2 Thermodynamic Fundamentals

2.1 INTRODUCTION

Metallurgical thermodynamics belongs to the field of chemical thermodynamics, which is employed to predict whether a chemical reaction is feasible. It also allows quantitative calculation of the state of equilibrium of a system in terms of composition, pressure, and temperature, as well as determination of heat effects of reactions and processes. Laws of thermodynamics are exact. Therefore, calculations based on them are, in principle, sound and reliable. There are standard books dealing with the basics of chemical-cum-metallurgical thermodynamics.[1,2] The following is a very brief review only, with special emphasis on topics of relevance to secondary steel making.

All reactions and processes tend towards the thermodynamic equilibrium. If sufficient time is allowed, then attainment of equilibrium is possible. Steelmaking reactions and processes are very fast due to their high temperatures. As a result, some of these have been found to approach equilibrium closely within the short processing time. Examples of this in secondary steelmaking are provided in subsequent chapters. Therefore, a full knowledge of thermodynamics is required for the understanding, control, design, and development of metallurgical processes.

A discussion of thermodynamics requires precise definitions of some terms. For example, a *system* is defined as any portion of the universe selected for consideration. The rest of the universe outside the system is known as *surroundings*. An *open* system exchanges both matter and energy, a *closed* system exchanges only energy, and an *isolated* system exchanges nothing with the ambient. The *state* of a system is defined at any instant by specifying all state variables and properties such as temperature, pressure, volume, surface tension, viscosity, etc. A complete listing of all the properties of a state is superfluous, because many of them are often mutually interdependent.

Pressure (P), volume (V), and temperature (T) are the most common state variables. When a state is described by such variables, assumptions are made implicitly or explicitly. For example, if there is no mention of magnetic field intensity, then it implies that the magnetic effect is insignificant. Similarly, if surface tension forces are ignored, then there is the underlying assumption that surface energy is negligible. Again P, V and T are interrelated. For example, for an ideal gas,

$$PV = nRT \tag{2.1}$$

where n is the number of moles occupying volume V. In general, for a *thermodynamic substance*, if $V/n = v$, where v is molar volume, then

$$v = f(P, T) \tag{2.2}$$

where the R.H.S. of Eq. (2.2) denotes some appropriate function of P and T. Therefore, the state of a thermodynamic substance can be defined by any two of the above three variables, provided that the only work done is against pressure.

It should be noted that, among these variables, V is a property that depends on the amount of substance under question. On the other hand, P and T are not dependent on mass. A variable such as volume, which depends on the amount of substance in the system, is known as an *extensive variable*. Variables such as temperature, pressure, etc., which do not depend on mass, are known as *intensive variables*. It goes without saying that, if an equation contains a variable denoting an extensive property, then there must also be a term denoting mass or mol as in Eq. (2.1). If the latter is missing, there is an implicit assumption that the extensive property is per mass/mol, such as v, in Eq. (2.2), which becomes an intensive property. Thermodynamic relations among intensive properties are of more general validity.

A state can be characterized by state variables only when the system has come to *equilibrium* with respect to those variables. Then and only then can the state be correctly defined in terms of these variables. This also implies that the magnitudes of related intensive properties throughout the system are the same.

Thermodynamic equilibrium necessarily requires the attainment of mechanical, thermal, and chemical equilibria. Mechanical interaction of a system with the surroundings is most commonly in the form of pressure. Therefore, in the absence of a field of force, *mechanical equilibrium* generally means pressure equilibrium, i.e., uniform pressure throughout the system. Similarly, *thermal equilibrium* implies uniformity of temperature, and *chemical equilibrium,* in a broad sense, means uniformity of chemical potential for all species in the system. At chemical equilibrium, there is no tendency for further reaction.

It is possible that the system is at equilibrium with respect to some variables but not some others. This is known as *partial equilibrium,* and thermodynamics is capable of handling this as well. However, a precondition for handling any chemical equilibrium is the establishment of mechanical and thermal equilibria.

2.2 FIRST AND SECOND LAWS OF THERMODYNAMICS

2.2.1 Statement of the First Law

$$dE = \delta q - \delta w, \text{ for an infinitesimal change} \tag{2.3}$$

where dE = an infinitesimal change in the *internal energy (E)* of the system
δq = an infinitesimal quantity of *heat absorbed* by the system
δw = an infinitesimal quantity of *work done* by the system

For a finite change,

$$\Delta E = q - w \tag{2.4}$$

The first law of thermodynamics is nothing but a statement of the *law of conservation of energy.* Careful experiments have revealed that q is not equal to w for many processes, apparently violating the law of conservation of energy. To make these findings conform to the law of conservation of energy, the concept of internal energy *(E)* was proposed. Internal energy is the energy stored in the system. In chemical thermodynamics, E is taken as the energy of atoms and molecules.

Experiments have proved that E is a *state property.* Ignoring other fields of forces, and for a closed system,

$$E = f(P, T) \tag{2.5}$$

Again, we do not know or cannot measure the absolute value of E. All we can measure are changes in E (ΔE for a finite change, dE for an infinitesimal change).

2.2.2 ENTHALPY AND SPECIFIC HEAT

Every substance, in a given state at a certain temperature, has a characteristic value of *heat content* or *enthalpy (H).*

By definition,

$$H = E + PV \tag{2.6}$$

and hence is a state property. Differentiating,

$$dH = (dE + P\ dV) + V\ dP = \delta q + Vdp \tag{2.7}$$

at constant P, $$dP = 0$$

and therefore, $$dH = \delta q \tag{2.8}$$

or, $$\Delta H = q \tag{2.9}$$

Therefore, at constant P, q is related to the change of state property (H) and hence can be calculated from the initial and final states only. We do not have to consider the path.

This is a great simplification. Most of the processes are carried out approximately at constant pressure. Even though the pressure fluctuates, it does not introduce any significant error if q is taken as ΔH. Molar ΔH (i.e., ΔH per mole) values for a variety of processes have been determined experimentally and are available in thermodynamic data books. Using them, heat requirements of processes can be calculated, and process heat balances can be worked out.

The *molar specific heat* of a substance is the heat required to raise temperature of one mole of a substance by 1 Kelvin. Specific heat at a constant pressure is given by

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{2.10}$$

Experimental C_p values are expressed as functions of temperature as

$$C_p = a + bT + \frac{c}{T^2} \tag{2.11}$$

where T is temperature in Kelvins, and a, b, and c are empirical constants. Values of C_p may be found in standard thermodynamic data books. Table 2.1 presents values of C_p and enthalpies of transformations for iron.

2.2.3 STATEMENT OF THE SECOND LAW

The second law of thermodynamics is based on universal experience. It may be stated in a variety of ways. For the purpose of the ensuing discussions, the following statement would be useful: "Spontaneous processes, i.e., processes taking place without any outside intervention, such as diffusion, free expansion of a gas, heat flow, etc., are not thermodynamically reversible."

TABLE 2.1
Specific Heats and Enthalpies of Transformation for Iron

Transformation Reaction	Temperature (K)	Specific heat (C_p) (Jmol^{-1} k^{-1})	Enthalpy change (ΔH) (J mol^{-1})
$Fe_\alpha \rightarrow Fe_\beta$	1033	$Fe_\alpha = 17.49 + 24.769 \times 10^{-3}\,T$	+ 5105
$Fe_\beta \rightarrow Fe$	1187	$Fe_\beta = 37.66$	+ 670
$Fe_\gamma \rightarrow Fe_\delta$	1665	$Fe_\gamma = 7.70 + 19.5 \times 10^{-3}\,T$	+ 837
$Fe_\delta \rightarrow Fe_{liq}$	1809	$Fe_\delta = 28.284 + 7.53 \times 10^{-3}\,T$	+13807
		$Fe_{liq} = 35.4 + 3.74 \times 10^{-3}\,T$	

Source: F.R. DeBoer, R. Boom, W.C.M. Mattens, A.R. Miedema, and A.K. Niessen, *Cohesion in Metals—Transition Metal Alloys,* Cohesion and Structure Series, North-Holland, Amsterdam (l988).

2.2.4 REVERSIBLE PROCESSES

Heat and work are not properties of state. They are energy in transition, and thus the magnitude of q and w would depend on the path that the process takes in going from an initial to the final state. That is why δq and δw rather than dq and dw have been employed in Eq. (2.3). This is a great mathematical limitation. Hence, considerable effort has been made by thermodynamicists to examine under what conditions δw and δq can be related to state properties. Obviously, the path has to be defined. This is where the concept of reversible processes has assumed importance.

In a reversible process, the system is displaced from equilibrium infinitesimally and then allowed to attain a new equilibrium, then again displaced infinitesimally and so on. Thus, it may be defined as "the hypothetical passage of a system through a series of equilibrium states." A reversible process is very slow and impractical. No practical process is reversible in strict sense. However, the concept is very useful and a key one in thermodynamics. The term *reversible* has been coined because such a process can be reversed along the same path without leaving any permanent change in the system or its surrounding.

2.2.5 ENTROPY (S)

A system may go from an initial to the final state by any of the innumerable paths available to it. These paths would be mostly irreversible. Some of them, however, would be or can be treated as reversible. It can be proved on the basis of *Carnot's Cycle* that the quantity $\delta q_{rev}/T$ is dependent only on the initial and final states, where δq_{rev} refers to δq along a reversible path. The following relationship has been thereby proposed.

$$\sum_{A \to B} \frac{\delta q_{rev}}{T} = S_B - S_A = \Delta S \tag{2.12}$$

or, in differential form,

$$\frac{\delta q_{rev}}{T} = dS \tag{2.13}$$

where A and B designate the initial and final states respectively, and S is a state function (i.e. state property) known as *entropy.*

According to the *third law of thermodynamics*, the entropy of a substance at zero Kelvins (i.e., absolute zero), and at complete internal equilibrium, is zero if there is perfect order in that state, e.g., in perfectly crystalline solids, but not in metastable vitreous phases. This allows evaluation of absolute values of entropy, which are also tabulated in the thermodynamic data books.

Example 2.1

Calculate (a) entropy (S^o) of 1 mole of liquid iron at 2000 K, and (b) enthalpy change $(\Delta H^\circ_{2000} - \Delta H^\circ_{298})$ in heating 1 mole of iron from 298 to 2000 K. Note that

$$(S^\circ_{298}(\alpha - Fe) \;=\; 27.15 \text{J mol}^{-1} K^{-1})$$

Solution

(a) Entropy of liquid iron at 2000 K, i.e.

$$S^o_{2000}(l) \;=\; S^o_{298}(\alpha - Fe) + \int_{298}^{1033} \frac{C_p(\alpha)}{T} dT + \frac{\Delta H_{a \to B}}{1033} + \int_{1033}^{1187} \frac{C_p(\beta)}{T} dT + \frac{\Delta H_{B \to \gamma}}{1187} +$$
$$\int_{1187}^{1665} \frac{C_p(\gamma)}{T} dT + \frac{\Delta H_{\gamma \to \delta}}{1665} + \int_{1665}^{1809} \frac{C_p(\delta)}{T} dT + \frac{\Delta H_m}{1809} + \int_{1809}^{2000} \frac{C_p(l)}{T} dT \qquad \text{(E1.1)}$$

Substituting the values of C_p and ΔH for various transformations from Table 2.1.

$$S^o_{2000(l)} \;=\; 27.15 + \int_{298}^{1033} \left[\frac{17.49}{T} + 24.769 \times 10^{-3}\right] dT + \frac{5105}{1033}$$

$$+ \int_{1033}^{1187} \left[\frac{37.66}{T}\right] dT + \frac{670}{1187} + \int_{1187}^{1665} \left[\frac{7.7}{T} + 19.5 \times 10^{-3}\right] dT + \frac{837}{1665}$$

$$+ \int_{1665}^{1809} \left[\frac{28.284}{T} + 7.531 \times 10^{-3}\right] dT + \frac{13807}{1809} + \int_{1809}^{2000} \left[\frac{35.4}{T} + 3.745 \times 10^{-3}\right] dT$$

$$= \; 105.5 \quad \text{J mol}^{-1} K^{-1} \quad \text{(Ans.)}$$

(b) Enthalpy change in heating 1 mole of iron from 298 to 2000 K

$$H^o_{2000(l)} - H^o_{298(s)} \;=\; \int_{298}^{1033} C_p(\alpha) dT + \Delta H_{\alpha \to b} + \int_{1033}^{1187} C_p(\beta)(dT + \Delta H_{\beta \to \gamma})$$

$$+ \int_{1187}^{1665} C_p(\gamma) dT + \Delta H_{\gamma \to \delta} + \int_{1665}^{1809} C_p(\delta) dT + \Delta H_m + \int_{1809}^{2000} C_p(l) dT \qquad \text{(E1.2)}$$

Substituting the values of C_p and ΔH from Table 2.1,

$$H^o_{2000(l)} - H^o_{298(s)} = \int_{298}^{1033} [17.49 + 24.769 \times 10^{-3} T] dT + 5105 + \int_{1033}^{1187} 37.66 \; dT + 670$$

$$+ \int_{1187}^{1665} [7.7 + 19.5 \times 10^{-3} T] dT + 837$$

$$+ \int_{1665}^{1809} [28.284 + 7.531 \times 10^{-3} T] dT + 13807$$

$$+ \int_{1809}^{2000} [35.4 + 3.745 \times 10^{-3} T] dT$$

$$= 24971 + 5105 + 5800 + 670 + 16972 + 837 + 5957 + 13807 + 7489 = 821788 \quad \text{J mol}^{-1}$$

(Ans.)

2.2.6 COMBINED EXPRESSIONS OF FIRST AND SECOND LAWS

For a reversible process and a closed system, if the only work done is against pressure, then combining the Eqs. (2.3) and (2.13) we obtain Eq. (2.14), i.e.,

$$dE = T\,dS - P\,dV \tag{2.14}$$

again,

$$dH = dE + P\,dV + V\,dP \tag{2.15}$$

Combining Eqs. (2.8) and (2.14),

$$dH = T\,dS + V\,dP \tag{2.16}$$

2.3 CHEMICAL EQUILIBRIUM

2.3.1 FREE ENERGY AND CRITERION OF EQUILIBRIUM

In Eq. (2.14), internal energy E is expressed as a function of entropy S and volume V, both of which are independent state variables. Experimental control of temperature and pressure is easier. Gibbs, therefore, defined a new function G, where

$$G = E + PV - TS = H - TS \tag{2.17}$$

G is known as *Gibbs free energy*, which is a state property from the definition of G. Differentiating Eq. (2.17),

$$dG = dE + P\,dV + V\,dP - T\,dS - S\,dT \tag{2.18}$$

For a closed system, and for a reversible process (or at equilibrium), if the only work done is against pressure, then combining Eqs. (2.14) and (2.18),

$$dG = V\,dP - S\,dT \tag{2.19}$$

at equilibrium, under constant temperature and pressure,

$$(dG)_{P,T} = 0, \text{ i.e. } (\Delta G)_{P,T} = 0, \text{ for a finite process} \tag{2.20}$$

For an irreversible (spontaneous) process, it can be shown that

$$dG < V\,dP - SdT \tag{2.21}$$

Therefore, at constant temperature and pressure, a spontaneous, (i.e., natural or irreversible) process would occur if

$$(dG)_{P,T} < 0, \text{ i.e. } (\Delta G)_{P,T} < 0, \text{ for a finite process} \tag{2.22}$$

Thus, the Gibbs free energy provides us with a criterion to predict equilibrium or possibility of occurrence of a spontaneous process at constant T and P.

2.3.2 ACTIVITY, EQUILIBRIUM CONSTANT

Consider the following isothermal reaction, which occurs at a temperature T.

$$aA + bB = lL + mM \tag{2.23}$$

Here A, B, L, and M are general symbols of chemical species and a, b, l, and m denote the number of moles of each. The word *isothermal* implies that the initial temperature at the beginning of the reaction and the final temperature (when equilibrium is reached) are the same. It is not necessary that the temperature remain unchanged throughout the progress of the reaction.

The free energy change for reaction represented by Eq. (2.23) may be expressed as

$$\Delta G = (1\overline{G}_L + m\overline{G}_M) - (a\overline{G}_A + b\overline{G}_B) \tag{2.24}$$

where $\overline{G}_i$ is the *partial molar free energy* of the species i. The *standard state* is the stablest state of the pure substance at the same temperature (T) and at a pressure of 1 atmosphere. The standard state could thus be a pure solid or liquid or ideal gas at 1 atmosphere of pressure. The magnitude of a variable for any standard state is indicated by a superscript o.

It can be shown that

$$\overline{G}_i - G_i^o = RT\ ln\ a_i \tag{2.25}$$

where, G_i^o = free energy of species i at its standard state

$a_i = \dfrac{f_i}{f_i^o}$ = *activity* of species i at partial molar free energy $\overline{G}_i$

f_i = the *fugacity* of i at the state under consideration

f_i^o = the fugacity at its standard state

For ideal gases, fugacity equals partial pressure, expressed in atm (i.e., standard atmosphere = 760 mm Hg).

By definition, activity a_i is 1 when species i is at its standard state. If all reactants and products are at their standard states, then for the reaction of Eq. (2.23),

$$\Delta G^o = (lG_L^o + mG_M^o) - (aG_A^o + bG_B^o) \tag{2.26}$$

where ΔG^o is the standard free energy change of reaction represented by Eq. (2.23) at temperature T. Combining Eqs. (2.24) through (2.26),

$$\Delta G = \Delta G^o + RT \ln \left[\frac{\mathrm{a}_L^1 \cdot \mathrm{a}_M^m}{\mathrm{a}_A^a \cdot \mathrm{a}_B^b} \right] \tag{2.27}$$

or,

$$\Delta G = \Delta G^o + RT \ln Q \tag{2.28}$$

where

$$Q = \frac{a_L^1 \cdot a_M^m}{a_A^a \cdot a_B^b} \tag{2.29}$$

Q is called the *activity quotient.*

Equation (2.27) has been derived assuming an isothermal condition, i.e., the same temperature for reactants and products. If it is further assumed that the reaction is isobaric, i.e., the initial and final pressures are the same, and also that thermodynamic equilibrium prevails, then $\Delta(G)_{P,T} = 0$ from Eq. (2.20). Combining this with Eq. (2.28),

$$\Delta G^o = -RT \ln[Q]_e = -RT \ln K \tag{2.30}$$

where K is the value of the activity quotient at equilibrium. K is known as the *equilibrium constant.*

Equation (2.27) is the basis for prediction of the feasibility of reactions. A reaction is spontaneous or feasible if $\Delta(G)_{p,T}$ is negative. It is impossible when $\Delta(G)_{p,T}$ is positive. Equation (2.30) is used to calculate the equilibrium condition of a reaction.

Thermodynamic predictions and calculations can be made if the following conditions are satisfied:

1. The process should take place isothermally (i.e., the initial and final temperature should be the same) and the temperature should be known.
2. The standard free energy change of reaction (ΔG^o) should be available.
3. Activity versus composition relations for all species involved should be known.

Since changes in pressure as encountered in metallurgy do not affect thermodynamic properties significantly, the condition that P should be constant is of no importance in situations we normally encounter. Hence, P = constant restriction shall be omitted from here on.

2.4 ΔG^0 FOR OXIDE SYSTEMS

In secondary steelmaking, we primarily encounter formation or decomposition of inorganic oxides. Therefore, a brief write-up is presented on free energies of oxide systems.

The standard free energies of formation reactions, representing formation of compounds from the elements, are now known for all inorganic compounds of interest in secondary steelmaking. These are called *standard free energies of formation* (ΔG_f^o). A number of books carry compilations of such data.[3–6] Some values of ΔG_f^o for compounds of interest in secondary steelmaking are presented in Appendix 2.1.

Consider formation of an oxide from the elements represented by the following general reaction:

$$\frac{2X}{Y}M + O_2(g) = \frac{2}{Y}M_XO_Y \tag{2.31}$$

where M denotes a metal. X and Y are general symbols for oxide stoichiometry. Traditionally, free energy data shown in diagrams would be for a reaction such as Eq. (2.31), where the formation reaction involves only one mole of oxygen. This would make it convenient to compare the data for different oxides.

If the metal, oxygen and oxide are in their standard states, then the free energy change is related to temperature as

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{2.32}$$

where ΔH_f^o and ΔS_f^o are standard heat and entropy of formation, respectively.

According to Kirchoff's law, in the absence of any phase transformation between T and T_1,

$$\Delta H_f^o = \Delta H_f^o(\text{at T}_1) + \int_{T_1}^{T}\Delta C_p^o dT \tag{2.33}$$

$$\Delta S_f^o = \Delta S_f^o(\text{at T}_1) + \int_{T_1}^{T}\frac{\Delta C_p^o}{T}dT \tag{2.34}$$

where ΔH_f^o and ΔS_f^o are standard heat and standard entropy of formation at temperature T, and ΔC_p^o is the difference of specific heats of products and reactants at standard states. The values of ΔC_p^o are generally very small and, therefore, one may assume that ΔH_f^o and ΔS_f^o are essentially independent of temperature. This allows us to express dependence of ΔG_f^o on temperature as:

$$\Delta G_f^o = A + BT \tag{2.35}$$

where A and B are constants.

Equation (2.35) is an approximate one. A more precise representation of ΔG_f^o as a function of T is

$$\Delta G_f^o = A + BT + CT\ \ln T \tag{2.36}$$

However, data at steelmaking temperatures in standard compilations are available in the form of Eq. (2.35), for the limited temperature range of steelmaking.

Appendix 2.1 provides values of *A* and *B* for oxides as well as some other compounds of importance in secondary steelmaking. Figure 2.1 presents a diagram for oxides. ΔG_f^o values are per gm mol of O_2. This normalization allows us to compare stabilities of oxides directly from such figures. For example, Al_2O_3 is stabler than SiO_2, since the free energy of formation of the former is more negative as compared to that of the latter.

Quantitatively speaking, we are interested in the following reaction:

$$\frac{4}{3}Al + SiO_2 = \frac{2}{3}Al_2O_3 + Si \tag{2.37}$$

ΔG^o [for the reaction of Eq. (2.37)] = ΔG_f^o $(2/3Al_2O_3) - (SiO_2)$ is a negative quantity, and hence the reaction is feasible if all reactants and products are at their respective standard states (i.e., pure substances) in accordance with free energy criteria [Eq. (2.22)]. However, if they are not pure (e.g., present as solution in molten iron or slag), then ΔG^o does not provide a correct guideline, and we have to find out ΔG by using Eq. (2.27). These will require knowledge of activity as a function of composition.

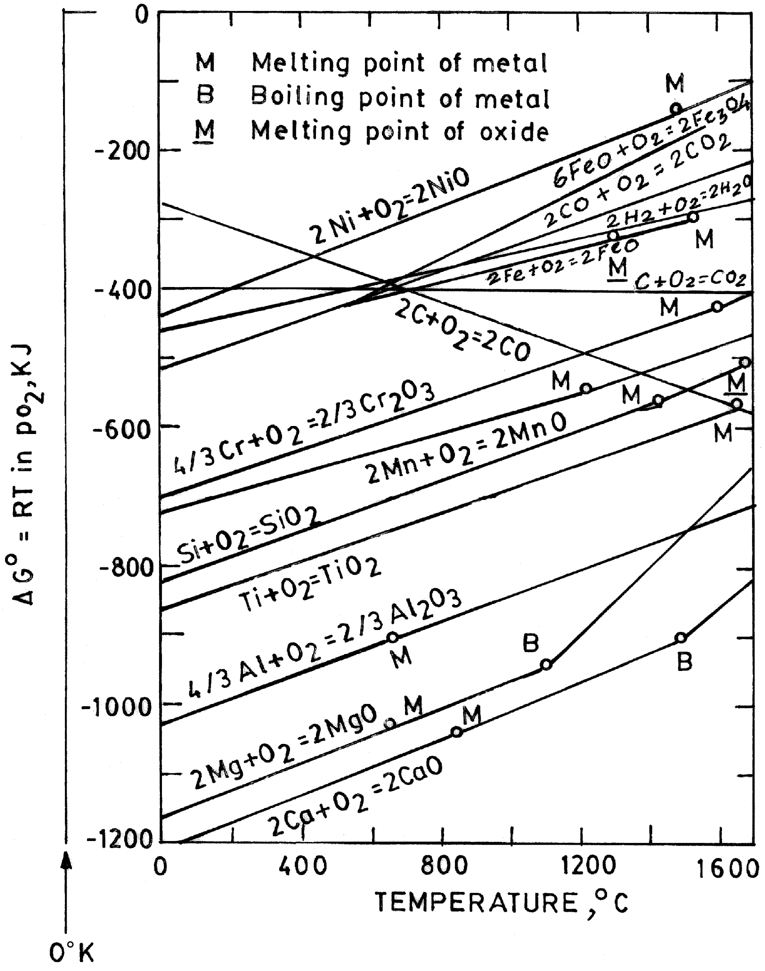

FIGURE 2.1 Standard free energy of formation for some oxides.

2.5 ACTIVITY–COMPOSITION RELATIONSHIPS: CONCENTRATED SOLUTIONS

Crudely speaking, activity is a measure of “free” concentration in a solution, i.e., concentration that is available for chemical reaction. Also, by definition, activity is dimensionless. In metallurgical processing, the gases behave as ideal, and molecules are free. Hence, activity of a component *i* in a gas mixture is equal to its concentration. Numerically, by convention, $a_i = p_i$, where p_i is partial pressure of *i* in atmosphere.

The composition of a solution can be altered significantly during processing only if mixing and mass transfer are rapid. Solid state diffusion is very slow. Hence, during the short processing time, its composition does not change. For example, a particle of CaO will remain CaO as long as it does not dissolve in slag. It may get coated by another solid such as Ca_2SiO_4 or CaS during steel processing. Here, solid CaO remains pure and its activity, by definition, is 1, since this is its standard state.

However, liquid steel contains variable concentrations of impurities and alloying elements. Molten slag is also a solution of oxides with a variety of compositions. Hence, activity versus composition relationships are required here for equilibrium calculations.

As already stated, a pure element or compound constitutes its conventional standard state. For example, pure Fe is the conventional standard state for liquid steel, and $a_{Fe} = 1$ for pure iron. Similarly, pure SiO_2 is the standard state for a slag containing silica. In the conventional standard state, an *ideal solution* obeys *Raoult’s law*, which states,

$$a_i = X_i \tag{2.38}$$

where X_i is mole fraction of solute *i* in the solution. For example, let liquid steel contain chromium and nickel. Then, X_{Cr} is to be calculated from weight percent composition as follows.

$$X_{Cr} = \frac{\dfrac{W_{Cr}}{M_{Cr}}}{\dfrac{W_{Cr}}{M_{Cr}} + \dfrac{W_{Ni}}{M_{Ni}} + \dfrac{W_{Fe}}{M_{Fe}}} \tag{2.39}$$

where W_i denotes weight percent and M_i molecular mass of species *i*.

Most real solutions do not obey Raoult’s law. They either exhibit positive or negative departures from it. For a binary solution (i.e., containing two species such as Fe + Ni or CaO + SiO_2), this is illustrated in Figure 2.2. For example, molten Fe-Mn, Fe-Ni, FeO-MnO solutions are ideal. Molten Fe-Si, CaO-SiO_2, FeO-SiO_2, MnO-SiO_2, etc. show negative departures. Liquid Fe-Cu exhibits positive departure.

Departures from Raoult’s law are quantified using a parameter, known as the *activity coefficient* (γ), which is defined as:

$$\gamma_i = a_i/x_i \tag{2.40}$$

Activities in slag systems use conventional standard states as reference. However, industrial slags are multicomponent systems. Hence, presentation of activity versus composition diagrams is more complex and different from that of a binary solution.

Figure 2.3 shows values of activity of SiO_2 in CaO-SiO_2-Al_2O_3 ternary system at 1550°C (1823 K).[4] These are in the form of isoactivity lines for SiO_2. Similarly, there would be diagrams presenting isoactivity lines for CaO and Al_2O_3. The liquid field is bounded by liquidus lines. In this diagram, Al_2O_3 has been written as $AlO_{1.5}$. This is because molecular mass of CaO, SiO_2, and $AlO_{1.5}$ are

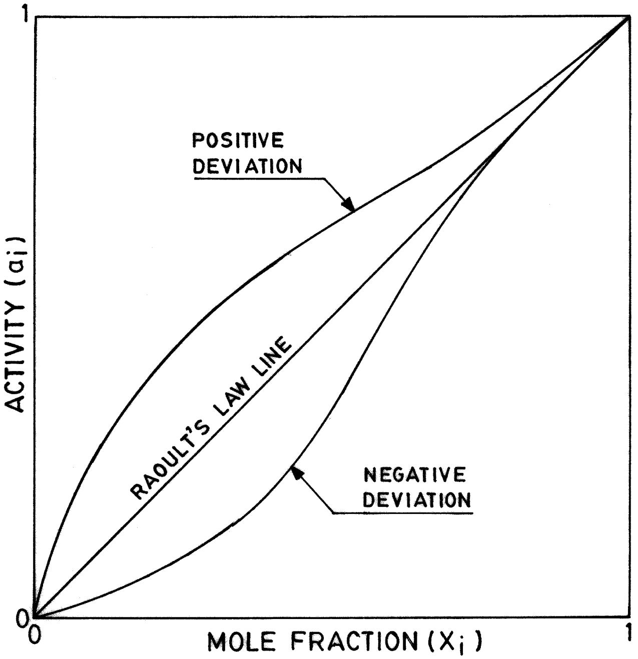

FIGURE 2.2 Raoult's law and real systems showing positive and negative deviations.

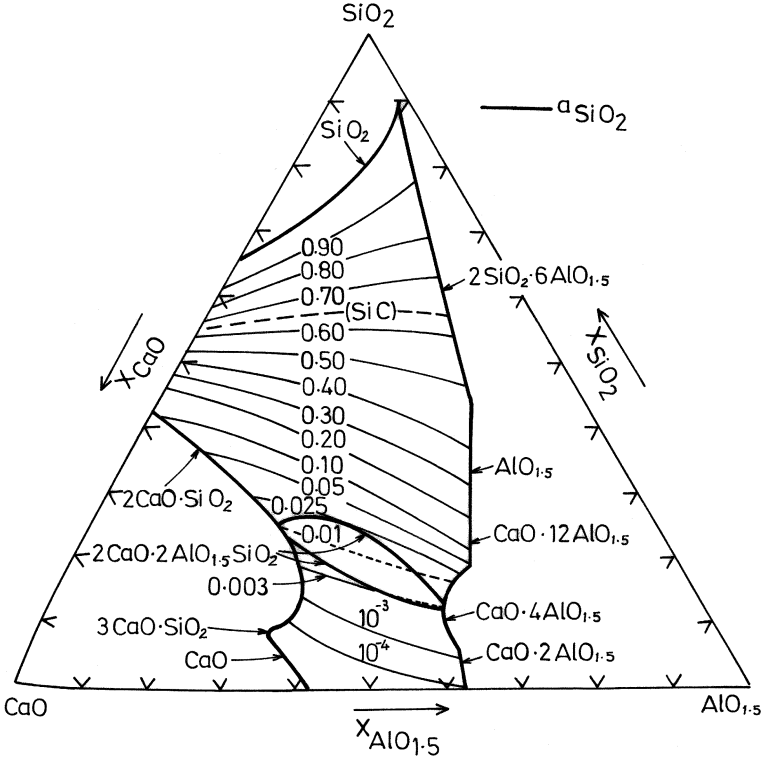

FIGURE 2.3 Activity of SiO_2 in CaO-SiO_2 – Al_2O_3 ternary system at 1823 K; the liquid at various locations on liquidus is saturated with compounds as shown.[4]

close, being equal to 56, 60, and 51, respectively. Therefore, the mole fraction scale is approximately the same as the weight fraction scale. Slag activity data are available from several sources, but the most comprehensive is the *Slag Atlas*.[7] However, this is quite unsatisfactory, since

1. slags are multicomponent and not ternary, and
2. thermodynamic calculations can be performed properly if the activity vs. composition relationship can be expressed by equations. This allows easier interpolations and extrapolations of laboratory experimental data in a composition regime.

Example 2.2

Solid iron is in contact with a liquid FeO-CaO-SiO_2 slag and gas containing CO and CO_2 at 1300°C. The activity of FeO in slag is 0.45, and the p_{CO}/p_{CO_2} ratio in gas is 20/1. Predict whether it is possible to oxidize iron. Also, calculate equilibrium value of p_{CO}/p_{CO_2} ratio in gas.

Solution

We are to consider the following reaction:

$$\mathrm{Fe(s) + CO_2\ (g) = (FeO) + CO(g)} \tag{E2.1}$$

For the reaction of Eq. (E2.1),

$$\Delta G^o = \Delta G_f^o[CO(g)] + \Delta G_f^o[FeO(s)] - \Delta G_f^o[CO_2(g)] \tag{E2.2}$$

The standard state for FeO is solid pure FeO, since its melting point is 1368°C.

With the help of Appendix 2.1,

$$\Delta G^o \text{ at } 1300°\text{C (1573 K)} = -249.8 - 161.3 + 395.7$$
$$= -15.38 \text{ kJ mol}^{-1} = -15.38 \times 10^3 \text{ J mol}^{-1}$$

(a) From Eq. (2.27),

$$\Delta G = \Delta G^0 + R \times T \ln\frac{p_{CO} \times (\mathrm{a_{FeO}})}{[a_{Fe}] \times p_{\mathrm{CO_2}}} \tag{E2.3}$$

As discussed earlier, solid iron would remain essentially pure in a limited time period. So, a_{Fe} may be taken as 1. Going through the calculations,

$$\Delta G = +\ 13.36 \text{ kJ mol}^{-1}$$

Since ΔG is positive, oxidation of Fe is not possible.

(b) At equilibrium,

$$\Delta G^o = -RT \ln K \tag{2.30}$$

where

$$K = \ln\left[\frac{p_{CO} \times (a_{Feo})}{[a_{Fe}] \times \mathrm{p}_{CO_2}}\right]_{\text{at equilibrium}}$$

Using the value of ΔG^o, the p_{CO}/P_{CO_2} ratio at equilibrium with Fe and the slag turns out to be 7.20. (Note that $R = 8.314$ J mol^{-1} K^{-1}.)

2.5.1 A NOTE ON SOLUTION MODELS FOR MOLTEN SLAGS

Whitley[8] made the earliest effort in this direction. He assumed the slag to consist of $2CaO \cdot SiO_2$, $3CaO \cdot P_2O_5$, etc. to estimate “free CaO” in slag as an index of $a_{CaO.}$ However, slags are really ionic liquids, and compounds like CaO, SiO_2, etc. do not exist as such. In contrast to these models, the other group of models has been termed as *ionic models*, where some kind of ionic structure is assumed.

The first ionic model of salt melts is that of Temkin (1945), who assumed ideal mixing (i.e., ideal solution) among cations and ideal mixing among anions but no interaction between cations and anions. The last assumption is too simplistic and has not been accepted. However, the first assumption, namely, ideal mixing among cations and among anions separately, constituted the basis for some later models.

Flood et al.[9] utilized it for reaction of sulfur between liquid steel and slag and obtained the analytical relation for the equilibrium constant as follows:

$$\log K_{h,S} = \sum_i X'_i \log K^i_{h,S} \tag{2.41}$$

where $K_{h,S}$ denotes the equilibrium constant for sulfur reaction between metal and slag containing several cations. i denotes a cation. X'_i is an electrically equivalent fraction of i among all cations. $K^i_{h,S}$ is the equilibrium constant if i is the only cation in slag. This is a useful equation. It allows calculation of $K_{h,S}$ in slag from knowledge of $K^i_{h,S}$ of various cations. Hence, this approach was later extended to the reaction of phosphorus as well.

Slag modeling for thermodynamic calculations is of considerable interest to steelmaking. Some recent studies[10] indicate efforts to apply the approach of Flood et al. with refinements. Of course, thermodynamic predictions are independent of structural considerations. This provides another approach. Analytical relations based on a regular solution model have proved to be the most popular among structure-independent predictions.

For a binary solution, the *regular solution model* predicts

$$RT \ln\gamma_1 = \alpha X_2^2 \tag{2.42}$$

where X_2 is the mole fraction of component 2 in the binary 1–2, and α is a constant. For a multicomponent solution, the general form of the equation for the regular solution model is[10]

$$RT \ln\gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \tag{2.43}$$

where α values are constants, known as interaction energies between subscripted solutes.

Ban-ya[11] has recently summarized mathematical expression of slag-metal reactions in steelmaking processes by quadratic formalism based on regular solution model. If the melt is not a strictly regular solution, then for a real solution,

$$RT \ln\gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k + I \tag{2.44}$$

where I has been termed the conversion factor of the activity coefficient from the hypothetical regular solution to the real solution.

Experimental data of various slag-metal and slag-gas equilibria for many slag compositions were statistically fitted with Eq. (2.44). These have yielded some values of α_{ij} and I.[11]

Example 2.3

Calculate γ_i in a multicomponent solution of slag at 1873 K. Composition of slag in weight percent is as follows:

$$MnO = 4,\ CaO = 50,\ Al_2O_3 = 35,\ SiO_2 = 8,\ FeO = 3$$

Take MnO as species i.

Solution

From Eq (2.39):

Mole fractions of various species in slag are

$$X_{MnO} = 0.0384,\ X_{CaO} = 0.6058,\ X_{Al_2O_3} = 0.2339, X_{SiO_2} = 0.091,\ X_{FeO} = 0.0284$$

Interaction energies between various cations are[11]

$$\alpha_{Mn\text{-}Ca} = -92050,\ \alpha_{Mn\text{-}Al} = -83680,\ \alpha_{Mn\text{-}Si} = -75310,$$

$$\alpha_{Mn\text{-}Fe} = 7110,\ \alpha_{Ca\text{-}Al} = -154810,\ \alpha_{Ca\text{-}Si} = -133890,$$

$$\alpha_{Ca\text{-}Fe} = -31380,\ \alpha_{Al\text{-}Si} = -127610,\ \alpha_{Al\text{-}Fe} = -41000,$$

$$\alpha_{Si\text{-}Fe} = -41840$$

For reaction MnO(s) = MnO (regular solution),

$$I = -32470 + 26.14T,\ \text{J}$$

Performing calculations on the basis of Eq. (2.44) and using the above data, $\gamma_{MnO} = 0.163$ (Ans.).

2.6 ACTIVITY–COMPOSITION RELATIONSHIPS: DILUTE SOLUTIONS

2.6.1 ACTIVITIES WITH ONE WEIGHT PERCENT STANDARD STATE

Liquid steel comes primarily in the category of dilute solution, where concentration of solutes (carbon, oxygen etc.) are mostly below 1 wt.% or so except for high alloy steels. Solutes in dilute binary solutions obey *Henry's law,* which is stated as follows:

$$a_i = \gamma_i^o X_i \tag{2.45}$$

where γ_i^o is a constant. Deviation from Henry's law occurs when the solute concentration increases.

Therefore, activities of dissolved elements in liquid steel are expressed with reference to Henry's law and not Raoult's law. Since we are interested in finding values directly in weight percent, the composition scale is weight percent, not mole fraction. With these modifications, in dilute solution of species i in liquid iron,

1. If Henry's law is obeyed by species *i*, then

$$h_i = W_i \tag{2.46}$$

2. If Henry's law is not obeyed by species *i*, then

$$h_i = f_i \, W_i \tag{2.47}$$

h_i is activity and f_i is the activity coefficient in the so-called *one weight percent standard state.* This is because, at 1 wt.%, $h_i = 1$, if Henry's law is obeyed.

Again, it can be shown that f_i is related to Raoultian activity coefficient γ_i as:

$$f_i = \frac{\gamma_i}{\gamma_i^o} \tag{2.48}$$

It is to be noted that the standard free energy change for reaction is not going to be the same if the standard state is changed. For example, at 1600°C,

$$\mathrm{Si(1)} + 0_2\mathrm{(g)} = \mathrm{SiO_2(s)}; \quad \Delta G^o_{49} = -571.5 \text{ kJ mol}^{-1} \tag{2.49}$$

with pure liquid silicon as standard state. However, for the 1 wt.% standard state of Si dissolved in liquid iron,

$$[\mathrm{Si}]_{\text{wt.pct.}} + 0_2\mathrm{(g)} = \mathrm{SiO_2(s)}; \quad \Delta G^o_{50} = -406.4 \text{ kJ mol}^{-1}\,* \tag{2.50}$$

ΔG^o_{49} and ΔG^o_{50} are related to each other as

$$\Delta G^o_{50} = \Delta G^o_{49} - [\bar{G}_{Si} + -G^o_{Si}]_{\text{at 1 wt. pct. std. state for Si in liquid iron}} \tag{2.51}$$

$$= \Delta G^o_{49} - [\bar{G}^m_{Si}]_{\text{at 1 wt. pct. std. state for Si in liquid iron}} \tag{2.52}$$

where $\bar{G}^m_i = \bar{G}_i - \bar{G}^o_i$ is known as the partial molar free energy of mixing of solute *i* into a solution. Again, from Eq. (2.25),

$$\bar{G}^m_{Si} = RT \ln [a_{Si}]_{\text{at 1 wt. pct. std. state Si in liquid iron}} \tag{2.53}$$

$$= RT \ln \gamma^o_{Si}[X_{Si}]_{\text{at 1 wt. pct.}} \tag{2.54}$$

With reference to Eq. (2.39), in Fe-Si binary,

$$X_{Si} = \frac{\dfrac{W_{Si}}{M_{Si}}}{\dfrac{W_{Si}}{M_{Si}} + \dfrac{W_{Fe}}{M_{Fe}}} \tag{2.55}$$

---

* *Note:* Si dissolved in liquid metal is denoted either as [Si] or $\underline{\mathrm{Si}}$, $\mathrm{SiO_2}$ dissolved in slag is indicated by ($\mathrm{SiO_2}$).

On the basis of Eq. (2.55), $X_{Si} = 0.02$ at $W_{Si} = 1$. Noting that $\gamma^{o}_{Si} = 1.25 \times 10^{-3}$, the value of ΔG^{o}_{50} in Eq. (2.50) was obtained.

Appendix 2.2 presents values of $\overline{G}^{m}_{i}$ for some solute in liquid iron.

2.6.2 Solute–Solute Interactions in Dilute Multicomponent Solutions

It has been found that solutes in a multicomponent solution interact with one another and thus influence activities of other solutes. Figure 2.4 illustrates this for activity of carbon and oxygen in liquid iron at 1833 K. In the Henry's law region of Fe-C binary (i.e., without any other added element), $f_C = 1$, i.e., $\log f_C = 0$. In the presence of a third element in liquid iron solution, f_C keeps changing systematically.

It has been derived that if, in a dilute multicomponent solution, A is solvent (Fe in case of liquid steel), and B, C,..., i, j, etc. are solutes, then

$$\log f_i = e_i^B \cdot W_B + e_i^C W_C + \dots + e_i^i W_i + e_i^j W_j + \dots\dots \tag{2.56}$$

where e values are constants. e_i^j is called the *interaction coefficient*, describing the influence of solute j on f_i, which is defined as

$$e_i^j = \left[\frac{\partial(\log f_i)}{\partial W_j}\right]_{W_j \to O} \tag{2.57}$$

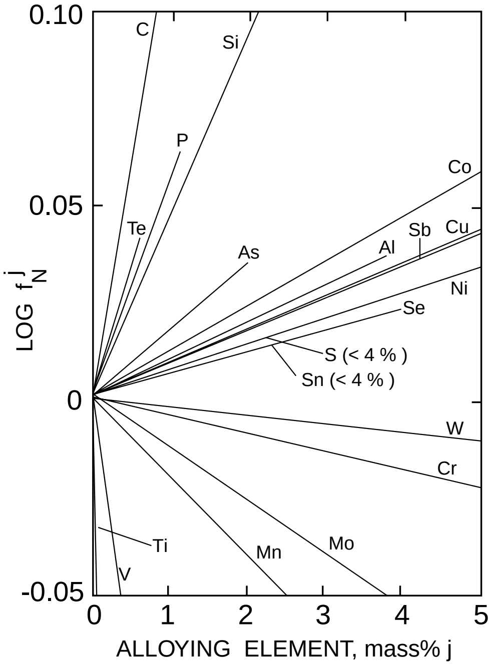

FIGURE 2.4 Influence of alloying elements on the activity coefficient of nitrogen dissolved in molten iron at 1823 K.

e_i^i is known as the *self interaction coefficient* and has a non-zero value only if Fe-i binary deviates from Henry's law. Again,

$$e_j^i = \left[\frac{\partial(\log f_j)}{\partial W_i}\right]_{W_i \to \mathrm{O}} = e_i^j \cdot \frac{M_j}{M_i} + 0.434 \times 10^{-2}\left[\frac{M_i - M_j}{M_i}\right] \tag{2.58}$$

Appendix 2.3 presents values of interaction coefficient for some common elements dissolved in liquid iron.

Equation (2.56) contains only first-order interaction coefficients. It is, in general, all right for dilute solutions of liquid iron. However, sometimes, even here, second-order interaction coefficients (r_i^j) are to be employed. On the other hand, if solute–solute interactions are not significant, log f_i vs. weight percent of the added element exhibit good linear behavior over a long range. This is demonstrated by Figure 2.4 for nitrogen dissolved in liquid iron. The figure is based on several data sources and taken from the review by Iguchi.[12] In such cases, Eq. (2.56) may be fairly all right up to reasonably high concentrations of solutes. Iguchi[12] has recently reviewed the subject, especially the work of Ban-ya and his coworkers, who had been active in this field for about two decades. The following two approaches have been seriously explored. The first approach is application of quadratic formalism, originally proposed by Darken and applied to several binary systems by Turkdogan and Darken.[10] Ban-ya examined its use in Fe-C-j ternary melts.

The second approach is application of the interstitial solution model originally proposed by Chipman.[13] Elements P, C, S, N, etc. may be treated as interstitial atoms, and this model has been applied to ternary iron alloys containing these elements to high concentrations. It predicts linearity between log ψ with Y_j, where ψ_i is a modified activity coefficient of i, and Y_j is atom ratio of j in a ternary containing i and j. Figure 2.5 shows its application to the effect of iron on the activity coefficient of nitrogen in Cr-Fe-N ternary melts. Good linear relation up to a high concentration of iron may be noted.

Example 2.4

Liquid steel is being degassed by argon purging in a ladle at 1873 K (1600°C). The gas bubbles coming out of the bath have 10 percent CO, 5 percent N_2, 5 percent H_2, and the rest Ar. Assuming these to be at equilibrium with molten steel, calculate the hydrogen, nitrogen, and oxygen concentrations in steel in parts per million (ppm). The steel contains 1 percent carbon, 2 percent manganese, and 0.5 percent silicon. The total gas pressure may be taken as 1 atm.

Solution

(a) For hydrogen, the reaction may be written as

$$[H]_{\text{wt.pct.}} = \frac{1}{2}\mathrm{H}_2(g) \tag{E4.1}$$

for which

$$\log K_H = \frac{1905}{T} + 1.591 \tag{E4.2}$$

Again, at equilibrium,

$$K_H = \frac{p_{\mathrm{H}_2}^{1/2}}{[\mathrm{h}_H]} \tag{E4.3}$$

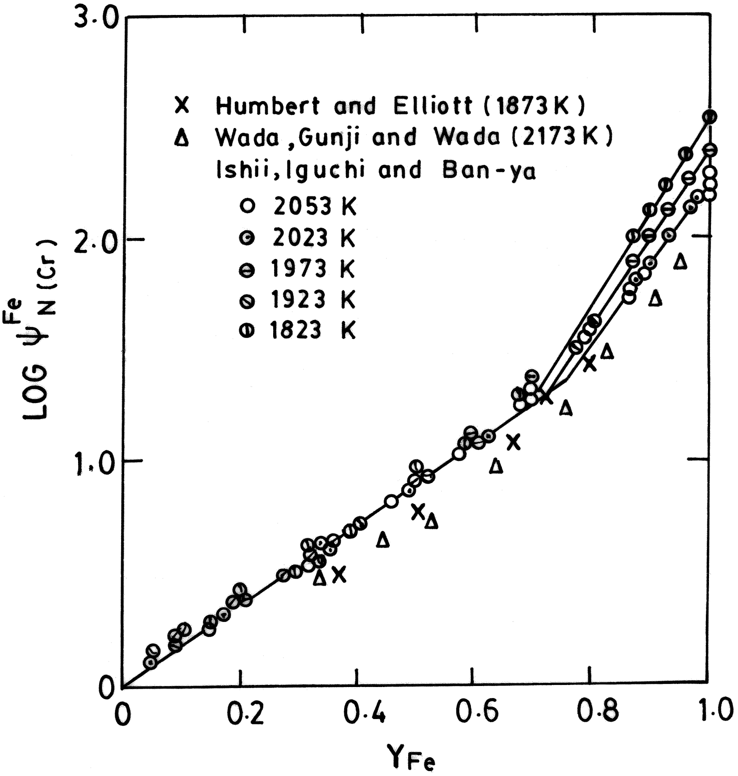

FIGURE 2.5 Effect of iron on the activity coefficient of nitrogen in liquid chromium.[13]

Now,

$$p_{H_2} = 0.05 \text{ atm, and } K_H = 405.58 \text{ at } 1873 \text{ K}$$

So,

$$h_H \text{ at equilibrium} = 5.513 \times 10^{-4} = f_H \cdot W_H$$

Again,

$$\log f_H = e_H^C \cdot W_C + e_H^{Mn} \cdot W_{Mn} + e_H^{Si} \cdot W_{Si} \tag{E4.4}$$

Assume interactions of dissolved H, N, and O on f_H as negligible. This is justified in view of their very small concentrations. Taking values of e_i^j from Appendix 2.3,

$$\log f_H = 0.06 \times 1 - 0.002 \times 2 + 0.027 \times 0.5$$

putting in values,

$$W_H = 4.69 \times 10^{-4} \text{ percent} = 4.69 \text{ ppm (Ans.)}$$

(b) For nitrogen, the reaction may be written as

$$[N]_{\text{wt.pct.}} = \frac{1}{2}\text{N}_2(\text{g}) \tag{E4.5}$$

for which

$$\log K_N = \frac{518}{\text{T}} + 1.063 \tag{E4.6}$$

Proceeding as for hydrogen,

$[h_N] = 0.01$, in 1 weight percent standard state

Now,

$$h_N = f_N \cdot W_N \tag{E4.7}$$

and

$$\log f_N = e_N^C \cdot W_C + e_N^{Mn} \cdot W_{Mn} + e_N^{Si} \cdot W_{Si} \tag{E4.8}$$

Proceeding as before,

$W_N = 0.0077$ wt.% = 77 ppm (Ans.)

(c) For oxygen, the reaction may be written as

$$[\text{C}]_{\text{wt.\%.}} + [\text{O}]_{\text{wt.\%.}} = \text{CO(g)} \tag{E4.9}$$

for which

$$\log K_O = \frac{1160}{T} + 2.003 \tag{E4.10}$$

Again, at equilibrium,

$$K_O = \frac{P_{CO}}{[h_C][h_O]} \tag{E4.11}$$

$$h_C = f_C \cdot W_C = f_C \cdot 1$$

$$\log f_C = e_C^C \cdot W_C + e_C^{Mn} \cdot W_{Mn} + e_C^{Si} \cdot W_{Si} \tag{E4.12}$$

(As in previous cases, assume interactions of $\underline{\text{H}}$, $\underline{\text{N}}$, and $\underline{\text{O}}$ on f_C as negligible.)

Putting in values, $f_C = 1.82$, and $h_C = 1.82$. So,

$$h_O = \frac{P_{CO}}{[K_O][h_C]} = \frac{0.1}{419 \times 1.82} = 1.31 \times 10^{-4}$$

Again,

$$W_O = h_O/f_O$$

and,

$$\log f_O = e_O^C \cdot W_C + e_O^{Mn} \cdot W_{Mn} + e_O^{Si} \cdot W_{Si} \tag{E4.13}$$

Putting in values (taking $e_O^C = -0.421$),

$$W_O = 4.1 \times 10^{-4} \text{ wt.\%} = 4.1 \text{ ppm} \quad \text{(Ans.)}$$

2.7 CHEMICAL POTENTIAL AND EQUILIBRIUM

So far, we have followed the approach in which the overall free energy change had been employed as the criterion for assessing the feasibility of a process. There is an alternative approach based on *chemical potential*.

Suppose that an element i is to be transferred from phase I to phase II. Then, we say that, for the transfer to be feasible thermodynamically,

$$\mu_i \text{ (I)} > \mu_i \text{ (II)} \tag{2.59}$$

and for equilibrium,

$$\mu_i \text{ (I)} = \mu_i \text{ (II)} \tag{2.60}$$

where μ_i (I) and μ_i (II) denote the chemical potential of species i in phases I and II, respectively.

μ_i is identical with partial molar free energy of solute i in a solution $(\overline{G}_i)$. On the basis of Eq. (2.25),

$$\mu_i \text{ (I)} = \mu_i^O \text{ (I)} + RT \ln a_i \text{ (I)} \tag{2.61}$$

$$\mu_i \text{ (II)} = \mu_i^O \text{ (II)} + RT \ln a_i \text{ (II)} \tag{2.62}$$

where μ_i^O denotes the chemical potential of i at its standard state. If the standard state of i is the same in both the phases, then

$$\mu_i^O \text{ (I)} = \mu_i^O \text{ (II)} \tag{2.63}$$

so, a_i(I) > a_i(II), for transfer from phase (I) to (II), and,

$$a_i\text{(I)} = a_i\text{(II)}, \text{ for equilibrium} \tag{2.64}$$

The chemical potential approach has the following advantages:

1. We can visualize a process better because of the similarity of the concept to some common physical processes. Just as heat flows from a higher heat potential (temperature) to a lower heat potential, and electricity flows from a higher electrical potential to a lower

one, in the same way a chemical species *i* is transferred spontaneously from higher μ_i to a lower μ_i.

2. It is not necessary to bother about the overall reaction; it is sufficient to find out the chemical potential of the species concerned only. Suppose we know μ_i(I). If another phase II is brought in contact with it, all we have to do is to calculate μ_i(II) to find out direction of transfer of *i*.

2.7.1 CHEMICAL POTENTIAL OF OXYGEN

In refining processes, we are primarily concerned about the transfer of oxygen. For the reduction of a metal from its oxide, the reaction environment must have a lower chemical potential than oxygen. Similarly, if impurities in a metal are to be preferentially oxidized in refining, then the environment must have a higher chemical potential than oxygen as compared to that in the impure metal. The chemical potential of oxygen (O_2) is expressed as

$$\mu_{O_2} = \mu^o_{O_2} + RT\ln a_{O_2} = \mu^o_{O_2} + RT\ln p_{O_2} \tag{2.65}$$

Since a_{O_2} may be equated to p_{O_2} for ideal gas, and $\mu^o_{O_2}$ is set equal to zero, then

$$\mu_{O_2} = RT\ln p_{O_2} \tag{2.66}$$

Calculation of the oxygen potential in a gas phase is relatively simple. For liquid metals, one should consider the reaction $O_2(g) = 2[O]$. For this,

$$\Delta G^o_h = -RT\ \ln\frac{[h_O]^2}{p_{O_2}} = -2RT\ \ln[h_O] + RT\ln p_{O_2} \tag{2.67}$$

Hence,

$$\mu_{O_2}(metal) = \Delta G^o_h + 2RT\ \ln\ [h_O] \tag{2.68}$$

For liquid slag in ironmaking, we consider the reaction

$$2[\mathrm{Fe}] + \mathrm{O_2(g)} = 2(\mathrm{FeO});\ \Delta G^o_{69} \tag{2.69}$$

$$\Delta G^o_{69} = -RT\ln K_{69} = -RT\ln\frac{(a_{\mathrm{FeO}})^2}{[a_{\mathrm{Fe}}]^2 p_{O_2}} \tag{2.70}$$

where p_{O_2} is partial pressure of O_2 in equilibrium with [Fe] and (FeO).

Since $a_{\mathrm{Fe}} \approx 1$ in ironmaking and steelmaking,

$$\mu_{O_2}(slag) = RT\ln p_{O_2} = \Delta G^O_{69} + 2RT\ln(a_{\mathrm{FeO}}) \tag{2.71}$$

If slag-metal equilibrium does not exist, Eq. (2.71) gives the μ_{O_2} in slag, because it is not dependent on the composition of iron. If slag-metal equilibrium exists, then it is μ_{O_2} in both slag and metal.

Of course, primary steelmaking slags contain Fe_2O_3 (i.e., Fe^{3+} ions) also. There μ_{O_2} is determined more by the following reaction:

$$4\,(FeO) + O_2(g) = 2(Fe_2O_3) \tag{2.72}$$

However, in secondary steelmaking, Eq. (2.71) is applicable, since the FeO concentration is low.

The above analysis does not mean that oxygen is present as O_2 in the slag or metal. As a matter of fact, it is far from being so, because oxygen exists as ions in slag and as dissociated atoms in metal. But, for thermodynamic calculations and concepts, this is unimportant.

Example 2.5

Calculate the chemical potential of oxygen in a CO/CO_2 gas mixture and slag as given in Example 2.2, and the chemical potential of nitrogen as per Example 2.4.

Solution

(a) Calculation of μ_{O_2} in CO/CO_2 gas mixture for the problem in Example 2.2:

Consider the reaction,

$$2CO(g) + O_2(g) = 2CO_2(g) \tag{E5.1}$$

$$\Delta G^o = -RT\ln\left[\frac{p^2_{CO_2}}{p^2_{CO} \times p_{O_2}}\right]_{\text{equilibrium}}$$

$$= RT\ln(p_{O_2})_e - 2RT\ln\frac{p_{CO_2}}{p_{CO}}$$

where $(p_{O_2})_e$ is in equilibrium with CO and CO_2.

Since

$$\frac{p_{CO}}{p_{CO_2}} = \frac{20}{1},\ \mu_{o_2} = RT\ \ln(p_{O_2})_e = \Delta G^o + 2RT\ \ln\left(\frac{1}{20}\right) \tag{E5.2}$$

At 1300°C (1573 K), for the reaction of Eq. (E5.1),*

$$\Delta G^o = 2[\Delta G^o_{f,\,CO_2} - \Delta G^o_{f,CO}] \tag{E5.3}$$

$$= 2[(-396.46 + 0.08 \times 10^{-3} \times 1573) + (118.0 + 84.35 \times 10^{-3} \times 1573)] = -291.32\ \text{kJ mol}^{-1}$$

Substituting in Eq. (E5.2),

$$\mu_{O_2} = -369.67\ \text{kJ mol}^{-1}O_2 \quad \text{(Ans.)} \tag{E5.4}$$

---

* From data in Appendix 2.1.

(b) Calculation of μ_{O_2} in FeO-CaO-SiO$_2$ slag for the problem in Example 2.2:

Consider the reaction

$$2\text{Fe(s)} + \text{O}_2\text{(g)} = 2\text{(FeO)} \qquad \text{(E5.5)}$$

Since $a_{Fe} = 1$, $a_{FeO} = 0.45$ (given), from Eq. (2.71),

$$\mu_{O_2} = 2\Delta G^o_{FeO(1)} + 2RT\ \ln(0.45) \qquad \text{(E5.6)}$$

From Appendix 2.1,

$$\Delta G^o_{FeO(1)} = -238.07 + 49.45 \times 10^{-3}T \quad \text{kJ mol}^{-1}$$

At 1573 K,

$$2\Delta G^o_{FeO(l)} = -320.57 \ \ \text{kJ mol}^{-1}$$

Therefore, from Eq. (E5.6),

$$\mu_{O_2}\ \text{(in slag)} = -341.46\ \text{kJ/mol}^{-1}\ \text{O}_2 \quad \text{(Ans.)}$$

μ_{O_2} in slag is different from μ_{O_2} in gas, because they are not at equilibrium.

(c) Calculation of μ_{N_2} for Example 2.4:

Since $p_{N_2} = 0.05$ atm in Example 2.4,

$$p_{N_2} = RT\ \ln\ p_{N_2} = RT\ \ln\ (0.05)$$

At $T = 1873$ K,

$$\mu_{N_2} = -46.65\ \text{kJ mol}^{-1}\ \text{N}_2\ \text{(Ans.)}$$

Since liquid steel and nitrogen in exit gas are at equilibrium, μ_{N_2} in liquid steel also shall be the same.

2.8 SLAG BASICITY AND CAPACITIES

Basicity of a slag increases with increased percentages of basic oxides in it. It is an important parameter governing refining. Steelmakers had always paid attention to it. In the early days, the numerical value of basicity was taken as the CaO/SiO$_2$ ratio, modified ratio, or excess base.

Since a basic oxide (e.g., CaO) tends to dissociate into a cation and oxygen ion (e.g., Ca^{2+}, O^{2-}), the concentration of free O^{2-} increases with increasing basicity. Therefore, from a thermodynamic viewpoint, the activity of oxygen ion $(a_{O^{2-}})$ may be taken as an appropriate measure of the basicity of slag. However, there is no method available for experimental determination of $(a_{O^{2-}})$.

2.8.1 OPTICAL BASICITY

A breakthrough came with the development of the concept of *optical basicity* (Λ) in the field of glass chemistry by Duffy and Ingram[14] in 1975–76. It was applied to metallurgical slags first by Duffy, Ingram, and Somerville.[15] From then on, numerous investigators have applied it to metallurgical slags for a variety of correlations.

Experimental measurements of optical basicity in transparent media such as transparent glass and aqueous solutions were carried out employing Pb^{2+} as the probe ion. In an oxide medium, electron donation by oxygen brings about a reduction in the 6s–6p energy gap, and this in turn produces a shift in frequency in UV spectral band.

$$\Lambda = \frac{\upsilon_{\text{free}} - \upsilon_{\text{sample}}}{\upsilon_{\text{free}} - \upsilon_{\text{CaO}}} \tag{2.73}$$

where υ_{free}, υ_{CaO} and υ_{sample} are frequencies at peak for free Pb^{2+}, Pb^{2+} in CaO, and Pb^{2+} in a sample, respectively. Therefore, $\Lambda = 1$ for pure CaO by definition. Hence, Λ is an expression for *lime character*, even though there may not be any CaO in sample.

Based on experimental measurements, the following empirical correlation was proposed by Duffy et al.[14,15]

$$\frac{1}{\Lambda_i} = 1.35(\alpha_i - 0.26) \tag{2.74}$$

where α_i is *Pauling electronegativity* of the cation in a single oxide i. This relationship has allowed estimation of Λ_i for a variety of oxides where experimental data are not available from the values of α_i. The estimated Λ_i is known as *theoretical optical basicity* ($\Lambda_{th.i}$).

For a multicomponent system such as slag or glass.

$$\Lambda_{th} \text{ (for slag/glass)} = \Sigma\, X_i' \Lambda_{th.i} \tag{2.75}$$

where X_i' = equivalent cation fraction of oxide i.

Slags are opaque. The same is true of glasses containing oxides of transition metals. Hence, Λ is to be estimated for slags. The most widely employed method of estimation is on the basis of Eqs. (2.74) and (2.75). Other, lesser-known methods also have been employed.[16]

Optical basicity of individual oxides was estimated from Eq. (2.74), where experimental data were not available. This was tantamount to suggesting that each oxide is characterized by a unique value of Λ_i, irrespective of medium and temperature. However, it has not been accepted by recent investigators. Moreover, assignment of correct values of Λ_{th} to transition metal oxides such as FeO, MnO is controversial, since Eq. (2.74) is not applicable for these from theoretical considerations. Differing findings and opinions have been published in the literature. Estimated values of Λ_i have been questioned, and other methods of estimation based on refractive index, electronic polarizability, and electron density have been employed besides Pauling's electronegativity.[17–19] Some metallurgical slags contain fluorides or chlorides. Here, fluoride or chloride ions also ought to be considered, in addition to oxygen, for their contribution toward basicity. Considerable efforts have been made to evaluate Λ_i for common fluorides such as CaF_2.

One important problem facing application of the optical basicity concept has been differing values of Λ_i proposed by different investigators, especially for transition metal oxides such as FeO, MnO, TiO_2, and others. The present status is shown in Appendix 2.4. The values of optical basicity recommended by Duffy and coworkers[18,20] were on the basis of electronegativity, electronic polarizability, and refractive index, whereas those by Nakamura et al.[21] were estimated from average electron density. It may be noted that there is both agreement as well as disagreement among various investigators. It is not presently possible to recommend one set over another.

Example 2.6

Calculate the optical basicity of a slag of composition same as in Example 2.3.

Solution

$X'_i = 2 \times 0.0384 + 2 \times 0.6058 + 3 \times 0.2339 + 4 \times 0.091 + 2 \times 0.0284 = 2.414$, for Example 2.3. Equivalent cation fractions of species are:

$$X'_{Mn^{2+}} = \frac{2 \times 0.0384}{2.414} = 0.031 \qquad X'_{Cn^{2+}} = \frac{2 \times 0.6058}{2.414} = 0.504$$

$$X'_{Al^{3+}} = \frac{3 \times 0.2339}{2.414} = 0.291 \qquad X'_{Si^{4+}} = \frac{4 \times 0.091}{2.414} = 0.151$$

$$X'_{\mathrm{Fe}^{2+}} = \frac{2 \times 0.028}{2.414} = 0.023$$

Optical basicity of various species (considering data of Nakamura et al.[21]; Appendix 2.4):

$$\Lambda_{\mathrm{MnO}} = 0.95, \ \Lambda_{\mathrm{CaO}} = 1.0, \ \Lambda_{\mathrm{Al_2O_3}} = 0.66, \ \Lambda_{\mathrm{SiO_2}} = 0.47, \ \Lambda_{\mathrm{FeO}} = 0.94$$

Substituting the values of X_i' and Λ_i in Eq. (2.75),

$$\Lambda_{\mathrm{th,slag}} = 0.82 \text{ (Ans.)}$$

2.8.2 SLAG CAPACITIES

Along with basicity, another concept, namely that of slag capacity, has evolved, and its use has become quite widespread. Richardson and Fincham[10] in 1954 defined *sulfide capacity* (C_s) as the potential capacity of a melt to hold sulfur as sulfide. Mathematically,

$$C_s = (\text{wt. \% S}^{2-}) \cdot p_{\mathrm{O_2}}^{1/2} / p_{\mathrm{S_2}}^{1/2} \tag{2.76}$$

where $p_{\mathrm{O_2}} \cdot p_{\mathrm{S_2}}$ are partial pressures of O_2 and S_2 in the gas at equilibrium with slag. Noting that the reaction is

$$1/2\ \mathrm{S_2}\ (g) + (\mathrm{O}^{2-}) = 1/2\ \mathrm{O_2}\ (g) + (\mathrm{S}^{2-}) \tag{2.77}$$

it can be shown that

$$C_s = \frac{\mathrm{K}_{77} \cdot a_{O^{2-}}}{\phi_{S_{2-}}} \tag{2.78}$$

where K_{77} is the equilibrium constant for the reaction of Eq. (2.77) and $\phi_{S^{2-}}$ is the activity coefficient of S^{2-} in slag in an appropriate scale.

Wagner[22] has critically discussed the concept of basicity and various capacity parameters such as sulfide capacity, phosphate capacity, carbonate capacity, etc. He has discussed interrelationships among capacities. He also suggested use of carbonate capacity as a method of measurement of basicity. Many papers have been published on measurements and application of these capacities, and relationships among these.[17,24]

The reaction of phosphorus under oxidizing condition may be written as

$$\frac{1}{2}P_2(g) + \frac{5}{4}O_2(g) + \frac{3}{2}(O^{2-}) = (PO_4^{3-}) \tag{2.79}$$

for which the phosphate capacity of slag may be defined as

$$C_p = \frac{(\text{wt. \% } PO_4^{3-})}{(P_{p2})^{1/2}(p_{O_2})^{5/4}} \tag{2.80}$$

From Eqs. (2.79) and (2.80),

$$C_p = K_{79} \cdot \frac{[a_{O^{2-}}]^{3/2}}{\phi_{PO_4^{3-}}} \tag{2.81}$$

where K_{79} is the equilibrium constant for the reaction of Eq. (2.79) and $\phi_{PO_4^{3-}}$ is the activity coefficient of PO_4^{3-} in slag in an appropriate scale.

The combination of Eqs. (2.78) and (2.81) leads to the following relation:

$$\log C_p = \frac{3}{2}\log C_s + \log K_{82} + \log\left[\frac{\phi_{S^{2-}}^{3/2}}{\phi_{PO_4^{3-}}}\right] \tag{2.82}$$

K_{82} is an equilibrium constant term and depends only on temperature. At a constant temperature, in the same slag system (e.g., Na_2O – SiO_2 system), $(\phi_{S^{2-}}^{3/2})/\phi_{PO_4^{3-}}$ parameter is expected to be constant,[22] Hence, a single straight line with slope of 3/2 is expected. Figure 2.6 is based on review by Sano et al.[24] It shows agreement with the above expectation. Of course, a corollary to this conclusion is that there is no universal correlation between log C_p and log C_s that will be applicable to all kinds of slag systems. Similar conclusions can be drawn about interrelationships of other capacities.

Optical basicity concept is being utilized by industries as well. Equation (2.75) forms the basis of estimation of optical basicity in slags. C_s increases with increasing $a_{O^{2-}}$ (i.e., increasing basicity) and hence ought to have a relation to optical basicity. Many workers have shown that

$$\log C_s = m\,\Lambda + n \tag{2.83}$$

where m and n are empirical constants. Figure 2.7[23] shows such an attempt for various slags at 1500°C.

Young et al.[18] have recently questioned applicability of a simple linear dependence of log C_s and log C_p on Λ. Capacities have been correlated with Λ, Λ^2, temperature, as well as some

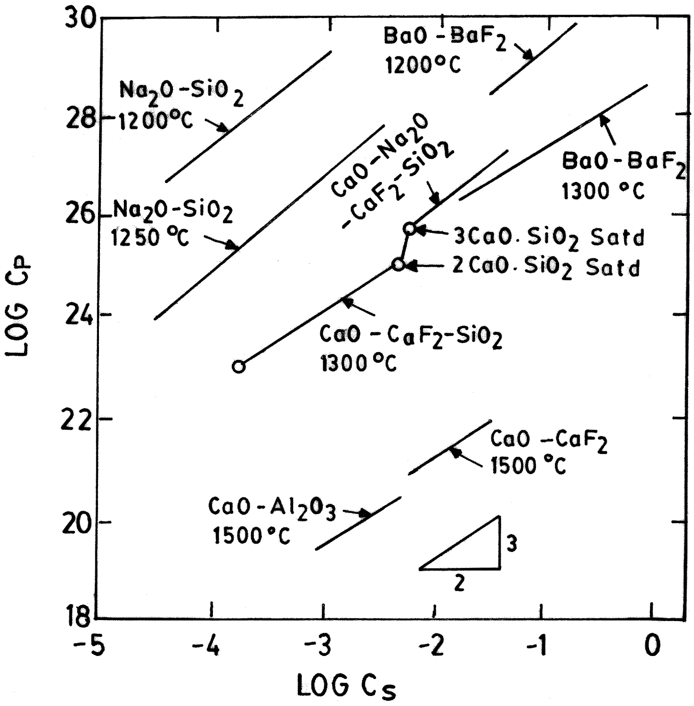

FIGURE 2.6 Relationship between sulfide capacities and phosphate capacities for various fluxes. *Source:* Sano, N., in *Proceedings of the Elliott Symposium,* ISS, Cambridge, Mass., reprinted by permission of the Iron & Steel Society, Warrendale, PA.

composition parameters. However, it has also been shown that, at values of C_s less than 0.01, Eq. (2.83) as employed in Figure 2.7[23] is also all right. Since, in secondary steelmaking, C_s lies in this range, a linear relationship as in Eq. (2.83) would be adequate for industrial uses.

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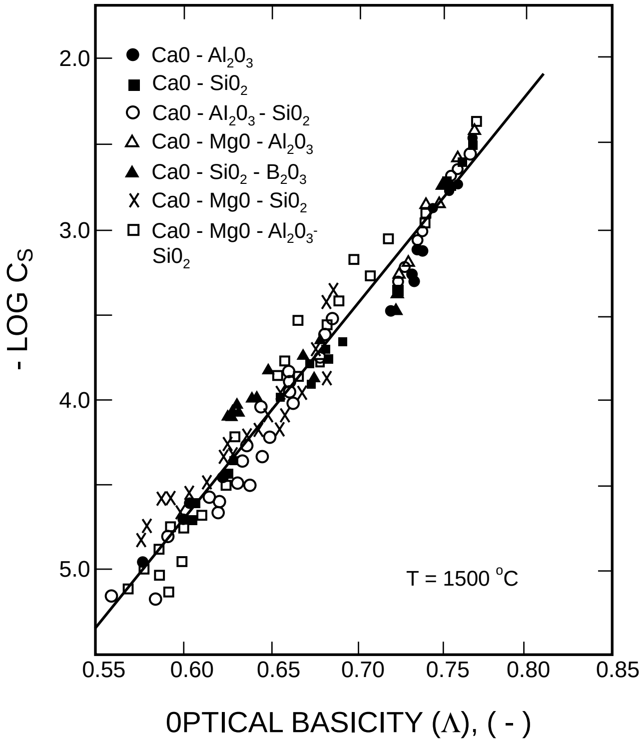

FIGURE 2.7 Logarithm of sulfide capacity vs. optical basicity at 1823 K.[23]

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