1. HETEROGENEOUS EQUILIBRIA

1.1. Generalization of equilibrium conditions

Thermodynamics is perhaps the most general discipline developed for direct application to physico-chemical systems. Classical thermodynamics deals with the macroscopical properties of matter in bulk and is not concerned with the atomic and molecular structure. All information about a system is contained in the equation[1]

$$S = S(U, V, N_1 \dots N_j) \tag{1.1}$$

where the entropy, S, is a function of extensive parameters, the internal energy, U, the volume, V, and the mole number of the chemical components, N_j. Equation (1.1) could also be solved uniquely for U as

$$U = U(S, V, N_1 \dots N_j). \tag{1.2}$$

This holds all the necessary information about the system in question as well. Such an approach was found useful in the case that the phenomena of mechanics and heat are discussed simultaneously. The application to chemical problems, however, requires another mathematical formalism.

In the laboratory, intensive parameters are more easily measured and controlled than the extensive ones. Through the Légendre transforms[1] of the function U (see eqn. (1.2)) of the extensive variables are replaced by intensive ones. From the experimental point of view the three following cases are the most important:

1) For an *isobaric system* the state function, H,

$$H = U + PV \tag{1.3}$$

called enthalpy is the partial Légendre transform of U where the volume, V, is replaced by the pressure, P, as the independent variable

$$H = H(S, P, N_1 \dots N_r) \tag{1.4}$$

2) For the case of an *isothermal mechanically isolated system* the Helmholtz free energy, F,

$$F = F(T, V, N_1 \dots N_j) = U - TS \tag{1.5}$$

is the most convenient and is a partial Légendre transform of U replacing the entropy, S, by the temperature, T, as the independent variable.

3) For an *isothermal and isobaric system* another Légendre transform of U is advantageously assigned with the Gibbs free energy, G,

$$G = G(T, P, N_1 \dots N_j) = H - TS \tag{1.6}$$

as a partial Légendre transform of U which simultaneously replaces the entropy by the temperature and the volume by the pressure as the independent variables.

In an homogeneous system, the infinitesimal reversible change of the internal energy, U, is given by

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V} dN_j \tag{1.7}$$

where partial derivatives define the intensive parameters of temperature, T, pressure, P, and chemical potentials, μ_i, respectively,

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T; \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial N_i}\right)_{S,V} = \mu_i. \tag{1.8}$$

Equation (1.7) can be written in the form called the Gibbs phenomenological relation

$$dU = TdS - PdV + \sum_i \mu_i dN_i. \tag{1.9}$$

Similarly, for the other state functions the following relations hold:

$$\begin{aligned} dH &= TdS + VdP + \sum \mu_i dN_i \\ dF &= -SdT - PdV + \sum \mu_i dN_i \\ dG &= -SdT + VdP + \sum \mu_i dN_i \end{aligned} \tag{1.10}$$

The problem of classical thermodynamics becomes the determination of the equilibrium state of a system (the properties of which are independent of time). This problem is solved on the basis of the postulate that in an isolated (i.e., composite) system, the equilibrium value of any (unconstrained) internal parameters characterizing the state of the system corresponds to the maximum of entropy for the given energy content or,

$$\text{for } U = \text{constant, } dS = 0 \qquad \text{and} \qquad d^2S < 0 \tag{1.11}$$

The task of determining the equilibrium state is hence reduced to the purely mathematical problem of finding the entropy maximum (see eqn. 1.1).

All natural processes taking place in an isolated system tend towards equilibrium. If a system attains equilibrium, then any conceivable change in it must be reversible. This puts the equilibrium conditions into various forms, each of general validity, e.g., for an isothermal and isobaric system

$$dG = 0 \qquad \text{and} \qquad d^2G > 0 \; (T = \text{constant, } P = \text{constant}). \tag{1.12}$$

Likewise, for constant volume and temperature the Helmholtz free energy becomes a minimum, $dF = 0$, and $d^2F > 0$. The second derivative expresses the conditions of the stability of the equilibrium state. In the case the equilibrium conditions are fulfilled for some different values of G and F than those for their lowest values compatible with the given external conditions, the system is considered to be in a *metastable equilibrium state*.

The advantage of a thermodynamic approach to the study of systems behavior results, in the first place, from the nature of the state functions U, S, H, F and G.

Although the absolute values of these functions are not known, it is easy to determine their relative changes. The choice of an appropriate standard state permits the use of the functions and their tabulation. Because the change of state function is not dependent on the path along which the systems move from the initial to the final state, thermodynamic considerations facilitate the determination of the most suitable way for the experimental measurement of data characterizing equilibria.

The method of classical thermodynamics has a very broad field of application[3,4]. The most important topics in chemistry and chemical engineering areas involve:

1) Quantitative description of the properties of homogeneous systems (pure substances, mixtures and solutions).

2) Prediction of the energy change accompanying a process in question (chemical reaction, phase change).

3) Prediction of the conditions under which various substances or phases exist in equilibrium.

4) Prediction of the direction of chemical reactions or phase changes under certain specified conditions.

1.2. Thermodynamic properties of substances

For most physico-chemical calculations[5,9] it is necessary to know both the properties of chemical individuals, mixtures, and solutions, as well as their dependence on the state variables such as pressure, temperature and composition. The behavior of perfect gases is expressed by the state equation for an ideal gas

$$PV = nRT \qquad (1.13)$$

where n is the number of moles and R is the gas constant. However, for real gases there exist various empirical relations[2,6]. For chemical calculations, particularly in the case of equilibria, it is convenient to employ the chemical potential, μ, expressed by means of the function called fugacity, f (Lewis et al.)[2]

$$\mathrm{d}\mu = RT\,\mathrm{d}\ln f. \qquad (1.14)$$

Fugacity, in other words, is a thermodynamic effective pressure and is defined by the equation, $V\mathrm{d}P = nRT\,\mathrm{d}\ln f$, and by the limit

$$\lim_{P\to 0} \frac{f}{P} = 1 \qquad (T = \text{constant}). \qquad (1.15)$$

It becomes equal to the pressure only at very low pressures (nearly perfect gas). For real gases, it can be calculated from experimental P–V–T data. A frequently used term is the fugacity coefficient, ν, given by the equation,

$$f/P = \nu. \qquad (1.16)$$

For perfect gases it is not difficult to derive the changes of the state functions, H, S, G, and F, with the temperature and/or pressure[2,6]. For real gases, it is sufficient to determine merely the deviation from the perfect state.

More important is the state behavior of gaseous mixtures. Besides the total pressure and temperature, it is necessary to consider also the composition, the value of which is commonly expressed by the mole fractions, x_j. In order to predict mixture behavior from the behavior of pure components, there are two approaches:

(*a*) *Dalton's law*

$$P = \sum_j p_j \tag{1.17}$$

and

(*b*) *Amagate's law*

$$V = \sum_j V_j \tag{1.18}$$

Enthalpy, entropy and heat capacity of such mixtures are also determined by approximate methods, as shown by Hougen and Watson[9].

The fugacity of a component, j, in a gaseous mixture is given by the Lewis relation[2]

$$f_j = f_j^\circ x_j \tag{1.19}$$

where x_j is the mole fraction of j-th component and f_j° is the fugacity of the pure component under the total pressure of the mixture whose state is adopted as the standard one. The relation between the chemical potential of j-th component and its fugacity is given by equation

$$\mathrm{d}\mu_j = RT \ln f_j \tag{1.20}$$

or in relation to a standard state ($^\circ$)

$$\mu_j - \mu_j^\circ = RT \ \ln f_j/f_j^\circ = RT \ \ln a_j \tag{1.21}$$

where f_j° is the fugacity in the reference state adopted and a_j is the activity (Lewis et al.[2]). The standard state is chosen in such a way that the resulting numerical values of activities corresponds to partial pressures or concentrations for a perfect system. For gases, unit fugacity ($f_j^\circ = 1$) is chosen for the standard state so that the component activity is equal to the fugacity which, for a perfect mixture [see eqns. (1.15) and (1.19)] is equal to the partial pressure.

For condensed systems, a pure component at the temperature and pressure of the system is chosen for the standard state; the component activity is then equal to the mole fraction. Generally it is valid that

$$a_j/x_j = \gamma_j \tag{1.22}$$

where x_j is the mole fraction and γ_j is the activity coefficient. The numerical value of γ_j is a matter of the standard state convention. Aqueous solutions are discussed by Lewis et al.[2], while organic substances are described by Hildebrand et al.[10]. The problem of ionic melts and solid solution[11] are discussed by Těmpkin[12], Driessens[13], Holba[14] and others[15].

Thermodynamic quantities, which characterize a given mixture, can be calculated from the free energy of mixing, ΔG^{M}, which is defined as the change of free energy associated with the formation of a solution from pure components at constant temperature and pressure

$$\Delta G^{\mathrm{M}} = \sum_j x_j \mu_j - \sum_j x_j \mu_j^{\circ} \,. \tag{1.23}$$

On combining eqns. (1.21) and (1.22) with (1.23) we obtain

$$\Delta G^{\mathrm{M}} = RT \sum_j x_j \ln x_j + RT \sum_j x_j \ln \gamma_j \tag{1.24}$$

where the first term on the right-hand side represents the free energy of mixing of a perfect solution and the second term its non-ideality which is often designated as the excess free energy, ΔG^{E}. The dependence of ΔG^{E} on the composition can be described by a power series

$$\Delta G^{\mathrm{E}} = x(1-x) \sum_{m=0}^{M} a_m x^m \tag{1.25}$$

the coefficients of which must be determined experimentally[10].

1.3. Energy balance

One of the basic problems often met in practice is the determination of heat liberated and/or absorbed during a reaction, the measurement of which is usually made under constant pressure. Such a calculation requires a knowledge[7,8] of:

(*a*) The specific heats of participating substances, the temperature function of which is usually given by

$$C_p = a_1 + a_2 T + a_3 T^2 \tag{1.26}$$

where a_1, a_2 and a_3 are constants to be determined experimentally.

(*b*) The enthalpy change of substances under consideration at the temperature of the phase transition.

(*c*) The enthalpy changes associated with the chemical reactions given for the standard state, usually chosen as 25 °C and 1 atm. The standard enthalpy of formation, expressing the enthalpy change which accompanies the formation of one mole of resulting compound from its elements under standard conditions, is tabulated.

The total enthalpy change for a reaction, ΔH_r°, is given by the law of Hess

$$\Delta H_r^\circ = \sum_j \nu_j \Delta H_{f\ j\,\mathrm{product}}^\circ - \sum_j \nu_j \Delta H_{f\ j\,\mathrm{reactants}}^\circ \tag{1.27}$$

where ν_j is the stoichiometric coefficient of the j-th component and ΔH_{fj}° is the standard enthalpy of formation of the j-th component. For recalculation of the enthalpy to another temperature, Kirchoff's law is used

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = \Delta C_p = \sum C_{p_{\mathrm{product}}} - \sum C_{p_{\mathrm{reactant}}}\,. \tag{1.28}$$

If an exothermic reaction is carried out adiabatically, the system may achieve a maximum temperature, the value of which can be calculated under the condition that all the heat liberated is consumed to heat up the product

$$-\Delta H_r^\circ = \int_{T_0}^{T} m C_{p_{\mathrm{product}}}\,\mathrm{d}T \tag{1.29}$$

where T_0 is the initial temperature of the system in question, ΔH_r° is the enthalpy change and C_p is the specific heat of the product which has the mass, m.

1.4. Thermodynamics of phase changes and chemical reactions

When eqns. (1.10) and (1.12) are applied to a homogeneous system at constant temperature and pressure, the conditions of equilibrium are

$$\mathrm{d}G = \sum_j \mu_j \mathrm{d}N_j = 0\,. \tag{1.30}$$

For a system composed of α-phases

$$\mathrm{d}G = \sum_\alpha \sum_j \mu_j \mathrm{d}N_j\,. \tag{1.31}$$

If no chemical reactions occurs, the total amount of each component in a closed system remains constant so that

$$\sum_\alpha (\mathrm{d}N_j)^\alpha = 0\,. \tag{1.32}$$

This gives the general condition for phase equilibrium

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \dots \mu_i^\alpha = \mu_i\,. \tag{1.33}$$

For the coexistence of two phases in a single-component system, eqn. (1.33) results in the Clapeyron equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{\Delta s}{\Delta v} = \frac{\Delta h}{T_{\mathrm{eq}} \Delta v} \tag{1.34}$$

where Δs, Δv and Δh are the changes of molar entropy, volume and enthalpy, respectively. This corresponds to the phase transformation $\alpha \rightarrow \beta$ at the equilibrium temperature, T_{eq}.

For a transition of the second order, where $\Delta s = 0$ and $\Delta v = 0$, the term $\Delta s/\Delta v$ is indefinite. It, however, can be determined by L'Hopital's rule to yield Ehrenfest's[16,17] equations

$$\frac{dP}{dT} = \frac{\Delta c_p}{Tv\Delta\alpha} \quad \text{and/or} \quad \frac{dP}{dT} = \frac{\Delta\alpha}{\Delta\mathcal{K}_T} \tag{1.35}$$

where $\Delta\alpha$, $\Delta\mathcal{K}_T$ and Δc_p are differences in the volume expansion coefficient, α, the isothermal compressibility, $\mathcal{K}_T$, and the molar heat capacity, c_p, of both phases, respectively. These quantities are defined by the relations:

$$\alpha = \frac{1}{v}\left(\frac{\partial V}{\partial T}\right)_P, \quad \mathcal{K}_T = \left(\frac{\partial V}{\partial P}\right)_T \quad \text{and} \quad c_p = \left(\frac{\partial H}{\partial T}\right)_P. \tag{1.36}$$

In most cases, the study of phase transitions is based on the direct investigation of conditions under which different phases can exist in equilibrium. Equations (1.34) and (1.35) enable the interpolation and/or the extrapolation of the changes in T and P and the direct calculation of the quantities, Δh, Δs and Δv. The measurement of the values, Δh, Δs and Δv, makes possible the construction of phase diagrams.

There is an extensive literature dealing with the individual types of tranformations; they are polymorphic transitions of crystals[18], order–disorder transformations[19], fusion[20], transformation of glasses[21,22], sublimation[23,24], and magnetic[25] and/or ferroelectric[26,27] transitions.

A similar situation is met through the investigation of phase diagrams in two-component systems[5]. For the coexistence of crystals of pure component (A) with an ideal solution of two components, A and B, eqn. (1.10) yields

$$\mu_A = \bar{v}_A dP - \bar{s}_A dT + RT d\ln x_A = v_A^\dagger dP - s_A^\dagger dT = \mu_A^\dagger \tag{1.37}$$

where $\bar{v}_A$ and $\bar{s}_A$ are the partial molar volume and the entropy of the component A in solution, respectively; $\mu_A^\dagger$, $v_A^\dagger$ and $s_A^\dagger$ are the chemical potential, the molar volume and the entropy of the pure crystalline component, A, respectively.
If $P =$ a constant, then

$$\frac{d\ln x_A}{dT} = \frac{\bar{s}_A - s_A^\dagger}{RT} = \frac{\Delta h_A}{RT^2} \tag{1.38}$$

where Δh_A is the molar change of enthalpy corresponding to the melting of the component A. This value can be calculated from a plot of $\ln x_A$ against $(1/T)$ as determined experimentally (see direct investigation of phase equilibria). From the value of Δh_A determined calorimetrically, the ideal solubility of A can be calculated. This indirect method makes possible the construction of a complete phase diagram from information concerning the behavior of solutions, temperatures, and enthalpy changes which correspond to the melting of the pure component.

The change of free energy associated with the formation of one mole of solution from the pure components A and B (as given by eqn. (1.24)) can be rewritten in the form

$$\Delta G^{M} = \Delta H^{M} - T\Delta S^{M} \tag{1.39}$$

where ΔH^{M} and ΔS^{M} are the changes of enthalpy and entropy, respectively. The expression, $-T\Delta S^{M}$, is always negative. If ΔH^{M} is also negative then ΔG^{M} is negative

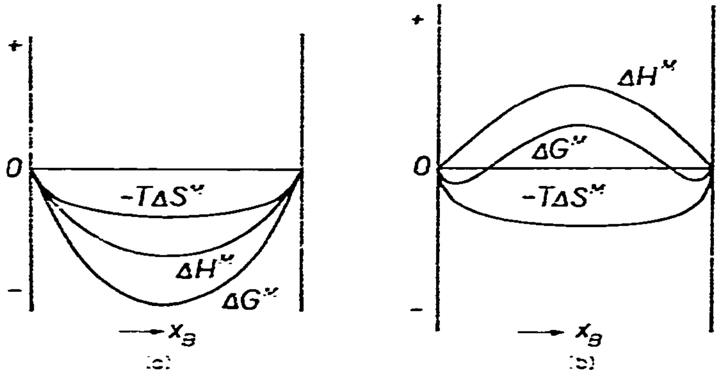

Fig. 1.1. Thermodynamic behavior of binary solutions. (a) Negative enthalpy of mixing and (b) positive enthalpy of mixing.

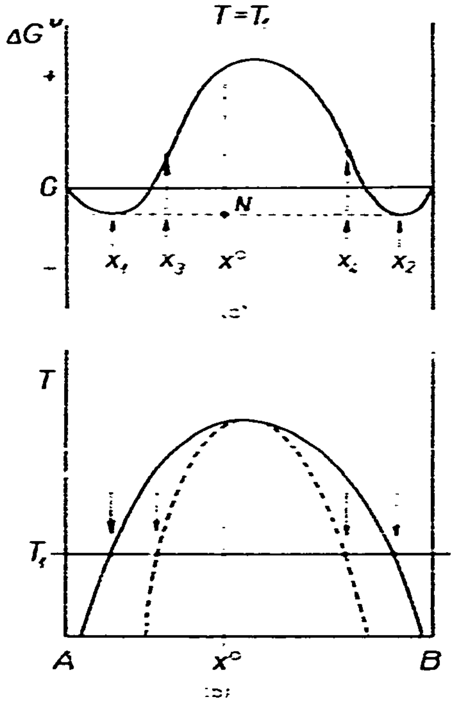

Fig. 1.2. Binary system with limited solubility. (a) Plot of free energy of mixing versus composition for temperature T_1, and (b) phase diagram—full line boundaries miscibility gap, dashed line (spinodal) boundaries unstable region.

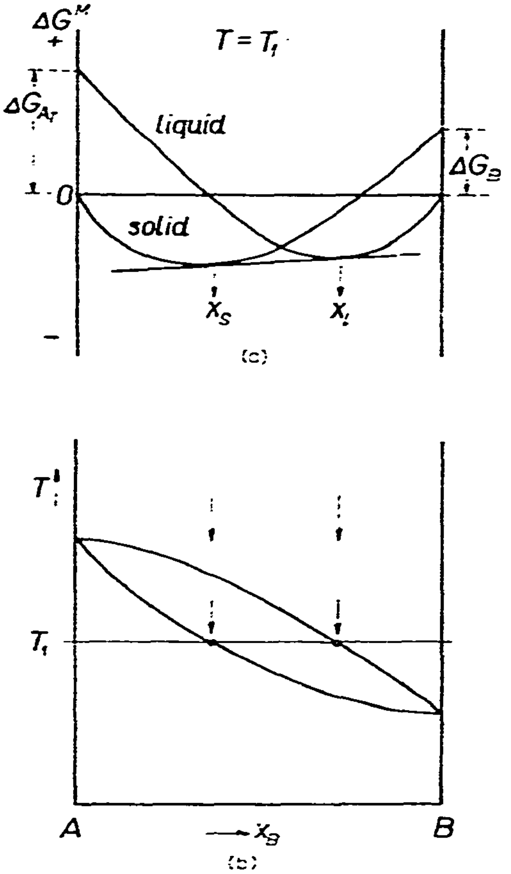

Fig. 1.3. Binary system with perfect miscibility in both solid and liquid states. (a) Plot of free energy of mixing versus composition for temperature T_1, and (b) phase diagram.

for all compositions (see Fig. 1.1a). However, if $\Delta H^M > 0$, then the ΔH^M term becomes, at lower temperatures, more important than the $-T\Delta S^M$ term. Consequently, the curve ΔG^M versus x_B tends to be concave upward over a range of composition and the complete curve takes the shape shown in Fig. 1.1b. Thus, a system in which the composition falls in the interval between x_1 and x_2 (Fig. 1.2a), is unstable. Such a system then tends to separate into two phases represented by the lowest free energy configuration. For the system of composition x° (Fig. 1.2), the lowest free energy configuration is given by N, laying on the common tangent to the curve ΔG^M. This stable configuration N consists of two solutions; one for the composition x_1 and the other for the composition x_2. The common tangent method can be applied to determine the composition of coexisting phases at the different temperatures as well as for the construction of the entire phase diagram (see Fig. 1.2b).

For the numerical calculation[28–31] of equilibrium compositions (x_1 and x_2) at different temperatures, the solution of the system of equations

$$\mu_A(x_1, T) = \mu_A(x_2, T)$$

and

$$\mu_B(x_1, T) = \mu_B(x_2, T) \qquad (1.40)$$

describing the equilibrium conditions, is more practical. This method is convenient when using computers.

In the case of a binary system with an unlimited solubility of both components in both liquid and solid phases, the calculation is analogous. The free energy of mixing of the pure components to solid and liquid solutions are referred to by an analogous reference state. In Fig. 1.3, pure solid A, and pure liquid B, at a given temperature, T, are adopted as the standard state. For liquid solutions,

$$\Delta G_l^M = RT[x\ln x + (1-x)\ln(1-x)] + (1-x)\,\Delta G_{A_T} + \Delta G_l^E \qquad (1.41)$$

and likewise for the solid solutions

$$\Delta G_s^M = RT[x\ln x + (1-x)\ln(1-x)] - x\Delta G_{B_T} + \Delta G_s^E \qquad (1.42)$$

where x is the mole fraction of the component B, and ΔG_{A_T} and ΔG_{B_T} are the changes of molar free energy of melting which correspond to the temperature, T. On the supposition that the standard enthalpy of melting, ΔH_A, is temperature independent, the following approximate formula for the ΔG_{A_T} calculation may be used:

$$\Delta G_{A_T} = \Delta H_A[1-(T/T_A)] \qquad (1.43)$$

where T_A is the normal melting point of component A.

The shape of ΔG_s^M and ΔG_l^M as functions of composition, are shown in Fig. 1.3. The common tangent then gives the composition of solid and liquid solutions which are in equilibrium under a given temperature. By repeating this procedure for a series of temperatures, the whole phase diagram can be obtained.

For numerical calculations (particularly using computers), the solution of the equations that follow is employed:

$$\begin{aligned} \mu_{A_s}(x_s, T) &= \mu_{A_l}(x_l, T) \\ \mu_{B_s}(x_s, T) &= \mu_{B_l}(x_l, T) \end{aligned} \qquad (1.44)$$

The same methods can be used for other types of the phase diagram calculations in binary[28,29] as well as in multicomponent systems[30,32].

If T = constant, eqn. (1.35) reduces to

$$\frac{\mathrm{d}\ln x_A}{\mathrm{d}P} = \frac{\bar{v}_A - v_A^{+}}{RT} = \frac{\Delta v_A}{RT} \qquad (1.45)$$

where Δv_A is the molar change of volume corresponding to the melting of pure component A. Equation (1.37) permits the calculation of the volume change, Δv_A, corresponding to the melting of component A (see direct investigation of phase equilibria) or the change of solubility of A if Δv_A is known as a function of pressure.

A chemical reaction

$$\nu_1' A_1 + \nu_2' A_2 + \ldots \rightleftharpoons \nu_3' A_3 + \nu_4' A_4 + \ldots \tag{1.46}$$

which takes place in a homogeneous system can be described by the more compact relationship

$$0 = \sum_j \nu_j A_j \tag{1.47}$$

where the stoichiometric coefficients, ν_i, are positive for products and negative for reactants. The change in mole number of each component is related to its stoichiometric coefficient by

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \ldots = d\xi \tag{1.48}$$

where ξ is a reaction parameter commonly called the "extent of reaction". Employing this notation, the free energy change in a system which arises from the reaction (at constant temperature and pressure) is given by

$$dG = \sum_j \mu_j dN_j = \sum_j \mu_j \nu_j d\xi \tag{1.49}$$

or

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \sum_j \mu_j \nu_j = \Delta G\,. \tag{1.50}$$

The symbol ΔG represents the change of total free energy per unit of reaction carried out under constant T and P. The condition of equilibrium (eqn. (1.12)) requires that

$$\Delta G = \sum_j \mu_j \nu_j = 0\,. \tag{1.51}$$

ΔG is negative for any natural process

$$\text{i.e. } \Delta G < 0. \tag{1.52}$$

Equation (1.51) may be expressed in terms of activities, defined by the relation (eqn. (1.21))

$$\mu_j = \mu_j^\circ + RT \ln a_j$$

(μ_j° is the chemical potential of the j-th component in the reference state). Equation (1.50) then has the form

$$\begin{aligned} \Delta G &= \sum_j \nu_j \mu_j^\circ + RT \ln \Pi_i\, a_j^{\nu_i} \\ &= \Delta G^\circ + RT \ln \Pi_j\, a_i^{\nu_i} \end{aligned} \tag{1.53}$$

which is often called the Van't Hoff reaction isotherm. Using eqn. (1.51), the equilibrium state is described as

$$\Delta G^\circ = -RT\ln \Pi_i (a_i^{\nu_i})_{eq} = -RT\ln K_a. \tag{1.54}$$

The standard change of free energy, ΔG°, represents the finite change in G associated with the transformation of the reactants to the products according to the stoichiometry, where $\Delta\xi = 1$, and where all components are in their standard states. From the value of ΔG°, the equilibrium constant, K_a, can be calculated. The composition at equilibrium can be determined from the known value of the equilibrium constant, K_a, and the initial composition of the system in question. On the other hand, if the equilibrium constant is directly determined by experimental measurement the corresponding value of ΔG° may be calculated. If multiple simultaneous reactions occur in the system, then for each of them the equilibrium criterion (eqn. (1.54) holds

$$\Delta G_k^\circ = -RT\ln K_{ak} \tag{1.55}$$

and the extent of k-th reaction (eqn. (1.48)) can be defined. The equilibrium composition in the system is then calculated by means of solution of a set of equations (eqn. (1.55)). A computer method for this is described by Zeleznik and Gordon[31].

1.5. *Thermodynamics of interfaces*

In the preceding part, the state of the system was considered to be only dependent on temperature, pressure and composition. In a real case, the surface and the curvature of the phase boundaries are also state determining, particularly if a new phase is formed. Gibbs[33] has shown that for a system composed of two phases, α and β, and separated by a surface of the area, A, the curvatures of which are c_1 and c_2, the total change in energy, U, associated with the displacement of the separating boundary is given by the equation

$$dU = TdS - P^\alpha dV^\alpha - P^\beta dV^\beta + \sum_j \mu_j dN_j + \sigma dA + \varphi_1 dc_1 + \varphi_2 dc_2 \tag{1.56}$$

where σ is the interface tension, φ_1 and φ_2 are the curvature coefficients, and P^α and P^β are the pressures in phases α and β, respectively.

Such a system is considered where the separating surface has a curvature which permits the deletion of terms, $\varphi_1 dc_1$ and $\varphi_2 dc_2$, then

$$dU = TdS - P^\alpha dV^\alpha - P^\beta dV^\beta + \sum_j \mu_j dN_j + \sigma dA \tag{1.57}$$

If the phase boundary is displaced by an amount dw perpendicular to the interface, A, while holding the total volume, energy, and composition constant, then $dV^\alpha = A\, dw$, $dV^\beta = -A\, dw$ and $dA = [(1/r_1) - (1/r_2)]A\, dw$, and

$$P^\beta - P^\alpha = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\sigma \tag{1.58}$$

where r_1 and r_2 are the main radii of curvature. For a spherical surface, $r_1 = r_2 = r$, and $P^\alpha - P^\beta = 2\sigma/r$. An exact analysis has been given in monographs[34,35].

When equilibrium conditions are assumed for a spherical particle of phase β within phase α in a single component system, then $\mu_r^\beta = \mu^\alpha$, and

$$\mu_r^\beta - \mu_\infty^\beta = v^\beta \frac{2\sigma}{r} \tag{1.59}$$

where μ_r^β, μ_∞^β and μ^α are chemical potentials of a particle of phase β of radius r, with flat surface ($r = \infty$) and of bulk phase α, respectively, and v^β is the molar volume of phase β. For the case where phase α is a liquid and phase β is an ideal gas, then

$$\ln \frac{P}{P_0} = \frac{2 v^\beta \sigma}{RTr} \tag{1.60}$$

where P_0 is the saturated partial pressure of phase β ($r = \infty$) at a given temperature, T; P is the equilibrium pressure in the whole system, and R is the gas constant.

By analogy, for a multicomponent system it is valid that for each component

$$\mu_{r_j}^\beta - \mu_{\infty j}^\beta = \bar{v}_j^\beta \frac{2\sigma}{r} \tag{1.61}$$

where $\bar{v}_j^\beta$ is the partial molar volume of the j-th component in phase β.

In the case of an isotropic solid phase, β, and a fluid phase, α, the above relations are retained for spherical particles[35]. Actually, the interfacial energy on the boundary solid–fluid is dependent on the crystallographic orientation. A detailed analysis can be found in refs. 34–36.

In a multicomponent system which is composed of two phases separated by interface A, it is valid that

$$\sum_j N_j^\sigma \mathrm{d}\mu_j + A\,\mathrm{d}\sigma = 0. \tag{1.62}$$

This is an analogy of the Gibbs–Duhem relations, where N_j^σ is the number of molecules of j-th component present in the surface layer separating the phases. Relating this amount to the surface area unit of the phase boundary the surface concentration, Γ_j, can be defined as $\Gamma_j = N_j^\sigma/A$. For zero surface concentration of one component in a two component liquid system, the surface concentration of the second component, Γ_2, can be described by the Gibbs adsorption isotherm

$$\Gamma_2 = -\frac{c_2}{RT}\frac{\mathrm{d}\sigma}{\mathrm{d}c_2} \tag{1.64}$$

where c_2 is the concentration in the bulk liquid which means that the interface layer is enriched by the second component in order to decrease the interphase energy, $(\mathrm{d}\sigma/\mathrm{d}c_2 < 0)$.

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