Chapter 2A

Equilibrium, Stability, and Displacements

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Introduction

The aims of Chapters 2A–2C are as follows: In Chapter 2A, we develop the physicochemical thermodynamic properties of matter in the particular cases of equilibrium states, equilibrium displacements, and equilibrium stability. The best way to treat this problem is to use the concept of chemical affinity introduced by De Donder and developed by Prigogine,

Defay, Glansdorff, and their co-workers. To do this, we base our formulation on the fundamental book of Prigogine and Defay (1967).

In Chapter 2B, we introduce the concept of irreversibility in a local way.

In Chapter 2C, we discuss surface phenomena, following the method of Bakker and Gibbs–Defay.

I. Thermodynamic Potentials

We shall briefly review some properties of the thermodynamic potentials developed exhaustively in Chapter 1.

First, as seen in Chapter 1, the classical definition of the second law is that, for all reversible changes in a closed system at a uniform temperature T,

$$dS = dQ/T \quad \text{(reversible)}. \tag{1.1}$$

For a closed system, the state is defined by the variables T, V, and ξ (ξ is the extent of reaction, or simply the reaction coordinates (see Chapter 1, Section XX), so that

$$S = S(T, V, \xi). \tag{1.2}$$

For all irreversible changes in a closed system,

$$dS > dQ/T \quad \text{(irreversible)}. \tag{1.3}$$

Following Clausius, we may now introduce a new quantity dQ' always positive, which represents the difference between $T\,dS$ and dQ in the course of an irreversible change. It is defined by

$$dS - (dQ/T) = dQ'/T > 0 \quad \text{(irreversible)}. \tag{1.4}$$

Equations (1.1) and (1.3) can now be combined to give

$$dS = dQ/T + dQ'/T, \tag{1.5}$$

with

$$dQ' = 0 \quad \text{(reversible)},$$
$$dQ' > 0 \quad \text{(irreversible)}.$$

Clausius called dQ' the *uncompensated heat*, which is always positive or zero; in classical thermodynamics, it played a purely qualitative part. It was used to delimit reversible changes for which $dQ' = 0$, and when

dealing with nonequilibrium states it was sufficient to write $dQ' > 0$ without attempting an explicit calculation of its value.

The term "uncompensated heat" is not a particularly happy choice. The uncompensated heat dQ' is never the heat received by the system, but arises from irreversible changes taking place in the *interior* of the system.

The entropy of a system can vary for *two reasons and for two reasons only*: either by the transport of entropy $d_e S$ to or from the surroundings through the boundary surface of the system, or by the *creation of entropy* $d_i S$ inside the system. We have then [see Chapter 1, Eq. (11.2)]

$$dS = d_e S + d_i S, \tag{1.6}$$

and for a closed system

$$d_e S = dQ/T \tag{1.7}$$

$$d_i S = dQ'/T. \tag{1.8}$$

The entropy created in the system is thus equal to the Clausius uncompensated heat divided by the absolute temperature; this gives the uncompensated heat a physical significance (see Chapter 1, Section XI).

The inequality (1.4) states that the creation of entropy is always positive, that is, irreversible processes can only create entropy, they cannot destroy it.

We note that for an *isolated* system

$$dS = d_i S > 0. \tag{1.9}$$

Now, thermodynamic potentials are special state functions whose properties may be characterized, if certain variables are maintained constant, by a decrease when irreversible processes take place in the system. Thus, the thermodynamic potentials indicate the presence of irreversible phenomena in changes in which the corresponding variables are maintained constant.

Limiting our work to systems submitted only to quasistatic work (see Chapter 1, Section VII), we use the following four sets of variables:

$$\begin{aligned} S, V, n_1, \ldots, n_c; && T, V, n_1, \ldots, n_c; \\ S, p, n_1, \ldots, n_c; && T, p, n_1, \ldots, n_c; \end{aligned} \tag{1.10}$$

where $n_1, \ldots, n_c$ are the numbers of moles of components $1, \ldots, c$. The other symbols are defined in Chapter 1.

It may be interesting to note that each set of variables constains a thermal variable (S or T), a mechanical variable (p or V), and chemical variables ($n_1, \ldots, n_c$) related to the extents of reactions ($\xi_1, \ldots, \xi_c$).

The choice of a set of variables is only governed by practical factors. To each set of variables there corresponds a thermodynamic potential.

Combining the first law of thermodynamics [see Chapter 1, Eqs. (8.3) and (7.1)]

$$dU = dQ - p\,dV \tag{1.11}$$

with the second law (1.5) expressed in a modern form by De Donder (1923) (see also Duhem, 1899, 1911; Planck, 1927, 1930; Poincare, 1908), we obtain

$$dQ = dU + p\,dV = T\,dS - dQ'. \tag{1.12}$$

We now put formula (1.12) into various forms corresponding to various experimental conditions under which physicochemical changes can take place:

1. *Internal energy U*

From (1.12), we get

$$dU = T\,dS - p\,dV - dQ'. \tag{1.13}$$

Thus, for all irreversible reactions taking place *at constant S and V*,

$$dU = -dQ' < 0. \tag{1.14}$$

Thus, an irreversible change at constant entropy and volume is accompanied by a *decrease* in the internal energy. The internal energy thus plays the part of an indicator of irreversible processes for changes at constant S and V.

2. *Enthalpy H*

From the definition of the heat content or enthalpy [see Chapter 1, Eq. (9.3)]

$$H = U + pV, \tag{1.15}$$

(1.13) may be written

$$dH = T\,dS + V\,dp - dQ'. \tag{1.16}$$

For an irreversible reaction at constant S and p, we have therefore

$$dH = -dQ' < 0. \tag{1.17}$$

Thus, an irreversible change at constant entropy and *pressure* is accompanied by a decrease in the *enthalpy*. The enthalpy is the thermodynamic potential associated with the physical variables S and p.

3. Helmholtz Free Energy F

We define the Helmholtz free energy F by the relation [see Chapter 1, Eq. (16.3)]

$$F = U - TS, \tag{1.18}$$

and we see, from (1.13) and (1.18), that

$$dF = -S\, dT - p\, dV - dQ'. \tag{1.19}$$

For an irreversible change at constant T and V, we have therefore

$$dF = -dQ' < 0; \tag{1.20}$$

the function F is the thermodynamic potential associated with the variables T, V.

Thus, an irreversible change at constant temperature and volume is accompanied by a decrease in the Helmholtz free energy.

4. Gibbs Free Energy G

We define the Gibbs free energy G by the relation

$$G = U - TS + pV = H - TS. \tag{1.21}$$

Combining (1.13) with (1.21), we have

$$dG = -S\, dT + V\, dp - dQ'. \tag{1.22}$$

For an irreversible change at constant T and p, (1.22) reduces to

$$dG = -dQ' < 0. \tag{1.23}$$

Thus, an irreversible change at constant temperature and pressure is accompanied by a decrease in the Gibbs free energy.

Remark. The function $-S$ is a thermodynamic potential corresponding to the variables U, V, n_1, ..., n_c. Indeed, (1.12) gives, at constant U and V,

$$-dS = -dQ'/T < 0. \tag{1.24}$$

This conclusion is expected because a closed system where U and V are maintained constant is in fact an *isolated system*. This is the classical statement that the entropy of an isolated system increases with time.

II. Affinity

We shall consider here uniform systems in the absence of gravity, i.e., systems where pressure, temperature and composition are the same within each phase.

The diffusion equilibrium is thus reached within each phase of the system. The mechanical equilibrium excludes the barycentric motion and the viscosity, while the thermal equilibrium excludes transport of heat.

In fact, it is well known that a real system submitted to variations of temperature and pressure is not strictly uniform. The concept of a uniform system is thus an idealization of reality, but the approximation may be accepted if the variations of T and p are very slow.

If chemical reaction and phase changes take place in the same manner at each point of the system and if the exchanges of heat with the external world are slow enough to maintain a uniform temperature throughout all the system, the only irreversible processes are then general changes which can be expressed in terms of a reaction coordinate ξ. The production of entropy must be determined solely by ξ, and with De Donder (1922) we may write

$$dQ' = A \, d\xi \geq 0. \tag{2.1}$$

The inequality corresponds to spontaneous reaction, while the equality corresponds to the equilibrium.

De Donder introduced the function of state A called the affinity of the reaction, which does not depend upon the kind of transformation considered but depends solely on the state of the system at a particular instant.

In fact, De Donder introduced his relation (2.1) as a hypothesis, but Defay (1938) showed afterwards that, for a given value of $d\xi$, dQ' will

be the same whatever may be the values of dp and dT during the change under consideration. With the variables T, p, ξ, we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial U}{\partial p}\right)_{T\xi} dp + \left(\frac{\partial U}{\partial \xi}\right)_{Tp} d\xi \qquad (2.2)$$

and also

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial V}{\partial p}\right)_{T\xi} dp + \left(\frac{\partial V}{\partial \xi}\right)_{Tp} d\xi. \qquad (2.3)$$

Let us define the following quantities (see Chapter 1, Section XVIII):

$$\left(\frac{\partial U}{\partial T}\right)_{p\xi} + p\left(\frac{\partial V}{\partial T}\right)_{p\xi} = C_{p\xi} \qquad (2.4)$$

$$\left(\frac{\partial U}{\partial p}\right)_{T\xi} + p\left(\frac{\partial V}{\partial p}\right)_{T\xi} = h_{T\xi} \qquad (2.5)$$

$$\left(\frac{\partial U}{\partial \xi}\right)_{Tp} + p\left(\frac{\partial V}{\partial \xi}\right)_{Tp} = -r_{Tp} \qquad (2.6)$$

The quantities $C_{p\xi}$ (heat capacity of the system at constant pressure and composition), $h_{T\xi}$ (latent heat of pressure change at constant temperature and composition), and r_{Tp} (heat of reaction at constant T and p) are the thermal coefficients in the variables T, p, and ξ.

Substitution in (1.11) then leads to

$$dQ = C_{p\xi}\, dT + h_{T\xi}\, dp - r_{Tp}\, d\xi. \qquad (2.7)$$

Now, we may write

$$dS = \left(\frac{\partial S}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial S}{\partial p}\right)_{T\xi} dp + \left(\frac{\partial S}{\partial \xi}\right)_{Tp} d\xi. \qquad (2.8)$$

Combining (2.7) and (2.8) with the Clausius equation

$$dQ' = T\, dS - dQ, \qquad (2.9)$$

we obtain

$$\frac{dQ'}{dt} = \left[T\left(\frac{\partial S}{\partial T}\right)_{p\xi} - C_{p\xi}\right]\frac{dT}{dt} + \left[T\left(\frac{\partial S}{\partial p}\right)_{T\xi} - h_{T\xi}\right]\frac{dp}{dt}$$
$$+ \left[T\left(\frac{\partial S}{\partial \xi}\right)_{Tp} + r_{Tp}\right]\frac{d\xi}{dt}, \qquad (2.10)$$

where dT/dt and dp/dt, which are the changes of the temperature and pressure in unit time, are quantities which can vary arbitrarily and may be given either positive or negative values. On the other hand, we consider the speed of reaction $d\xi/dt$ as a function of state (Prigogine and Defay, 1967, p. 18; De Donder, 1937, p. 936, 1938, p. 15), so that

$$d\xi/dt = \mathbf{v}(T, p, \xi). \tag{2.11}$$

Moreover, the three coefficients of dT/dt, dp/dt, and $d\xi/dt$ are functions of T, p, ξ. Equation (2.10) shows that, for a given state of the system, if the coefficients of dT/dt and dp/dt are not zero, then by assigning dT/dt and dp/dt suitable values, we may give dQ'/dt any value we wish; in particular, we can make dQ'/dt negative, which is contrary to the second law. It is thus necessary for these coefficients to be zero, that is,

$$T\left(\frac{\partial S}{\partial T}\right)_{p\xi} - C_{p\xi} = 0; \qquad T\left(\frac{\partial S}{\partial p}\right)_{T\xi} - h_{T\xi} = 0. \tag{2.12}$$

Equation (2.10) reduces then to the form (2.1) with

$$A = r_{Tp} + T(\partial S/\partial \xi)_{Tp}. \tag{2.13}$$

Because r_{Tp} and S are functions of T, p, and ξ, it results that A is also a function of T, p, and ξ, and thus it is a function of the state of the system.

Combining De Donder's inequality (2.1) with (2.11), we may write

$$dQ'/dt = A \, d\xi/dt = A \cdot \mathbf{v} \geq 0, \tag{2.14}$$

whence,

$$
\begin{aligned}
A > 0, \qquad & \mathbf{v} \geq 0 \\
A < 0, \qquad & \mathbf{v} \leq 0 \\
A = 0, \qquad & \mathbf{v} = 0,
\end{aligned}
$$

for, if we had $\mathbf{v} \neq 0$ with $A = 0$, we should have a chemical reaction proceeding at a finite rate in a reversible manner, which is impossible.

CONCLUSIONS

(a) The affinity is always of the same sign as the rate of reaction and thus gives the sign of the rate.

(b) When the affinity is zero, the system is in equilibrium.

The converse of this second statement is, however, not true:

$$\mathbf{v} \neq 0, \quad \text{whence} \quad dQ' > 0 \quad \text{and} \quad A\mathbf{v} > 0 \quad \begin{cases} \mathbf{v} > 0 \quad \text{gives } A > 0 \\ \mathbf{v} < 0 \quad \text{gives } A < 0 \end{cases}$$

$$\mathbf{v} = 0, \quad \text{whence} \quad dQ' = 0 \quad \text{and} \quad A\mathbf{v} = 0 \quad \begin{cases} \mathbf{v} = 0 \quad \text{and} \quad A = 0: \\ \qquad \text{true equilibrium} \\ \mathbf{v} = 0 \quad \text{and} \quad A \neq 0: \\ \qquad \text{false equilibrium.} \end{cases}$$

We describe a system as being in a state of false equilibrium when no reaction proceeds even though the affinity of the reaction is not zero. The necessary and sufficient conditions for true equilibrium in a chemical reaction is then given by

$$A(T, p, \xi) = 0. \tag{2.15}$$

In place of (2.2), we may write, in the variables T, V, ξ,

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V\xi} dT + \left(\frac{\partial U}{\partial V}\right)_{T\xi} dV + \left(\frac{\partial U}{\partial \xi}\right)_{TV} d\xi. \tag{2.16}$$

By comparing (2.16) and (1.11), we may write

$$dQ = C_{V\xi}\, dT + l_{T\xi}\, dV - r_{TV}\, d\xi, \tag{2.17}$$

where

$$(\partial U/\partial T)_{V\xi} = C_{V\xi}, \tag{2.18}$$

$$(\partial U/\partial V)_{T\xi} + p = l_{T\xi}, \tag{2.19}$$

$$(\partial U/\partial \xi)_{TV} = -r_{TV}. \tag{2.20}$$

The quantity $C_{V\xi}$ is the heat capacity at constant volume and composition. $l_{T\xi}$ is the latent heat of volume change of the system, and r_{TV} is the heat of reaction at constant T and V.

The same arguments as above [see (2.12)] lead to

$$T(\partial S/\partial T)_{V\xi} - C_{V\xi} = 0; \qquad T(\partial S/\partial V)_{T\xi} - l_{T\xi} = 0. \tag{2.21}$$

and

$$A = r_{TV} + T(\partial S/\partial \xi)_{TV}. \tag{2.22}$$

It is easy to see that, at low temperatures, a measurement of r_{TV} gives as first approximation the value of the affinity A according to Berthelot's

point of view. But, generally, A and r_{TV} are different because of the term $T(\partial S/\partial \xi)_{TV}$. If this term is important, then it is possible to obtain

$$A > 0 \quad \text{with} \quad r_{TV} < 0 \quad \text{(endothermic reaction)}.$$

III. Affinity and Thermodynamic Potentials

Now combining (2.1) respectively with (1.13), (1.16), (1.19), and (1.22), we obtain (Prigogine and Defay, 1967, Chapter IV)

$$dU = T\, dS - p\, dV - A\, d\xi \tag{3.1}$$

$$dH = T\, dS + V\, dp - A\, d\xi \tag{3.2}$$

$$dF = -S\, dT - p\, dV - A\, d\xi \tag{3.3}$$

$$dG = -S\, dT + V\, dp - A\, d\xi. \tag{3.4}$$

For a closed system, we have then

$$U = U(S, V, \xi), H = H(S, p, \xi), F = F(T, V, \xi), G = G(T, p, \xi). \tag{3.5}$$

We now compare (3.1)–(3.4) with the corresponding total differentials, and so obtain the connection between (1) an extensive thermal variable S and an intensive thermal variable T, (2) an extensive mechanical variable V and an intensive mechanical variable p, and (3) an extensive chemical variable ξ and an intensive chemical variable A:

$$\left(\frac{\partial U}{\partial S}\right)_{V\xi} = T, \qquad \left(\frac{\partial U}{\partial V}\right)_{S\xi} = -p, \qquad \left(\frac{\partial U}{\partial \xi}\right)_{VS} = -A; \tag{3.6}$$

$$\left(\frac{\partial H}{\partial S}\right)_{p\xi} = T, \qquad \left(\frac{\partial H}{\partial p}\right)_{S\xi} = V, \qquad \left(\frac{\partial H}{\partial \xi}\right)_{pS} = -A; \tag{3.7}$$

$$\left(\frac{\partial F}{\partial T}\right)_{V\xi} = -S, \qquad \left(\frac{\partial F}{\partial V}\right)_{T\xi} = -p, \qquad \left(\frac{\partial F}{\partial \xi}\right)_{VT} = -A; \tag{3.8}$$

$$\left(\frac{\partial G}{\partial T}\right)_{p\xi} = -S, \qquad \left(\frac{\partial G}{\partial p}\right)_{T\xi} = V, \qquad \left(\frac{\partial G}{\partial \xi}\right)_{Tp} = -A; \tag{3.9}$$

the affinity is thus equal to the *slope* with respect to ξ of the thermodynamical potential related to the appropriate variables.

It is now easy to find the so-called Gibbs–Helmholtz equation by combining (1.18) and (3.8); we then find

$$U = F - T(\partial F/\partial T)_{V\xi}. \tag{3.10}$$

We may now derive a further set of important relations from (3.6)–(3.9). With the second derivatives, we have, for example, in the variables T, V, ξ and T, p, ξ,

$$\left(\frac{\partial S}{\partial V}\right)_{T\xi} = \left(\frac{\partial p}{\partial T}\right)_{V\xi}, \quad \left(\frac{\partial S}{\partial \xi}\right)_{TV} = \left(\frac{\partial A}{\partial T}\right)_{V\xi}, \quad \left(\frac{\partial p}{\partial \xi}\right)_{TV} = \left(\frac{\partial A}{\partial V}\right)_{T\xi},$$
(3.11)

$$\left(\frac{\partial S}{\partial p}\right)_{T\xi} = -\left(\frac{\partial V}{\partial T}\right)_{p\xi}, \quad \left(\frac{\partial S}{\partial \xi}\right)_{Tp} = \left(\frac{\partial A}{\partial T}\right)_{p\xi}, \quad \left(\frac{\partial V}{\partial \xi}\right)_{Tp} = -\left(\frac{\partial A}{\partial p}\right)_{T\xi}.$$
(3.12)

Other groups of equations and many applications are given in the fundamental book of Prigogine and Defay (1967, p. 54).

From a general point of view, we observe that a partial derivative of a thermal variable (T or S) with respect to one of the mechanical variables (p or V) is equal to the partial derivative of the conjugate mechanical variable (V or p) with respect to the other thermal variable (S or T). Similar statements hold for the other pairs of variables (T, S) and (A, ξ) and (p, V) and (A, ξ).

In further sections, we will see some applications of Eq. (3.12).

IV. The Gibbs Chemical Potential

A. THE CHEMICAL POTENTIAL

Let us suppose that the functions of state U and S introduced by the first and second laws of thermodynamics also exist in open systems, so that we may write

$$U = U(T, V, n_1, \ldots, n_c) \equiv U(S, V, n_1, \ldots, n_c) \tag{4.1}$$

$$S = S(T, V, n_1, \ldots, n_c). \tag{4.2}$$

Now, in closed systems, we used the symbols dn_y and dV to represent the changes, respectively, in number of moles n_y and in volume in the time dt ($dt > 0$). However, in open systems, we have to introduce a new symbol for differentiation, δ, to avoid any confusion with the symbol d. The δn_y are chosen quite arbitrarily and they represent virtual or true variations of any kind in the number of moles n_y.

From (3.1), we then have

$$\delta U = \left(\frac{\partial U}{\partial S}\right)_{Vn} \delta S + \left(\frac{\partial U}{\partial V}\right)_{Sn} \delta V + \sum_{\gamma} \left(\frac{\partial U}{\partial n_{\gamma}}\right)_{SVn_{\beta}} \delta n_{\gamma}, \qquad (4.3)$$

where the subscript n means that all the n_{γ} remain constant during the derivation and the subscript n_{β} means that all n's except n_{γ} remain constant.

We may write now the following equalities:

$$\left(\frac{\partial U}{\partial S}\right)_{Vn} = \left(\frac{\partial U}{\partial S}\right)_{V\xi} \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{Sn} = \left(\frac{\partial U}{\partial V}\right)_{S\xi} \qquad (4.4)$$

because the state of an open system in which all the n_{γ} remain constant changes exactly as it would in a closed system in which ξ remains constant.

Combining (4.4), (4.3), and (3.6), we obtain

$$\delta U = T \,\delta S - p \,\delta V + \sum_{\gamma} \left(\frac{\partial U}{\partial n_{\gamma}}\right)_{VSn_{\beta}} \delta n_{\gamma}. \qquad (4.5)$$

If we use H, F, and, G, we obtain

$$\delta H = T \,\delta S + V \,\delta p + \sum_{\gamma} \left(\frac{\partial H}{\partial n_{\gamma}}\right)_{pSn_{\beta}} \delta n_{\gamma} \qquad (4.6)$$

$$\delta F = -S \,\delta T - p \,\delta V + \sum_{\gamma} \left(\frac{\partial F}{\partial n_{\gamma}}\right)_{TVn_{\beta}} \delta n_{\gamma} \qquad (4.7)$$

$$\delta G = -S \,\delta T + V \,\delta p + \sum_{\gamma} \left(\frac{\partial G}{\partial n_{\gamma}}\right)_{Tpn_{\beta}} \delta n_{\gamma}. \qquad (4.8)$$

Nevertheless, we can write δH, δF, and δG in another way; i.e., from (4.5) and the definitions (1.15), (1.18) and, (1.21), we deduce that

$$\delta H = T \,\delta S + V \,\delta p + \sum_{\gamma} \left(\frac{\partial U}{\partial n_{\gamma}}\right)_{SVn_{\beta}} \delta n_{\gamma} \qquad (4.9)$$

$$\delta F = -S \,\delta T - p \,\delta V + \sum_{\gamma} \left(\frac{\partial U}{\partial n_{\gamma}}\right)_{SVn_{\beta}} \delta n_{\gamma} \qquad (4.10)$$

$$\delta G = -S \,\delta T + V \,\delta p + \sum_{\gamma} \left(\frac{\partial U}{\partial n_{\gamma}}\right)_{SVn_{\beta}} \delta n_{\gamma}. \qquad (4.11)$$

Comparing these equations with (4.6), (4.7), and (4.8), we thus have [see Chapter 1, Eqs. (16.5), (16.8)]

$$\delta U = T\,\delta S - p\,\delta V + \sum_\gamma \mu_\gamma\,\delta n_\gamma \tag{4.12}$$

$$\delta H = T\,\delta S + V\,\delta p + \sum_\gamma \mu_\gamma\,\delta n_\gamma \tag{4.13}$$

$$\delta F = -S\,\delta T - p\,\delta V + \sum_\gamma \mu_\gamma\,\delta n_\gamma \tag{4.14}$$

$$\delta G = -S\,\delta T + V\,\delta p + \sum_\gamma \mu_\gamma\,\delta n_\gamma, \tag{4.15}$$

where the symbol μ_γ, called by Gibbs (see Prigogine and Defay (1967), p. 68) the chemical potential of component γ, is the common value of the derivatives

$$\mu_\gamma \equiv \left(\frac{\partial U}{\partial n_\gamma}\right)_{SVn_\beta} = \left(\frac{\partial H}{\partial n_\gamma}\right)_{Spn_\beta} = \left(\frac{\partial F}{\partial n_\gamma}\right)_{TVn_\beta} = \left(\frac{\partial G}{\partial n_\gamma}\right)_{Tpn_\beta} \tag{4.16}$$

As the thermodynamic potentials are extensive functions, the chemical potential μ_γ is an intensive quantity; it is the partial molar quantity corresponding to a thermodynamic potential. Thus, the chemical potential describes the *local* properties of the system (for electrochemical systems, see Sanfeld (1968a)).

If the system is composed of many phases $(\alpha, \delta, \ldots)$ at the same pressure and the same temperature, it is easy to show (Prigogine and Defay, 1965, p. 75) that, for example, (4.15) and (4.16) must be replaced by

$$\delta G = -S\,\delta T + V\,\delta p + \sum_\alpha \sum_\gamma \left(\frac{\partial G}{\partial n_\gamma{}^\alpha}\right)_{Tpn_{\beta\neq\gamma}^\delta} \delta n_\gamma{}^\alpha \tag{4.17}$$

$$\mu_\gamma{}^\alpha = \left(\frac{\partial U}{\partial n_\gamma{}^\alpha}\right)_{VSn_\beta^\delta} = \left(\frac{\partial H}{\partial n_\gamma{}^\alpha}\right)_{Spn_\beta^\delta} = \left(\frac{\partial F}{\partial n_\gamma{}^\alpha}\right)_{TVn_\beta^\delta} = \left(\frac{\partial G}{\partial n_\gamma{}^\alpha}\right)_{Tpn_\beta^\delta} \tag{4.18}$$

B. Affinity and Thermodynamic Potentials as Functions of the Chemical Potentials

In accordance with the *principle of conservation of mass*, the stoichiometric equation for a reaction r may be written [see Chapter 1, Eq. (20.3)]

$$\sum_\alpha \sum_\gamma \nu_{\gamma r}^\alpha M_\gamma = 0, \tag{4.19}$$

where M_y is the molecular weight of component y. Now, from Eqs. (4.19) and (4.18) and the form of A given by (3.9), combined with [see Chapter 1, Eq. (20.2)]

$$d\xi_r = d_r n_y{}^\alpha / v_{yr}^\alpha, \tag{4.20}$$

we obtain

$$A_r = -\sum_\alpha \sum_y v_{yr}^\alpha \frac{\partial G}{\partial n_y{}^\alpha} = -\sum_\alpha \sum_y v_{yr}^\alpha \mu_y{}^\alpha. \tag{4.21}$$

At the true equilibrium of reaction, we have

$$A_r = 0 \tag{4.22}$$

or

$$\sum_\alpha \sum_y v_{yr}^\alpha \mu_y{}^\alpha = 0 \qquad (r = 1, 2, \ldots, r). \tag{4.23}$$

Practical examples of chemical and passage equilibrium will be given in further sections.

Now, the extensive function G given by (4.17) is homogeneous of the first degree with the extensive variables $n_1{}^1, \ldots, n_y{}^\alpha, \ldots, n_c{}^\delta$ as independent variables. We may then apply to G Euler's theorem for homogeneous functions, i.e.,

$$G = \sum_\alpha \sum_y n_y{}^\alpha \mu_y{}^\alpha. \tag{4.24}$$

The chemical potentials $\mu_y{}^\alpha$ of the y constituents in the α phases of the system are thus functions of the independent variables $T, p, n_1{}^1, \ldots, n_y{}^\alpha, \ldots, n_c{}^\delta$. On the one hand, they define all the thermodynamic properties of the system studied, and on the other hand they enable us to write the conditions of chemical equilibrium in the form (4.23) which is at once both simple and general.

The total volume V of the system can be written in function of the volume of each homogeneous phase V^α so that

$$V = \sum_\alpha V^\alpha(T, p, n_1{}^\alpha, \ldots, n_c{}^\alpha). \tag{4.25}$$

In the same way, if we neglect all the surface energies and entropies between the phases, then the thermodynamic potentials may be written as

$$G = \sum_\alpha G^\alpha \tag{4.26}$$

and the chemical potential may be written simply as

$$\mu_\gamma{}^\alpha = \left(\frac{\partial G}{\partial n_\gamma{}^\alpha}\right)_{Tpn_\beta^\delta} = \left(\frac{\partial G^\alpha}{\partial n_\gamma{}^\alpha}\right)_{Tpn_\beta^\delta} \tag{4.27}$$

Similarly, it is easy to show that

$$h_\gamma{}^\alpha = \left(\frac{\partial H^\alpha}{\partial n_\gamma{}^\alpha}\right)_{Tpn_\beta^\delta} \tag{4.28}$$

$$s_\gamma{}^\alpha = \left(\frac{\partial S^\alpha}{\partial n_\gamma{}^\alpha}\right)_{Tpn_\beta^\delta}; \tag{4.29}$$

$\mu_\gamma{}^\alpha$, $h_\gamma{}^\alpha$, and $s_\gamma{}^\alpha$ are thus the partial molar quantities corresponding, respectively, to the extensive functions G^α, H^α, and S^α.

C. THE GIBBS–DUHEM EQUATION

The differentiation of (4.24) combined with the corresponding equation (4.17) gives the fundamental Gibbs–Duhem equation

$$S\,\delta T - V\,\delta p + \sum_\alpha \sum_\gamma n_\gamma{}^\alpha\,\delta\mu_\gamma{}^\alpha = 0. \tag{4.30}$$

If the system is described by the variables T, p, $\mu_1{}^1$, ..., $\mu_\gamma{}^\alpha$, ..., $\mu_c{}^\delta$, one of these variables is not independent. The relation (4.30) enables us to calculate one of the increments δT, δp, or $\delta\mu_\gamma{}^\alpha$ when the others are known.

For an isothermal, isobaric change, (4.30) reduces to

$$\sum_\alpha \sum_\gamma n_\gamma{}^\alpha\,\delta\mu_\gamma{}^\alpha = 0 \tag{4.31}$$

Applying Euler's theorem, (4.31) becomes (now dropping all the subscripts related to the number of moles)

$$\sum_\alpha \sum_\gamma n_\gamma{}^\alpha\left(\frac{\partial\mu_\gamma{}^\alpha}{\partial n_\beta{}^\alpha}\right)_{Tp} = 0. \tag{4.32}$$

Or, from the so-called reciprocity relation (Prigogine and Defay, 1967, p. 70)

$$\left(\frac{\partial\mu_\gamma{}^\alpha}{\partial n_\beta{}^\alpha}\right)_{Tp} = \left(\frac{\partial\mu_\beta{}^\alpha}{\partial n_\gamma{}^\alpha}\right)_{Tp} \qquad (\gamma, \beta = 1, 2, \ldots, c), \tag{4.33}$$

Eq. (4.32) may be rewritten as

$$\sum_\alpha \sum_\gamma n_\gamma{}^\alpha \left(\frac{\partial \mu_\beta{}^\alpha}{\partial n_\gamma{}^\alpha}\right)_{Tp} = 0. \tag{4.34}$$

Remark. From the second partial derivative of $G(T, p, n_1, \ldots, n_c)$ and from Eq. (4.15) and (3.9), we have

$$\left(\frac{\partial \mu_\gamma}{\partial T}\right)_{pn} = -\left(\frac{\partial S}{\partial n_\gamma}\right)_{Tp} = -s_\gamma \tag{4.35}$$

$$\left(\frac{\partial \mu_\gamma}{\partial p}\right)_{Tn} = \left(\frac{\partial V}{\partial n_\gamma}\right)_{Tp} = v_\gamma. \tag{4.36}$$

Differentiating $H = U + pV$ and $G = U - TS + pV$, we obtain

$$h_\gamma = u_\gamma + pv_\gamma \tag{4.37}$$

$$\mu_\gamma = u_\gamma - Ts_\gamma + pv_\gamma. \tag{4.38}$$

The specific molar entropy s_γ determines the variation of μ_γ with T, while the specific molar enthalpy determines the variation of μ_γ/T with T. Indeed, from (4.37) and (4.38), we find

$$\mu_\gamma = h_\gamma - Ts_\gamma, \tag{4.39}$$

and thus

$$\partial(\mu_\gamma/T)/\partial T = -h_\gamma/T^2. \tag{4.40}$$

D. COMPARISON WITH THE FORMULATION OF LEWIS AND RANDALL[*]

As we have seen previously, the affinity A is a function of the instantaneous state of the system given by the derivative of the thermodynamic potential G with respect to ξ, at constant T and p for *each* state of the matter [see Eq. (3.9)]

$$A = -(\partial G/\partial \xi)_{Tp}. \tag{4.41}$$

Now, the symbol ΔG used by Lewis and Randall means a *finite* variation of the function, e.g.,

$$\Delta G = G_{\text{final}} - G_{\text{initial}} \quad \text{(two states)}. \tag{4.42}$$

In fact, the fundamental difference between A and ΔG is not related to

[*] Lewis and Randall (1923).

the existence of two states of matter, because, in $A = A(T, p, \xi)$, the extent of reaction ξ is also related to the initial state of matter:

$$\xi = (n_\gamma - n_\gamma{}^i)/\nu_\gamma, \tag{4.43}$$

where $n_\gamma{}^i$ is the number of moles of the components γ when $t = 0$. The difference comes from the relation (4.24). For one phase, Eq. (4.24) reduces to

$$G = \sum_\gamma n_\gamma \mu_\gamma, \tag{4.44}$$

and thus

$$\Delta G = \left(\sum_\gamma n_\gamma \mu_\gamma \right)_{\text{final}} - \left(\sum_\gamma n_\gamma{}^i \mu_\gamma{}^i \right)_{\text{initial}}. \tag{4.45}$$

Since μ_γ does not necessarily have the same value in the initial and in the final states,

$$\Delta G \neq \sum_\gamma \mu_\gamma (n_\gamma - n_\gamma{}^i). \tag{4.46}$$

From (4.43) and (4.46), we obtain the inequality

$$\Delta G_\xi \neq \sum_\gamma \nu_\gamma \mu_\gamma, \tag{4.47}$$

where

$$\Delta G_\xi = \Delta G / \xi. \tag{4.48}$$

According to the Lewis approach, the chemical potentials μ_γ are implicitly considered as constant, or have a mean value so that, if $\xi = 1$,

$$\Delta G = \sum_\gamma \nu_\gamma \langle \mu_\gamma \rangle. \tag{4.49}$$

This hypothesis is quite correct if the initial composition, temperature, and pressure are only weakly modified by the chemical reactions. Strictly speaking, for a chemical reaction

$$\nu_A A + \nu_B B = \nu_C C + \nu_D D,$$
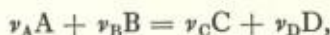
A, for a given well-defined state, is

$$A = \nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B, \tag{4.50}$$

and thus does not simply represent a decrease in free energy or a difference between two states. Because the use of a mean value gives rise to some

difficulties in the neighborhood of equilibrium, where G takes a minimum value, it would be better to define ΔG as a single operator of the type (4.50). For details about this problem, see the fundamental work of Prigogine and Defay (1967, Chapter V).

E. PASSAGE FROM A CLOSED TO AN OPEN SYSTEM

As we already saw, the functions $A(T, p, \xi)$ and $G(T, p, \xi)$ are well defined in closed systems, with the definition (2.1),

$$A \, d\xi = dQ',$$

the relation [Eqs. (3.9)]

$$A = -(\partial G/\partial \xi)_{Tp},$$

and the formula [Eq. (3.4)]

$$\delta G = -S \, \delta T + V \, \delta p - A \, \delta \xi.$$

For an open system, we *presumed* that the function G must also exist in the form

$$G = G(T, p, n_1, \ldots, n_c). \tag{4.51}$$

Now, when an open system undergoes a change in which all the n_γ remain constant, the change is exactly as it would be in a closed system in which ξ remains constant, so that the two first derivatives of (3.9) become

$$(\partial G/\partial T)_{pn} = -S \tag{4.52}$$

$$(\partial G/\partial p)_{Tn} = V. \tag{4.53}$$

The last derivative of (3.9) can also be written in the form

$$\left(\frac{\partial G}{\partial \xi}\right)_{Tp} = \sum_\gamma \left(\frac{\partial G}{\partial n_\gamma}\right)_{Tp} \frac{dn_\gamma}{d\xi} \tag{4.54}$$

because, in $G = G(T, p, \xi)$, ξ depends on n_γ. Now, the derivative $dn_\gamma/d\xi$ means $d_i n_\gamma/d\xi$, because, in closed systems, the change dn_γ in the number of moles of γ in a time interval dt will be only the change arising as a result of internal (subscript i) chemical reactions, and

$$d_i n_\gamma/d\xi = \nu_\gamma. \tag{4.55}$$

On the other hand, from the form (4.51), it results that in the derivative $(\partial G/\partial n_\gamma)_{Tp}$ the variations of n_γ are of any kind, e.g., result from transport across the boundaries of the system to or from the surroundings.

Combining (4.54), (4.55), and (4.16), we obtain the well-known passage equation from closed to open systems

$$(\partial G/\partial \xi)_{Tp} = \sum_\gamma \nu_\gamma \mu_\gamma. \qquad (4.56)$$

Inserting Eq. (4.55) and (4.21) in Eq. (3.4) then gives *for open systems*

$$\delta G = -S\,\delta T + V\,\delta p + \sum_\gamma \mu_\gamma\,\delta n_\gamma. \qquad (4.15)$$

The passage from a closed system (where the function A is well defined) to an open one (where the intensive functions μ_γ are locally defined) is thus realized without any difficulty.

V. The Phase Rule

A. General Demonstration

We will now consider the number of phases which can coexist and the relationship of the properties of each component to the equilibrium behavior of the system. First, let us remember that a phase composed of one or several components is a macroscopic homogeneous portion of a system.

Since all gases are completely miscible, there can never be more than one gas phase; however, a number of independent liquid or solid phases may be formed. The phase rule, like all basic thermodynamic relationships, is independent of assumptions pertaining to the particular nature of matter; it is not concerned with the quantities of the various phases, but only with *intensive variables*. The Gibbs phase rule only permits us to *fix arbitrarily a certain number of intensive variables when the system is in equilibrium.*

We consider a system with c components, ϕ phases at the same pressure and the same temperature, and r' distinct chemical reactions (omitting those which consist solely of the passage reactions).

In the systems considered here,[*] composed of c constituents and ϕ phases, the intensive variables are

$$T, p, N_1^1, \ldots, N_c^1, \ldots, N_1^\phi, \ldots, N_c^\phi, \tag{5.1}$$

where the mole fractions N_γ^α of γ in the phase α are defined by

$$N_\gamma^\alpha = n_\gamma^\alpha / \sum_\gamma n_\gamma^\alpha. \tag{5.2}$$

Nevertheless, the $(2 + c\phi)$ intensive variables are not all independent, and, at equilibrium, general relations bind these variables.

Whatever the state of the system, we have ϕ relations of the type

$$\sum_\gamma N_\gamma^\alpha = 1. \tag{5.3}$$

The equilibrium conditions are:

(1) There are $c(\phi - 1)$ conditions of transfer equilibrium of each constituent among the various phases

$$\mu_\gamma^1 = \mu_\gamma^2 = \cdots = \mu_\gamma^\phi \qquad (\gamma = 1, \ldots, c). \tag{5.4}$$

(2) There are r' conditions of equilibrium for the chemical reactions,

$$A_r = - \sum_\gamma \sum_\alpha \nu_{\gamma r} \mu_\gamma^\alpha = 0 \qquad (r = 1, \ldots, r'). \tag{5.5}$$

The number of relations among the $2 + c\phi$ intensive variables is thus

$$\phi + c(\phi - 1) + r'. \tag{5.6}$$

The variance or the number of degrees of freedom, i.e., *the number of independent intensive variables*, is thus given by (Gibbs, 1928; De Donder, 1920; Jouguet, 1921; Bowden, 1938)

$$w = 2 + (c - r') - \phi. \tag{5.7}$$

Remark. If a component is insoluble in the phase α, the supplementary insolubility condition

$$N_\gamma^\alpha = 0 \tag{5.8}$$

gives rise to a loss of a condition like (5.4). Thus, the phase rule (5.7) remains valid.

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[*] For charged systems, see Sanfeld (1968). For anisotropic systems, see Steinchen (1970).

B. Examples

1. *One-component systems, $c = 1$ and $r' = 0$*

For a one-component system, a phase diagram is usually a plot of pressure against temperature.

a. Water Phase Diagram. The behavior of water is shown in a limited region in Fig. 1. The lines represent the equilibrium between the phases, and thus establish the fixed relationship between pressure and temperature. We consider three cases:

(*i*) The system consists of only one phase (vapor, liquid, or solid): $\phi = 1$ and $w = 2$. The system is divariant and the areas between the lines representing the equilibrium between the phases correspond to regions in which only a single phase exists and in which T and p may be varied independently.

(*ii*) The system consists of two phases (liquid and vapor, liquid and solid, or solid and vapor): $\phi = 2$ and $w = 1$. The system is monovariant. If the pressure is fixed, then the equilibrium temperature of the coexisting two phases will be a function of the chosen pressure. Equilibrium between any two phases can exist only if the value of T for a particular p falls on the line dividing the areas (see Fig. 1), e.g., liquid and gas. At each line grouping the representative points of two-phase systems, the affinity of passage of the substance from one phase to the other is zero.

(*iii*) The system consists of three phases (vapor, liquid, and solid): $\phi = 3$ and $w = 0$. We cannot fix either T or p arbitrarily and the three phases coexist only at the point of intersection of the three equilibrium
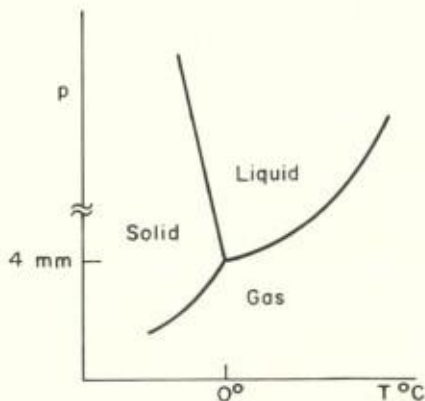

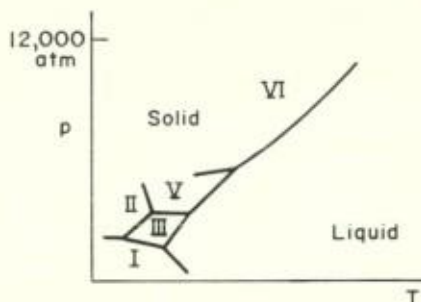FIG. 1.   Phase diagram for water in the vicinity of the triple point.

FIG. 2.   Phase diagram for water at high pressure.

lines. This triple point is invariant. For water, the coexistence of the three phases occurs at a temperature of $+7.6 \cdot 10^{-3}$ °C and a pressure of 4.6 mm of mercury.

At high pressures, a number of different crystalline forms (different phases) of ice have been observed. The phase diagram (see Fig. 2) is not complete because only limited information is available. Four triple points corresponding to the coexistence of the three forms of ice (ice II, III, and IV) are shown.

More than three independent phases cannot coexist in equilibrium in a one-component system.

b. *Sulfur Phase Diagram.* The four phases, clinorhombic, orthorhombic, liquid, and vapor, cannot all be in simultaneous equilibrium (Fig. 3). Any two of these are separated by a line along which they can coexist, while there are three triple points corresponding to the different forms of sulfur. Along the line *AC*, there is equilibrium between orthorombic (OR) and clinorhombic (CR); along *DA*, between orthorhombic and vapor (V); along *AB*, between clinorhombic and vapor; along *BE*, between vapor and liquid (L), etc.

The systems composed of three phases are invariant and their states are represented by isolated points or triple points (*A*, *B*, and *C*). At the equilibrium, it is impossible to find systems composed of four phases because the variance would then be less than zero.

2. *Binary Systems*

The phase diagrams, particularly for binary or ternary systems, are of great practical importance in metallurgy and physical chemistry, and much work has been done on their classifications.
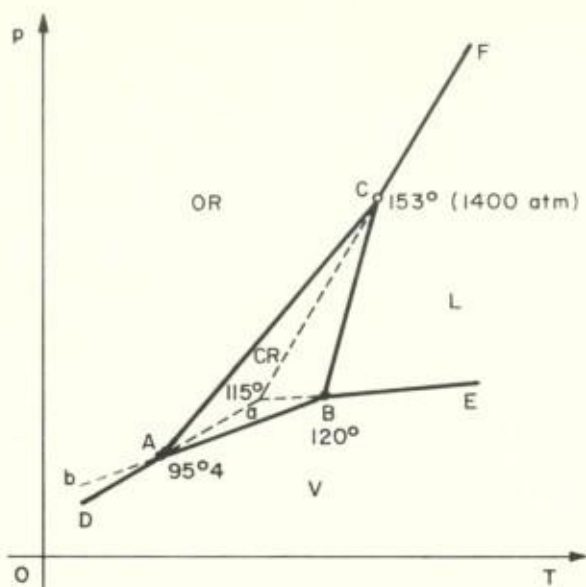
FIG. 3. Phase diagram of sulfur.

Here we have several cases:

(*i*) $\phi = 1$, $w = 3$. For example, two components in a vapor state without chemical reaction. The temperature, the pressure, and the composition can be fixed arbitrarily.

(*ii*) $\phi = 2$, $w = 2$. A mixture of alcohol and water in the presence of their vapor (without air). Two variables (the pressure and the temperature, or the pressure and the composition in one phase, or the temperature and the composition in one phase) can be fixed arbitrarily.

a. Equilibrium between Vapor and Liquid. (1) We consider first the case where the temperature has been taken as constant. The total pressure will be determined by the composition of either phase. Thus, we may represent the composition of either phase by the abscissa in a rectangular system of coordinates, and the pressures at constant temperature as ordinate (see Fig. 4).

The vaporization curve $p(N_2')$ gives the equilibrium pressure, i.e., the vapor pressure of the solution at the considered temperature T and for a given composition of solution, N_2'. For the same pressure (for example, p_D), the vapor phase (C'') is in equilibrium with the solution (C'). Nevertheless, the composition of the vapor phase N_2'' is generally
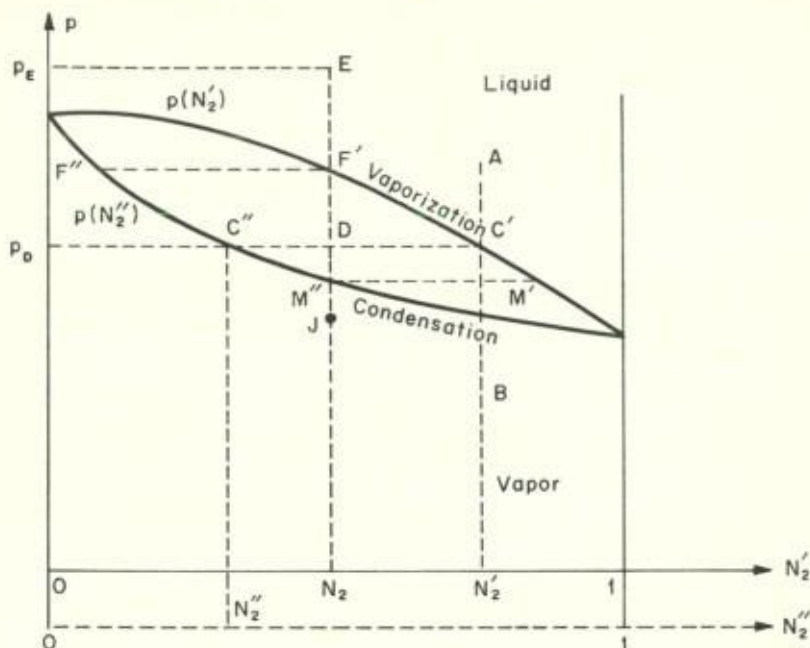
FIG. 4. Vapor–liquid phase diagram at constant temperature.

different from that of the liquid phase. The curve $p(N_2'')$ is called *condensation curve*.

The point A situated above curve $p(N_2')$ only represents a liquid phase, although the point B situated behind curve $p(N_2'')$ only represents a vapor phase.

Excluding all the false equilibria, the point D within the area enclosed by two curves represents a two-phase system consisting of the liquid C' and the vapor C'' in such proportions that the overall composition of the whole system is N_2. If n is the total number of moles in the system, it is easy to see that

$$\frac{n''}{n} = \frac{N_2' - N_2}{N_2 - N_2''} = \frac{DC'}{C''D}. \tag{5.9}$$

Thus, when D approaches the condensation curve, more and more of the system will be vaporized, and when D is close to the vaporization curve, the system will nearly all be in the liquid phase.

Fractional distillation. Let us assume that initially we have a solution in the state E. The decrease of pressure from p_E to p_D yields a partial

vaporization and results in the formation of two phases C' and C''. The proportion of these two phases is given by (5.9).

The mechanism is very simple: (1) From E to F' no vaporization. (2) At F', the vaporization begins. The state of the vapor phase produced is represented by F'' ($N_1^{F''} > N_1^{F'}$). (3) In the liquid phase, the fraction of the component 1 decreases, and thus F' goes down to C' along the vaporization curve, while the state of the vapor phase sinks along the condensation curve from F'' to C''.

If the pressure decreases from p_D to $p_{M''}$, all the liquid phase becomes a vapor phase, and, below this pressure, only the vapor phase subsists with the same composition as the initial E liquid phase (point J).

Now, let us assume that we stop the vaporization or the condensation when the composition of the two obtained phases is different. This phase is then submitted to a new partial vaporization or condensation, and so on. This process is called fractional distillation.

From the experimental point of view, a one-step separation can occur on a plate of a fractionation column (Keeson, 1939; Bosnjakovic, 1935; Brown *et al.*, 1955; Ponchon, 1921; Savarit, 1922; Daniels and Alberty, 1961); the number of plates (separation steps) required to give the desired fractionation depends on the shape of the phase diagram. The effectiveness of a given fractionation column is indicated by the number of *theoretical plates* corresponding to the number of separation steps which it performs.

(2) We now consider the case where the pressure has been taken as constant. The independent variables are p and N_2'. The curve $T(N_2')$, boiling point as a function of liquid composition N_2', is called the *boiling curve* (Fig. 5).

A horizontal line cuts the boiling and condensation curves at P' and P''. These points, corresponding to the same temperature, give the composition of the liquid, N_2', and the vapor, N_2'', which are in equilibrium with one another at the temperature T. If we neglect the effect of surface tension, a bubble containing vapor and the solution represents two phases at the same pressure.

Azeotropic mixtures. Maximum- or minimum-boiling mixtures are called *azeotropes* (Fig. 6). An argument based on the Gibbs–Konovalow theorem shows that the composition of the two phases must be identical at the point of maximum or minimum.

In an azeotropic system, one phase may be transformed to the other at *constant temperature, pressure* and *composition* without affecting the
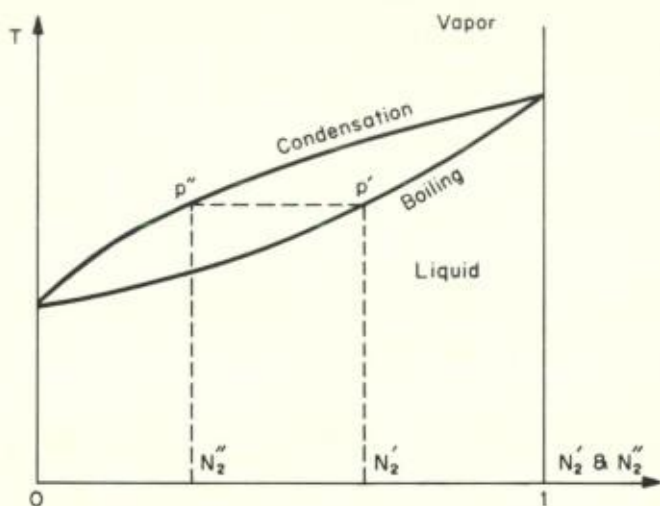
FIG. 5.   Vapor–liquid phase diagram at constant pressure.

equilibrium state (Fig. 6) (see, for example, Wade and Merriman (1911)).

The azeotrope behaves in some respects like a pure substance, since it distils at constant temperature and pressure without change in composition. If, however, the pressure at which the distillation is carried out is altered, the composition is also altered (see Fig. 7), and hence the substance corresponds to a mixture, and not a pure one. Azeotropic mixtures are not uncommon.

Water and hydrogen chloride form an azeotropic mixture with a maximum boiling point of $108.6°C$ at 1760 mm Hg pressure, when the
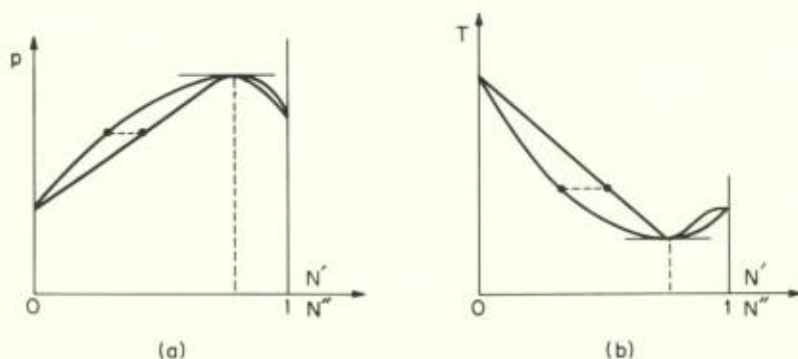
FIG. 6.   Vapor–liquid equilibrium in a binary system forming an azeotrope.
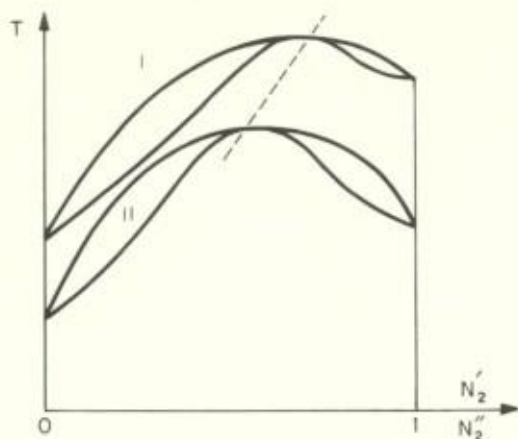
FIG. 7.   Variation of the azeotropic maximum with pressure.

weight per cent of HCl is 20.222. Ethylalcohol and water form an azeo-trope with a minimum boiling point of 78.15°C (95.57% ethanol). For azeotropic data on a large number of systems, see Horsley (1952) and MacDougall (1926, p. 181).

Remark. At each minimum in the isobaric curves, there corresponds a maximum in the isothermal curves, and conversely.

b. Equilibrium between Solution and Crystal. (1) *Melting-point curves. Solid solution.* The phase diagram is similar in many respects to that for

FIG. 8.   Solid–liquid equilibrium (p = const) where solid solutions are formed.

the vapor pressure of binary liquids. Examples are the systems $Ni + Cu$ (Fig. 8) and $HgBr_2 + HgI_2$ (Fig. 9). The liquidus gives the composition of the liquid phase, and the solidus gives the composition of the solid solution in equilibrium with the liquid solution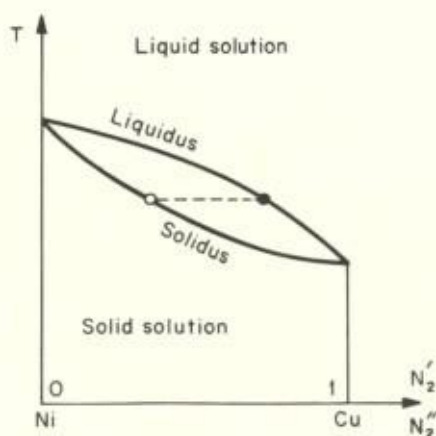. An extremum in the phase diagram might be expected if the two components form an intermediate compound. However, the extremum itself is not a proof of the existence of such a compound.
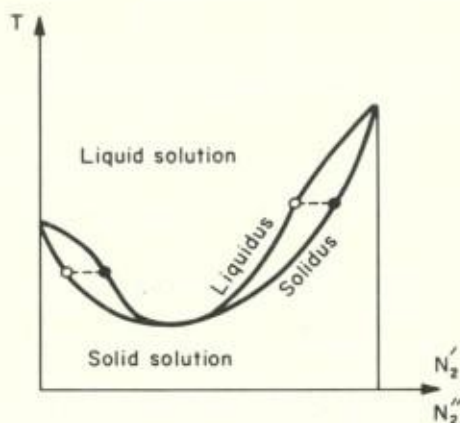
FIG. 9.   Azeotropic liquid–solid phase diagram.

If the composition at which the maximum occurs is independent of the pressure, then it is probably associated with a compound. The pressure test is useful in the study of vapor–liquid mixtures.

For the solid-state problem, an X-ray examination of the crystal structure provides more reliable evidence.

(2) *Melting-point curves. Eutectics.* The two phases give a divariant system where p and N_2' are arbitrary. The phase diagram is given in Fig. 10. Here, A and B are the melting points of pure components 1 and 2, AE is the equilibrium curve for the solution (composition N_2') and the crystals of pure component 1, and BE is the equilibrium curve for the solution (composition N_2') and the crystals of pure component 2. The point of intersection of these two curves is called the eutectic point. At this point, the system has the eutectic composition at the eutectic temperature and the solution is in equilibrium with pure crystals of 1 and 2. The system is thus univariant, and the coexistence of the three phases is governed by the arbitrary choice of the pressure.
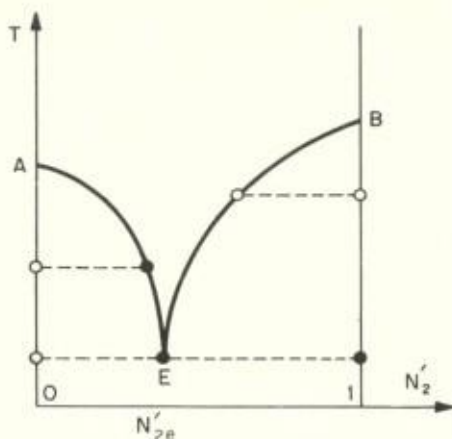
FIG. 10.   Freezing-point curves of a binary system forming a eutectic (p = const).

In the presence of air, the variance is not altered, because air can be regarded as a single component, since its composition remains constant throughout (aside from the vapors derived from the solution).

(3) *False binary systems.* If the two components A and B of a binary system react together to form an addition component C so that $A + B = C$, the variance is not affected, because $c = 3$, $r' = 1$, $c - r' = 2$. Figure 11 shows the appearance of the phase diagram when the two pure substances form an addition compound.
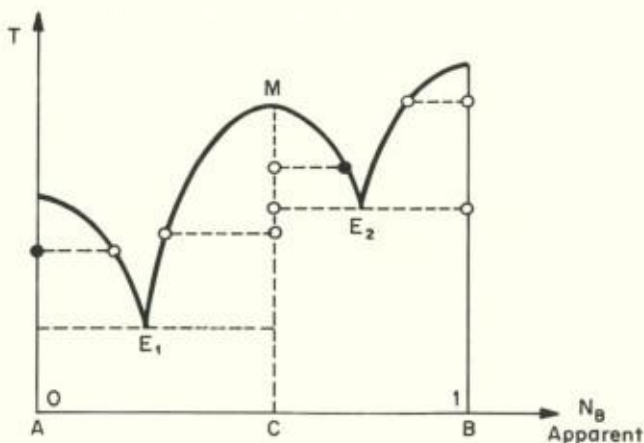
FIG. 11.   Eutectic phase diagram for binary systems forming an addition compound.

As abscissa, we plot the apparent molar fraction of component B, i.e., the molar fraction given by the experimentator which ignores the existence of the addition compound.

In the absence of solid solutions, we obtain two eutectics E_1 and E_2. At E_1, there is an equilibrium: solution + crystal A + crystal C; at E_2, there is an equilibrium: solution + crystal C + crystal B.

The maximum M represents the melting point of a well-defined compound, the crystal C. At this maximum, the apparent composition remains constant when the pressure is changing.

One speaks of a congruent melting point (Prigogine and Defay, 1967, p. 377) when the solid compound melts to form a liquid phase which has the same composition as the solid. In the $NaF-MgF_2$ system (Eggers *et al.*, 1964, p. 263–265), the intermediate compound has the formula $NaMgF_3$. Two eutectics are observed, $NaF-NaMgF_3$ and $NaMgF_3-MgF_2$.

An eutectic may disappear, and is then replaced by a *transition point* r where there are three phases in equilibrium (Fig. 12).

One speaks of an incongruent melting point for the intermediate compound if, when melting occurs, the liquid has a composition different from that of the compound and a new solid phase is also formed.

According to Counts *et al.* (1953), (see also Eggers *et al.* (1964)), the compound CaF_2-BeF_2 is unstable above 890°C. During the transition in the melting process, we have three different phases in equilibrium, and the system is at an invariant point called *peritectic* one.
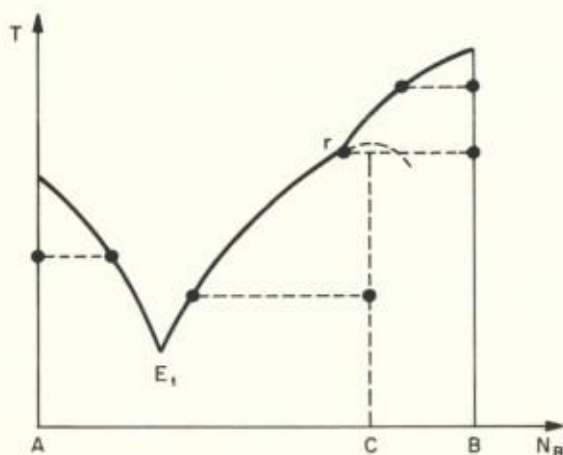

FIG. 12.   Eutectic phase diagram with a transition point.

3. *Ternary Systems*

On account of the great complexity of the phenomena observable in the case of three-component systems, we shall have to be content with a brief discussion of some of the simpler cases (Vogel, 1937). The composition of a ternary mixture is best represented by a point in an equilateral triangle whose vertices 1, 2, and 3 represent the three pure components. If the side of the triangle is taken as unity, then the mole fractions N_1, N_2, and N_3 in the solution under consideration are given by the distances, measured along lines parallel to the sides of the triangle, of the point P from the sides of the triangle remote from vertices 1, 2, and 3, respectively (Figs. 13 and 14). This representation ensures auto-
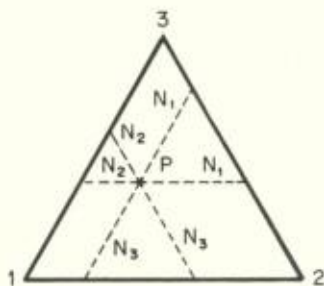
FIG. 13. Ternary phase diagram.
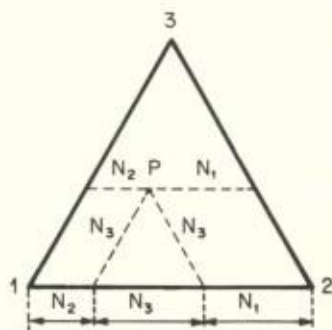
FIG. 14. Ternary phase diagram.

matically that $N_1 + N_2 + N_3 = 1$. The sides of the triangle represent the binary systems $(1 + 2)$, $(2 + 3)$, $(3 + 1)$, and the vertices represent pure components. Now let us consider systems without chemical reactions. Different cases are possible: $\phi = 1$, $w = 4$ (case A); $\phi = 2$, $w = 3$ (case B); $\phi = 3$, $w = 2$ (case C); $\phi = 4$, $w = 1$ (case D); $\phi = 5$, $w = 0$ (case E).

Example 1. *Case A.* A gas mixture with three components. The variables p, T, N_2, N_3 are given arbitrarily.

Example 2. *Case B.* Solidification of a ternary solution without solid solution. With two phases, the system is trivariant; we can, for example, consider the pressure and composition of the solution N_2', N_3' and see how the equilibrium temperature changes with these variables. If the pressure is taken as constant, then we may construct a diagram in which the equilibrium temperature between liquid and one of the solid phases

is shown as a function of N_2' and N_3'. We obtain a surface in three-dimensional space.

Example 3. Case E. Ternary eutectic in the presence of vapor of the solution without air. An example of a classical ternary system with binary and ternary eutectics is the alloy system Bi + Pb + Sn [for details see Prigogine and Defay (1962), p. 185, MacDougall (1926)].

Remarks. (1) The diagrams become very complicated if the various components can form solid solutions in one another (Findlay, 1951).

(2) If the three components are linked by a chemical reaction, the variance is reduced by one and the behavior is simplified. Example: $CaCO_3$ (solid) $\rightleftharpoons$ CaO (solid) $+ CO_2$ (gas). The system here is monovariant, and, at equilibrium, its state is completely specified when the temperature is fixed.

(3) To cover a complete specification of the state of a system in terms of both *intensive* and *extensive* variables, we must calculate how many variables must be fixed to *determine completely* the equilibrium state of a closed system. This problem, related to the *conditions of enclosure* (Prigogine and Defay, 1967, p. 186), is treated exhaustively in the work of Duhem (1899, vol. IV).

VI. The Equilibrium Constant

A. INTRODUCTION

In Sections II and IV, we discussed the conditions of thermodynamic equilibrium in a system subject to various constraints, and found that the conditions could be expressed by saying that chemical affinity is zero when equilibrium prevails. Now, the chemical affinity is determined by the temperature, pressure, and composition of the system, so that, if this function is a known function of the variables just mentioned, then the thermodynamic behavior of the system can be readily predicted. Because the affinity and the chemical potentials are connected by Eq. (4.21), in order to obtain specific numerical answers for the equilibrium composition in a particular system, we must know the explicit form of the equation of state

$$\mu = \mu(T, p, N_1{}^1, \ldots, N_c{}^s).$$

In this section, it will be part of our work to show somewhat more explicitly how the state of equilibrium depends on the quantities of the various substances present, first, when all the substances are ideal gases, and second, when the system is a dilute solution.

From a practical point of view, if substances which can react with one another are brought together, it will be found that, in general, when all change *seems* to have ceased, the original substances are still present, although their concentrations may be extremely small.

We commonly say that the original and final substances are in chemical equilibrium.

Experimenters are especially interested in determining the extent to which a given chemical reaction will take place and in finding out how the final state of equilibrium depends, not only on the temperature and the pressure, but on the concentrations of the reacting substances.

B. The Single-Component Perfect Gas

The perfect gas is a fictitious substance, defined by certain properties which are not possessed by any actual substance, but which are supposed to be approached by every actual gas as its pressure is indefinitely diminished. We may state, then, that the perfect gas is a substance which fulfills the two following conditions:

(1) Its internal energy is a function of temperature alone (Joule's law), or, in other words,

$$\partial U(T)/\partial V = 0. \tag{6.1}$$

(2) At constant temperature, the volume V occupied by a given number of moles of gas varies in inverse proportion to the pressure (Boyle's law)

$$pV = nf(T), \tag{6.2}$$

where $f(T)$ is a function independent of the nature of the gas.

The combination of these two laws gives the well-known equation of state

$$pV = nRT, \tag{6.3}$$

where R is the gas constant ($R = 0.08205$ l atm deg^{-1} mol^{-1} or 1.987 cal mol^{-1} deg^{-1}).

Now let us assume that no chemical reaction can occur in the gas. Any transformation of a system remaining uniform is reversible, and, thus, from (1.13), (6.3), and (2.18), we have, per mole,

$$ds = c_v(T)\, d(\ln T) + R\, d(\ln v), \tag{6.4}$$

where c_v is the partial molar heat capacity at constant volume. Integration of (6.4) from the initial state $s^i(T^i, v^i)$ to the final state $s(T, v)$ gives (for an application, see Chapter 8, Section VIII)

$$s = s^*(T) - RT \ln p, \tag{6.5}$$

where

$$s^*(T) = s^i(T^i, v^i) + \int_{T^i}^{T} \frac{c_v(T)}{T}\, dT - R \ln v^i + R \ln RT. \tag{6.6}$$

Combining (6.5), (6.3), and (4.38), we obtain

$$\mu = \mu^*(T) + RT \ln p. \tag{6.7}$$

For the free energy F of a perfect gas, Eq. (1.18), (6.5), and (6.1) give

$$F = n[f^*(T) + RT \ln(n/V)], \tag{6.8}$$

where

$$f^*(T) = e(T) - Ts^*(T) + RT \ln RT. \tag{6.9}$$

C. The Multicomponent Perfect Gas

We first suppose that we have several *separate* single-component perfect gases. If they are mixed together and if the free energy of the mixture is equal to the sum of the free energies that each of the gases would have if it alone were to occupy the same volume at the same temperature, then they make a multicomponent perfect gas.

Applying Eq. (6.8), we obtain

$$F = \sum_\gamma F_\gamma(T, V, n_\gamma) = \sum_\gamma n_\gamma[f_\gamma^*(T) + RT \ln(n_\gamma/V)]. \tag{6.10}$$

To find the equation of state, we must use (3.8) and (6.10):

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T, n_1, \ldots, n_c} = \sum_\gamma n_\gamma \frac{RT}{V}, \tag{6.11}$$

and thus

$$pV = nRT, \tag{6.12}$$

where $n = \sum_\gamma n_\gamma$. The equation of state is thus formally identical to the corresponding equation of state of a single-component perfect gas.

From (6.10), (3.8), and (3.10), it is then easy to show that

$$S = \sum_\gamma S_\gamma(T, V, n_\gamma), \tag{6.13}$$

$$U = \sum_\gamma U_\gamma. \tag{6.14}$$

Let us *define* the partial pressure p_γ of the component γ by

$$p_\gamma = pN_\gamma. \tag{6.15}$$

This definition is true whether the gases in the mixture are perfect or not. It follows then from (6.15) and (6.11) that

$$p = \sum_\gamma p_\gamma, \qquad p_\gamma = n_\gamma RT/V = C_\gamma RT \qquad \text{(Dalton's law).} \tag{6.16}$$

The partial pressure of γ is thus equal to the pressure which would be exerted by n_γ moles of pure γ in the same volume, and at the same temperature. It is a purely mathematical construct with no direct physical meaning.

The chemical potential of the γ component in the mixture is most conveniently computed by recalling that [see Eq. (4.16)]

$$\mu_\gamma = (\partial F/\partial n_\gamma)_{TVn_\beta}. \tag{6.17}$$

Evaluating this derivative from Eqs. (6.10) and (6.17) gives

$$\boxed{\mu_\gamma = \mu_\gamma^*(T) + RT \ln p_\gamma,} \tag{6.18}$$

where

$$\mu_\gamma^*(T) = f_\gamma^*(T) + RT + RT \ln RT. \tag{6.19}$$

The chemical potential of a single component γ in a mixture of perfect gases is equal to the chemical potential that component would have alone if it were at the same temperature and the reduced pressure p_γ.

We now evaluate the chemical affinity by applying (4.21) and (6.18). This gives

$$A = RT \ln[K_p(T)/p_1^{\nu_1}, \ldots, p_c^{\nu_c}], \tag{6.20}$$

where the function $K_p(T)$ is *defined* by

$$K_p(T) = \exp\left\{-\left[\sum_\nu \nu_\gamma \mu_\gamma^*(T)\right]\Big/RT\right\}. \tag{6.21}$$

At the equilibrium, $A = 0$ and (6.20) reduces to the well known law of Guldberg–Waage

$$K_p(T) = p_1^{\nu_1}, \ldots, p_c^{\nu_c}. \tag{6.22}$$

The quantity $K_p(T)$, called the equilibrium constant, is characteristic of the reaction under consideration and is a function only of the temperature.

The partial pressures used in (6.22) are equilibrium quantities.

If reactants and products (assumed to be perfect) are mixed under nonequilibrium conditions, a spontaneous change is expected until the partial pressure quotient reaches the equilibrium value. In certain circumstances, it is more convenient to express the equilibrium constant as a molar fraction or a concentration quotient.

Replacing in (6.18) p_γ respectively by pN_γ and $C_\gamma RT$ as in Eqs. (6.15) and (6.16), we get

$$\mu_\gamma = \mu_\gamma^\circ(T, p) + RT \ln N_\gamma \tag{6.23}$$

and

$$\mu_\gamma = \mu_\gamma^{\circ\circ}(T) + RT \ln C_\gamma, \tag{6.24}$$

where

$$\mu_\gamma^\circ(T, p) = \mu_\gamma^*(T) + RT \ln p \tag{6.25}$$

and

$$\mu_\gamma^{\circ\circ}(T) = \mu_\gamma^*(T) + RT \ln RT. \tag{6.26}$$

A similar treatment as above may be developed by using (4.21) and (6.23) or (6.24). We then obtain

$$\boxed{A = RT \ln[K_N(T, p)/N_1^{\nu_1}, \ldots, N_c^{\nu_c}]} \tag{6.27}$$

$$\boxed{A = RT \ln[K_c(T)/C_1^{\nu_1}, \ldots, C_c^{\nu_c}],} \tag{6.28}$$

where the functions K_N and K_e are *defined* by

$$K_N = \exp\left\{-\left[\sum_\gamma v_\gamma \mu_\gamma{}^\circ(T, p)\right]\Big/RT\right\} \tag{6.29}$$

$$K_e = \exp\left\{-\left[\sum_\gamma v_\gamma \mu_\gamma{}^{\circ\circ}(T)\right]\Big/RT\right\}. \tag{6.30}$$

At the equilibrium, (6.27) and (6.28) then reduce to

$$K_N(T, p) = N_1^{v_1}, \ldots, N_e^{v_e} \tag{6.31}$$

$$K_e(T) = C_1^{v_1}, \ldots, C_e^{v_e}. \tag{6.32}$$

The equilibrium constants may be used to evaluate the chemical affinity, or, alternatively, the latter may be used to evaluate the equilibrium constants. From (6.25), (6.26), (6.29), and (6.30), it is easy to show that the three equilibrium constants are related by the formulas

$$K_N(T, p) = p^{-v}K_p(T) \tag{6.33}$$

$$K_e(T) = (RT)^{-v}K_p(T), \tag{6.34}$$

where v is the algebraic sum of the stoichiometric coefficients for the reaction and is given by

$$v = \sum_\gamma v_\gamma. \tag{6.35}$$

For the reaction considered as a multicomponent ideal gas

$$4HCl(g) + O_2(g) = 2H_2O(g) + 2Cl_2(g),$$
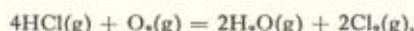
we have

$$K_p(T) = p_{H_2O}^2 p_{Cl_2}^2 / p_{HCl}^4 p_{O_2}$$

$$K_N(T, p) = N_{H_2O}^2 N_{Cl_2}^2 / N_{HCl}^4 N_{O_2}$$

$$K_e(T, p) = C_{H_2O}^2 N_{Cl_2}^2 / C_{HCl}^4 C_{O_2}$$

and the three constants are related by

$$K_N(T, p) = pK_p(T) = CK_e(T, p)$$

where $C = \sum_\gamma C_\gamma$; thus, $K_N(T, p)$ is here proportional to pressure.

D. Dependence of the Equilibrium Constant on Temperature and Pressure

1. *The Clausius–Kirchhoff Equations*

Let us first show how the thermal coefficients are interrelated. Thus, we will be able to find the dependence of the equilibrium constant on temperature and on pressure.

The internal energy U being a function of T, V, and ξ, we have the identities

$$\frac{\partial^2 U}{\partial V\,\partial T} = \frac{\partial^2 U}{\partial T\,\partial V}, \quad \frac{\partial^2 U}{\partial V\,\partial \xi} = \frac{\partial^2 U}{\partial \xi\,\partial V}, \quad \frac{\partial^2 U}{\partial T\,\partial \xi} = \frac{\partial^2 U}{\partial \xi\,\partial T}. \qquad (6.36)$$

Thus from (2.17)–(2.20), we obtain

$$\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial \xi}\right)_{TV} = -\left(\frac{\partial r_{TV}}{\partial T}\right)_{V\xi} = \left(\frac{\partial C_{V\xi}}{\partial \xi}\right)_{TV} \qquad \text{(Kirchhoff–Clausius)}$$
$$(6.37)$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial \xi}\right)_{TV} = -\left(\frac{\partial r_{TV}}{\partial V}\right)_{T\xi} = \left[\frac{\partial(l_{T\xi} - p)}{\partial \xi}\right]_{TV} \quad \text{(De Donder)}$$

$$\left.\begin{array}{c} \\ \\ \end{array}\right\} \quad (6.38)$$

$$\left(\frac{\partial C_{V\xi}}{\partial V}\right)_{T\xi} = \left[\frac{\partial(l_{T\xi} - p)}{\partial T}\right]_{V\xi} \qquad \text{(Clausius).}$$

We may proceed in an analogous manner in the variables T, p, and ξ. From (1.15) and (2.4)–(2.6), we may write

$$C_{p\xi} = (\partial H/\partial T)_{p\xi} \qquad (6.39)$$

$$V + h_{T\xi} = (\partial H/\partial p)_{T\xi} \qquad (6.40)$$

$$r_{Tp} = -(\partial H/\partial \xi)_{Tp}. \qquad (6.41)$$

The enthalpy H being a function of T, p, and ξ, we then have from (2.7)

$$\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial \xi}\right)_{Tp} = -\left(\frac{\partial r_{Tp}}{\partial T}\right)_{p\xi} = \left(\frac{\partial C_{p\xi}}{\partial \xi}\right)_{Tp} \qquad \text{(Kirchhoff–Clausius)}$$
$$(6.42)$$

$$\left(\frac{\partial C_{p\xi}}{\partial p}\right)_{T\xi} = \left[\frac{\partial(h_{T\xi} + V)}{\partial T}\right]_{p\xi} \qquad \text{(Clausius)} \qquad (6.43)$$

$$\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial \xi}\right)_{Tp} = -\left(\frac{\partial r_{Tp}}{\partial p}\right)_{T\xi} = \left[\frac{\partial(h_{T\xi} + V)}{\partial \xi}\right]_{T} \qquad \text{(Clausius).} \qquad (6.44)$$

Now, since $C_{p\xi}$ is a function of state of the system, we have

$$\left(\frac{\partial C_{p\xi}}{\partial \xi}\right)_{Tp} = \sum_{\gamma}\left(\frac{\partial C_{p\xi}}{\partial n_{\gamma}}\right)_{Tpn_{\beta}}\frac{dn_{\gamma}}{d\xi} = \sum_{\gamma}\nu_{\gamma}c_{p\gamma}, \tag{6.45}$$

where $c_{p\gamma}$ is the partial molar heat capacity of γ at constant pressure, defined by

$$c_{p\gamma} = (\partial C_{p\xi}/\partial n_{\gamma})_{Tpn_{\beta}}. \tag{6.46}$$

Combining (6.45) and (6.42), we obtain

$$\boxed{(\partial r_{Tp}/\partial T)_{p\xi} = -\sum_{\gamma}\nu_{\gamma}c_{p\gamma} \qquad \text{(Kirchhoff).}} \tag{6.47}$$

This equation is of importance since it enables us to calculate the heat of a reaction at any temperature provided that it is known at one temperature, and that we know the partial molar heat capacities of the components taking part in the reaction (see the example in Section VIII).

The Clausius–Kirchhoff equations are quite general because they do not suppose any particular state of matter (perfect or nonperfect gas, ideal liquid or nonideal liquid, solid).

2. Influence of Temperature on Equilibrium Constants

The influence of temperature on the equilibrium constant is now easy to establish. Indeed, the entropy being a function of state, we have

$$\partial^2 S/\partial T\,\partial\xi \equiv \partial^2 S/\partial\xi\,\partial T, \tag{6.48}$$

and then, from the first of Eqs. (2.12), combined with (2.13) and (6.41), we can write

$$\boxed{\frac{\partial(A/T)}{\partial T} = -\frac{r_{Tp}}{T^2}.} \tag{6.49}$$

Thus, combining (6.49) and (6.27), we find the well-known equation of van't Hoff

$$\boxed{\left(\frac{\partial[\ln K_N(T,p)]}{\partial T}\right)_p = -\frac{r_{Tp}}{RT^2}.} \tag{6.50}$$

From (6.50) and (6.33), we also obtain

$$\frac{d[\ln K_p(T)]}{dT} = -\frac{r_{Tp}}{RT^2},$$

(6.51)

or, in another form,

$$\frac{d[R \ln K_p(T)]}{d(1/T)} = r_{Tp}.$$

(6.52)

If the reaction is accompanied by an absorption of heat $(r_{Tp} < 0)$, the equilibrium constant increases with temperature, while, for an exothermic reaction $(r_{Tp} > 0)$, it decreases.

Example. For the dissociation of water vapor, $2H_2O = 2H_2 + O_2$, the reaction is endothermic and thus is favored by a high temperature.

These equations enable us to calculate the rate at which the equilibrium constant is changing with the temperature when r_{Tp} is known; and if we know r_{Tp} as a function of the temperature, then (6.51), may be integrated. Thus, from the equilibrium constant at any temperature, we may calculate its value at any other temperature.

By integration of (6.51) between T^i (initial) and T, we get

$$\ln K_p(T) - \ln K_p(T^i) = -\int_{T^i}^{T} (r_{Tp}/RT^2) \, dT.$$

(6.53)

From (6.47), it is then possible to know the explicit form of $r_{Tp}(T)$ and then to calculate the integral (6.53). A detailed example is given in Section VIII.

Remarks. (1) The same equations as above may be written in the variables T, V, and ξ. To derive the relationship between the thermal coefficients $C_{V\xi}$, $l_{T\xi}$, and r_{TV} with T, V, and ξ as variables, it is most convenient to consider first the total differential dU in the variables T, V, and ξ [see Eq. (2.16)] and then to replace dV by the value given in terms of T, p, and ξ [see Eq. (2.3)].

Employing Eqs. (2.2), (2.4)–(2.6), and (2.18)–(2.20), we can write the required general relations between the thermal coefficients in the two sets of variables T, V, ξ and T, p, ξ (see Chapter 1, Section XVIII):

$$C_{p\xi} = C_{V\xi} + l_{T\xi}(\partial V/\partial T)_{p\xi}$$

(6.54)

$$h_{T\xi} = l_{T\xi}(\partial V/\partial p)_{T\xi}$$

(6.55)

$$r_{Tp} = r_{TV} - l_{T\xi}(\partial V/\partial \xi)_{Tp}.$$

(6.56)

For a perfect gas, (2.19) and (6.55) reduce, respectively, to

$$l_{T\xi} = p \qquad \text{(perfect gas)} \qquad (6.57)$$

$$h_{T\xi} = p(\partial V/\partial p)_{T\xi} = -V \qquad \text{(perfect gas).} \qquad (6.58)$$

Furthermore,

$$(\partial V/\partial T)_{p\xi} = nR/p \qquad \text{(perfect gas)} \qquad (6.59)$$

$$(\partial V/\partial \xi)_{Tp} = \nu RT/p \qquad \text{(perfect gas).} \qquad (6.60)$$

Equations (6.54) and (6.56) thus become

$$C_{p\xi} - C_{V\xi} = nR \qquad \text{(Mayer's formula)} \qquad (6.61)$$

$$r_{Tp} - r_{TV} = -\nu RT. \qquad (6.62)$$

It is then easy to show that Eqs. (6.49) and (6.51) may be written in the form

$$\left(\frac{\partial (A/T)}{\partial T} \right)_{V\xi} = -\frac{r_{TV}}{RT^2} \qquad (6.63)$$

$$\frac{d[\ln K_c(T)]}{dT} = -\frac{r_{TV}}{RT^2}. \qquad (6.64)$$

(2) From the experimental point of view, if r_{Tp} is independent of T, then (6.53) may be written

$$\ln K_p(T) = (r_{Tp}/RT) + \text{const.} \qquad (6.65)$$

An example of a reaction for which $\ln K_p$ is a linear function of $1/T$ over a wide temperature range is given in Section VIII.

(3) Influence of pressure on the equilibrium constants. Let us write the last of Eqs. (3.12) as

$$(\partial A/\partial p)_{T\xi} = -(\partial V/\partial \xi)_{Tp} = -\Delta_{Tp}, \qquad (6.66)$$

where Δ_{Tp} is the change in the volume of the system produced by the chemical reactions at constant T and p,

$$\Delta_{Tp} = \sum_{\gamma} \nu_\gamma v_\gamma. \qquad (6.67)$$

The variation of the affinity of reaction with the pressure is seen to be appreciable only if the reaction is accompanied by a considerable change

in volume when it takes place at constant temperature and pressure. If a reaction is accompanied by an increase in volume when the pressure is kept constant, an increase in pressure will reduce the affinity of the reaction.

Example. For the gas reaction $2H_2 + O_2 = 2H_2O$, $\Delta_{Tp} < 0$ and the affinity of the reaction increases with pressure. From the experimental point of view, according to this, it could be interesting to work at high pressure.

Combining (6.67) and (6.27), we obtain

$$\partial[\ln K_N(T, p)]/\partial p = -\Delta_{Tp}/RT. \tag{6.68}$$

An increase in pressure increases the equilibrium constant if the reaction is accompanied by a decrease in volume ($\Delta_{Tp} < 0$); and, conversely, if $\Delta_{Tp} > 0$, the equilibrium constant is decreased (Le Chatelier's principle). For a perfect gas mixture, (6.67) and (6.16) give

$$\Delta_{Tp} = vRT/p, \tag{6.69}$$

so that (6.68) reduces to the formula

$$p\{\partial[\ln K_N(T, p)]/\partial p\} = -v. \tag{6.70}$$

E. Ideal Systems

In order to discuss the behavior of ideal systems, we need to express the chemical potentials of the components in a form in which the molar fractions or the partial pressures appear explicitly.

One-Phase System

An ideal system may be defined by the equation

$$\mu_\gamma = \zeta(T, p) + RT \ln N_\gamma. \tag{6.71}$$

Mixtures of perfect gases and very dilute solutions are referred to as ideal systems. If the solution is ideal for all values of N_γ and for all γ, it is then called a perfect solution.

Pure components are always ideal systems because

$$\mu_\gamma = \mu_\gamma(T, p). \tag{6.72}$$

Now, combining (4.21) and (6.71), we obtain

$$A = RT \ln[K_N(T, p)/N_1^{r_1}, \ldots, N_c^{r_c}], \tag{6.73}$$

where $K_N(T, p)$ is defined by the equation

$$RT \ln K_N(T, p) = - \sum_\gamma \nu_\gamma \zeta_\gamma(T, p) \tag{6.74}$$

At the equilibrium,

$$A = 0 \quad \text{and} \quad K_N(T, p) = N_1^{r_1}, \ldots, N_c^{r_c} \quad \text{(Guldberg–Waage)}, \tag{6.75}$$

and we obtain again the van't Hoff expression (6.50) and Eq. (6.68) valid here for an ideal system,

$$\left\{ \frac{\partial[\ln K_N(T, p)]}{\partial T} \right\}_p = - \frac{r_{Tp}}{RT^2} \quad \text{(van't Hoff)} \tag{6.76}$$

$$\left\{ \frac{\partial[\ln K_N(T, p)]}{\partial p} \right\}_T = - \frac{\Delta_{Tp}}{RT}. \tag{6.77}$$

F. MULTIPHASE SYSTEMS

When each of the phases is ideal, we have following the definition [see (6.71)]

$$\mu_\gamma^\alpha = \zeta_\gamma^\alpha(T, p) + RT \ln N_\gamma^\alpha, \tag{6.78}$$

and the multiphase system is then called an ideal system.

Passage Reaction

If the reaction consists in a transfer of a component γ from one phase (') to another (''), we have, from (4.21), (6.78), and (6.73),

$$A_\gamma = \mu_\gamma' - \mu_\gamma'' = RT \ln K_{\gamma N}(T, p) - RT \ln(N_\gamma''/N_\gamma'); \tag{6.79}$$

when the equilibrium of transfer is attained, (6.79) reduces to the well-known Nernst distribution law

$$N_\gamma''/N_\gamma' = K_{\gamma N}(T, p). \tag{6.80}$$

It is physically obvious, and also an experimental fact, that, for trivariant systems (for example, three components and two phases), the composition of γ in one phase, N_γ'', at constant temperature and pressure

varies proportionally to the composition of γ in the other phase, N_γ', following (6.80). For a divariant system, both the temperature and pressure can be fixed arbitrarily. For example, we can study a pure liquid in the presence of a gaseous phase such as nitrogen. Neglecting the weak solubility of nitrogen in the liquid (subscript l), (6.80) becomes

$$N_l^V = K_{lN}(T, p),$$

where V designates the vapor phase. The composition of the vapor of the liquid in the vapor phase is thus only a function of T and p.

For a monovariant system—for example, a pure liquid in the presence of its own vapor—the Nernst law $K_{lN}(T, p) = 1$ shows that the pressure depends only upon the temperature. This result is consistent with the phase rule.

Example. Chemical reactions between two different phases. For the thermal dissociation of calcium carbonate in air,

$$CaCO_3(s) = CaO(s) + CO_2(g),$$
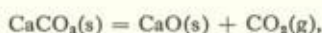
let us assume that each reacting component is present in one phase and that $CO_2(g)$ + air is a mixture of perfect gas. Then it is easy to see that

$$A = RT \ln[K_N(T, p)/N_{CO_2}]$$

For equilibrium, $N_{CO_2} = K_N(T, p)$, or $p_{CO_2} = pK_N(T, p)$, which shows that the equilibrium partial pressure of CO_2 depends both upon the total pressure p and the temperature.

In the absence of air ($N_{CO_2} = 1$), we find $K_N(T, p) = 1$, and the equilibrium pressure of carbon dioxide depends only upon the temperature.

Remark. If the condensed phases (liquids and solids) in a heterogeneous system are pure components and the gas is a mixture, it is more convenient, from a practical point of view, to express the equilibrium constant in terms of partial pressures.

Applying (4.21) and (6.18) to our system, we obtain

$$A = - \sum_i \nu_i \mu_i(T, p) - \sum_j \nu_j \mu_j^*(T) - RT \sum_j \nu_j \ln p_j, \qquad (6.81)$$

where the subscripts i and j refer, respectively, to the condensed pure constituents and to the gaseous components. We then may write
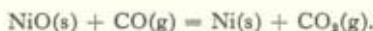
$$A = RT \ln(K_N/\prod_j p_j^{\nu_j}), \qquad (6.82)$$

where

$$RT \ln K_N = - \sum_i \nu_i \mu_i(T, p) - \sum_j \nu_j \mu_j^*(T). \tag{6.83}$$

As for condensed phases, the chemical potentials $\mu_i(T, p)$ are practically independent of pressure (Prigogine and Defay, 1967, p. 163); the constant K varies only with the temperature.

Example:

$$NiO(s) + CO(g) = Ni(s) + CO_2(g).$$

For equilibrium, (6.82) reduces to $K_N = p_{CO_2}/p_{CO}$ and K_N does not depend upon the total pressure.

VII. Standard Functions and Functions of Mixing

A. STANDARD FUNCTIONS

In general, every intensive thermodynamic quantity θ in a uniform system $\theta = \theta(T, p, N_1, \ldots, N_e)$, can be split up arbitrarily into the sum of two functions—for example, a standard part $\theta^s(T, p)$ which depends only upon the temperature and the pressure, and a function of mixing $\theta^m(T, p, N_1, \ldots, N_e)$:

$$\theta = \theta^s(T, p) + \theta^m(T, p, N_1, \ldots, N_e). \tag{7.1}$$

For example, an ideal system characterized by (6.87) gives

$$\mu_\gamma^s = \zeta_\gamma(T, p) \tag{7.2}$$

$$\mu_\gamma^m = RT \ln N_\gamma. \tag{7.3}$$

The affinity of such a system is written

$$A = A^s + A^m, \tag{7.4}$$

where

$$A^s = - \sum_\gamma \nu_\gamma \zeta_\gamma(T, p) \tag{7.5}$$

$$A^m = - \sum_\gamma \nu_\gamma RT \ln N_\gamma. \tag{7.6}$$

The chemical potential being the partial molar quantity corresponding

to the Gibbs free energy G, we have, from (3.9),

$$\partial \mu_y / \partial T = -s_y, \tag{7.7}$$

where the partial molar entropy of y is defined by

$$s_y = (\partial S / \partial n_y)_{Tp}. \tag{7.8}$$

Now, combining (7.2), (7.3), and (7.7), we find

$$s_y = -(\partial \zeta_y / \partial T) - R \ln N_y \tag{7.9}$$

and

$$s_y^s = -\partial \zeta_y / \partial T \tag{7.10}$$

$$s_y^m = -R \ln N_y. \tag{7.11}$$

In the same manner, the entropy of reaction can be written as

$$\left(\frac{\partial S}{\partial \xi} \right)_{Tp} = \left(\frac{\partial S}{\partial \xi} \right)^s_{Tp} + \left(\frac{\partial S}{\partial \xi} \right)^m_{Tp} = \sum_y \nu_y s_y = - \sum_y \nu_y \frac{\partial \zeta_y}{\partial T}$$
$$- R \sum_y \nu_y \ln N_y. \tag{7.12}$$

The quantity $(\partial S / \partial \xi)^s_{Tp}$ is often called the standard entropy of reaction.

As the partial molar volume for an ideal system is only a function of T and p, we may write

$$v_y = v_y^s = \partial \mu_y^s / \partial p = \partial \zeta_y / \partial p \tag{7.13}$$

and

$$\Delta_{Tp} = \Delta_{Tp}^s + \Delta_{Tp}^m = \sum_y \nu_y v_y^s. \tag{7.14}$$

It is easy to show that, for ideal systems,

$$r_{Tp} = r_{Tp}^s = - \sum_y \nu_y h_y = - \sum_y \nu_y h_y^s = T^2 \sum_y \nu_y \, \partial(\zeta_y/T)/\partial T \tag{7.15}$$

and

$$c_{py} = \partial h_y / \partial T = \partial h_y^s / \partial T, \tag{7.16}$$

where h_y is the partial molar enthalpy of y.

For perfect solutions, h_y^s, s_y^s and v_y^s are equal to the molar enthalpy, molar entropy, and molar volume of the pure component, respectively, On the other hand, the identity

$$\frac{\partial(\zeta_y/T)}{\partial T} = \frac{1}{T} \frac{\partial \zeta_y}{\partial T} - \frac{\zeta_y}{T^2} \tag{7.17}$$

enables us to show that

$$r^{s}_{Tp} + T\left(\frac{\partial S}{\partial \xi}\right)^{s}_{Tp} = A^{s} \tag{7.18}$$

and

$$\frac{\partial r^{s}_{Tp}}{\partial T} = -\sum_{\gamma} \nu_{\gamma} c^{s}_{p\gamma}. \tag{7.19}$$

From (2.13) and (7.5),

$$r^{m}_{Tp} + T\left(\frac{\partial S}{\partial \xi}\right)^{m}_{Tp} = A^{m}. \tag{7.20}$$

The following equations are also easily verified

$$\left[\frac{\partial(A^{s}/T)}{\partial T}\right]_{p} = -\sum_{\gamma} \nu_{\gamma} \frac{\partial(\zeta_{\gamma}/T)}{\partial T} = \frac{r^{s}_{Tp}}{T^{2}}, \tag{7.21}$$

$$\left(\frac{\partial A^{s}}{\partial p}\right)_{T} = -\sum_{\gamma} \nu_{\gamma} \frac{\partial \zeta_{\gamma}}{\partial p} = -\sum_{\gamma} \nu_{\gamma} v_{\gamma}^{s} = -\varDelta^{s}_{Tp}. \tag{7.22}$$

As, in general, every property $(\partial X/\partial \xi)_{Tp}$, where X is any extensive variable, can be added together in the same way as chemical reactions, it is immediately clear that this is particularly true for A^{s}, r^{s}_{Tp}, $(\partial S/\partial \xi)^{s}_{Tp}$, and $\varDelta^{s}_{Tp}$. More explicitly, *standard affinities, standard heats of reaction, standard expansions, and standard entropies of reaction can be added together in the same way as the chemical equations for the reactions themselves.*

Now, from (6.75) and (7.5), we see that

$$K_{N}(T, p) = \exp(A^{s}/RT). \tag{7.23}$$

This equation enables us to calculate the equilibrium constant of any reaction which can be obtained by a linear combination of known reactions.

B. STANDARD FUNCTION OF FORMATION

Many tables give values of the standard affinities and heats of reaction at a temperature of 298.17°K (25°C) and a pressure of 1 atm (symbols A° and r°_{Tp}). It is much more convenient to consider standard affinities of reaction than equilibrium constants. This is because standard affinities can be added and subtracted in just the same way as stoichiometric equations, so that the standard affinity and the equilibrium constant of a reaction not included in the table is easily calculated.

A reaction involving a compound produced from its elements (these elements being taken in their normal physical state under specified conditions), is called a *formation reaction.*

It is also necessary to specify the physical condition of the compound which is formed, although this need not necessarily be the stable state under the conditions considered.

At 298.16°K and 1 atm pressure, the normal physical state of the elements are the gas state (for example, hydrogen, oxygen, fluorine), the liquid state (for example, mercury, bromine), the solid state (for example, sodium, rhombic sulfur, iodine). The standard values for the formation of an element in the stable physical state are, by definition, zero.

For example, $A_{I_2}^\circ$ is equal to zero for the formation of solid iodine, $I_2(s) \to I_2(s)$, but for the formation of gaseous atomic hydrogen, $\frac{1}{2}H_2(g) \to H(g)$, the standard affinity at 298.16°K and 1 atm is not zero, because atomic hydrogen is not stable at this temperature and this pressure.

In general, the standard affinity of formation $A_\gamma{}^\circ$, the standard heat of formation $r_{Tp\gamma}^\circ$, and the standard entropy change of formation $(\partial S^\circ/\partial \xi_\gamma)_{Tp}$ are defined as the standard affinity, standard heat, and standard entropy of the formation reaction of the component γ. Equation (7.18) then becomes

$$A_\gamma{}^\circ = r_{Tp\gamma}^\circ + 298.16\left(\frac{\partial S^\circ}{\partial \xi_\gamma}\right)_{Tp}. \tag{7.24}$$

In Table I, values of $r_{Tp\gamma}^\circ$ and $A_\gamma{}^\circ$ are given for some compounds (Prigogine and Defay, 1967, p. 99). The values of $(\partial S^\circ/\partial \xi_\gamma)$ are easily calculated from (7.24).

Unstable compounds such as O_3, NO, and NO_3 have negative standard affinities of formation at 218°K and 1 atm, while for the other inorganic compounds they are usually positive. For elements in an unstable physical state, A° is negative [S (monoclinic) and Cl(g)].

Now, from a practical point of view, the standard affinity A^s of a reaction can be evaluated from the knowledge of the equilibrium constant (7.23). This last quantity is given by measuring the mole fractions of the various components at the equilibrium. Conversely, if the standard affinity is known, we can evaluate the position of equilibrium.

A large positive standard affinity of formation means that the compound will not decompose spontaneously into its elements under the standard conditions, since the synthesis reaction is practically complete.

TABLE I

STANDARD THERMODYNAMIC FUNCTIONS OF FORMATION AT $T = 298.16°K$, $p = 1$ ATM

Substance	State	r_{Tp}° (kcal mol^{-1})	A° (kcal mol^{-1})	s° (cal mol^{-1} $^{\circ}$K^{-1})
Ca	s	0	0	9.95
CaCO$_3$ (calcite)	s	288.450	269.780	22.2
(aragonite)	s	288.490	269.530	21.2
CaO	s	152.800	145.360	7.8
Hg	l	0	0	18.5
Hg$_2$	g	-27.100	—	—
Na	s	0	0	12.48
NaCl	s	98.232	91.785	17.3
H$_2$	g	0	0	31.211
H	g	-52.089	-48.575	27.393
F$_2$	g	0	0	48.6
Cl$_2$	g	0	0	53.286
Cl	g	-29.012	-25.192	39.457
Br$_2$	l	0	0	36.4
	g	-7.340	-0.751	58.639
I$_2$	s	0	0	27.9
	g	-14.876	-4.630	62.280
I	g	-25.482	-16.766	43.184
HI	g	-6.200	-0.310	49.314
O$_2$	g	0	0	49.003
O	g	-59.159	-54.994	38.469
O$_3$	g	-34.000	-39.060	56.8
H$_2$O	g	$+57.798$	54.635	45.106
	l	$+68.317$	56.690	16.716
H$_2$O$_2$	aq. ($m = 1$)	45.680	31.470	—
S (rhombic)	s	0	0	7.62
(monoclinic)	s	-0.071	-0.023	7.78
N$_2$	g	0	0	45.767
N	g	-85.566	-81.476	36.615
NO	g	-21.600	-20.719	50.339
NH$_3$	g	$+11.040$	3.976	46.01
CO	g	26.416	32.808	47.301
CO$_2$	g	94.052	94.260	51.061
CH$_4$	g	17.889	12.140	44.50
CH$_3$OH	g	48.100	38.700	56.8
	l	57.036	39.750	30.3
C$_2$H$_5$OH	g	56.240	40.300	67.4
	l	66.356	41.770	38.4
CH$_3$COOH	l	116.400	93.800	38.2

This does not prove, however, that the compound will not decompose to form a more stable compound.

As an example, hydrogen peroxide at 25°C and 1 atm will not decompose spontaneously to H_2 and O_2, but will completely to $H_2O(l)$ and $O_2(g)$:

$$A° = -A°_{H_2O_2} + A°_{H_2O} + \tfrac{1}{2}A°_{O_2} = 25{,}220 \quad \text{cal mol}^{-1}.$$

Other important examples are found in organic chemistry.

But the affinity only indicates the *tendency* of a reaction to proceed and says nothing about the kinetics of the reaction. In organic chemistry, we frequently find that a number of different substances can be formed from the same starting materials, so that it is usually necessary to employ a specific catalyst to accelerate the required reaction. An interesting example is given by the oxidation of acetone (Prigogine and Defay, 1967, p. 98).

Remark. In American tables, we find the mean value

$$A = -(\Delta G/\Delta \xi)_{Tp} \quad \text{and} \quad \Delta \xi = 1.$$

Furthermore, in place of ΔG, the symbol used usually is ΔF, so that in American tables we find the quantity

$$\Delta F = -A.$$

C. Variation of Standard Affinity with Temperature and Pressure

Let us integrate (7.21) between two temperatures T and $T_0 = 298.1°K$ at constant pressure $p_0 = 1$ atm. We find

$$\frac{A^s(T, p°)}{T} - \frac{A^s(T°, p°)}{T°} = -\int_{T°}^{T} \frac{r^s_{Tp}}{T^2}\, dT. \tag{7.25}$$

The quantity $A^s(T°, p°)$ can be evaluated with the help of the standard affinity of formation and r^s_{Tp} can be calculated with the help of (7.19).
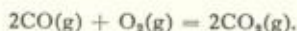
Now, to know the influence of the pressure upon the standard affinity, we must integrate (7.22) at constant temperature. The molar volumes are experimental quantities.

Finally, to calculate the affinity, we may use Eqs. (7.4)–(7.6),

$$A = A^s(T, p) - RT \sum_{\gamma} \nu_{\gamma} \ln N_{\gamma}. \tag{7.26}$$

VIII. Numerical Examples

Example 1. We consider a perfect gas mixture resulting from the reaction

$$2CO(g) + O_2(g) = 2CO_2(g).$$

(1) r_{Tp}^s at 1 atm is a function of the temperature, following Kirchhoff's law (6.47)

$$r_{Tp}^s = -\int \sum_\gamma \nu_\gamma c_{p\gamma}\, dT + \beta, \tag{8.1}$$

where β is the constant of integration.

Now, the molar heat capacities are usually expressed in an empirical power series of the form (Bryant, 1933; Ewell, 1940; Thacker *et al.*, 1941; Kelley, 1960; Spencer, 1945)

$$c_p = a + bT + cT^2 + \cdots$$

CO: $6.25 + 2.091 \times 10^{-3}T - 0.459 \times 10^{-6}T^2$

CO_2: $6.85 + 8.533 \times 10^{-3}T - 2.475 \times 10^{-6}T^2$

O_2: $6.26 + 2.746 \times 10^{-3}T - 0.770 \times 10^{-6}T^2.$

We then obtain

$$r_{Tp}^s = \beta + 5.06T - 5.069 \times 10^{-3}T^2 + 1.087 \times 10^{-6}T^3. \tag{8.2}$$

At 298.16°K, $r_{Tp}^s = \sum_\gamma \nu_\gamma r_{Tp\gamma}^\circ$, and, from the Table I, $r_{Tp}^s = 135{,}272$ cal. Putting this value in Eq. (8.2) for $T = 298.16°K$, we get the expression for r_{Tp}^s

$$r_{Tp}^s = 134{,}185 + 5.06T - 5.069 \times 10^{-3}T^2 + 1.087 \times 10^{-6}T^3. \tag{8.3}$$

(2) We now calculate the affinity as a function of the temperature by using (7.25). From Table I,

$$A^s(298.16°, 1 \text{ atm}) = \sum_\gamma \nu_\gamma A_\gamma{}^\circ = 122{,}904 \quad \text{cal};$$

thus,

$$A^s(T, 1 \text{ atm}) = \frac{122{,}904}{298} T - T \int_{298.16}^T \frac{r_{Tp}^s}{T^2}\, dT. \tag{8.4}$$

Putting (8.3) in the integral of (8.4), we find

$$A^s(T, 1 \text{ atm}) = 134{,}185 - 10.49T - 5.06T \ln T + 5.069 \times 10^{-3}T^2$$
$$- 0.543 \times 10^{-6}T^3. \tag{8.5}$$

(3) The equilibrium constants $K_N(T, p)$ and $K_p(T)$ can be calculated with the help of (7.23) and (6.33). The combination of (7.23), (8.5), and (6.33) gives

$$\log_{10} K_p(T) = \log_{10} K_N(T, 1 \text{ atm}) = (29.427/T) - 1.11 \log_{10} T$$
$$+ 5.069 \times 10^{-3}T^2 - 0.543 \times 10^{-6}T^3. \tag{8.6}$$

Applying (6.22) to our reaction, we can write

$$K_p(T) = p_{CO_2}^2 / p_{CO}^2 p_{O_2}, \tag{8.7}$$

where $K_p(T)$ is not a function of the pressure, but only of the temperature (Fig. 15).

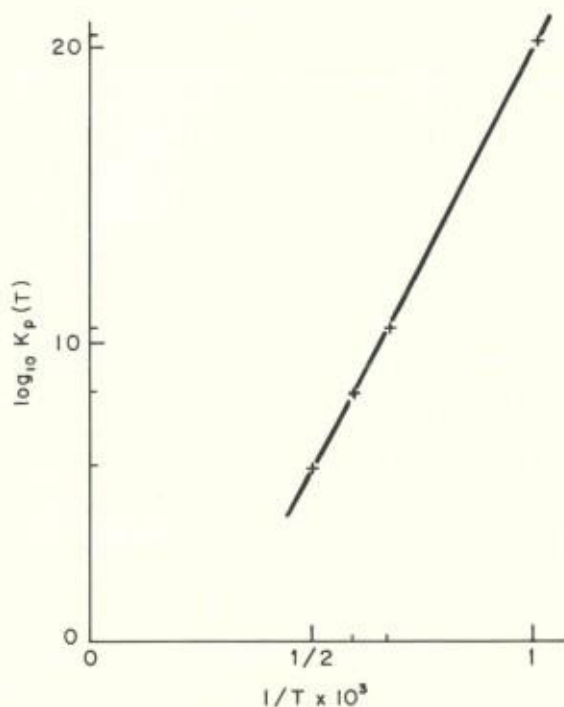
FIG. 15. Equilibrium constant as a function of temperature for the reaction $2CO + O_2 = 2CO_2$.

It follows immediately from (6.15) and (8.7) that

$$K_p(T) = \frac{1}{p} \frac{N_{CO_2}^2}{N_{CO}^2 N_{O_2}}. \tag{8.8}$$

Let us now introduce the degree of dissociation α in such a way that we have at equilibrium α moles of CO, $\alpha/2$ moles of O_2, and $(1 - \alpha)$ moles of CO_2.

Equation (8.8) then becomes

$$K_p(T) = (1 - \alpha)^2(2 + \alpha)/p\alpha^3. \tag{8.9}$$

For any value of α and p, we are thus able to calculate the equilibrium temperature with the help of the Fig. 15.

For example, at $\alpha = 10^{-3}$: for $p = 1$ atm, $K_p(T) = 2 \times 10^9$ atm^{-1} and $T = 1600°K$; for $p = 0.1$ atm, $K_p(T) = 2 \times 10^{10}$ atm^{-1} and $T = 1520°K$.

Example 2. In the thermal dissociation of calcium carbonate, $CaCO_3(s)$ (aragonite) $= CaO(s) + CO_2(g)$, each constituent occurs in one phase only.

(1) r_{Tp} at 1 atm as a function of the temperature. The empirical values of the molar heat capacities are

$$
\begin{aligned}
CaCO_3: &\quad 26.35 \quad (290°K–1030°K) \\
CO: &\quad 11.78 \\
CO_2: &\quad 7 + 7.1 \times 10^{-3}T - 1.86 \times 10^{-6}T^2.
\end{aligned}
$$

From Kirchhoff's law (6.47), we thus obtain

$$r_{Tp}^s = \beta + 7.57T - 3.55 \times 10^{-3}T^2 + 0.62 \times 10^{-6}T^3. \tag{8.10}$$

At $298.16°K$, from Table I, we have $r_{Tp}^s = -41,638$ cal, and (8.10) then becomes

$$r_{Tp}^s = -43,600 + 7.57T - 3.55 \times 10^{-3}T^2 + 0.62 \times 10^{-6}T^3. \tag{8.11}$$

At $1200°K$, $r_{Tp}^s = 38,500$ cal.

(2) From Table I, we have

$$A^s(298.16, 1 \text{ atm}) = \sum_\gamma \nu_\gamma A_\gamma^\circ = -29,910 \quad \text{cal.}$$

Now, from (7.21) and (8.11), it results

$$A^s(T, 1 \text{ atm}) = -43,600 - 17.4T \log_{10} T + 86.2T + 3.6 \times 10^{-3}T^2$$
$$- 0.3 \times 10^{-6}T^3. \tag{8.12}$$

At 900°K, $A^s(900°, 1 \text{ atm}) \simeq -9700$ cal.

(3) From (7.23), the equilibrium constant at 900°K and 1 atm is then equal to $K_N \simeq 3.8 \times 10^{-3}$.

(4) If the reaction is studied in the presence of air, $K_N(T, p) = N_{CO_2}$ and $p_{CO_2} = pN_{CO_2}$, and thus, at 900°K and 1 atm, $N_{CO_2} \simeq 3.8 \times 10^{-3}$, $p_{CO_2} \simeq 3.8 \times 10^{-3}$ atm.

(5) The affinity of the reaction can be calculated with the help of (7.26).

At 1 atm and 900°K and for $N_{CO_2} = 10^{-3}$,

$$A = A^s RT \ln N_{CO_2} = -9700 - RT \ln 3.8 \times 10^{-3} \simeq 2600 \text{ cal. } (8.13)$$

In the absence of air, $N_{CO_2} = 1$ and $p = p_{CO_2}$, and $K_N(T, p) = 1$, which shows that the equilibrium pressure of carbon dioxide depends only on the temperature.

Example 3. Let us now consider the synthesis of ammonia, $N_2 + 3H_2 = 2NH_3$, as a mixture of perfect gases. Using Eq. (6.67), we obtain

$$\Delta_{Tp} = 2v_{NH_3} - v_{N_2} - 3v_{H_2} = -2v_{H_2}. \tag{8.14}$$

From (6.66), we see, then, that the affinity of the reaction increases with pressure.

Combining (6.66) and (8.14), we can write

$$\partial A/\partial p = 2RT/p, \tag{8.15}$$

or

$$A(T, p) - A(T, 1 \text{ atm}) = 2RT \ln p;$$

at 10^3 atm, $A(T, p) - A(T, 1 \text{ atm}) \simeq 8000$ cal. This reaction is exothermic because $r_{Tp} > 0$; $r_{Tp}^s = 22,800$ cal (see Table I). From (6.50), we see that the synthesis of ammonia is favored by a decrease of temperature.

Example 4. We may examine the formation of methanol in a mixture of gases

$$CO(g) + 2H_2(g) = CH_3OH(g). \tag{8.16-I}$$
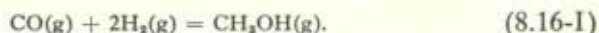
The heats of combustion of H_2, CO, and CH_3OH at 298.16°K and 1 atm are (see Table I)

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) \qquad\qquad r^s_{Tp(II)} = 68{,}317 \quad cal \qquad (8.16\text{-}II)$$

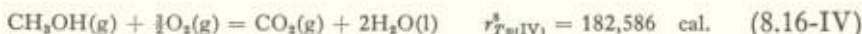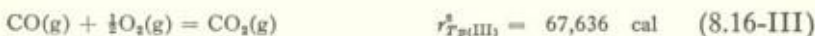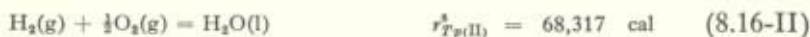$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g) \qquad\qquad r^s_{Tp(III)} = 67{,}636 \quad cal \qquad (8.16\text{-}III)$$

$$CH_3OH(g) + \tfrac{1}{2}O_2(g) = CO_2(g) + 2H_2O(l) \quad r^s_{Tp(IV)} = 182{,}586 \quad cal. \qquad (8.16\text{-}IV)$$

The heat of reaction of (I) is then equal to

$$r^s_{Tp(I)} = r^s_{Tp(III)} + 2r^s_{Tp(II)} - r^s_{Tp(IV)} = 21{,}684 \quad cal.$$

Using Table I, we find the same result for the reaction (I),

$$r^s_{Tp(I)} = r^o_{Tp CH_3OH} - r^o_{Tp CO} = 21{,}684 \quad cal.$$

The standard affinity $A^o_{(I)}$ for the reaction (I) is equal to 5892 cal. Using (7.18), we can also obtain $A^o_{(I)}$:

$$s^o_{CH_3OH(g)} = 56.8 \quad cal, \qquad s^o_{CO(g)} = 47.3 \quad cal, \qquad s^o_{H_2(g)} = 31.21 \quad cal,$$

$$A^o_{(I)} = r^o_{Tp(I)} + T \sum_\gamma \nu_\gamma s_\gamma^{\,o} = 5908 \quad cal.$$

Example 5. *Entropy of a gas.* We now consider the vaporization of methanol

$$CH_3OH(l) = CH_3OH(g). \qquad (8.17)$$

We shall calculate the standard entropy of the vapor of methanol (assumed here to be perfect) $s^s_{(g)}$ (298.16, 1 atm), knowing the corresponding value of the liquid $s^s_{(l)}$ (298.16, 1 atm) and the heat of vaporization of CH_3OH at 298.16°K and 0.163 atm.

From (6.5), we find at 0.163 atm and 298.16°K

$$s^s_{(g)}(298.16°K, 1\ atm) = s^s_{(g)}(298.16°K, 0.163\ atm) + R \ln 0.163. \quad (8.18)$$

On the other hand,

$$s^s_{(g)}(298.16°K, 0.163\ atm) = s^s_{(l)}(298.16°K, 0.163\ atm) + \Delta S_{vap}, \quad (8.19)$$

where ΔS_{vap} is the entropy of vaporization, equal to the heat of vaporization divided by the temperature. From Table I, we take the values of

$$r^o_{Tp CH_3OH(g)} = 48{,}100 \quad cal, \qquad r^o_{Tp CH_3OH(l)} = 57{,}036 \quad cal.$$

· The heat of reaction $r_{T_p}^s$ of (8.16-I) is thus equal to -8936 cal and the heat of vaporization to 8936 cal. The entropy of vaporization is thus

$$\Delta S_{vap} = 8936/298.16 \simeq 29.98 \quad \text{cal } °K^{-1}.$$

We then obtain

$$s_{(g)}^s(298.16°K, 0.163 \text{ atm}) = s_{(1)}^s(298.16°K, 0.163 \text{ atm}) + 29.98. \quad (8.20)$$

As a first approximation, we neglect the effect of pressure upon the entropy of the liquid. We thus have, from Table I,

$$s_{(1)}^s(298.16°K, 0.163 \text{ atm}) \simeq s_{(1)}^s(298.16°K, 1 \text{ atm}) = 30.3 \text{ cal}. \quad (8.21)$$

Combining (8.18), (8.20), and (8.21), we find

$$s_{(1)}^s(298.16°K, 1 \text{ atm}) = 56.68 \quad \text{cal}.$$

It is interesting to know the influence of pressure on the entropy of liquid methanol. For methanol, the value of the dilatation coefficient is known,

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = 0.1199 \times 10^{-3}. \quad (8.22)$$

The specific mass is about 0.8 g cm^{-3} and the molar volume is equal to 40 cm^3. It is easy now to calculate the derivative $(\partial s/\partial p)_T$ with the help of (3.12). We then obtain

$$(\partial s/\partial p)_T = -0.1199 \times 40 \times 10^{-6} = -4.8 \times 10^{-6} \quad 1 \, °K^{-1}. \quad (8.23)$$

Integrating (8.23), we find

$$s_{(1)}^s(0.163 \text{ atm}) = s_{(1)}^s(1 \text{ atm}) + 4.02 \times 10^{-6} \quad 1 \text{ atm } °K \simeq 30.3 \quad \text{cal}$$

Thus, the pressure has no influence on the entropy of the liquid.

IX. Real Gases

A. INTRODUCTION

The ideal gas law may be derived directly on the basis of simple kinetic assumptions in which the translation energy of molecular motion is the main consideration.

All gases behave like ideal gases at sufficiently high temperatures and sufficiently high molar volumes. As the molar volume is decreased, however, real gases exhibit a more complicated behavior. As a gas is compressed, its properties at first deviate only slightly from those of an ideal gas. Under sufficient compression, however, every real gas undergoes a condensation to the liquid or solid state, in which condition it deviates very far indeed from ideal gas behavior. The result is that all real gases must be treated by a more realistic equation of state in such a way as to explain such phenomena as condensation, intermolecular collisions, and a variety of transport properties, such as diffusion and viscosity. The modification of the perfect gas model involves the inclusion of attractive and repulsive intermolecular forces. A detailed discussion of the intermolecular forces in gases and of the state equations is to be found in several fundamental books (Fowler and Guggenheim, 1939; Mayer and Mayer, 1940; Hirschfelder et al., 1965).

Our purpose here consists in the evaluation of the thermodynamic functions from the virial equation of state, and in the introduction of the notion of fugacity.

B. The Virial Equation of State

Kammerling-Onnes (1902) suggested that, with decreasing molar volume v, the properties of every real gas can be expressed in a power series in $1/v$ of the form

$$\frac{p}{T} = \frac{R}{v}\left(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \cdots\right), \tag{9.1}$$

where the coefficients $B(T)$, $C(T)$, ..., are functions of the temperature. The forms of these functions depend on the types of intermolecular forces in the gas. The function $B(T)$ is called the *second virial coefficient*, $C(T)$ the *third virial coefficient*, etc. Enough terms are taken to accomodate the accuracy of the data available. The well-known equation of van der Waals may be shown to be correct only in terms to $B(T)$.

Nevertheless, for a slightly imperfect gas, we need only retain two terms of the expression, giving

$$p = \frac{nRT}{V}\left(1 + \frac{Bn}{V}\right). \tag{9.2}$$

The virial coefficients are often expressed in terms of $cm^3 \, mol^{-1}$, but $B(T)$ is not the volume of the mole, because it passes through zero

and becomes negative at low temperature. It has a maximum at a high temperature and then declines with rising T. The temperature corresponding to $B(T) = 0$ is called the Boyle temperature. At this temperature, the Boyle–Mariotte law $pv = \text{const}$ is observed.

C. Free Energy and Chemical Potential

We now consider a mixture of real gases defined by the variables $T, V, n_1, \ldots, n_c$.

Knowledge of $F(T, V, n_1, \ldots, n_c)$ immediately gives the state equation, because

$$p = -\partial F(T, V, n_1, \ldots, n_c)/\partial V. \tag{9.3}$$

Conversely, the knowledge of a state equation permits us to calculate the thermodynamic functions of a gas. This fact is more interesting because F is not an experimental quantity. Furthermore, observable properties of a gas are usually summarized in the form of an equation of state.

If the volume tends to infinity, the free energy F tends toward the value F^* corresponding to a perfect gas, so that, by integrating (9.3), we find

$$F(T, V, n_1, \ldots, n_c) - \lim_{V_0 \to \infty} F^*(T, V_0, n_1, \ldots, n_c)$$
$$= - \lim_{V_0 \to \infty} \int_{V_0}^{V} p \, dV. \tag{9.4}$$

For a perfect gas, we may write (9.4) in the form

$$F^*(T, V, n_1, \ldots, n_c) - \lim_{V_0 \to \infty} F^*(T, V_0, n_1, \ldots, n_c)$$
$$= - \lim_{V_0 \to \infty} \int_{V_0}^{V} p^* \, dV, \tag{9.5}$$

where

$$p^* = nRT/V. \tag{9.6}$$

Combining (9.4) and (9.5), we find

$$F(T, V, n_1, \ldots, n_c) - F^*(T, V, n_1, \ldots, n_c) = - \lim_{V_0 \to \infty} \int_{V_0}^{V} (p - p^*) \, dV. \tag{9.7}$$

Substituting (9.2) and (9.6), in (9.7), we have

$$F = F^* + B(RTn^2/V) \tag{9.8}$$

and, from (4.16),

$$\mu = \mu^*(T, V) + 2(BRTn/V). \qquad (9.9)$$

We have, therefore, from (6.7) and (9.9), the value of the chemical potential of a real gas

$$\mu = \mu^*(T) + RT \ln(nRT/V) + 2(BRTn/V) \qquad (9.10)$$

D. FUGACITY

The fugacity of a pure real gas is a corrected pressure, defined in such a way that the chemical potential μ can be expressed in a classical form

$$\mu = \mu^*(T) + RT \ln \varphi. \qquad (9.11)$$

This intensive quantity gives the effects of intermolecular forces on the thermodynamic properties of gases.

Comparing (9.11) and (9.10), we may write

$$\ln \varphi = \ln(nRT/V) + 2(Bn/V). \qquad (9.12)$$

For a slightly imperfect gas, $2Bn/V$ is small compared with unity and (9.12) becomes, as a first approximation,

$$\varphi = \frac{nRT}{V}\left(1 + 2B\frac{n}{V}\right). \qquad (9.13)$$

Comparing this relation with (9.2) yields

$$\varphi - p = n\frac{RT}{V}\frac{Bn}{V} \qquad (9.14)$$

or

$$\varphi = 2p - p^*. \qquad (9.15)$$

Now, in the limit of zero total pressure, the fugacity φ is identical with the pressure.

Example. At $T = 382°K$, the saturation vapor pressure of fluoro-benzene is equal to 1.974 atm and the molar volume $v = 15 \times 10^3$ cm³ mol⁻¹. We then obtain $p^* = 2.085$ atm, $\varphi = 1.86$ atm.

Remark. At the Boyle temperature, $\varphi = p = p^*$.

E. INTERNAL ENERGY

It is well known that in a Joule expansion a real gas tends to cool. This fact is a direct consequence of the dependence of the internal energy on the volume. Indeed, substituting (9.8) in (3.10), we find

$$U = U^* - n^2(RT^2/V) \, dB/dT, \tag{9.16}$$

where

$$U^* = F^* - T \, \partial F^*/\partial T. \tag{9.17}$$

We thus have

$$\left(\frac{\partial U}{\partial V}\right)_T = n^2 \frac{RT^2}{V^2} \frac{dB}{dT}. \tag{9.18}$$

The derivative dB/dT being positive, the interval energy increases with V. As in a Joule expansion, $dU = 0$, and, because V increases, T must decrease in order to maintain U constant.

F. MIXTURE OF REAL GASES

The state equation for a mixture of two slightly imperfect gases is

$$p = \frac{n_1 + n_2}{V} RT + \frac{RT}{V^2} [B_{11}n_1^2 + 2B_{12}n_1n_2 + B_{22}n_2^2], \tag{9.19}$$

where the coefficients B_{11}, B_{12}, and B_{22} are related to the interaction, respectively, between molecules of type 1, of types 1 and 2, and of type 2.

The free energy can thus be obtained by substituting (9.19) in (9.7):

$$F = F^* + (RT/V)[B_{11}n_1^2 + 2B_{12}n_1n_2 + B_{22}n_2^2], \tag{9.20}$$

and, from (4.16),

$$\mu_1 = \mu_1^*(T) + RT \ln \frac{n_1 RT}{V} + \frac{2RT}{V} [B_{11}n_1 + B_{12}n_2]$$

$$\mu_2 = \mu_2^*(T) + RT \ln \frac{n_2 RT}{V} + \frac{2RT}{V} [B_{12}n_1 + B_{22}n_2]. \tag{9.21}$$

Now, in order to obtain the fugacity in terms of the virial coefficients, let us assume that for real gases (6.15) applies in the same manner, and thus

$$\sum_\gamma p_\gamma = p \sum N_\gamma = p. \tag{9.22}$$

Nevertheless, in this case, the partial pressure of a component is not necessarily equal to the pressure of the same component alone occupying the same volume at the same temperature.

In a real gas mixture, we may retain the simple form of (6.18) by use of the fugacity

$$\mu_\gamma = \mu_\gamma^*(T) + RT \ln \varphi_\gamma, \tag{9.23}$$

where $\mu_\gamma^*(T)$ is the same function as for the perfect gases.

Combining (9.23), (9.21), and (6.18), we obtain

$$\ln \varphi_1 = \ln \frac{n_1 RT}{V} + 2 \frac{B_{11}n_1 + B_{12}n_2}{V},$$
$$\ln \varphi_2 = \ln \frac{n_2 RT}{V} + 2 \frac{B_{12}n_1 + B_{22}n_2}{V}. \tag{9.24}$$

On the other hand, from (4.21) and (9.23), the affinity of a reaction is readily expressed in terms of fugacities

$$A = - \sum_\gamma \nu_\gamma \mu_\gamma^*(T) - RT \sum_\gamma \nu_\gamma \ln \varphi_\gamma. \tag{9.25}$$

We then have

$$A = RT \ln[K_p(T)/\varphi_1^{\nu_1}\varphi_2^{\nu_2} \cdots \varphi_c^{\nu_c}], \tag{9.26}$$

where

$$\ln K_p(T) = -\left[\sum_\gamma \nu_\gamma \mu_\gamma^*(T)\right]\Big/ RT. \tag{9.27}$$

The equilibrium then gives the extension to real gases of the Guldberg–Waage law of mass action

$$K_p(T) = \varphi_1^{\nu_1} \cdots \varphi_c^{\nu_c}. \tag{9.28}$$

Instead of the fugacities used in the expression of chemical potential, it is sometimes advantageous to use a corrected mole fraction a_γ called the activity of component γ. Let us define this activity a_γ by

$$a_\gamma = \exp[(\mu_\gamma - \mu_\gamma^\circ)/RT], \tag{9.29}$$

where μ_γ° is the same function as in perfect gases; i.e., from (6.23) and (6.25),

$$\mu_\gamma^\circ(T, p) = \mu_\gamma^*(T) + RT \ln p, \tag{9.30}$$

but here p is the pressure of the real gas.

The chemical potential is then

$$\mu_\gamma = \mu_\gamma^\circ(T, p) + RT \ln a_\gamma. \tag{9.31}$$

The activity is thus an intensive function of $T, p, N_1, \ldots, N_c$, and contains all the effects arising from the interactions. This quantity has been introduced by Lewis and Randall (1923).

Usually, the chemical potential is expressed in a more explicit manner:

$$\mu_\gamma = \mu_\gamma^\circ(T, p) + RT \ln f_\gamma N_\gamma \tag{9.32}$$

where the coefficient f_γ, called the activity coefficient, is a function of $T, p, N_1, \ldots, N_c$. This coefficient may then be defined by the relation

$$f_\gamma = a_\gamma / N_\gamma. \tag{9.33}$$

In the limit of zero total pressure, the activity a_γ is identical to the mole fraction N_γ, and thus the activity coefficient is equal to unity. Accordingly, for a perfect gas mixture, all the activity coefficients are unity.

Now, it is easy to calculate the activity when one knows the fugacity. Indeed, comparing (9.32) to (9.23) and (9.30), we find

$$\varphi_\gamma = p f_\gamma N_\gamma. \tag{9.34}$$

For a pure constituent γ, $N_\gamma = 1$ and

$$\varphi_\gamma = p f_\gamma. \tag{9.35}$$

The activity coefficient of a pure gaseous component differs from unity because $\varphi \neq p$.

The chemical potential of an isolated component may then be written, following (9.30) and (9.32),

$$\mu_\gamma = \mu_\gamma^\circ(T, p) + RT \ln f_\gamma = \mu_\gamma^*(T) + RT \ln p + RT \ln f_\gamma. \tag{9.36}$$

The quantity μ_γ° corresponds to the chemical potential of an isolated component in a perfect gaseous state at pressure p and temperature T. It is called the standard chemical potential μ_γ^*, while the quantity $RT \ln f_\gamma N_\gamma$ is the function of mixing μ_γ^m.

Let us express now the affinity in terms of activity. From (4.21) and (9.32), we find

$$A = -\sum_\gamma \nu_\gamma \mu_\gamma^\circ(T, p) - RT \sum_\gamma \nu_\gamma \ln f_\gamma N_\gamma \tag{9.37}$$

and thus

$$A = RT \ln[K_N(T, p)/(N_1 f_1)^{\nu_1} \cdots (N_c f_c)^{\nu_c}], \qquad (9.38)$$

where

$$\ln K_N(T, p) = -\left[\sum_\gamma \nu_\gamma \mu_\gamma{}^\circ(T, p)\right]\Big/ RT. \qquad (9.39)$$

The quantity $-\sum_\gamma \nu_\gamma \mu_\gamma{}^\circ(T, p)$ is called the standard affinity A^s, and thus

$$K_N(T, p) = \exp[A^s/RT]. \qquad (9.40)$$

At equilibrium, the Guldberg–Waage equation becomes

$$K_N(T, p) = (N_1 f_1)^{\nu_1} \cdots (N_c f_c)^{\nu_c}. \qquad (9.41)$$

As $K_N(T, p)$ is the same function as in the perfect gas, we also find [see Eq. (6.33)]

$$K_N(T, p) = p^{-\nu} K_p(T). \qquad (9.42)$$

The other standard functions (superscript s) and mixing functions (superscript m) are given as follows:

$$h_\gamma = -T^2 \frac{\partial(\mu_\gamma/T)}{\partial T}, \qquad\qquad h_\gamma{}^s = -T^2 \frac{\partial(\mu_\gamma{}^\circ/T)}{\partial T},$$

$$h_\gamma{}^m = -RT^2 \frac{\partial(\ln f_\gamma)}{\partial T} \qquad\qquad\qquad\qquad (9.43)$$

$$s_\gamma = -\frac{\partial\mu_\gamma}{\partial T}, \qquad\qquad\qquad s_\gamma{}^s = -\frac{\partial\mu_\gamma{}^\circ}{\partial T},$$

$$s_\gamma{}^m = -R \ln f_\gamma N_\gamma - RT \frac{\partial(\ln f_\gamma)}{\partial T} \qquad\qquad (9.44)$$

$$v_\gamma = \frac{\partial\mu_\gamma}{\partial p}, \qquad\qquad\qquad v_\gamma{}^s = \frac{\partial\mu_\gamma{}^\circ}{\partial p},$$

$$v_\gamma{}^m = RT \frac{\partial(\ln f_\gamma)}{\partial p} \qquad\qquad\qquad\qquad (9.45)$$

$$r_{Tp} = -\sum_\gamma \nu_\gamma h_\gamma, \qquad\qquad r_{Tp}^s = -\sum_\gamma \nu_\gamma h_\gamma{}^s,$$

$$r_{Tp}^m = -\sum_\gamma \nu_\gamma h_\gamma{}^m \qquad\qquad\qquad\qquad (9.46)$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{Tp} = \sum_\gamma \nu_\gamma s_\gamma, \qquad\qquad \left(\frac{\partial S}{\partial \xi}\right)_{Tp}^s = \sum_\gamma \nu_\gamma s_\gamma{}^s,$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{Tp}^m = \sum_\gamma \nu_\gamma s_\gamma{}^m. \qquad\qquad\qquad (9.47)$$

The variation of the equilibrium constant with temperature and pressure can be calculated in the same manner as for the perfect gases [see Eqs. (6.50), (6.68), and (7.21)–(7.23)]:

$$\frac{\partial[\ln K_N(T, p)]}{\partial T} = \frac{1}{R} \frac{\partial(A^s/T)}{\partial T} = -\frac{1}{R} \sum_\gamma v_\gamma \frac{\partial(\mu_\gamma{}^\circ/T)}{\partial T}$$

$$= -\frac{r_{Tp}^s}{RT^2} \tag{9.48}$$

$$\frac{\partial[\ln K_N(T, p)]}{\partial p} = \frac{1}{RT} \frac{\partial A^s}{\partial p} = -\frac{1}{RT} \sum_\gamma v_\gamma \frac{\partial \mu_\gamma{}^\circ}{\partial p}$$

$$= \frac{-\sum_\gamma v_\gamma v_\gamma{}^s}{RT} = -\frac{\Delta_{Tp}}{RT}. \tag{9.49}$$

Remark. The standard entropy of a constituent in a perfect gas mixture is equal to the entropy of the isolated constituent at the same temperature and pressure. But this is not true for real gases. Indeed, Eq. (9.44) reduces, for a real isolated gas, to

$$s_\gamma{}^m = -R \ln f_\gamma - RT\, \partial(\ln f_\gamma)/\partial T. \tag{9.50}$$

The entropy of real isolated gases can be evaluated by calorimetric measurements. To obtain the standard entropy $s_\gamma{}^s$ (see Table I), we must subtract the above value of $s_\gamma{}^m$ from the experimental value.

X. Stability of Chemical Systems

In this section, we shall discuss the stability of equilibrium states and present some conclusions concerning the properties of thermodynamic variables in stable equilibrium systems.

A. De Donder's Method

If, in a closed system P, a reaction may take place, its state is characterized by two physical variables x and y (for example, T and p) and by a chemical variable ξ. We have

$$dn_\gamma = v_\gamma\, d\xi \qquad (\gamma = 1, 2, \ldots, c). \tag{10.1}$$

Let us assume that, at time t, the system is in an equilibrium state.

The rate of reaction $\mathbf{v}_P$ is thus zero,

$$\mathbf{v}_P = 0. \tag{10.2}$$

At the same time, let us consider another system P' characterized by the same physical variables x and y as the system P but by a different chemical variable $\xi + d\xi$.

The system P' is not in general in an equilibrium state and its rate of reaction $\mathbf{v}_{P'}$ is then

$$\mathbf{v}_{P'} \neq 0. \tag{10.3}$$

In comparison with the system P, the system P' is thus a perturbed system. The perturbation consists here in the virtual displacement from ξ to $\xi + d\xi$ with constant values of x and y.

Now, we know that [see Chapter 1, Eq. (20.2)]

$$n_y = n_y{}^\circ + \nu_y \xi. \tag{10.4}$$

The considered perturbation $d\xi$ is thus identical to a slight change of all the n_y proportionally to $d\xi$,

$$\delta n_y = \nu_y \, d\xi. \tag{10.5}$$

At constant x and y, the system P is said to be stable with respect to the perturbations if the rate of reaction of the perturbed system P' tends to bring this system to the equilibrium state P (De Donder, 1942; Duhem, 1911, Chapter XVI).

Let us now represent the systems P and P' on the $xy\xi$ axes (see Fig. 16) and let us assume that the system P is stable. There are two cases:

(1) $\delta\xi > 0$ (system P'), $\mathbf{v}_{P'}$ is directed in the direction opposite to the ξ axis; the rate of reaction $d\xi/dt = \mathbf{v}_{P'}$ is then negative.

(2) $\delta\xi < 0$ (system P''), the rate of reaction $\mathbf{v}_{P''}$ is directed in the same direction as the ξ axis and is positive.

The criterion of stability is thus

$$\mathbf{v}_{P'} \, \delta\xi < 0. \tag{10.6}$$

There are two kinds of perturbations: those in which $\delta\xi$ can have only one sign (unilateral perturbations), and those in which $\delta\xi$ can be either positive or negative (bilateral perturbations). An example of a unilateral perturbation is the appearance of a vapor bubble in a system which was

initially completely liquid, while the reverse reaction is impossible as long as there is no vapor phase.

If a stable system is perturbed, it reverts to the initial equilibrium; if it is unstable, the perturbation proceeds to a finite extent.
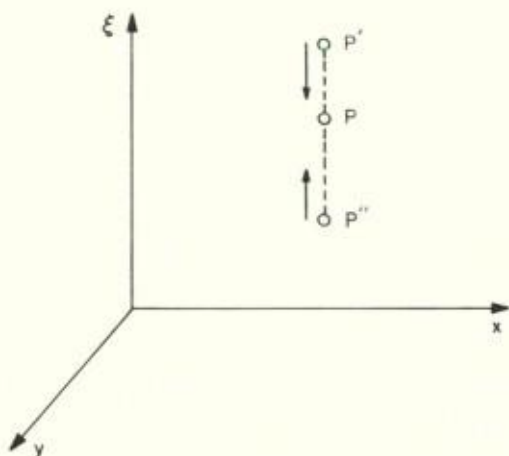

FIG. 16.   Equilibrium stability of a system P.

Remark. A perturbation is not necessarily related to any external action on the system. Molecular fluctuations lead to small variations of the macroscopic quantities from their equilibrium values. There is, in fact, a relation between the probability of a fluctuation and the production of entropy which accompanies it.

B. THE PRIGOGINE–DEFAY METHOD

The method adopted by Prigogine (see Prigogine and Defay (1967), p. 205) is based upon the direct evaluation of the entropy production in the course of a perturbation and so permits a discussion of stability with respect to any kind of perturbation. The entropy production corresponding to a change from a state $P(x, y, \xi_P)$ to a state $P'(\xi_{P'})$ is given from (2.1) by

$$Q'_{PP'} = \int_{\xi_P}^{\xi_{P'}} A(\xi)\, d\xi, \tag{10.7}$$

where, for a specified process, the physical variables x and y are functions completely determined by ξ.

Developing the affinity in the form of a Taylor series, (10.7) becomes

$$Q'_{PP'} = A_P \Delta\xi + \frac{1}{2}\left(\frac{dA}{d\xi}\right)_P (\Delta\xi)^2 + \cdots + \frac{1}{n!}\frac{d^{(n-1)}A}{d\xi^{(n-1)}}(\Delta\xi)^n, \quad (10.8)$$

where $A_P = A(\xi_P)$ and $\Delta\xi = \xi_{P'} - \xi_P$.

For a small variation $\Delta\xi$, we have two cases:

(i) $\qquad A_P \neq 0 \qquad$ and $\qquad Q'_{PP'} = A_P\,\delta\xi;$ $\hspace{3cm}$ (10.9)

(ii) $\qquad A_P = 0 \qquad$ and $\qquad Q'_{PP'} = \frac{1}{2}(dA/d\xi)_P(\delta\xi)^2.$ $\hspace{1.7cm}$ (10.10)

The transformations characterized by Eqs. (10.8)–(10.10) are called *perturbations, where P is an equilibrium state*. They are related to the infinitesimal change $\delta\xi$ and to the conditions under which they are carried out. If, for example, x and y remain constant during the perturbations, (10.10) becomes

$$Q'_{PP'} = \frac{1}{2}(\partial A/\partial\xi)_{xyP}(\delta\xi)^2. \quad (10.11)$$

Now, the state P is said to be stable with respect to the transformation $P \to P'$ if the production of entropy accompanying it is *negative*, and thus

$$\boxed{Q'_{PP'} < 0.} \quad (10.12)$$

On the other hand, for the inverse spontaneous process, $P' \to P$, the production of entropy is positive.

C. THERMODYNAMIC CONDITIONS OF STABILITY. UNILATERAL PERTURBATIONS

The unilateral perturbation is characterized by the fact that $\delta\xi$ can have only one sign; for example, let us take $\delta\xi > 0$. Thus, for a reaction

$$d\xi/dt \geq 0, \quad (10.13)$$

and, from (2.1), it follows that the system will be in equilibrium provided that

$$A \leq 0. \quad (10.14)$$

If $A_P \neq 0$ (10.12) and Eq. (10.9) yield the condition of stability

$$A_P < 0, \tag{10.15}$$

which is in fact the condition of equilibrium.

If $A_P = 0$, Eq. (10.10) gives the condition of stability

$$(dA/d\xi)_P < 0, \tag{10.16}$$

or, if x and y remain constant,

$$(\partial A/\partial \xi)_{xyP} < 0. \tag{10.17}$$

Now, combining (3.6) and (10.15), we find that, if P is a stable equilibrium state, the internal energy U increases in the perturbations,

$$(\partial U/\partial \xi)_{VSP} > 0, \tag{10.18}$$

where U is a function of ξ only (V and S are maintained constant).

On the other hand, we have from (10.10), (10.17), and (3.6)

$$(\partial U/\partial \xi)_{VSP} = 0, \qquad (\partial^2 U/\partial \xi^2)_{VSP} > 0. \tag{10.19}$$

and the internal energy U has a horizontal tangent at P; it increases during a perturbation if P is a stable equilibrium state.

With regard to the stability of phases, the initial system (unperturbed) consists of a single phase, while the final system (perturbed) contains, in addition to the original phase, a small amount of a new phase whose properties (partial molar volume, volume, composition, etc.) differ only infinitesimally from those of the original phase, or differ from them by a finite, nonzero, amount. Usually, we say that the initial phase is stable when it is stable with respect to all other phases whether infinitesimally different from them or not. In this case, the phase can never give rise spontaneously to a new phase in macroscopic amounts.

The initial phase is called a metastable phase when it is stable with respect to phases infinitesimally different from it, but there is at least one other phase with respect to which it is not stable. This means that, in the absence of nuclei, the system may remain indefinitely in equilibrium without the appearance of a new phase (supercooled liquids).

Finally, the initial phase is called an unstable phase when it is unstable with respect to the phases infinitesimally different from it. Practically, this means that the phase will disappear and give rise to one or more neigh-

boring phases (molecular fluctuations) until we arrive at a phase which is stable with respect to adjacent phases.

Remark. Instead of (10.18), we may write the classical conditions

$$(\partial H/\partial \xi)_{pS} > 0, \tag{10.20}$$

$$(\partial F/\partial \xi)_{VT} > 0, \tag{10.21}$$

$$(\partial G/\partial \xi)_{Tp} > 0. \tag{10.22}$$

If $A_P = 0$, then we have

$$(\partial H/\partial \xi)_{pS} = 0, \qquad (\partial^2 H/\partial \xi^2)_{pS} > 0 \tag{10.23}$$

$$(\partial F/\partial \xi)_{VT} = 0, \qquad (\partial^2 F/\partial \xi^2)_{VT} > 0 \tag{10.24}$$

$$(\partial G/\partial \xi)_{Tp} = 0, \qquad (\partial^2 G/\partial \xi^2)_{Tp} > 0. \tag{10.25}$$

D. STABILITY WITH RESPECT TO BILATERAL PERTURBATIONS

We have seen earlier (Section II), that false equilibrium may be characterized by $\mathbf{v} = 0$ and $A \neq 0$. Thus, if such a system is perturbed, it does not revert to its initial situation. Only true equilibrium could be stable. The first condition of stability is thus $A_P = 0$ in a state P.

Furthermore, in the perturbed state P', the system must take a rate satisfying the inequality (10.6). We may calculate $A_{P'}$

$$A_{P'} = A_P + (\partial A/\partial \xi)_{xyP} \, \delta \xi. \tag{10.26}$$

From the stability condition $A_P = 0$, Eq. (10.26) reduces to

$$A_{P'} = (\partial A/\partial \xi)_{xyP} \, \delta \xi. \tag{10.27}$$

Now, from De Donder's inequality (2.14),

$$A_{P'} \mathbf{v}_{P'} > 0, \tag{10.28}$$

which characterizes a spontaneous process; it follows that the sign of $\mathbf{v}_{P'}$ is given by the inequality

$$(\partial A/\partial \xi)_{xyP} \, \delta \xi \mathbf{v}_{P'} > 0. \tag{10.29}$$

This relation is consistent with the criterion of stability only if

$$(\partial A/\partial \xi)_{xyP} < 0. \tag{10.30}$$

Thus, two conditions, $A_P = 0$ and (10.30), are necessary and sufficient to express the stability of a system.

Remark. At constant T and p, the two conditions are

$$A = 0, \qquad (\partial A/\partial \xi)_{Tp} = 0. \tag{10.31}$$

At constant T and V, we have

$$A = 0, \qquad (\partial A/\partial \xi)_{TV} = 0. \tag{10.32}$$

In Section III, we saw that

$$A = -\left(\frac{\partial U}{\partial \xi}\right)_{VS} = -\left(\frac{\partial H}{\partial \xi}\right)_{pS} = -\left(\frac{\partial F}{\partial \xi}\right)_{TV} = -\left(\frac{\partial G}{\partial \xi}\right)_{Tp}. \tag{10.33}$$

The conditions of stability $A = 0$ and (10.30) are:

(*i*) $\quad (\partial U/\partial \xi)_{VS} = 0, \qquad (\partial^2 U/\partial \xi^2)_{SV} > 0; \tag{10.34}$

when S and V are maintained constant, U is thus minimum in a stable equilibrium state (Fig. 17).

(*ii*) $\quad (\partial H/\partial \xi)_{Sp} = 0, \qquad (\partial^2 H/\partial \xi^2)_{Sp} > 0; \tag{10.35}$

in a stable equilibrium state, H is minimum at constant S and p.

(*iii*) $\quad (\partial F/\partial \xi)_{TV} = 0, \qquad (\partial^2 F/\partial \xi^2)_{TV} > 0; \tag{10.36}$

in a stable equilibrium state, F is minimum at constant T and V.

(*iv*) $\quad (\partial G/\partial \xi)_{Tp} = 0, \qquad (\partial^2 G/\partial \xi^2)_{Tp} > 0; \tag{10.37}$

in a stable equilibrium state, G is minimum at constant T and p.

The inequality (10.37) may be rewritten as

$$a_{Tp} < 0, \tag{10.38}$$

where

$$a_{Tp} = (\partial A/\partial \xi)_{Tp} = -(\partial^2 G/\partial \xi^2)_{Tp}. \tag{10.39}$$

Thus, from (10.33) and (4.21),

$$a_{Tp} = -\sum_\gamma \nu_\gamma \, \partial\mu_\gamma/\partial \xi = -\sum_\gamma \sum_\beta \nu_\gamma \nu_\beta \mu_{\gamma\beta} < 0, \tag{10.40}$$

where

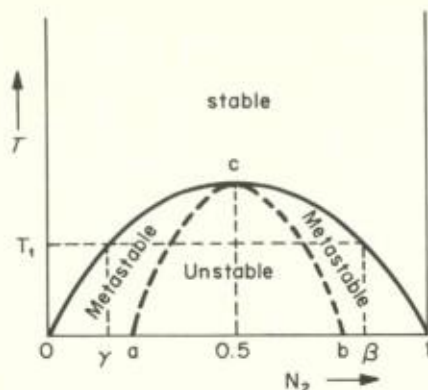$$\mu_{\gamma\beta} = \partial\mu_\gamma/\partial n_\beta. \tag{10.41}$$

FIG. 17. Minimum internal energy for a stable equilibrium state.

Equation (10.40) can be rewritten in the form

$$a_{Tp} = \tfrac{1}{2} \sum_{\gamma} \sum_{\beta} \mu_{\gamma\beta} n_{\gamma} n_{\beta} \left(\frac{v_{\gamma}}{n_{\gamma}} - \frac{v_{\beta}}{n_{\beta}} \right)^{2} < 0. \tag{10.42}$$

This condition is satisfied if $\mu_{\gamma\beta}$ is negative for all $\gamma \neq \beta$.

Prigogine and Defay (1967, Eq. (7.13)) showed that this condition is always satisfied by ideal systems. Thus, all stable states of an ideal system are stable equilibrium states at constant T and p.

E. EXPLICIT FORMS OF THE STABILITY CONDITIONS

For a system at constant energy and volume [see Eq. (3.1)], the stability condition gives

$$\delta S \leq 0 \qquad (E, V \text{ constant}). \tag{10.43}$$

Systems which are maintained at constant energy and volume are by definition *isolated* systems. For such systems, entropy is *maximum* for stable equilibrium and

$$(\delta S)_{\text{eq}} = 0 \qquad \text{(equilibrium)} \tag{10.44}$$

$$(\delta S)_{\text{eq}} < 0 \qquad \text{(stability)} \tag{10.45}$$

$$(\delta^{2} S)_{\text{eq}} < 0. \tag{10.46}$$

Let us now derive a relation for the second-order quantity $\delta^{2}s$, where s

is the specific mass entropy. For a system in equilibrium, the Gibbs relation (4.12) may then be written in the classical form

$$T \, \delta s = \delta u + p \, \delta v - \sum_\gamma \mu_\gamma \, \delta N_\gamma, \tag{10.47}$$

where u is the specific mass internal energy, v the specific volume, N_γ the molar fraction, and μ_γ is here the chemical potential per unit mass. Let us first calculate $\delta^2 s$ using as independent variables u, v, N_γ; then $\delta^2 u = 0$, $\delta^2 v = 0$, and $\delta^2 N_\gamma = 0$, and the Gibbs formula (10.47) gives us directly

$$\delta^2 s = \delta T^{-1} \, \delta u + \delta(pT^{-1}) \, \delta v - \sum_\gamma \delta(\mu_\gamma T^{-1}) \, \delta N_\gamma. \tag{10.48}$$

Combining (10.47) and (10.48), we obtain

$$T \, \delta^2 s = -\delta T \, \delta s + \delta p \, \delta v - \sum_\gamma \delta\mu_\gamma \, \delta N_\gamma. \tag{10.49}$$

Let us now express the variation of the chemical potentials $\delta\mu_\gamma$ in the variables T, p, N_γ. We obtain the quadratic form [see Chapter 1 (16.11)–(16.13), (16.17), (18.3), (18.4), (18.18)–(18.20), (18.23), (18.25)],

$$\delta^2 s = -\frac{1}{T}\left[\frac{c_v}{T}(\delta T)^2 + \frac{\varrho}{\chi}(\delta v)^2 + \sum_{\gamma\beta} \mu_{\gamma\beta} \, \delta N_\gamma \, \delta N_\beta\right], \tag{10.50}$$

where

$$c_v = \left(\frac{\partial e}{\partial T}\right)_{vN_\gamma} = T\left(\frac{\partial s}{\partial T}\right)_{vN_\gamma} \tag{10.51}$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_{pN_\gamma} \tag{10.52}$$

$$\chi = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{TN_\gamma} \tag{10.53}$$

$$c_p - c_v = \frac{T}{\chi v}\left(\frac{\partial v}{\partial T}\right)_{pN_\gamma}^2 \tag{10.54}$$

$$\mu_{\gamma\beta} = \left(\frac{\partial \mu_\gamma}{\partial N_\beta}\right)_{TpN_\beta}. \tag{10.55}$$

Now, in the system of variables ϱu, ϱ_γ, it is easy to show that

$$\delta^2(\varrho s) = \varrho \, \delta^2 s, \tag{10.56}$$

ϱs being the volume entropy density; it becomes easy to calculate the quantity $\delta^2 s$.

The quadratic form has to be positive definite. From the inequality (10.46), this leads to the following stability conditions:

$$c_v > 0 \qquad \text{(thermal stability)} \tag{10.57}$$

$$\chi > 0 \qquad \text{(mechanical stability).} \tag{10.58}$$

Both the specific heat (at constant volume) and the isothermal compressibility have to be positive.

In addition, we also have

$$\sum_{\gamma\beta} \mu_{\gamma\beta}\, \delta N_\gamma\, \delta N_\beta > 0 \qquad \text{(stability with respect to diffusion).} \tag{10.59}$$

Let us consider, for example, a perturbation which consists in the appearance of a heterogeneity in the composition of a binary system which is initially uniform. The inequality (10.59) guarantees that the response of the system will restore the initial homogeneity.

The inequalities (10.57) and (10.58) ensure stability with respect to thermal and mechanical disturbances, while (10.59) ensures stability in respect to diffusion.

F. PHASE SEPARATION IN BINARY MIXTURES

As a simple illustration of the stability condition (10.59), let us consider phase separations in binary mixtures. The stability conditions are then

$$\mu_{11} > 0, \qquad \mu_{22} > 0 \tag{10.60}$$

$$\begin{vmatrix} \mu_{11} & \mu_{21} \\ \mu_{12} & \mu_{22} \end{vmatrix} \geq 0. \tag{10.61}$$

On the other hand, from (4.33) we have

$$\mu_{12} = \mu_{21} \tag{10.62}$$

$$\begin{aligned} n_1\mu_{11} + n_2\mu_{21} &= 0, \\ n_1\mu_{12} + n_2\mu_{22} &= 0. \end{aligned} \tag{10.63}$$

Thus, the determinant in (10.61) vanishes and we have only to consider

the first two inequalities. Moreover,

$$n_1^2\mu_{11} = n_2^2\mu_{22} \tag{10.64}$$

and this implies that the two inequalities in (10.60) are equivalent and that

$$\mu_{12} = \mu_{21} < 0. \tag{10.65}$$

For mixtures of perfect gases and "perfect solutions" formed by components of similar molecules, the influence of the activity coefficient f_γ may be neglected and the chemical potentials take the form [see Eq. (9.32)]

$$\mu_\gamma = \mu_\gamma{}^\circ(T, p) + RT \ln N_\gamma, \tag{10.66}$$

and it is easy to show that the inequalities (10.60) and (10.65) are verified. However, this is no longer necessarily so for regular solutions (Prigogine, 1957). Indeed, in this case,

$$\mu_1 = \mu_1{}^\circ(T, p) + RT \ln(1 - N_2) + \alpha N_2{}^2 \tag{10.67}$$

$$\mu_2 = \mu_2{}^\circ(T, p) + RT \ln N_2 + \alpha(1 - N_2)^2, \tag{10.68}$$

where α is a constant defined by

$$\alpha = N_{Av} z [\varepsilon_{12} - \tfrac{1}{2}(\varepsilon_{11} + \varepsilon_{22})], \tag{10.69}$$

with N_{Av} the Avogadro number, z the number of nearest neighbors of a molecule in the considered medium, and $\varepsilon_{\gamma\beta}$ is the interaction energy between a molecule γ and a molecule β. Now,

$$\mu_{12} = \frac{\partial \mu_1}{\partial N_2} = -\frac{RT}{1 - N_2} + 2\alpha N_2. \tag{10.70}$$

If

$$2\alpha/RT > 4, \tag{10.71}$$

there exists a range of mole fractions where the stability conditions are not satisfied. We then obtain phase separations, and the phase diagram is represented schematically in Fig. 18.

There exists a critical point $N_2 = 0.5$, $T_c = (\alpha/2)R$. Above this critical point, the two components are mixable in all proportions. Below, we find two coexisting phases (for example, at $T = T_1$, we have two phases corresponding to $N_2 = \gamma$ and $N_2 = \beta$). Inside the region acb, the stability
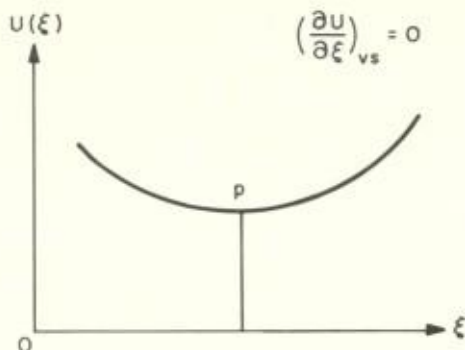
FIG. 18.   Phase separation in a regular solution at constant p.

condition (10.60–10.61) is violated. This curve is called the spinodal. It separates unstable states from metastable states.

For metastable states, the stability conditions as derived in Section X, E are satisfied; however, the Gibbs free energy (if we work at constant p and T) is higher for the homogeneous mixtures than for a system formed by two coexisting phases. Metastable systems are stable with respect to small perturbations (the second-order stability conditions are satisfied, but the system is unstable with respect at least to some finite perturbations).

Remark. The limitations of the Gibbs–Duhem theory, the comparison with the kinetic theory of stability, and the important problem of the thermodynamic stability conditions for nonequilibrium states are discussed in detail by Glansdorff and Prigogine (1970).

XI. Equilibrium Displacements in Closed Systems

A. GENERAL LAWS

The problems encountered when considering equilibrium displacements are similar to those met when studying stability. If the modification is due to the variables T and p as well as to ξ, and if we maintain constant the perturbed values $p + \delta p$ and $T + \delta T$, a stable system may tend to return to a *new* equilibrium state different from the initial state. This modification is called the displacement of thermodynamic equilibrium.

Let us assume, for example, that only p and T are perturbed, respectively, to $p + \delta p$ and $T + \delta T$. We thus pass from an initial system in an equilibrium state P to a perturbed system P'. Then we maintain $p + \delta p$ and $T + \delta T$ constant and the system evolves toward to a new equilibrium state P'' (Fig. 19). At each point of the line PP'', we have

$$A = 0 \tag{11.1}$$

Generally, a displacement on the surface $A = 0$ is called an equilibrium displacement. Along an equilibrium displacement,

$$\delta A = 0 \tag{11.2}$$

and thus

$$\frac{\partial A}{\partial T}\, \delta T + \frac{\partial A}{\partial p}\, \delta p + \frac{\partial A}{\partial \xi}\, \delta \xi = 0. \tag{11.3}$$

Now each derivative may be rewritten. From (2.13) and (3.12), we find

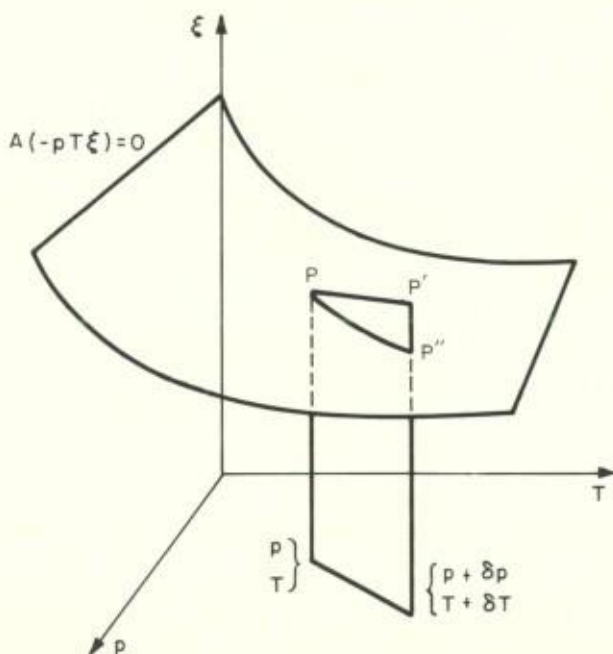$$\partial A / \partial T = (A - r_{T_p}) / T. \tag{11.4}$$

FIG. 19.   Equilibrium displacement.

From (3.12),

$$\partial A/\partial p = - \sum_{\gamma} \nu_{\gamma} v_{\gamma} = -\Delta_{Tp}. \tag{11.5}$$

From (10.39),

$$\partial A/\partial \xi = a_{Tp}. \tag{11.6}$$

Combining the above six equations, we obtain the general law of the *equilibrium displacement*:

$$(r_{Tp}/T)\, \delta T + \Delta_{Tp}\, \delta p - a_{Tp}\, \delta \xi = 0. \tag{11.7}$$

1. *Isobaric Displacement*, $\delta p = 0$

Equation (11.7) then reduces to the De Donder formula (see De Donder (1925, 1927), Schottky *et al.* (1929, p. 492))

$$\left(\frac{\partial \xi}{\partial T} \right)_p = \frac{1}{a_{Tp}} \frac{r_{Tp}}{T}. \tag{11.8}$$

As the condition of stability is given by the inequality (10.38), Eq. (11.8) expresses the *van't Hoff theorem*; if a reaction is exothermic ($r_{Tp} > 0$), then $\partial \xi/\partial T < 0$, and thus an increase in temperature moves the equilibrium position of the reaction back ($\delta \xi < 0$). If the reaction is endothermic ($r_{Tp} < 0$), a rise in temperature advances the equilibrium position ($\delta \xi > 0$).

Further, De Donder's formula (11.8) makes it possibile for us to calculate the value of the derivative $(\partial \xi/\partial T)_p$.

Example. The reaction $2H_2 + O_2 = 2H_2O$ is exothermic. At ordinary temperature, we have a false equilibrium. True equilibrium exists at high temperatures and is stable at given temperature and pressure. If the temperature increases, ξ decreases, and thus water vapour dissociates partially into H_2 and O_2.

Remark. The conclusions obtained here are consistent with the equation (6.50) giving the variation of $K_N(T, p)$ with T. But, from a practical point of view, Eqs. (6.49) and (6.50) are only interesting in the case of perfect gases, where the chemical potentials are known.

2. *Isothermal Displacement*, $\delta T = 0$

From (11.7), we then have the De Donder formula

$$(\partial \xi/\partial p)_T = \Delta_{Tp}/a_{Tp}. \tag{11.9}$$

The condition of stability (10.38) and Eq. (11.9) express *Le Chatelier's theorem*: if a reaction is accompanied by an increase in volume ($\Delta_{Tp} > 0$), an increase in pressure leads to a reduction of the extent of reaction ($\delta\xi < 0$), and inversely.

3. *Isomassic Displacement,* $\delta\xi = 0$

We may write

$$\left(\frac{\partial p}{\partial T}\right)_{\xi} = -\frac{1}{\Delta_{Tp}}\frac{r_{Tp}}{T}. \tag{11.10}$$

Equation (11.10) is called the De Donder–Clapeyron–Clausius formula.

Let us assume that, in a chemical reaction, the composition of each constituent remains constant; then we are able to calculate the variation of the pressure with the temperature.

B. A Particular Case: $A = A(T, p)$

Let us consider a pure constituent in two phases (Fig. 20). Here, the affinity is independent of ξ because

$$A = \mu'(T, p) - \mu''(T, p). \tag{11.11}$$

Thus,

$$A = A(T, p), \tag{11.12}$$

and (11.7) reduces to the Clapeyron formula

$$\frac{\delta p}{\delta T} = -\frac{1}{\Delta_{Tp}}\frac{r_{Tp}}{T}. \tag{11.13}$$

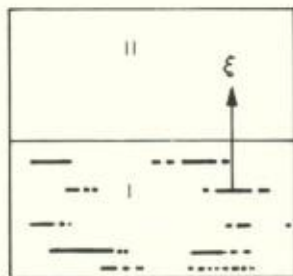Here, $\Delta_{Tp} = v'' - v'$ and $-r_{Tp}$ is the latent heat L.

Fig. 20. Matter transfer of a pure constituent between two phases.

For example, in vaporization, v' may be neglected with repect to v'', and, for a perfect gas,

$$v'' = RT/p. \tag{11.14}$$

Combining (11.13) and (11.14), we find

$$\delta(\ln p)/\delta T = L/RT^2. \tag{11.15}$$

Integrating (11.15), we obtain

$$\ln p = -(L/RT) + \text{const.} \tag{11.16}$$

For chloroform (Fig. 21), we find for the latent heat $L_v \approx 7200$ cal mol^{-1} and for the entropy of vaporization $(\Delta S_v)_{500\text{mmHg}} \simeq 28$ cal mol^{-1} °K^{-1}.

Remark. From Eq. (2.13) at equilibrium, we may write

$$r_{T_p} = -T(\partial S/\partial \xi)_{T_p} = -T(s'' - s'). \tag{11.17}$$

Substituting (11.17) in (11.13) gives

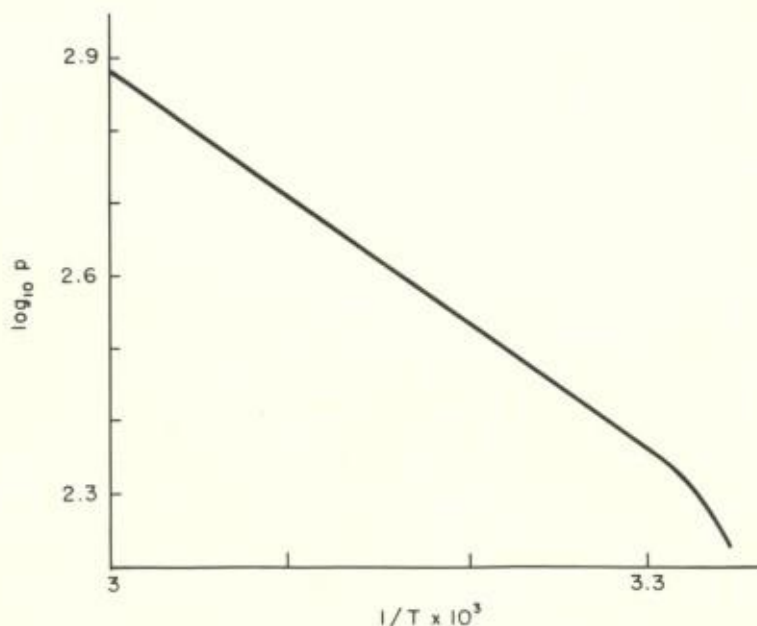$$\delta p/\delta T = (s'' - s')/(v'' - v'). \tag{11.18}$$

FIG. 21. Vapor pressure as a function of temperature for chloroform.

C. The Le Chatelier–Braun Theorem of Moderation

The van't Hoff and Le Chatelier theorems are characterized by the fact that in both cases the reaction occurs in such a way that it exhibits moderation of the factor perturbed.

If we increase the temperature, the reaction absorbs heat, and this tends to moderate the increase of temperature. If we increase the pressure, the reaction occurs in such a way that the volume decreases and thus tends to moderate the increase of pressure.

But these theorems of restraint or of moderation cannot be applied in the same manner when we use other variables. If we decrease the volume of a system, the reaction produced does not tend to moderate this decrease.

The problem of moderation must be studied by considering the *real* transformation produced by the system when the system is perturbed. An unambiguous answer can be deduced by using the fundamental inequality $Av > 0$.

XII. Equilibrium Displacements in Open Systems

A. Method

In open systems, the equilibrium conditions may be modified by the addition of certain constituents; for example, the addition of KOH to the mixture $HNO_3 + KOH$.

In fact, equilibrium displacement in open systems can be studied by noting the properties of equilibrium curves or equilibrium surfaces.

Furthermore, it is more convenient to use here the variables $T, p, N_1, \ldots, N_c$ or $T, p, \mu_1, \ldots, \mu_c$. Nevertheless, the fundamental problem is also related to the two equations

$$A = 0 \tag{12.1}$$

$$\delta A = 0, \tag{12.2}$$

with δA a function of the chemical potentials.

B. Two-Phase System

We consider a two-phase system and c constituents with only passage reactions from one phase to the other (Fig. 22). The equilibrium condi-

tions (12.1) applied to the passages are

$$A_\gamma = \mu_\gamma' - \mu_\gamma'' = 0 \qquad (\gamma = 1, \ldots, c). \qquad (12.3)$$

The equilibrium displacement condition (12.2) then becomes

$$\delta\mu_\gamma'' = \delta\mu_\gamma' = \delta\mu_\gamma \qquad (\gamma = 1, \ldots, c), \qquad (12.4)$$

where $\delta\mu_\gamma$ is the common value of $\delta\mu_\gamma'$ and $\delta\mu_\gamma''$.
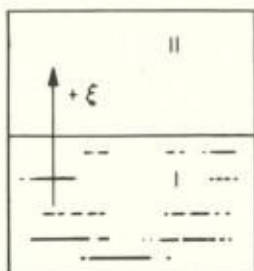

FIG. 22.   Matter transfer between two phases.

Let us now write the Gibbs–Duhem equation (4.30) for each phase:

$$-s'\,\delta T + v'\,\delta p - \sum_\gamma N_\gamma'\,\delta\mu_\gamma = 0$$
$$-s''\,\delta T + v''\,\delta p - \sum_\gamma N_\gamma''\,\delta\mu_\gamma = 0 \qquad (12.5)$$

where

$$s' = S'/\sum_\gamma n_\gamma', \qquad v' = V'/\sum_\gamma n_\gamma', \qquad N_\gamma' = n_\gamma'/\sum_\gamma n_\gamma'. \qquad (12.6)$$

By subtraction, Eq. (12.5) becomes

$$-(s'' - s')\,\delta T + (v'' - v')\,\delta p - \sum_\gamma (N_\gamma'' - N_\gamma')\,\delta\mu_\gamma = 0. \qquad (12.7)$$

Because the variance of the system is [see Eq. (5.7)]

$$w = 2 + c - \phi = c, \qquad (12.8)$$

the two equations (12.5) permit us to calculate the variation of two variables of $T, p, \mu_1, \ldots, \mu_c$ when the variations of the c other variables are given.

For a pure constituent (subscript 1) in each phase, we have $N_1' = N_1''$ $= 1$ and (12.7) reduces to

$$\delta p / \delta T = (s'' - s')/(v'' - v'). \qquad (12.9)$$

We here again find the Clapeyron equation (11.18).

C. THE GIBBS–KONOVALOW THEOREMS

1. *Isothermal Equilibrium Displacement*

At constant temperature, (12.7) gives

$$(v'' - v') \, \delta p - \sum_{\gamma} (N_\gamma'' - N_\gamma') \, \delta \mu_\gamma = 0. \qquad (12.10)$$

If, during the equilibrium displacement, a state is characterized by

$$N_\gamma' = N_\gamma'' \qquad (\gamma = 1, \ldots, c), \qquad (12.11)$$

then (12.10) reduces simply to

$$\delta p = 0; \qquad (12.12)$$

the pressure must pass through an extreme value (maximum, minimum, or inflection at horizontal tangent).

Equation (12.11) means that the two phases have the same composition. Such a system is called azeotropic (see Section V,B,2a). The above *Gibbs–Konovalow theorem* may then be stated in the form: If, in an isothermal equilibrium displacement of a two-phase binary system, the composition of the phases becomes the same, then the pressure must pass through an extreme value.

Example 1. Two constituents, two phases, and only passage reactions. The system is thus bivariant. If T and μ_2 are the independant variables, we thus have $\mu_1 = \mu_1(T, \mu_2)$. At constant temperature, (12.10) can be written in the form

$$(v'' - v') \frac{\delta p}{\delta \mu_2} = (N_1'' - N_1') \left(\frac{\partial \mu_1}{\partial \mu_2} \right)_T + (N_2'' - N_2'). \qquad (12.13)$$

For $N_1'' = N_1'$ and $N_2'' = N_2'$, we find

$$\delta p / \delta \mu_2 = 0 \qquad \text{(horizontal tangent).} \qquad (12.14)$$

From the curve $p = p(\mu_2)$ at constant temperature, we thus obtain a horizontal tangent. As μ_2 increases with N_2, the curves $p = p(N_2')$ and $p = p(N_2'')$ at T constant will give an extremum of p for the state $N_2' = N_2''$ (see Fig. 6).

Example 2. Three constituents, two phases, and only passage reactions. The system is thus trivariant. We choose T, μ_2, and μ_3 as independent variables.

If, at constant temperature, μ_2 and μ_3 vary (Fig. 23), the maximum of the surface corresponds to the state of same composition

$$N_1' = N_1'', \qquad N_2' = N_2'', \qquad N_3' = N_3''. \tag{12.15}$$

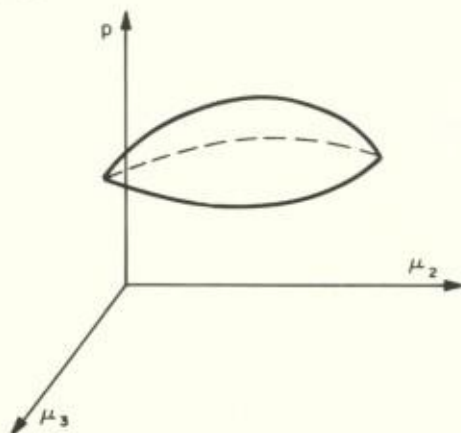The chemical potential of a constituent as a function of its composition is given in Fig. 24.

Fig. 23.   Variation of the chemical potential with pressure.

2. *Isobaric Equilibrium Displacement*

In this case, (12.7) reduces to

$$(s'' - s')\, \delta T + \sum_\gamma (N_\gamma'' - N_\gamma')\, \delta\mu_\gamma = 0. \tag{12.16}$$

If the composition of the two phases is the same,

$$N_\gamma'' = N_\gamma' \qquad (\gamma = 1, \ldots, c)$$
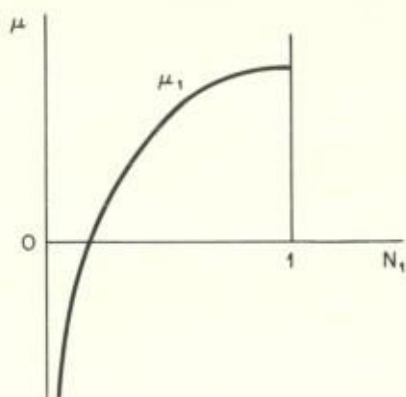
and

$$\delta T = 0. \tag{12.17}$$

FIG. 24.   Variation of the chemical potential with the composition.

This second theorem, also called *the Gibbs–Konovalow theorem*, may be expressed in the form: In an equilibrium displacement at constant pressure of a binary system, the temperature of coexistence passes through an extreme value (maximum, minimum, or inflection with a horizontal tangent) if the composition of the two phases is the same (Fig. 6).

D. The Reciprocal of the Gibbs–Konovalow Theorems

1. *Isothermal Transformation*

For a binary system, let us give $\delta\mu_2 \neq 0$ at constant temperature. The equations (12.5) can be written

$$v' \, \delta p - N_1' \, \delta\mu_1 = N_2' \, \delta\mu_2$$
$$v'' \, \delta p - N_1'' \, \delta\mu_1 = N_2'' \, \delta\mu_2. \tag{12.18}$$

Thus,

$$\delta p = \delta\mu_2 \left\{ (N_1'' - N_1') \middle/ \begin{vmatrix} v' & N_1' \\ v'' & N_1'' \end{vmatrix} \right\}. \tag{12.19}$$

If the pressure passes through an extreme value, $\delta p = 0$ at this point, and, from (12.19), the phases must be of the same composition ($N_1'' = N_1'$ and $N_2'' = N_2'$).

2. *Isobaric Transformation*

Similarly, it is easy to show that, if the temperature of coexistence passes, at constant pressure, through an extremum, then the two phases must have the same composition.

XIII. Thermodynamics of Solutions

A. INTRODUCTION

A solution is a condensed phase (liquid or solid) composed of several components. Molecules of liquids and solids are strongly interacting, but the molecules of liquids are randomly distributed, while the molecules in solids are located in a regular array.

In the vicinity of the *critical temperature* and *critical pressure*, the distinction between gases and liquids vanishes. In this section, we develop the fundamental principles of the thermodynamics of solutions. In order to aid in this investigation, it is convenient to distinguish between ideal solutions and nonideal solutions. The fundamental quantity is the activity coefficient described in asymmetrical and symmetrical reference systems. This coefficient can be evaluated by different methods involving the knowledge of vapor pressures. Finally, the last subsection is devoted to a brief study of the excess functions.

B. IDEAL SOLUTIONS

An ideal solution is defined in such a way that the chemical potential of each substance composing the solution has a simple functional dependence on a concrete composition variable. Under appropriate conditions, the properties of a large class of real substances may be adequately represented by the properties of ideal substances. This is often observed for dilute solutions. It is found by experiment and from molecular considerations (Prigogine, 1957) that a suitable form of the chemical potential of an ideal component γ can be written

$$\mu_\gamma = \mu_\gamma{}^\circ(T, p) + RT \ln N_\gamma, \tag{13.1}$$

where $\mu_\gamma{}^\circ(T, p)$ is some reference value of the chemical potential. If (13.1) is valid, then the solution is called a perfect solution. From

(13.1), we have

$$v_\gamma = \frac{\partial \mu_\gamma}{\partial p} = \frac{\partial \mu_\gamma{}^\circ(T, p)}{\partial p} \tag{13.2}$$

$$\frac{h_\gamma}{T^2} = -\frac{\partial(\mu_\gamma/T)}{\partial T} = -\frac{\partial(\mu_\gamma{}^\circ/T)}{\partial T}. \tag{13.3}$$

Thus, at constant T and p, the molar volumes v_γ and the molar enthalpies h_γ are constant over the whole region of ideality. On the other hand, it is easy to show that, for a binary solution,

$$v = (1 - N_2)v_1 + N_2 v_2, \tag{13.4}$$

where

$$v = V/n = \sum_\gamma N_\gamma v_\gamma. \tag{13.5}$$

As v_1 and v_2 are constant at a given temperature and pressure, the molar volume v is thus a linear function of the mole fraction.

For a perfect solution, v_1 and v_2 are the molar volumes of the pure components and the mixing process is accompanied by neither expansion nor contraction. In the same way, if the molar global enthalpy h is defined by

$$h = H/n = \sum_\gamma N_\gamma h_\gamma, \tag{13.6}$$

the mixing of two components at constant T and p is accompanied by neither an absorption nor evolution of heat.

For example (Fig. 25), the mixing of two systems by passage of component 1 from a pure phase ($''$) to a phase ($'$) (solution of components 1 and 2) is characterized by the heat of reaction (see Section II)
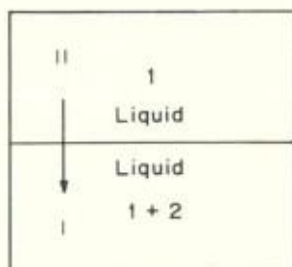
$$r_{Tp} = h_1{}'' - h_1{}'. \tag{13.7}$$

Fig. 25. Matter transfer of a pure constituent 1 ($''$) to a solution $1 + 2$ ($'$).

Since in a perfect solution h_1' is only a function of T and p, (13.7) reduces to $r_{Tp} = 0$. In other words, if, at constant pressure $(dp = 0)$, the mixing is carried out adiabatically $(dQ = 0)$, no temperature change occurs. Indeed, it is clear from (2.7) that

$$C_{p\xi}\, dT = r_{Tp}\, d\xi.$$

As $r_{Tp} = 0$, $dT = 0$.

C. Vapor Pressure of Perfect Solutions

The equilibrium condition between a solution (l) and its vapor (v) is given for two components 1 and 2 by

$$\mu_1^l = \mu_1^v, \qquad \mu_2^l = \mu_2^v. \tag{13.8}$$

Let us now assume that the solution is perfect and that the vapor is a mixture of perfect gases. Then, combining (13.8) with (13.1) and (6.18), we obtain

$$p_1 = k_1 N_1, \qquad p_2 = k_2 N_2, \tag{13.9}$$

where

$$k_1 = \exp\left\{\frac{\mu_1^{ol}(T, p) - \mu_1^{v*}(T)}{RT}\right\}$$
$$k_2 = \exp\left\{\frac{\mu_2^{ol}(T, p) - \mu_2^{v*}(T)}{RT}\right\}. \tag{13.10}$$

At ordinary conditions, μ_1° and μ_2° are practically independent of pressure, and thus k_1 and k_2 are functions of T only.

The vapor pressure of each component in a perfect solution is thus proportional to its mole fraction.

For $N_1 = 1$, p is the vapor pressure p_1° of pure component γ, and thus $k_1 = p_1^\circ$. The so-called Raoult law is

$$p_1 = p_1^\circ N_1, \qquad p_2 = p_2^\circ N_2 \tag{13.11}$$

and the total pressure p of a perfect solution is a linear function of the molar fraction. Indeed,

$$p = p_1 + p_2 = p_1^\circ(1 - N_2) + p_2^\circ N_2. \tag{13.12}$$

D. Dilute Real Solutions

A large class of dilute real solutions may be considered as ideal systems. Equation (13.1) is then verified from $N_2 = 0$ to $N_2 = N_2$ (2 is the index of the solute). This limit of N_2 depends upon the nature of the system. For nonelectrolytes, the range of validity is much larger than for strong electrolytes. Equation (13.9) holds in the neighborhood of $N_2 = 0$, $N_1 = 1$. At $N_1 = 1$, $k_1 = p_1°$, and

$$(p_1° - p_1)/p_1° = N_2. \tag{13.13}$$

The Raoult law (13.11) is valid only for the solvent. It is interesting to note that the relative lowering of the vapor pressure of the solvent is a function of the molar fraction of the solute; it is independent of the nature of the dissolved substance.

For the solute, (13.9) is often called Henry's law.

E. Real Solutions

In this section, we consider a real mixture of components for which the laws of Raoult and Henry are not satisfied.

This fact must be related to the form of the chemical potential. Let us arbitrarily choose a standard function $\mu_\gamma°(T, p)$ and let us define a new quantity called activity of the component γ by the relation

$$a_\gamma = \exp\left\{\frac{\mu_\gamma(T, p, N_1, \dots, N_c) - \mu_\gamma°(T, p)}{RT}\right\} \tag{13.14}$$

or

$$\mu_\gamma = \mu_\gamma°(T, p) + RT \ln a_\gamma. \tag{13.15}$$

The activity a_γ is a function of T, p, $N_1, \dots, N_c$.

The decomposition of μ_γ into two functions $\mu_\gamma°(T, p)$ and $a_\gamma(T, p, N_1, \dots, N_c)$ is arbitrary; the quantity a_γ is then related to the choice of a reference system based on the limit of the ratio a_γ/N_γ for particular conditions. This ratio is called the activity coefficient f_γ. Deviations from the laws of perfect solutions may be expressed formally by introducing the activity coefficients f_γ in the expression for the chemical potential of a perfect solution. The method due to Lewis and Randall (1923) permits one formally to extend the properties of perfect solutions to actual solutions in a most elegant way. The chemical potential now

takes the form

$$\mu_\gamma = \mu_\gamma{}^\circ(T, p) + RT \ln f_\gamma N_\gamma. \tag{13.16}$$

In this case, (13.9) must be replaced by

$$p_1 = k_1 N_1 f_1, \qquad p_2 = k_2 N_2 f_2, \tag{13.17}$$

where $k_1(T)$ and $k_2(T)$ are given by (13.10).

As the affinity is given by the classical relation

$$A = - \sum_\gamma \nu_\gamma \mu_\gamma, \tag{13.18}$$

we obtain from (13.16) the general expression

$$A = RT \ln[K_a(T, p)/(f_1 N_1)^{\nu_1} \cdots (f_c N_c)^{\nu_c}], \tag{13.19}$$

where

$$- \sum_\gamma \nu_\gamma \mu_\gamma{}^\circ(T, p) = RT \ln K_a(T, p). \tag{13.20}$$

At equilibrium, $A = 0$ and the Guldberg–Waage law may be written

$$(f_1 N_1)^{\nu_1} \cdots (f_c N_c)^{\nu_c} = K_a(T, p) \tag{13.21}$$

F. Asymmetrical Reference System

In the asymmetrical reference system, the dilute ideal solution is taken as reference system for a study of less dilute solutions. As the solution becomes more dilute, (13.16) approaches (13.1) with the same standard function. In this case, the asymmetrical property

$$\begin{aligned} N_2 &\rightarrow 0, & f_1 &\rightarrow 1 \\ N_1 &\rightarrow 1, & f_2 &\rightarrow 1 \end{aligned} \tag{13.22}$$

means that

$$f_1 \rightarrow 1 \quad \text{for} \quad N_2 \rightarrow 0$$

while

$$f_1 \rightarrow 1 \quad \text{for} \quad N_1 \rightarrow 1.$$

In other words, (13.17) becomes

$$p_1 = p_1{}^* f_1, \qquad p_2 = p_2{}^* f_2, \tag{13.23}$$

where

$$p_1{}^* = p_1{}^\circ N_1, \qquad p_2{}^* = k_2 N_2. \tag{13.24}$$

In Fig. 26, $p_1{}^*$ and $p_2{}^*$ are represented, respectively, by the Raoult line P_1O_2 and Henry line O_1Q_1. These two lines are tangential to the real experimental curves p_1 and p_2. From the curves p_1 and p_2 and from the Raoult and Henry laws, it is easy to calculate the activity coefficients. Indeed, from (13.23), we find

$$f_1 = p_1/p_1{}^*, \qquad f_2 = p_2/p_2{}^*. \tag{13.25}$$

Unfortunately, f_2 is given by the way of the tangent O_1Q_1, and this line cannot be drawn with good precision.
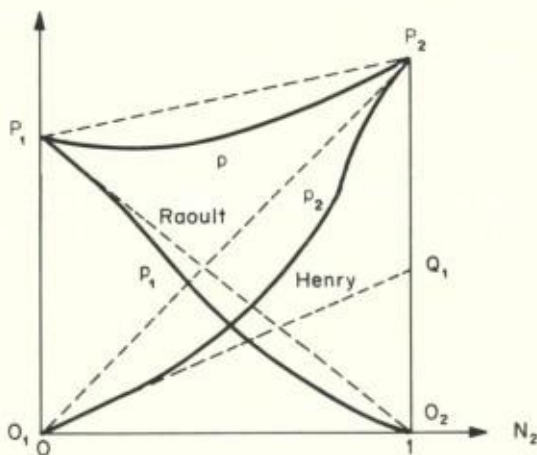

FIG. 26.   The Raoult and Henry laws.

From a practical point of view, it is more convenient to use the relation between f_1 and f_2 derived from the Gibbs–Duhem equation. We shall use this method in the symmetrical reference system (see Section H on Boissonnas' Method).

G. SYMMETRICAL REFERENCE SYSTEM

Let us now study the properties of a solution in the range $N_2 = 0$ (pure solvent) to $N_2 = 1$ (pure solute). In the symmetrical reference

system, we define $\mu_\gamma{}^\circ(T, p)$ by the relation

$$\mu_\gamma{}^\circ(T, p) = \mu_\gamma(T, p, N_\gamma = 1), \tag{13.26}$$

where $\mu_\gamma(T, p, N_\gamma = 1)$ is the chemical potential of the pure component. From (13.26) and (13.16),

$$f_\gamma = 1 \quad \text{for} \quad N_\gamma = 1, \tag{13.27}$$

which means that the activity coefficient of each pure component is equal to the unity. Equations (13.17) give

$$\begin{aligned} N_1 &= 1, & p_1{}^\circ &= k_1, \\ N_2 &= 1, & p_2{}^\circ &= k_2, \end{aligned} \tag{13.28}$$

and thus

$$p_1 = p_1{}^*f_1, \qquad p_2 = p_2{}^*f_2, \tag{13.29}$$

where

$$p_1{}^* = p_1{}^\circ N_1, \qquad p_2{}^* = p_2{}^\circ N_2; \tag{13.30}$$

thus,

$$f_1 = p_1/p_1{}^*, \qquad f_2 = p_2/p_2{}^*. \tag{13.31}$$

The "ideal" pressures $p_1{}^*$ and $p_2{}^*$ are the Raoult lines P_1O_2 and O_1P_2 (Fig. 27).

From the experimental values of the total pressure p, it becomes easy to calculate f_1 and f_2. Indeed

$$p_1 = pN_1{}^V, \qquad p_2 = pN_2{}^V. \tag{13.32}$$

The curves p_1 and p_2 can be calculated by titrating the solution ($N_1{}^V$ and $N_2{}^V$ are then known). The deviations from ideality are described as negative or positive. In the first case, this means that the total pressure p in less than the ideal pressure (line P_1P_2) or that $f_\gamma < 1$ (example: chloroform + ethyl ether solutions). In the second case, $f_\gamma > 1$ (example: methylal + carbon disulphide) (Prigogine and Defay, 1967, pp. 338–339).

Remarks. (1) From a molecular point of view, we say that the vapor pressure is constant with respect to the composition if the interactions between the molecules 1–1, 1–2, and 2–2 are equal. If the attractions 1–2 < 1–1, 1–2, the vapor pressure is raised and $f_\gamma > 1$. Alternatively, if 1–2 > 1–1, 1–2, then $f_\gamma < 1$. However, entropy effects also modify the activity coefficients (Prigogine, 1957).
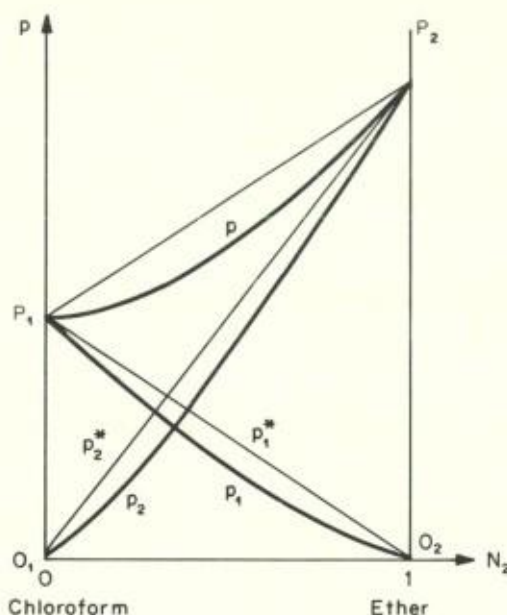
FIG. 27. Deviation from ideality for the system chloroform–ether.

(2) If deviations from ideality are large enough, the total vapor pressure p passes through a maximum or a minimum (azeotropy).

H. The Boissonnas Method

If the composition of the vapor is unknown, p_1 and p_2 can be still calculated.

From the Gibbs–Duhem relation [Eq. (4.30)] at constant T and p,

$$\sum_{\gamma} N_{\gamma}\, d\mu_{\gamma} = 0, \tag{13.33}$$

and thus, (13.16) leads to

$$N_1\left[\frac{\partial(\ln f_1)}{\partial N_2}\right]_{Tp} + N_2\left[\frac{\partial(\ln f_2)}{\partial N_2}\right]_{Tp} = 0. \tag{13.34}$$

In the symmetrical reference system, (13.34) reduces to the well-known Duhem–Margules relation

$$N_1\left[\frac{\partial(\ln p_1)}{\partial N_2}\right]_{T} + N_2\left[\frac{\partial(\ln p_2)}{\partial N_2}\right]_{T} = 0. \tag{13.35}$$

This equation is valid only for an ideal vapor phase. Equation (13.35) can be transformed into

$$\frac{\partial p_2}{\partial N_2} = \frac{1}{1 - (p_1/p_2)(N_2/N_1)} \frac{\partial p}{\partial N_2}.$$ (13.36)

For a very dilute solution, $p_1 = p_1°N_1$, and thus

$$dp_1 = p_1° \, dN_1 \quad \text{and} \quad dp_2 = dp + p_1° \, dN_2.$$ (13.37)

Boissonnas (1939) suggested that the composition range be divided into a number of equal intervals ΔN_2 and that Eqs. (13.36) and (13.37) be used in the approximate forms

$$\Delta p_2 = \frac{\Delta p}{1 - (p_1/p_2)(N_2/N_1)}$$ (13.38)

with

$$\Delta p_2 = \Delta p + p_1° \, \Delta N_2 \quad \text{(for } N_2 = 0\text{)}.$$ (13.39)

From the curves p_1 and p_2, it is easy to calculate f_1 and f_2.

Remark. For an azeotrope, the two phases have the same composition at the extremum and $p_1/N_1 = p_2/N_2$. The relation (13.36) then becomes wrong in the neighborhood of the extremum. Practically, we apply the method of Boissonnas first from $N_2 = 0$ to a point neighboring the extremum and then from $N_1 = 0$ until the vicinity of the azeotrope. If, at the temperature considered, the vapor pressure p_2 (solute) is small in comparison with p_1 (solvent), we may write

$$p = p_1.$$ (13.40)

From the experimental value of p, it becomes easy to calculate f_1, because

$$f_1 = p_1/p_1°N_1.$$ (13.41)

On the other hand, integrating Eq. (13.34), we find the value of f_2

$$\ln f_2 = - \int_{N_2=1}^{N_2} (N_1/N_2) \, d(\ln f_1).$$ (13.42)

An interesting example of this case (butyl sebacate at 20°C dissolved in methanol) was studied by Colmant (1954).

Analytical forms of activity coefficients are given in several publications (Prigogine and Defay, 1967, p. 339).

1. *Fugacity in Solution*

The fugacity φ_γ of a component γ is defined in a solution by the relation

$$\mu_\gamma = \mu_\gamma^*(T) + RT \ln \varphi_\gamma, \tag{13.43}$$

where $\mu_\gamma^*(T)$ is the standard function of a perfect gas.

When a solution (l) is in equilibrium with its vapor (v), we have

$$\begin{aligned} \mu_\gamma^l &= \mu_\gamma^*(T) + RT \ln \varphi_\gamma^l \\ \mu_\gamma^v &= \mu_\gamma^*(T) + RT \ln \varphi_\gamma^v, \end{aligned} \tag{13.44}$$

where φ_γ^l is the fugacity in the solution and φ_γ^v that in the vapor. At equilibrium,

$$\varphi_\gamma^l = \varphi_\gamma^v. \tag{13.45}$$

This means that, for two phases in equilibrium, each component has the same fugacity in the two phases.

Now, combining (13.43) and (13.18), we find the affinity of a reaction in solution

$$A = RT \ln[K_\varphi(T)/\varphi_1^{\gamma_1} \cdots \varphi_c^{\gamma_c}]. \tag{13.46}$$

Nevertheless, as vapor pressures of numerous dissolved substances are small, fugacities are not frequently used.

2. *Molar Concentration and Molality*

We know that the molar concentration of a solute C_s is given by

$$C_s = n_s/V = N_s/(N_1 v_1 + \sum_s N_s v_s). \tag{13.47}$$

If the solution is very dilute, $N_1 \simeq 1$, and

$$C_s \simeq N_s/v_1^\circ, \tag{13.48}$$

where v_1° is the specific molar volume of the pure solvent; the chemical potential given by (13.16) then reduces to

$$\mu_s = \mu_s^{\circ\circ}(T, p) + RT \ln f_s^c C_s \tag{13.49}$$

where

$$\mu_s^{\circ\circ}(T, p) = \mu_s^\circ(T, p) + RT \ln v_1^\circ(T, p). \tag{13.50}$$

For a reaction between dissolved substances, the affinity is given by

$$A = RT \ln[K^\circ(T, p)/(f_2^c C_2)^{\nu_2} \cdots (f_e^c C_e)^{\nu_e}], \tag{13.51}$$

where

$$RT \ln K^\circ(T, p) = -\sum_s \nu_s \mu_s^{\circ\circ}(T, p). \tag{13.52}$$

It follows that

$$K^\circ(T, p) = K(T, p)(v_1^\circ)^{-\nu}, \tag{13.53}$$

and, at equilibrium,

$$(f_2^c C_2)^{\nu_2} \cdots (f_e^c C_e)^{\nu_e} = K^\circ(T, p). \tag{13.54}$$

On the other hand, the molality of a dissolved substance m_s is defined by

$$m_s = 1000 n_s/n_1 M_1 = 1000 N_s/N_1 M_1. \tag{13.55}$$

For a dilute solution, $N_1 \simeq 1$ and

$$m_s \simeq 1000 N_s/M_1. \tag{13.56}$$

The chemical potential given by (13.16) then reduces to

$$\mu_s = \mu_s^\dagger(T, p) + RT \ln f_s^m m_s \tag{13.57}$$

where

$$\mu_s^\dagger(T, p) = \mu_s^\circ + RT \ln(M_1/1000). \tag{13.58}$$

The affinity of a reaction between dissolved substances is given by

$$A = RT \ln[K^\dagger(T, p)/(f_2^m m_2)^{\nu_2} \cdots (f_e^m m_e)^{\nu_e}] \tag{13.59}$$

and

$$K^\dagger(T, p) = K(T, p)(M_1/1000)^{-\nu}. \tag{13.60}$$

At equilibrium, we have

$$(f_2^m m_2)^{\nu_2} \cdots (f_e^m m_e)^{\nu_e} = K^\dagger(T, p). \tag{13.61}$$

Remarks. (1) In the three systems, the molar fractions, the concentrations and molalities, and the activity coefficients (f_s, f_s^c, f_s^m) have the same values in a dilute solution, but the three activities $(f_s N_s, f_s^c C_s, f_s^m m_s)$ are different.

(2) The standard affinities usually found in the literature are quantities related to molalities in dilute solutions.

I. EXCESS FUNCTIONS

The main problem with which we shall be concerned in this section is the effect of mixing two or more substances. In other words, we shall compare the properties of the mixture to those of the pure substances. In order to separate the effects of mixing from the effects of changes in temperature or pressure, we shall always compare the mixture to the pure components taken at the same pressure and temperature. The total volume V° of separate components with specific volumes v_γ° is given by

$$V^\circ = \sum_\gamma n_\gamma v_\gamma^\circ. \tag{13.62}$$

The change of the volume due to mixing V_m, is then

$$V_m = V - V^\circ = \sum_\gamma n_\gamma (v_\gamma - v_\gamma^\circ), \tag{13.63}$$

where V is the real volume of the solution.

Similarly, we have the enthalpy of mixing, the entropy of mixing, and the Gibbs free energy of mixing:

$$H_m = \sum_\gamma n_\gamma (h_\gamma - h_\gamma^\circ) \tag{13.64}$$

$$S_m = \sum_\gamma n_\gamma (s_\gamma - s_\gamma^\circ) \tag{13.65}$$

$$G_m = \sum_\gamma n_\gamma (\mu_\gamma - \mu_\gamma^\circ), \tag{13.66}$$

where the index $^\circ$ refers to the pure components in the same physical state as into the solution.

Other important quantities of the same kind are the molar functions

$$v_m = \sum_\gamma N_\gamma (v_\gamma - v_\gamma^\circ) \tag{13.67}$$

$$h_m = \sum_\gamma N_\gamma (h_\gamma - h_\gamma^\circ) \tag{13.68}$$

$$s_m = \sum_\gamma N_\gamma (s_\gamma - s_\gamma^\circ) \tag{13.69}$$

$$g_m = \sum_\gamma N_\gamma (\mu_\gamma - \mu_\gamma^\circ). \tag{13.70}$$

The enthalpy of mixing H_m is the heat absorbed by the system at

constant T and p because

$$\int dQ = \int dH = H - H_0 = H_m. \qquad (13.71)$$

Now, a solution will be described as perfect if the Gibbs free energy of mixing $g_m{}^p$ takes the following simple form

$$g_m{}^p = RT \sum_\gamma N_\gamma \ln N_\gamma. \qquad (13.72)$$

The corresponding heat of mixing $h_m{}^p$ and volume of mixing $v_m{}^p$ are zero. Alternatively, these properties may be used to test the validity of the laws of perfect solutions for a given mixture. For the entropy of mixing in a perfect solution, we find the positive expression

$$s_m{}^p = -R \sum_\gamma N_\gamma \ln N_\gamma > 0. \qquad (13.73)$$

Thus, in a perfect solution, all thermodynamic functions of mixing except those containing the entropy are zero.

The entropy of mixing (13.73) has a simple meaning. To obtain its interpretation, we must make use of the Boltzmann formula relating the number of accessible configurations of the system to the entropy. This problem is developed by Prigogine (1957).

From the experimental point of view, the discrepancies between real and perfect systems are better illustrated by the excess functions. The difference between the thermodynamic functions of mixing and the value corresponding to a perfect solution (superscript p) at the same T and p and composition will be called the thermodynamic excess function (denoted by subscript e). Thus,

$$v_e = v_m, \quad h_e = h_m, \quad s_e = s_m - s_m{}^p, \quad g_e = g_m - g_m{}^p. \qquad (13.74)$$

The Gibbs free energy of mixing may be represented by the following expressions [cf. (13.16) and (13.70)]

$$g_m = RT \sum_\gamma N_\gamma \ln f_\gamma N_\gamma, \qquad (13.75)$$

where f_γ is defined in the symmetrical reference system. On the other hand, since

$$\frac{\partial \mu_\gamma}{\partial p} = v_\gamma, \quad \frac{\partial \mu_\gamma}{\partial T} = -s_\gamma, \quad \frac{\partial(\mu_\gamma/T)}{\partial T} = -\frac{h_\gamma}{T^2}, \qquad (13.76)$$

we obtain

$$v_m = RT \sum_\gamma N_\gamma \, \partial(\ln f_\gamma)/\partial p$$

$$h_m = -RT^2 \sum_\gamma N_\gamma \, \partial(\ln f_\gamma)/\partial T \qquad (13.77)$$

$$s_m = -R \sum_\gamma N_\gamma \ln f_\gamma N_\gamma - RT \sum_\gamma n_\gamma \, \partial(\ln f_\gamma)/\partial T;$$

the excess thermodynamic quantities then become

$$v_e = RT \sum_\gamma N_\gamma \, \partial(\ln f_\gamma)/\partial p \qquad (13.78)$$

$$h_e = -RT^2 \sum_\gamma N_\gamma \, \partial(\ln f_\gamma)/\partial T \qquad (13.79)$$

$$s_e = -R \sum_\gamma N_\gamma \ln f_\gamma - RT \sum_\gamma N_\gamma \, \partial(\ln f_\gamma)/\partial T \qquad (13.80)$$

where the excess entropy is defined by

$$Ts_e = h_e - g_e. \qquad (13.81)$$

The excess volume v_e is found by measuring the mixing volume, h_e by the mixing heat, and g_e by vapor-pressure curves. The relation (13.81) then gives the value of the excess entropy. The orders of magnitude of the excess free energy, excess enthalpy, and excess entropy for mixtures of saturated hydrocarbons are shown in Figs. 28–31 for four systems studied by different authors.[*]

We observe that the contribution of the excess enthalpy and of the excess entropy (multiplied by T) to the excess free energy are of comparable magnitude.

In the case n-heptane + n-hexadecane (Fig. 28), g_e is negative (activity coefficients smaller than 1) and we have negative deviations from Raoult's law, since, when the activity coefficients are smaller than one, the partial vapor pressures are smaller than those of perfect solutions. However, for the other systems, we have positive deviations from Raoult's law and the partial vapor pressures are higher than those of a perfect

[*] For the system n-heptane + n-hexadecane at 20°C, see Brönsted and Koefeld (1946), Van der Waals and Hermans (1949). For the systems h-hexane + cyclohexane at 20°C and n-octane + tetraethylmethane at 50°C, see Prigogine and Mathot (1950a,b). For the system 2,2,4-trimethylpentane + hexadecane at 24.9°C, see Van der Waals (1950).
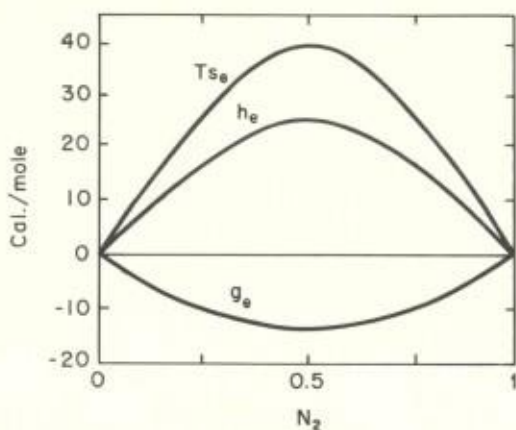
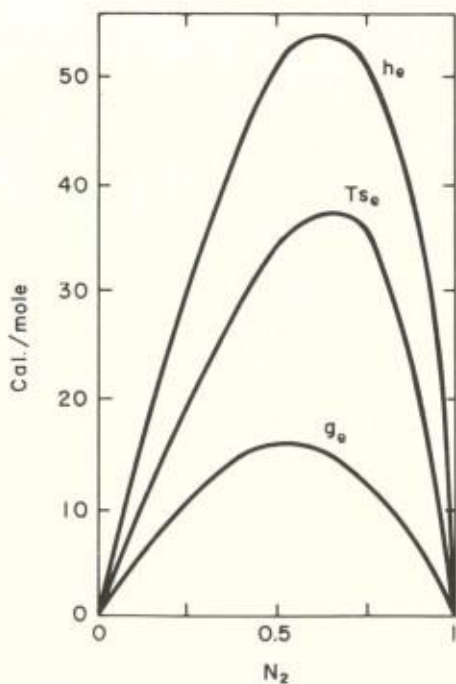FIG. 28. Excess functions for the system (1) n-heptane + (2) n-hexadecane at 20°C.

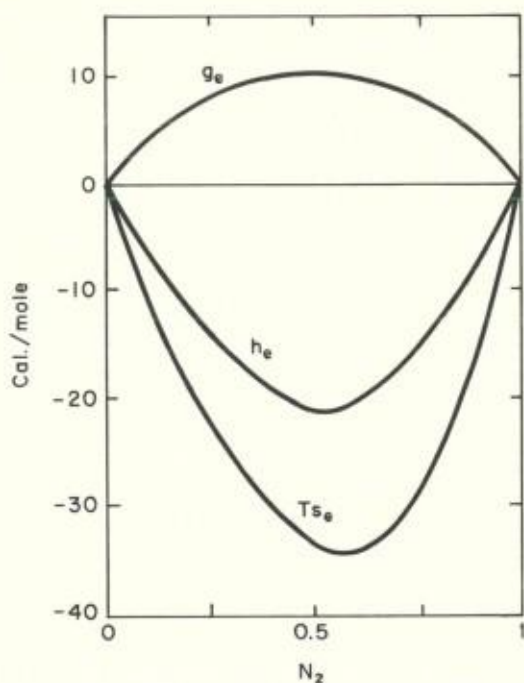FIG. 29. Excess functions for the system (1) n-hexane + (2) cyclohexane at 20°C.

FIG. 30. Excess functions for the system 2-2-4-trimethylpentane (1) + n-hexadecane (2) at 24.9°C.
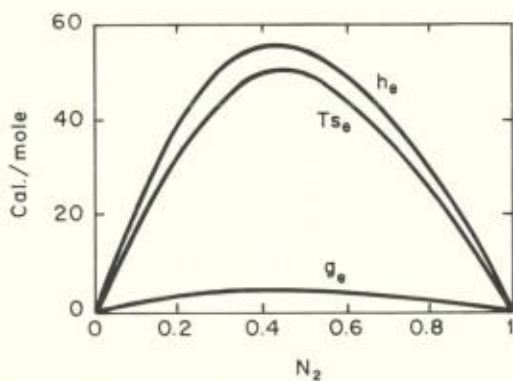

FIG. 31. Excess functions for the system (1) n-octane + (2) tetraethylmethane at 50°C.

solution. Generally, the excess functions have a simple parabolic form, but for some systems (like systems containing alcohol or water), they may be more complicated. The discrepancies to ideality are due to energy and entropy effects [difference of interactions (h_e) 1–1, 2–2, 1–2; entropy effects (s_e) related to the differences in molecular size].

In the system 2,2,4-trimethylpentane + hexadecane (Fig. 30), the entropy effect partially compensates the energy effect in such a way that $g_e \simeq 0$ (perfect solutions at 24.9°C). In the system n-octane + tetraethylmethane (Fig. 31), the excess entropy is negative, and this means that the mixing entropy is smaller than its value corresponding to a perfect solution. The orientation disorder is larger in the pure substance than in the mixture.

An interesting case is the system water + triethylamine (Fig. 32) (Haase and Rehage, 1955). The excess entropy s_e is negative and larger in absolute value than s_m^p; the mixing real entropy s_m is then negative. Nevertheless, the mixing exists because of the effect of the mixing en-
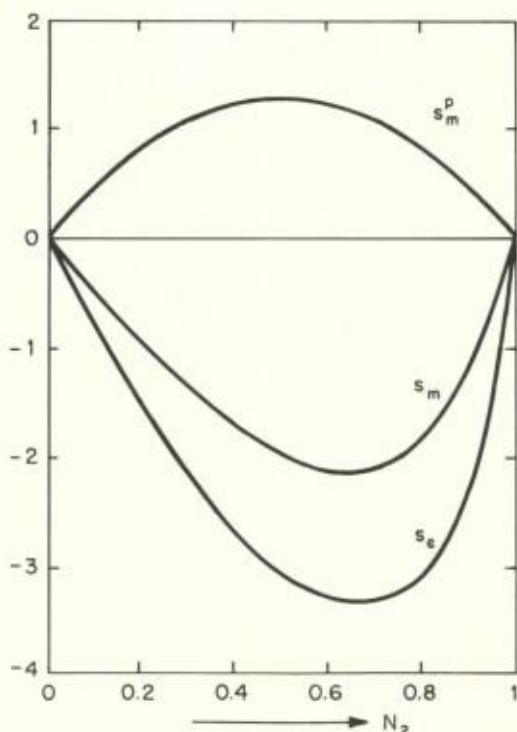

FIG. 32.   Excess entropy for the system triethylamine + water.

thalpy h_m. The condition of stability of miscibility is given by $g_m < 0$, and thus $h_m - Ts_m < 0$, which means that, if s_m is negative, h_m is also negative and large in absolute value. The mixture is exothermic.

Now, it is interesting to consider two limit cases for which the discrepancies are only related, on one hand, to the energetic effects, and on the other hand, to the entropy effects. First, from the above relations, it is easy to show that

$$\partial G_e/\partial T = -S_e, \tag{13.82}$$

where

$$G_e = RT \sum_\gamma n_\gamma \ln f_\gamma \tag{13.83}$$

$$\partial G_e/\partial n_\gamma = RT \ln f_\gamma \tag{13.84}$$

$$H_e = -RT^2 \sum_\gamma n_\gamma \partial(\ln f_\gamma)/\partial T \tag{13.85}$$

$$\partial H_e/\partial n_\gamma = -RT^2 \partial(\ln f_\gamma)/\partial T. \tag{13.86}$$

1. Regular Solutions

The term "regular solutions" was introduced by Hildebrand[*] to describe mixtures whose excess entropy was found experimentally to be zero. Deviations from ideality arise entirely from the energetic term:

$$|h_e| \gg T|s_e|, \qquad g_e \simeq h_e, \qquad s_e \simeq 0. \tag{13.87}$$

For a binary system, we obtain

$$\partial S_e/\partial n_1 = 0, \qquad \partial S_e/\partial n_2 = 0 \tag{13.88}$$

and

$$\partial^2 G_e/\partial T \, \partial n_1 = 0, \qquad \partial^2 G_e/\partial T \, \partial n_2 = 0, \tag{13.89}$$

$$\partial(RT \ln f_1)/\partial T = 0, \qquad \partial(RT \ln f_2)/\partial T = 0, \tag{13.90}$$

so that

$$\ln f_1 \propto 1/T, \qquad \ln f_2 \propto 1/T. \tag{13.91}$$

The activity coefficients for regular solutions are thus inversely proportional to the absolute temperature.

[*] See Fowler and Guggenheim (1939), Hildebrand (1929), Guggenheim (1935), Prigogine (1957).

2. Athermal Solutions

Here, the deviations from ideality arise entirely from the entropy term, the mixing heat being zero (this is the origin of the term athermal):

$$T \mid s_e \mid \gg \mid h_e \mid, \qquad g_e \simeq -Ts_e, \qquad h_e \simeq 0. \qquad (13.92)$$

For a binary system,

$$\partial H_e / \partial n_1 = 0, \qquad \partial H_e / \partial n_2 = 0, \qquad (13.93)$$

so that

$$\partial(\ln f_1)/\partial T = 0, \qquad \partial(\ln f_2)/\partial T = 0. \qquad (13.94)$$

The activity coefficients of athermal solutions are independent of temperature.

XIV. Osmotic Pressure

Measurements of osmotic pressure are frequently used to determine activity coefficients and solution molecular weights. The measurements are particularly useful in the determination of the properties of polymer solutions. The system under consideration consists of a liquid solution of components (phase ') separated from pure liquid (phase ") by a non-deformable heat-conducting membrane permeable to component 1 alone (Fig. 33). The temperature is assumed to be uniform in the system.

The affinity of passage of component 1 from the phase " to the phase ' is

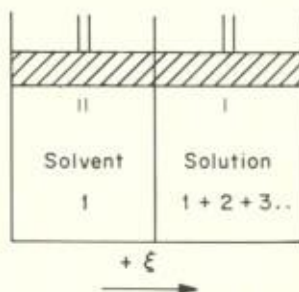$$A = \mu_1'' - \mu_1' = \mu_1°(T, p'') - \mu_1°(T, p') - RT \ln f_1' N_1', \quad (14.1)$$

FIG. 33. Osmotic phenomena.

where μ_1° is the same function in the two phases. Let us assume now that $p'' = p'$. Equation (14.1) reduces to

$$(A)_{p''-p'} = -RT \ln f_1' N_1'. \tag{14.2}$$

This affinity cannot be equal to zero unless $N_1' = 1$, which means that the solvent is pure in each phase. In other words, when substances are dissolved in the solution, we have $N_1' < 1$ and the affinity $(A)_{p''-p'}$ is positive; the solvent tends to pass from the pure solvent ($''$) to the solution ($'$) and increases in this solution phase. Hence, equilibrium cannot be established unless $p'' \neq p'$. The difference

$$\Pi = p' - p'' \tag{14.3}$$

is called osmotic pressure.

At equilibrium, (14.1) reduces to

$$\mu_1^\circ(T, p'') - \mu_1^\circ(T, p') = RT \ln f_1' N_1'. \tag{14.4}$$

For a displacement along an equilibrium line at T constant, we have

$$\frac{\partial \mu_1^\circ}{\partial p''} \delta p'' - \frac{\partial \mu_1^\circ}{\partial p'} \delta p' = RT \, \delta(\ln f_1' N_1'). \tag{14.5}$$

with

$$\frac{\partial \mu_1^\circ}{\partial p''} = v_1^s(T, p''), \qquad \frac{\partial \mu_1^\circ}{\partial p'} = v_1^s(T, p'), \tag{14.6}$$

where the quantity v_1^s is the standard molar volume.

Neglecting the compressibility of component 1, (14.5) and (14.3) give

$$\delta \Pi = -(RT/v_1^\circ) \, \delta(\ln f_1' N_1'), \tag{14.7}$$

where v_1° is the molar volume of the solvent extrapolated to zero pressure. Integrating (14.7) from $N_1' = 1$ ($\Pi = 0$) to $N_1' = N_1'$, we obtain

$$\Pi = -(RT/v_1^\circ) \ln f_1' N_1'. \tag{14.8}$$

For a sucrose solution of $0.88 \text{ mol } 1^{-1}$, the experimentally observed (Eucken, 1934) osmotic pressure is about 27 atm.

Instead of characterizing deviations from ideality of the solvent by its activity coefficient f_1, it is often advantageous to introduce the osmotic coefficient Γ of Bjerrum and Guggenheim defined by the equality

$$\Gamma \ln N_1 = \ln f_1 N_1. \tag{14.9}$$

Comparing this with (14.8), we see that

$$\Pi = -\Gamma(RT/v_1^\circ) \ln N_1'. \tag{14.10}$$

For very dilute solutions, (14.10) reduces to

$$\Pi = \Gamma RT \sum_s C_s'. \tag{14.11}$$

For an ideal dilute solution $(C_s' \leq 10^{-6} \text{ mol l}^{-1})$, we find the classical van't Hoff equation

$$\Pi = RT \sum_s C_s', \tag{14.12}$$

which shows that the osmotic pressure is independent of the nature of the solvent.

For a weak electrolyte $AB \rightleftharpoons A^- + B^+$, Eq. (14.11) may be rewritten

$$\Pi = \Gamma RT(1 + \alpha)C_{AB}^\circ, \tag{14.13}$$

where α is the dissociation degree and C_{AB}° the total concentration of AB. The coefficient Γ may be calculated if we know the experimental values of Π and α (known, for instance, by electrical conductivity measurements).

Remark. Comparing (14.2) to (14.8), it follows that the affinity for $p'' = p'$ is given by

$$(A)_{p'=p''} = v_1^\circ \Pi. \tag{14.14}$$

XV. Equilibrium Curves between Two Phases

A. Generalization of the Nernst Distribution Law

We know that the affinity A_γ of transfer of component γ from one phase (') to the other ('') is given by

$$A_\gamma = \mu_\gamma' - \mu_\gamma'' = \mu_\gamma'^\circ(T, p) - \mu_\gamma''^\circ(T, p) + RT \ln(f_\gamma' N_\gamma'/f_\gamma'' N_\gamma''). \tag{15.1}$$

At equilibrium,

$$f_\gamma'' N_\gamma''/f_\gamma' N_\gamma' = K_\gamma(T, p), \tag{15.2}$$

where we have put

$$RT \ln K_\gamma(T, p) = \mu_\gamma'(T, p) - \mu_\gamma''(T, p). \tag{15.3}$$

For ideal phases, (15.2) reduces to the classical Nernst distribution law
(see 6.80)

$$N_\gamma''/N_\gamma' = K_{\gamma N}(T, p). \tag{15.4}$$

The quantity K_γ is called the distribution or partition coefficient. At
T and p constant, the equilibrium constant K_γ is independent of mole
fractions.

Remark. The distribution law of matter in an electric field was estab-
lished a few years ago by Sanfeld and co-workers (1968c).

B. Van Laar Relation

For a general displacement along an equilibrium line, (15.2) becomes

$$\delta\left[\ln \frac{f_\gamma'' N_\gamma''}{f_\gamma' N_\gamma'}\right] = \delta[\ln K_\gamma(T, p)] = \frac{\partial(\ln K_\gamma)}{\partial p} \delta p + \frac{\partial(\ln K_\gamma)}{\partial T} \delta T. \tag{15.5}$$

We thus find from (9.48) and (9.49) that

$$\delta\left[\ln \frac{f_\gamma'' N_\gamma''}{f_\gamma' N_\gamma'}\right] = -\frac{r_{Tp}^s(\gamma)}{RT^2} \delta T - \frac{\Delta_{Tp}^s(\gamma)}{RT} \delta p \tag{15.6}$$

This is the well-known van Laar equation, which we now apply to dif-
ferent cases:

1. *Binary Systems Forming a Eutectic*

Let us consider first the equilibrium between the solution (') and one
pure solid phase ('') and the transfer of component 1 from the solution
to the solid phase (''):

$$N_1'' = 1, \qquad N_2'' = 0, \qquad f_1'' = 1.$$

Applying the van Laar relation (15.6) for a displacement at constant p,
we obtain

$$\delta(\ln f_1' N_1') = \frac{L_{f_1}}{R} \frac{\delta T}{T^2}, \tag{15.7}$$

where

$$L_{f_1} = r_{Tp}^s(1) \tag{15.8}$$

is the latent heat of fusion at the pressure considered.

For a pure system, $N_1' = 1$ and $N_1'' = 1$, the variance is equal to unity and we called T_{10} the fusion temperature of component 1 at the pressure considered.

Integrating (15.7) from a point $N_1' = 1$ ($f_1' = 1$, $T = T_{10}$) to the required value of N_1', we obtain the equilibrium curve of a solution with crystals 1:

$$\ln f_1' N_1' = \frac{L_{f_1}}{R} \left[\frac{1}{T_{10}} - \frac{1}{T} \right]. \tag{15.9}$$

If we assume the solution phase to be perfect, this simplifies to

$$\ln N_1' = \frac{L_{f_1}}{R} \left[\frac{1}{T_{10}} - \frac{1}{T} \right], \tag{15.10}$$

where $T < T_{10}$.

This approximate equation is that of the line of coexistence at a given pressure given in Fig. 34.
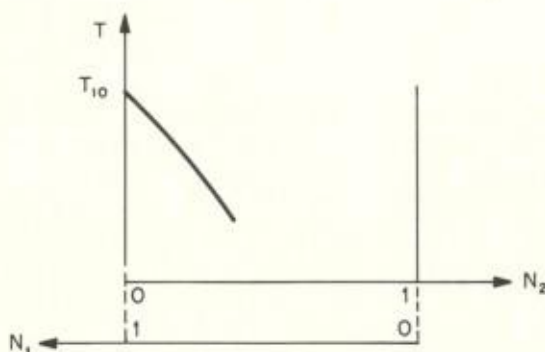
FIG. 34.   Shape of freezing-point curve.

We define the depression θ of the freezing point of the solution by

$$\theta = T_{10} - T.$$

For very dilute solutions, $\theta \ll T$ and $1/T \simeq \theta/T_{10}^2$; thus, (15.9) reduces to

$$\frac{L_{f_1} \theta}{R T_{10}^2} \simeq \Gamma \sum_s N_s', \tag{15.11}$$

where the osmotic coefficient Γ is defined by (14.9).

The lowering of the freezing point is then given by

$$\theta = \Gamma \frac{RT_{10}^2}{L_{f_1}} \sum_s N_s'. \tag{15.12}$$

If a solution is both very dilute and ideal, $\Gamma = 1$, and we have, in terms of molalities,

$$\theta = \frac{RT_{10}^2}{L_{f_1}} \frac{M_1}{1000} \sum_s m_s' = \theta_c \sum_s m_s'; \tag{15.13}$$

the quantity θ_c is called the cryoscopic or freezing-point constant. It depends only on the nature of the solvent. For water, $\theta_c = 1.86$, while for benzene, $\theta_c = 5.08$.

For a substance 2, the coexistence line BE (Fig. 35) is represented by the equation

$$\ln f_2' N_2' = \frac{L_{f_2}}{R} \left[\frac{1}{T_{20}} - \frac{1}{T} \right]. \tag{15.14}$$

At the eutectic point, crystals of both 1 and 2 and the solution coexist in equilibrium and the two equations (15.9) and (15.14) are simultaneously satisfied.

If the solution is perfect, N_{2e}' and T_e (values at the eutectic point) can be calculated from

$$\ln N_{2e}' = \frac{L_{f_2}}{R} \left[\frac{1}{T_{20}} - \frac{1}{T_e} \right]$$
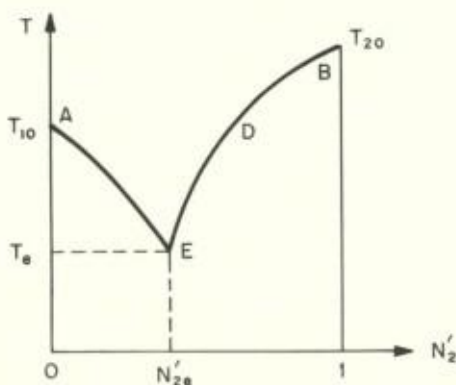$$\ln(1 - N_{2e}') = \frac{L_{f_1}}{R} \left[\frac{1}{T_{10}} - \frac{1}{T_e} \right]. \tag{15.15}$$

FIG. 35. Crystallization or freezing-point curves at constant pressure, with eutectic point.

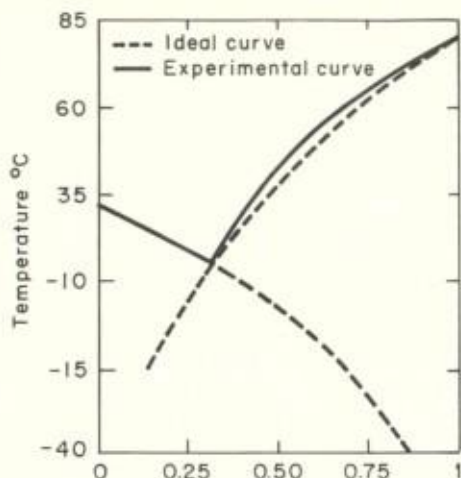FIG. 36. Freezing point curves for $o + p$-chloronitrobenzene.

An example (Hollman, 1900; Kohman, 1925; Timmermans, 1936, p. 54) is given in Fig. 36.

Remarks. (1) In the case of saturated salt solutions (excluding the formation of mixed crystals)—for example, $H_2O + NaCl$—the line AE is called the freezing curve, while the line EB is called the solubility curve of e.g., NaCl. A better definition is "crystallization" curves.

The solubility is obtained by solving Eq. (15.14); it increases with the temperature (line ED).

The heat of fusion of ice in the presence of aqueous solutions of NaCl and $CaCl_2 \cdot 6H_2O$ has been calculated by Defay and Sanfeld (1959).

(2) The equilibrium between a crystalline substance i and its ions in solution is governed by the equation

$$\mu_i^s(T, p) = \nu_+ \mu_+ + \nu_- \mu_-, \tag{15.16}$$

where μ_i^s is the chemical potential of the solid. For example, for the system $NaCl = Na^+ + Cl^-$, the equilibrium condition is

$$\mu_{NaCl}^s = \mu_{Na^+} + \mu_{Cl^-} = \mu_{Na^+}^\circ(T, p) + \mu_{Cl^-}^\circ(T, p) + RT \ln f_{Na^+}^c C_{Na^+}$$
$$\times f_{Cl^-}^c C_{Cl^-}) \tag{15.17}$$

or

$$f_{Na^+}^c C_{Na^+} f_{Cl^-}^c C_{Cl^-} = \exp\left\{ \frac{\mu_{NaCl}^s - \mu_{Na^+}^\circ - \mu_{Cl^-}^\circ}{RT} \right\}. \tag{15.18}$$

At a given temperature and pressure, the product of activities is thus a constant called the solubility product K_S. For very dilute solutions, (15.18) reduces to

$$C_{Na^+}C_{Cl^-} = K_S(T, p). \tag{15.19}$$

Since the equilibrium Nernst tension of a cell depends on ion concentrations, it is clear that the solubility product K_S can be determined by electromotive-force measurements (Petré *et al.*, 1969).

2. *Mixed Crystals*

Let us now consider the same components in a liquid and a solid phase. At constant pressure, N_2'' and N_2' can be calculated with the aid of the van Laar equations (15.6):

$$\delta\left[\ln\frac{f_1''N_1''}{f_1'N_1'}\right] = -\frac{r_{Tp}^s(1)}{RT^2}\,\delta T$$

$$\delta\left[\ln\frac{f_2''N_2''}{f_2'N_2'}\right] = -\frac{r_{Tp}^s(2)}{RT^2}\,\delta T. \tag{15.20}$$

Details of calculations are given by Prigogine and Defay (1967, Chapter XXIII). For the system Cu + Ni, the theoretical and experimental curves (Seltz, 1934) are in good agreement, showing that this system is nearly ideal (Fig. 37).
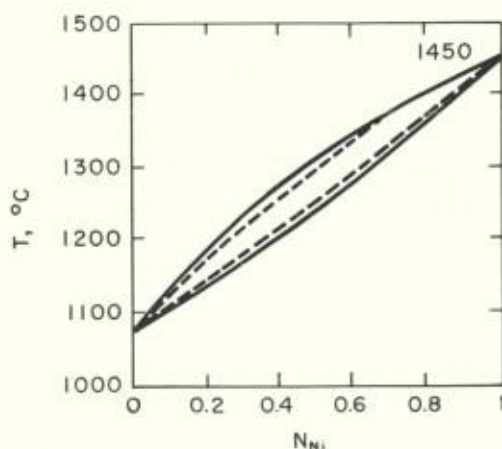

FIG. 37. Phase diagram of system Cu + Ni (———) observed; (– – – –) ideal.

On the other hand, treating the two phases as regular solutions, Scatchard and Hamer (1935) have calculated the liquidus and solidus curves. The results for the systems Ag + Pd and Au + Pt (Scatchard and Hamer, 1935; Doerinckel, 1907; Grigorjew, 1929) are shown in Figs. 38 and 39.
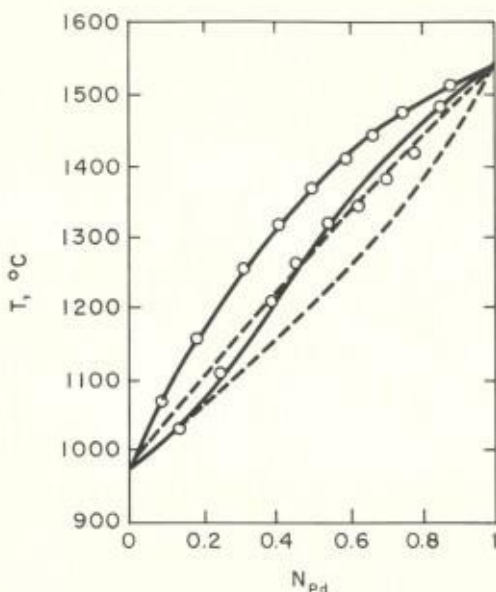

FIG. 38. Freezing-point diagram for the system Ag + Pd.

Remarks. (1) The systems Mn–Cu, Fe–V, Ni–Pd form azeotropes (see Section V).

(2) Transition from mixed crystals to addition compounds and eutectics with the phenomenon of miscibility gaps has been observed for many systems (Timmermans, 1936, p. 76).

3. *Boiling-Point Law*

When a solute species 2 may be regarded as nonvolatile, the vapor phase ($''$) contains only the component 1 (Fig. 40). We then have $N_1'' = 1$ and $f_1'' = 1$, and, at p constant, (15.6) reduces to

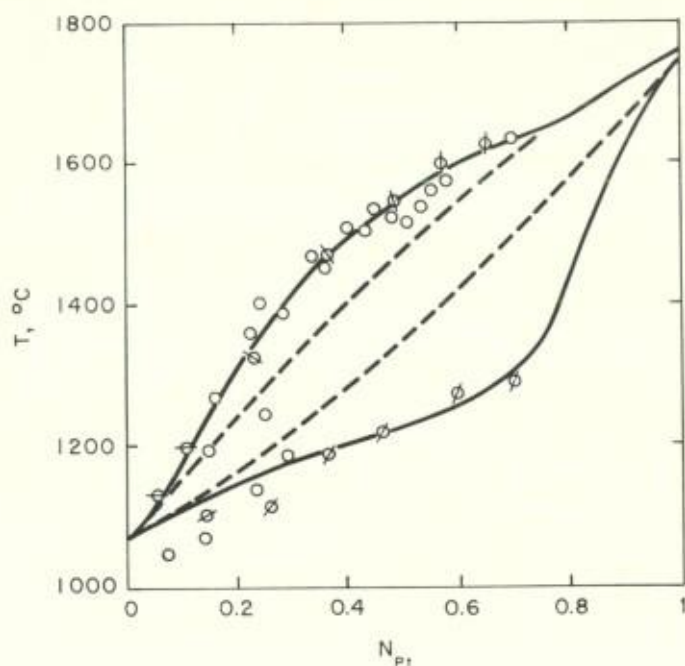$$\delta(\ln f_1' N_1') = \frac{r_{Tp}^3(1)}{RT^2} \delta T, \tag{15.21}$$

FIG. 39. Freezing-point diagram for the system Au + Pt. (———) calculated; (————) ideal; (○) measured (Doerinckel); (∅) measured (Grigorjew).
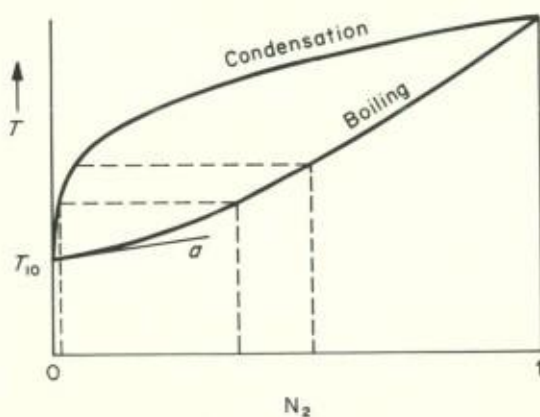

FIG. 40. Boiling-point and condensation curves for solution of nonvolatile solute.

where $r_{Tp}^s(T)$ has a negative value (to permit vaporization, the system must absorb an amount of heat), and thus

$$r_{Tp}^s(1) = -L_v(1), \tag{15.22}$$

where $L_v(1)$ is the heat of vaporization of pure component 1, boiling at the considered temperature.

Integrating (15.21), we find the equation of the boiling curve

$$\ln f_1' N_1' = \frac{L_v(1)}{R} \left[\frac{1}{T} - \frac{1}{T_{10}} \right]. \tag{15.23}$$

For a perfect solution,

$$\ln N_1' = \frac{L_v(1)}{R} \left[\frac{1}{T} - \frac{1}{T_{10}} \right], \tag{15.24}$$

and thus $T > T_{10}$, which means an elevation of boiling temperature resulting from the addition of a nonvolatile solute.

Equation (15.23) may be rewritten in molalities (see Eqs. 15.11), (15.12), and (15.13)

$$\theta = \Gamma \theta_e \sum_s m_s', \tag{15.25}$$

where the boiling point or ebullioscopic constant θ_e is defined in dilute solutions by

$$\theta_e = \frac{RT_{10}^2}{L_v(1)} \frac{M_1}{1000}. \tag{15.26}$$

In a perfect binary solution, the elevation of boiling point is proportional to the molality of the dissolved substance. The coefficient θ_e is only a function of the solvent. For water, $\theta_e = 0.51°C$; for benzene, $\theta_e = 2.53°C$.

4. Boiling Curves for Immiscible Liquids

For immiscible liquids (for example, hydrocarbon + water), we observe a eutectic-point vapor–liquid (Fig. 41). The only difference between this system and the liquid–solid system is that here the condensed phase is the liquid state. Two immiscible liquid components boil at the vapor–liquid eutectic-point.

Example. The boiling point of cooking fat is about 170°C. An addition of water decreases this temperature to under 100°C. Neglecting the small effect of surface tension, the pressure inside the bubble is identical to
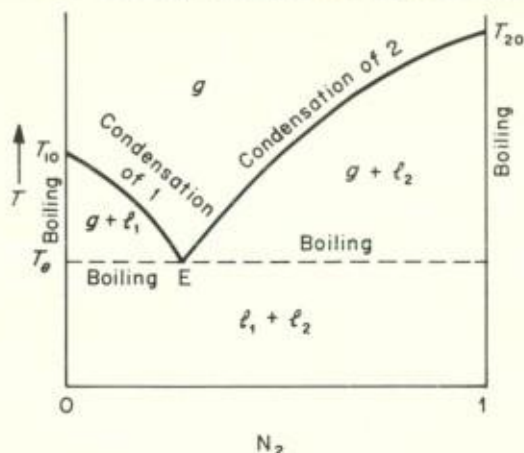
FIG. 41. Evaporation of immiscible liquids at constant pressure.

that in the liquid. If the bubble forms at the boundary of two liquids (1 and 2), the pressure in the bubble is equal to the pressure p in the liquid, but $p = p_1 + p_2$, where p_1 and p_2 are the partial vapor pressures of components 1 and 2. At atmospheric pressure, $p = p_a$ and the boiling point occurs at a temperature lower than that which should give $p_1 = p_a$ and $p_2 = p_a$. This phenomenon has an industrial application: steam distillation. Let us now calculate the boiling temperature of two liquids in contact. The evaporation of immiscible liquids at constant temperature is given in Fig. 42.
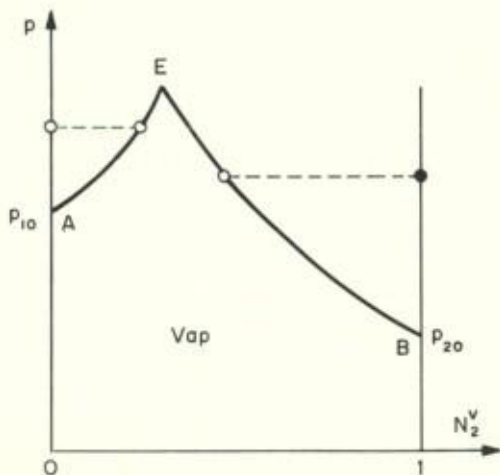

FIG. 42. Evaporation of immissible liquids at constant temperature.

Applying the van Laar relation at T constant, we obtain for the vapor phase ($''$)

$$\delta(\ln N_1'') = -\frac{\Delta_{Tp}^s(1)}{RT}\,\delta p, \tag{15.27}$$

where $\Delta_{Tp}^s(1)$ is the dilatation related to the transfer of component 1 from the liquid to the vapor. As a first approximation, let us assume that

$$\Delta_{Tp}^s(1) \simeq RT/p. \tag{15.28}$$

Putting (15.28) in (15.27) and integrating from $N_1'' = 1$ to N_1'', we get

$$\ln N_1'' = \ln(p_{10}/p) \tag{15.29}$$

curve AE: $N_1'' = p_{10}/p$

curve BE: $N_2'' = p_{20}/p.$

At the eutectic point, we have

$$N_{1e}'' = p_{10}/p_e, \qquad N_{2e}'' = p_{20}/p_e; \tag{15.30}$$

thus,

$$N_{1e}''/N_{2e}'' = p_{10}/p_{20} \tag{15.31}$$

$$p_e = p_{10} + p_{20}. \tag{15.32}$$

The ratio of the molar fractions of the two components in the eutectic vapor phase is equal to the ratio of the vapor pressures of the pure substances. The eutectic vapor–liquid pressure at a given temperature is equal to the sum of the vapor pressures of the pure substances at this temperature (Gay-Lussac's law).

Remark. Vapor–liquid equilibria of partially miscible systems can also be found (Prigogine and Defay, 1967, p. 356).

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