

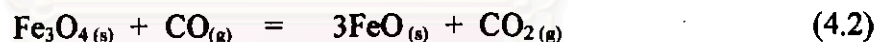
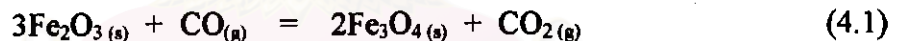
CHAPTER FOUR

THERMODYNAMIC CONSIDERATIONS

The iron-reduction distillation process consists of two reduction stages. The first reduction stage involves the reduction of iron oxide, zinc ferrite, and production of hazardous elements like cadmium. For the second reduction stage, the thermodynamics of reduction of zinc and lead oxide are considered.

4.1 FIRST REDUCTION STAGE

Carbon monoxide is the most common gaseous reductant used for the reduction of iron oxides. Equations 4.1 to 4.3 show the sequential reduction of iron oxides by carbon monoxide :



By making two assumptions, the equilibrium constants for these reactions can be expressed as :

$$K = p_{\text{CO}_2}/p_{\text{CO}} \quad (4.4)$$

The assumptions are that the activities of carbon monoxide and carbon dioxide are equal to their partial pressures and the activities of the iron species are equal to unity. The equilibrium constants for Reaction 4.1 to 4.3 are all equal to $p_{\text{CO}_2}/p_{\text{CO}}$ but all are not equal in value as can be seen from Figure 4.1 (Ross, 1980). The equilibrium constants can be calculated at any temperature by using the standard Gibbs free energy changes for these reactions in Equation 4.5 .

$$\Delta G^\circ = -RT \ln [p_{\text{CO}_2}/p_{\text{CO}}] \quad (4.5)$$

Equilibrium gas phase compositions for Reactions 4.1 to 4.3, at temperatures between 200 to 1600 °C are shown in Figure 4.1 (Ross, 1980), for the case where the sum of the partial pressures of carbon monoxide and carbon dioxide equals one atmosphere. Between the curves, the stable iron phase is indicated. The figure shows that below 570 °C, wustite is unstable and at low temperatures magnetite can be reduced to metal directly. The figure also shows that as the temperature increases, a greater concentration of carbon monoxide in the gas is required to reduce oxides to metal. For example, a gas containing 50% carbon monoxide and 50% carbon dioxide can reduce hematite to metal at 300 °C whereas at 1000 °C the same gas can reduce hematite only to wustite.

Figure 4.1 also contains the curve for the Boudouard reaction :



At temperatures below this curve, the back reaction occurs and carbon monoxide disproportionates into carbon and carbon dioxide. The Boudouard curve crosses the iron/wustite curve at about 700 °C and the wustite/magnetite curve at about 650 °C and these are the minimum temperatures at which carbon will reduce wustite to metallic iron and magnetite to wustite. Thermodynamically, below these temperatures wustite and magnetite respectively cannot be reduced by carbon monoxide because carbon monoxide will decompose to carbon and carbon dioxide. However, gaseous reduction of iron oxides proceeds faster than the reverse of Reaction 4.6 and reduction at low temperatures does occur in practice due to the presence of metastable mixtures of carbon monoxide and carbon dioxide. For the same reason, gas mixtures supersaturated with respect to carbon (gas composition above the Boudouard curve) may also be established (Rosenquist, 1983). These mixtures can react with iron to form cementite :



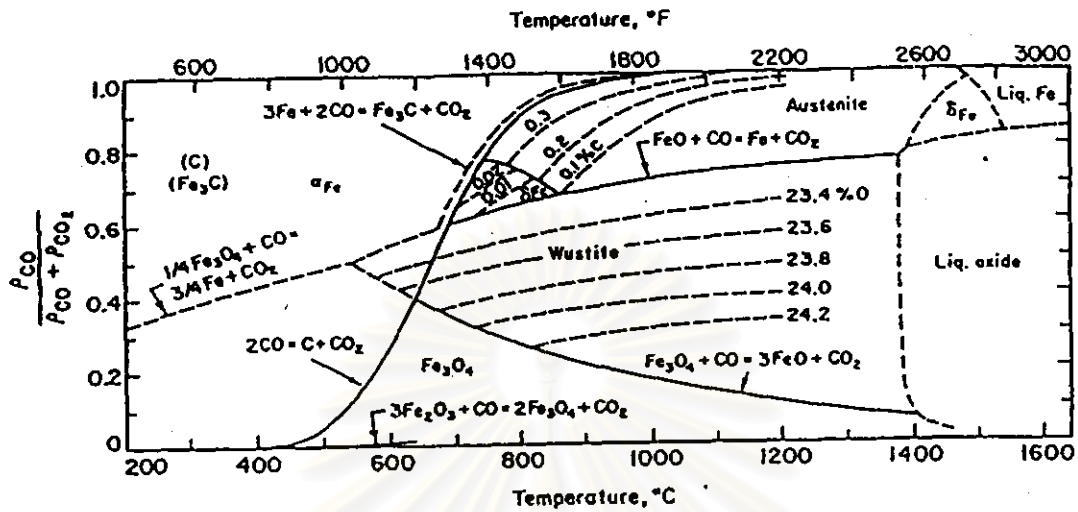
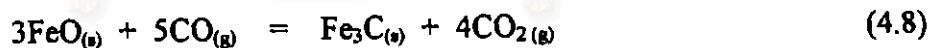


Figure 4.1: The Iron-Carbon-Oxygen System (Ross, 1980).

Cementite can also be formed by the reduction of wustite and magnetite at temperature about 700 °C according to the following reactions :



Metastable equilibria for cementite formation have been determined by Elliott *et al.* (1963) and are also represented in Figures 4.1 and 4.2 by dashed lines (Rosenqvist, 1983).

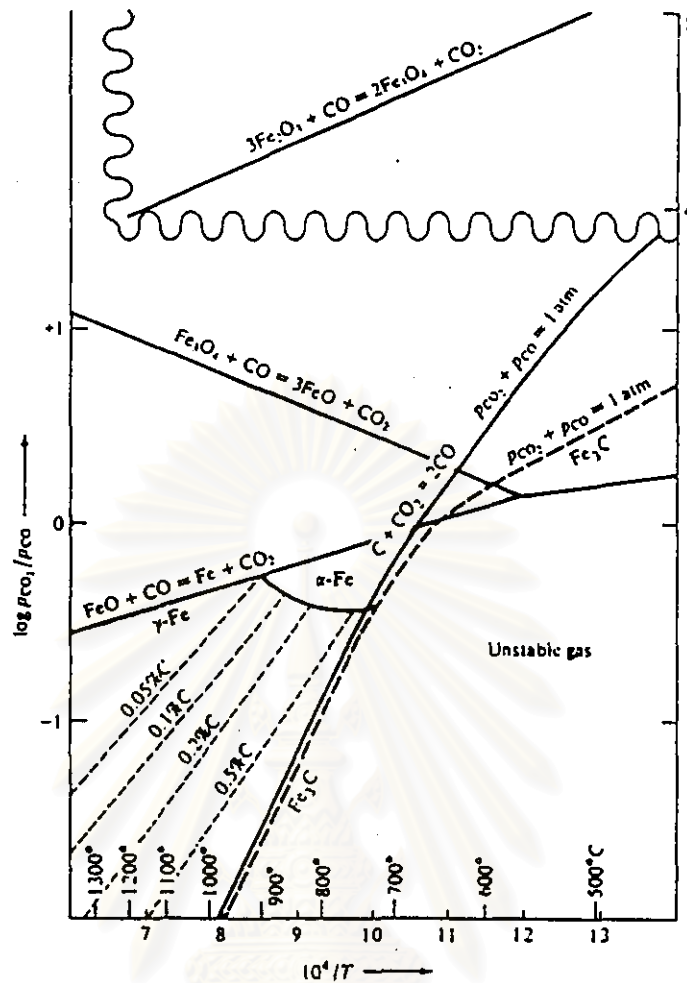
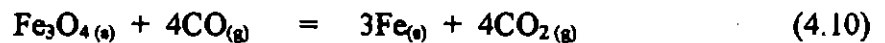


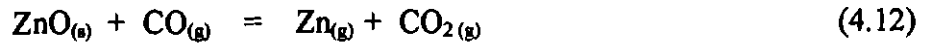
Figure 4.2: Equilibrium ratio $p_{\text{CO}_2}/p_{\text{CO}}$ for the reduction of iron oxides. Metastable equilibria for the formation of Fe_3C as well as equilibrium carbon contents in austenite are given by dashed lines (Rosenqvist, 1983).

In the first reduction stage, the basic reaction for iron oxide reduction is shown as follows:



$$\Delta G^\circ = -27,440 + 39.8T \text{ J/mol} \quad (4.11)$$

Iron oxide is preferentially reduced to metallic iron by carbon monoxide gas at about 700-800 °C and highly reduction atmosphere ($p_{\text{CO}}/p_{\text{CO}_2} = 3-10$), while most of the zinc oxide is unreacted. The reduction of zinc oxide by carbon monoxide gas is shown below:

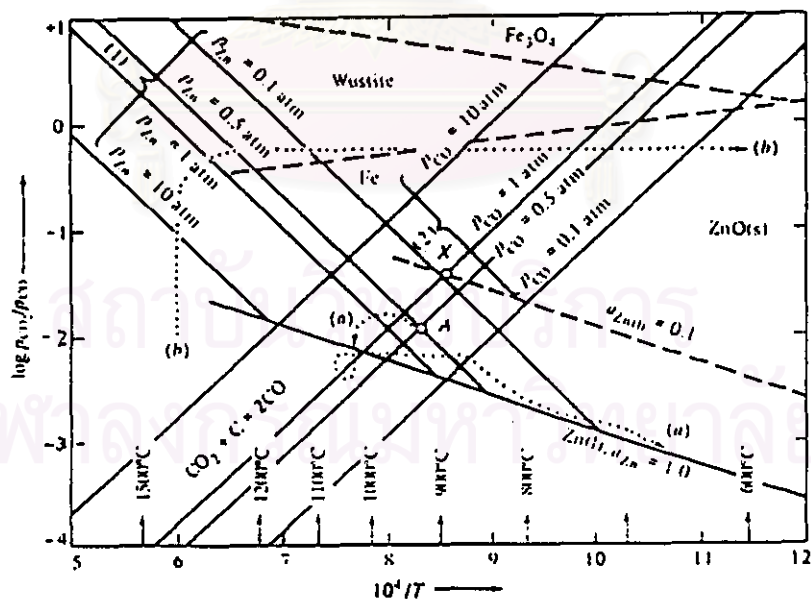


The equilibria for Reaction 4.12 must be simultaneously satisfied in order for ZnO to be carbothermally reduced. The minimum temperature at which this occurs is about 920°C for a total pressure of 1 atmosphere. For the reduction of pure zinc oxide, the equilibrium reaction constant can be expressed as :

$$K_{4.12} = \frac{(p_{\text{CO}_2} \cdot p_{\text{Zn}})}{p_{\text{CO}}} \quad (4.13)$$

assuming the activity of zinc oxide equals one, the activities of the gaseous species equal to their partial pressures and the sum of these partial pressures equals the total pressure. At temperatures above 920 °C, the equilibrium gas phase is primarily composed of metallic zinc and carbon monoxide.

Equilibrium gas ratios for Reaction 4.12, at temperatures between 600-1500 °C are shown in Figure 4.3 (Rosenqvist, 1983).

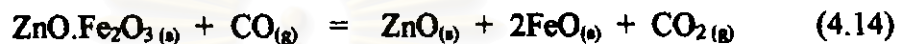


Equilibrium gas ratios for reduction of ZnO(s) to Zn(l) ($a_{\text{Zn(l)}} = 1.0$ and 0.1) as well as to Zn(g) ($p_{\text{Zn}} = 0.1, 0.5, 1.0$, and 10 atm), and for the Boudouard reaction for $p_{\text{CO}} = 0.1, 0.5, 1.0$, and 10 atm. Continuous reduction of ZnO with carbon at $p_{\text{tot}} = 1$ atm starts at point A. By further heating in the retort process and subsequent cooling and condensation the gas ratio follows the path (a)-(a). For the Imperial Smelting Processes blast furnace the gas ratio follows the path (b)-(b). Reduction of ZnO(s) to brass with $a_{\text{Zn(l)}} = 0.1$ and $p_{\text{CO}} = 1$ atm takes place at point X.

Figure 4.3: The Iron-Zinc-Carbon-Oxygen System (Rosenqvist, 1983).

From these thermodynamic considerations, the reduction of zinc oxide by carbon monoxide gas does not proceed at the temperature condition for iron oxide reduction (700-800 °C). Therefore, in the first reduction stage the zinc in EAF dust is still in the form of zinc oxide.

The reduction of zinc ferrite by carbon monoxide gas is also preferentially reduced to zinc oxide and wustite, after that wustite is reduced to metallic iron by carbon monoxide respectively.



$$\Delta G^\circ = 14,540 + 41.78T \text{ J/mol} \quad (4.15)$$



$$\Delta G^\circ = -18,700 + 22.5T \text{ J/mol} \quad (4.17)$$

Reaction 4.18 shows that, cadmium oxide is reduced and evaporates completely in the first reduction stage.

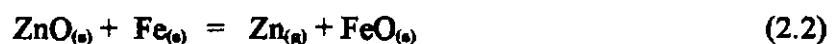


$$\Delta G^\circ = 82,630 - 122.2T \text{ J/mol} \quad (4.19)$$

For Equation 4.19, the minimum temperature at which this occurs is about 403 °C (676 K) for a total pressure of 1 atmosphere, therefore, above this temperature, the reaction of cadmium oxide by carbon monoxide would be expected.

4.2 SECOND REDUCTION STAGE

In the second reduction stage zinc oxide that remains in the EAF dust is reduced. The basic reaction for zinc oxide reduction stated previously in the Section 2.2.2 is shown as follows:



$$\Delta G^\circ = 204,066.8 - 1388.33T \text{ J/mol} \quad (2.3)$$

For Equation 2.2, the Van't Hoff free energy equation can be written as :

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{p_{Zn} \cdot a_{FeO}}{a_{ZnO} \cdot a_{Fe}} \right] \quad (4.20)$$

Let suppose that the reaction is now allowed to proceed under conditions of constant pressure and temperature. As the reaction proceeds, the activities of the species, or the value of the logarithmic term in Equation 4.20 which is call the activity quotient will change, and in due course the reaction will reach a state of equilibrium. For the reaction at equilibrium, $\Delta G = 0$, provided the pressure and temperature remain altered. So, from Equation 4.20, find that

$$\Delta G^\circ = -RT \ln \left[\frac{p_{Zn} \cdot a_{FeO}}{a_{ZnO} \cdot a_{Fe}} \right] \quad (4.21)$$

By making two assumptions, that the activities of zinc vapour is equal to its partial pressure and the activities of the iron species and zinc oxide are equal to unity. At any given temperature, the equilibrium constant (K) which is equal to p_{Zn} can be calculated directly from the value of ΔG° using the relationship as follow :

$$K = p_{Zn} = \exp(-\Delta G^\circ / RT) \quad (4.22)$$

If ΔG° is known at a series of temperatures, the corresponding values of p_{Zn} can readily be evaluated at each of these temperatures. Figure 4.4 shows the partial pressure of zinc calculated by Equation 4.22 between 700 to 1200 °C.

At the temperature of 1200 °C, a zinc partial pressure is equal to 1 atmosphere. Therefore the reduction at this temperature will give 1 atmosphere of zinc vapour. On the other hand if the reduction temperatures are decreased, the amounts of zinc vapour product will also decrease. For example at 800 °C only 0.002 atmosphere of zinc vapour will be produced.

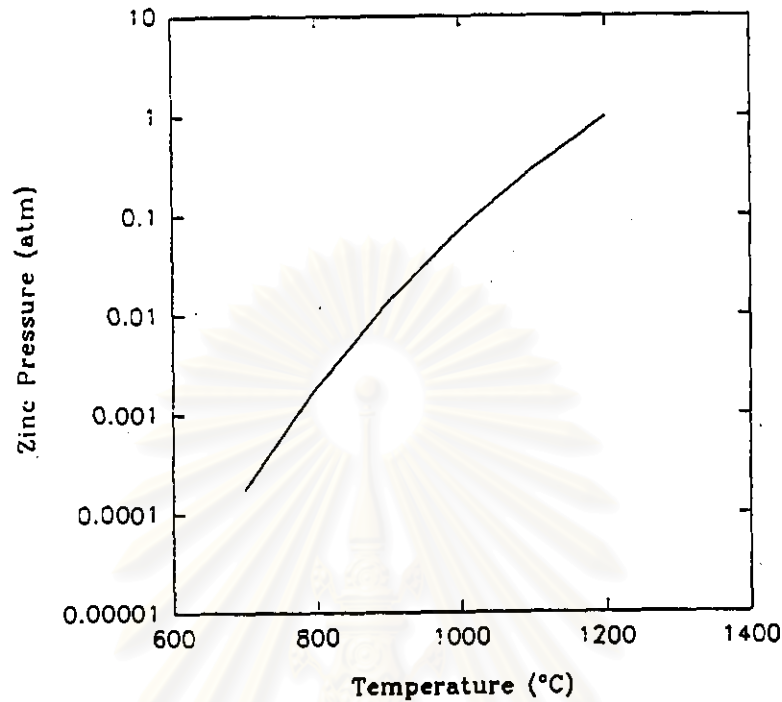
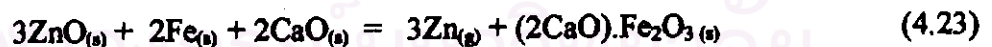


Figure 4.4: Partial pressure of zinc for the reduction of zinc oxide with iron at temperatures between 700 and 1200 °C.

In EAF dust, calcium is presented in the form of calcium oxide (lime) which may affect the equilibrium conditions by forming reaction products, such as dicalcium ferrite which reduces the activity of iron oxide. This is shown in the following reaction:

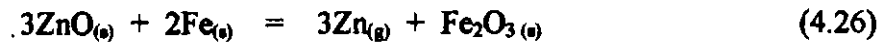


$$\Delta G^\circ = 561,312.4 - 379.1T \text{ J/mol (per mol of zinc oxide)} \quad (4.24)$$

The equilibrium constant for Reaction 4.23 is

$$K_{4.21} = \left[\frac{p_{\text{Zn}}^3 \cdot a_{(2\text{CaO})\cdot\text{Fe}_2\text{O}_3}}{a_{\text{ZnO}}^3 \cdot a_{\text{Fe}}^2 \cdot a_{\text{CaO}}^2} \right] \quad (4.25)$$

Reaction 4.23 shows that, in the presence of lime, the iron is present in the reaction products as ferric iron (Fe^{3+}) rather than ferrous iron (Fe^{2+}), as is indicated in Reaction 2.2 for the reaction without lime. The overall reaction in the presence of lime can be written as:



Also, the hematite forms a dicalcium ferrite solid solution, thereby reducing the activity of the iron oxide which will decrease the free energy change of Reaction 4.23. The standard free energy change of Reaction 4.26 is given as follows, per mole of zinc oxide :

$$\Delta G^\circ = 187,060 - 126T \text{ J/mol} \quad (4.27)$$

Lead oxide can also be reduced by metallic iron according to the following reaction:



$$\Delta G^\circ = -51,178.0 - 29.74T \text{ J/mol} \quad (4.29)$$

However, since lead has a relatively high boiling point ($T_{bp} = 1620 \text{ }^\circ\text{C}$: Perry *et al.*, 1984) compared to the other volatile constituents of the dust, the reduced lead phase will be present as a liquid at partial pressures of lead above its equilibrium vapour pressure. That is, the lead is reduced to a vapour phase only at partial pressures of lead below $1.8 \cdot 10^{-3}$ atm at $1000 \text{ }^\circ\text{C}$, $1.8 \cdot 10^{-2}$ atm at $1200 \text{ }^\circ\text{C}$ and $1.0 \cdot 10^{-1}$ atm at $1400 \text{ }^\circ\text{C}$.

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