Contents:

Preamble

Equilibrium between phases

Activity of solution

Raoult's law

Henry's law

Interaction parameter

Key words: Solution, steelmaking, Raoult's law, Henry's law

Preamble

In steelmaking, the impurities like carbon, silicon, manganese, phosphorus and sulphur are removed from hot metal through a combination of gas/metal, gas/slag and gas/metal/slag reactions so as to produce steel of desired chemistry and cleanliness (cleanliness refers to the inclusions). Science of steelmaking involves equilibrium concentration of an impurity between the phases and the rate of transfer of an impurity from the hot metal.

Equilibrium between the phases:

The phases in steelmaking are hot metal, molten slag and gas. Hot metal is a multi-component solution in which impurities like carbon, silicon, manganese, phosphorus and sulphur are dissolved in very low amount (total concentration of all the impurities is approximately 5% to 6%) in iron. Slag is a solution of predominantly oxides with small amounts of sulphides, phosphides, silicates etc. Composition of the solutions in steelmaking is conveniently expressed either as weight% (Wt%) or mole fraction(N). The mole fraction of the ith component in a solution of n components is

$$N_i = X_i / \sum X_i, \qquad\qquad 1)$$

where X_i is the number of moles of ith component. The equilibrium of a component between the liquid phases is expressed in terms of integral molar free energy. Integral molar free energy of solution

$$G^m = \sum G_i^m N_i = \sum G_i N_i - \sum G_i^o N_i = RT \sum N_i \ln a_i, \qquad\qquad 2)$$

$G_i N_i$ represents free energy of solution and $G_i^o N_i$ is the free energy of pure components before entering into the solution. The quantity G_i^m is the partial molar free energy of mixing of component i and represent the change of energy or work which a mole of pure component i can make available.

Chemical potential is a useful concept to describe chemical equilibrium between liquid phases. At chemical equilibrium the chemical potential of any component is identical in all phases. Knowledge of chemical potential is important in steelmaking because an impurity can transfer in the gaseous or slag phase only when its chemical potential is lower than in hot metal.

The criterion for equilibrium at constant temperature and pressure is the change in the integral molar free energy of the solution, $(dG)_{T,P}$, i.e.

$$(dG)_{T,P} = 0 \text{ for an infinitesimal process and} \qquad\qquad 3)$$

$$(\Delta G)_{T,P} = 0 \text{ for a finite process}$$

Where $(dG)_P$ is change in integral molar free energy

At constant temperature and pressure when $(dG)_{T,P} < 0$, a process occurs spontaneously. For an isothermal chemical reaction say $A + B = C + D, (\Delta G) = \Delta G^o + RT \ln J$, where J is activity quotient and ΔG^o is the standard free energy change. At equilibrium

$$\Delta G^o = -RT \ln (J)_{eq} = -RT \ln K, \text{ where K is equilibrium constant.} \qquad\qquad 4)$$

Activity of solution

In dealing with chemical reactions in solution it is important to define the activity of a component. Activity of a component denotes its effective concentration. It is related to fugacity as

$$a_i = f_i/f_i^0 \hspace{4cm} 5)$$

f_i is the fugacity of component i in solution and f_i^0 is the fugacity of a component in its standard state (standard state could be either pure element or compound at 1 atmospheric pressure) So at standard state activity equals 1. In an ideal gas activity of a component i is equal to its partial pressure.

Raoults's Law

An ideal solution obeys Raoult's law, in which activity of a component a_i equals to its mole fraction N_i

$$a_i = N_i \hspace{4cm} 6)$$

Real solutions exhibit either positive or negative deviation from Raoult's law for a binary solution. Deviation from Raoult' law is taken care by activity coefficient γ_i

$$\gamma_i = a_i / N_i, \hspace{4cm} 7)$$

The Fe-Mn forms an ideal solution, whereas the Fe-Cu exhibits strong positive deviation and the Fe-Si strong negative from Raoult's law. Physically it implies that in Fe-Cu solution copper has a strong tendency to segregate, and in Fe-Si solution silicon has a strong tendency to form chemical compound with iron.

In binary liquid oxides, FeO-MnO behaves ideally, whereas most binary silicates i.e. $CaO - SiO_2, FeO - SiO_2, MgO - SiO_2$ show negative deviation from Raoult's law.

Henry's law

Liquid steel, and to a reasonable extent hot metal primarily fall in the category of dilute solution. In a dilute binary solution activity of a solute obeys Henry's law, which is stated as

$$a_i = \gamma_i^o \ N_i, \hspace{4cm} 8)$$

where γ_i^o is a constant (activity coefficient for the solute in dilute binary) and N_i is the mole fraction of the specie i. Solutes in all infinite dilute solutions obey Henry's law. Deviation from Henry's law occurs when the solute concentration increases.

In steelmaking the concentration of solute in molten steel is expressed in weight percent. It is frequently most convenient to choose the infinitely dilute solution expressed in terms of weight percent as the standard state. This is defined as

$$h_i / (Wt\% \, i) \; = \; 1 \text{ when } wt\% \, i \; \to \; 0 \qquad\qquad 9)$$

For weight percent i other than zero

$$h_i \; = \; f_i \, Wt\%_i \qquad\qquad 10)$$

Interaction parameter

Molten steel contains several dissolved solutes in dilute scale. For example, molten steel contains C, S, P, Si, Mn etc. This steel is a multi-component solution. In multi-component solution solutes interact with one another and thus influence activities of other solutes. If Fe is the solvent, and 1, 2….k are solutes in dilute state, then

$$\text{Log } f_i \; = \; e_i^1 Wt \%1 \; + \; e_i^2 \, Wt \%2 \; + \; e_i^3 Wt \%3 \; + \; e_i^4 Wt \%4 \; + \; ….e_1^J \, Wt \% \, J \quad 11)$$

The term e_i^j is known as interaction parameter describing the influence of solute j on the activity coefficient of solute i. The value of interaction parameter can be found in any book on thermodynamics.

The concept of interaction parameter is very important in estimating the activity of a solute element in presence of other solute elements. For example we want to calculate the activity of sulphur in hot metal of composition C = 4%, Si = 1.5%, Mn =1% and S = 0.04% at 1600 °C. By assuming infinite dilute solution as the standard state, the activity of sulphur is given by

$$h_S \; = \; f_S \, Wt\%S$$

$$\log f_S \; = \; e_S^S Wt \%S \; + \; e_S^C Wt \%C \; + \; e_S^{Si} Wt \%Si \; + \; e_s^{Mn} Wt \%Mn$$

Substituting the value of $e_S^S \; = \; -0.028, e_S^C \; = \; 0.24, \; eS^{Si} \; = \; 0.066 \text{ and } eS^{Mn} \; = \; -0.025$, we get $f_S \; = \; 10.78$ and activity of sulphur is 0.43.

References

A.Ghosh and A. Chatterjee: Ironmaking and steel making