Chapter 2 Chemical Thermodynamics

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Problems

2.1   Applications of Thermodynamics to Light-Water Reactor Materials

It is generally recognized that material failure limits both the maximum burnup attainable by LWR fuel and the lifetime of structural alloys in and around the core. The processes that affect the behavior of these materials are both equilibrium and nonequilibrium; or, processes exhibit both thermodynamic and kinetic aspects. The nonequilibrium kinetic features are dominant in cladding corrosion by the coolant and production of defects in metals by irradiation. In other processes, thermodynamic properties either completely dictate the nature of the response of the materials to reactor conditions or control the driving force for kinetic steps. Thermodynamics plays a particularly important role in the following:

- Pressure-temperature-volume properties (equations of state): water, fuel, fission gas
- Vapor pressures: fuel, coolant, fission products
- Thermal properties: specific heat capacity; coefficient of thermal expansion
- Phase diagrams; single component and binary
- Chemical and physical state of fission products in fuel
- Hydrides in cladding and nitrides in steel
- Corrosion of metals and alloys
- Response of the O/U ratio in nonstoichiometric uranium dioxide to the oxygen pressure of the environment
- Thermal stability of point defects in solids
- Corrosion of cladding by steam

This chapter is devoted to a brief review of chemical thermodynamics that is intended to serve as the basis of applications encountered in subsequent chapters.

2.2 Thermodynamics

2.2.1 Basic Properties
Thermodynamic properties depend only on the state or condition of the system but not on the process or the path by which the particular state was achieved. Five fundamental thermodynamic properties cannot be derived from other thermodynamic properties. These are, with their common symbols:

T = temperature
p = hydrostatic pressure
V = volume
U = internal energy
S = entropy

In addition, there are two derived thermodynamic properties that are combinations of the primitive properties:

$$H = U + pV = \text{enthalpy} \tag{2.1a}$$
$$G = H - TS = \text{Gibbs energy} \tag{2.1b}$$

These particular combinations of fundamental properties define new properties that describe commonly encountered processes. For example, when pressure and temperature are fixed, thermodynamic equilibrium is achieved when the Gibbs energy of a closed system is a minimum. With the same constraints, the heat absorbed or evolved in a chemical reaction is the change in enthalpy.

The basic thermodynamic properties can be classified as *intensive* or *extensive*. An intensive property is independent of the quantity of substance. Temperature and pressure, for example, are intensive properties. All of the others (except T) are extensive can be made intensive by dividing by the quantity of the substance. Taking the number of moles, n, as the measure of quantity, the intensive counterparts of V,.....G are v = V/n, …. g = G/n. For these quantities, lower-case designations denote *specific*, or *molar* values of the property. The molar volume v is the reciprocal of the molar density.

Other thermodynamic properties are defined as partial derivatives of one of the properties with respect to temperature or pressure. The heat capacities:

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V \qquad\qquad C_P = \left(\frac{\partial h}{\partial T}\right)_p \tag{2.2}$$

represent the increases in internal energy and enthalpy, respectively, per degree of temperature increase. They are written as partial derivatives because of the constraints indicated by the subscripts on the derivatives. For C_V, the increase in temperature is required to occur at a fixed volume. For C_p, on the other hand, the pressure is maintained constant during the increase in temperature.

The *coefficient of thermal expansion* α and the *coefficient of compressibility* β involve the fractional changes in volume as temperature or pressure is increased:

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad\qquad \beta = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \tag{2.3}$$

Since the specific volume (or reciprocal of mass density)of a substance depends on both temperature and pressure, α and β are defined as partial derivatives in order to indicate the property that is held constant during the increase of the other property. Both α and β are positive numbers, which accounts for the negative sign in the definition of β.

Four of the basic properties have absolute values: T, p, v, and s. Assignment of zero entropy to crystalline solids at 0 K is a consequence of the 3rd law of thermodynamics. The energy-like properties u, h and g are relative. Any one of them may be given an arbitrary value at a *standard state* (e.g., specified pressure and temperature).

To a good approximation, the internal energy and the enthalpy of both gases and condensed phases (liquids and solids) are nearly independent of pressure (or volume). This simplification permits Eq (2.2) to be integrated:

$$u(T) - u(T_o) = \int_{T_o}^{T} C_V(T')dT' \cong C_V(T - T_o) \tag{2.4}$$

$$h(T) - h(T_o) = \int_{T_o}^{T} C_P(T')dT' \cong C_P(T - T_o) \tag{2.5}$$

where T_o is an arbitrary reference temperature (usually 298 K) and T' is the variable of integration (any letter would do). The second equalities in Eqs (2.4) and (2.5) follow from the commonly-employed approximation of temperature-independent specific heats.

Other important properties of pure (i.e., one-component) substances are the enthalpy changes that accompany phase changes. For the solid-liquid transition, the molar enthalpy of melting, or fusion, is:

$$\Delta h_M = h_L - h_S \tag{2.6}$$

where h_L and h_S are the molar enthalpies of the liquid and solid phases, respectively. Conversion of a liquid to its vapor is characterized by the enthalpy of vaporization:

$$\Delta h_{vap} = h_g - h_L \tag{2.7}$$

These molar enthalpy changes are measured by the heat absorbed as the phase with the lower enthalpy is converted to the phase with the higher enthalpy. Consequently, Δh_M and Δh_{vap} are positive quantities.

Relations similar to Eqs (2.6) and (2.7) can be written for all types of phase transitions. Of particular importance are the transformations of crystalline solids from one type of crystal structure to another type.

2.2.2 Heat and work

The concepts of heat and work are fundamentally different from the properties of a material. *Heat*, in particular, is often confused with the thermodynamic properties temperature and internal energy. It is neither. To say that a body (or system) contains a certain quantity of heat is incorrect; the body or system possesses internal energy. Heat appears as this energy crosses the system's boundary in the form of conduction, convection, or radiation.

Work is a term for forms of energy transfer that have in common that they are not heat but are in principle completely interconvertible among themselves. The most common form of work is that produced by a force F acting over a distance ΔX, which represents displacement of the system boundary. This action involves a quantity of work given by $W = F\Delta X$. If we multiply ΔX by A, the area over which the force acts, and divide F by A, the work equation becomes $W = (F/A)(A\Delta X)$. Since F/A defines pressure p, and since the product $A\Delta X$ is the volume change ΔV, the work involved can also be written as $W = p\Delta V$. This form of mechanical work done on (or by) the system is called "pV" work.

Another common form of mechanical work is *shaft* work, by which a system exchanges work with its surroundings by means of rotational motion rather than expansion or contraction, as in the pV form. For example, shaft work is performed as high-pressure steam spins a turbine in an electric power plant. A third form of work is *electrical* work, which is best exemplified by a battery that runs a motor by means of the electrical current generated by a chemical reaction. These non-pV forms of work are known collectively as *external work*, denoted by W_{ext}.

2.2.3 Thermodynamic laws

The *First law of thermodynamics* is an empirical observation, never refuted, that the change in the internal energy of a closed system resulting from addition of heat and performance of work is given by:

$$\Delta U = Q - W \tag{2.8}$$

where

$\Delta U = U(\text{final}) - U(\text{initial}) = $ change in system internal energy
$Q = $ heat added *to* the system
$W = $ work done *by* the system

Equation (2.8) applies to a *closed system*, which is a region of space whose boundaries enclose the substance characterized by the properties such as T and p (heat and work are *not* properties of a system). The material outside of the system boundaries is called the *surroundings*. The law of energy conservation states that the sum of the energy changes of the system (ΔU) and surroundings (ΔU_{surr}) is a constant:

$$\Delta U + \Delta U_{surr} = 0 \tag{2.9}$$

For simplicity, potential and kinetic energies have been neglected. U refers to the system.

In the microscopic view of thermodynamics, entropy characterizes the state of disorder of a system. Consequently, entropy changes are closely related to heat, but are not associated with work. The connection of heat and entropy is embodied in the following statement of the Second Law:

$$\Delta S \geq \int \left(\frac{Q}{T} \right) \tag{2.10}$$

where ΔS and the integral represent changes from an initial state to a final state. The equality in Eq (2.10) applies if the process is *reversible* (i.e. one that can be made to go backward without any change in the system or the surroundings).

The total entropy change of the system (ΔS) and the surroundings (ΔS_{surr}) is:

$$\Delta S + \Delta S_{surr} \geq 0 \tag{2.11}$$

where the equality applies to reversible processes. Contrary to the energy analog given by Eq (2.9), entropy is not conserved in irreversible processes.

In common with enthalpy changes, entropy changes are associated with phase changes of a pure substance. For melting:

$$\Delta s_M = s_L - s_S \tag{2.12}$$

where s_L and s_S are the molar entropies of the liquid and solid phases, respectively. Conversion of a liquid to its vapor is characterized by the entropy of vaporization:

$$\Delta s_{vap} = s_g - s_L \tag{2.13}$$

Both Δs_M and Δs_{vap} are positive quantities.

The First law (Eq (2.8)) written in differential form for a unit quantity of substance is $du = \delta Q - \delta W$. For reversible changes, the second law (Eq (2.10)) is $\delta Q = Tds$ and if only expansion/contraction work is permitted, $\delta W = pdv$. The combined First and Second laws takes the form:

$$du = Tds - pdv \tag{2.14}$$

Equation (2.14) also applies to irreversible processes because it involves only properties of the system. For the same reason, it is equally valid if the system performs external (non-pV) work.

Analogous differential forms of the combined First and Second laws can be derived for the other two energy-like properties. For example, the molar enthalpy function is defined by: $h = u + pv$. The differential of this property is $dh = du + pdv + vdp$, which, when combined with Eq (2.14), gives:

$$dh = Tds + vdp \tag{2.15}$$

at constant pressure, Eq (2.15) gives:

$$ds = \frac{dh}{T} = \frac{C_p dT}{T}, \text{or in integral form: } s(T) - s(T_o) = \int_{T_o}^{T} \frac{C_P(T')}{T'} dT' \tag{2.15a}$$

where T_o is a reference temperature.

For the Gibbs function, $g \equiv h - Ts$, the differential is $dg = dh - Tds - sdT$. Substituting Eq (2.15) gives:

$$dg = -sdT + vdp \tag{2.16}$$

At constant temperature, the above gives:

$$dg = vdp, \text{or in integral form: } g(p) - g(p_o) = \int_{p_o}^{p} v(p')dp' \tag{2.16a}$$

where p_o is a reference pressure, usually 1 atm $\cong$ 0.1 megapascal (MPa).

2.3 Equations of State

Equations of state (EOS) provide mathematical relationships between p, v, and T of a single-phase, single-component system (or a solution of fixed composition). Rather than total properties, molar properties are more conveniently used here.

2.3.1 Gases
The EOS of gases are frequently represented by the ideal-gas law:

$$pv = R_g T \tag{2.17}$$

The *gas constant,* R, is the product of Avogadro's number and Boltzmann's constant:

$$R = 6.023\times10^{23} \text{ (molecules/mole)}\times1.3804\times10^{-23} \text{ J/molecule-K)} = 8.314 \text{ J/mole-K} \quad (2.18)$$

As is obvious from its genesis in two fundamental constants, the gas constant is not restricted to gases. Nonetheless, it is so often used with gases that its value in units compatible with Eq (2.17) is needed. Using the unit identities: J = N-m = Pa – m³. Eq (2.18) converts to:

$$R_g = 8.314\frac{\text{Pa}-\text{m}^3}{\text{mole}-\text{K}} \text{x}9.87\text{x}10^{-6}\frac{\text{atm}}{\text{Pa}} \text{x}10^6\frac{\text{cm}^3}{\text{m}^3} = 82.1\frac{\text{atm}-\text{cm}^3}{\text{mole}-\text{K}} \quad (2.19)$$

Non-ideal behavior in gases (Ref [1], p. 51) arises from attractive and repulsive forces between colliding atoms or molecules. A frequently-used modification of Eq (2.17) is the Van der Waals equation:

$$(p + a/v^2)(v – b) = R_g T \quad (2.20)$$

a and b are unique to each gas. The constant a accounts for attraction between atoms or molecules. If $p + a/v^2$ is thought of as an equivalent pressure in Eq (2.17), because it is larger than p, a reduction in v is required. This is what attraction should do: pull the gas together. The constant b represents the repulsive force; if v – b is considered to be an equivalent volume, an increase of p is needed to satisfy the right-hand side of Eq (2.17). Intermolecular repulsion requires a greater pressure to hold the gas.

Example #1 Nonideality of rare gases
The table below gives the Van der Waals' constants for the rare gases:

Gas	a, cm⁶-atm/mole²	mkml, cm³/mole
He	3.5×10^4	24
Xe	4.25×10^6	51

What are the deviations from ideality at T = 600 K and v = 2.5×10^3 cm³/mole?
The pressure of an ideal gas at this temperature and specific volume is 19.7 atm. The pressures calculated from Eq (2.20) and the errors incurred using the ideal gas law are:
He: p = 19.9 atm (0.9% error)   Xe: p = 19.4 atm (1.4% error)
The Van der Waals' constants are to be used with caution. At lower temperatures and higher pressures than in the above example, a more accurate EOS, such as the hard-sphere EOS (Sect. 19.3) is needed.

2.3.2 Condensed phases
Another way of describing the EOS is by:

$$\frac{dv}{v} = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p dT + \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T dp \quad (2.21)$$

For ideal gases, this gives:

$$\frac{dv}{v} = \frac{dT}{T} - \frac{dp}{p} \quad (2.22)$$

For condensed phases (liquids or solids), on the other hand, an EOS can be represented by substituting the coefficients of expansion (α) and compressibility (β) from Eq (2.3) into Eq (2.21):

$$dv/v = \alpha dT - \beta dp \quad (2.23)$$

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Although α and β vary with temperature and pressure, the dependence is slight enough that Eq (2.23) can be integrated:

$$\ln[v(T,p)/ v(T_o,p_o)] = \alpha(T - T_o) - \beta(p - p_o) \qquad (2.24)$$

The subscript o signifies a reference state where the molar volume is known. Typical values of α are 10^{-5} K^{-1}, so that a 100 K temperature change increases the molar volume by 0.1%.

2.4 Criteria of Thermodynamic Equilibrium

Thermodynamic equilibrium in a closed system contains three sub-equilibrium requirements. For thermal equilibrium there can be no temperature gradients in the system; mechanical equilibrium implies a constant pressure throughout the system. Chemical equilibrium, which fixes the composition of the system, is not as obvious.

The combined First and Second laws of thermodynamics, expressed by Eq (2.14), allows only for work due to expansion or contraction (pV work). If the system performs external work, such as shaft work or work derived from a chemical reaction, δW_{ext} must be subtracted from the right hand side of Eq (2.14). δW_{ext} also appears in the right hand sides of Eqs (2.15) and (2.16). With the constraints of constant T and p, Eq (2.16) reduces to:

$$dG_{T,p} = -\delta W_{ext} \qquad (2.25)$$

A useful definition of a system in equilibrium is one that cannot perform useful (non-expansion) work. Applying this notion to Eq (2.25), the criterion of equilibrium for closed systems constrained by fixed T and p is:

$$dG_{T,p} = 0 \qquad (2.26)$$

or: a*t equilibrium, the Gibbs energy of a constant T-p closed system is a minimum.*

This criterion of equilibrium is useful chiefly for systems with more than one phase or more than one component. For a single-phase, single-component system, fixing any two properties determines the others. For heterogeneous (multiphase) systems or homogeneous (single-phase) systems containing chemically reacting constituents, Eq (2.26) provides the essential starting point for determining the state of equilibrium.

2.5 Single-component phase Equilibria

A pure substance can exist in one, two or three phases, as long as the *phase rule* (Sect. 2.6) is satisfied. Important two-phase mixtures, and the process by which one phase is transformed to the other, include: liquid-gas (vaporization); solid-gas (sublimation); solid-liquid (melting, or fusion); solidI - solidII (allotropy).

At fixed pressure and temperature, the condition of equilibrium between two phases which satisfies Eq (2.26) is:

$$g_I = g_{II} \qquad (2.27)$$

from which:

$$g_{II} - g_I = \Delta g_{tr} = \Delta h_{tr} - T\Delta s_{tr} = 0, \text{ or:} \qquad \Delta s_{tr} = \Delta h_{tr}/T \qquad (2.27a)$$

tr signifies transition between phases.

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2.5.1 Liquid-Vapor Equilibria

An important application of Eqs (2.27) and (2.27a) is to liquid-gas transformation (vaporization), where I = L(liquid) and II = g(gas). At equilibrium, $g_L = g_g$. For a small move from equilibrium to another equilibrium state, $dg_g = dg_L$, or from Eq (2.16), $-s_g dT + v_g dp = -s_L dT + v_L dp$ and:

$$\frac{dp}{dT} = \frac{s_g - s_L}{v_g - v_L} = \frac{\Delta s_{vap}}{\Delta v_{vap}} = \frac{\Delta h_{vap}}{T \Delta v_{vap}} \cong \frac{\Delta h_{vap}}{T v_g} \cong \frac{p \Delta h_{vap}}{RT^2}$$

In this equation, Δs_{vap} has been replaced by $\Delta h_{vap}/T$ according to Eq (2.27a), v_L has been neglected compared to v_g, which has been approximated by Eq (2.17).

Since the two phases are at equilibrium, p and T are connected. The link can be considered either as p_{sat}, the *saturation pressure*, or *vapor pressure,* at temperature T, or T_{sat}, the *saturation temperature* as a function of p. The former representation is most commonly used. Δh_{vap} can be constructed by applying Eq (2.5) to the vapor and the liquid and subtracting, yielding:

$$\Delta h_{vap}(T) = \Delta h_{vap}(T_o) + (C_{Pg} - C_{PL})(T - T_o)$$

This second term on the right-hand side of this equation is important for water, and at 350 K reduces Δh_{vap} by ~ 11%. However, for the refractory metals and ceramics with which we deal in this book, the first term in the above equation dominates the second term. Δh_{vap} is a essentially independent of temperature, and as a consequence, dp/dT can be integrated to yield:

$$\ln\left(\frac{p_{sat}}{p_{sat}^o}\right) = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{2.28}$$

where p_{sat}^o is the vapor pressure at the reference temperature T_o.

A formula of the same mathematical form but with Δh_{sub} in place of Δh_{vap} applies to vaporization from the solid phase. The saturation pressure is now called the *sublimation pressure.*

$$\ln\left(\frac{p_{sat}}{p_{sat}^M}\right) = \frac{\Delta h_{sub}}{R}\left(\frac{1}{T_M} - \frac{1}{T}\right) \tag{2.29}$$

The reference temperature has been chosen as the melting temperature, T_M, where the vapor/sublimation pressure is p_{sat}^M. The heats of sublimation, vaporization and melting are related by:

$$\Delta h_{sub} = \Delta h_{vap} + \Delta h_M \tag{2.30}$$

Figure 2.1 shows the saturation pressures of selected metals. Sublimation pressures are shown as solid lines and vaporization pressures as dashed lines. In each region, the lines are straight because both Δh_{vap} and Δh_{sub} are very nearly temperature-independent. The slopes of the lines are $-\Delta h_{sub}/R$ for the solid-gas transition and $-\Delta h_{vap}/R$ for the liquid-gas phase change. The changes in slope at the melting temperature for Ca, Zn, and Cd in Fig. 2.1 are due to the replacement of Δh_{sub} by Δh_{vap}. According to Eq (2.30), the difference between these two enthalpy changes is the heat of fusion. The changes in slope are barely discernible because the heats of fusion are only ~ 4 – 5% of the heats of sublimation for all metals.

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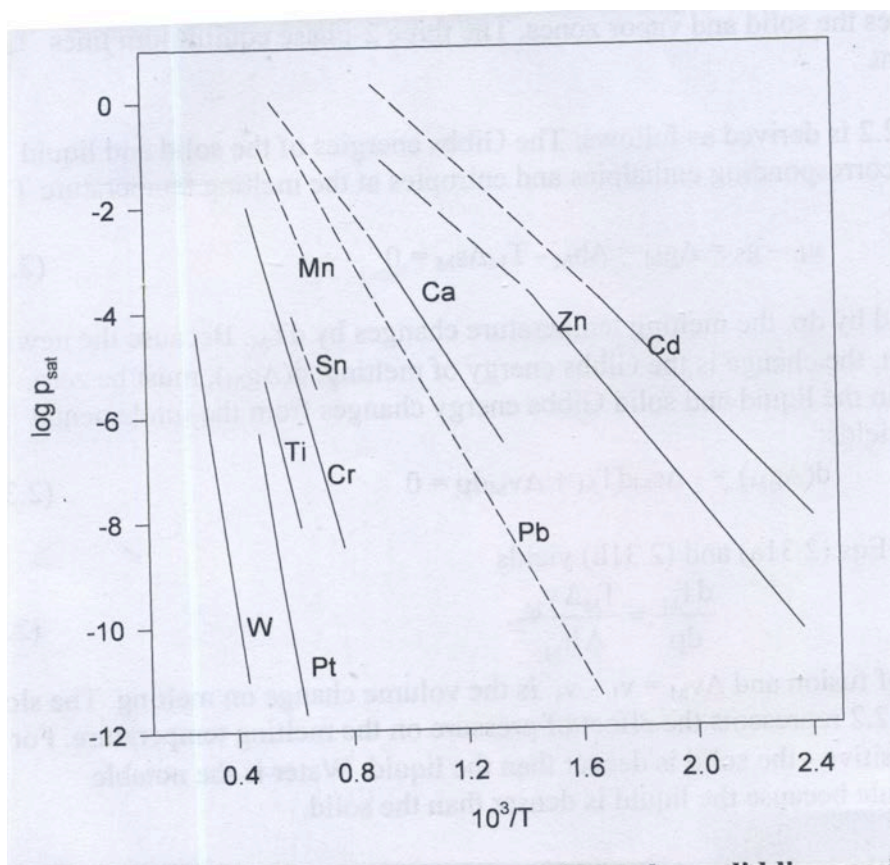
Fig. 2.1 Vapor pressures of selected metals – solid lines: sublimation; dashed lines – vaporization. Pressure in atm and temperature in Kelvins (*from G. V. Samsonov, Handbook of the Physicochemical Properties of the Elements*, **Plenum (1968))**

2.5.2 Solid-liquid Equilibria

In addition to the vapor pressure formulas of Eqs (2.29a) and (2.29b), the phase relations of a pure substance include the solid-liquid equilibrium. These three equilibria are shown graphically on a *phase diagram*. The most familiar graphical representation of the phase relationships of a pure substance is the p-T diagram such as that shown in Fig. 2.2. These representations contain three lines that intersect at the triple point. At this unique combination of pressure and temperature, all three phases coexist at equilibrium. In the areas labeled "solid", "liquid", and "vapor/gas", a single phase is stable over a range of temperature and pressure. The line separating the liquid and vapor regions is the liquid vapor pressure equation given by Eq (2.29a). Equation (2.29b) separates the solid and vapor zones. The three 2-phase equilibrium lines intersect at the triple point.

The melting line in Fig. 2.2 is derived as follows: The Gibbs energies of the solid and liquid phases are related to the corresponding enthalpies and entropies at the melting temperature T_M, where $g_L = g_S$, or:

$$g_L - g_S = \Delta g_M = \Delta h_M - T_M \Delta s_M = 0 \qquad (2.31a)$$

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If the pressure is increased by dp, the melting temperature changes by dT_M. Since the new state is still in equilibrium, the change is the Gibbs energy of melting, $d(\Delta g_M)$, must be zero. Obtaining the difference in the liquid and solid Gibbs energy changes from the fundamental differential of Eq (2.16) yields:

$$d(\Delta g_M) = -\Delta s_M dT_M + \Delta v_M dp = 0 \qquad (2.31b)$$

Eliminating Δs_M between Eqs (2.31a) and (2.31b) yields

$$\frac{dT_M}{dp} = \frac{T_M \Delta v_M}{\Delta h_M} \qquad (2.32)$$

here Δh_M is the enthalpy of fusion and $\Delta v_M = v_L - v_s$ is the volume change on melting. The slope of the melting line in Fig. 2.2 represents the effect of pressure on the melting temperature. For most materials, Δv_M is positive - the solid is denser than the liquid. Water is the notable exception to this general rule because the liquid is denser than the solid near the melting point.

A related aspect of the melting process is the variation of Δg_M with temperature at constant pressure. Under these conditions, the solid and liquid are no longer in equilibrium, so $\Delta g_M \neq 0$. In Eq (2.31b), setting $dp = 0$ for the constant-pressure requirement and replacing T_M by the variable temperature T yields:

$$\left(\frac{\partial \Delta g_M}{\partial T} \right)_p = -\Delta s_M = -\frac{\Delta h_M}{T_M}$$

where Eq (2.31a) has been used to eliminate Δs_M. Assuming Δh_M to be independent of temperature, this equation can be integrated to give:
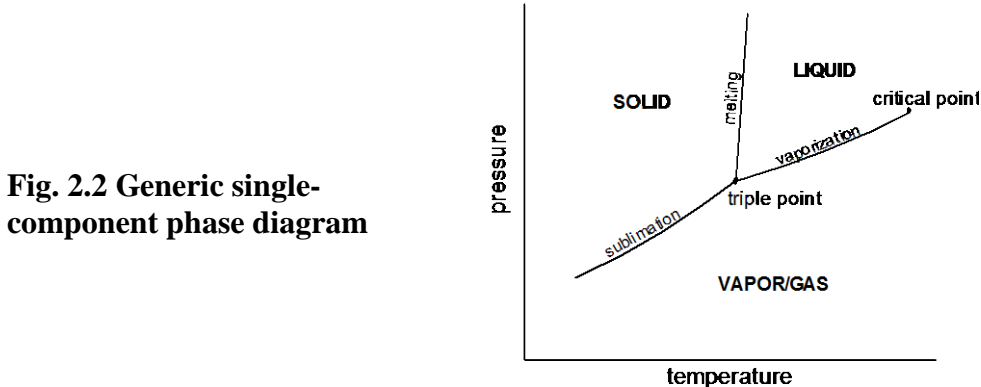
Fig. 2.2 Generic single-component phase diagram

$$\Delta g_M(T) = \Delta h_M \left(1 - \frac{T}{T_M} \right) \qquad (2.33)$$

If $T > T_M$, Δg_M is negative, implying that the liquid has a lower Gibbs energy than the solid, and hence in a single-component system, is the stable phase. Conversely, if $T < T_M$, only the solid exists at equilibrium. This sharp demarcation of phase stability breaks down in multicomponent systems; a component can exist in a liquid solution at temperatures well below its melting point when pure.

2.6 The Phase Rule

Analysis of systems other than pure substances requires understanding of the notions of phase, components and degrees of freedom. *Components* are distinct chemical constituents whose quantities can be independently varied. The relative amounts of the components are designated by compositions, for which mole fraction is a common measure. *Phases* are regions of a system in which all properties are uniform and are separated from other regions in the same system by a physical boundary, or *interface*. The number of system variables (e.g., properties, composition) that can be independently specified without changing the phase(s) are called d*egrees of freedom.* The numbers of components (C), phases ($\mathcal{P}$), and degrees of freedom ($\mathcal{F}$) are related by the *Gibbs Phase Rule*:

$$\mathcal{F} = C + 2 - \mathcal{P} \tag{2.34}$$

Temperature and pressure are included in $\mathcal{F}$. For single-component systems ($C = 1$), Eq (2.34) reduces to $\mathcal{F} = 3 - \mathcal{P}$. This relation can be understood using Fig. 2.2. The areas labeled SOLID, LIQUID, and VAPOR/GAS permit both p and T to be varied. This corresponds to $\mathcal{P} = 1$, and $\mathcal{F} = 3 - 1 = 2$. Or, these single-phase regions possess two degrees of freedom. Two phases are present for p – T combinations that fall on the sublimation, vaporization, and melting lines in Fig. 2.2. These correspond to $\mathcal{P} = 2$ and $\mathcal{F} = 2$. The single degree of freedom can be either p or T; specification of one fixes the other according to Eqs (2.29a) or (2.29b). When three phases coexist at equilibrium, $\mathcal{F} = 0$. This means that the three-phase mixture occurs at a unique combination of p and T (the triple point).

Application of the phase rule to multicomponent systems is not as straightforward as it is for single-component systems. For example, take the problem of identifying the number of components in a gas containing H_2, O_2 and H_2O. At low temperature and in the absence of an ignition source, the hydrogen does not burn and the mixture is a true three-component, single-phase system. Temperature, pressure and two mole fractions can be independently specified, which in Eq (2.34) corresponds to $C = 3$ and $\mathcal{F} = 3 + 2 - 1 = 4$. At high temperatures, on the other hand, the chemical reaction $2H_2(g) + O_2(g) = 2H_2O(g)$ provides a relation between the mole fractions of the three molecular components. This restraint effectively reduces the number of components from three to two. The two components are the elements H and O, irrespective of their molecular forms. The sole composition variable is the H/O element mole ratio. With $C = 2$, the phase rule gives $\mathcal{F} = 3$, which corresponds to the variables p, T and H/O needed to fix the equilibrium composition of the molecular constituents.

If a phase does not change composition in a process, a binary system can be treated as a pseudo single-component substance. Thus, analysis of air flowing through an orifice need not consider N_2 and O_2 as distinct components as long as the properly-averaged properties are used.

2.7 Solution Thermodynamics

The objective of this section is to understand the thermodynamics of single-phase, two-component (binary) systems. These include mixtures of ideal gases and the simplest models of

nonideal binary solid or liquid solutions. The terms "mixture" and "solution" are nearly, but not quite, synonymous. A *solution* unequivocally refers to a phase of two or more constituents.. The term is applied to condensed phases, but not to gases. Gaseous "solutions" are called *mixtures.* Thus air is a mixture, not a solution, of O_2 and N_2. These semantic distinctions between mixtures and solutions are usually clear from the context in which the words are used. Whether a single-phase mixture or a solution, the composition is denoted by the mole fractions of the constituents present:

$$x_i = n_i / n \qquad \text{where} \qquad n = \sum n_i \qquad (2.35)$$

n is the total moles of a phase and n_i is the number of moles of constituent i. By definition, the sum of the mole fractions is equal to unity.

To a good approximation, gas mixtures and many liquid and solid solutions can be considered to be ideal. In an ideal gas mixture, there are effectively no intermolecular interactions between the constituents. Pure solids and liquids must exhibit strong intermolecular attractions simply to exist as condensed phases. A binary solution of A and B is ideal if the average of the A-A and B-B intermolecular forces is equal to the strength of the A-B interaction.

With some exceptions, the properties of an ideal solution are mole-fraction-weighted averages of the properties of the pure components. If Q denotes an extrinsic property (i.e., for n moles of mixture or solution), and q_A and q_B are the properties per mole of the two pure components, the mixture property is:

$$Q = n_A q_A + n_B q_B \qquad \text{or} \qquad q = Q / n = x_A q_A + x_B q_B \qquad (2.36)$$

q is the intensive value of the property, or the value of the property per mole of mixture or solution. Equation (2.36) applies to the volume V, the internal energy U, the enthalpy H, and the heat capacities C_P and C_V. The entropy, however, contains an additional term that arises from the increased randomness afforded by mixing. When two pure substances are mixed at constant temperature and pressure, the entropy change, or the *entropy of mixing* is given by:

$$\Delta s_{mix} = -R(x_A \ln x_A + x_B \ln x_B) \qquad (2.37)$$

where R = 8.314 J/mole-K is the gas constant. Since the definitions of the Gibbs energy includes the entropy, the right hand side of Eq (2.37) appears in g analogous to Eq (2.36):

$$G = n_A g_A + n_B g_B - RT(n_A \ln x_A + n_B \ln x_B) \qquad (2.38a)$$

Non-ideal behavior is a common characteristic of condensed-phase solutions. Departure from ideality in a binary solution occurs when the mean of the A-A and B-B bond strengths differs from the A-B bond strength. Departure from ideal behavior can be positive or negative. Quantitative treatment of nonideality in a binary system is achieved by modification of Eq (2.36). The entropy of mixing, Eq (2.37) is unchanged and is handled just as for ideal solutions.

2.7.1 Partial molar properties
Thermodynamic equilibrium analyses are based on minimization of the Gibbs energy of an isothermal, isobaric closed system. The non-ideal equivalent of Eq (2.36) is expressed in terms

of this property. The total Gibbs energy of a binary solution at a specified temperature and pressure and its value per mole of solution are given by:

$$G = n_A \overline{g}_A + n_B \overline{g}_B \quad \text{or} \quad g = x_A \overline{g}_A + x_B \overline{g}_B \tag{2.38b}$$

where $\overline{g}_A$ and $\overline{g}_B$ are the *partial molar Gibbs energies* of constituents A and B in the solution. $\overline{g}_A$ depends on the nature of constituent B with which it shares the solution. In addition to depending on temperature (and to a lesser extent, on pressure), $\overline{g}_A$ depends on the solution composition. The same characteristics apply to $\overline{g}_B$. These two partial molar quantities include the entropy of mixing. Formulas analogous to Eq (2.38b) hold for other thermodynamic properties (h, s).

It is often necessary to express partial molar properties in terms of the molar property (of the solution) and its variation with composition. Consider the molar volume, which is easy to measure as the composition is changed. The inverted relations are (Ref [1], p. 193):

$$\overline{v}_A = v + x_B \frac{dv}{dx_A} \qquad\qquad \overline{v}_B = v + x_A \frac{dv}{dx_B} \tag{2.38c}$$

2.7.2 The chemical potential

The partial molar Gibbs energy of a component in solution is called the *chemical potential* of the component, or $\mu_i = \overline{g}_i$. With this replacement, Eq (2.38b) becomes:

$$G = n_A \mu_A + n_B \mu_B \quad \text{or} \quad g = x_A \mu_A + x_B \mu_B \tag{2.39}$$

The physical meaning of the chemical potential is best appreciated by recognizing that the total Gibbs energy of a binary solution depends on the number of moles of A and B as well as on temperature and pressure. Taking the differential of $G(T,p,n_A,n_B)$ holding T and p constant gives:

$$dG = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} dn_B \qquad \text{or} \qquad dG = \mu_A dn_A + \mu_B dn_B \tag{2.40}$$

The partial derivatives in the first form of dG define the chemical potentials in the second form:

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} \qquad\qquad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} \tag{2.40a}$$

This equation shows that μ_A represents the change in the Gibbs energy of the system when a small quantity of A is added while the amount of B is held constant.

Equation (2.40) can be "integrated" in a physical sense by simultaneously adding the pure components to a vessel at rates proportional to their concentrations in the final solution. This procedure maintains all concentrations constant during the process, so that the integral of Eq (2.40) is identical to the first equality in Eq (2.39). This procedure demonstrates that μ_A and μ_B in Eq (2.40) are identical to those in Eq (2.39) as expressed by Eq (2.40a).

2.7.3 The Gibbs-Duhem relation

Another important relation involving the chemical potentials can be derived from the total differential of Eq (2.39), $dG = \mu_A dn_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B$. Eliminating dG using Eq (2.40) and dividing by n to convert mole numbers to mole fractions yields:

$$x_A d\mu_A + x_B d\mu_B = 0 \tag{2.41}$$

This relation is known as the *Gibbs-Duhem equation*. As will be seen below, it is very important in analyzing nonideal solutions.

2.7.4 Standard-state Gibbs energy

The basic data for solving chemical equilibria are the Gibbs energies of the compounds involved in the reaction. The pressure is specified as 1 atm, which defines the *standard state*. With this restriction:

g_i^o = **Gibbs energy of pure constituent i (compound) at temperature T and 1 atm, J/mole.**

g_i^o identical to the *standard Gibbs energy of formation* of the compound, ΔG_i^f.

g_i^o (or ΔG_i^f) is zero if i is an element in its stable state (e.g., O_2).

ΔG_i^f is related to measurable properties of the substance, namely its enthalpy and entropy of formation by:

$$\Delta G_i^f = \Delta H_i^f - T\Delta S_i^f \tag{2.42}$$

The enthalpy of formation of a constituent at a reference temperature T_o and 1 atm pressure is:

$$\Delta H_i^f(T_o) = h_i^o(T_o) - \sum_{elements} \nu h_{reactant}^o(T_o)$$

ν is the balancing number of an element in the formation reaction.

Since there is no absolute value of enthalpy, all $h_{reactant\ element}^o(T_o)$ are set equal to zero. At temperature T:

$$\Delta H_i^f(T) = \Delta H_i^f(T_o) + \int_{T_o}^{T} \left[C_{pi}(T') - \sum_{elements} \nu C_{p\,reactant}(T') \right] dT' \tag{2.42a}$$

where C_p is the specific heat.

The analog of Eq (2.42a) for the entropy $\Delta S_i^f(T)$ is:

$$\Delta S_i^f(T) = \Delta S_i^f(T_o) + \int_{T_o}^{T} \left[\frac{C_{pi}(T')}{T'} - \sum \nu \frac{C_{p\,reactant\ elements}(T')}{T'} \right] dT' \tag{2.42b}$$

where:
$$\Delta S_i^f(T_o) = s_i^o(T_o) - \sum_{elements} \nu s_{reactant}^o(T_o) \tag{2.42c}$$

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Example #2a Standard enthalpy of formation of methane at 1000 K
The formation reaction is: $C(s) + 2H_2(g) = CH_4(g)$
The enthalpy of formation of methane at 298 K is – 75 kJ/mole.
The heat capacity of methane is: $C_{pCH_4} = 20.6 + 0.051 \times T$ J/mole-K.

The first integral in the above equation between 298 K and 1000 K is 37.5 kJ/mole.
The average heat capacity of graphite over the same temperature range is ~ 12 J/mole-K, so the contribution to the sum is 8 kJ/mole.
The average heat capacity of H_2 gas over the same range is ~ 15 J/mole-K, so the integral of Cp_{H2} is 21 J/mole-K. In Eq (2.42a):

$$\Delta H_i^f(1000) = -75 + [37.5 - 8 - 2 \times 21] = -88 \text{ kJ/mole}$$

Example #2b Standard entropy of formation of methane at 1000 K

Data are (in J/mole-K): $\quad s_{CH_4}^o(300) = 186 \quad s_C^o(300) = 6 \quad s_{H_2}^o(300) = 131$

from Eq (2.42c): $\quad \Delta S_{CH_4}^f(300) = 186 - 6 - 2 \times 131 = -82$

for CH_4, $C_p = 20.6 + 0.051T$, and the first integral in Eq (2.42b) is 60.5 J/mole-K
for C, $\quad C_P = 1.05 + 0.022\ T$, and the 2nd integral in Eq (2.42b) is 18.5 "
for H_2 $\quad$ the 3rd integral in Eq (2.42) is 35 J/mole-K
The second term on the right-hand side of Eq (2.42b) = 60.5 – 18.5 - 2×35 = - 28 J/mole-K

From Eq (2.42b): $\quad \Delta S_{CH_4}^f(1000) = -82 - 28 = -110 \text{ J/mole} - K = 0.11 \text{ kJ/mole} - K$

Applying Eq (2.42): $\quad \Delta G_{CH_4}^f(1000) = -88 - 1000(-0.11) = 22 \text{ kJ/mole}$

Instead of the cumbersome calculations in Examples #2a and 2b, the tabulation in the URL of the National Institute of Science and Technology (NIST), **www.kinetics.nist.gov/janaf/,** provides tabulations of $\Delta G_i^f(T)$ for most important compounds.

2.7.5 Activity and activity coefficient
Although the thermodynamic behavior of a constituent in solution is ultimately tied to its chemical potential, a connection between this property and the concentration of the constituent is needed. This relationship is made via the *activity* of a solution constituent which is related to the chemical potential by:

$$\mu_i = g_i^o + RT \ln a_i \tag{2.43}$$

The activity a_i tends to unity for pure i and μ_i reduces to g_i^o, the molar Gibbs energy of pure i in its standard state. When component i becomes infinitely dilute in the solution, $a_i \to 0$ and its logarithm approaches -∞. This is also the limit of the chemical potential of i at infinite dilution. This inconvenient behavior of the chemical potential at zero concentration is avoided by using the activity in practical thermodynamic calculations.

For real solutions, the *activity coefficient* of constituent i is the ratio of its activity and mole fraction by:

$$\gamma_i = a_i/x_i \tag{2.44}$$

Combining the above two equations gives:

$$\mu_i = g_i^o + RT \ln \gamma_i + RT \ln x_i \tag{2.44a}$$

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The first term on the right side represents the property of pure component i; the second term accounts for nonideality and the third term is incorporated into the entropy of mixing of Eq (2.37).

A useful connection between the activity coefficients of constituents in a solution is obtained by eliminating a_i between Eqs (2.43) and (2.44) and substituting the resulting equation into the Gibbs-Duhem equation, Eq (2.41). For two-component (A-B) solutions, this procedure yields:

$$x_A d\ln\gamma_A + x_B d\ln\gamma_B = 0. \tag{2.45}$$

The activity coefficient is an important characterization of non-ideal behavior in condensed solution phases. The significance of Eq (2.45) is that measurement of the activity coefficient of one constituent as a function of composition determines the activity coefficient of the other constituents by integration (via Eq (2.45) for two constituents).

2.7.6 Excess Properties

An alternative to partial molar properties as a means of characterizing nonideality in solutions is the concept of *excess properties.* A partial molar property and the corresponding excess property are not independent quantities (Ref [1], p. 194). Instead of Eq (2.38), the Gibbs energy of a binary solution can be expressed by:

$$g = g^o + g^{ex} - T\Delta s_{mix} = x_A g_A^o + x_B g_B^o + h^{ex} - Ts^{ex} - T\Delta s_{mix} \tag{2.46}$$

where g_A^o and g_B^o are the Gibbs energies of the pure constituents in the standard state ($p^o = 1$ atm) at the specified temperature. These terms and $T\Delta s_{mix}$ represent the Gibbs energy of the solution if it were ideal. The nonideal features are contained in the g^{ex} term, which has been broken into enthalpy and entropy contributions according to the definition the Gibbs energy in Eq (2.1). The motivation of this last step arises from the possibility of attaching physical meaning to h^{ex} and s^{ex}.

Formulas analogous to Eq (2.46) apply to other thermodynamic properties. For example, the volume and enthalpy of a binary solution are given by:

$$v = x_A v_A + x_B v_B + v^{ex} \quad \text{and} \quad h = x_A h_A + x_B h_B + h^{ex} \tag{2.47}$$

The excess property that governs nonideality in solutions is the excess Gibbs energy, g^{ex}. This is determined from Eq (2.39) wherein the chemical potentials are expressed by Eq (2.43), giving:

$$g = x_A(g_A^o + RT\ln a_A) + x_B(g_B^o + RT\ln a_B) = x_A g_A^o + x_B g_B^o + RT(x_A\ln a_A + x_B\ln a_B)$$

here a_A and a_B are the activities of A and B in the solution. Activities can be expressed in terms of activity coefficients by use of Eq (2.44), so the above equation is:

$$g = (x_A g_A^o + x_B g_B^o) + RT(x_A\ln x_A + x_B\ln x_B) + RT(x_A\ln\gamma_A + x_B\ln\gamma_B)$$

The middle term is the ideal mixing entropy, so the last term is the excess Gibbs energy:

$$g^{ex} = RT(x_A\ln\gamma_A + x_B\ln\gamma_B) \tag{2.48}$$

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Since $g^{ex} = h^{ex} - Ts^{ex}$, the right-hand side of Eq (2.48) includes both h^{ex} and s^{ex}.

The excess volume and enthalpy are directly measurable, but a direct measure of g^{ex} requires measurement of activity coefficients, which are usually obtained from measurements of the partial pressures of A and B over the solution.

Example #3 Excess enthalpy and excess volume
When 50 cm^3 of 20°C water are mixed with 50 cm^3 of sulfuric acid at the same temperature in an insulated vessel, the temperature rises to 123°C, and after cooling, the final volume is 90 cm^3. These changes are direct measures of v^{ex} and h^{ex}. The moles of each component are:

$n_w = 50 \text{ cm}^3 \times 1 \text{ g}/\text{cm}^3 \div 18 \text{ g}/\text{mole} = 2.78 \text{ moles water}$

$n_A = 50 \text{ cm}^3 \times 1.83 \text{ g}/\text{cm}^3 \div 98 \text{ g}/\text{mole} = 0.93 \text{ moles acid}$

$x_w = 2.78/3.71 = 0.75; \quad x_A = 0.25$

The molar volumes of the pure components are:

$v_w = 18 \text{ g}/\text{mole} \div 1 \text{ g}/\text{cm}^3 = 18 \text{ cm}^3/\text{mole} \qquad v_A = 98 \text{ g}/\text{mole} \div 1.83 \text{ g}/\text{cm}^3 = 53.6 \text{ cm}^3/\text{mole}$

For an ideal solution: $v_{id} = x_w v_w + x_A v_A = 0.75 \times 18 + 0.25 \times 53.6 = 26.9 \text{ cm}^3/\text{mole}$
The measured volume per mole: $v = 90/3.71 = 24.3 \text{ cm}^3/\text{mole}$. From Eq (2.44):
$$\therefore v^{ex} = 24.3 - 26.9 = -2.6 \text{ cm}^3/\text{mole}$$

Take the standard states of the two liquids to be at room temperature, so $h_w = h_A = 0$ and from Eq (2.47), $h = h^{ex}$. By cooling, heat is removed from the solution, which means that its enthalpy has decreased, so the final enthalpy of the solution is:
$$h = -\overline{C}_P \Delta T = -(x_w C_{Pw} + x_A C_{PA})\Delta T$$
$C_{Pw} = 4.19 \text{ J/g-K} \times 18 \text{ g/mole} = 75.4 \text{ J/mole-K}; \quad C_{PA} = 1.38 \text{ J/g-K} \times 98 \text{ g/mole} = 135.2 \text{ J/mole-K}$
$$\therefore h^{ex} = -(0.75 \times 75.4 + 0.25 \times 135.2)(123 - 20) = -9300 \text{ J/mole}$$

In this example, water and sulfuric acid interact strongly and produce highly negative deviations from ideality.

2.7.7 Regular Solutions
For ideal solutions, both h^{ex} and s^{ex} are zero. The behavior of a fair number of nonideal condensed solution phases can be adequately represented by the *regular solution* model. In this model, the molecules mix randomly as they do in ideal solutions, so that $s^{ex} = 0$ and the excess Gibbs energy reduces to the excess enthalpy. The analytical formulation of h^{ex} in terms of composition is restricted by the limiting behavior as the solution approaches pure A and pure B. In these limits, h^{ex} must be zero at $x_A = 0$ and at $x_B = 0$. The simplest function that obeys these restraints is the symmetric expression:
$$h^{ex} = \Omega x_A x_B \tag{2.49}$$
where Ω is a temperature-independent property of the A-B binary pair called the *interaction energy*. The form of Eq (2.49) is supported by molecular modeling, which suggests that Ω is equal to the difference between the energy of attraction (bond energy) of the A-B pair and the mean of the bond energies of the A-A and B-B interactions.

For regular solutions (i.e., solutions that obey Eq (2.49)), the activity coefficients can be shown to be (Sect. 7.7.2 of Ref [1]):

$$RT\ln\gamma_A = \Omega x_B^2 \quad \text{and} \quad RT\ln\gamma_B = \Omega x_A^2 \tag{2.50}$$

These activity coefficients satisfy the Gibbs-Duhem equation, Eq (2.41).

2.7.8 Mixtures of ideal gases

Contrary to condensed-phase solutions, gas mixtures are generally nearly ideal (Sect.2.3.1). Consider the following isothermal process:

- **Process No. 1** - two pure ideal gases (x_A moles A and x_B moles B) at the same p are combined at constant pressure

The mixture occupies a volume V equal to the sum of the initial volumes. Each constituent obeys the ideal gas law, but its pressure is termed the *partial pressure*. Denoting these by p_A and p_B, the ideal gas law applies to each constituent:

$$p_A V = n_A RT \qquad\qquad p_B V = n_B RT \tag{2.51}$$

The total pressure of the mixture (as measured by a gauge) is the sum of the partial pressures:

$$p_A + p_B = p \tag{2.52}$$

and $n = n_A + n_B$ is the total moles of gas.

The mixture also obeys the ideal gas law (Sect. 2.3.1), as can be seen by adding Eqs (2.51) and using Eq (2.52) to eliminate the partial pressures:

$$pV = nRT$$

Dividing each of Eqs (2.51) by the above equation relates the partial pressures to the mole fractions

$$\frac{p_A}{p} = \frac{n_A}{n} = x_A \qquad\qquad \frac{p_B}{p} = \frac{n_B}{n} = x_B \tag{2.53}$$

Equations (2.52) and (2.53) are known as Dalton's law.

The mixing rules for ideal gases for the volume, internal energy, and enthalpy follow the generic form of Eq (2.39). However, in addition, the Gibbs energy of the mixture must also include the entropy of mixing. In particular, the entropy change of process No. 1 (above) is Δs_{mix} of Eq (2.37).

An important related question is:
How are the chemical potentials of a mixture of x_A moles of A and x_B moles of B at temperature T and 1 atm related to the partial pressures in the mixture?

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To answer this question, we consider isothermal process No. 2 divided into two steps:

- **Process No. 2** –
  2a. The pure gases are reduced from 1 atm pressure to their partial pressures in the mixture p_A and p_B.
  2b. The pure gases are mixed.

Since the total pressure p = 1 atm and the mole numbers x_A and x_B are fixed, the partial pressures in the mixture are given by Eq (2.54): $p_A = x_A p$ and $p_B = x_B p$. In order to calculate the Gibbs energy change of step *2a*, we use the equation obtained by combining Eq (2.16) with the ideal gas law. For constant temperature, this gives:

$$\frac{dg_i}{dp_i} = v_i = \frac{RT}{p_i} \tag{2.54a}$$

where i = A or B. Integrating from initial pressures p_A^o and p_B^o tto partial pressures p_A and p_B:

$$g_A = g_A^o + RT \ln(p_A / p_A^o) \qquad g_B = g_B^o + RT \ln(p_B / p_B^o) \tag{2.54b}$$

g_A^o and g_B^o are the molar free energies of A and B at the initials pressure (and the specified temperature).

The initial pressures are chosen as 1 atm and the condition is known as the *standard state* of the pure gas. The Gibbs energy at the termination of step 2a is:

$$g = x_A g_A + x_B g_B = x_A (g_A^o + RT \ln p_A) + x_B (g_B^o + RT \ln p_B)$$

In step *2b*, there is no change in either the entropy or the Gibbs energy (see Ref. **1**, Fig. 7.3). From Eq (2.39) and the above equation,

$$g = x_A \mu_A + g_B \mu_B = x_A (g_A^o + RT \ln p_A) + x_B (g_B^o + RT \ln p_B)$$

from which:

$$\mu_A = g_A^o + RT \ln p_A \qquad \mu_B = g_B^o + RT \ln p_B \tag{2.55}$$

Equation (2.55) relates the partial pressures to the chemical potentials. The partial pressures p_A and p_B must be in units of atmospheres.

2.8 Two-Phase Equilibria

An important application of the thermodynamics of solutions summarized in the preceding section is to the analysis of equilibrium of multiple components distributed between multiple phases. The most common combinations are a gas phase and one or two condensed phases. The latter includes liquid-solid, liquid-liquid, and solid-solid pairs. The two coexisting phases are denoted by I and II, but the number of components is restricted to two, labeled A and B. The total Gibbs energy of this two-phase mixture is $G = G_I + G_{II}$. A change in the state of the system at constant temperature and pressure is provoked by moving dn_{AI} moles of component A from phase I to phase II. If the system is at equilibrium, this movement does not change the system's

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Gibbs energy, and Eq (2.26) results in $dG = dG_I + dG_{II} = 0$. The Gibbs energy changes of each phase are related to the chemical potentials according to Eq (2.40), which yields:

$$\mu_{A(I)}dn_{A(I)} + \mu_{B(I)}dn_{B(I)} + \mu_{A(II)}dn_{A(II)} + \mu_{B(II)}dn_{B(II)} = 0$$

where $n_{A(I)} \ldots n_{B(II)}$ are the numbers of moles of each constituent in each phase and $\mu_{A(I)} \ldots \mu_{B(II)}$ are their chemical potentials. Conserving component A, $dn_{A(II)} = - dn_{A(I)}$, and because component B is not exchanged, $dn_{B(I)} = dn_{B(II)} = 0$. Applying these constraints to the above equation yields:

$$\mu_{A(I)} = \mu_{A(II)} \tag{2.56}$$

A similar equation applies to component B. Equation (2.56) is the multicomponent generalization of the equilibrium condition for two coexisting phases of a pure substance, namely $g_I = g_{II}$, where g is the molar Gibbs energy. If phase I is a gas and phase II a condensed phase, the equilibrium criterion of Eq (2.56) becomes $\mu_{A(g)} = \mu_{A(L)}$. Using Eq (2.55) for $\mu_{A(g)}$ and the combination of Eqs (2.43) and (2.44) for $\mu_{A(L)}$, the equilibrium condition becomes:

$$\frac{p_A}{\gamma_A x_A} = \exp\left(-\frac{g^o_{A(g)} - g^0_{A(L)}}{R_g T}\right)$$

For pure A, $\mu_{A(L)} = g^o_{A(L)}$ and $\mu_{A(g)} = g^o_{A(g)} + RT\ln p_{sat,A}$, so the right hand side of the above equation is the saturation pressure of pure liquid A, and the above equation becomes:

$$p_A = \gamma_A x_A p_{sat,A} \tag{2.57}$$

This equation forms the basis for all analyses of phase equilibria in multicomponent systems involving a gas phase. A formula similar to Eq (2.57) applies to component B, and to all other components if the system contains more than two constituent. It equally valid for a solid solution of A and B. The dependence of p_A on composition is in general nonlinear because the activity coefficient of A in the condensed phase, γ_A, is a function of composition if the solution is nonideal and not infinitely dilute in A.

2.8.1 Raoult's and Henry's laws

If the solution is ideal, $\gamma_A = 1$ for all x_A, and Eq (2.57) reduces to *Raoult's law*:

$$p_A = x_A p_{sat,A} \tag{2.58}$$

Component B also obeys Raoult's law because Eq (2.45) shows that if $\gamma_A = 1$, then $\gamma_B = 1$ as well. In nonideal solutions, $\gamma_A \rightarrow$ constant $\neq 1$ as the solution becomes dilute in A. Equation (2.57) reduces to *Henry's law*:

$$p_A = k_{HA}x_A \tag{2.59}$$

where the Henry's law constant, k_{HA}, is the product of the composition-independent activity coefficient of A in solution and the saturation pressure of pure A. In the concentration range where A follows Henry's law, component B must obey Raoult's law. This is a consequence of the Gibbs-Duhem equation, Eq (2.41).

Figure 2.3 shows typical examples of nonideal solution behavior. The curves represent Eq (2.57) for positive and negative deviations from ideality (i.e., $\gamma_A > 1$ or $\gamma_A < 1$). The limiting cases of Raoult's and Henry's law are shown as dashed lines.

2.8.2 Binary Phase Diagrams

Equilibrium between condensed phases in two-component systems is displayed as a *binary phase diagram*[1]. Most common phase diagrams illustrate regions of a single- or two-phase stability in plots with temperature as the ordinate and composition as the abcissa. The total pressure is constant (usually 1 atm). The gas phase is usually ignored in this representation because the effect of pressure on the phase diagram is small. In two-phase regions, Eq (2.56), and the analogous equation for component B, serve to determine the compositions of the two phases. The chemical potentials of A and B in each phase are expressed in terms of composition by the equation obtained by eliminating the activity between Eqs (2.43) and (2.44).

Assuming that the phases present are known, this method of constructing phase diagrams, melting in an ideal system is illustrated with Phase I a solid and phase II is liquid. All four activity coefficients are unity (ideal behavior is assumed). With these restrictions, the conditions of equilibrium become:

$$g_{AL} + RT\ln x_{AL} = g_{AS} + RT\ln x_{AS} \tag{2.60a}$$

$$g_{BL} + RT\ln x_{BL} = g_{BS} + RT\ln x_{BS} \tag{2.60b}$$

The differences $g_{AL} - g_{AS}$ and $g_{BL} - g_{BS}$ are the Gibbs energy changes on melting of the pure constituent. These are related to the melting properties of A and B by Eq (2.31a). Since $x_{AL} + x_{BL} = 1$ and $x_{AS} + x_{BS} = 1$, the above equations contain two unknowns. Solving yields:

$$x_{BL} = \frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}} \qquad \text{and} \qquad x_{BS} = e^{\beta}\left(\frac{1 - e^{\alpha}}{e^{\beta} - e^{\alpha}}\right) \tag{2.61}$$

with

$$\alpha = \left(1 - \frac{T}{T_{MA}}\right)\frac{\Delta h_{MA}}{RT} \qquad \beta = \left(1 - \frac{T}{T_{MB}}\right)\frac{\Delta h_{MB}}{RT} \tag{2.62}$$

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[1] see Chap. 10 for a more extensive treatment of this topic
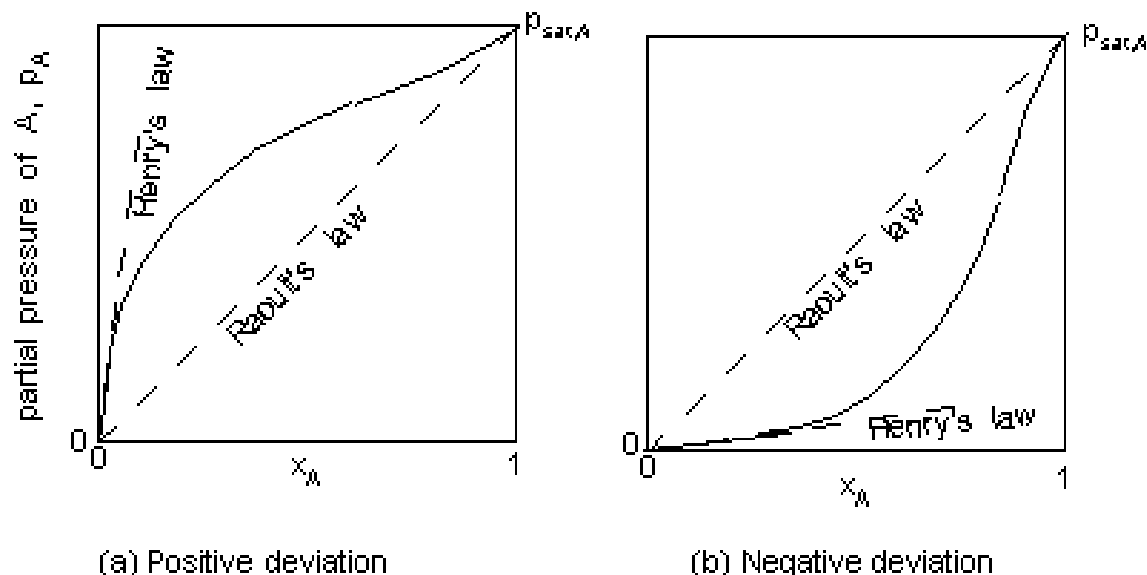
Fig. 2.3 Equilibrium pressures of component A over an A-B solution. Temperature is fixed.

Figure 2.4 shows the phase diagram for an ideal binary system calculated from Eqs (2.61) using the melting properties of metals U and Zr. The upper line (representing T Vs $x_{B(L)}$) is called the *liquidus.* All points lying above this line are completely liquid. Similarly, all points below the lower curve (the *solidus*, or T - $x_{B(S)}$) are completely solid. In the region bounded by the solidus and the liquidus, two phases coexist.

The left-hand panel of Fig. 2.4 represents the actual phase diagram. In the right-hand panel, the horizontal and vertical lines are superimposed on the phase diagram in order to illustrate important characteristics of the melting process. If the solid solution with a composition $x_B = 0.4$ is heated, the intersection of the vertical line with the solidus (at point A) shows that the first liquid appears at 1630 K and has a composition $x_{BL} = 0.21$ (at point B). As the temperature is increased to 1700 K, the system lies at point P. Here a liquid phase with composition $x_{BL} = 0.31$
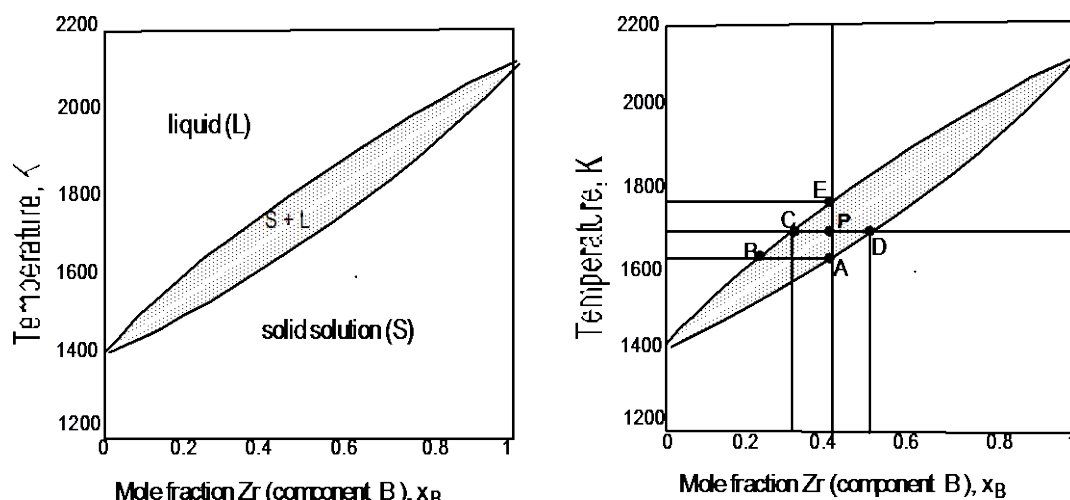
Fig. 2.4 Phase diagram of the U-Zr binary system with ideal behavior in both liquid and solid

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(point C) and a solid phase with $x_{BS} = 0.49$ (point D) coexist. The fraction of the mixture present as liquid at point P is obtained from the mole balance known as the *lever rule*:

$$\text{Fraction liquid at point P} = \frac{\overline{PD}}{\overline{CD}} = \frac{x_{BS} - x_B}{x_{BS} - x_{BL}} = \frac{0.49 - 0.4}{0.49 - 0.31} = 0.50 \tag{2.63}$$

Upon heating from point P, the last solid disappears at $T = 1790$ K (point E). Melting of this binary system at this particular overall composition is spread over a 160 K temperature range.

In the above example, both solid and liquid phases were assumed to behave ideally, However, the majority of condensed-phase systems exhibit non-ideal behavior. In a limiting version of such a system, the condensed phases exhibit positive deviations from ideality, so that there is negligible solubility of A in B or B in A. That is, molecules of B and A repel each other so strongly that solutions of one in the other are not possible. On the other hand, A-rich and B-rich liquid solutions exist and may even exhibit negative deviations from ideality (attraction between A and B on the molecular level).

For pure solid A in equilibrium with an A-rich liquid, Eq (2.56) becomes:

$$g_{AS} = g_{AL} + RT \ln(\gamma_{AL} x_{AL}) \tag{2.64}$$

Solving for x_{AL}, the A-rich portion of the phase diagram is expressed by:

$$x_{AL} = e^{-\alpha} / \gamma_{AL} \tag{2.65}$$

where α is the temperature-dependent function given by Eq (2.62). To complete this portion of the phase diagram, γ_{AL} must be known as a function of temperature and composition (e.g., by Eq (2.49) if the liquid obeys regular solution theory).

An entirely analogous treatment applies to the portion of the phase diagram in which pure solid B coexists with a B-rich liquid. The equilibrium condition is given by Eq (2.64) with A replaced by B, and the composition-temperature equation is:

$$x_{BL} = e^{-\beta} / \gamma_{BL} \tag{2.66}$$

with β given by Eq (2.62). Again, γ_{BL} must be known as a function of temperature and composition.

The gold-silicon binary system is representative of systems that exhibit this type of phase behavior. This phase diagram is shown in Fig. 2.5. With A = Au, the Au-rich liquidus in the figure is a plot of Eq (2.65) and the Si-rich liquidus represents Eq (2.66). The two liquidus curves intersect at a point called the *eutectic* (Greek for "lowest melting"). At this point, three phases coexist: the two pure solids and the liquid of the eutectic composition. At lower temperatures, only the two pure solids are present When A and B are mutually soluble in each other, the phase diagram takes on the general appearance of the one shown in Fig. 2.6. Compared to Fig. 2.5, two single-phase regions, labeled

At this juncture, it is constructive to examine how binary phase diagrams relate to the phase rule (Sect. 2.6). For a two component system, Eq (2.34) permits $\mathcal{F} = 4 - \mathcal{P}$ degrees of freedom. Since the diagrams deal only with condensed phases, they are minimally affected by total pressure. Ignoring the total pressure reduces the number of degrees of freedom by one, thereby allowing $3 - \mathcal{P}$ properties to be independently varied. In the single phase ($\mathcal{P} = 1$) portions of the phase diagram, two degrees of freedom are permitted. These are the temperature T and the composition, represented by the mole fraction of one of the constituents, say x_B. Single-phase regions appear as areas in the phase diagram.

In two-phase regions ($\mathcal{P} = 2$), only one system property can be specified. Fixing the temperature, for example, determines the compositions of the two coexisting condensed phases. These temperature-composition relationships appear in the phase diagram as lines (or curves) called *phase boundaries*. A three-phase system ($\mathcal{P} = 3$) has no degrees of freedom and is represented by a point on the phase diagram. An example of this is the eutectic point in Fig. 2.5.

 The distinction between overall compositions and the compositions of individual phases is essential to understanding phase diagrams. For single-phase zones, the two are identical. When two phases coexist, the overall composition is the mole-weighted average of the compositions of the two phases (i.e., the lever rule, Eq (2.63)).

When A amd B are mutually soluble, the phase diagram typically looks like Fig. 2.6. Compared to Fig. 2.5, two single-phase regions, labeled α and β, have been added to the diagram. The α phase retains the crystal structure of pure A but some component B is dissolved in it, usually by substituting for A atoms in the lattice. The curves ab and bc represent the *terminal solubility* of B in A. Compositions along these curves are the maximum concentrations of B that the α phase can sustain. Additional B added to the system causes precipitation of a new phase, which is the solid β phase below the eutectic temperature or the liquid above this temperature.
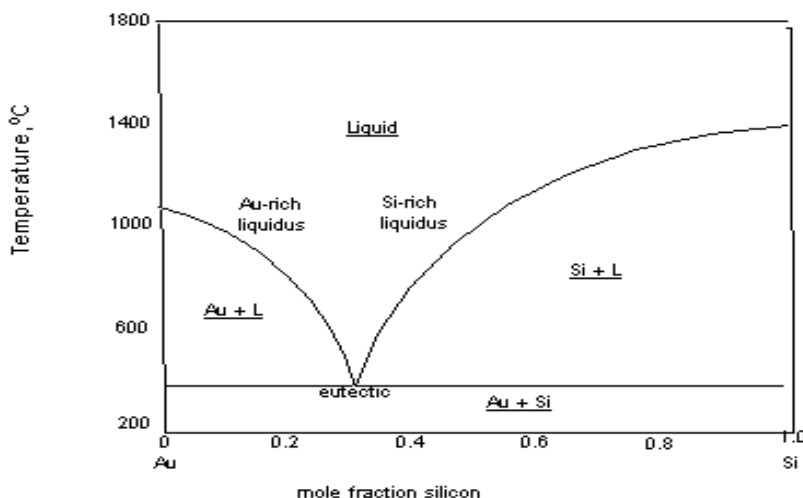
Fig. 2.5   The gold-silicon phase diagram
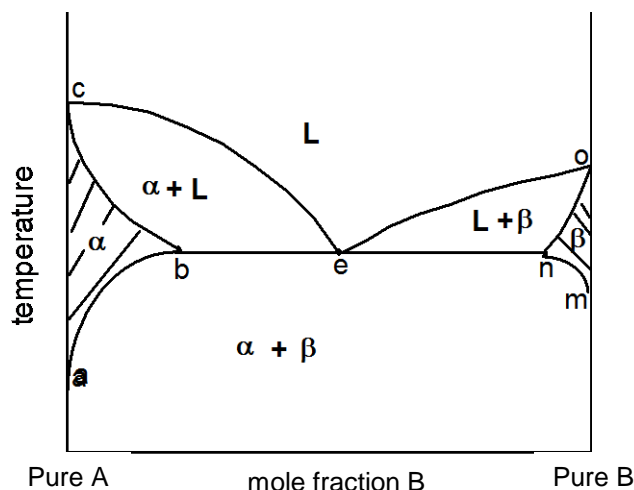
Fig. 2.6 Generic eutectic phase diagram

An analogous portion of the diagram is present on the right hand side of Fig. 2.6. If point b is moved to the left-hand ordinate and point n displaced to the right-hand ordinate, the phase diagram reduces to that shown in Fig. 2.5.

The iron-uranium phase diagram of Fig. 2.7 exhibits two eutectic points located between high-melting entities called *intermetallic compounds*. The vertical lines at uranium fractions of 0.33 and 0.86 represent Fe_2U and FeU_6, respectively. These are true compounds, with fixed and invariant Fe/U ratios, that are crystallographically distinct from the pure metals and have definite melting points. They form the boundaries of eutectic features in the phase diagram. Except for the presence of three allotropes of pure iron (the αFe, γFe, and δFe phases), the portion of the diagram between Fe and Fe_2U is the same as in Fig. 2.5. The region from Fe_2U to FeU_6 is exactly like Fig. 2.5. The zone between FeU_6 and pure U is complex, owing to the presence of the three phases of uranium (αU, βU, and γU) and the limited solubility of Fe in these phases. The α-U, β-U, and γ-U phases indicated on the extreme right of the diagram are analogs of the β region in Fig. 2.6. Except in these three single-phase solids and the liquid region, a point in Fig. 2.7 indicates the coexistence of two phases. The coexisting phases lie at the intersections of a horizontal line through the point and the boundaries of adjacent single phases. The lever rule gives the relative proportions of the two phases. Applying the lever rule (Eq(2.62)), an overall composition of 50 atom percent U at 1000^oC (B) consists of 23 mole % (BC/AC) Fe_2U (A) and 77 mole % liquid (AB/AC) of 55 mole % U (C).
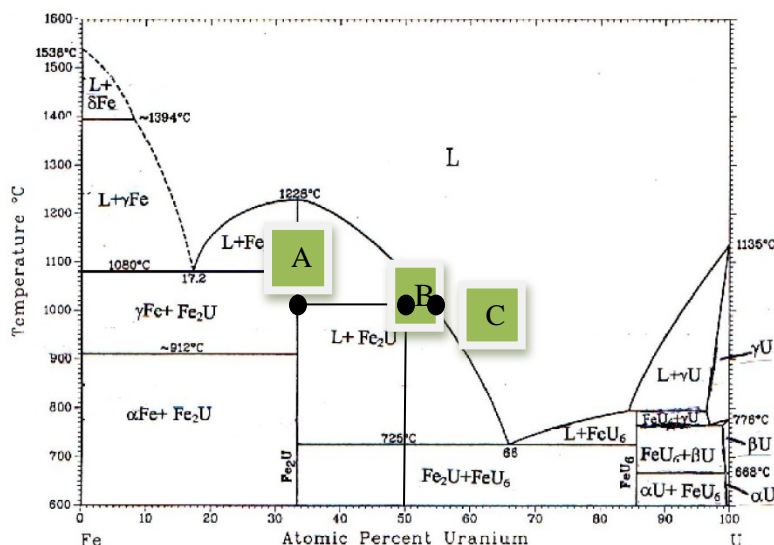
Fig. 2.7   The iron-uranium phase diagram

2.9 Chemical Equilibrium

Chemical reactions entail exchange of atoms between molecules. A system is designated as *homogeneous* if all constituents involved are in a single phase, or *heterogeneous* if the constituents are in two or more phases. Typically a homogeneous system may be a gas, solid or a liquid. A common heterogeneous reaction is metal oxidation, which involves a gas (containing oxygen) and two solid phases (the metal and its oxide).

Equilibrium analysis of chemical reactions provides an equation relating the mole fractions of all constituents. When supplemented with specified ratios of the elements involved, the composition of the equilibrium system is fixed. These generalities can be made more specific by considering the generic reaction between *reactant* constituents A and B to form *product* constituents C and D:

$$aA + bB = cC + dD \tag{2.67}$$

The coefficients of the reactant and product constituents (a, b, c and d) are the *stoichiometric coefficients* or *balancing numbers* that conserve elements on the two sides of the reaction. The equal sign indicates that the four constituents are present at equilibrium. At equilibrium, there is no distinction between reactants and products; Eq (2.67) could just as well have been written with C and D on the left and A and B on the right.

As in any system at constant temperature and pressure, thermodynamic equilibrium is attained when the Gibbs energy of the system containing all constituents involved is a minimum, or $dG = 0$. Extending the second equality in Eq (2.40) to include constituents C and D yields:

$$\mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D = 0$$

The changes in the mole numbers, $dn_A, \ldots dn_D,$ are related to each other by the balancing numbers in Eq (2.67); For example, for every **a** moles of *A* consumed, **b** moles of *B* disappear and **c** and **d** moles of *C* and *D*, respectively, are produced. These stoichiometric restraints are

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equivalent to: $dn_B = \frac{b}{a} dn_A$; $dn_C = -\frac{c}{a} dn_A$; $dn_D = -\frac{d}{a} dn_A$, and the equilibrium condition reduces to:

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D \qquad (2.68)$$

The equation applies to an equilibrium in a single phase or involving multiple phases.

2.9.1 Law of Mass Action

For a homogeneous gas-phase reaction, the chemical potentials are expressed in terms of the partial pressures by Eq (2.55), and Eq (2.68) becomes:

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \exp\left(-\frac{cg_C^o + dg_D^o - ag_A^o - bg_B^o}{RT}\right) = \exp\left(-\frac{\Delta G^o}{RT}\right) \qquad (2.69)$$

where K_P is the *equilibrium constant* in terms of partial pressures. It depends on both temperature and total pressure. The effect of the latter variable can be made explicit by replacing the partial pressures using Dalton's rule, Eq (2.53). With this substitution, the equilibrium constant becomes:

$$K_P = Kp^m, \qquad \text{where} \qquad m = c + d - a - b \qquad (2.70)$$

$$K = \frac{x_C^c x_D^d}{x_A^a x_B^b} \qquad (2.71)$$

K is the equilibrium constant in terms of gas-phase mole fractions, and is usually the preferred method for expressing equilibrium in a mixture. Equations (2.69) and (2.71) relating compositions to K_P and K are sometimes called the *law of mass action*.

Equation (2.67) is applicable to reactions involving both solids and gases. For example, the equilibrium constant for the reaction:

$$aA(g) + bB(s) = A_aB_b(g) \qquad (2.72)$$

is:

$$K_p = p_{A_aB_b} / p_A^a \qquad (2.72a)$$

provided that B is a pure solid, for which the activity is unity.

An important class of reactions involves solution species as well as gases and pure phases. A typical reaction of this type is:

$$M^{z+}(soln) + \tfrac{1}{2}zH_2(g) = M(s) + zH^+(soln) \qquad (2.73)$$

where z is the valence of the metal ion. "soln" denotes an ion in an aqueous solution for which the chemical potential is given by a modification of Eq (2.44a):

$$\mu_i = \mu_i^o + RT\ln[i] \qquad (2.73a)$$

μ_i^o is the chemical potential of species i in its standard state, which is 1 M aqueous solution of i.

[i] denotes the concentration of species i in moles per liter (molarity, M).. Equilibrium is defined by the general formula, Eq (2.68), applied to reaction (2.73) with:
-      for the solution species μ in the form of Eq (2.44a) with x_i replaced by [i]

- for the gas as applied to Eq (2.72)
- for pure solid components there is no composition dependence

The result is:

$$\Delta\mu^o = \mu_M^o + z\mu_{H^+}^o - \mu_{M^{z+}}^o - \tfrac{1}{2}zg_{H2_2}^o = -RT\ln\left(\frac{[H^+]^z}{[M^{z+}]p_{H2_2}^{z/2}}\right) \tag{2.73b}$$

The ratio in parentheses is the equilibrium constant for reaction (2.73). For a reaction with equilibrium constant K, the aqueous analog of Eq (2.69) is:

$$\Delta\mu^o = -RT\ln K \tag{2.69a}$$

2.9.2 Standard Gibbs energy of reaction

ΔG^o in Eq (2.69) is the *standard Gibbs energy* of reaction (2.67). It is expressed in terms of the *Gibbs energies of formation* ΔG_i^f (see Eq (2.42)). For reaction (2.67):

$$\Delta G^o = c\Delta G_C^f + d\Delta G_D^f - a\Delta G_A^f - b\Delta G_B^f \tag{2.74}$$

the superscript o indicates that it is to be evaluated at 1 atm pressure. The effect of pressure is contained in the integer m. Equation (2.71) applies to reactions in which the reactants and products are in any phase, not just the gas phase. If one or more of the components of the reaction are liquid or solid, their stoichiometric coefficients are not included in m of Eq (2.70).

One of the most convenient sources of ΔG_i^f is the compilation known as the JANAF (stands for Joint Army-Navy-Air Force) tables, which have been maintained by the National Institute of Science & Technology (NIST)[2] .

Knowledge of ΔG^o permits K_P to be obtained from Eq (2.69). Armed with the equilibrium constant K_P, Eq (2.71) determines the composition of the equilibrium mixture. The closed system initially contains specified moles of constituents A, B, C and D. In achieving equilibrium, the initial numbers of moles change to new values. Let $a\xi$ be the number of moles of A reacted in achieving equilibrium. The changes in the number of moles of B, C, and D are related to $a\xi$ by the stoichiometric coefficients of reaction (2.67). Table 2.1 gives the initial and final (equilibrium) mole numbers. In the last column, n_T^0 is the sum of the initial moles of

Table 2.1 Initial and Equilibrium mole numbers in gas-phase reaction aA + bB = cC + dD

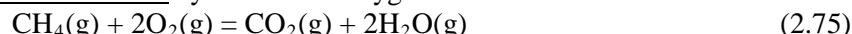| Moles	A	B	C	D	Total
Initial	n_A^0	n_B^0	n_C^0	n_D^0	n_T^0
Equilibrium	$n_A^0 - a\xi$	$n_B^0 - b\xi$	$n_C^0 + c\xi$	$n_D^0 + d\xi$	$n_T^0 + m\xi$

the four constituents and m is the combination of the stoichiometric coefficients shown in Eq (2.70). The mole fractions in the equilibrium system are obtained by dividing the moles of A, B, C, and D in the last row by the total moles in this row. Substituting these mole fractions into the law of mass action given by Eq (2.71) yields:

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[2] at the URL www.kinetics.nist.gov/janaf

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$$K = \frac{\left(n_C^o + c\xi\right)^c \left(n_D^o + d\xi\right)^d}{\left(n_A^o - a\xi\right)^a \left(n_B^o - b\xi\right)^b \left(n_T^o + m\xi\right)^m} \qquad (2.74)$$

This equation is solved for ξ (in general numerical solution is required) and from this result, the mole fractions at equilibrium are calculated.

Example #4: Combustion of 1 mole of methane by 2 moles of oxygen at 2000 K. The reaction is:
$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g) \qquad (2.75)$$
The letter g in parentheses following each constituent indicates it is a gas.

Application of the phase rule: two degrees of freedom are taken by fixing temperature and total pressure, So the remaining degrees of freedom are (Eq (2.34)):
$\mathcal{F}$ = C –P = 3(elements C, O and H) – 1(gas phase only) = 2
One degree of freedom is consumed by the equilibrium of reaction (2.75)
The last degree of freedom is eliminated by specification of the 2:1 ratio of O_2:CH_4 in the initial charge.

From the NIST tabulation, the formation reactions and their Gibbs-energies (in kJ/mole) at 2000 K are:

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) \qquad \Delta G_{H_2O}^f = -136 \qquad (a)$$

$$C(s) + O_2(g) = CO_2 \qquad \Delta G_{CO_2}^f = -395 \qquad (b)$$

$$C(s) + 2H_2(g) = CH_4(g) \qquad \Delta G_{CH_4}^f = 131 \qquad (c)$$

Algebraically, reaction (2.75) = 2(a) + (b) – (c), so the standard Gibbs energy change of the reaction is
$$\Delta G^o = \Delta G_{CO_2}^f + 2\ \Delta G_{H_2O}^f - \Delta G_{CH_4}^f = -395 + 2(-136) - (-131) = -798 \text{ kJ/mole},$$
According to Eqs (2.69) and (2.70), the equilibrium constant is $K_P = K = 7.5 \times 10^{20}$.

To solve for the composition of the equilibrium gas, a table similar to Table 2.1 is constructed with $A = CH_4$, $B = O_2$, $C = CO_2$ and $D = H_2O$. Second, Eq (2.74) is specialized for this reaction. In the latter method, the input parameters are: a (CH_4) = 1; b (O_2) = 2; c (CO_2)= 1; d (H_2O)= 2; m = 0 and $n_A^0 = 1$; $n_B^0 = 2$; $n_C^0 = 0$; $n_D^0 = 0$. Substituting these values into Eq (2.74) yields:

$$7.4 \times 10^{20} = \left(\frac{\xi}{1-\xi}\right)^3$$

In this case, analytical solution is possible, yielding $1 - \xi = 2.1 \times 10^{-7}$. The corresponding mole fractions at equilibrium are: $x_A = 4 \times 10^{-8}$; $x_B = 8 \times 10^{-8}$; $x_C = 0.333$; $x_D = 0.667$. The reaction goes nearly to completion (i.e., essentially all reactants are consumed).

2.9.3 Stability diagrams

The class of heterogeneous reactions in which an element reacts with a diatomic gas to form a compound is both of practical importance and amenable to simple thermodynamic analysis. Reactions in this category include oxidation, nitriding, and hydriding of metals and halogenation of the electronic material silicon. The simplicity of the thermodynamics stems from the immiscibility of the reactants and products. Consider oxidation of a metal (M) to form a dioxide (MO_2):
$$M(s) + O_2(g) = MO_2(s) \qquad (2.76)$$

The letter s in parentheses indicates a solid phase; in this case there are two solid phases because the metal and its oxide are essentially insoluble in each other. Since M and MO_2 are practically pure substances, their chemical potentials are equal to their molar Gibbs energies. The chemical potential of oxygen gas is dependent on its partial pressure, and is given by Eq (2.55). With $a(M) = b(O_2) = c(MO_2) = 1$ and $d = 0$, the general criterion, Eq (2.68), becomes:

$$g_M^o + g_{O_2}^o + RT \ln p_{O_2} = g_{MO_2}^o \qquad (2.77)$$

Rearranging this equation into more convenient forms gives:

$$\ln p_{O_2} = \frac{\Delta G_{MO_2}^f}{RT} = \frac{\Delta H_{MO_2}^f}{RT} - \frac{\Delta S_{MO_2}^f}{R} \qquad (2.78a)$$

or

$$RT \ln p_{O_2} = \Delta G_{MO_2}^f = \Delta H_{MO_2}^f - T\Delta S_{MO_2}^f \qquad (2.78b)$$

where

$$\Delta G_{MO_2}^f = g_{MO_2}^o - g_{O_2}^o - g_M^o = g_{MO_2}^o \qquad (2.79)$$

is the standard Gibbs energy of formation of the oxide MO_2. By definition, the standard Gibbs energies of formation of the elements are zero. The standard state is the substance at a total pressure of 1 atm and the specified temperature. $\Delta H_{MO_2}^f$ and $\Delta S_{MO_2}^f$ are the enthalpy and entropy of formation (reaction (2.72)). The former is the heat released when one mole of metal is oxidized.

Equations (2.78a) and (2.78b) are plotted in Fig. 2.8. These plots are called *stability diagrams* because the lines separate regions in which only one of the two phases is present. The line represents the p_{O_2} - T combinations where both the metal and its oxide coexist.
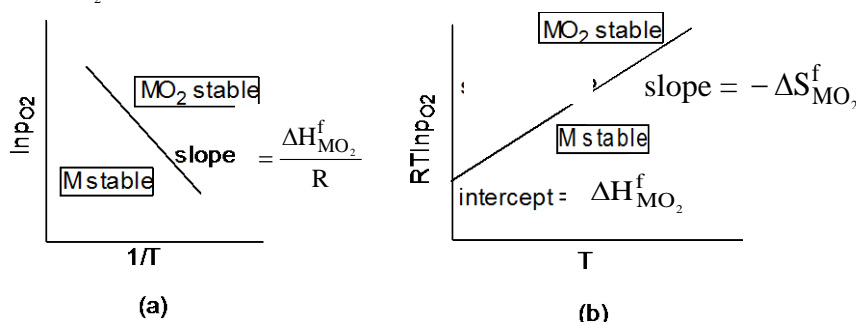
Fig. 2.8 Stability diagrams for the M + MO$_2$ Couple.

The oxide-metal stability diagram is a solid-phase analog of the p-T phase diagram of a single substance such as water, where lines separate existence regions of solid, liquid, and vapor phases (see Fig.2.2).

Example #5: Oxygen pressure over Ni/NiO
Powdered nickel metal is contacted with a flowing mixture of CO_2 and CO at 1 atm total pressure in a furnace at 2000 K. The quantity of metal is limited, but because of continual flow, the quantity of the gas mixture is unlimited. Therefore, the oxygen pressure established in the gas phase is imposed on the metal, and determines whether or not it oxidizes.
At what CO_2/CO ratio do both Ni and NiO coexist?

The O_2 pressure in the gas is fixed by the equilibrium: $2CO(g) + O_2(g) = CO_2(g)$. At 2000 K, the equilibrium constant is $K_P = 4.4 \times 10^5$. The law of mass action for this equilibrium reaction is:

$$\left(p_{O_2}\right)_{gas} = (p_{CO_2} / p_{CO})^2 / K_P$$

The nickel/nickel oxide equilibrium reaction is: $2Ni + O_2 = 2NiO$, for which

$\Delta G^f_{NiO} = $ -46 kJ/mole at 2000 K[3]. According to Eq (2.71a), for coexisting Ni and NiO in the solid phase, the oxygen pressure is:

$$\left(p_{O_2}\right)_{solid} = \exp\left(\Delta G^f_{NiO} / RT\right) = 6.3 \times 10^{-2} \text{ atm}$$

The mixed solid and the mixed gas are in equilibrium when $(p_{O_2})_{gas} = (p_{O_2})_{solid}$. From the above equations, this condition yields the required ratio of CO_2 to CO in the gas:

$$p_{CO_2} / p_{CO} = \sqrt{K_P \left(p_{O_2}\right)_{solid}} = \sqrt{\left(4.4 \times 10^5\right)\left(6.3 \times 10^{-2}\right)} = 166$$

2.9.4 Ellingham diagrams

A common method of expressing the relative stabilities of metal oxides, chlorides and fluorides is the *Ellingham diagram*. As shown in Fig. 2.9, the temperature dependence of the standard Gibbs energies of formation of the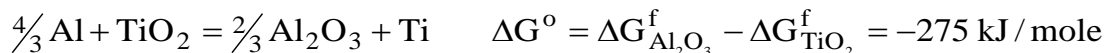 oxides are plotted against T. The ordinate expresses $\Delta G^f_{M_2O_3}$ per mole of O_2, for the generic metal M with oxide M_aO_b reaction:

$$\tfrac{2a}{b} M + O_2 = \tfrac{2}{b} M_a O_b$$
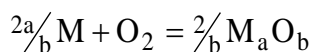
The reason for the per-mole-O_2 units is to permit easy assessment of the relative stabilities of the oxides. For example, application of Fig. 2.9 to Al_2O_3 and TiO_2 at 800°C yields:

$$\tfrac{4}{3} Al + O_2 = \tfrac{2}{3} Al_2O_3 \qquad \Delta G^f_{Al_2O_3} = -975 \text{ kJ / mole } O_2$$

$$Ti + O_2 = TiO_2 \qquad \Delta G^o_{TiO_2} = -700 \text{ kJ / mole } O_2$$

Subtracting the Ti reaction from the Al reaction gives:

$$\tfrac{4}{3} Al + TiO_2 = \tfrac{2}{3} Al_2O_3 + Ti \qquad \Delta G^o = \Delta G^f_{Al_2O_3} - \Delta G^f_{TiO_2} = -275 \text{ kJ / mole}$$

The negative standard Gibbs energy change indicates that the reaction favors the right hand side and, given sufficient aluminum, all TiO_2 is reduced to the metal. Used this way, the Ellingham reactions are analogous to half-cell reactions in electrochemistry.

The Gibbs energy of formation of M_aO_b can be written as:

$$\Delta G^f_{M_aO_b} = \Delta H^f_{M_aO_b} - T\Delta S^f_{M_aO_b}$$

Because $\Delta H^f_{M_aO_b}$ and $\Delta S^f_{M_aO_b}$ are very nearly temperature-independent, $\Delta G^f_{M_aO_b}$ Vs T is a straight line with a slope equal to $-\Delta S^f_{M_aO_b}$ and an intercept at 0 K of $\Delta H^f_{M_aO_b}$

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[3] the free energy of formation is per mole of O_2, not per mole of NiO.

$$\Delta S^f_{M_aO_b} = \tfrac{2}{b}s^o_{M_aO_b} - \tfrac{2a}{b}s^o_M - s^o_{O_2} \qquad \Delta H^f_{M_aO_b} = \tfrac{2}{b}h^o_{M_aO_b} - \tfrac{2a}{b}h^o_M - h^o_{O_2}$$

where the lower-case letters apply to a property per mole of the constituent and the superscript o indicates the standard state of 1 atm. Because the oxide and the metal are solids, their entropies are small compared to the entropy of O_2. This means that $\Delta S^f_{M_aO_b} \cong -s^o_{O_2}$, so that $\Delta G^f_{MO_2}$ is approximately:

$$\Delta G^f_{M_aO_b} \cong \Delta H^f_{M_aO_b} + Ts^o_{O_2}$$

This is why the slopes of the lines in the Ellingham diagram are positive and nearly the same for all metals.

The intercepts at 0 K (not shown on Fig. 2.9) are all negative (because $\Delta H^f_{M_aO_b}$ is negative) and vary greatly with the metal. The sum of the enthalpies of the metal and oxygen is greater than that of the oxide, or that most metals burn with considerable release of heat. The noble metals Au, Ag, Pd, etc. are not shown on Fig. 2.9. For these metals, $\Delta H^f_{M_aO_b}$ is positive.

The letters on Fig. 2.9 indicate the three phase changes discussed in Sects. 2.4.1 and 2.4.2: sublimation, vaporization and melting. At the boiling point of the metal (**B** on the diagram), the slope of the line increases . The slopes of the lines with the metal liquid and vapor are:

$$\text{slope liquid} = -\Delta S^f_{M_aO_b} = -(\tfrac{2}{b}s^o_{M_aO_b} - \tfrac{2a}{b}s^o_{M(L)} - s^o_{O_2})$$

$$\text{slope vapor} = -\Delta S^o_{M_AO_b} = -(\tfrac{2}{b}s^o_{M_aO_b} - \tfrac{2a}{b}s^o_{M(g)} - s^o_{O_2})$$

so that the change in slope at the boiling point is the difference in the molar entropies of the vapor and liquid metal, or $s^o_{M(g)} - s^o_{M(L)} = \Delta s_{vap,M}$. Because $\Delta g_{vap,M} = 0$ at equilibrium, $\Delta s_{vap,M} = \Delta h_{vap,,M}/T_{vap,M}$.

<u>Example #6: Slope of the boiling line in Fig. 2.9</u>
For M = Al, the enthalpy of vaporization is 295 kJ/mole and the boiling temperature (at 1 atm) is 2740 K, so $\Delta s_{vap,Al}$= 0.11 kJ/mole-K. The slope of the Al(L) line in Fig. 2.9 is ~ 0.20 kJ/mole-K, so the slope of the Al(vap) should be 0.31 kJ/mole-K. The slope of the Al(vap) line from Fig. 2.9 is ~ 0.35 kJ/mole-K, which is close enough.

There is a similar change in slope at the melting point of the metal. However the enthalpy of melting divided by the melting temperature is too small for the expected change in slope to be visible on Fig. 2.9.

O_b,

2.10 Aqueous Electrochemistry and Ionic Reactions

The chemical reactions between aqueous ions and metals are called *electrochemical reactions*. Such reactions are the source of some of the most important materials problems in the nuclear industry. Corrosion of the metal components in the core and the primary circuit of light water reactors is a prime example of practical electrochemistry (see Chap. 15).

The elements that, as ions, take part in electrochemical reactions often have more than one *valence state,* or *oxidation state* (z), that are stable in, or in contact with, water. Iron, for example, commonly occurs in the elemental (Fe^0), ferrous (Fe^{2+}), and ferric (Fe^{3+}) oxidation states. Hydrogen occurs as the diatomic molecule H_2 dissolved in water or as the hydrogen ion H^+. The forms of oxygen include OH^- and the dissolved gas O_2. Both hydrogen and oxygen

appear in H_2O, which often takes part in electrochemical reactions. For an element to participate in an electrochemical reaction, it must change valence state in the reaction. For example, the *overall reaction*:

$$M^{z+} + \tfrac{1}{2}zH_2 = M + zH^+ \qquad (2.80)$$

involves reduction of M^{z+} dissolved in water to the metal M. Accompanying reduction of one element is oxidation of another. In this case, hydrogen in its elemental state as H_2 (either in solution or in the gas phase) is oxidized to the 1+ state in solution.

Positive ions in solution are called *cations*, whereas negative ions, called *anions,* must accompany the positive ions to maintain electrical neutrality of the solution. Anions are not explicitly included in Eq (2.80). The reason is that most anions exhibit only one charge state in aqueous solution. If an ionic constituent is not capable of changing oxidation state, it cannot participate in the electrochemical reaction. Typical anions include Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}.

 Many (but not all) electropositive elements are immune from electrochemical effects because they exhibit only one stable oxidation state. Sodium, for example, is always present in solution as Na^+; reduction to the element in water is not possible. The phases occupied by the constituents in the above overall reaction are not indicated, but are usually evident: the metal M is a solid; H_2 is a gas; both cations are in solution.

Reaction (2.80) can be viewed as the transfer of z electrons from the hydrogen molecule to the metal ion. As a result, M decreases in valence from z+ to 0 and is said to be *reduced*. Hydrogen increases its valence from 0 to 1+, or is *oxidized.*

In overall electrochemical reactions, the exchange of the electrons is not physically manifest because it occurs in an intimate mixture of reactants and products. However, in a device known as an *electrochemical cell*, participants in a reaction are physically separated in a manner that makes it possible for the electron transfer process to be observed, utilized for doing work, or measured to provide information useful in understanding processes such as corrosion. This is accomplished by separating the overall reaction into *half-cell reactions*, in which the oxidation and reduction portions are shown explicitly. For example, the half-cell reactions corresponding to reaction (2.80) are:

$$M^{z+} + ze = M \qquad (2.81a)$$
$$2H^+ + 2e = H_2 \qquad (2.81b)$$

where e denotes an electron. By convention, the reduced species is on the right-hand side of the equal sign. The overall reaction is (2.81a) minus ½z of (2.81b), which gives (2.80). The rule for writing half-cell reactions is: *electrons on the left*.

2.10.1 Faraday Constant

Because electrochemistry deals with movement of electrons between species, a fundamental constant called the *Faraday constant* is frequently encountered. The Faraday constant F is the product of Avogadro's number and the electronic charge:

$$F = eN_{Av} = (1.602 \times 10^{-19})(6.02 \times 10^{23}) = 96,500 \text{ Coulombs/mole electrons.}$$

A Coulomb is a Joule per Volt, so:

$$F = 96.5 \ \frac{kJ}{Volt - mole \ electrons}$$

2.10.2 The electric potential

Figure 2.10 illustrates an electrochemical cell in which the half-cell reactions take place in individual compartments. Each half-cell contains a metal *electrode*. The left-hand half cell contains the metal M and the specified aqueous concentration of M^{z+} In the right-hand half cell, the inert metal (platinum) electrode permits reaction (2.81b) to proceed efficiently. The concentration of H^+ and the H_2 pressure in the gas saturating the solution are both specified. The *bridge* separating the two compartments permits anions (associated with M^{z+} and H^+) to move in order to maintain electrical neutrality.

The two metal electrodes are connected by wires to one of two devices: a voltmeter or a battery. Shown in the figure is a meter that measures the voltage, or *electric potential*, between the two electrodes. In this mode, no current flows and the system is at electrical equilibrium, but not chemical equilibrium.

If instead of the voltmeter, a battery is placed in the line, the applied voltage causes a current to flow as reactions (2.81a) and (2.81b) proceed in the two half cells; the metal is either dissolved or electroplated, depending on the direction of current flow. The half cell in which oxidation (increase in valence) occurs is the *anode* and the one supporting reduction is the *cathode*.

From a thermodynamic point of view, the great utility of the electrochemical cell is that its electric potential is proportional to the difference in the Gibbs energies of the mixtures in the two electrodes – that is, $\Phi_{M,H}$ is a direct measure of the equilibrium constant of the overall cell reaction (2.80). This connection is established by considering a nonequilibrium cell and equating the electrical work (cell potential times the charge transferred, $z(eN_{Av})\Phi_{MH}$, to the maximum possible work in a process at constant temperature and pressure (equal to the decrease of the Gibbs energy, Eq (2.25)). The result is:

$$\Delta G = -zF\Phi_{MH} \tag{2.82}$$

ΔG is the difference in the Gibbs energy between the product and reactant sides of the reaction. The cell in Fig. 2.10 functions as an equilibrium cell since no current flows and no change occurs with time. However, this does not mean that the ion concentrations in the two electrodes are those that would be found if the two half-cell solutions were part of the same solution, which is equivalent to short-circuiting the cell in Fig. 2.10. In this case, the concentrations of M^{z+} and H^+
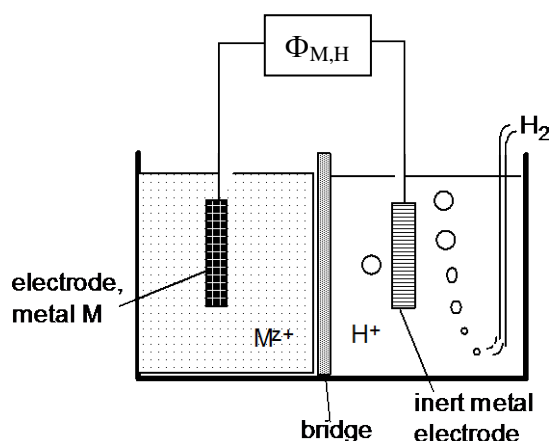
Fig. 2.10 An aqueous electrochemical cell with a metal half-cell and a hydrogen half-cell.

adjust until the equilibrium criterion of Eq (2.68) is satisfied for overall reaction (2.80). In the configuration of Fig. 2.10, on the other hand, the ion concentrations can be arbitrarily fixed and the potential $\Phi_{M,H}$ reflects the imbalance of the chemical potentials in the two half cells. Instead of the equilibrium condition of Eq (2.68), ΔG is nonzero and is given by:

$$\Delta G = \mu(M) + z\mu(H^+) - \mu(M^{z+}) - \frac{z}{2}\mu(H_2) \tag{2.83}$$

The chemical potential of H_2 depends on its partial pressure according to Eq (2.55):

$$\mu_{H2} = g^o_{H2} + RT \ln p_{H2} \tag{2.84a}$$

The chemical potential of H_2 dissolved in water is the same as that of the gas (see Eq (2.56)).

- the chemical potential of pure metal M is equal to its molar Gibbs energy.
- the chemical potentials of ions in solution are related to the concentrations by:

$$\mu(H^+) = \mu^o(H^+) + RT\ln[H^+] \qquad\qquad \mu(M^{z+}) = \mu^o(M^{z+}) + RT\ln[M^{z+}] \tag{2.84b}$$

[i] is the concentration of constituent i in moles per liter of solution (molarity, denoted by M). $\mu^o(i)$ is the standard-state chemical potential for ion i in a 1 M solution. Nonideality due to interaction of the ions with the surrounding water molecules is contained in the chemical potential in this standard state. All that is required is that the ion-water interaction be

independent of [i], which is acceptable as long as the solution is not too concentrated in constituent i.

Substituting Eqs (2.84a) and (2.84b) into Eq (2.83) and eliminating ΔG using Eq (2.82) gives:

$$\Phi_{MH} = -\frac{\Delta\mu^o}{zF} - \frac{RT}{zF}\ln\left(\frac{[H^+]^z}{[M^{z+}]p_{H2}^{z/2}}\right) \qquad (2.84c)$$

where:
$$\Delta\mu^o = \mu^o(M) - \mu^o(M^{z+}) + z\mu^o(H^+) - \tfrac{1}{2}zg_{H2}^o\,]$$

The standard chemical potentials are converted to electric potentials of the half-cells:

$$\mu^o(M) - \mu^o(M^{z+}) = -zF\phi_M^o \qquad\qquad \tfrac{1}{2}g_{H2}^o - \mu^o(H^+) = -F\phi_H^o$$

ϕ_H^o and ϕ_M^o are the *standard electrode potentials* of the two half-cell reactions. All half-cell potentials are with respect to the *standard hydrogen electrode* (acronym SHE), which is a H^+/H_2 half-cell containing $[H^+] = 1$ M and $p_{H2} = 1$ atm. The standard electrode potential of the SHE is defined as $\phi_H^o = 0$.

Combining the above equations gives:

$$\frac{\Delta\mu^o}{zF} = \phi_H^o - \phi_M^o$$

Inserting this equation into Eq (2.84c) yields:

$$\Phi_{MH} = \phi_M^o - \phi_H^o - \frac{RT}{zF}\ln\left(\frac{[H^+]^z}{[M^{z+}]p_{H2}^{z/2}}\right) \qquad (2.84d)$$

2.10.3 The standard electrode potential

Cell potentials for overall reactions such as that of reaction (2.80) have been split into two *half-cell potentials* that characterize reactions (2.81a) and (2.81b) such that $\Phi_{MH} = \phi_M - \phi_H$, where:

For $M^{z+} + ze = M$:
$$\phi_M = \phi_M^o - \frac{RT}{zF}\ln\left(\frac{1}{[M^{z+}]}\right) \qquad (2.85a)$$

For $2H^+ + 2e = H_2$:
$$\phi_H = \phi_H^o - \frac{RT}{2F}\ln\left(\frac{p_{H2}}{[H^+]^2}\right) \qquad (2.85b)$$

Figure 2.10a shows the sequence of electrochemical cells which permit proceeding from standard electrode potentials to potentials of the overall cell reaction. The voltmeter reads the difference between the half-cell potentials.

In No. 1, a standard hydrogen electrode (SHE) is coupled to a half cell containing H^+ at 1 M and hydrogen gas at 1 atm. Since the latter is the definition of the SHE, the potential of this overall cell is zero.

No. 2 contains the same components as No. 1 except that the H^+ concentration and p_{H2} in the left-hand half cell are not unity. The potential of this H^+/H_2 overall cell is given by Eq (2.85b), again with $\phi_H^o = 0$

No. 3 couples a SHE and a half cell containing the metal M and a 1 M concentration of the metal ion . The measured voltage is ϕ_M^o .

No. 4 contains the same constituents as cell No. 3 except that the metal ion concentration is no longer specified as 1 M. The potential of this cell is given by Eq (2.85a).

No. 5 mates the hydrogen half cell of No. 2 and the metal half cell of No. 4 to give the overall potential of the electrochemical cell in Fig. 2.10. The potential produced by this cell is:

$$\Phi_{MH} = \phi_M - \phi_H = \phi_M^o - \frac{RT}{zF} \ln\left[\frac{[H^+]^z}{[M^{z+}]p_{H_2}^{z/2}} \right] \tag{2.86}$$
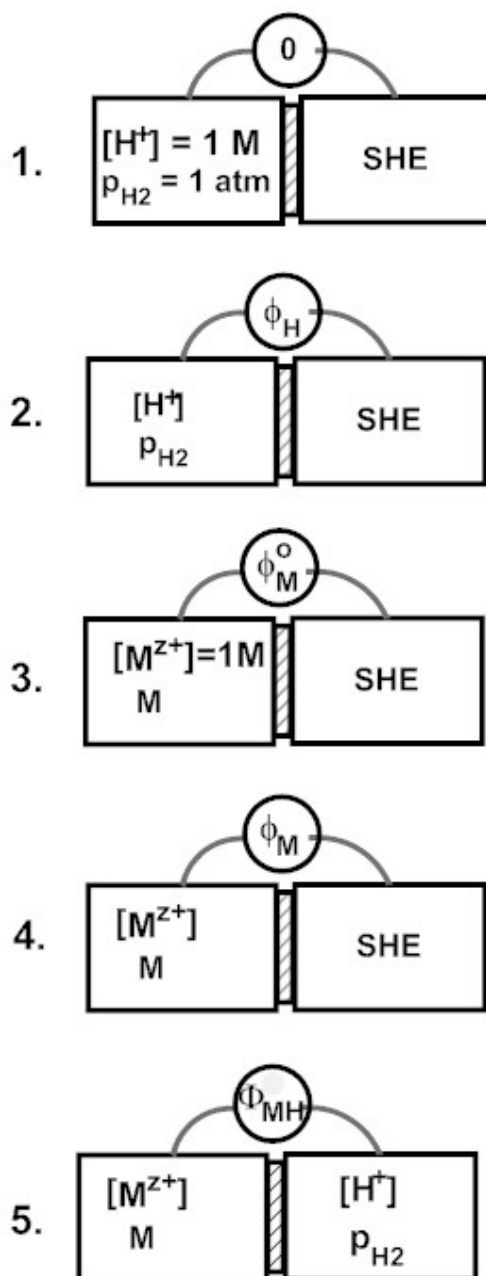
Fig. 2.10a Electrochemical cells

At this point, one might ask: "Of what use are electrochemical potentials?" The most important information is obtained by short-circuiting cell No. 5, which is equivalent to setting $\Phi_{MH} = 0$ in the above equation. This yields:

$$\frac{[M^{z+}]p_{H2}^{z/2}}{[H^+]^z} = \exp\left(-\frac{z\,F\phi_M^o}{RT}\right)$$

(2.87)

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The right hand side is the equilibrium constant of reaction (2.80). The standard electrode potentials thus provide important equilibrium information for aqueous reactions. For a general reaction written as lhs = rhs, the law of mass action is:

$$K = \frac{[rhs]}{[lhs]}$$

where [rhs] denotes the product of the concentrations of solution species on the right-hand side of the reaction. The same applies to [lhs]. The generalization of Eq (2.87) is:

$$lnK = -\frac{zF}{RT}\left(\phi^o_{ox,rhs} - \phi^o_{ox,lhs}\right) \tag{2.87a}$$

The subscripts *ox,rhs* and *ox,lhs* denote the oxidized species on the two sides of the reaction. Problem 2.8 is a typical application of Eq (2.87a).

The basic database for aqueous electrochemistry consists of the standard electrode potentials. Since most aqueous systems are at room temperature (with the notable exception of the coolant in light water reactors), a single table at 25^oC suffices to accommodate the entire database. An abridged table of standard electrode potentials is given in Table 2.2.

The last two columns of the top set of half-cell reactions refer to the conditions of the aqueous solution. ϕ^o for the hydrogen reaction (No 3 in the table) is zero because this is the reference half-cell (the SHE).

As shown in the examples below, the standard electrode potential for a half-cell reaction not found in Table 2.2 can often be derived from reactions that appear in the table. Standard electrode potentials are temperature-independent.

Table 2.2 Standard Electrode Potentials

Half-cell Reaction ϕ^o, Volts

Involving H_2 and O_2

1.	$\frac{1}{2}O_2 + 2H^+ + 2e = H_2O$	1.23
1a.	$\frac{1}{2}O_2 + H_2O + 2e = 2OH^-$	0.40
2.	$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.77
3.	$2H^+ + 2e = H_2$	0
3a.	$2H_2O + 2e = H_2 + 2OH^-$	-0.83

Nos. 1a and 3a are obtained from Nos. 1 and 3
using $H_2O = H^+ + OH^-$

Involving metals

4.	$Au^{3+} + 3e = Au$	1.50
5.	$Cu^{2+} + 2e = Cu$	0.34

Fig. 2.10a Electrochemical cells

6.	$Ni^{2+} + 2e = Ni$	- 0.25
7.	$Fe^{2+} + 2e= Fe$	- 0.44
8.	$Na^+ + e = Na$	- 2.75

Involving only ions

9.	$Fe^{3+} + e = Fe^{2+}$	0.77
10.	$UO_2^{2+} + 4H^+ + 2e = U^{4+} + 2H_2O$	0.34
11.	$PuO_2^{2+} + 4H^+ + 2e = Pu^{4+} + 2H_2O$	2.04
12.	$Pu^{4+} + e = Pu^{3+}$	0.98
13.	$Cu^{2+} + e = Cu^+$	0.16

Involving solid oxides or hydroxides

14.	$UO_2^{2+} + 2e = UO_2(s)$	-0.43
15.	$Fe_2O_3(s) +6H^+ + 2e = 2Fe^{2+} + 3H_2O$	0.68
15a	$FeO(s) + 2H^+ + 2e = Fe(s) +H_2O$	-0.03
16.	$Cu_2O(s) + H_2O + 2e = 2Cu(s) + 2OH^-$	- 0.36
17.	$Cu(OH)_2(s) + 2e = Cu(s) + 2OH^-$	- 0.22

Example #7a: the half-cell reaction $Fe^{+3} + 3e = Fe$
This half-cell reaction is the sum of reactions 7 and 9 in Table 2.2, so:

$$\phi^o (Fe^{3+} / Fe) = \phi_7^o + \phi_9^o = -0.44 + 0.77 = 0.33 \text{ V}$$

Example #7b: Standard electrode potential for No. 15 in Table 2.2
This reaction can be decomposed into the following:

(7) $Fe^{2+} + 2e = Fe$
(a) $2Fe + 3/2O_2 = Fe_2O_3$
(1) $½ O_2 + 2H^+ + 2e = H_2O$
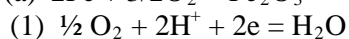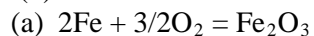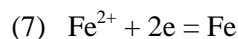
No. 15 is obtained by algebraically combining the three reactions as:
$$(15) = -(a) - 2(7) +3(1)$$
However, the electrode potential of half-cell reaction No. 15 cannot be determined simply by combining standard electrode potentials as in Example #7a because (a) does not involve either aqueous ions or

electrons. Instead, we only have the Gibbs energy of formation of Fe_2O_3 at 25ºC, $\Delta\mu_a^o$. In order to combine the t

hree component equations, ϕ_1^o and ϕ_7^o must first be converted to $\Delta\mu_1^o$ and $\Delta\mu_7^o$ using the analog of Eq (2.82):

$$\Delta\mu_i^o = \text{-z } \boldsymbol{F}\phi_i^o \tag{2.82a}$$

and the $\Delta\mu_i^o$ values combined to determine $\Delta\mu_{15}^o$:

$$\Delta\mu_{15}^o = -\Delta\mu_a^o - 2\Delta\mu_7^o + 3\Delta\mu_1^o$$

From Table 2.2,

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$$\phi_1^o = 1.23 \text{ V, so} \qquad \Delta\mu_1^o = -2\times96.5\times(1.23) = -237 \text{ kJ/mole } H_2Ol;$$

and

$$\phi_7^o = -0.44 \text{ V, so} \qquad \Delta\mu_7^o = -2\times96.5\times(-0.44) = 85 \text{ kJ/mole Fe}$$

from Fig. 2.9, $\Delta\mu^o$ (or ΔG^o) of Fe_2O_3 is - 500 kJ per mole of O_2 . So for reaction (a) as written:

$$\Delta\mu_a^o = 3/2(-500) = -750 \text{ kJ/mole } Fe_2O_3$$

Combining:

$$\Delta\mu_{15}^o = -(-750) - 2(85) + 3(-237) + = -132 \text{ kJ/mole}$$

and from Eq (2.82a), the standard half-cell potential is:

$$\phi_{15}^o = -(-132)/(2\times96.5) = 0.68 \text{ V}$$

2.10.4 The Nernst equation

Half-cell reactions such as Eqs (2.85a) and (2.85b) are written with electrons on the left and in the corresponding potential equations, the reduced species is in the numerator and the oxidized portion in the denominator:

For oxid + ne = red: $$\phi^N = \phi^o - \frac{RT}{nF}\ln\left(\frac{\text{red.}}{\text{oxid.}}\right) = \phi^o - \frac{2.3RT}{nF}\log\left(\frac{\text{red.}}{\text{oxid.}}\right) \qquad (2.88)$$

This general form of the half-cell potential is called the *Nernst equation*. At 25°C, 2.3RT/F = 0.059 V. It is important to remember that the Nernst equation applies to half-cell reactions such as (2.81a) and (2.81b), not to overall reactions of which (2.80) is an example. The potential ϕ^N in Eq (2.88) is termed the *Nernst potential* of the half-cell. It is measured in a full cell relative to an SHE. n is the coefficient of e in the half-cell reaction taken from Table 2.2. It need not be the same as the charge on the ion. For example, n = 2 for half-cell reactions 1 – 3a even though the charge of the moving ion is +1 or -1.

Example #8 : Nernst potential of half-cell 10 in Table 2.2

for the following concentrations: $[H^+] = 0.01$ M, $[UO_2^{2+}] = 2.0$ M, $[U^{4+}] = 0.1$ M. The Nernst equation for this half-cell is:

$$\phi_{10}^N = \phi_{10}^o - \frac{0.059}{2}\log\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right) = 0.34 - \frac{0.059}{2}\log\left(\frac{0.1}{0.01^4\times2.0}\right) = 0.14 \text{ V}$$

The Nernst equation, expressed in its general form by Eq (2.88), has three very important applications: i) it gives the voltage (or potential) of an electrochemical cell consisting of two arbitrary half cells; ii) it provides a means of converting the data in Table 2.2 to the equilibrium constant of ionic reactions in a single solution; iii) it offers a systematic method for assessing the tendency for metals to corrode in water. The last of these applications is deferred until Chap. 15

The first two applications of Eq (2.88) are closely related and can be illustrated by the reaction by which tetravalent plutonium is reduced to the trivalent state by addition of ferrous ion:

$$Fe^{2+} + Pu^{4+} = Fe^{3+} + Pu^{3+} \tag{2.89}$$
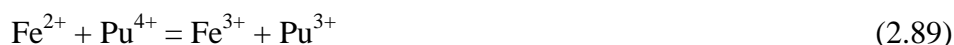
This reaction can be considered either as an overall reaction for an electrochemical cell consisting of electrodes with the half-cell reactions:

$$Fe^{3+} + e = Fe^{2+} \qquad Pu^{4+} + e = Pu^{3+} \tag{2.90}$$
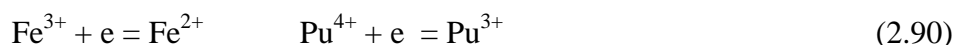
or as an equilibrium reaction with all four ions in the same solution. These two interpretations are shown schematically in Fig. 2.11.

(a) separate half-cells   **(b) solution**
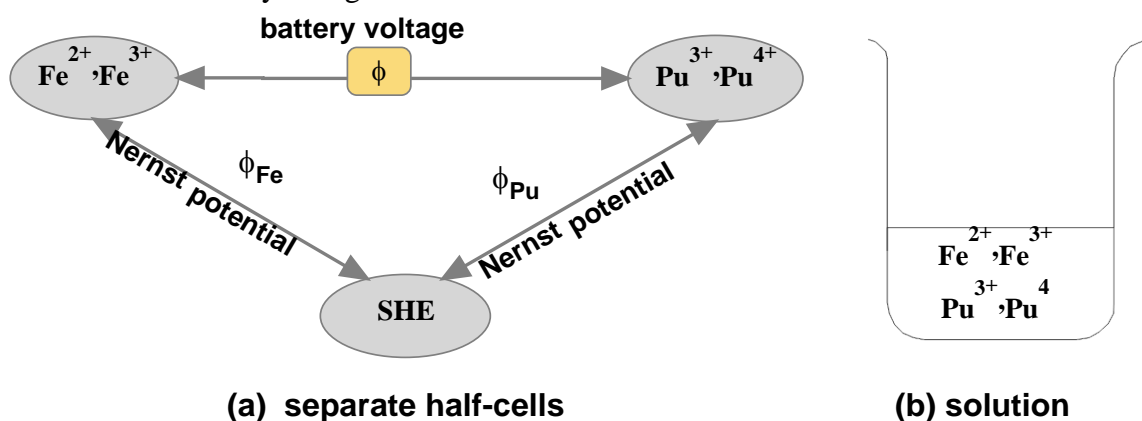
Fig. 2.11 Two ways of interpreting the plutonium-iron reaction in solution.

As components of an electrochemical cell, the Nernst potentials of the Fe and Pu half-cells are, using Eq (2.88):

$$\phi_{Pu}^{N} = \phi_{Pu}^{o} - 0.059 \log\left(\frac{[Pu^{3+}]}{[Pu^{4+}]}\right)$$

$$\phi_{Fe}^{N} = \phi_{Fe}^{o} - 0.059 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) \tag{2.91}$$

When the Fe and Pu electrodes are joined (top of Fig. 2.11(a)), the potential of this full electrochemical cell is:

$$\phi = \phi_{Fe}^{N} - \phi_{Pu}^{N} = (\phi_{Fe}^{o} - \phi_{Pu}^{o}) - 0.059 \log\left(\frac{[Fe^{2+}][Pu^{4+}]}{[Fe^{3+}][Pu^{3+}]}\right) \tag{2.92}$$

This equation has two interpretations. If ϕ represents an applied voltage, the ratios $[Pu^{4+}]/[Pu^{3+}]/$ and $[Fe^{3+}]/[Fe^{2+}]$ adjust so that Eq (2.92) is satisfied. If the concentration ratios are fixed, ϕ adjusts according to Eq (2.92) and the combination forms a battery.

Example #9: Pu^{4+}/Fe^{2+} battery

The Pu half-cell contains equal concentrations of trivalent and tetravalent plutonium and the iron half-cell consists of a 5:1 concentration ratio of Fe^{2+} to Fe^{3+}.

The electrode reactions are numbers 9 and 12 in Table 2.2. From Eq (2.91), the Nernst potentials are: $\phi_{Pu}^{N} = 0.98$ V and $\phi_{Fe}^{N} = 0.73$ V. The overall cell potential is $\phi = 0.73 - (0.98) = -0.25$ V.

2.10.5 Ionic equilibria

An important feature of the standard electrode potentials in Table 2.2 is their utility in calculating equilibrium constants for ionic reactions in aqueous solutions. The electrochemistry of ions contained in a single solution (Fig. 2.11(b)) is equivalent to short-circuiting the connection between the Fe and Pu half cells (setting $\phi = 0$ in Fig. 2.11(a) is equivalent to mixing the two together as in Fig. 2.11b).

The condition for equilibrium in a solution containing the constituents of half-cells A and B is the equality of their Nernst potentials:

$$\phi_A^N = \phi_B^N \tag{2.93}$$

Two examples of utilizing this equation are given below.

Example #10 The Pu^{4+}/Fe^{2+} reaction
The solution is made by mixing equal volumes of 1M $FeSO_4$ and 0.5 M $Pu(SO_4)_2$. Find the concentration ratio Pu^{4+}/Pu^{3+} at equilibrium.
Element conservation for the two metals is:

$$[Fe^{2+}] + [Fe^{3+}] = 0.5 \qquad\qquad [Pu^{4+}] + [Pu^{3+}] = 0.25$$

The total concentrations of the two elements are one half of their initial values because two equal volumes are mixed, which doubles the volume of solution.

The condition of charge neutrality requires that the total cation charges in the solution equal the total anion charges. This gives:

$$2[Fe^{2+}] + 3[Fe^{3+}] + 3[Pu^{3+}] + 4[Pu^{4+}] = 2[SO_4^{2-}] = 2[0.5 + 0.5] = 2$$

The two 0.5 numbers in the brackets account for 1 M SO_4^{2-} concentrations in each of the solutions prior to mixing.

With $\phi = 0$ in Eq (2.92), the law of mass action for reaction (2.89) is:

$$K = \frac{[Fe^{3+}][Pu^{3+}]}{[Fe^{2+}][Pu^{4+}]} = 10^{(\phi_{Pu}^o - \phi_{Feu}^o)/0.059} \tag{2.94}$$

Using the ϕ_{Fe}^o and ϕ_{Pu}^o values for half-cell reactions 9 and 12 in Eq (2.94) gives K = 3600.

To solve the above four equations for the four unknowns, it is convenient to simplify the notation using:

$$x = [Fe^{2+}] \quad [Fe^{3+}] = y \quad [Pu^{3+}] = u \quad [Pu^{4+}] = v$$

the above equations become:

x + y = 0.5	(a)	2x + 3y + 3u + 4v = 2	(c)
u + v = 0.25	(b)	yu/xv = K	(d)

The first step is to substitute (a) and (b) into (c), which yields $\qquad$ u = 0.5 - x $\qquad$ (e)
Substituting (a) and (b) into (d) yields:

$$K = \frac{(0.5 - x)u}{(0.25 - u)x}$$ which, when u is eliminated using (e) gives a quadratic equation for x:

$$(K - 1)x^2 - (0.25K - 1)x - 0.25 = 0$$

for K >> 1, this reduces to:

$$4Kx^2 - Kx - 1 = 0, \text{ or } \quad x = \tfrac{1}{8}\left[1 + \sqrt{1 + {}^{16}\!/_K}\right] \cong 0.25 + 1/K$$

using this result in (e) gives u = 0.25 - 1/K and from (b), v = 1/K. The Pu^{4+}/Pu^{3+} ratio at equilibrium is
v/u = 1/(0.25K - 1) $\cong$ 4/K = 4/3600 = 1.1×10^{-3}
Thus, addition of a ferrous ion solution to a solution of tetravalent plutonium very effectively reduces
99.9% of the latter to Pu^{3+}.

Example #11 Water dissociation: $H_2O = H^+ + OH^-$
The half-cell reactions from Nos. 1 and 2 in Table 2.2 and their Nernst equations are:

(1) $\quad\quad 2H^+ + \tfrac{1}{2}O_2 + 2e = H_2O \quad\quad\quad \phi_H = 1.23 - \tfrac{1}{2}\times 0.059\log\left(\dfrac{1}{[H^+]^2\sqrt{p_{O2}}}\right)$

(2) $\quad\quad \tfrac{1}{2}O_2 + H_2O + 2e = 2OH^- \quad\quad \phi_{OH} = 0.40 - \tfrac{1}{2}\times 0.059\log\left(\dfrac{[OH^-]^2}{\sqrt{p_{O_2}}}\right)$

At equilibrium, $\phi_H = \phi_{OH}$, which yields: $[H^+][OH^-] = K_W = 10^{-14}$

2.10.6 Solubility Product

Solubility product is an equilibrium constant for the dissolution of a solid compound into ions in
water. For a metal hydroxide, for example, the reaction is:

$$M(OH)_z(s) = M^{z+} + zOH^-$$
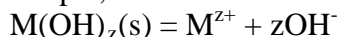
which can be divided into half-cell reactions and the associated Nernst equations:

$$M^{z+} + ze = M \quad\quad\quad \phi_M^N = \phi_M^o - \tfrac{1}{z}\times 0.059\log\left(1/[M^{z+}]\right)$$

$$M(OH)_z(s) + ze = M + zOH^- \quad\quad \phi_{M(OH)_z}^N = \phi_{M(OH)_z}^o - \tfrac{1}{z}\times 0.059\log[OH^-]^z$$

setting $\phi_M^N = \phi_{M(OH)_z}^N$ yields $[M^{z+}][OH^-]^z = 10^{-z\left(\phi_M^o - \phi_{M(OH)_z}^o\right)/0.059}$

Example #12   Solubility of $Ni(OH)_2$ in water

For the above Nernst equations, $\phi_{Ni}^o = -0.23\,V \quad\quad\quad \phi_{Ni(OH)_2}^o = -0.66\,V$

Solubility product = $K_{SP} = [Ni^{2+}][OH^-]^2 = 10^{-2(\phi_{Ni}^o - \phi_{Ni(OH)_2}^2)/0.059} = 2.6\times 10^{-15}$

i) In neutral water; $[Ni^{2+}] = 2.6\times 10^{-15}/(10^{-7})^2 = 0.26\,M$

ii) in acid of pH = 5

K_{SP} is unchanged but $[OH^-] = K_W/[H^+] = 10^{-14}/10^{-5} = 10^{-9}\,M$

$[Ni^{2+}] = 2.6\times 10^{-15}/(10^{-9})^2 = 26\,M$

This high concentration of nickel in the acid will never be achieved. Either all of the $Ni(OH)_2$ will be
dissolved or other solid solubility reactions will limit the amount of Ni in solution
(e.g., $NiO + H_2O = Ni^{2+} + 2OH^-$).

2.10.7 Electrolysis of water

A classic application of the electrochemical cell is dissociation (electrolysis) of water, for which the overall reaction is:
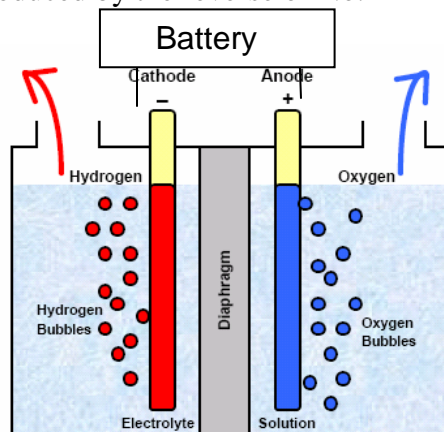
$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad\qquad (2.95)$$

The cell (Fig. 2.12) consists of two platinum electrodes immersed in salt water.
The cathodic reaction (reduction) is No. 3 in Table 2.2:

$$2H^+ + 2e \rightarrow H_2 \qquad\qquad (2.95a)$$

The negative connection of the battery supplies the electrons for this reaction.
At the anode, oxygen gas is produced by the reverse of No. 1 in Table 2.2:

Fig. 2.12 Cell for electrolysis of water

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e \qquad\qquad (2.95b)$$

The positive pole of the battery consumes the electrons produced by this reaction.

The H^+ converted to H_2 by Eq (2.95a) at the cathode must be supplied by the H^+ produced by the anode reaction (2.95b). Unless a very large potential is applied to effect the autoionization of water, the electrolysis of pure water proceeds very slowly because the electrical conductivity of water is low.

A water-soluble *electrolyte* (typically Na_2SO_4) is added to increase the electrical conductivity of water. The electrolyte disassociates into cations and anions; the anions move towards the anode and neutralize the buildup of positively charged H^+ there; similarly, the cations move towards the cathode and neutralize the buildup of negatively charged OH^-. This allows the continued flow of electricity.

For the cathodic reaction, the Nernst equation is:

$$\phi_{cath}^{N} = 0.0 - \frac{0.059}{2}\log\left(\frac{p_{H_2}}{[H^+]^2}\right)$$

Similarly, for the anodic reaction:

$$\phi_{anod}^{N} = 1.23 - \frac{0.059}{2} \log\left(\frac{1}{[H^+]^2 \sqrt{p_{O_2}}}\right)$$

The battery voltage is the difference between ϕ_{cath} and $\phi_{anod.}$:

$$\phi = \phi_{anod}^{N} - \phi_{cath}^{N} = 1.23 + \frac{0.059}{2} \log\left(p_{H_2} \sqrt{p_{O_2}}\right) \qquad (2.96)$$

For the two gases leaving the anode and cathode at 1 atm pressure, this equation gives $\phi = 1.23$ V. Water does not decompose at potentials less than this value.

2.11 Computational thermochemistry

Computational thermochemistry deals with the analysis of chemical equilibria using the extensive databases, software and computer power that have become available in the last 20 years. The objectives include calculation of thermodynamic functions (e.g., equilibrium constants of chemical reactions, oxygen potentials of complex solids, and especially, phase diagrams). The field was initiated in 1958 by White et al [2] and further developed in the 1970s by Eriksson [3].

By chemical equilibrium is meant a unique combination of constituents and phases that yield the lowest total Gibbs energy of a multicomponent, multiphase closed system[4] at fixed temperature and total pressure. The computational effort arises from the minimization of the system's Gibbs energy, which is the condition of thermodynamic equilibrium (Eq (2.26)). The numerical approach has been applied to materials of various kinds, such as slags, ceramics, alloys and semiconductors. Recently considerable effort has been devoted to using computational methods to analyze nuclear materials, with emphasis on fuel, cladding and fission-product behavior in both normal and off-normal operating conditions.

There are several ways of dealing with complex thermochemical problems. One is the classic approach described in Sect. 2.9, in which the input information consists of the Gibbs energies of formation of the chemical constituents involved, from which the standard Gibbs energy changes of the reactions (ΔG^o) are formed (e.g., Eq (2.73)). ΔG^o provides the equilibrium constant that relates the concentrations of the constituents in the reaction (as in Eq (2.69)). This is called the *Law of Mass Action* method.

The problem with this approach is the complexity of the algebra if more than one or two reactions are simultaneously taking place. The equilibrium equations (i.e., laws of mass action) are nearly always highly nonlinear and special techniques are required for their solution. While a single reaction such as methane combustion may be reducible to an analytic solution, as in Example #3, treatment of two simultaneous reactions almost always involves a numerical solution. Treating, say, thirty simultaneous reactions by this method is out of the question.

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[4] A *closed* system is contained in a boundary through which matter cannot pass. Heat can pass through the boundary (unless it is adiabatic) and expansion-contraction (pV) work can be performed (unless the boundary is rigid)

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Computer codes are designed to deal with complex thermochemical systems without the difficulties associated with the law-of-mass-action method. Starting from Ericksson's SOLGASMIX [4], *FactSage*, an extensive thermochemical database and calculational modules have been developed [5,6].

These computational systems can handle ~ 100 constituents (molecular or atomic), 20 elements and as many as 10 solution phases. In addition to a single gas phase, the condensed phases can be solid or liquid solutions (with variable composition) or solids or liquids of fixed composition (i.e., stoichiometric).

 Figure 2.13 summarizes the notation describing phases, constituents and elements. The right-hand sketch depicts phases: 1 gas phase and q solution phases; *Phase* is designated by index p. The middle sketch shows the *constituents* (molecular or elemental) that are contained in phase p. Each constituent is denoted by an integer i and there are m_p constituents in phase p. The moles of constituent i is labeled n_{ip} and the total moles of constituents in phase p is N_P. The left-hand diagram in Fig. 2.13 breaks the constituents into *elements,* with b_{jp} specifying the number of moles of element j in phase p. The b_{jp} are not input numbers because the initial mixture in general will not have the same number of phases and compositions in the phases as the equilibrium mixture. However, summing the quantity of element j in all phases, B_j is a specified quantity. The collection of all phases is termed the *system.* .

Fig. 2.13 Notation for describing a multicomponent, multiphase system
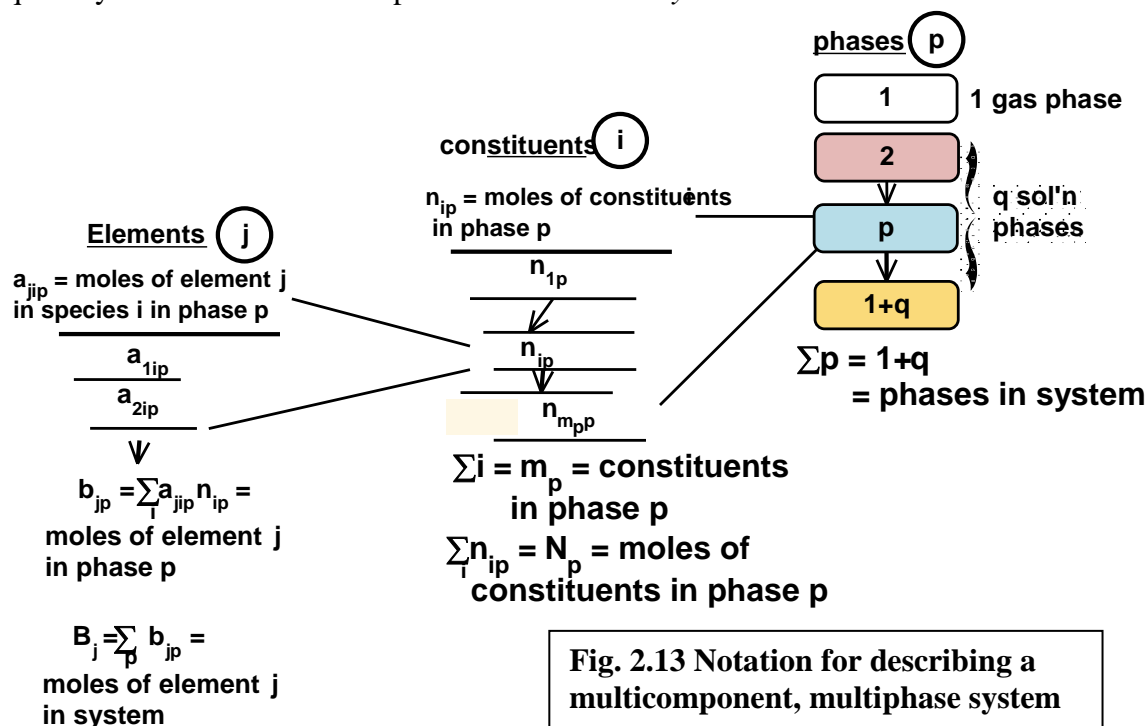
The number of phases and the number of components are constrained by the phase rule (Sect. 2.6); with temperature and pressure specified, the remaining degrees of freedom are

$$\mathcal{F} = \sum_j B_j - \sum p - \sum rxns \qquad (2.97)$$

The last sum represents all of the equilibrium reactions in the system. The degrees of freedom that remain are consumed by specification of the initial material charged to the system.

2.11.1 Gibbs energy minimization

Many computer thermochemistry codes use the method of *Lagrange multipliers* applied in a method known as *Gibbs energy minimization*. This technique potentially simplifies the problem and makes use of one of many readily-available equation solvers.

This method starts from the total Gibbs energy of the system. All phases and all constituents are contained in the following single equation for this property:

$$G = \sum_{i=1}^{m_1} n_{i1}\left[g_i^o + RT\ln\left(\frac{n_{i1}}{N_1}\right)\right] + \sum_{p=2}^{q+1}\sum_{i=1}^{m_p} n_{ip}\left[g_i^o + RT\ln a_{pi}\right] \tag{2.98}$$

$$\underbrace{\text{gas phase } (p = 1)} \qquad\qquad \underbrace{\text{solution phases}}$$

R = gas constant = 8.314 K/mole-K
T = temperature in K

g_i^o = standard Gibbs energy of pure constituent i at temperature T and 1 atm given by Eq (2.42). The other symbols Eq (2.98) are explained in Fig. 2.13. In the second term on the right-hand side, the inner sum adds constituents in a phase and the outer sum adds the solution phases in the system.

Example #13   Hydrocarbon combustion by Gibbs energy minimization
Consider oxidation of methane (CH_4) and ethylene (C_2H_4) at p = 1 atm, T = 2000 K. The reactions:
:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{2.99a}$$
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \tag{2.99b}$$

take place in one <u>phase</u> (gas), contain 5 <u>constituents</u> ($n_1 = C_2H_4$, $n_2 = CH_4$, $n_3 = O_2$, $n_4 = CO_2$, $n_5 = H_2O$)   and 3 <u>elements</u> ($B_H = H$, $B_C = C$ and $B_O = O$). For reactions (2.99a) and (2.99b), the degrees of freedom from Eq (2.97) are $\mathcal{F} = 3 - 1 - 2 = 0$. Or, there is a unique solution to this equilibrium.

Since there is only one phase, the notation is simplified by dropping the second subscript:
$$n_{i1} \rightarrow n_i \text{ and } N_1 \rightarrow N$$
The relations between constituent numbers and element numbers are:

$$4n_1 + 4n_2 + 2n_5 = B_H \qquad 2n_1 + n_2 + n_4 = B_C \qquad n_5 + 2n_4 + 2n_3 = B_O \tag{2.100}$$

These three equations serve as *constraints* on the solution.

From Eq (2.100), the total moles are:
$$N = \sum_{i=1}^{5} n_i = \tfrac{1}{4}B_H + \tfrac{1}{2}B_O \tag{2.101}$$

For only a gas phase, Eq (2.98) becomes:

$$\frac{G}{RT} = \sum_{i=1}^{5_i} n_i \left[\frac{g_i^o}{RT} + \ln\left(\frac{n_i}{N}\right) \right] \qquad (2.98a)$$

The values of n_i at the minimum of G, which is the condition of equilibrium (see Eq (2.26)), is determined by the method of Lagrange multipliers (one for each element)[5]

$$\frac{1}{RT}\frac{\partial G}{\partial n_i} + \lambda_H \frac{\partial B_H}{\partial n_i} + \lambda_C \frac{\partial B_C}{\partial n_i} + \lambda_O \frac{\partial B_O}{\partial n_i} = 0 \qquad , i = 1, \ldots 5 \qquad (2.102)$$

Equations (2.100) and (2.102) provide 8 equations for determining 8 unknowns
($n_1, \ldots n_5$, λ_H, λ_C and λ_O). The partial derivatives of B_H, B_C and B_O are obtained from Eq (2.100) and the $\partial G/\partial n_i$ terms from Eqs (2.98a). With these conditions, Eqs (2.102) become:

$$\frac{g_1^o}{RT} + \ln\left(\frac{n_1}{N}\right) + 4\lambda_H + 2\lambda_C = 0 \qquad\qquad \frac{g_2^o}{RT} + \ln\left(\frac{n_2}{N}\right) + 4\lambda_H + \lambda_C = 0$$

$$\frac{g_3^o}{RT} + \ln\left(\frac{n_3}{N}\right) + 2\lambda_O = 0 \qquad\qquad \frac{g_4^o}{RT} + \ln\left(\frac{n_4}{N}\right) + 2\lambda_O = 0 \qquad (2.103)$$

$$\frac{g_5^o}{RT} + \ln\left(\frac{n_5}{N}\right) + 2\lambda_H + \tfrac{1}{2}\lambda_O = 0$$

To simplify the notation, these equations are redefined using:

$$[i] = \frac{g_i^o}{RT} + \ln\left(\frac{n_i}{N}\right), \quad i = 1,\ldots 5$$

so that:

$$[1] + 4\lambda_H + 2\lambda_C = 0 \qquad\qquad [2] + 4\lambda_H + \lambda_C = 0$$
$$[3] + 2\lambda_O = 0 \qquad\qquad [4] + \lambda_C + 2\lambda_O = 0 \qquad (2.103a)$$
$$[5] + 2\lambda_H + \lambda_O = 0$$

First, the Lagrange multipliers are eliminated in terms of the [i]:

$$\lambda_H = -\tfrac{1}{2}[5] + \tfrac{1}{4}[3]; \qquad \lambda_C = [2] - [1] \qquad \lambda_O = -\tfrac{1}{2}[3] \qquad (2.104)$$

Next, mole numbers are converted to mole fractions ($x_i = n_i/N$), so that Eqs (2.100) become:

$$4x_1 + 4x_2 + 2x_5 = \beta_H \qquad 2x_1 + x_2 + x_4 = \beta_C \qquad x_5 + 2x_4 + 2x_3 = \beta_O \qquad (2.100a)$$

where:

$$\beta_H = \frac{B_H}{\tfrac{1}{4}B_H + \tfrac{1}{2}B_O} \qquad \beta_C = \frac{B_C}{\tfrac{1}{4}B_H + \tfrac{1}{2}B_O} \qquad \beta_O = \frac{B_O}{\tfrac{1}{4}B_H + \tfrac{1}{2}B_O} \qquad (2.105)$$

The Lagrange multipliers are eliminated by substituting Eqs (2.104) into Eqs (2.103a), a step that results in only two equations:

$$-[1] + 2[2] + [3] - 2[5] = 0 \quad \text{and} \quad -[1] + [2] - [3] + [4] = 0$$

or, replacing [i] by its definition:

$$\frac{-g_1^o + 2g_2^o + g_3^o - 2g_5^o}{RT} + \ln\left(\frac{x_2^2\, x_3}{x_5^2\, x_1}\right) = 0 \qquad \frac{-g_1^o + g_2^o - g_3^o + g_4^o}{RT} + \ln\left(\frac{x_2\, x_4}{x_1\, x_3}\right) = 0 \qquad (2.106)$$

---

[5] For details on Lagrange multipliers, try Google

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Numerical Example

Specify (arbitrarily) $B_H = 3$, $B_C = 1$ and $B_O = 2$, so that from Eq (2.105),

$$\beta_H = 1.71 \quad \beta_C = 0.57 \quad \beta_O = 1.14.$$

Looking up the g_i^o in the NIST tables[6] at 1000 K (in kJ/mole):

$$g_1^o(C_2H_4) = 119 \quad g_2^o(CH_4) = 19 \quad g_3^o(O_2) = 0 \quad g_4^o(CO_2) = -396 \quad g_5^o(H_2O) = -193$$

So that Eqs (2.106) become:

$$\frac{x_2^2 x_3}{x_5^2 x_1} = 1.2 \times 10^{-16} \qquad \frac{x_2 x_4}{x_1 x_3} = 1.2 \times 10^{26} \qquad (2.106a)$$

There are now five equations ((2.100a) and (2.106a)) for the five mole fractions. Fortunately, because of the magnitudes of the g_i^o, they are easily solved. The g_i^o are identical to the Gibbs energies of formation of the constituents (Sect. 2.7.4), so the more negative the value, the more stable is the compound. This rule-of-thumb suggests that CH_4 is much more stable than C_2H_4, or $x_1 \ll x_2$. Similarly, the stable forms of oxygen are CO_2 and H_2O, so $x_3 \cong 0$.

From the first two of Eqs (2.100a), x_4 and x_5 are expressed in terms of x_2 by:

$$x_4 = \beta_C - 2x_1 - x_2 \cong \beta_C - x_2 \qquad 2x_5 = \beta_H - 4(x_1 + x_2) \cong \beta_H - 4x_2 \qquad (2.100b)$$

With x_3 neglected, the last of Eqs (2.100a) yields:

$$x_2 \cong \tfrac{1}{4}(\tfrac{1}{2}\beta_H + 2\beta_C - \beta_O) = \tfrac{1}{4}(\tfrac{1}{2}\times1.71 + 2\times0.57 - 1.14) = 0.21 \qquad (2.107)$$

Also, x_3 is eliminated by multiplying the two Eqs (2.106a):

$$\frac{x_2^3 x_4}{x_1^2 x_5^2} = 1.4 \times 10^{10} \qquad (2.106b)$$

Substituting Eqs (2.100b) into (2.106b):

$$\frac{x_2^3 (\beta_C - x_2)}{x_1^2 (\beta_H - 4x_2)^2} = 3.5 \times 10^9 \qquad (2.108)$$

The very large right-hand side of this equation is consistent with assumed small value of x_1:

$$x_1 = 1.7 \times 10^{-5} \left[\frac{x_2^3 (\beta_C - x_2)}{(\beta_H - 4x_2)^2} \right]^{1/2} = 1.7 \times 10^{-5} \left[\frac{0.21^3 (0.57 - 0.21)}{(1.71 - 4 \times 0.21)^2} \right]^{1/2} = 1.2 \times 10^{-6}$$

Finally, from Eqs(2.100b):

$$x_4 = 0.57 - 0.21 = 0.36 \qquad x_5 = \tfrac{1}{2}(1.71 - 4\times0.21) = 0.43$$

x_3 can be calculated from either of Eqs (2.106a):

$$x_3 = 1.2 \times 10^{-16} \frac{0.43^2 (1.2 \times 10^{-6})}{0.21^2} = 6 \times 10^{-22} \qquad x_3 = \frac{1}{1.2 \times 10^{26}} \frac{0.21 \times 0.36}{1.2 \times 10^{-6}} = 5 \times 10^{-22}$$

x_3 from the two equations agree satisfactorily.

---

[6] **www.kinetics.nist.gov/janaf/**

To verify the above solution $\sum n_i$ (neglecting x_3 and x_1) = 0.21 + 0.36 + 0.43 = 1.00 - OK

g2.11.2 Compound-energy formalism

Recently, considerable effort has gone into understanding the thermodynamics of nuclear materials by a method called *compound-energy formalism*. This theoretical approach to solid-state thermodynamics started in 1970 and modern reviews of the modeling and its applications are presented in Refs [3] and [4]. It is a complicated method, so we introduce the approach with a simple case and then extend the model to the actinide oxides in Chap. 16. Compound-energy formalism is employed in calculations of thermodynamic equilibria in multicomponent, multiphase systems, including: i) modeling complex metallic and oxide phases; ii) acquisition of thermodynamic data for a wide range of inorganic chemicals; iii) design of alloys and ceramics and solving problems in industrial materials processing. The behavior of nuclear fuels and cladding during normal operation and accident conditions is a significant component of this activity. The methodology employed in developing such models is called the *CALPHAD (*Calculation of Phase Diagrams) method. There is a journal by this name and a book explaining the method [7]. The CALPHAD method provides a framework for applying experiment and theory to thermodynamic equilibria in various materials.

In Chap. 3, the structure of a solid was treated as a single lattice for metals or anion and cation lattices for ionic solids. In the present method, each of these lattices is considered as a *sublattice*. The structure of the interstitial sites is treated as a distinct sublattice as well. Each sublattice contains one or more *constituents*, here defined as an atomic entity occupying all or part of a sublattice. Examples of solids and their description in terms of sublattices and constituents are listed in Table 2.3.

System	Sublattice	Constituents
Fe, Cr, N	metal	Fe, Cr
	interstitial	N, V_I
UO_2	cation	U^{4+}
	anion	O^{2-}
UO_{2-x}	cation	U^{3+}, U^{4+}
	anion	O^{2-}, V_O
UO_{2+x}	cation	U^{4+}, U^{5+}
	anion	O^{2-}
	anion interstitial	I_O, V_I

Table 2.3 Examples of sublattices and constituents in solids

- The first solid is an iron-chromium alloy with dissolved nitrogen. The bcc structure of the metal provides the first sublattice. The second sublattice is made up of the interstitial sites in the alloy, in which the constituents are N atoms or vacancies (unoccupied interstitial sites).
- The second example is stoichiometric UO_2, in which the cation sublattice is filled with U^{4+} ions and the sole occupant of the anion sublattice is O^{2-}
- In UO_{2-x}, the cation sublattice contains trivalent and tetravalent uranium ions as constituents. The constituents of the anion sublattice are oxygen ions or oxygen vacancies, denoted by V_O. The presence of U^{3+} is required in order to maintain electrical neutrality in the hypostoichiometric oxide (see Sect. 16.3.3)

- In UO_{2+x}, electrical neutrality implies oxidation of some U^{4+} to U^{5+} because of the excess oxygen. The latter is present in a separate sublattice that consists of anion interstitials (I_O) and empty interstitial sites (V_I).

The symbolism for an arbitrary system consisting of two sublattices and their constituents, is:

$$(A:B)(\alpha:\beta)_n \tag{2.109}$$

The parentheses signify a sublattice. The symbols A, B, α and β represent the constituents in each sublattice; they may be atoms, ions, or point defects, such as vacancies or interstitials, but not molecules. The colon separates constituents of a sublattice. In Eq (2.109), A and B occupy the first sublattice and α and β are the tenants of the second sublattice. The subscript n indicates that the number of sites in the second sublattice is n times larger than the number of sites in the first. For example UO_{2-x} is designated as $(U^{3+}:U^{4+})(O^{2-}:V_O)_2$. Hyperstoichiometric urania is written as $(U^{4+}:U^{5+})(O^{2-})_2(I_O:V_I)$; the number of oxygen interstitial sites is the same as the number of cation sites (Eq (16.22)).

Compositions are defined by the *site fractions* of the constituents on each of the sublattices. These are y_A and y_B on the first sublattice and y_α and y_β on the second sublattice, where:

$$y_A + y_B = 1 \qquad \text{and} \qquad y_\alpha + y_\beta = 1 \tag{2.110}$$

End members are the molecules or elements that are formed if each sublattice is filled with only one constituent. For the two-sublattice system defined by Eq (2.109), the end members are $A\alpha_n$, $A\beta_n$, $B\alpha_n$ and $B\beta_n$. These combinations may or may not be actual molecular compounds for which thermodynamic data are available Nonetheless they are assigned standard Gibbs energies:

$$g^o_{A\alpha_n} \quad g^o_{A\beta_n} \quad g^o_{B\alpha_n} \quad g^o_{B\beta_n}$$

The Gibbs energy of a phase is expressed by Eq (2.46):

$$g = g^o - T\Delta s_{mix} + g^{ex} \tag{2.111}$$

Similar equations apply to each phase and the total Gibbs energy is the mole-weighted sum of each g.

The method by which the site fractions on the sublattices and the end-member Gibbs energies are combined to produce g^o in Eq (2.111) is demonstrated by the dissolution of nitrogen in an iron-chromium alloy.

Example # 14 - Solubility of nitrogen in a Fe,Cr alloy
In sublattice symbolism, nitrogen dissolved in the alloy is denoted by $(Fe:Cr)(N:V_I)_n$. The two metals form the (Fe:Cr) sublattice (fcc or bcc) and nitrogen atoms (N) and vacancies (V_I) occupy a separate <u>interstitial</u> sublattice, $(N:V_I)_n$, whose sites are interspersed between the metal sites (Chap. 4). The metals do not enter the interstitial sublattice, nor do nitrogen or vacancies occupy sites in the metal sublattice. Depending on the metal's crystal structure, n could be either 1 or 3; here we have assumed the austenitic metal crystal structure, for which n = 1.

The way that the g^o term in Eq (2.111) is determined is illustrated in Figure 2.14, which is a small section of the $(Fe:Cr)(N:V_I)$ system. Circles denote the metal sublattice and stars represent the interstitial sublattice. The metal sublattice is filled with either Fe or Cr and the interstitial sublattice with either N atoms or nothing (vacancy). Site-filling equations are:

$$y_{Fe} + y_{Cr} = 1 \quad \text{and} \quad y_N + y_V = 1 \tag{2.110a}$$

y_V denotes the fraction of interstitial sites that are vacant. To illustrate, suppose the site fractions are:
$$y_{Fe} = 3/4 \quad \text{and} \quad y_{Cr} = 1/4 \quad \text{in the metal sublattice}$$
$$y_N = 1/4 \quad \text{and} \quad y_V = 3/4 \quad \text{in the interstitial sublattice}$$

The left side of Fig. 2.14 illustrates the compound-energy-formalism representation of the metal containing dissolved nitrogen. There are 16 sites for the metal sublattice and 16 for the interstitial sublattice. Metal atoms and nitrogen atoms are randomly distributed on the two sublattices. The fundamental assumption of the compound-energy model is that the only contributors to the Gibbs energy are adjacent atoms (i.e., "compounds") Thus Fig. 2.14 shows three Fe-N combinations (solid ovals), one Cr-N (dotted oval), three Cr-Va (rectangle) and the remainder Fe-Va (not indicated). These are counted as follows: (Gibbs energies are divided by R_gT)
- Probability of Fe in a metal-atom site <u>and</u> an N in an adjacent interstitial site

$$= y_{Fe} \ y_N = \tfrac{3}{4} \times \tfrac{1}{4} = \tfrac{3}{16}$$

These three combinations contribute $\tfrac{3}{16} \ g^o_{FeN}$ to the Gibbs energy g^o.

Similarly, additions to the Gibbs energy from the remaining combinations are:

- probabity of adjacent Cr & N $= \tfrac{1}{4} \times \tfrac{1}{4};$ Gibbs energy $= \tfrac{1}{16} \ g^o_{CrN}$

- probability of adjacent Fe & $V_I = \tfrac{3}{4} \times \tfrac{3}{4};$ Gibbs energy $= \tfrac{9}{16} \ g^o_{Fe}$

- probability of adjacent Cr & $V_I = \tfrac{3}{4} \times \tfrac{1}{4};$ Gibbs energy $= \tfrac{3}{16} g^o_{Cr}$

Adding the above contributions gives g^o for this example:

$$g^o = [\tfrac{3}{16} \ g^o_{FeN} + \tfrac{9}{16} \ g^o_{Fe} + \tfrac{1}{16} \ g^o_{CrN} + \tfrac{3}{16} \ g^o_{Cr}] \times (N_{Av}/16)$$

The reason for the factor $N_{Av}/16$ in the above equation is that the illustration contained only 16 sites in each sublattice, whereas the actual system contains 1 mole (Avogadro's number) of metal sites and 1 mole of interstitial sites. The Gibbs energies are per mole of the end members (the nitrides FeN, CrN, and the pure metals Fe and Cr)

Also, the above result applies only for the fixed composition (site fractions) selected for the two portions of the sublattices. For any combination of site fractions in the two full-size sublattices,

$$g^o = y_{Fe} y_N g^o_{FeN} + y_{Fe} y_V g^o_{Fe} + y_{Cr} y_N g^o_{CrN} + y_{Cr} y_V g^o_{Cr} \tag{2.112}$$

Adding the entropies of mixing (Eq (2.37)) in the two sublattices gives the complete expression for the Gibbs energy of the metal phase containing dissolved nitrogen:

$$g = g^o + RT[y_{Fe} \ln y_{Fe} + y_{Cr} \ln y_{Cr}] + RT[y_N \ln y_N + y_V \ln y_V] \tag{2.113}$$

The name "compound energy" arises from the assignment of a Gibbs energy to each adjacent metal/N pair.

Thermochemical data is required for the end members, which in this example are actual compounds or elements; they are the nitrides FeN ($y_{Fe}=1$, $y_N=1$) and CrN ($y_{Cr}=1$, $y_N=1$) and the

metals are Fe ($y_{Fe}=1$, $y_V=1$) and Cr ($y_{Cr}=1$, $y_V=1$). The data required are the molar Gibbs energies, g^o_{FeN}, g^o_{Fe}, g^o_{CrN} and g^o_{Cr} (divided by RT) at the specified temperature and total pressure (g^o_{Fe}, and $g^o_{Cr} = 0$ because they are elements). y_{Fe} (and hence y_{Cr}) is specified. However, the fractional occupancy of the interstitial sites (y_N or y_{VI}) depends on the temperature and the N_2 pressure to which the metal is exposed. The connection is made by representing the dissolution process by the reaction:
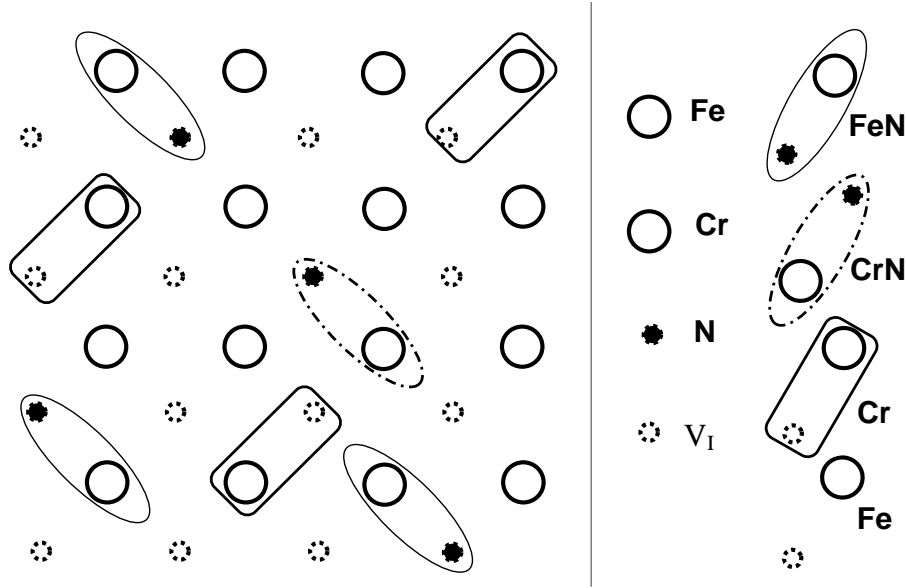
Fig. 2.14 Sublattice model for the (Fe:Cr)(N:V$_I$) system

$$\tfrac{1}{2}\,N_2(g) + V_I = N(diss) \tag{2.114}$$

By which N_2 dissociates and one atom enters a vacant site in the interstitial sublattice and becomes a N atom on this sublattice. Equilibrium is expressed by casting Eq (2.114) in the form of Eq (2.67) from which the balance of chemical potentials of Eq (2.68) is specialized to:

$$\tfrac{1}{2}\mu_{N_2} = \mu_N - \mu_{VI} \tag{2.115}$$

From Eq (2.55):

$$\mu_{N_2} = g^o_{N_2} + RT\ln p_{N_2} \tag{2.116}$$

The chemical potentials in the interstitial sublattice (Gibbs energies no longer divided by RT) are:

$$\mu_N = \frac{\partial g}{\partial y_N} = y_{Fe}g^o_{FeN} + y_{Cr}g^o_{CrN} + RT(\ln y_N + 1) \tag{2.117a}$$

$$\mu_{VI} = \frac{\partial g}{\partial y_{VI}} = RT(\ln y_{VI} + 1) \tag{2.117b}$$

where the derivatives with respect to y_N and y_{VI} were obtained from Eqs (2.113) and (2.112). Substituting Eqs (2.116) and (2.117) into Eq (2.115) yields:

$$\tfrac{1}{2}g^o_{N_2} + RT\ln\sqrt{p_{N_2}} = y_{Fe}\left(g^o_{FeN} - g^o_{Fe}\right) + y_{Cr}\left(g^o_{CrN} - g^o_{Cr}\right) + RT(\ln y_N - \ln y_V) \tag{2.118a}$$

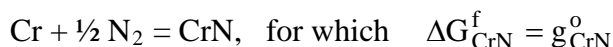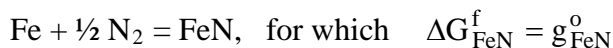Light Water Reactor Materials © Donald R. Olander and Arthur T. Motta,
9/7/2015

From the site-filling requirement, $y_V = 1 - y_N$. Rearranging this equation produces:

$$\frac{y_N}{(1 - y_N)\sqrt{p_{N_2}}} = \exp\left(-\frac{\Delta G^o}{RT}\right) \tag{2.119}$$

where

$$\Delta G^o = y_{Fe}(g_{FeN}^o) + y_{Cr}(g_{CrN}^o) \tag{2.120}$$

The reaction Gibbs energy can be understood in terms of formation Gibbs energies of the rections:

$$Fe + \tfrac{1}{2} N_2 = FeN, \quad \text{for which} \quad \Delta G_{FeN}^f = g_{FeN}^o$$

$$Cr + \tfrac{1}{2} N_2 = CrN, \quad \text{for which} \quad \Delta G_{CrN}^f = g_{CrN}^o$$

So that:
$$\Delta G^o = y_{Fe}\Delta G_{FeN}^f + y_{Cr}\Delta G_{CrN}^f \tag{2.121}$$

klAs in the previous section, the detailed method has led to an expression that could have been obtained (much more easily) from the law of mass action. However, as shall be shown below, the compound energy formalism provides other important advantages over the standard thermodynamic methodology.

Example # 15 Nitrogen solubility in a metal alloy
At 1000 K, what is the solubility of nitrogen in an iron-chromium alloy with 25 mole % Fe in a gas with an N_2 partial pressure of 0.1 atm? The Gibbs energies of formation of CrN and FeN are – 37 kJmole and -25 kJ/mole, respectively.

From Eq (2.121), $\Delta G^o = 0.25 \times (-25) + 0.75 \times (-37) = -34$ kJ/mole, so, from Eq (2.119),

$$\frac{y_N}{1 - y_N} = \sqrt{0.1}\,\exp\left(-\frac{-34,000}{8.314 \times 1000}\right) = 19$$

or $y_N = 0.94$; the alloy is $(Fe_{0.25}Cr_{0.75})N_{0.94}$.

Solubility of nitrogen in a Fe,Cr alloy by standard thermodynamics
In the approach to gas-solid phase equilibria reviewed in Sect. 2.8, nitrogen dissolution is:
$$N_2(g) = 2N(diss) \tag{2.122}$$
and the equilibrium is governed by:
$$\mu_{N2} = 2\mu_N \tag{2.123}$$
Expressing the chemical potentials as in Eqs (2.55) for N_2 and (2.43)/(2.44) for N(diss) ultimately leads to a Henry's law-type equation:
$$p_{N_2} = k_H x_N^2 \tag{2.124}$$
Where k_H is a Henry's law constant that contains the standard-state Gibbs energies of N_2 and N(diss). The mole fraction of dissolved nitrogen is related to the site fraction of N by:
$$x_N = \frac{y_N}{1 + y_N} \tag{2.125}$$

However, the standard-thermodynamic approach provides no information on the Henry's law constant k_H, which simply must be measured. The compound energy formalism, on the other hand, relates the nitrogen solubility in the alloy to the known Gibbs energies of formation of the metal nitrides.

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Problems

2.1 What is the standard electrode potential for half-cell No. 3a?

2.2
0.35 moles of FeS and 0.65 moles of O_2 are equilibrated at 1000 K and 1 atm total pressure. All of the Fe is converted to Fe_2O_3 and all of the S remains in the gas phase as SO_2 and SO_3. Using the method of Sect. 2.11.1, find the following:

  (a) the total Gibbs energy of the gas phase, g_g, in terms of the mole numbers n_{O2}, n_{SO2} and n_{SO3}.
  (b) the Gibbs energy of the solid, g_S

note: all Gibbs energies are divided by RT.

  (c) the auxiliary equations connecting the quantities in parts (a) and (b)

  (d) the equilibrium composition of the gas phase.

At 1000 K the standard Gibbs energies of the pure gas constituents (relative to RT) are:
$$g_{SO3}^o = -683 \qquad g_{SO2}^o = -568 \qquad g_{O2}^o = -221$$

2.3 From standard electrode potentials Nos. 3 and 3a in Table 2.2, determine the dissociation constant of water.