_{T,n} - T\left(\frac{\partial P}{\partial T}\right)_{V,n} \text{ (Maxwell)} \qquad (15.21)$$

so that:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -P + T\left(\frac{\partial P}{\partial T}\right)_{V,n} = 0 \text{ for an ideal gas} \qquad (15.22)$$

Note 15.2

The dependence of entropy change on volume at constant temperature, T, and chemical amount, n can also be shown using the Maxwell relationship. This avoids the consideration of the path-dependent quantities of heat, q, and work, w. Thus:

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} \quad \text{(Maxwell)} \qquad (15.23)$$

so that:

$$\Delta S = \int_{V_i}^{V_f}\left(\frac{\partial P}{\partial T}\right)_{V,n} \cdot \mathrm{d}V = nR\int_{V_i}^{V_f}\left(\frac{1}{V}\right) \cdot \mathrm{d}V \text{ for an ideal gas} = \mathrm{nR}\ \ln\left(\frac{\mathrm{V_f}}{\mathrm{V_i}}\right) = \mathrm{nR}\ \ln\left(\frac{\mathrm{P_i}}{\mathrm{P_f}}\right) \qquad (15.24)$$

so leading to the equation:

$$S = S^o + RT\ln\left(\frac{P}{P^o}\right) \qquad (15.25)$$

Note 17.1

In relation to Frame 6, section 6.3 it should be noted that W is a pure number and so is dimensionless so that logarithms can be legitimately taken in equation (17.1).

Note 17.2

Imagine three dipoles with *horizontal* arrows depicted: →→→, there will be:

$2 = 2^1$ possible arrangements of *one* dipole (i.e. → *and* ←);

$4 = 2^2$ possible arrangements of *two* dipoles (i.e. →→, →←, ←→ *and* ←←);

$8 = 2^3$ possible arrangements of *three* dipoles (i.e. →→→, →→←, →←→,

←→→, ←←→, ←→←, →←← *and* ←←←)

and hence for N dipoles there would be 2^N possible arrangements.

Note 18.1

It should be noted here that, as we shall see later (Frames 50 (section 50.1) and 53 (section 53.2)), the equation (18.9) in the form: $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$ is not universally true, the more general form is that given in equation (50.3) in Frame 50. For equation (18.9) to be true the following conditions are actually required:

- that (i) the system is closed (although not necessarily non-reactive);

and

- that there (ii) should be no other kind of work other than '*pV*' work (Frame 1, Frame 8, section 8.3 and Frame 9) to consider for the system.

and

- that (iii) the process, to which the equation (18.9) is applied, is fully reversible (i.e. mechanical, thermal and chemical)
- that (iv) in equation (50.3), Frame 50, all dn (same species in different phases if the system is multiphase or different species in the same phase) = 0. To expand on this condition provided that there is no work other than mechanical then later we shall see that:

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum \mu_\mathrm{i}\mathrm{d}n_\mathrm{i} \qquad (50.3)$$

where i represent the various individual phases of the system. For a pure phase (only one component) – signified by a '*' symbol, then:

$$\mathrm{d}G^* = V^*\mathrm{dP} - S^*\mathrm{d}T + \mu^*\mathrm{dn} = V^*\mathrm{dP} - S^*\mathrm{d}T + G^*_\mathrm{m}\mathrm{dn} \qquad (18.15)$$

We can define molar Gibbs energy and Gibbs energy, G^* for the pure phase divided by amount of material present (n):

$$G^*_{\text{m}} = \frac{G^*}{\text{n}} \tag{18.16}$$

so that:

$$G^* = G^*_{\text{m}}\text{n} \tag{18.17}$$

and so using the Product Rule (Table 3.1, Frame 3):

$$\text{d}G^* = \text{d}[G^*_{\text{m}}\text{n}] = G^*_{\text{m}}\cdot\text{dn} + \text{n}\cdot\text{d}G^*_{\text{m}} \tag{18.18}$$

so that:

$$\text{d}[G^*_{\text{m}}\text{n}] - G^*_{\text{m}}\cdot\text{dn} = \text{n}\cdot\text{d}G^*_{\text{m}} \tag{18.19}$$

and from equations (18.16) and (18.18):

$$\text{d}G^* - G^*_{\text{m}}\text{dn} = V^*\text{dP} - S^*\text{d}T = \text{n}\cdot\text{d}G^*_{\text{m}} \tag{18.20}$$

so that:

$$\text{d}G^*_{\text{m}} = \left(\frac{V^*}{\text{n}}\right)\cdot\text{dP} - \left(\frac{S^*}{\text{n}}\right)\cdot\text{d}T = V^*_{\text{m}}\text{dP} - S^*_{\text{m}}\text{d}T \tag{18.21}$$

More generally (see later Frame 27), because Gibbs energy is a function of state and because a state is defined by temperature, T, pressure, P, and chemical amounts, n_{i}:

$$\begin{aligned}\text{d}G &= \left(\frac{\partial G}{\partial T}\right)_{P,\,all\,ni}\cdot\text{d}T + \left(\frac{\partial G}{\partial P}\right)_{T,\,all\,ni}\cdot\text{d}P + \sum_i\left(\frac{\partial G}{\partial n_{\text{i}}}\right)_{P,\,T,\,ni\neq i}\cdot\text{d}n_{\text{i}}\\ &= \left(\frac{\partial G}{\partial T}\right)_{P,\,all\,ni}\cdot\text{d}T + \left(\frac{\partial G}{\partial P}\right)_{T,\,all\,ni}\cdot\text{d}P + \sum_i u_{\text{i}}\cdot\text{d}n_{\text{i}} \qquad \text{(by definition of } \mu_{\text{i}})\end{aligned} \tag{18.22}$$

and this equation can, because of its generality, be applied to the restricted case above, leading to:

$$\left(\frac{\partial G}{\partial T}\right)_{P,\,all\,ni} = -S; \quad \left(\frac{\partial G}{\partial P}\right)_{T,\,all\,ni} = V; \quad \sum_i \mu_{\text{i}}\cdot\text{d}n_{\text{i}} = 0 \tag{18.23}$$

However, the first two relationships in equation (18.23) are in fact *generally* true, *e.g.*, a graph of G against T (both state functions) at constant P and all n_{i} is not related to the way T is changed. The right-hand relationship in (18.23) is however restricted by (i), (ii) and (iii) above – importantly, it leads to:

- constancy of μ for a common component in phase equilibria;
- $\sum_i \nu_i\mu_i = 0$ for chemical equilibria.

But, *in general*, equation (18.10) in the form: $\text{d}G = -S\text{d}T + V\text{d}P + \sum_i \mu_i\text{d}n_i$ reduces:

- to $\text{d}G_{\text{m}} = -S_{\text{m}}\text{d}T + V_{\text{m}}\text{d}P$ *only for a one-component phase* (*open or closed*) as is shown above.

Note 26.1

Strictly speaking (Frame 6 and Appendix) equation (26.10) should not contain the illegal 'ln P' term but should be written either as ln kP where k is a constant having dimensions of [PRESSURE]$^{-1}$ or else as ln (P/P^o) or as ln (P/bar) etc. to ensure that the argument of the logarithm is dimensionless. However k would cancel at the stage of reaching equation (26.11)

Note 26.2

Note: *negative sign* in front of $\Delta_{\text{vap}}H^o/R$ term here.

Note 26.3

The so-called *normal* boiling point of a liquid is for 1 atm pressure, but it could be redefined here at being at 1 bar if we wished.

Note 27.1

An alternative approach which could be adopted to treat both physical and chemical equilibria is to consider

- the ‘completely general’ (open or closed; reversible or irreversible change, provided only ‘PV’ work is done) equation:

$$dG = -SdT + VdP + \sum_{i} \mu_i \cdot dn_i \tag{27.29}$$

  as starting point with the:
- restricted (closed system, PV work only, change completely reversible (= near equilibrium) for which $\sum \mu_i \cdot dn_i = 0$

$$dG = -SdT + VdP \tag{27.30}$$

  being the result of the fact that:

$$\sum \mu_i \cdot dn_i (= dG(T, P)) = \{\sum_{i} \upsilon_i \cdot dn_i\} \cdot d\xi = 0 \text{ so that} \sum_{i} \mu_i \cdot dn_i = 0 \tag{27.31}$$

Note 29.1 Alternative Approach

As is so often the case in thermodynamics one can look at a given problem slightly differently and achieve a similar result. Thus, as an example, if we recognised that for a spontaneous process, then:

$$dG < 0 \tag{29.30}$$

and so equation (29.6) leads to:

$$\sum_{i=1}^{n} \mu_i \cdot dn_i < 0 \tag{29.31}$$

Thus for a system consisting of just two phases, A and B, which is closed (i.e. nothing can be transferred from outside the system, although transfer can take place internally between the phases) and containing *one species of material* then we can reduce equation (29.31) to:

$$\mu_A \cdot dn_A + \mu_B \cdot dn_B < 0 \tag{29.32}$$

Furthermore if the material is lost from phase A, it is gained by phase B and vice versa so that:

$$dn_A = -dn_B \tag{29.33}$$

so that condition (29.32) becomes:

$$(\mu_A - \mu_B) \cdot dn_A < 0 \tag{29.34}$$

Suppose that the chemical potential of the material when present in phase A, μ_A is larger than when the material is present in phase B, μ_B:

$$\mu_A > \mu_B \tag{29.35}$$

then in order for condition (29.32) to be true:

$$dn_A(= -dn_B) < 0 \tag{29.36}$$

in other words material will *spontaneously* be transferred out (hence dn_A is negative) of phase A – the phase with the higher chemical potential – and move into the phase (B) in which its chemical potential, μ_B will then be lower. This process will continue until the chemical potential of the material is the same in both phase A and phase B, when, in general:

$$\sum_{i=1}^{n} \mu_i \cdot dn_i = 0 \tag{29.37}$$

and the Gibbs energy change is then zero and equilibrium is reached.

In summary then a material will move spontaneously from a higher to a lower chemical potential in order to establish equilibrium.

Note 30.2

Percentages are similar except that they add up to 100 (instead of 1). Thus if we defined the various components in terms of their weight percent = % age of component 1 present in mixture, then we would only need to define this for $(c - 1)$ of the components since {weight % for component c} = {100 – [sum of weight percentages of components 1 to $(c - 1)$}. The same is of course true when we use mole fractions.

Note 34.1

Cross multiplying the outer terms of equation (34.11) leads to:

$$y_A[P_B^* + x_A(P_A^* - P_B^*)] = x_A P_A^* \tag{34.23}$$

and hence:

$$y_A P_B^* = x_A[P_A^* - (P_A^* - P_B^*)y_A] \tag{34.24}$$

so that:

$$x_A = \frac{y_A P_B^*}{[P_A^* - (P_A^* - P_B^*)y_A]} \tag{34.12}$$

Note 34.2

Arranging terms on the right-hand side of equation (34.13) over a common denominator:

$$P = \frac{\{P_B^*[P_A^* - y_A(P_A^* - P_B^*)] + y_A P_B^*(P_A^* - P_B^*)\}}{[P_A^* - y_A(P_A^* - P_B^*)]} \tag{34.26}$$

leads to:

$$P = \frac{\{P_B^* P_A^* - y_A P_A^* + y_A P_B^* + y_A P_B^* P_A^* - y_A P_B^*\}}{[P_A^* - y_A(P_A^* - P_B^*)]} \tag{34.27}$$

giving:

$$P = \frac{P_B^* P_A^*}{[P_A^* - y_A(P_A^* - P_B^*)]} \tag{34.28}$$

Note 40.1

If the student is in need of further information here, Appendix A provides a complete discussion of the issues involved.

Note 40.2

In many text books this same equilibrium constant may well be denoted as K_c and is sometimes written down as being equal to:

$$K_c = \frac{\{([\mathrm{C}])^{\mathrm{c}}([\mathrm{D}])^{\mathrm{d}}\}}{\{([\mathrm{A}])^{\mathrm{a}}([\mathrm{B}])^{\mathrm{b}}\}} \tag{40.4}$$

However this is incorrect and is misleading since [A], [B], [C] and [D] represent concentrations and each term has an individual unit. Then for K_c evaluating expression (40.4) would then lead us to a value for K_c which would have units (after substitution of the concentrations in the expression) of $[\text{concentration}]^{\mathrm{c+d-a-b}}$. To avoid this, if we assume that the units to be used for concentration are mol dm^{-3} a correct form of equation (40.4) would be to write:

$$K_{c/co} = \left\{\left(\frac{[\mathrm{C}]}{\mathrm{c^o}}\right)^{\mathrm{c}}\left(\frac{[\mathrm{D}]}{\mathrm{c^o}}\right)^{\mathrm{d}}\right\} \Big/ \left\{\left(\frac{[\mathrm{A}]}{\mathrm{c^o}}\right)^{\mathrm{a}}\left(\frac{[\mathrm{B}]}{\mathrm{c^o}}\right)^{\mathrm{b}}\right\}; \quad c^o = 1\ \mathrm{mol\ dm^{-3}} \tag{40.15}$$

Note 41.1

Most of the time we will be dealing with reactions at (near) atmospheric pressure, in units of bar (1 bar = 100 kPa 10^5 Pa) and for which the standard pressure, $P = P^o = 1$ bar. In older textbooks pressure in atmospheres is employed, where $P = P^o = 1$ atm (1 atm = 1.013×10^5 Pa) but the principles above remain the same whichever standard is used.

In connection with a change in standard pressure from 1 bar with a standard chemical potential denoted as μ_i^{o1} to 101.325 Pa or 1 atm with a standard chemical potential denoted by μ_i^{o2} then:

$$\Delta_r G^{o2} = \sum \upsilon_i \mu_i^{o2} = \sum \upsilon_i(\mu_i^{o1} + RT\ln(1.01325) = \Delta_r G^{o1} + RT\ln(1.01325\sum \upsilon_i) = \Delta_r G^{o1} + RT\ln(1.01325) \tag{41.24}$$

where $\Sigma\upsilon_i$ is the so-called stoichiometric sum (Frame 1) = (c + d − a − b) in equation (41.1). If we are concenred only with formation reactions then sub-r ($_r$) can be replaced by sub-f ($_f$). $R\ln(1.01325) = 0.109$ J K^{-1} mol^{-1} which makes the magnitude of $RT\ln(1.01325) \approx 30$ J mol^{-1} = 0.03 kJ mol^{-1} at 'ordinary' temperatures which is neither here nor there.

Note 41.2

For a fuller discussion of the notation see Appendix. In many textbooks $K_{p/po}$ in our equation (41.12) is simply written as K_p. The notation used in this text is preferred by the author since it is:

- more informative about the nature of the terms used to construct the equilibrium constant;

and is

- more consistent with the nature of logarithmic arguments (Frame 6, section 6,3).

Note 43.1

Equation (43.8) could, of course, be derived more directly from $\Delta G^o = -RT\ln K_a$ but it was felt more informative to take the longer route here.

Note 43.2

In equation (43.9) the two activity coefficients, γ_i are generally different and are often symbolised by γ_c and γ_m so that a more general representation of equation (43.9) would be to write:

$$a_i = \gamma_c\left(\frac{c_i}{c^o}\right) = \gamma_m\left(\frac{m_i}{m^o}\right)^*;\quad c^o = 1\text{ mol dm}^{-3};\quad m^o = 1\text{ mol kg}^{-1} \tag{43.19}$$

It is true however that both γ_c and γ_m become 1 for ideal dilute solutions. For aqueous solutions at common ambient temperatures they are similar:

$$\lim \gamma_c = \mu - \lim\limits_{m\to 0}\left[\mu - RT\ln\left(\frac{c}{c^o}\right)\right] - RT\ln\left(\frac{c}{c^o}\right) \tag{43.20}$$

$$\lim \gamma_m = \mu - \lim\limits_{m\to 0}\left[\mu - RT\ln\left(\frac{m}{m^o}\right)\right] - RT\ln\left(\frac{m}{m^o}\right) \tag{43.21}$$

Since γ_c and γ_m are independent of the standard molality/concentration choices. If we (arbitrarily) choose that $m^o =$ 1 mol kg^{-1} and $c^o = 1$ mol dm^{-3} then for aqueous solutions $\text{m/m}^o \approx \text{c/c}^o$ making the two very nearly equal.

Note 46.1

Some texts refer to this equation (46.12) as the van't Hoff Isochore (Frame 1) (but there is no constancy of volume involved) .

Note 46.2

The *van't Hoff Equation* can also be written in the form:

$$\left(\frac{1}{K_{p/po}}\right)\cdot\frac{\mathrm{d}K_{p/po}}{\mathrm{dT}} = \frac{\Delta H}{RT^2} \tag{46.29}$$

Note 46.3

If ΔH^o is *not* constant over the temperature range T_1 to T_2 however we would have to retain the ΔH^o term *within* the integral and express ΔH^o as a function of temperature – typically this might take the form:

$$\Delta H^o = f(T) = \Delta H^o_{298} + a\cdot T + {}^1\!/_2 b\cdot T^2 + c/T + 1/3d\cdot T^{3+}\ldots.\text{etc.}$$

where a, b, c and d are constants and treated in a similar fashion to that when integrating C_p in Frame 2.

Note 49.1

An alternative treatment could be as follows: For reaction (45.23):

$$K_{p/po} = \left(\frac{p_X}{P^o}\right)^2 \Big/ \left(\frac{p_{X2}}{P^o}\right) = \frac{(p_X)^2}{(p_{X2}\cdot P^o)} \tag{49.12}$$

with:

$$p_{X2} = x_{X2}\cdot P = (1 - x_X)\cdot P \tag{49.13}$$

and:

$$p_X = x_X\cdot P \tag{49.14}$$

where $P =$ total pressure so that:

$$K_{p/po} = \left(\frac{x_X\cdot P}{P^o}\right)^2 \Big/ \left(\frac{(1 - x_X)\cdot P}{P^o}\right) \tag{49.15}$$

and therefore:

$$x_X^2 + \frac{P^o\cdot K_{p/po}}{P\cdot x_X} - \frac{P^o\cdot K_{p/po}}{P} = 0 \tag{49.16}$$

and solving the quadratic equation in x_x (Frame 6):

$$x_X = {}^1\!/_2\left[\frac{-P^o\cdot K_{p/po}}{P} + \left\{P^{o2}\cdot\left(\frac{K_{p/po}}{P}\right)^2 + \frac{4\cdot P^o\cdot K_{p/po}}{P}\right\}^{1/2}\right] \tag{49.17}$$

a function of the fixed $K_{p/po}$ and the chosen total pressure P/P^o.

Note 52.1

This is not precisely true, a liquid boils when its vapour pressure equals that of the surrounding atmosphere (i.e. when its vapour pressure = 1 atm – and not 1 bar). However these pressures are so closely similar that the distinction becomes unimportant. One can have boiling points at other pressures, of course, at 1 atm. We usually speak of the *normal* boiling point.

Appendix 1

Cancellation: $0.1\ \text{bar}/1\ \text{bar} = 0.1;\quad 10000\ \text{Pa}/100000\text{Pa} = 0.1$ (A.47)

Unit conversion: $10000\ \text{Pa}/1\text{bar} = 10000\ \text{Pa bar}^{-1} = 10000\text{Pa}\ (100000\text{Pa})^{-1} = 0.1$ (A.48)

It does not matter what units partial pressures are expressed in. Neither does it matter, *once the standard pressure p^o has been decided*, what units p^o is expressed in. For example p^o could be 1 bar, but if expressed as 100 kPa this is still the same. Taking equation (A4) as an example, with all partial pressures expressed in 1 atm (say) and $p^o = 1$ bar, we have:

$$K_p = \frac{p_C}{p_A\cdot p_B} \tag{A.4}$$

so that:

$$K_{p/po} = \frac{p_C\cdot p^o}{p_A\cdot p_B} \tag{A.49}$$

and

$$\begin{aligned}K_{p/po} &= \frac{p_C\cdot p^o}{p_A\cdot p_B} = \frac{(1\ \text{atm})\cdot(1\ \text{bar})}{(1\ \text{atm})\cdot(1\ \text{atm})}\\ &= 1\ \text{bar atm}^{-1} = (1\ \text{bar})\cdot(1.01325\ \text{bar})^{-1} = \frac{1}{1.01325} = 0.98692\end{aligned} \tag{A.50}$$

or

$$\begin{aligned}K_{p/po} &= \frac{p_C\cdot p^o}{p_A\cdot p_B} = \frac{(1.01325\ \text{bar})\cdot(1\ \text{bar})}{(1.01325\ \text{bar})\cdot(1.01325\ \text{bar})}\\ &= \frac{1}{1.01325} = 0.98692\end{aligned} \tag{A.51}$$

or

$$\begin{aligned}K_{p/po} &= \frac{p_C\cdot p^o}{p_A\cdot p_B} = \frac{(760\ \text{Torr})\cdot(1\ \text{bar})}{(760\ \text{Torr})\cdot(760\ \text{Torr})}\\ &= \left(\frac{1}{760}\right)\ \text{bar Torr}^{-1} = \left(\frac{1}{760\ \text{bar}}\right)\cdot\left(\frac{1.01325}{760\ \text{bar}}\right)^{-1} = \frac{1}{1.01325} = 0.98692\end{aligned} \tag{A.52}$$

so that once you have decided on p^o you always get the same final value for the equilibrium constant ($K_{p/po}$) – although unit conversion is necessary to evaluate it.

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