Lecture 15: Thermodynamics of roasting

Contents

Key words: roasting, dead roasting, Predominance area diagram

Preamble

Roasting is gas/solid reaction in which sulphide is converted to oxide or sulphate or even to metal. Whether roast product is oxide or sulphate or partially sulphide would depend on temperature and partial pressures. The purpose of this lecture is to determine thermodynamic conditions for roasting.

Phase rule

Gibbs phase rule is

$$P + F = C + 2$$

P is the number of phases and C is the minimum number of chemical components requiresconstituting all the phases in the system. F is the number of degrees of freedom in the system also referred to as the variance of the system). The integer in the Gibbs phase rule is related to the number of intensive parameters such as temperature and pressure that are being considered.

In roasting we have 3 components, that is metal, sulphur and oxygen. Also pressure has no effect on condensed phases. Mostly roasting is carried out at a constant pressure. The phase rule as applied to a 3- component system at constant temperature and pressure reduces to

$$F = 3 - P.$$

For a given temperature the composition of the gas mixture is defined by the partial pressure of gaseous components, p_{O_2} and p_{SO_2}. Thus the phase relations in the ternary system as constant temperature may be described in two dimensional diagram where p_{SO_2} and p_{O_2} are the two coordinates. Such a diagram is called predominance- area diagram.

Predominance area diagram

Figure 15.1 shows predominance area diagram for $Ni - S - O$ system, at constant temperature. The phases are shown in the figure.
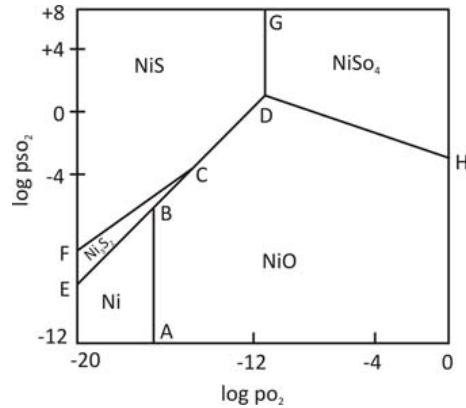

Figure 15.1: predominance area diagram for $Ni - S - O$ system at constant temperature.

In the figure at points B C and D, three condensed phases area at equilibrium for a particular value of p_{O_2} and p_{SO_2}. Degree of freedom is zero. For example at point B $Ni_3S_2/Ni/NiO$ can co-exist at fixed p_{O_2} and p_{SO_2}, at point C $NiS - Ni_3S_2 - NiO$ and at point D $NiS - NiSO_4 - NiO$ can $co - exist$. Thus these points are called invariant point.

The lines describe the equilibrium between any two condensed phases. Along the lines degree of freedom $F = 1$, which means we can vary either p_{O_2} or p_{SO_2} to obtain the phases. For example line EB is equilibrium between Ni_3S_2 and Ni, where along line BC equilibrium exists between Ni_3S_2 and NiO. Along lines AB and GD equilibrium exists between Ni and NiO, and NiS and $NiSO_4$. This shows that NiO/Ni or NiS/$NiSO_4$ equilibrium is independent of p_{SO_2}.

The figure also shows predominance areas for a single phase, for example in the area ABCDHNiO is a stable phase, whereas in the area FCDG, NiS is a stable phase. In the area degree of freedom is 2 which means both p_{SO_2} and p_{O_2} can be varied to obtain a phase within the area.

Method of construction

The predominance area diagram depends on the system and temperature. In a two dimensional diagram, temperature is fixed. These are the equilibrium diagrams and hence we have to consider all the phases which can form in a systems.

Consider $Ni - S - O$ system in which Ni, NiO, Ni_3S_2, Ni SO_4 and NiS phase can form. Let us write chemical equation representing equilibrium between any two condensed phases
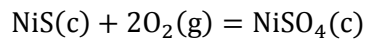
$$Ni(c) + \frac{1}{2}O_2(g) = NiO(c).$$
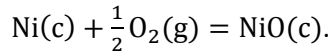
$$K_1 = \frac{1}{\left(p_{O_2}\right)^{0.5}}$$

Since Ni and NiO are pure and hence their activities are unity.

$$LogK_1 = -0.5 \text{ kg } p_{O_2}$$

We see that Ni/NiO equilibrium is independent of p_{SO_2} and hence it is a vertical line AB in diagram 15.1. The actual values of p_{SO_2} and p_{O_2} can be obtained from free energy values.

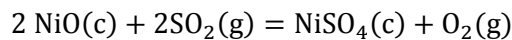Similarly line DG represents equilibrium between NiS and $NiSO_4$

$$NiS(c) + 2O_2(g) = NiSO_4(c)$$

Since activity of condensed phase is unity

$$\log K_2 = -2\log p_{O_2}$$

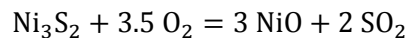DG line is also a vertical line.

Consider $NiO - NiSO_4$ equilibrium

$$2\,NiO(c) + 2SO_2(g) = NiSO_4(c) + O_2(g)$$

$$K_3 = \frac{p_{O_2}}{\left(p_{SO_2}\right)^2}$$

$$\log p_{SO_2} = 0.5\,(\log p_{O_2} + \log K_3)$$

We not that equilibrium between NiO and $NiSO_4$ can be attained by varying p_{SO_2} and p_{O_2} both and the line DH shows the variation of $\log p_{SO_2}$ against $\log p_{O_2}$.

Similarly

$$Ni_3S_2 + 3.5\,O_2 = 3\,NiO + 2\,SO_2$$

$$\log p_{SO_2} = 0.5\log K_2 + 1.75\log p_{O_2}$$

The line BC is the variation between log pSO2 and log po2 for Ni_3S_2/NiO equilibrium.

The predominance area diagram can be constructed easily by writing $\Delta G°$ values for each reaction.

Utility of predominance – area diagram (PAD)

1. PAD shows the stable phase under different conditions (gas pressures)
2. PAD predicts possible processing routes.

3. One can predict the conditions for formation of a particular phase. In dead roasting of PbS, PbO can form several compounds like $PbSO_4 . 4PbO$, $PbSO_4 . 2PbO$ and $PbSO_4 . PbO$. Dead roasting of PbS is likely to produce PbO and $PbSO_4$.
4. It is possible thermodynamically to produce metal from sulphide by controlling p_{O_2}.

Roasting of complex sulphide ores

Additional reactions may occur during the roasting of complex sulphide ore.

Differentsulphide may form solid solutions and even complex sulphides. In iron-copper sulphide ores, numberof ternary phases and also solid solutions of FeS in Cu_2S may form during roasting.

Another phenomenon is the formation of $ZnO - Fe_2O_3$ in roasting of sulphide ores. Since in a complex phase the chemical activity of a given compound is less than the pure compound, its predominance area will expand.

Technology of roasting

Roasting may be carried out in different furnaces. Multiple hearth furnace was dominant for a long time for roasting of sulphide ores. Now flash roasting is developed. Fluidized bed roasting is also being in use. A problem on fluidized bed roasting is discussed is lecture 17.

Roasting is strongly exothermic process. The calculation of adiabatic temperature is important and will be discussed in lecture 17.

A copper concentrate may be roasted autogenously in a multiple hearth furnace provided sulphur is not eliminated completely. Dead roasting would require additional thermal energy. Heat balance calculations will be taken in subsequent lectures. Material balance will also be illustrated first because heat balance cannot be done without materials balance. In subsequent lectures attempt has been made to illustrate materials and heat balance.

Conclusions:

In this lecture thermodynamics of roasting is briefly presented to impart a feel about the formation of different phases during roasting of sulphide ore. In this connection predominance area diagram is a very useful one to obtain the conditions for the formation of a phase.

Reference:

1) Resenquist : principles of extractive metallurgy

2) Ray, H S; Sridhar, R and Abraham, K.P: Extraction of non ferrous metals