CHAPTER 5

METALLURGICAL THERMODYNAMICS

D.R. GASKELL

School of Materials Engineering
Purdue University
West Lafayette, IN 47907, USA

R.W. Cahn and P. Hansen, eds.
Physical Metallurgy: fourth, revised and enhanced edition
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1. Introduction

Metallurgical thermodynamics is concerned with the equilibrium states of existence available to systems, and with the effects of external influences on the equilibrium state. The thermodynamic state of a system is defined in terms of state variables (or state functions) and the state variables occur in two categories: intensive variables such as pressure, \( P \), and temperature, \( T \), the values of which are independent of the size of the system, and extensive variables such as internal energy, \( U \), and volume, \( V \), the values of which are dependent on the size of the system. The simplest equation of state is the ideal gas law,

\[
P V = nRT
\]

where \( n \) is the number of moles of the gas and \( R \) is the universal gas constant. In considering a fixed quantity of ideal gas, only two of the state functions in eq. (1) are independent and the other is dependent. Thus, in a three-dimensional diagram employing \( P, V \) and \( T \) as coordinates, the equilibrium states of existence of the fixed quantity of gas lie on a definite surface. In any reversible change of state of the gas the path of the process lies on this equilibrium surface, such that, in moving from the initial to the final state, the gas passes through a continuum of equilibrium states. Under such conditions the work, \( w \), done on or by the gas during the process is given by:

\[
w = \int_{V_i}^{V_f} P dV,
\]

and thus the magnitude of \( w \) is dependent on the actual process path taken over the equilibrium surface between the final and initial states. In an irreversible process the state of the gas momentarily leaves the equilibrium surface while moving between the initial and final states.

1.1. The First and Second Laws of Thermodynamics

When a system undergoes a process in which it moves from one state to another, the change in the internal energy of the system, \( \Delta U \), is given by:

\[
\Delta U = U_f - U_i = q - w_i
\]

where \( q \) is the heat entering or leaving the system and \( w \) is the work done on or by the system during the change of state. For an increment of the process the change is:

\[
\Delta U = dq - dw
\]

Equations (3) and (4) are statements of the First Law of Thermodynamics. By convention, heat entering the system and work done by the system are positive quantities. Equation (3) is remarkable in that, although the individual values of \( q \) and \( w \) are dependent on the path taken by the system between the initial and final states, their algebraic sum (which is the difference between \( U_f \) and \( U_i \)) is independent of the process path. Thus integration of eq. (4) to obtain eq. (3) requires that the process path be known and that the process be conducted reversibly.

The Second Law of Thermodynamics states that, for a reversible change of state, the integral of \( dq/T \) is independent of the process path. As one of the properties of a state function is that the difference between the values of the function in any two thermodynamic states is independent of the process path, taken by the system in moving between the two states, the term \( dq/T \) is the differential of a state function. The state function entropy, \( S \), is thus defined as:

\[
dS = dq/T
\]

If change in volume against an external pressure is the only form of work performed during a reversible change of state of a closed system, the work performed is given by eq. (2), and substitution of eqs. (2) and (5) into eq. (4) gives:

\[
dU = T dS - P dV
\]

Equation (6), which is a combination of the First and Second Laws of Thermodynamics, gives the variation of \( U \) as the dependent variable with \( S \) and \( V \) as the independent variables.

From consideration of the difference between reversible and irreversible processes and the Second Law, eq. (6) gives the following criteria for thermodynamic equilibrium in a closed system of fixed composition:

(i) \( S \) is a maximum at constant \( U \) and \( V \);

(ii) \( U \) is a minimum at constant \( S \) and \( V \).

Equation (6) involves the extensive thermodynamic properties \( S \) and \( U \) as independent variables. Although it is possible to measure and, with sufficient ingenuity on the part of the experimenter, to control the volume of a system, experimental control of the entropy of a system is virtually impossible, and consequently the criteria for equilibrium obtained from eq. (6) are not of practical use. From the practical point of view it would be desirable to have an equation as simple in form as eq. (6) but in which the independent variables are the intensive properties \( P \) and \( T \), both of which are amenable to experimental measurement and control. Such an equation would also provide a criterion for equilibrium in a constant pressure-constant temperature system.

1.2. Auxiliary thermodynamic functions

The required auxiliary state functions are generated by Legendre transformations of \( U \). For example, in eq. (6), written as:

\[
U = U(S, V)
\]

a Legendre transform, \( H \), of \( U \) is obtained using:

\[
-H = \left( \frac{\partial U}{\partial V} \right)_{S, T} = \frac{U - H}{V - 0}.
\]

At constant \( S \), the tangent to the variation of \( U \) with \( V \) passes through the points \( U = U \), \( V = V \) and \( U = H \), \( V = 0 \). Rearrangement of eq. (7) gives:

References: p. 469.
\[ H = U + PV, \]

which, on differentiation, gives:

\[ \frac{dH}{dV} = dU + PdV + Vdp. \]  

(8)

Substitution of eq. (6) into eq. (8) gives:

\[ dH = \frac{dH}{dS} dS + Vdp. \]  

(9)

in which the extensive variable \( V \) has been replaced by the intensive variable \( P \). The transform \( H \) is called the \textit{enthalpy}.

Writing eq. (9) as

\[ H = H(S, P), \]

a Legendre transform, \( G \), of \( H \) is obtained as:

\[ G(S, P) = H - TS, \]  

(10)

which, on differentiation, gives:

\[ \frac{dG}{dS} = dH - TdS - SdT = -SdT + Vdp. \]  

(11)

in which the extensive variable \( S \) has been replaced by the intensive variable \( T \). This transform, \( G \), is called the \textit{Gibbs free energy}. Being dependent on the independent variables \( T \) and \( P \), the Gibbs free energy is the most useful of thermodynamic functions and provides the practical criterion that, at constant \( T \) and \( P \), thermodynamic equilibrium is established when the Gibbs free energy is minimized.

A third Legendre transform yields the \textit{Helmholtz free energy}, or work function \( A \), defined as

\[ A = U - TS. \]

In a multicomponent system containing \( n_i \) moles of component \( i \), \( i \) moles of component \( j \), etc.,

\[ G = G(T, P, n_1, n_2, \ldots, n_i) \]

and thus,

\[ dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP + \left( \frac{\partial G}{\partial n_i} \right)_T dn_i + \ldots \left( \frac{\partial G}{\partial n_j} \right)_T dn_j, \]  

(12)

The derivative

\[ \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \]

is of particular significance and is called the \textit{chemical potential}, \( \mu_i \), or the partial molar free energy, \( G_i \), of the component \( i \). Thus, in view of eq. (11), eq. (12) can be written as

\[ dG = -SdT + Vdp + \sum \mu_i dn_i, \]  

(13)

and the equilibrium state of any system undergoing any type of reaction at constant temperature and pressure can be determined by application of this equation.

2. **Metallurgical thermochemistry**

2.1. The measurement of changes in enthalpy

In order to distinguish between the value of an extensive property of a system containing \( n \) moles and the molar value of the property, the former will be identified by the use of a prime (') e.g., with respect to enthalpy, \( H' = nH \).

From eqs. (5) and (9), for a process occurring reversibly at constant pressure \( P \):

\[ dH' = dq_r, \]

which, on integration, gives:

\[ \Delta H' = q_r. \]

Thus, in a system undergoing a process in which the only work performed is the work of expansion or contraction against the constant pressure \( P \), the change in enthalpy, \( \Delta H' \), can be measured as the heat \( q_r \) entering or leaving the system during the constant pressure process. In the case of heat entering the system the process involves an increase in the temperature of the system and the \textit{constant pressure molar heat capacity}, \( c_p \), is defined as:

\[ c_p = \left( \frac{dq}{dT} \right)_P. \]  

(14)

The constant pressure molar heat capacity of a system can be measured by the methods of calorimetry. In metallurgical applications the measured values are fitted to an equation of the form

\[ c_p = a + bT + cT^{-2}. \]

For example, the constant pressure molar heat capacity of solid silver varies with temperature in the range 298–1234 K as:

\[ c_{p,Ag(s)} = 21.3 + 8.54 \times 10^{-3}T + 1.51 \times 10^{5}T^{-2} \text{ J/K mole} \]

and hence, from eq. (14), the difference between the molar enthalpy of solid Ag at a temperature \( T \) and the molar enthalpy at 298 K is
\[ \Delta H = \int_{298}^{T} c_p, Ag \, dT \]
\[ = 21.3(T - 298) + 4.27 \times 10^{-3}(T^2 - 298^2) \]
\[ - 1.51 \times 10^{5} \left( \frac{1}{T} - \frac{1}{298} \right) \mathrm{J/mole}, \]
which is thus the quantity of heat required to raise the temperature of one mole of solid Ag from 298 K to T.

Transformation of a low-temperature phase to a high-temperature phase involves the absorption of the latent heat of the phase change, e.g., the transformation of one mole of silver from the solid to the liquid state at the normal melting temperature of 1234 K requires a heat input of 11.09 kJ. Thus at 1234 K the molar enthalpy of melting of Ag, \( \Delta H_m \), is
\[ \Delta H_{m, Ag} \text{ at 1234 K} = H_{Ag(l)1234 K} - H_{Ag(s)1234 K} = 11.09 \text{kJ}. \]

The molar heat capacity of liquid Ag is independent of temperature, \( c_{p, Ag(l)} = 30.5 \text{ J/K mol} \), and the difference between the molar enthalpy of liquid Ag at a temperature \( T \) and the molar enthalpy of solid Ag at 298 K is
\[ H_{Ag(l)T} - H_{Ag(s)298 K} = \int_{298}^{T} c_{p, Ag(l)} \, dT + \Delta H_{m, Ag} \text{ at 1234 K} + \int_{298}^{T} c_{p, Ag(l)} \, dT. \]

As chemical reactions involve the absorption or evolution of heat, they also necessarily involve changes in enthalpy. For example, when conducted at 298 K, the oxidation reaction
\[ 2Ag(s) + \frac{1}{2}O_2(g) = Ag_2O(s) \]
is accompanied by the evolution of 30.5 kJ of heat per mole of \( Ag_2O \) produced. Thus,
\[ q = \Delta H = -30.5 \text{kJ}, \]
or the system existing as one mole of \( Ag_2O \) has an enthalpy of 30.5 kJ less than the system existing as two moles of Ag and half a mole of oxygen gas at 298 K.

As the enthalpies of substances are not measurable quantities, i.e., only changes in enthalpy can be measured (as the evolution or absorption of heat), it is conventional to designate a reference state in which the relative enthalpy is zero. This reference state is the elemental substance existing in its stable form at 298 K and \( P = 1 \text{ atm} \). In practice the designation of \( P = 1 \text{ atm} \) is relatively unimportant as the enthalpies of condensed phases are not significantly dependent on pressure and the enthalpy of an ideal gas is independent of pressure. Thus, in the above example:
\[ \Delta H_{298} = H_{Ag_2O(s)298} - 2H_{Ag(s)298} - \frac{1}{2} H_{O_2(g)298}. \]

As \( H_{Ag_2O298} \) and \( H_{O_2298} \) are arbitrarily assigned values of zero, the relative molar enthalpy of \( Ag_2O \) at 298 K is simply equal to the experimentally measured molar heat of formation of \( Ag_2O \) at 298 K. At any other temperature \( T \):
\[ \Delta H_T = H_{Ag_2O(T)} - 2H_{Ag(T)} - \frac{1}{2} H_{O_2(T)} \]
\[ = H_{Ag_2O298} + \int_{298}^{T} c_{p, Ag_2O} \, dT - 2H_{Ag298} - 2\int_{298}^{T} c_{p, Ag} \, dT \]
\[ - \frac{1}{2} H_{O_2298} - \int_{298}^{T} c_{p, O_2} \, dT \]
\[ = \Delta H_{298} + \int_{298}^{T} \Delta c_v \, dT, \]
where
\[ \Delta c_v = c_{p, Ag_2O} - 2c_{p, Ag} - \frac{1}{2} c_{p, O_2}. \]
The enthalpy–temperature diagram for the oxidation of silver is shown in fig. 1.

2.2. The measurement of entropy
From eqs. (5) and (14), we find:
\[ dS = \frac{dq}{T} = \frac{c_v \, dT}{T}. \]
Thus, the variation of entropy with temperature at constant pressure is obtained from measured heat capacities as
\[ S_T = S_0 + \int_0^T \frac{c_v \, dT}{T}. \]

Nernst's heat theorem, which is also known as the Third Law of Thermodynamics, states that all substances at complete internal equilibrium have zero entropy at 0 K, i.e., \( S_0 = 0 \). Thus, in contrast to enthalpies, the entropies of substances have absolute values.

According to Gibbs, entropy is a measure of the degree of disorder in a system. Thus the entropy of the gaseous state is greater than that of the liquid state, which, in turn, is greater than that of the solid state. The transformation of a solid to a liquid at the normal melting temperature, \( T_m \), involves the absorption of \( \Delta H_m \) per mole. Thus, at \( T_m \), the molar entropy of the liquid exceeds that of the solid by the molar entropy of fusion, \( \Delta S_m \), given by eq. (5) as:
\[ \Delta S_m = \Delta H_m / T_m. \]
This corresponds with the fact that the liquid state is more disordered than the solid state, and \( \Delta S_m \) is a measure of the difference in degree of order. For simple metals, with similar crystal structures and similar liquid structures, \( \Delta S_m \) lies in the range 8–16 J/K.

This correlation is known as Richard's rule. Similarly, at the normal boiling temperature, \( T_b \), the molar entropy of boiling, \( \Delta S_b \), is obtained from the molar heat of boiling as:

References: p. 469.
which, from eq. (1), gives:

$$
\Delta S' = \frac{q^2}{nR} \cdot \frac{dV}{V} = -\frac{q^2}{nR} \cdot d\ln P.
$$

Thus

$$
S'_T - S'_T = nR \cdot \ln \left( \frac{P_2}{P_1} \right),
$$

which corresponds with the fact that a gas at high pressure is a less disordered state than a gas at low pressure.

As changes in entropy are caused by the transfer of heat, chemical reactions involving heat changes necessarily involve changes in entropy. At 298 K and 1 atm pressure, the molar entropies of Ag(s), O_{2}(g) and Ag_{2}O(s) are 42.7, 205 and 122 J/K, respectively. Thus the entropy change for the oxidation

$$
2\text{Ag(s)} + \frac{1}{2} \text{O}_{2}(g) = \text{Ag}_{2}\text{O(s)}
$$

at 298 is:

$$
\Delta S = 122 - (2 \times 42.7) - (0.5 \times 205) = -65.9 \text{ J/K mole}.
$$

This can be viewed in two ways: (i) the entropy decrease is due to the loss of the heat of oxidation from the reacting system, or (ii) the degree of disorder in the system existing as one mole of Ag_{2}O is less than that when the system exists as two moles of Ag and half a mole of oxygen gas at 1 atm pressure.

The variation, with temperature, of the entropy change for the reaction is determined by the heat capacities of the reactants and products as:

$$
\Delta S_T = \Delta S_{298} + \int_{298}^{T} \left[ \Delta C_p/T \right] dT.
$$

The entropy–temperature diagram corresponding to fig. 1 is shown in fig. 2.

From the definition of Gibbs free energy, eq. (10), the change in Gibbs free energy due to a chemical reaction occurring at a temperature $T$, $\Delta G_T$, is

$$
\Delta G_T = \Delta H_T - T \Delta S_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT - T \Delta S_{298} - T \int_{298}^{T} \left( \Delta C_p/T \right) dT.
$$

Thus, the variation of the change in Gibbs free energy with temperature can be determined from measurement of the variation, with temperature, of the constant pressure molar heat capacities of the reactants and products and measurement of the enthalpy change of the reaction at one temperature. For the oxidation of solid silver, such data give

$$
\Delta G_T = -34200 + 87.9T - 1.767 \ln T - 10.8 \times 10^{-3} T^2 + 3.2 \times 10^{7} T^{-1} \text{ J/mole Ag}_2\text{O}.
$$

References: p. 469.
3. Phase equilibrium in a one-component system

At constant $T$ and $P$ the equilibrium state is that in which the Gibbs free energy has its minimum possible value. In a one-component system the states of existence available are the gaseous and liquid states and the various allotropic or polymorphic forms of the solid state. At any $T$ and $P$ the state with the lowest Gibbs free energy is the stable state. For the transformation

$$
\Delta G_m(P, T) = G_m(P, T) - G_m(P, T) = \Delta H_m(P, T) - T\Delta S_m(P, T)
$$

(17)

If $\Delta G_m$ is negative, the transformation decreases the Gibbs free energy of the system and hence the liquid is stable relative to the solid. Conversely, if $\Delta G_m$ is positive the solid is stable relative to the liquid. As absolute values of enthalpy cannot be measured it follows that absolute values of Gibbs free energy cannot be measured. Thus only changes in $G$ can be measured.

The solid and liquid phases coexist in equilibrium with one another in that state at which $\Delta G_m=0$, i.e. where $G_m=G_m$. From eq. (15), at any pressure $P$ this equilibrium occurs at the temperature $T_m$ given by

$$
T_m = \frac{\Delta H_m}{\Delta S_m},
$$

and hence $T_m$ is the equilibrium melting temperature of the solid at the pressure $P$. From eq. (10), $G$ is decreased by decreasing $P$ and increasing $T$ and hence nature prefers states of low enthalpy and high entropy. As $H_m > H_m$ and $S_m > S_m$ the enthalpy contribution to $G$ favors the solid as the stable state and the entropy contribution favors the liquid as the stable state. In eq. (17) the entropy contribution to $AG$ is temperature-dependent and the enthalpy contribution is not. Thus, at high temperatures the former contribution dominates, at low temperatures the latter contribution dominates, and at a unique temperature $T_m$ the two contributions cancel to make $AG=0$.

For the two-phase equilibrium to exist,

$$
G_m = G_m,
$$

and maintenance of the two-phase equilibrium with variation in $T$ and $P$ requires that $T$ and $P$ be varied in such a manner that

$$
dG_m = dG_m,
$$

or, from eq. (11), such that

$$
-S_m dT + V_m dP = -S_m dT + V_m dP,
$$

i.e.,

$$
\left(\frac{dP}{dT}\right)_m = \left(\frac{S_m - S_m}{V_m - V_m}\right) = \frac{\Delta S_m}{\Delta V_m}
$$

As equilibrium between the two phases is maintained, $\Delta H_m = T\Delta S_m$:

$$
\left(\frac{dP}{dT}\right)_m = \frac{\Delta H_m}{T\Delta S_m}.
$$

Equation (18) is the Clapeyron equation, which, on integration, gives the variation of $T$ and $P$ required for maintenance of the two-phase equilibrium. Strictly, integration requires knowledge of the pressure and temperature dependences of $\Delta H_m$ and $\Delta V_m$.

However, for relatively small departures from the state $P=1$ atm, $T_m$, $\Delta H_m$ and $\Delta V_m$ can be taken as constants, in which case:

$$
P_2 - P_1 = \frac{\Delta H_m}{\Delta V_m} \ln \left(\frac{T_2}{T_1}\right)
$$

Equation (18) can be applied to condensed phase-vapor phase equilibria by making the approximation $\Delta V_m = V_m$, assuming ideal behavior of the vapor phase, i.e., $V_m = RT/P$, i.e.,

$$
\left(\frac{dP}{dT}\right)_m = \frac{P_2H_m}{RT^2}
$$

Equation (19) is the Clausius-Clapeyron equation.

References, p. 469.
If \( \Delta H_b \) (the molar enthalpy of boiling) is not a function of temperature (which requires \( C_{T0} = C_{T0} \)), integration of eq. (19) gives

\[
\ln P = -\frac{\Delta H_b}{RT} + \text{const.,}
\]

and if \( \Delta H_b \) is a linear function of \( T \) (which requires that \( \Delta c_p \) be independent of temperature) given by \( \Delta H_b = \Delta H_b + \Delta c_p T \), integration gives

\[
\ln P = -\frac{\Delta H_b}{RT} + \frac{\Delta c_p}{R} \ln T + \text{const.}
\]

as either (i) the variation of the saturated vapor pressure with temperature or (ii) the variation of the equilibrium boiling temperature with pressure. Experimentally measured vapor pressures are normally fitted by an equation of the type

\[
\ln P = -A/T + B \ln T + C.
\]

The solid, liquid, and vapor states exist on surfaces in \( G-T-P \) space. The solid- and liquid-surfaces intersect at a line (along which \( G_S = G_L \)) and projection of this line onto the basal \( P-T \) plane of the \( G-T-P \) diagram gives the pressure dependence of \( T_m \). Similarly the vapor- and liquid-surfaces intersect at a line, projection of which onto the basal \( P-T \) plane gives the variation, with temperature, of the saturated vapor pressure of the liquid. Similar projection of the line of intersection of the surfaces for the solid and vapor states gives the variation, with temperature, of the saturated vapor pressure of the solid. The three lines of two-phase equilibrium in \( G-T-P \) space intersect at a point, called the triple point, at which all three phases are in equilibrium with one another. Consideration of the geometry of the intersections of the surfaces in \( G-T-P \) space shows that, in a one-component system, a maximum of three phases can exist in equilibrium. Alternatively, as the three phases coexist in equilibrium at fixed values of \( T \) and \( P \) the equilibrium is invariant, i.e., has no degrees of freedom. The phase diagram for \( H_2O \) is shown in fig. 3 and a schematic representation of the section of \( G-T-P \) space at 1 atm pressure is shown in fig. 4. In fig. 4, the slope of any line at any point is \( -S \) for that state and hence the "steepness" of the lines increases in the order solid, liquid, vapor. Also the curvatures of the lines are \( \left( \frac{\partial^2G}{\partial T^2} \right)_p = -\left( \frac{\partial S}{\partial T} \right)_p = -c_p/T \).

4. Chemical reaction equilibrium

From eq. (13), at constant \( T \) and \( P \), the Gibbs free energy varies with composition in a chemically reacting system as

\[
dG' = \sum G_i \Delta n_i.
\]

The reaction proceeds spontaneously in that direction which involves a decrease in Gibbs free energy, and reaction equilibrium is attained when, thereby, the Gibbs free energy is minimized, i.e., when \( dG' = 0 \).

Consider the water-gas reaction

\[
H_2O(g) + CO_2(g) = H_2(g) + CO_2.
\]

At equilibrium,

\[
dG = \sum G_i \Delta n_i + \sum G_i \Delta n_i - \sum G_i \Delta n_i = 0
\]

or, in view of the stoichiometry requirement

\[
\sum \Delta n_i = 0 = \Delta n_{H_2O} = \Delta n_{CO_2}
\]

Thus, at equilibrium,

\[
\sum G_i = \sum G_i.
\]

The isothermal transfer of a mole of ideal gas \( i \) from the pure state at the pressure \( P_i \) and temperature \( T \) to an ideal gas mixture at the partial pressure \( p_i \) involves a change in Gibbs free energy:

\[
\Delta G = G_i - G_i = RT \ln \left( \frac{p_i}{P_i} \right)
\]
Again, as only changes in Gibbs free energy can be measured, it is convenient to select a standard state for the gas and consider the Gibbs free energy of the gas in any other state in terms of the difference between the free energy of the gas in this state and the free energy of the gas in the standard state. The standard state for an ideal gas at the temperature \( T \) is the pure gas at 1 atm pressure and in this state the Gibbs free energy is the standard free energy, designated \( G^0 \). Thus eq. (21) can be written as:

\[
G^0_i = G^0 + RT \ln P_i.
\]

(22)

Substitution of eq. (22) into eq. (20) and rearrangement gives:

\[
(G^0_{H_2} + G^0_{CO_2} - G^0_{H_2O} - G^0_{CO}) = -RT \ln \frac{P_{H_2} P_{CO_2}}{P_{H_2O} P_{CO}}.
\]

(23)

Being the difference between the standard free energies of the products and the standard free energies of the reactants, the left-hand side of eq. (23) is termed the standard free energy for the reaction at the temperature \( T \), \( \Delta G^0 \), and, being dependent only on \( T \), it has a definite fixed value at any \( T \). Consequently the quotient of the partial pressures of the reactants and products occurring in the logarithm term on the right-hand side of eq. (23) has a fixed value at any \( T \). This term is called the equilibrium constant, \( K_p \), and hence the equilibrium state in any reacting system is such that

\[
\Delta G^0_p = -RT \ln K_p.
\]

(24)

For the general reaction

\[
aA + bB = cC + dD; \quad K_p = \frac{P^c P^d}{P^a P^b}.
\]

Dalton's law of partial pressures in an ideal gas mixture gives

\[
P_i = X_i P,
\]

where \( X_i \), being the ratio of the number of moles of \( i \) in the gas to the total number of moles of all species, is the mole fraction of \( i \) in the gas and \( P \) is the total pressure of the gas.

Thus

\[
K_p = \frac{X^c X^d}{X^a X^b} P^{c+d-a-b} = K_a P^{c+d-a-b},
\]

(25)

where \( K_a \) is the equilibrium constant expressed in terms of the mole fractions of the reactants and products occurring at reaction equilibrium. From the definition of \( \Delta G^0 \), \( K_p \) is independent of pressure and hence, from eq. (25), \( K_p \) is only independent of pressure if \( c + d - a - b = 0 \).

Thus

\[
\Delta G^0_p = -RT \ln K_p = \Delta H^0_p - T \Delta S^0_p.
\]

For the water-gas reaction:

\[
CO + H_2O = CO_2 + H_2;
\]

\[
\Delta G^0_p = -36400 + 32.0TJ/mole;
\]

thus

\[
K_p = \exp \left( \frac{36400}{8.3144T} \right) \exp \left( \frac{-32.0}{8.3144} \right)
\]

The reaction of \( a \) moles of CO with \( b \) moles of \( H_2O \) produces \( x \) moles of each \( CO_2 \) and \( H_2 \) and leaves \( (a-x) \) moles of CO and \( (b-x) \) moles of \( H_2 \). Thus at any point along the reaction coordinate in a reacting mixture at the constant pressure \( P \):

References: p. 469.
on the right-hand side of eq. (31) is negligibly small and hence eq. (31) can be written as:

$$G_{A_{(g)}}^0 + RT \ln p_{A_{(g)}} = G_{A_{(g)}}^0$$

(32)

Similarly, eq. (30) can be written as:

$$G_{A_{(g)}}^0 + RT \ln p_{A_{(g)}} = G_{A_{(g)}}^0$$

(33)

Substitution of eqs. (32) and (33) into eq. (28) gives:

$$2G_{A_{(g)}}^0 + \frac{1}{2} G_{O_{2(g)}}^0 + RT \ln p_{O_{2(g)}} = G_{A_{(g)}}^0$$

or

$$\Delta G_f^0 = -RT \ln \frac{1}{P_{O_{2(g)}}}$$

(34)

where $\Delta G_f^0$ is the standard free energy change for the reaction given by eq. (26) and $P_{O_{2(g)}}$ is the value of $p_{O_{2}}$ required for equilibrium between $A_{g}$, $A_{g}O_{2}$, and oxygen gas at temperature $T$. The variations of $\Delta H_f^0$, $-T\Delta S_f^0$ and $\Delta G_f^0$ [given by eq. (16)] are shown in fig. 5. Thus, from eq. (34), $p_{O_{2(g)}} = 1$ atm, at which temperature $\Delta G_f^0 = 0$. At $T<485$ K, $\Delta G_f^0$ is a negative quantity and hence $p_{O_{2(g)}} < 1$ atm. At $T>485$ K, $\Delta G_f^0$ is a positive quantity and hence $p_{O_{2(g)}} > 1$ atm.

5. Ellingham diagrams

In 1944 ELLINGHAM published diagrams showing the variation, with temperature, of the standard free energies of formation of a number of oxides and sulphides, and pointed out that these diagrams "would show at a glance the relative stabilities of the various substances within a given class at any temperature, and would thus indicate, in a direct fashion, the range of conditions required for their reduction to the corresponding elements. It would provide, in fact, what might be described as a ground plan of metallurgical possibilities with respect to the reduction of compounds of the specified class". Such diagrams, which are now available for a wide range of classes of compounds, are known as Ellingham diagrams, and the Ellingham diagram for oxides is shown in fig. 6. (See also ch. 14, § 2.1).

In order to facilitate comparison of the stabilities of the various oxides, the standard free energies for the reaction

$$(2v+y)M + O_{2(g)} = (2v+y)M_{2O}$$

i.e., for reactions involving the consumption of one mole of $O_{2}$. By choosing this basis:

$$\Delta G_f^0 = RT \ln p_{O_{2(g)}}$$

and hence, in addition to being a plot of $\Delta G_f^0$ versus temperature, the Ellingham diagram is a plot of the variation, with temperature, of the oxygen pressure, $p_{O_{2(g)}}$, required for equilibrium between the metal and its oxide. The free energy change for the change of state $O_{2}(T, P=1$ atm) $\rightarrow$ $O_{2}(T, P=p_{O_{2}})$ is:

References: p. 469.
\[ \Delta G^f = RT \ln P_{O_2}, \]

and thus, in the Ellingham diagram, lines of constant \( P_{O_2} \) radiate from the origin, \( \Delta G^f = 0 \), \( T=0 \) K, with slopes of \( R \ln P_{O_2} \). Consequently, a nomographic scale of \( P_{O_2} \) can be placed on the edges of the diagram and \( P_{O_2}^{\text{eq}} \) at any point on an Ellingham line is obtained as the reading on the nomographic scale which is collinear with the given point and the origin of the diagram. The Ellingham diagram is thus a stability diagram, in that any point in the diagram lying above the Ellingham line for a given oxide is a state in which \( P_{O_2}^{\text{eq}} > P_{O_2}^{\text{eq}} \) and hence, in all states above the line the oxide is stable relative to the metal. Conversely, any point lying below the Ellingham line for the given oxide is a state in which \( P_{O_2}^{\text{eq}} < P_{O_2}^{\text{eq}} \) and hence, below the line, the metal is stable relative to the oxide. The Ellingham line thus divides the diagram into stability fields and, if it is required that a given oxide be reduced, the thermodynamic state must be moved from a point above the Ellingham line for the oxide to a point below the line, i.e., must be moved from a position within the oxide stability field to a position within the metal stability field.

The magnitude of \( \Delta G^f \) is a measure of the relative stability of the oxide and hence, with increasing stability, the Ellingham lines occur progressively lower in the diagram. Consequently, in principle, the element A can reduce the oxide \( B_2O_3 \) if, in the diagram,
the Ellingham line for \( \text{A}_2\text{O}_3 \) lies below that for \( \text{B}_2\text{O}_3 \).

Over the ranges of temperature in which no phase transitions occur the Ellingham lines are virtually linear, being given by

\[
\Delta G^\circ = A + BT
\]

In this expression, \( A \), the intercept of the line with the \( T=0 \) \( K \) axis, is identified with \( \Delta H^\circ \), the standard enthalpy change for the oxidation, and \( B \), the slope of the line, is identified with \( -\Delta S^\circ \), the standard entropy change for the reaction. The Ellingham lines for the oxidation of solid and liquid metals are more or less parallel with one another, with slopes corresponding to the disappearance of one mole of oxygen gas in the standard oxidation equation. Consequently, the stabilities of these oxides are determined primarily by the magnitudes of their enthalpies of formation.

At the temperature of a phase change the slope of the Ellingham line changes by an amount equal to the entropy change for the phase transition. The slope increases at the transition temperatures of the metal and decreases at the transition temperatures of the oxide. These changes in slope are most noticeable at normal boiling temperatures, e.g., at 1090°C the slope of the Ellingham line for \( \text{MgO} \) increases by 190.3 \( \text{J/K} \), which is the entropy of boiling of \( \text{Mg} \), and at 1484°C the slope of the Ellingham line for \( \text{CaO} \) increases by 174.2 \( \text{J/K} \), the entropy of boiling of \( \text{Ca} \).

Carbon is unique in that it forms two gaseous oxides, \( \text{CO} \) and \( \text{CO}_2 \), and the positions of the Ellingham lines for these oxides are of particular significance in extraction metallurgy. The Ellingham line for \( \text{CO} \) has a negative slope due to the fact that the oxidation

\[
2\text{C} + \text{O}_2 = 2\text{CO}
\]

Involves the net production of one mole of gas, and, because the oxidation

\[
\text{C} + \text{O}_2 = \text{CO}_2
\]

Does not involve a change in the number of moles of gas, the Ellingham line for \( \text{CO}_2 \) is virtually horizontal. The enthalpy change for the oxidation of \( \text{C} \) to form \( \text{CO} \) as \( \text{C} + \frac{1}{2}\text{O}_2 \)

\[
= \text{CO} \]

Is \(-111,700 \) \( \text{J} \) and the enthalpy change for the oxidation of \( \text{CO} \) to \( \text{CO}_2 \) as \( \text{CO} + \frac{1}{2}\text{O}_2 \)

\[
= \text{CO}_2
\]

Is \(-282,400 \) \( \text{J} \). Thus the standard enthalpy change for the Ellingham line for \( \text{CO} \)

\[
is 2 \times (-111,700) = -223,400 \text{ J}
\]

And the standard enthalpy change for the Ellingham line for \( \text{CO}_2 \)

\[
is (-111,700) + (-282,400) = -394,100 \text{ J}
\]

Thus, on the basis that the stability of an oxide is determined primarily by the magnitude of \( \Delta H^\circ \), it would appear that \( \text{CO}_2 \) should be more stable than \( \text{CO} \). However, as the Ellingham line for \( \text{CO} \) has a negative slope, which means that the stability of \( \text{CO} \) increases with increasing temperature, the Ellingham lines for the two oxides intersect. Consequently, although \( \text{CO}_2 \) is more stable than \( \text{CO} \) at lower temperature, the reverse is the case at higher temperatures. The gaseous phase in equilibrium with solid carbon is a \( \text{CO} \)-\( \text{CO}_2 \) mixture in which the ratio \( \frac{\text{p}_{\text{CO}}}{\text{p}_{\text{CO}_2}} \) increases with increasing temperature. For a total pressure of 1 atm, the equilibrium gas contains less than 1% \( \text{CO} \) at temperatures less than 400°C, contains less than 1% \( \text{CO}_2 \) at temperatures greater than 980°C, and is an equimolar mixture at 674°C. The "carbon line" in the diagram, which is the continuum of states in which carbon is in equilibrium with a \( \text{CO} \)-\( \text{CO}_2 \) mixture at 1 atm pressure, follows the \( \text{CO}_2 \) Ellingham line up to about 400°C and then curves down gently to tangentially meet and join the Ellingham line for \( \text{CO} \) at about 1000°C. Along the carbon line the ratio \( \frac{\text{p}_{\text{CO}}}{\text{p}_{\text{CO}_2}} \) is fixed by the equilibrium

\[
\text{C} + \text{CO}_2 = 2\text{CO},
\]

And, by virtue of the equilibrium

\[
\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2
\]

The oxygen pressure is also fixed. Thus the carbon line divides the other oxides into two classes, those with Ellingham lines which lie above the carbon line, and those with Ellingham lines which lie below the carbon line. With respect to the former class, the carbon line lies in the stability field of the metal and hence carbon is a potential reducing agent for these oxides, whereas, with respect to the latter class, the carbon line lies in the oxide stability field and hence cannot reduce the oxide. Furthermore, if the Ellingham line for a metal oxide intersects the carbon line, the temperature of intersection is the minimum temperature at which the oxide may be reduced by carbon. Thus, for example, \( \text{FeO} \) cannot be reduced by carbon at temperatures less than 675°C.

Whether or not carbon can be used as a reducing agent is determined by the stability of any carbide phase which may form, i.e., by the sign of the standard free energy for formation of the carbide from metal and carbon. For example, in the Ellingham diagram the carbon line intersects with the Ellingham line for \( \text{SiO}_2 \) at 1676°C, and hence above this temperature liquid \( \text{Si} \) is stable relative to \( \text{SiO}_2 \) in the presence of \( \text{C} \) and its equilibrium \( \text{CO} \)-\( \text{CO}_2 \) gas mixture at 1 atm pressure. However, for the reaction

\[
\text{Si} + \text{C} = \text{SiC},
\]

The standard free energy change is \( \Delta G^\circ = -122,600 + 37.07 \) \( \text{J} \) and hence \( \text{SiC} \) is stable relative to liquid \( \text{Si} \) in the presence of carbon at 1676°C and \( P = 1 \) atm.

The stability fields in the system \( \text{Si-O-C} \) at 1676°C are shown in Fig. 7 as functions of \( \log p_{\text{CO}} \) and \( \log p_{\text{CO}_2} \). Line A is the variation of \( p_{\text{CO}} \) and \( p_{\text{CO}_2} \) required for the equilibrium

\[
\text{Si} + 2\text{CO} = \text{SiO}_2 + 2\text{CO},
\]

Line B is the corresponding variation required for the equilibrium

\[
\text{Si} + 2\text{CO} = \text{SiC} + \text{CO}_2,
\]

And line C is the variation for the equilibrium

\[
\text{SiC} + 3\text{CO}_2 = \text{SiO}_2 + 4\text{CO}.
\]

These lines divide the diagram into stability fields for \( \text{Si} \), \( \text{SiC} \) and \( \text{SiO}_2 \) and meet at the values of \( p_{\text{CO}} \) and \( p_{\text{CO}_2} \) required for the four-phase equilibrium involving the three condensed phases \( \text{Si} \), \( \text{SiC} \) and \( \text{SiO}_2 \) and the \( \text{CO} \)-\( \text{CO}_2 \) gas phase. Line D is the variation of \( p_{\text{CO}} \) and \( p_{\text{CO}_2} \) required for the equilibrium between carbon and the gas phase at 1676°C.
Fig. 7. The stability diagram for the system Si-O-C at 1949 K.

and, as such, represents the compositions of CO-CO₂ gas mixtures which are saturated with carbon. The field below line D is designated "unstable" gas, as any gas mixture in this field is supersaturated with carbon and hence will spontaneously undergo the carbon deposition reaction

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2. \]

until, thereby, the composition of the gas lies on line D. The dashed line is the \( (P_{\text{CO}} + P_{\text{CO}_2}) \) atm isobar. Consequently, the system containing solid carbon and a gas phase at 1 atm pressure exists at the state a, and this state is in the field of stability of SiC. SiO₂ is not reduced to Si by carbon at 1676°C. However, if the standard free energy for formation of SiC had been positive, lines B and C would have occurred below line D in the diagram and, as shown by the dashed-dotted extension of line A, the equilibrium Si-SiO₂-C would occur at the state a, which is the state of intersection of the carbon line with the Ellingham line for SiO₂ in the Ellingham diagram.

6. The thermodynamic properties of solutions

6.1. Mixing processes

The relationship between entropy and the "degree of mixed-up-ness" is quantified by Boltzmann's expression as:

\[ S' = k \ln W, \]

where \( S' \) is the entropy of the system and \( W \) is the number of microstates available to the system. In the simplest of mixing processes, \( W \) is the number of distinguishable arrangements of the constituent atoms on the sites available to them. Consider the mixing of \( N_A \) atoms of solid A and \( N_B \) atoms of solid B as the process:

- state 1 \( \rightarrow \) state 2,
- i.e., unmixed A and B \( \rightarrow \) mixed A and B.

In state 1, interchange of the positions of A atoms in the crystal of pure A and/or interchange of the positions of B atoms in the crystal of pure B does not produce a distinguishably different arrangement and hence \( W_{\text{sub1}} = 1 \). However, the \( N_A \) atoms of A and \( N_B \) atoms of B can be placed on the \( N_A + N_B \) lattice sites of the mixed crystal (state 2) in \( (N_A + N_B)! \) ways, of which \( (N_A + N_B)!/N_A!N_B! \) are distinguishable. Thus

\[ W_1 = \frac{(N_A + N_B)!}{N_A! N_B!}. \]

Thus, for the process:

\[ \Delta S = S_2 - S_1 = k \ln W_1 - k \ln W_2 = k \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right). \]

If \( N_A \) and \( N_B \) are sufficiently large numbers, Stirling's theorem can be applied as

\[ \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right) = (N_A + N_B) \ln (N_A + N_B) - N_A \ln N_A - N_B \ln N_B = -N_A \ln X_A - N_B \ln X_B, \]

where, respectively, \( X_A \) and \( X_B \) are the mole fractions of A and B in the mixed crystal.

Thus, the change in entropy, \( \Delta S^M \), due to mixing, is

\[ \Delta S^M = k \ln (N_A \ln X_A + N_B \ln X_B). \]

and, if \( N_A + N_B = N_0 \) (Avogadro's number) then the molar entropy of mixing is

\[ \Delta S^M = k \ln N_0, \]

The equivalence between this definition of entropy and the definition in terms of heat flow (§4.1) is demonstrated in general terms in many texts; a particularly clear treatment is provided in ch. 2 of Fact's book (see bibliography).

References: p. 469.
\[ \Delta S^m = -R (X_A \ln X_A + X_B \ln X_B) \]  

This increase in entropy is caused by the increase in the number of spatial configurations made available to the system as a result of the mixing process and, hence, is configurational in origin. If there is no change in enthalpy on mixing, the Gibbs free energy change due to the mixing process is given by

\[ \Delta G^m = -T \Delta S^m = RT \left( X_A \ln X_A + X_B \ln X_B \right) \]  

Alternatively, consider the following. Consider that \( p_A^0 \) and \( p_B^0 \) are the saturated vapor pressures of pure A and pure B at temperature \( T \) and that \( p_A \) and \( p_B \) are the partial pressures of A and B exerted by the mixed crystal (or solid solution) of composition \( X_A \) at temperature \( T \). Consider that one mole of A is isothermally evaporated from pure solid A to form A vapor at the pressure \( p_A^0 \), that the mole of A vapor is isothermally expanded to the pressure \( p_A \) and is then isothermally condensed into a large quantity of the pure solid. As the evaporation and condensation processes are conducted at equilibrium, they do not involve any change in Gibbs free energy and hence the change in Gibbs free energy for the three-step process is simply that caused by the change in pressure from \( p_A^0 \) to \( p_A \), i.e.,

\[ \Delta G = \Delta G_{\text{vap}} = R T \ln \left( \frac{p_A}{p_A^0} \right) \]

Similarly, for the corresponding three-step process for B,

\[ \Delta G = \Delta G_{\text{cond}} = R T \ln \left( \frac{p_B}{p_B^0} \right) \]

Thus, for the mixing of \( n_A \) moles of A and \( n_B \) moles of B:

\[ \Delta G^m = \Delta G_{\text{vap}} + \Delta G_{\text{cond}} = R T \ln \left( \frac{p_A}{p_A^0} \right) + R T \ln \left( \frac{p_B}{p_B^0} \right) \]

which, from eqs. (37) and (38), can be written for one mole of solution as

\[ \Delta G^m = R T \left( X_A \ln \left( \frac{p_A}{p_A^0} \right) + X_B \ln \left( \frac{p_B}{p_B^0} \right) \right) \]

Comparison of eqs. (37) and (39) indicates that, if the mixing process does not involve a change in enthalpy,

\[ p_A = X_A p_A^0 \quad \text{and} \quad p_B = X_B p_B^0 \]

Equation (40) is an expression of Raoult’s Law and a solution conforming with this behavior is said to exhibit Raoultian ideal behavior. If the energies of the pure states and the solution are considered to be the sums of the pair-wise bond energies between neighboring atoms, Raoultian ideal mixing requires that:

\[ E_{A\text{B}} = \frac{E_{A\text{A}} + E_{B\text{B}}}{2} \]

where \( E_{A\text{B}} \), \( E_{A\text{A}} \), and \( E_{B\text{B}} \) are the pair-wise bond energies of A–B, A–A and B–B pairs, respectively. If the condition given by eq. (41) is not met, the isothermal mixing process is accompanied by the evolution or absorption of heat, which, for mixing at constant pressure, represents a change in the enthalpy of the system. In such a situation random mixing of A and B atoms does not occur and hence the entropy of mixing is no longer given by eq. (36).

Any change in the enthalpy on mixing arises from a redistribution of the atoms among their quantized energy levels and this gives rise to a change in the thermal (as distinct from the configurational) component of the entropy of the system. Boltzmann’s equation can be written as

\[ S_{\text{total}} = S_{\text{conf}} + S_{\text{thermal}} = k \ln \left( \frac{W_{\text{conf}} W_{\text{thermal}}}{} \right) \]

where \( W_{\text{conf}} \) is the number of distinguishable ways in which the atoms can be distributed on the available sites and \( W_{\text{thermal}} \) is the number of ways in which the energy of the system can be distributed among the particles. Thus, for the mixing process,

\[ \Delta S^m = k \ln \left( \frac{W_{\text{conf}} W_{\text{thermal}}}{} \right) \]

and hence \( \Delta S^m \) is only given by eq. (35) if \( W_{\text{thermal}} \) is \( W_{\text{thermal}} \), i.e., if no redistribution of the energy occurs, and hence no change in enthalpy occurs. This condition is required for Raoultian ideal mixing. If

\[ |E_{A\text{B}}| > \frac{(|E_{A\text{A}}| + |E_{B\text{B}}|)}{2} \]

the solution exhibits a tendency towards ordering, i.e., towards maximizing the number of A–B contacts, and if

\[ |E_{A\text{B}}| < \frac{(|E_{A\text{A}}| + |E_{B\text{B}}|)}{2} \]

the solution exhibits a tendency towards clustering or phase separation, i.e., towards minimizing the number of A–B contacts.

Configurational entropy is responsible for the occurrence of vacancies in metals. Consider a perfect single crystal containing \( N \) atoms on \( N \) lattice sites. If a single atom is removed from a lattice position within the crystal and is placed on the surface of the crystal, random placement of the vacancy on \( N + 1 \) sites gives rise to a configurational entropy of

\[ S = k \ln \left( \frac{(N + 1)!}{N!} \right) \]

This process involves an enthalpy change \( \Delta H \), and, as the vibration frequencies of the nearest-neighbor atoms to the vacancy are altered, a change occurs in the thermal entropy, \( \Delta S_w \). Thus, for the formation of \( N \) vacancies,

References: p. 469.
\[ \Delta G' = \Delta H' - T\Delta S' \]
\[ = N_c \Delta H_s - N_c \Delta S_w T + kT \ln \left( \frac{(N_c + N_v)}{N_c N_v} \right) \]
\[ = N_c \left( \frac{\Delta H_s}{N_c} + \frac{\Delta S_w}{k} \right) + \left[ N_c \ln \left( \frac{N_c}{N_c + N_v} \right) + N_v \ln \left( \frac{N_v}{N_c + N_v} \right) \right] \quad (42) \]

The formation of vacancies in an initially perfect crystal is thus a spontaneous process which proceeds until, thereby, the Gibbs free energy of the crystal is minimized, in which state
\[ \frac{\partial \Delta G'}{\partial N_v} = 0. \]

From eq. (42), this condition occurs when
\[ \frac{N_c}{N_c + N_v} = \exp \left( \frac{-\Delta H_s}{kT} \right) \exp \left( \frac{\Delta S_w}{k} \right). \]

The fraction of vacant sites in a crystal can be determined from simultaneous measurements of the thermal expansion of a sample, \( \Delta L / L \), and the change in the lattice parameter, \( \Delta a_0 / a_0 \), as measured by X-ray diffraction (see ch. 18, §2.2.2.2). As the former is influenced by both the increase in the average spacing between lattice planes and the creation of vacancies, and the latter is a measure only of the average spacing between planes, the increase in the fraction of vacant lattice sites is proportional to the difference between \( \Delta L / L \) and \( \Delta a_0 / a_0 \). Measurements of this type on aluminium give:
\[ \frac{N_v}{N_c + N_v} = 11 \exp \left( \frac{-8820}{T} \right). \]

from which \( \Delta H_s = 73.3 \text{ kJ/mole} \) and \( \Delta S_w = 20 \text{ J/K mole} \). At the melting temperature of 660°C this gives the fraction of vacant sites as 9 × 10⁻⁴.

The thermodynamic properties of solutions which do not exhibit Raoultian ideal behavior are dealt with by introducing the concept of activity. The activity, \( a_i \), of the component \( i \) in a solution is defined as:
\[ a_i = p_i / p_i^0 \quad (43) \]
and, from eq. (40), is equal to the mole fraction, \( X_i \), in a Raoultian ideal solution. Thus, the molar free energy of formation of a binary A–B solution, \( \Delta G^M \), is given by
\[ \Delta G^M = RT \left( X_A \ln a_A + X_B \ln a_B \right). \quad (44) \]

The free energy of formation of \( n \) moles of a solution, \( \Delta G^{Mn} \), can be written in terms of the partial molar free energies of mixing of the components as:

or, the molar free energy, \( \Delta G^M \), as:
\[ \Delta G^M = X_A \Delta G_A^M + X_B \Delta G_B^M, \quad (45) \]

where \( \Delta G^M = \bar{G}_i^M - G_i^M \) (the difference between the molar free energy of \( i \) in the solution and the molar free energy of pure \( i \) is termed the partial molar free energy of mixing of \( i \) in the solution). The partial molar free energy of mixing of \( i \) and the molar free energy of formation of the solution are related as:
\[ \Delta G_i^M = \Delta G^M + \left( 1 - X_i \right) \frac{\partial \Delta G^M}{\partial X_i} \left|_{X_i} \right. \quad (46) \]

Comparison of eqs. (39) and (45) shows that in a Raoultian ideal solution
\[ \Delta G_i^M = RT \ln X_i, \]
and comparison of eqs. (39) and (44) shows that, generally,
\[ \Delta G_i^M = RT \ln a_i. \quad (47) \]

A typical ideal variation of \( \Delta G^M \) with composition is shown in fig. 8. In this figure the tangent drawn to the free energy curve at any composition intersects the \( X_A = 1 \) axis at \( \Delta G_A^M \) and intersects the \( X_B = 1 \) axis at \( \Delta G_B^M \). This construction is a geometric representation of eq. (46). Also, as \( X_i \to 0, a_i \to 0 \) and hence, from eq. (47), \( \Delta G_i^M \to -\infty \), i.e., the vertical axes are tangents to the curve at its extremities. The relationship between the variations of the tangential intercepts with composition is given by the Gibbs–Duhem equation:
\[ X_A \ln a_A + X_B \ln a_B = 0. \quad (48) \]

Usually, the activity of only one component of a solution is amenable to experimental measurement, and the activity of the other component, and hence \( \Delta G^M \), are obtained from integration of the Gibbs–Duhem equation.

The activity coefficient, \( \gamma_i \), is defined as \( \gamma_i = a_i / X_i \), and hence eq. (44) can be written as:
\[ \Delta G^M = RT (X_A \ln X_A + X_B \ln X_B) + RT (X_A \ln \gamma_B + X_B \ln \gamma_A). \quad (49) \]

The first term on the right-hand side of eq. (49) is the molar free energy of formation of a Raoultian ideal solution, \( \Delta G_{\text{mix}}^M \), and the second term, being the difference between the actual molar free energy of solution and the ideal value, is called the excess molar free energy of mixing, \( G^m \).

6.2. Regular solution behavior

A regular solution is one which has an ideal entropy of mixing and a nonzero enthalpy of mixing. The properties of such a solution are best examined by means of a
simple statistical model of the mixing of \( N_A \) atoms of \( A \) and \( N_B \) atoms of \( B \). If the internal energy, \( U' \), of the solution can be taken as the sum of the pair-wise bond energies then

\[
U' = P_{AB}E_{AB} + P_{AA}E_{AA} + P_{BB}E_{BB},
\]

where \( P_i \) is the number of \( i-j \) pairwise bonds and \( E_i \) is the energy of the bond relative to \( i \) and \( j \) at infinite separation. If the coordination number of an atom is \( z \), the number of bonds involving \( A \) atoms, \( N_Az \), is given by \( 2P_{AA} + P_{AB} \) and, similarly, the number of bonds involving \( B \) atoms, \( N_Bz \), is given by \( 2P_{BB} + P_{AB} \). Thus:

\[
P_{AA} = \frac{1}{2} N_A z - \frac{1}{2} P_{AB} \quad \text{and} \quad P_{BB} = \frac{1}{2} N_B z - \frac{1}{2} P_{AB},
\]

substitution of which into eq. (50) gives:

\[
U' = \frac{1}{2} N_A z E_{AA} + \frac{1}{2} N_B z E_{BB} + P_{AB} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right].
\]

The first two terms on the right-hand side represent the internal energies of \( N_A \) atoms of \( A \) and \( N_B \) atoms of \( B \) before mixing and hence, for the mixing process:

\[
\Delta U' = P_{AB} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right].
\]

If the mixing process, conducted at constant pressure, does not involve a change in volume, then, as \( PAV = 0 \), \( \Delta H' = \Delta U' \) and eq. (51) is the expression for the enthalpy of mixing. As random mixing of the atoms is assumed, the number of \( A-B \) bonds is calculated as the product of the probability of occurrence of an \( A-B \) pair and the number of pairs of atoms. The former is given by:

\[
\frac{2}{N_A + N_B} \frac{N_A - N_B}{N_A + N_B},
\]

and the latter is \( \frac{1}{2}(N_A + N_B)x_2 \), and hence:

\[
\Delta H' = \frac{N_A - N_B}{N_A + N_B} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right].
\]

For the mixing of \( n_A \) moles of \( A \) (=\( n_A N_A \) atoms of \( A \)) and \( n_B \) moles of \( B \) (=\( n_B N_B \) atoms of \( B \)), eq. (52) becomes:

\[
\Delta H' = \frac{n_A - n_B}{n_A + n_B} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right],
\]

or, per mole of solution:

\[
\Delta H' = \frac{N_A - N_B}{N_A + N_B} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right].
\]

If \( |E_{AA}| < |E_{AB}| + E_{BB}/2 \), \( \Delta H' \) is negative, which leads to exothermic mixing, and if \( |E_{AA}| > |E_{AB}| + E_{BB}/2 \), \( \Delta H' \) is positive, which leads to endothermic mixing. On the other hand, if \( E_{AB} \) is the average of \( E_{AA} \) and \( E_{BB} \), \( \Delta H' \) is zero and Raoultian ideal mixing occurs. For any given system,

\[
\Delta H' = \frac{N_A - N_B}{N_A + N_B} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right],
\]

is a constant, and hence, in a regular solution, \( \Delta Q' \) is a parabolic function of composition, given by:

\[
\Delta Q' = \Omega X_A X_B,
\]

and

\[
\Delta S' = -k \frac{1}{X_A \ln X_A + X_B \ln X_B}.
\]

For any extensive thermodynamic property \( Q \), the relationship between \( \Delta Q' \) and \( \Delta Q^M \) in a binary system is given by:

\[
\Delta Q' = \Delta Q^M + (1 - X_i) \left( \frac{\partial \Delta Q^M}{\partial X_i} \right)
\]

and thus, in a regular solution, from eq. (53):

References: p. 469.
\[ \Delta H^M = \Omega (1 - X_i)^2, \]

and from eq. (36):
\[ \Delta S^M_i = -R \ln X_i. \]

The partial molar free energy of mixing of \( i \) can be expressed variously as
\[ \Delta G^M_i = \Delta H^M_i - T \Delta S^M_i = \Delta G^R_i + \Delta G^M_i = RT \ln X_i + RT \ln \gamma_i, \]

and hence, in a regular solution:
\[ \Delta G^M_i = \Delta H^M_i = RT \ln \gamma_i = \Omega (1 - X_i)^2. \]

Consequently, the limiting values of \( \gamma_i \) as \( X_i \to 1 \) and \( X_i \to 0 \) are unity and \( \exp(1/RT) \), respectively; i.e., with increasing dilution, the solvent approaches Raoultian ideal behavior and the activity coefficient of the solute approaches a constant value designated \( \gamma^0_i \). The tendency of \( \gamma_i \) towards a constant value as \( X_i \to 0 \) is expressed as Henry's Law, i.e.,
\[ \gamma_i \to \gamma^0_i \text{ as } X_i \to 0, \]

and if \( \gamma_i \) is constant over some finite range of composition of dilute solution of \( i \), component \( i \) is said to exhibit ideal Henrian behavior in this range, its activity being given by:
\[ a_i = \gamma^0_i X_i. \]

Application of the Gibbs-Duhem relation, eq. (48), shows that, over the composition range in which the solute B exhibits ideal Henrian behavior, the solvent A exhibits ideal Raoultian behavior.

The occurrence of Henrian ideal behavior gives rise to the concept of the Henrian standard state, illustrated in fig. 9 which shows the activity of B as a function of composition in the system A-B. The Raoultian standard state is pure B, located at the point R where \( a_B = 1 \). If, however, pure B behaved as it does in dilute solution in A, extrapolation of its activity along the Henry's Law line would give an activity of \( \gamma^0_B \) in the hypothetical pure state at \( X_B = 1 \), relative to the Raoultian standard state. This hypothetical pure state is the Henrian standard state, located at the point H in fig. 9, and, relative to this standard state, the activity of B in any solution, \( h_B \), is
\[ h_B = f_B X_B, \]

where \( f_B \) is the Henrian activity coefficient. In the range of dilute solutions over which B exhibits Henrian ideal behavior, \( f_B \approx 1 \) and hence:
\[ h_B = X_B. \]

If the vapor pressure of B in the Raoultian standard state is \( p_B^0 \), then the vapor pressure of B in the Henrian standard state is \( \gamma_B^0 p_B^0 \), and hence the change of standard state,
\[ a_{B}(\text{relative to standard state}) = \frac{p_B^{0(\text{vap})}}{p_B^{0(\text{solid})}} = \exp\left(\frac{\Delta G_B^0}{RT}\right). \]

Fig. 9. Illustration of the Raoultian and Henrian standard states.

7. The thermodynamic origin of phase diagrams

In the definition of activity, given by eq. (43), \( p_i \) is the vapor pressure of pure \( i \) at the temperature of interest. However, depending on the convenience of the situation, either pure solid \( i \) or pure liquid \( i \) can be chosen as the standard state. At temperatures below the triple point, \( p_i^{(\text{vap})} < p_i^{(\text{liquid})} \), and so the activity of \( i \) in a solution, relative to pure solid \( i \) as the standard state, is larger than the activity relative to pure liquid \( i \) as the standard state. Conversely, at temperatures higher than the triple point temperature the reverse is the case. The activities on the two activity scales are related as
\[ a_i(\text{relative to solid standard state}) = \frac{p_i^{(\text{vap})}}{p_i^{(\text{solid})}} = \frac{p_i^{(\text{liquid})}}{p_i^{(\text{solid})}} = \exp\left(\frac{\Delta G_i^0}{RT}\right). \]

References: p. 469.
Consider the molar free energies of mixing in the system A–B, the phase diagram for which is shown in fig. 10a. For simplicity of discussion it will be assumed that both the solid and liquid solutions exhibit ideal Raoultian behavior. The molar free energies, at temperature T, are shown in fig. 10b. Pure liquid A and pure solid B are chosen as the reference states and are located at points a and b respectively. $G^0_A$ is located at c, where $G^0_A - G^0_B - \Delta G_m^{ab}$ at temperature T, and $G^0_B$ is located at d where $G^0_B - G^0_A = \Delta G_m^{ab}$ at temperature T. Thus, relative to unmixed pure liquid A and pure solid B as the reference state, the molar free energy of the unmixed pure liquids (given by line ad) is $X_A \Delta G_m^{ab}$ and the corresponding free energy of the unmixed pure solids (given by line eb) is $-X_B \Delta G_m^{ab}$. Upon mixing to form Raoultian ideal solutions, the molar free energies decrease by $RT(X_A \ln X_A + X_B \ln X_B)$ and hence, relative to the chosen reference state:

$$\Delta G^M_{\text{solid solutions}} = -X_A \Delta G_m^{ab} + RT(X_A \ln X_A + X_B \ln X_B),$$

and

$$\Delta G^M_{\text{liquid solutions}} = X_B \Delta G_m^{ab} + RT(X_A \ln X_A + X_B \ln X_B).$$

The double tangent drawn to the two free energy curves touches the curve for the solid solutions at g and the curve for the liquid solutions at f, with the intercepts at $X_A = 1$ and $X_B = 1$ being e and h respectively. As the equilibrium state is that of minimum free energy, points f and g divide the composition range into three regions. At compositions between a and f the homogeneous liquid solution has the lowest possible free energy and at compositions between g and b the homogeneous solid solution has the lowest possible free energy. However, at compositions between f and g, a two-phase mixture of liquid solution of composition f and solid solution of composition g, the free energy of which lies on line fg, has a lower free energy than both the homogeneous solid solution and the homogeneous liquid solution. Thus point f is the limit of solution of B in liquid A and g is the limit of solution of A in solid B, and so points f and g are, respectively, the liquidus and solidus compositions at temperature T.

Furthermore, for phase equilibrium:

$$\bar{G}_A \text{ (in liquid solution f)} = \bar{G}_A \text{ (in solid solution g)},$$

and:

$$\bar{G}_B \text{ (in liquid solution f)} = \bar{G}_B \text{ (in solid solution g)}$$

or

$$\Delta \bar{G}^{M}_{A} \text{ (in liquid f)} = \Delta \bar{G}^{M}_{A} \text{ (in solid g)},$$

and:

$$\Delta \bar{G}^{M}_{B} \text{ (in liquid f)} = \Delta \bar{G}^{M}_{B} \text{ (in solid g)}.$$

These requirements state that, for phase equilibrium, the tangent to the molar free energy curve for the liquid solutions at the liquidus composition f is also the tangent to the molar free energy curve for the solid solutions at the solidus composition g. Geometrically, this condition is such that, simultaneously,

$$ca + ae = ce \text{ and } db + bh = dh,$$

where:

$$ce = \Delta \bar{G}^{M}_{A} \text{ (relative to solid A as the standard state)} = RT \ln X_A \text{ (at the composition g),}$$

$$ae = \Delta \bar{G}^{M}_{A} \text{ (relative to liquid A as the standard state)} = RT \ln X_A \text{ (at the composition f),}$$

$$dh = \Delta \bar{G}^{M}_{B} \text{ (relative to liquid B as the standard state)} = RT \ln X_B \text{ (at the composition f),}$$

and

$$bh = \Delta \bar{G}^{M}_{B} \text{ (relative to solid B as the standard state)} = RT \ln X_B \text{ (at the composition g).}$$

References: p. 469.
Thus eqs. (54) become:

\[ \Delta G^0_{m,A} + RT \ln X_A(\text{liquidus}) = RT \ln X_A(\text{solidus}), \]

and

\[ -\Delta G^0_{m,B} + RT \ln X_B(\text{solidus}) = RT \ln X_B(\text{liquidus}). \]

As \( X_A(\text{liquidus}) + X_B(\text{liquidus}) = 1 \) and \( X_A(\text{solidus}) + X_B(\text{solidus}) = 1 \), the solidus and liquidus compositions in a Raoultian system are thus uniquely determined by the values of \( \Delta G^0_{m,A} \) and \( \Delta G^0_{m,B} \) as:

\[ X_A(\text{liquidus}) = \frac{1 - \exp(-\Delta G^0_{m,B}/RT)}{1 - \exp(-\Delta G^0_{m,B}/RT) \exp(\Delta G^0_{m,A}/RT)} \]  \hspace{1cm} (55)

and

\[ X_A(\text{solidus}) = \frac{\exp(\Delta G^0_{m,A}/RT) - 1 + \exp(-\Delta G^0_{m,B}/RT)}{1 - \exp(-\Delta G^0_{m,B}/RT) \exp(\Delta G^0_{m,A}/RT)} \]  \hspace{1cm} (56)

The phase diagram for the system Si–Ge, calculated from eqs. (55) and (56) and the known variations of \( \Delta G^0_{m,A} \) and \( \Delta G^0_{m,B} \) with temperature, is compared, in fig. 11, with the liquidus and solidus lines determined experimentally by thermal and X-ray analysis. As is seen, the behavior in the system is very close to Raoultian.

Raoultian behavior is very much the exception rather than the rule, and even complete mutual solid solubility between A and B requires that A and B have the same crystal structure, similar atomic sizes, similar electronegativities, and similar valences. The requirement of similar atomic size arises from the introduction of a strain energy into the lattice when the solvent and substitutional solute atoms are of differing size. This strain energy always increases the Gibbs free energy and, hence, can significantly influence the phase relationships in the system. It is found that terminal solid solutions extend only a few atomic percent into a binary system if the atomic diameters differ by more than 14%. Significant differences in electronegativity cause the formation of intermetallic compounds such as MgSi, MgSn, and MgPb, and differences in valences can cause the formation of electron compounds such as occur in the systems Cu–Zn and Cu–Sn.

Although Cu and Ag are chemically similar, the atomic radius of Ag is 13% larger than that of Cu and hence, as shown in fig. 12a, Cu and Ag form a simple eutectic system. In this system it is presumed that Ag exhibits Raoultian ideal behavior in the Ag-rich \( \alpha \)-solid solution and that Cu exhibits Raoultian ideal behavior in the Cu-rich \( \beta \)-solid solution. Consequently Cu in \( \alpha \) and Ag in \( \beta \) exhibit Henrian ideal behavior and, at 1000 K, the activities of the components, relative to the pure solids at standard states, are as shown in fig. 12b. At 1000 K, saturation of the \( \alpha \)-phase with Cu occurs at \( X_{Ag} = 0.9 \), and hence, as Ag obeys Raoult's law in the \( \alpha \)-phase, \( a_{Ag} = 0.9 \) at this composition. Phase equilibrium between \( \alpha \) saturated with Cu and \( \beta \) saturated with Ag requires that the activities of both Ag and Cu be the same in both phases, and hence \( a_{Ag} = 0.9 \) in the Ag-saturated \( \beta \)-phase of composition \( X_{Ag} = 0.9 \). Similarly, \( a_{Cu} = 0.96 \) in the Ag-saturated \( \beta \) (at \( X_{Ag} = 0.96 \)) and in the Cu-saturated \( \alpha \) (at \( X_{Ag} = 0.9 \)). Thus, in the \( \alpha \)-phase, Henrian behavior of Cu is given by:

\[ a_{Cu} = 9.6X_{Cu}, \]  \hspace{1cm} (57)

and in the \( \beta \)-phase, Henrian behavior of Ag is given by:

\[ a_{Ag} = 22.5X_{Ag}. \]  \hspace{1cm} (58)

8. Reaction equilibrium involving solutions and the Gibbs phase rule

8.1. The dependence of the equilibrium state on activity

In §4 it was shown that, at constant temperature and pressure, equilibrium is established in the reaction

\[ aA + bB = cC + dD, \]

when

\[ a\bar{G}_A + b\bar{G}_B = c\bar{G}_C + d\bar{G}_D. \]  \hspace{1cm} (58)

References: p. 469.
where the quotient in the logarithm term is $K_r$, the equilibrium constant for the reaction.

Consider the oxidation, at $1000 \, \text{K}$, of Cu from an Ag–Cu alloy of $X_{\text{Cu}} = 0.08$. From eq. (57), the activity of Cu in this alloy, relative to pure solid Cu as the standard state, is

$$a_{\text{Cu}} = 9.6 \times 0.08 = 0.768.$$ 

For the reaction:

$$4\text{Cu} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow 2\text{Cu}_2\text{O}(\text{g})$$

$$\Delta G_f^o = -336810 + 142.57 \times 10^3 \text{J}.$$ 

Thus, $\Delta G_f^{o,1000} = -8.3144 \times 10^4 \ln K_{\text{fGMO}}$ and so:

$$K_{1000} = 1.41 \times 10^{10} = \frac{a_{\text{Cu}}^2}{a_{\text{Cu}_2\text{O}}^\gamma}.$$ 

(59)

Oxidation of the Cu occurs when the oxygen pressure in the system has been increased to the level at which $a_{\text{Cu}} = 1$. From eq. (59) this oxygen pressure is:

$$P_o_2 = \left(\frac{0.768}{1}\right)^{1.41 \times 10^{10}} = 2.04 \times 10^{-10} \text{atm.}$$

From eq. (16), $\Delta G_f^{o,1000}$ for the reaction

$$2\text{Ag} + \frac{1}{2} \text{O}_2(\text{g}) = \text{Ag}_2\text{O}(\text{g})$$

has the value 31 062 J. Thus:

$$K_{1000} = \frac{a_{\text{Ag}}^2}{a_{\text{Ag}_2\text{O}}^\gamma} = 0.024.$$ 

Thus, with $a_{\text{Ag}} = 0.92$ (Raoultian behavior in the $\alpha$–solid solution) and $P_o_2 = 2.04 \times 10^{-10}$ atm:

$$a_{\text{Ag}_2\text{O}} = 2.9 \times 10^{-7},$$

which shows that the equilibrium oxide is virtually pure Cu$_2$O. As the oxygen pressure in the system is further increased, the Cu content in the alloy decreases in accordance with eq. (59). Thus the alloy in equilibrium with virtually pure Cu$_2$O and air (oxygen fraction 0.21) at $1000 \, \text{K}$ is that in which

$$a_{\text{Cu}} = \left[\frac{1}{1.41 \times 10^{10} \times 0.21}\right]^{1/4} = 0.0043,$$

or $X_{\text{Cu}} = a_{\text{Cu}}/a_{\text{Ag}} = 9.6 = 4.5 \times 10^{-4}.$

At this oxygen pressure the activity of Ag$_2$O in the equilibrium oxide phase, with $a_{\text{Ag}} = 1$, is:

References: p. 469.
\[ a_{\text{Ag}_2\text{O}} = 0.024 \times 1 \times 0.21^{4/7} = 0.011, \]

and so the equilibrium oxide phase is still essentially pure Cu$_2$O.

### 8.2. The Gibb's phase rule

The complete description of a thermodynamic system containing \( C \) components existing in \( P \) phases requires specification of the temperatures, pressures and compositions of each of the \( P \) phases. As the composition of each phase is defined when the concentrations of \( C - 1 \) of its components are known, the total number of variables in the description is \( P \) pressures + \( P \) temperatures + \( P(C - 1) \) concentrations = \( P(C + 1) \). For thermodynamic equilibrium in the system, each of the \( P \) phases must be at the same temperature and same pressure and the activity (or partial molar free energy) of each of the individual components must be the same in each of the \( P \) phases. Thus, for equilibrium, there are \( (P - 1) \) equalities of temperature, \( (P - 1) \) equalities of pressure and \( (P - 1)C \) equalities of activity, and hence the total number of equilibrium conditions, given as the number of equations among the variables of the system, is \( (P - 1)(C + 2) \). The number of degrees of freedom, \( F \), which the equilibrium system may have, is defined as the maximum number of variables which may be independently altered in value without disturbing the equilibrium in the system. This number is obtained as the difference between the total number of variables available to the system and the minimum number of equations among these variables that is required for maintenance of the equilibrium, i.e.,

\[
F = P(C + 1) - (P - 1)(C + 2) = C + 2 - P.
\]

Equation (60) is the Gibb's phase rule and is a powerful tool in the determination of possible equilibria which may occur in multicomponent, multiphase systems.

In the simplest of applications, i.e., in a one-component system, \( F = 3 - P \). Thus, with reference to the phase diagram for H$_2$O, shown in fig. 3, for the existence of a single phase \( F = 2 \) and so the pressure and temperature can be varied independently without disturbing the equilibrium. In a two-phase state the pressure and temperature can be varied independently without disturbing the equilibrium, i.e., with \( F = 2 \) the state of the system can be moved about within the area of stability of the single phase in the pressure-temperature diagram. However, for a two-phase equilibrium the state of the system must lie on one of the lines in fig. 3 and thus only the pressure or the temperature can be varied independently. From the phase rule, \( F = 1 \) and hence the two-phase equilibrium is univariant. The triple point, where the three phases are in equilibrium, occurs at fixed values of temperature and pressure, in accordance with \( F = 0 \) from the phase rule. The three-phase equilibrium is thus invariant and three is the maximum number of phases which can be in equilibrium with one another in a one-component system.

In a binary system, the inclusion of a second component adds an extra degree of freedom to each equilibrium and hence the maximum number of phases which can be in equilibrium with one another in a two-component system is four. However, phase diagrams for binary systems of metallurgical interest are normally presented for a pressure of 1 atm, i.e., they are the 1 atm isobaric sections of the phase equilibria occurring in pressure-temperature-composition space, and hence one of the degrees of freedom is used in specifying the pressure. Thus, at an arbitrarily selected pressure such as 1 atm, the maximum number of phases which can exist in equilibrium with one another in a binary system is three (unless, by chance, the arbitrarily selected pressure happens to be that at which an invariant four-phase equilibrium occurs). In the binary system A-B, considered at constant pressure, the available variables are \( T \), \( a_a \) and \( a_b \). For the existence of a single phase, such as \( \alpha \), \( \beta \) or liquid in fig. 12a, the phase rule gives \( F = 2 \), and hence any two of \( T \), \( a_a \) and \( a_b \) may be varied independently. For any two-phase equilibrium, \( F = 1 \) and hence the specification of any one of the three variables fixes the state of the system. For example, specification of the temperature at which the two-phase equilibrium exists fixes the compositions of the equilibrated phases on the appropriate liquidus, solidus or solvus lines; and specification of the composition of one of the equilibrated phases fixes the temperature at which the chosen composition lies on the appropriate liquidus, solidus or solvus line and fixes the composition of the second phase at the other end of the tie-line between the two equilibrated phases. The three-phase equilibrium with \( F = 0 \) is invariant, and, in fig. 12a, the eutectic equilibrium occurs at a fixed temperature at which the compositions of the \( \alpha \), \( \beta \) and liquid phases are also fixed.

If some, or all, of the components of a system can react chemically with one another to produce new chemical species, a distinction must be drawn between the terms component and species. For example the components silver and oxygen in the binary system Ag-O are capable of reacting to form the new species Ag$_2$O, and hence an equilibrium among the three species Ag, Ag$_2$O and O$_2$ can occur in the two-component system. The equilibrium among Ag, Ag$_2$O and O$_2$ is called an independent reaction equilibrium. In a system containing \( N \) species and existing in \( P \) phases among which there are \( R \) independent reaction equilibria, the number of variables is \( P(N + 1) \), i.e., \( P \) pressures + \( P \) temperatures + \( P(N - 1) \) concentrations. However, if the species \( i \) and \( j \) react to form the species \( k \), reaction equilibrium requires that

\[
\mathcal{G}_i + \mathcal{G}_j = \mathcal{G}_k,
\]

and this is an additional equation required among the variables. Thus, if \( R \) independent reaction equilibria occur, the number of equations among the \( P(N + 1) \) variables, required for equilibrium is \( (P - 1) \) equalities of temperature + \( (P - 1) \) equalities of pressure + \( (P - 1)N \) equalities of activity + \( R = (P - 1)(N + 2) + R \), and hence the number of degrees of freedom, \( F \), is

\[
F = P(N + 1) - (P - 1)(N + 2) - R = (N - R) + 2 - P.
\]

Comparison with eq. (60) indicates that

\[
C = N - R,
\]

References: p. 459.
i.e., the number of components in a system equals the number of species present minus the number of reaction equilibria. Equation (61) is normally used to calculate the number of independent reaction equilibria from knowledge of the number of components and the number of species. For example, in the two-component system Ag-O, the independent reaction equilibrium among the three species is

$$2\text{Ag} + \frac{1}{2} \text{O}_2 = \text{Ag}_2\text{O}.$$  

For equilibrium among the phases metal, metal oxide and oxygen gas in the two-component system, $F = 1$ and thus only $T$ or $p_0$ can be selected as the single degree of freedom. Selection of $T$ fixes $\Delta G^0_f$ and hence, via eq. (34), fixes $p_0$, and vice versa.

Consider the various equilibria which can occur in the ternary system Si-C-O, for which a stability diagram is shown in fig. 7. It can be considered that this system contains the six species Si, SiO$_2$, SiC, C, CO and CO$_2$, and hence $R = 6 - 3$, i.e., there are three independent reaction equilibria. These are derived as follows. The chemical reaction for formation of each compound from its elements is written:

- Si + O$_2$ = SiO$_2$,
- Si + C = SiC,
- C + O$_2$ = CO$_2$,
- C + $\frac{1}{2}$ O$_2$ = CO.

These equations are then combined in such a way as to eliminate any elements which are not considered as species in the system, and the minimum number of equations so obtained, is the number of independent reaction equilibria, $R$. In this case oxygen is not considered as species, and elimination of O$_2$ gives:

- C + CO$_2$ = 2CO, \hspace{1cm} (i)
- Si + C = SiC, \hspace{1cm} (ii)

and

- Si + 2CO$_2$ = SiO$_2$ + 2CO \hspace{1cm} (iii)

as the independent equilibria. From the phase rule, the maximum number of phases which can coexist in equilibrium is five (the condensed phases Si, SiO$_2$, SiC, C and the gas phase CO$_2$). This equilibrium is invariant and occurs at the temperature $T_m$ at which $\Delta G^0_f = 0$ and at the pressure $P = p_{CO} + p_{CO_2}$ at which $K_{SiO_2} = p_{CO}p_{CO_2}$ and $K_{SiC} = (p_{CO}p_{CO_2})^2$ are simultaneously satisfied. If the temperature is arbitrarily fixed, as is the case in fig. 7, the maximum number of phases which can coexist in equilibrium is four (three condensed phases and a gas phase). One such equilibrium occurs in fig. 7 at point b. For the coexistence of two condensed phases and a gas phase at the arbitrarily selected temperature, $F = 1$, and such equilibria lie on the univariant lines A, B, C and D in fig. 7, and for equilibrium between a single condensed phase and a gas phase, $F = 2$, corresponding to areas of single condensed phase stability in fig. 7.

Occasionally situations are found in which it might appear, at first sight, that the phase rule is not obeyed, and usually, in such situations a degree of freedom is used by a condition of stoichiometry in the system. For example, in the reduction of ZnO by graphite to produce Zn vapor, CO and CO$_2$, it might appear that the three-phase equilibrium (ZnO, C and the gas phase) in the three-component system (Zn-O-C) has $F = 3 - 3 = 0$ degrees of freedom, and that, with the five species ZnO, C, Zn$_{\text{vap}}$, CO and CO$_2$, two independent reaction equilibria occur, which can be selected as

$$\text{ZnO}_{(s)} + C_{(s)} = \text{Zn}_{(l)} + \text{CO}_{(g)}$$  \hspace{1cm} (iv)

and

$$2\text{ZnO}_{(s)} + C_{(s)} = 2\text{Zn}_{(l)} + \text{CO}_2_{(g)}$$  \hspace{1cm} (v)

for which

$$K_{(s)} = p_{CO}p_{Zn},$$  \hspace{1cm} (vi)

and

$$K_{(l)} = p_{Zn}^2p_{CO_2}.$$  \hspace{1cm} (vii)

However, selecting $T$, which fixes the values of $K_{(s)}$ and $K_{(l)}$ and any one of $p_{Zn}, p_{CO}$ or $p_{CO_2}$ as the two apparent degrees of freedom does not fix the state of the system, i.e., does not allow simultaneous solution of eqs. (vi) and (vii). This difficulty arises because the stoichiometric requirement has not been taken into consideration, i.e. that, as all the Zn and O occurring in the gas phase originates from the stoichiometric ZnO, the condition

$$n_{Zn} = n_{CO} + 2n_{CO_2},$$

$$\frac{n_{Zn}}{n_{CO}} = \frac{p_{CO} + 2p_{CO_2}}{p_{CO}}$$  \hspace{1cm} (viii)

must also be satisfied. This stoichiometric requirement decreases $F$ to unity and hence selecting $T$ as the single degree of freedom fixes the partial pressures of Zn, CO and CO$_2$ as the values required for simultaneous solution of eqs. (vi), (vii) and (viii).

9. The thermodynamics of surfaces and interfaces

9.1. The Gibbs adsorption isotherm

In passing from one phase to another in a heterogeneous system, some of the properties undergo significant changes as the boundary between the two phases is traversed. The thin region over which these changes occur is called the interface, and a complete thermodynamic analysis of the system requires consideration of the thermodynamic properties of the interface.

Consider fig. 13 which shows the variation of the concentration, $c_1$, of the component 1 across the interface region in a system comprising equilibrated $\alpha$ and $\beta$ phases. Calculation of the total number of moles of component 1 in the system as the sum $c_1^\alpha V^\alpha + c_1^\beta V^\beta$, where $V^\alpha$ and $V^\beta$ are the volumes of the phases, involves the assumption

References: p. 460
that the values $c^\alpha_1$ and $c^\beta_1$ occur up to some plane in the interface region, and evaluation of $c^\alpha_1 V^\alpha + c^\beta_1 V^\beta$ requires that a mathematical plane be located somewhere in the interface region. In fig. 13 it is seen that the number of moles of component 1 in the system, calculated as $c^\alpha_1 V^\alpha + c^\beta_1 V^\beta$, is only equal to the actual number of moles of 1 in the system, $n_1$ when the boundary plane X–X is located such that the shaded areas in fig. 13 are equal. If the boundary plane is located to the right of X–X, say at X'–X', then:

$$n_1 < c^\alpha_1 V^\alpha + c^\beta_1 V^\beta$$

or, if the boundary plane is located to the left of X–X:

$$n_1 > c^\alpha_1 V^\alpha + c^\beta_1 V^\beta.$$

The difference between $n_1$ and $c^\alpha_1 V^\alpha + c^\beta_1 V^\beta$ defines the surface concentration of component 1, $\Gamma_1$ (moles/cm$^2$), as:

$$\Gamma_1 A = n_1 - (c^\alpha_1 V^\alpha + c^\beta_1 V^\beta),$$

where $A$ is the area of surface between the two phases. Thus, with the boundary located to the left of X–X, $\Gamma_1$ is a positive quantity and with the boundary located to the right of X–X, $\Gamma_1$ is a negative quantity. In a single-component system where the boundary is between a condensed phase and a vapor phase, it is logical to locate the boundary at X–X so that the surface concentration is zero. However, with two or more components in the system it is not generally possible to locate the interface at a position at which more than one of the surface concentrations are zero. In such a case X–X is located such that the surface concentration of the solvent, $\Gamma_\gamma$, is zero and the surface concentration of the solute, $\Gamma_\delta$, is not zero. This is illustrated in fig. 14.

Fig. 14. The variations, with distance, of the concentrations of solvent and solute on passing through an interface, and illustration of the origin of surface concentration of the solute.

The definition of surface free energy per unit area, $G_s$, is analogous to that for the surface concentration, i.e.:

$$G_s A = G^* - \sum \bar{G}^\alpha n^\alpha - \sum \bar{G}^\beta n^\beta,$$  \hspace{1cm} (62)

where $G^*$ is the total free energy of the system.

The surface tension, $\sigma$, is defined as:

$$\sigma = \left( \frac{\partial G^*}{\partial A} \right)_{T,P,n},$$

and hence, when surfaces are included in the discussion, eq. (13) is written as:

$$dG^* = -S^* dT + V^* dP + \sigma dA + \sum \bar{G} \, dn,$$  \hspace{1cm} (63)

If the surface area is increased by $dA$ at constant $T$, $P$, and $n$, combination of eqs. (62) and (63) gives:

$$G_s dA = \sigma dA + \left( \sum \bar{G}^\alpha n^\alpha + \sum \bar{G}^\beta n^\beta \right).$$  \hspace{1cm} (64)

As phase equilibrium is maintained, $\bar{G}_1^* = \bar{G}_\delta^*$; mass balance requires that:

$$dn^\alpha + dn^\beta = -\Gamma_\gamma dA,$$

in which case eq. (64) can be written as:

$$G_s dA = \sigma dA + \sum \bar{G} \Gamma dA$$

References: p 469.
or:

\[ G_s = \sigma + \sum G_{sr}, \]  

(65)

i.e., the surface free energy is the surface tension plus the free energy due to the surface concentrations of the components.

Complete differentiation of eq. (65) gives:

\[ dG_s = d\sigma + \sum G_{dr}d\Gamma_r + \sum \Gamma_rdG_r, \]  

(66)

and the differential of \( G_s \) for conditions of fixed surface area and fixed \( P \) gives:

\[ dG_s = -SdT + \sum G_{dr}d\Gamma_r, \]  

(67)

Combination of eqs. (66) and (67) gives:

\[ d\sigma = -SdT - \sum \Gamma_rdG_r, \]  

(68)

which is Gibbs' equation for surface tension. At constant \( T \), eq. (68) gives, for the binary system \( A-B \) in which \( \Gamma_A = 0 \):

\[ \Gamma_B = -\left( \frac{\partial \sigma}{\partial \Gamma_B} \right)_T = -\left( \frac{\partial \sigma}{RTd \ln a_B} \right)_T, \]  

(69)

Equation (69), which is known as the Gibbs adsorption isotherm, indicates that any solute which lowers the surface tension has a positive value of \( \Gamma \) and hence is concentrated in the surface, and, conversely, any solute which raises the surface tension has a lower concentration in the surface than in the bulk phase.

The influence of dissolved oxygen on the surface tension of liquid iron at 1550°C is shown in fig. 15 as the variation of \( \sigma \) with the activity of oxygen relative to the 1 weight percent standard state. The surface concentration of oxygen at any concentration of oxygen in the bulk phase is obtained from the slope of the line and the Gibbs adsorption isotherm. At high oxygen contents the slope of the line approaches the constant value of \(-240 \text{ dyne/cm}\), which corresponds to saturation coverage of the surface by adsorbed oxygen. From the Gibbs adsorption isotherm this saturation coverage is calculated as

\[ \Gamma_o = 6.023 \times 10^{21} \times \frac{240}{8.3144 \times 10^7 \times 1823} = 9.5 \times 10^{14} \text{ atoms/cm}^2. \]

9.2. The Langmuir adsorption isotherm

Consider the equilibrium between the component \( i \) in a vapor phase and \( i \) adsorbed on the surface of a condensed phase. If it is considered that the atoms of \( i \) are adsorbed on specific adsorption sites on the surface of the condensed phase, the limit of adsorption occurs when all of the available sites are occupied by adsorbed atoms. This limit corresponds to the surface being covered by a monolayer of adsorbed atoms at the surface concentration \( \Gamma_i^\circ \). At surface concentrations, \( \Gamma_i \), less than that corresponding to monolayer coverage, the fraction of surface sites occupied, \( \theta_i \) (or the fractional saturation of the surface) is defined as:

\[ \theta_i = \frac{\Gamma_i}{\Gamma_i^\circ}. \]  

(70)

At equilibrium, the rates of adsorption and desorption of \( i \) are equal, the former being proportional to the pressure of \( i \) in the vapor phase, \( p_i \), and the fraction of unoccupied surface sites, \( (1 - \theta_i) \), and the latter being proportional to the fraction of surface sites occupied by \( i \), i.e.:

\[ k_a p_i (1 - \theta_i) = k_d \theta_i, \]

where \( k_a \) and \( k_d \) are the rate constants for the adsorption and desorption reactions, respectively. Thus:

\[ p_i = K_i \frac{\theta_i}{1 - \theta_i}, \]  

(71)

where

\[ K_i = k_d/k_a = \exp\left(-\frac{\Delta G_i^\circ}{RT}\right). \]

Reference: p. 469.
and $\Delta G^o_i$ is the change in molar free energy accompanying the transfer of one mole of $i$ from the vapor state at 1 atm pressure to the adsorbed layer on the surface at the surface concentration $\Gamma_i^0$. Equation (71), which is Langmuir's adsorption isotherm, shows that $\theta_i$ is proportional to $p_i$ at small $\theta_i$ and $(1 - \theta_i)$ is inversely proportional to $p_i$ at large $\theta_i$.

Alternatively, eq. (71) can be written as:

$$a_i = K_i^o \frac{\theta_i}{1 - \theta_i}.$$  \hspace{1cm} (72)

Belton has combined the Gibbs and Langmuir adsorption isotherms by substitution of eqs. (70) and (72) into eq. (69) to give:

$$\frac{d\sigma}{d\ln a_i} = -RT \Gamma_i^0 = -RT \theta_i^0 \Gamma_i^0 = \frac{K_i^o a_i}{1 + K_i^o a_i},$$

which, on integration between the composition limits $X_i^f$ and $X_i^g$, becomes:

$$\sigma' = \sigma^f = -RT \frac{\Gamma_i^0}{\ln(1 + K_i^o a_i)}.$$  \hspace{1cm} (73)

If Langmuir's isotherm holds at all compositions, one limit can be taken as the pure solvent, in which case eq. (73) becomes

$$\sigma^p - \sigma = -RT \frac{\Gamma_i^0}{\ln(1 + K_i^o a_i)}.$$  \hspace{1cm} (74)

where $\sigma^p$ refers to the surface tension of the pure solvent. Curve-fitting of eq. (74) with the experimental data shown in fig. 16 and $\sigma^p = 1788$ dyne/cm, $\Gamma_i^0 = 240$ dyne/cm, gives $K_i^o = 220$. Thus, if oxygen adsorbed on liquid iron exhibits ideal Langmuir behavior:

$$\theta^o = \frac{220 \cdot [\text{wt} \% \text{O}]}{1 + 220 \cdot [\text{wt} \% \text{O}]}.$$  \hspace{1cm} (75)

Equation (75) is shown in fig. 16 in comparison with the variation of $\theta^o$ obtained from the slopes in fig. 15 as $\theta^o = \frac{1}{1 + \theta^o} \Gamma^0_o$.

A number of applications of the Gibbs and Langmuir adsorption isotherms will be found in ch. 13, §§2 and 4.

9.3. Curved interfaces

The existence of surface tension gives rise to the interesting phenomenon that the equilibrium vapor pressure exerted by a spherical droplet is a function of the radius of curvature of the droplet. This phenomenon, which was first discussed by Kelvin in 1871, is of importance with respect to the dependence of the limit of solid solution of one component in another on the particle size of the second phase.

The general equation

$$dG' = -S'dT + V'dP + \sigma dA_i + \sum \Gamma_i d\theta_i$$  \hspace{1cm} (63)

was tacitly applied to systems containing flat interfaces. However, provided that $\sigma$ is not a function of the radius of curvature of the interface, and that the interface within the system does not influence the exterior pressure, eq. (63) can be applied to the transfer of matter across curved interfaces. The partial molar free energy, $G_i'$, defined from eq. (63) as:

$$G_i' = \frac{\partial G'}{\partial n_i}$$

pertains to the addition of $i$ to the system in such a manner that $A_i$ remains constant. However, in a process involving the transfer of matter to a small spherical droplet, $A_i$, being dependent on the volume, and hence on the amount of matter in the droplet, is not an independent variable. The incremental increase in volume of a droplet caused by the addition of $dn_i$ moles of the various components is:

$$dV' = \sum \overline{V}_i d\theta_i,$$

where $\overline{V}_i$ is the partial molar volume of $i$ in the system. From the relationship between the surface area and the volume of a sphere,

$$dA_i = \frac{2dV'}{r} = \sum \frac{2\overline{V}_i}{r} d\theta_i,$$

substitution of which into eq. (63) gives:

References: p. 465.
systems can be expected to provide, at best, some fundamental understanding of the nature of these interactions or, at least, a basis for correlation of the behavior, which can then be used for extrapolations of the behavior of more complex systems.

The molar free energy of formation of a solution or compound from its pure components is obtained from the activities via eq. (44) and as the various phase equilibria occurring in a materials system are determined by the variations, with composition, temperature and pressure, of the relative free energies of the various phases, such equilibria can be most precisely determined by accurate measurement of activity. Also, the activity of a component in a solution is a measure of the minimum free energy required to convert the component from its state in solution to the pure state in any proposed extraction or refining process.

In the majority of the experimental methods the activity of only one component is measured. In such cases the activities of the other components can be obtained by integration of the Gibbs-Duhem equation. For constant temperature and total pressure this expression is \( \sum \dot{X}_i \ln a_i = 0 \) or, in a more convenient form, \( \sum \dot{X}_i \ln \gamma_i = 0 \) where \( \gamma_i = a_i / \dot{X}_i \) is the activity coefficient of \( i \). Applied to the binary system A–B in which the variation of \( \gamma_A \) is known across the entire range of composition:

\[
\ln \gamma_A(\dot{X}_B) = \int_{\dot{X}_B=1}^{\dot{X}_B} \frac{X_B}{X_{B\text{sol}}} \ln \gamma_B.
\]

### 10.1. Determination of activity by experimental measurement of vapor pressure

The experimental technique for the measurement of vapor pressure is determined by the magnitude of the pressure to be measured, and the various techniques which have been developed can be classified as absolute methods (direct and indirect static methods) and indirect methods (effusion and transpiration methods).

The earliest activity measurements were made on binary alloys of Hg with Zn, Au, Ag and Tl at temperatures near the boiling point of Hg. The partial pressure of Hg exerded by an amalgam is so much greater than the partial pressure of the other component that the former can be equated with the total vapor pressure of the amalgam. In the first studies the alloy was used as the sealing liquid in a U-tube null-point manometer. The vapor in equilibrium with the alloy is contained in the closed arm of the manometer, and hydrogen, the pressure of which is measured at a second manometer, is introduced to the other arm until the meniscuses in both arms are at the same level. The vapor pressures of amalgams at lower temperatures have been measured using various devices such as membrane manometers, quartz spiral manometers and ionization gages.

The partial pressures of Zn and Cd over \( \alpha \)-Ag–Zn–Cd alloys and of Zn over \( \alpha \)-brasses have been measured by resonance absorption spectroscopy. In studying the Zn alloys, light produced by a spark between Zn electrodes, is passed through a sample of vapor in equilibrium with the alloy, and the absorption of the 3076 Å resonance line is measured. As absorption of the 3035 Å resonance line does not occur, it is used as an internal standard and the vapor pressure, \( p \), of Zn is obtained from Beer’s Law as

\[
-\ln(I_{0\text{Abs}}/I_{0\text{Abs}}) = Kp/dT
\]

where \( I \) is the intensity of the transmitted light, \( K \) is the absorp-
tion coefficient, \( T \) is the absolute temperature and \( d \) is the distance travelled by the light through the sample of vapor.

The **dew point method** is well-suited to systems containing a distinctly volatile component and has been applied to measurement of the activity of Zn in binary alloys containing Cu, Al, Ag, Au, Zn, Th, U, and Y, and the activity of Cd in Ag-Cd alloys. Experimentally, the alloy is placed at one end of a long initially evacuated tube which is heated to the desired temperature \( T_e \). The temperature of the outer end of the tube is lowered until condensation of the volatile component is observed at the temperature \( T_e \). As the pressure within the tube is uniform, the partial pressure of the volatile component exertsed by the alloy at \( T_e \) equals the saturated vapor pressure of the pure volatile component at \( T_e \). The use of fused silica tubes, which permits visual observation of condensation at the cooler end, has limited the temperature to less than 1100\(^\circ\)C, and generally, measurements have been made in the range 400–900\(^\circ\)C. In a similar **isoplastic technique**, the pure volatile component is placed in the cool end of an initially evacuated tube maintained in a known temperature gradient, and weighed quantities of the pure second component are placed at intervals along the temperature gradient. The volatile component is transferred from the vapor phase to the specimen of nonvolatile component until the alloys in equilibrium with the prevailing pressure of the volatile component are formed. In this technique, which has been applied to measurement of the activities of Al in solid Al-Fe and Al-Ni alloys, the compositions of the equilibrated alloys are determined gravimetrically.

Application of the dew point and isoplastic techniques to measurement of activity requires knowledge of the temperature dependence of the saturated vapor pressure of the volatile component.

In the **transpiration technique**, an inert carrier gas is passed over a sample at a flow rate which permits evaporation of the alloy to occur to the extent necessary to saturate the carrier gas. This technique has been used to measure the activities in liquid Fe-Cu and Fe-Ni alloys. The material evaporated from the sample is condensed downstream and is chemically analyzed. The total amount of vaporization into unit volume of the carrier gas at the total pressure \( P \) is determined by measuring the weight loss of the sample or by quantitative analysis of the amount of condensate recovered from a known volume of gas. If \( n_{\text{Fe}}, n_{\text{Cu}} \) and \( n_{\text{Ni}} \) are the numbers of moles of Fe, Cu and He carrier gas in the sampled volume, the partial pressure of Fe is calculated, from the ideal gas law, as \( P_{\text{Fe}} = P n_{\text{Fe}}/(n_{\text{Fe}} + n_{\text{Cu}} + n_{\text{He}}) \). An advantage of this technique is that the activities of both components are measured and hence internal consistency of the results can be checked using the Gibbs–Duhem equation. However, in order that surface depletion of the more volatile component be avoided, the rates of diffusion in the alloy must be faster than the rates of evaporation.

In the **effusion technique** the alloy to be studied is placed in a **Knudsen cell** (a sealed crucible containing a small orifice in its lid) and the crucible is heated in vacuum to the desired temperature. Phase equilibrium is established between the vapor phase and the condensed phase in the cell and, if the dimensions of the orifice are small in comparison with the mean free path of the vapor species, the passage of vapor species through the orifice is not disturbed by collisions. Thus the rates of effusion of the vapor species are proportional to their vapor pressures within the cell. From gas kinetic theory, the number of particles in a vapor phase striking unit area of the containing wall in unit time is \( 0.25 n \sqrt{2} \), where \( n \) is the density of vapor species and \( \sqrt{2} \) is the average speed of the particles. Consequently, the **weight lost**, \( W \), due to effusion through an orifice of area \( A \) in time \( t \) is \( p A t / (2 R T / M)^{1/2} \) and hence the pressure, \( p \), of the species in the cell is \( p = (W / A t) (2 R T / M)^{1/2} \). If a radioactive tracer is added to the alloy, the very small amounts of effusing substance can be detected. For example, gamma-ray spectrometry of neutron-irradiated Au–Cu alloys has facilitated estimation of quantities as small as \( 10^{-6} \) g.

The transpiration and effusion techniques require that the molecular weights of the vapor species be known and hence they can only be used to study systems in which no complex vapor molecules are formed.

The problems caused by complex molecule formation can be eliminated by mass-spectrometric analysis of the vapor effusing from the Knudsen cell. In the **Knudsen cell-time of flight mass-spectrometer** combination, the beam of particles effusing from the cell is introduced to the ionization chamber of the mass-spectrometer through a slit. Ionization is produced by a pulsing electron beam and after each pulse the ionization chamber is cleared of ions by a pulse of small negative potential. The ions are then subjected to a continuously maintained high negative potential which accelerates them into a field-free drift tube, and the time required for a given ion to traverse the drift tube and be detected is proportional to \( (v / e)^{1/2} \). The ion current, \( I_i \), measured for the species \( i \) is related to the vapor pressure of \( i \) as:

\[
I_i = K_i T_i \frac{P_i}{N_i}
\]

where the constant \( K \) is determined by the ionization cross-section of the ion, the detector sensitivity and the geometry of the Knudsen cell–ion source. The application of the technique to measurement of activities in binary systems was greatly facilitated by a manipulation of the Gibbs–Duhem equation which allows the variations, with composition, of the activity coefficients of the individual components to be obtained from the corresponding measured ratio of the activity coefficients as:

\[
\ln \gamma_i (at X_i) = -\int_1^{X_i} X_a d \ln \frac{P_A}{P_i}
\]

From eq. (80):

\[
\frac{I_i}{P_i \sqrt{2}} \propto \frac{P_A}{P_i} \frac{\gamma_i X_i}{\gamma_a X_a}
\]

substitution of which into eq. (81) gives:

\[
\ln \gamma_i (at X_i) = -\int_1^{X_i} X_a d \left( \ln \frac{I_i}{I_a} - \frac{X_i}{X_a} \right)
\]

Use of a mass-spectrometer requires that a pressure of less than \( 10^{-4} \) atm be maintained in the areas of the ion source, analyzer and detector. This technique has been applied to

References: p. 469.
measurement of activities in a large number of binary and ternary systems containing V, Cr, Fe, Co, Ni, Cu, Ag, Au, Al, Ti, Pb, Sn, Bi, Sb, and In.

10.2. Determination of activity by establishing heterogeneous equilibrium

Heterogeneous equilibrium at constant temperature and pressure requires that the partial molar free energy, and hence activity, of each component of the system be the same in each of the phases present, i.e., \( a_i \) (in phase I) = \( a_i \) (in phase II) = \( a_i \) (in phase III) = ... Thus, if the activity of a component can be fixed at a known value in any one of the phases, its value in every other phase is known.

One of the more simple heterogeneous equilibria involves a binary liquid, saturated with one of its components. In a simple binary eutectic system exhibiting virtually complete mutual immiscibility in the solid state, the saturated liquids on the liquidus lines are in equilibrium with virtually pure solids. Thus, in the melt of A-lipidus composition at the liquidus temperature \( T \), the activity of \( A \) relative to pure liquid \( A \) as the standard state equals the activity of pure solid \( A \) relative to liquid \( A \) as the standard state, both being given by \( a_A = \exp\left( -\Delta G_{m,A}^0 / RT \right) \) where \( \Delta G_{m,A}^0 \) is the molar free energy of melting of \( A \) at temperature \( T \). Activities have been calculated in this manner along liquidus lines in such systems as Al-Si and Ag-Pb.

Fe and Ag are virtually immiscible in the liquid state, and when Si is added as a solute to coexisting liquid Fe and Ag it is distributed between the two liquids such that its activity is the same in both phases. The activities of Si in liquid Fe and liquid Fe-C alloys have been determined by chemical analysis of equilibrated Fe and Ag liquids containing Si, and knowledge of the activity of Si in Al-Si alloys. In a similar manner the activity of Ag in Al-Fe alloys has been determined from measurement of the equilibrium partitioning of Ag between the virtually immiscible liquids Al and Pb, and the activity of Al in Al-Co alloys has been determined by partitioning Al between the virtually immiscible liquids Ag and Co.

The respective equilibrium constants for the reactions CO\(_2\)+C\(_{\text{graphite}}\)=2CO and CO+\( \text{O}_2\)=CO\(_2\) are:

\[
K_4 = \frac{p_{\text{CO}}}{p_{\text{CO}_2}a_{c}}
\]

(82)

and

\[
K_5 = \frac{p_{\text{CO}_2}}{p_{\text{CO}}a_{\text{O}_2}}
\]

(83)

Thus, at a fixed temperature, which determines the values of \( K_4 \) and \( K_5 \), a CO-CO\(_2\) gas mixture of known \( p_{\text{CO}} \) and \( p_{\text{CO}_2} \) has an activity of carbon given by eq. (82) and a partial pressure of oxygen given by eq. (83). Similarly, by virtue of the equilibrium \( \text{H}_2 + \text{O}_2 = \text{H}_2\text{O} \), an \( \text{H}_2-\text{H}_2\text{O} \) mixture of known \( p_{\text{H}_2} \) and \( p_{\text{H}_2\text{O}} \) exerts a unique partial pressure of oxygen at any temperature; by virtue of the equilibrium \( \text{H}_2 + \text{S}_2 = \text{H}_2\text{S} \), an \( \text{H}_2-\text{H}_2\text{S} \) mixture of known \( p_{\text{H}_2} \) and \( p_{\text{H}_2\text{S}} \) exerts a unique partial pressure of sulfur at any temperature; and by virtue of the equilibrium \( \text{C}_{\text{graphite}} + 2\text{H}_2 = \text{CH}_4 \), a \( \text{CH}_4-\text{H}_2 \) mixture of known \( p_{\text{CH}_4} \) and \( p_{\text{H}_2} \) has a unique activity of carbon at any temperature. Consequently, CO-CO\(_2\) and \( \text{CH}_4-\text{H}_2 \) mixtures can be used as gas phases of fixed activity of carbon for use in the establishment of heterogeneous equilibria between a gas phase and a condensed phase. Similarly, CO-CO\(_2\) and \( \text{H}_2-\text{H}_2\text{O} \) mixtures can be used as gas phases of fixed oxygen pressure and \( \text{H}_2-\text{H}_2\text{S} \) mixtures can be used as gas phases of fixed sulfur pressure. The activities of carbon in liquid and solid iron have been determined by equilibrating iron with CO-CO\(_2\) and \( \text{CH}_4-\text{H}_2 \) mixtures and measuring the equilibrium carbon content of the metal phase, and the activities of oxygen and sulfur in liquid iron have been determined by equilibrating iron with \( \text{H}_2\text{O-}\text{H}_2 \) and \( \text{H}_2\text{S-}\text{H}_2 \) mixtures, respectively. In more simple gas-metal equilibria the activities of hydrogen and nitrogen in iron have been determined by measuring the solubilities of the gases as functions of gas pressure. Activities in the system Fe-Fe\(_2\text{O}_3\) have been determined by experimental observation of the variation of the composition of small samples of condensed phases with temperature and oxygen pressure imposed by an equilibrating gas phase. The variation, with composition, of the activity of Fe in the system is determined by Gibbs-Duhem integration of the corresponding measured variation of the equilibrium partial pressure of oxygen. The oxygen content of liquid iron in equilibrium with pure liquid iron oxide at 1600°C is 0.23 wt%.

If the oxide of a less noble metal than iron is dissolved in the liquid iron oxide, the activity of iron oxide, and hence the equilibrium oxygen content of the liquid iron are decreased. If the latter is \( x \) wt%, the activity of FeO, relative to pure Fe-saturated iron oxide as the standard state, in the oxide solution is \( x/0.23 \). This technique has been used to determine the activity of FeO in CaO-FeO and CaO-FeO-SiO\(_2\) melts saturated with liquid iron.

One step more complex is the establishment of equilibrium between a gas phase and two condensed phases. The equilibrium between manganese, manganese oxide and a CO-CO\(_2\) mixture, expressed as Mn+CO\(_2\)=MnO+CO requires:

\[
K = \frac{p_{\text{CO}}a_{\text{Mn}}}{p_{\text{CO}_2}a_{\text{MnO}}}
\]

(84)

Thus, at a given temperature, the equilibrium between pure Mn (at unit activity) and Mn-saturated pure MnO (at unit activity) occurs at a unique value of the ratio \( p_{\text{CO}}/p_{\text{CO}_2} \) given by eq. (84). If a metal more noble than Mn is embedded in an excess of MnO and subjected to a lower \( p_{\text{CO}}/p_{\text{CO}_2} \) ratio, manganese is transferred from the MnO to the metal phase until the activity of Mn required by eq. (84) and the imposed \( p_{\text{CO}}/p_{\text{CO}_2} \) is established. The manganese content of the alloy corresponding to the imposed activity is determined by chemical analysis. The other component of the alloy must be sufficiently more noble than Mn that formation and solution of its oxide in the MnO phase is negligible. The activity of Mn in Mn-Pt alloys has been determined in this manner. Having determined this relationship, the activity of MnO in oxide melts containing oxides more stable than MnO can be determined by equilibrating a small sample of Pt with an excess of oxide melt and a CO-CO\(_2\) gas mixture. Again, as Mn is distributed between the Pt-Mn alloy and the oxide melt in accordance with eq. (84) and the imposed
The chemical analysis of the equilibrated Pt–Mn alloy yields $\alpha_{\text{Mn}}$ and hence, from eq. (84), the value of $\alpha_{\text{MnO}}$ in the oxide melt. In this application, the other oxide component must be of a metal which is sufficiently less noble than Mn that the extent of its solution in the Pt Mn phase is negligible. This technique has been used to determine the activity of MnO in systems such as MnO–SiO$_2$, MnO–TiO$_2$, MnO–Al$_2$O$_3$, MnO–B$_2$O$_3$, and MnO–CaO–SiO$_2$.

Other examples of determination of activities by establishing equilibrium between a binary alloy, a nonmetallic phase of known composition and a gas phase include:

- Fe($\text{Fe–Ni alloys}) + \text{H}_2\text{O} = \text{FeO} + \text{H}_2$
- 2Cr($\text{Cr–Ni alloys}) + 3\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 3\text{H}_2$
- 3Mn($\text{Mn–Cu alloys}) + \text{C} = \text{Mn}_3\text{C} + 2\text{H}_2$
- 2Cu($\text{Cu–Au alloys}) + \text{H}_2\text{S} = \text{Cu}_2\text{S} + \text{H}_2$
- 3Si($\text{Si–Ag alloys}) + \text{N}_2$ in $\text{N}_2$–H$_2$ mixtures = Si,N$_4$

Again, in this application, the “inert” metal must be sufficiently more noble than the primary component metal that its occurrence in the equilibrium nonmetallic phase is negligible. Corrections are required in systems where the nonmetallic phase is not a pure compound. Thus, for example, in eq. (85), the activity of FeO is that in the wustite equilibrated with the imposed partial pressure of oxygen, relative to Fe-saturated wustite as the standard state. Equation (85) has also been used to determine the activity of FeO in FeO–SiO$_2$ melts by establishing the equilibrium Fe + $\text{H}_2\text{O} = \text{FeO} + \text{H}_2$ in FeO–SiO$_2$ melts.

If the difference between the nobilities of the metals is small enough that an oxide solution is produced in equilibrium with the binary alloy phase a different approach is taken. For example, if a small specimen of an Fe–Mn alloy is equilibrated with an excess of an FeO–MnO solid solution, the exchange equilibrium Fe + MnO = Mn + FeO is established, wherein $K = \alpha_{\text{Mn}}\alpha_{\text{FeO}}/\alpha_{\text{Fe}}\alpha_{\text{MnO}}$. From chemical analysis of the equilibrated Fe–Mn alloy and knowledge of the activities in the system Fe Mn, the ratio $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$ in the equilibrating oxide solution is obtained as:

$$\gamma_{\text{FeO}}/\gamma_{\text{MnO}} = K = \alpha_{\text{Mn}}\alpha_{\text{FeO}}/\alpha_{\text{Fe}}\alpha_{\text{MnO}}$$

and Gibbs–Duhem integration of the variation of this ratio with composition in the oxide solution according to eq. (81) yields the individual activity coefficients, and hence activities, of the components of the oxide solution. This technique has been used to determine activities in the systems Fe$_2$SiO$_4$–Co$_2$SiO$_4$ and Fe$_2$SiO$_4$–Mn$_2$SiO$_4$.

Activities have been determined by establishing equilibrium among three condensed phases and a gas phase. As an example, the activity of SiO$_2$ in CaO–MgO–Al$_2$O$_3$–SiO$_2$ melts has been determined by establishing the equilibrium

$$\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}$$

in systems comprising a silicate melt, solid graphite, liquid iron and CO gas at 1 atm pressure, and by establishing the equilibrium $\text{SiO}_2 + 2\text{SiC} = 3\text{Si} + 2\text{CO}$ in systems comprising a silicate melt, solid SiC, liquid iron and CO gas at 1 atm pressure. The activity of SiO$_2$ is obtained from chemical analysis of the equilibrated liquid phases, knowledge of the equilibrium constants for the reactions given by eqs. (86) and (87) and knowledge of the activity of Si in Fe–Si–C melts. Gibbs–Duhem integration of the results yields activities in the systems CaO–SiO$_2$, CaO–Al$_2$O$_3$, MgO–SiO$_2$, MgO–Al$_2$O$_3$–SiO$_2$, MgO–CaO–SiO$_2$ and MgO–Al$_2$O$_3$–SiO$_2$.

### 10.3. Electrochemical measurement of activity

The EMF of a reversible galvanic cell, $\epsilon$, is related to the free energy change, $\Delta G$, for the cell reaction as $\Delta G = -F\epsilon$, where $F$ is Faraday’s constant and $z$ is the number of Faradays required for the cell reaction. Thus, in a concentration cell of the type

$$\text{pure metal A} \text{ionic conductor containing metal A ions of valence} \times \text{alloy A–B}$$

the cell reaction is $A\text{pure} \rightarrow A\text{in the A–B alloy}$ for which $\Delta G = R T \ln \alpha_A$ (in the A B alloy). Thus the activity of A in the alloy is obtained as $\ln \alpha_A = -z\epsilon/F$. The determination of activity by measurement of the EMF of an electrochemical cell requires that the electrolyte be a purely ionic conductor and that the valency $z_k$ be defined. A further requirement is that the extent of the reaction occurs at the cathode–electrolyte interface between B in the alloy and in the electrolyte be negligible. If this condition is not met, the measured EMF contains a contribution of unknown magnitude arising from the transfer of electrolyte between regions of different composition. In practice, the extent of the reaction is rendered negligible by ensuring that B is significantly more noble than A. Moltken chlorides are purely ionic conductors and hence these melts are popular as liquid electrolytes. The concentrations of low valent cations in the electrolyte are minimized by dissolving the chlorides in mixtures of alkali chlorides.

The activity of Al in Al–Ag melts in the range 700–800°C has been obtained from measurement of the EMFs of cells of the type

$$\text{Al}_{11/3}\text{Al}^{2+}\text{(in KCl-NaCl)}\text{Al–Ag}_{11/3}$$

Similarly the activities of Cd in Cd–Pb, Cd–Bi, Cd–Sb and Cd–Sn alloys, and the activities of Cu in Cu–Au melts and Ag in Ag–Au melts have been determined from concentration cells with liquid chloride electrolytes.

The cell

$$\text{Mg}_{11/3}\text{MgCl}_{2(11\text{Cl}_{1/3})\text{mm}}$$

is a formation cell in which the cell reaction is $\text{Mg} + \text{Cl}_2 = \text{MgCl}_2$. With pure liquid Mg, pure liquid MgCl$_2$ and Cl$_2$ at 1 atm pressure, the free energy change is the standard free energy change, $\Delta G^\circ$, and the EMF is the standard EMF, $\varepsilon = -\Delta G^\circ/2F$. Allowing the anode with a more noble metal such as Al alters the free energy change for the cell reaction to $\Delta G = \Delta G^\circ - R T \ln \alpha_A$ (in the alloy) and hence the cell EMF to

$$\varepsilon = e^{\epsilon} + \frac{RT}{2F} \ln \alpha_A$$

### References

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Equation (88) has been used to determine the activities of Mg in Mg–Al melts from EMF measurements in the range 700–880°C.

Similarly, the formation cell

\[ \text{Pb}_{(l)}|\text{PbO}_{(s)}|\text{O}_{2(g)}|\text{air} \]

has a standard EMF of \( \varepsilon = -\Delta G^\circ / 2F \). Alloying the PbO electrolyte with the oxide of a less noble metal, such as SiO\(_2\), changes the cell EMF to:

\[ \varepsilon = \varepsilon^0 - \frac{RT}{2F} \ln a_{\text{PbO}} \] (in PbO–SiO\(_2\)),

and this has been used as the basis for electrochemical determination of the activities in the system PbO–SiO\(_2\) in the range 850–1050°C.

Within wide ranges of temperature and oxygen pressure, ZrO\(_2\), ThO\(_2\), and TiO\(_2\) in the fluorite structure, stabilized by solid solution with CaO and Y\(_2\)O\(_3\), respectively, exhibit unusually high conductivities and transport numbers for O\(^2\)- of essentially unity. Consequently CaO–ZrO\(_2\) and Y\(_2\)O\(_3\)–ThO\(_2\) have been used as solid electrolytes in oxygen concentration cells of the type

\[ \text{Pt}, \text{O}_{2(g)}|\text{alumina} \| \text{CaO–ZrO}_2 \| \text{O}_{2(g)}|\text{alumina} | \text{Pt}, \]

in which the cell reaction is \( \text{O}_{2(g)} \rightarrow \text{O}_{2(g)} \) and the cell EMF is \( \varepsilon = -\Delta G^\circ / 4F = -(RT/4F) \) in \( \text{Pt}/\text{Pt} \). The oxygen pressure at the electrodes can be fixed by using equilibrated metal–metal–oxide couples, e.g., with Fe–FeO and Ni–NiO the cell becomes Fe, FeO|CaO–ZrO\(_2\), Ni, NiO,

with a cell reaction of \( \text{NiO} + \text{Fe} = \text{FeO} + \text{Ni} \). With the electrodes Fe–FeO and (Fe–Ni)|FeO, the cell reaction is \( \text{Fe}_{\text{pure}} \rightarrow \text{Fe}_{\text{Ni-Al alloy}} \) and the cell EMF is

\[ \varepsilon = \frac{RT}{2F} \ln a_{\text{Fe}} \] (in the alloy). (89)

This method is similar to that discussed in connection with eq. (85). In the chemical equilibrium technique the oxygen pressure is imposed, and the Fe–Ni alloy equilibrium with FeO and the imposed oxygen pressure is produced in the experimental apparatus. In the EMF technique the oxygen pressure in equilibrium with a given Fe–Ni alloy and FeO is measured. Equation (89) has been used as the basis for electrochemical determination of the activities in a large number of solid and liquid binary alloy systems, the majority of which contains Fe, Co, Ni or Cu as the less noble metal. The activity of Si in Fe–Si alloys at 1550°C and 1600°C has been determined with electrodes of Cr, Cr\(_2\)O\(_3\), and SiO\(_2\). Fe–Si and activities in the systems Ta–W and Ta–Mo have been determined with a \( \text{Y}_2\text{O}_3–\text{ThO}_2 \) electrolyte and Ta, TaO\(_2\), and Ta–X, TaO\(_2\), electrodes. The activities of SnO in SnO–SiO\(_2\) melts and PbO in PbO–SiO\(_2\) melts have been determined from cells of the type M, MO|CaO–ZrO\(_2\)|M, MO–SiO\(_2\).

Other solid electrolytes which have been used include ß-alumina and soft soda glass for measurement of the activity of sodium in alloys, and glasses containing K\(^+\) and Ag\(^+\) for study of K and Ag alloys, respectively. It can be expected that, as new solid state electrolytes are developed for possible use in fuel cells, they will be applied to the determination of activities by EMF measurements.

Bibliography