Metal Production: Ellingham Diagrams

The change in Gibbs free energy caused by the oxidation of a pure metal to form the pure metal oxide is called the standard Gibbs free energy of formation of the oxide, ΔG° (where the pure metal and the pure oxide are the designated standard states), and is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1}$$

where ΔH° is the standard enthalpy change and ΔS° is the standard entropy change for the oxidation reaction. Oxidation reactions are exothermic which, by convention, makes ΔH° a negative quantity and, as the formation of a condensed oxide from a condensed metal involves the consumption of oxygen gas, ΔS° is a negative quantity. If the oxidation reaction does not involve a change in the heat capacity of the system then ΔH° and ΔS° are independent of temperature, in which case ΔG° is a linear function of temperature and a plot of ΔG° vs. temperature gives the standard Ellingham line on an Ellingham diagram. In an Ellingham diagram the value of ΔH° is given by the intersection of the Ellingham line with the $T = 0\,\mathrm{K}$ axis and the value of ΔS° is the negative of the slope of the line.

The equilibrium constant, K_p, is obtained from the standard Gibbs free energy of formation of the oxide as

$$\Delta G^\circ = -RT \ln K_p \tag{2}$$

where, for an oxidation reaction

$$x\mathrm{M} + \mathrm{O_2(g)} = \mathrm{M}_x\mathrm{O}_2 \tag{3}$$

the equilibrium constant gives the required combination of the activities of the metal and the oxide and the partial pressure of oxygen gas required for the three-phase metal–oxide–gas equilibrium as

$$K = \frac{a_{\mathrm{M}_x\mathrm{O}_2}}{a_M^x \cdot p(\mathrm{O_2})} \tag{4}$$

The choice of the pure metal and the pure oxide a standard states makes the activities of M and $\mathrm{M}_x\mathrm{O}_2$ have values of unity in Eqn. (4), in which case the combination of Eqns. (1), (2), and (4) gives

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT \ln p(\mathrm{O_2(eq)}) \tag{5}$$

Equation (5) gives the variation of the partial pressure of oxygen, $p(\mathrm{O_2(eq)})$, with temperature required for equilibrium between the pure metal, the pure oxide, and the gaseous phase containing oxygen. The application of Eqn. (5) to the Ellingham diagram creates a phase stability diagram.

The standard Gibbs free energies of formation of the various oxides of iron are as follows:

(a) for $2\mathrm{Fe(s)} + \mathrm{O_2} = 2\mathrm{FeO(s)}$
$\Delta G^\circ = -529\,800 + 113.0\ T\ \mathrm{J}$

(b) for $1.5\mathrm{Fe(s)} + \mathrm{O_2} = \mathrm{Fe_3O_4(s)}$
$\Delta G^\circ = -553400 + 148.0\ T\ \mathrm{J}$

(c) for $4\mathrm{Fe_3O_4(s)} + \mathrm{O_2} = 6\mathrm{Fe_2O_3(s)}$
$\Delta G^\circ = -498900 + 281.3\ T\ \mathrm{J}$

(d) for $6\mathrm{FeO(s)} + \mathrm{O_2} = 2\mathrm{Fe_3O_4(s)}$
$\Delta G^\circ = -624400 + 250.2\ T\ \mathrm{J}$.

The reactions given by Eqns. (a)–(d) above are written for the consumption of one mole of oxygen gas in order that $\Delta G^\circ = RT\ln p(\mathrm{O_2})$ for each reaction can be plotted as a function of T on a single Ellingham diagram. Wustite ("FeO") and magnetite ($\mathrm{Fe_3O_4}$) exhibit ranges of nonstoichiometry. Thus in reaction (a) iron-saturated wustite is chosen as the standard state for FeO and in reaction (d) oxygen-saturated wustite is chosen as the standard state for FeO. Similarly, in reaction (b), iron-saturated magnetite is chosen as the standard state for $\mathrm{Fe_3O_4}$ and in reaction (c) oxygen-saturated magnetite is the standard state for $\mathrm{Fe_3O_4}$. The Ellingham lines for the equilibria given by Eqns. (a)–(d) are shown in Fig. 1. Every point in an Ellingham diagram represents a unique thermodynamic state (combination of temperature and partial pressure of oxygen). Any point is a pair of values of T and $RT\ln p(\mathrm{O_2})$ and substitution of the value of T into the value of $RT\ln p(\mathrm{O_2})$ gives the corresponding value of the partial pressure of oxygen. Isotherms in an Ellingham diagram are vertical lines and Eqn. (5) shows that oxygen isobars are straight lines which radiate from the origin of the diagram ($\Delta G^\circ = 0$, $T = 0\,\mathrm{K}$) with a slope of $R\ln p(\mathrm{O_2})$. This allows a nomographic scale for oxygen pressure to be placed along the right-hand edge of the diagram and the oxygen isobar for $p(\mathrm{O_2}) = 10^{-8}\,\mathrm{atm}$ is shown as a broken line in Fig. 1. The oxygen pressure at any point in the diagram is read from the scale as being colinear with a line drawn from the origin of the diagram through the point of interest to the nomographic scale. For example, the state identified as c' in Fig. 1 is the state $T = 1635\,^\circ\mathrm{C}$ and $p(\mathrm{O_2}) = 10^{-8}\,\mathrm{atm}$.

A three-phase equilibrium (metal–oxide–gas) in a binary system (Fe–O) has one degree of freedom, which can be selected as temperature or partial pressure of oxygen. Thus line C in Fig. 1 represents the variation of oxygen pressure with temperature required to maintain phase equilibrium between the condensed phases magnetite and hematite ($\mathrm{Fe_2O_3}$) and the gas phase. This is the equilibrium oxygen pressure. If the state of the system is moved off the Ellingham line the equilibrium is destroyed and one of the condensed phase disappears. For example, moving the thermodynamic state from a point on the Ellingham line C to a less negative value of ΔG° at constant temperature increases the partial pressure of oxygen to a value higher than that required for the equilibrium at that temperature and thus the magnetite becomes unstable. Similarly, moving the thermodynamic state from a point on line C to a state of more negative free

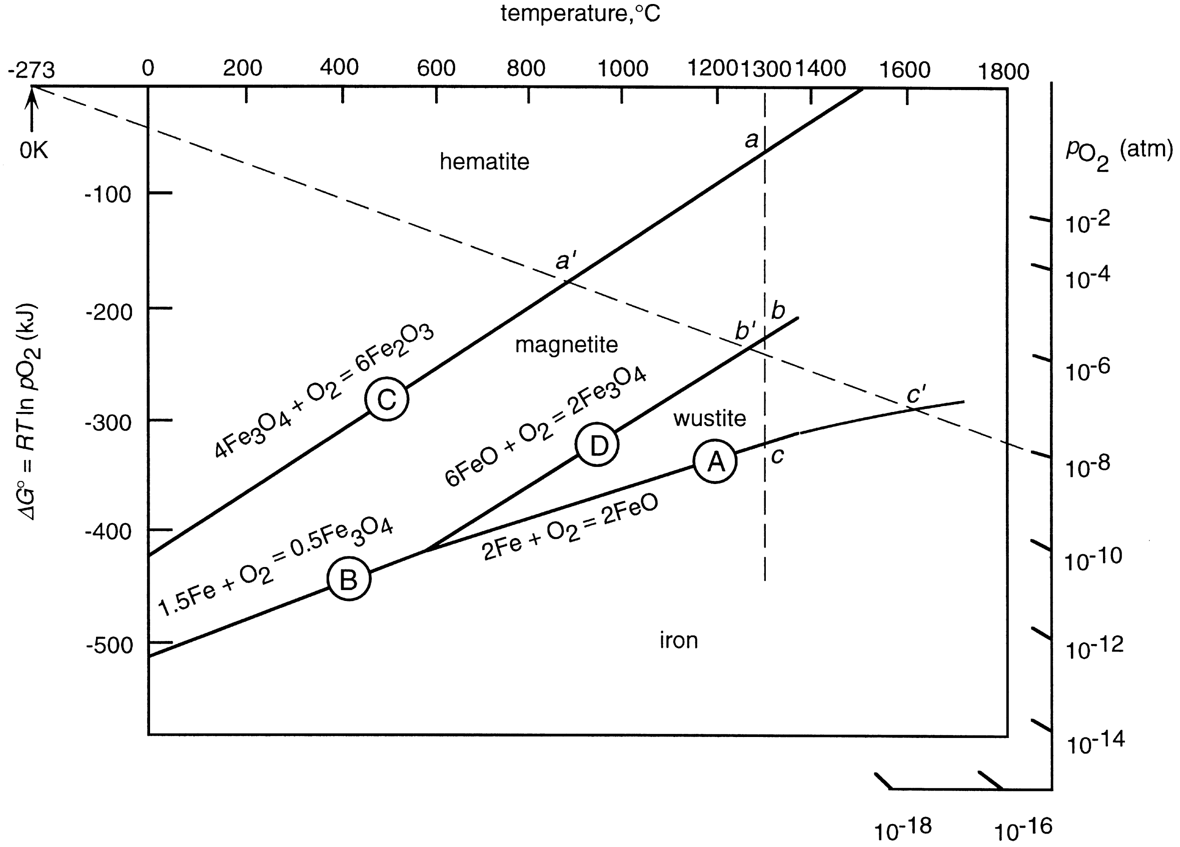

Figure 1
Phase stability in the system Fe–Fe_2O_3 as a function of ΔG° and temperature.

energy at constant temperature decreases the partial pressure of oxygen to a value less than that required for equilibrium at that temperature and thus the hematite phase disappears. Line C is thus the boundary between the phase stability fields of magnetite and hematite. Similarly line B is the variation, with temperature, of the oxygen pressure required to maintain equilibrium between iron and magnetite. In states above the line the oxygen pressure is higher than that required for the equilibrium and thus magnetite is stable relative to iron. Conversely, iron is the stable state below the line. Thus in any reduction–oxidation equilibrium the oxidized state is stable above the Ellingham line and the reduced state is stable below the line. Line D is the boundary between the phase stability fields of magnetite and wustite and line A is the boundary between the phase stability fields of iron and wustite. Lines A, B, and D meet at the invariant state ($T = 560\,°C$, $p(O_2) = 4 \times 10^{-24}$ atm) at which the eutectoid equilibrium iron–wustite–magnetite equilibrium occurs in the system. The change in the slope of line A occurs at the eutectic point (1371 °C) at which equilibrium exists between solid iron, wustite and liquid oxide. Line A at temperatures higher than 1371 °C is for equilibrium between solid iron, and liquid iron oxide. The increase in the entropy when wustite melts to form liquid oxide causes a decrease in the standard entropy change for the reaction, which produces an "elbow" in the Ellingham line. The four Ellingham lines define the phase stability fields of iron, wustite, magnetite, and hematite.

The Ellingham diagram shows that the production of a metal from its oxide requires that the thermodynamic state be moved from a point within the phase stability field of the oxide to a point within the phase stability field of the metal. Figure 1 shows that this change of state can be accomplished by: (i) decreasing the oxygen pressure at constant temperature; (ii) increasing the temperature at constant oxygen pressure; or (iii) a combination of increasing the temperature and decreasing the oxygen pressure. Consider the vertical broken line at 1300 °C in Fig. 1. At $\Delta G^\circ = 0$ ($p(O_2) = 1$ atm) the system exists as hematite. Decreasing the oxygen pressure at constant temperature moves the thermodynamic state to the point *a* on line C at $p(O_2) = 1.3 \times 10^{-2}$ atm in which

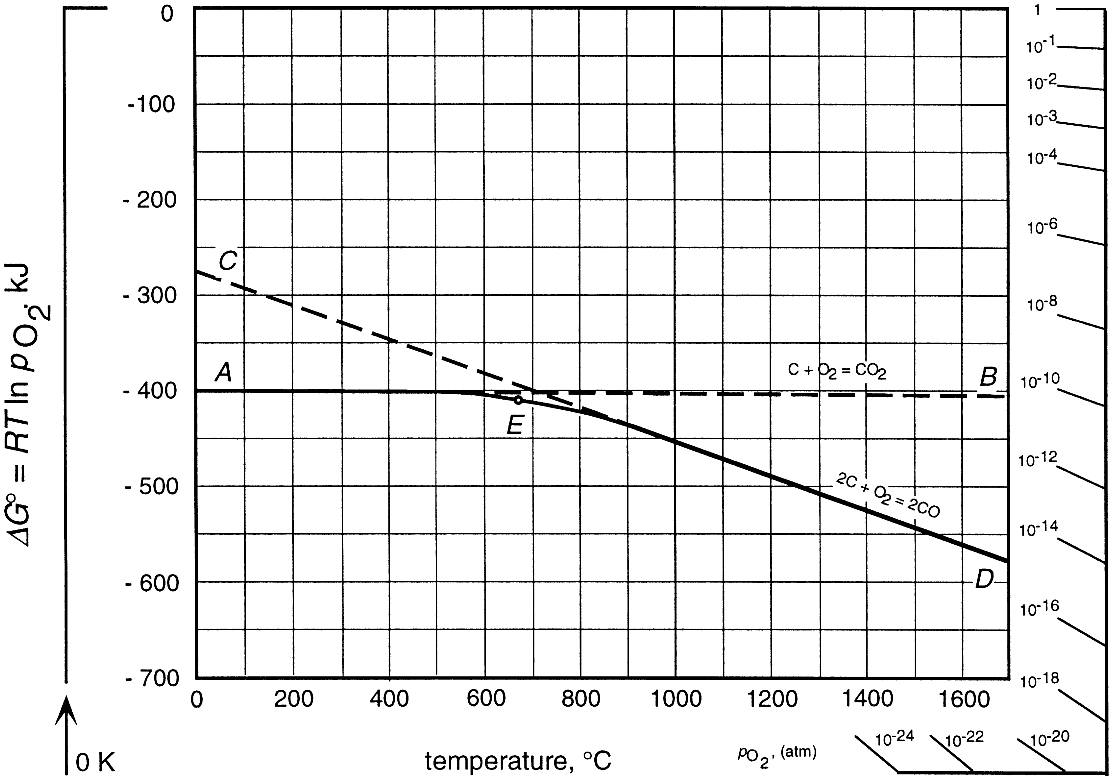

Figure 2
The carbon line in the Ellingham diagram.

state magnetite is in equilibrium with hematite. Further decrease in the oxygen pressure moves the system through the magnetite phase field to the state *b* at $p(O_2) = 2.2 \times 10^{-8}$ atm in which state magnetite is in equilibrium with wustite. Decreasing the oxygen pressure below 2.2×10^{-8} moves the system into the wustite phase field and at $p(O_2) = 2 \times 10^{-12}$ atm, the state *c*, iron is produced in equilibrium with wustite. Iron is the stable phase at 1300 °C and an oxygen pressure of less than 2×10^{-12} atm. The influence of increasing the temperature at a constant partial pressure of 10^{-8} atm is shown as the broken line. The state moves from the hematite phase field to the magnetite phase field at *a′* (875 °C), from the magnetite field to the wustite field at *b′* (1275 °C), and from the liquid iron oxide field to the liquid iron field at *c′* (1635 °C). Thus at a partial pressure of oxygen of 10^{-8} atm liquid iron is the stable phase at temperatures higher than 1635 °C.

The standard Ellingham lines for CO_2 and CO (with 1 atm pressure as the standard state) are shown in Fig. 2 as AB and CD, respectively. The line AB is virtually horizontal because the reaction $C + O_2 = CO_2$ involves the consumption of one mole of gas (O_2) and the production of one mole of gas (CO_2), with the consequence that the standard entropy change is virtually zero. In contrast, the line CD has a negative slope because the reaction $2C + O_2 = 2CO$ involves the consumption of one mole of gas (O_2) and the production of two moles of gas (CO) with the consequence that the standard entropy change is a positive quantity. A gaseous atmosphere containing oxygen gas in equilibrium with carbon thus contains both CO and CO_2, but the different thermodynamic stabilities of two gases causes the ratio $p(CO)/p(CO_2)$ in the gas in equilibrium with carbon to be a significant function of temperature. At lower temperatures CO_2 is more stable than CO and hence the gas in equilibrium with carbon is predominantly CO_2. The composition of the gas mixture in equilibrium with pure carbon (at unit activity) is determined by the equilibrium

$$C + CO_2 = 2CO \tag{6}$$

for which

$$\Delta G^\circ = 170{,}700 - 145.5T = -RT\ln\left(\frac{p^2(CO)}{p(CO_2)}\right) \tag{7}$$

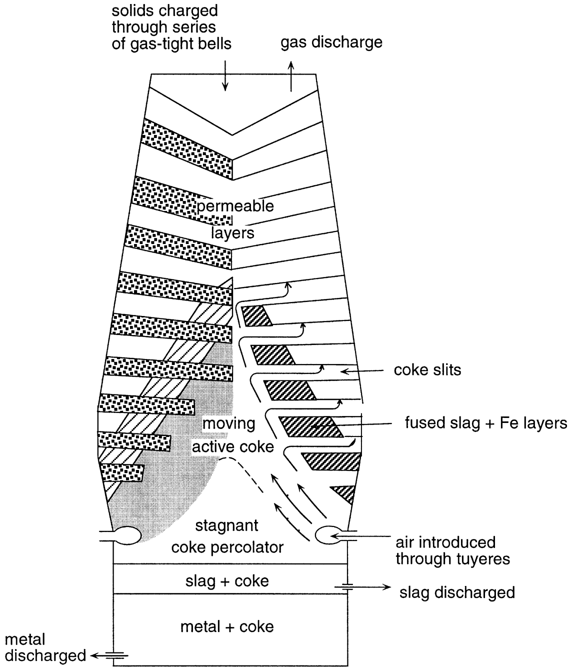

Figure 3
The internal structure of a large blast furnace.

and by

$$p(\mathrm{CO})+p(\mathrm{CO_2}) = P_{\mathrm{total}} \qquad (8)$$

At a total pressure of 1 atm and a temperature of 200 °C the ratio $p(\mathrm{CO_2})/p(\mathrm{CO})$ in the gas phase in equilibrium with carbon has the value 7.4×10^4. Conversely, at high temperatures CO is more stable than CO_2 and thus the gas in equilibrium with carbon is predominantly CO. At a total pressure of 1 atm and a temperature of 1600 °C the ratio $p(\mathrm{CO_2})/p(\mathrm{CO})$ in the gas in equilibrium with carbon has the value 4.4×10^{-5}. The gas in equilibrium with carbon in which $p(\mathrm{CO}) = p(\mathrm{CO_2}) = 0.5$ atm occurs at 674 °C at the state labeled E in Fig. 2. Thus the thermodynamic state of CO–CO_2 gas at a pressure of 1 atm in equilibrium with carbon varies with temperature along the full line AED in Fig 2, and this line called the *carbon line*. The CO–CO_2 gas in equilibrium with carbon exerts a partial pressure of oxygen by means of the gaseous equilibrium

$$2\mathrm{CO}+\mathrm{O_2} = 2\mathrm{CO_2} \qquad (9)$$

and this oxygen pressure can be obtained from the nomographic scale for partial pressure of oxygen in Fig. 2.

Iron ore is reduced in an iron blast furnace, which is a continuously-operating counter-current vertical retort in which the solid burden, charged at the top, moves down and the gas, introduced at the bottom, moves up. The internal structure of a large blast furnace is shown in Fig. 3. The charge is introduced to the furnace as alternating layers of coke, ore pellets, and flux and the region above the hearth, in the fusion zone, consists of alternating layers of coke and melting gangue, flux and iron, which have persisted from the charging sequence. Air, introduced through the tuyeres, reacts with the coke and the gas produced rises through the furnace. The sequence of reactions is shown in Fig. 4. Air, which is introduced at 1000 °C, enters the furnace at the state A. It reacts with the solid to produce mainly CO and the exothermic reaction heats the gas and moves its thermodynamic state from A to B. At B it is in equilibrium with the coke, has a partial pressure of oxygen of 10^{-14} atm and is at 2000 °C. The gas then ascends and moves through the layer of melted iron, gangue, and partially-melted slag during which the reaction

$$\mathrm{FeO}+\mathrm{CO} = \mathrm{Fe}+\mathrm{CO_2} \qquad (10)$$

moves the state of the gas from B on the carbon line to C on the Fe/FeO line. The gas then passes through another layer of coke, during which the reaction given by Eqn. (6) moves the state of the gas back to the carbon line at D. The occurrence of the reaction given by Eqn. (6) restores the reducing potential of the gas. As the gas continues to rise through the furnace its alternating passage through layers of coke and layers of ore causes its state to oscillate between the carbon line and the Fe/FeO line as shown in Fig 3. The temperature of the gas decreases and at 800 °C its partial pressure on the carbon line is 10^{-20} atm. The carbon and Fe/FeO lines intersect at 625 °C, which is thus the minimum temperature at which FeO can be reduced by carbon. The carbon line passes through the field of phase stability of magnetite between 60 and 560 °C, in which range of temperature carbon reduces hematite to magnetite.

Two comments can be made about Fig. 4. The carbon line is drawn for a total pressure of 1 atm. Modern blast furnaces operate at pressures higher than 1 atm and increasing the gas pressure rotates the carbon line in an anticlockwise direction about the point E in the figure. Secondly, the Fe/FeO line in the figure is drawn for unit activities of Fe and FeO. Slag fusion in the blast furnace occurs at the temperature at which CaO and MgO, added with the charge as fluxing agents, react with the SiO_2 and the Al_2O_3, which occur as the coke ash, to form a liquid slag. The oxidation potential in the slag fusion zone is such that the FeO concentration in the slag is negligibly small. Consequently the FeO occurs at a low activity which lowers the position of the Fe/FeO line in the diagram and decreases the magnitude of oscillation from states B to C. Operating at high gas pressure, which raises the position of the carbon line in the diagram, further

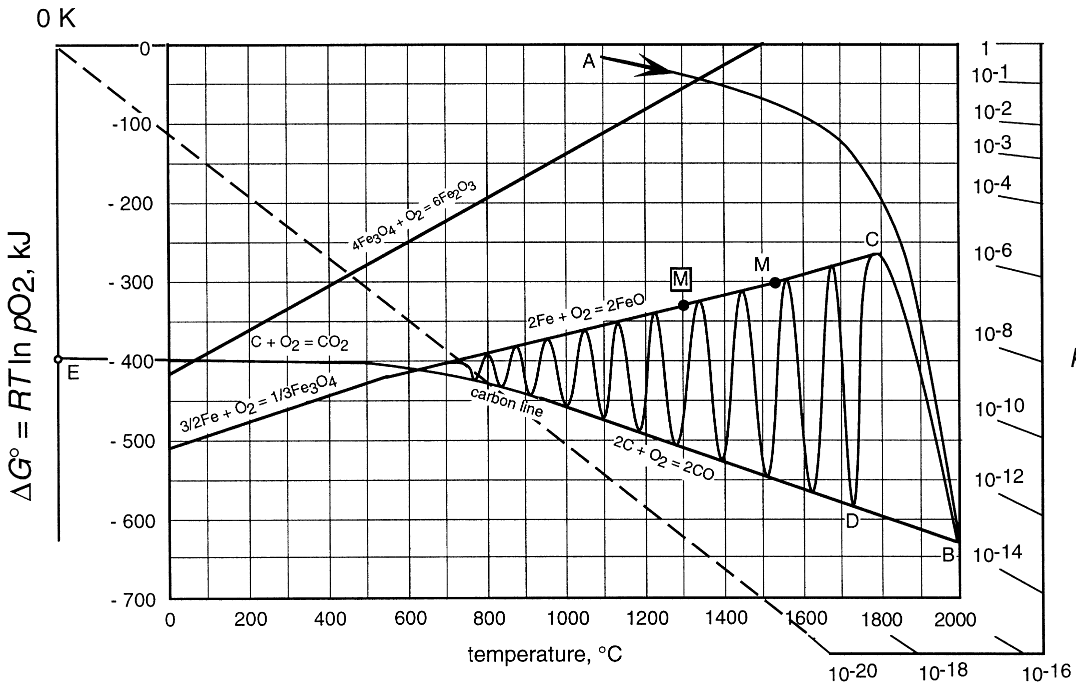

Figure 4
The change in thermodynamic state of a packet of gas as it passes through the iron blast furnace.

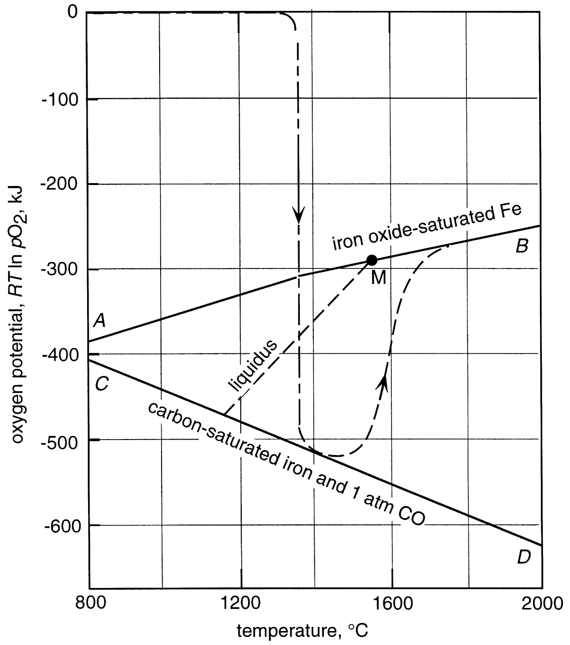

Figure 5
The progress of the blow in a basic oxygen furnace.

decreases the magnitude of the oscillation from state B to state C. The liquid metal produced by the iron blast furnace is carbon-saturated iron called hot metal.

Steel is produced by oxidizing carbon, silicon, and manganese from a mixture of hot metal, scrap, and flux charged to a Basic Oxygen Furnace. The oxidation is achieved by impinging a supersonic jet of liquid oxygen on to the free surface of the liquid in the furnace. The decarburization process is shown in Fig. 5. The line AB is for iron oxide–saturated iron and the line CD is the carbon line (carbon-saturated iron and CO gas at 1 atm pressure). Upon contact with the melt the oxygen is heated to the temperature of the melt (1370 °C) and dissolves in the melt. The state of the system follows the vertical dash–dot line to the carbon line during which time iron is oxidized to liquid FeO, silicon in solution is oxidized to SiO_2 which dissolves in the iron oxide to form a liquid iron silicate, and the fluxing agent, CaO, dissolves in the melt to form the steelmaking slag. When the state of the system reaches the carbon line the dissolved oxygen begins to react with the carbon in solution to produce CO gas, which rises through the melt and leaves the furnace. The decarburization reaction decreases the carbon concentration and increases the oxygen concentration and the state of the system moves along the broken line in the direction of the arrow. The sensible heat evolved by the oxidation reactions is sufficient to maintain the temperature of the melt above the liquidus and decarburization ceases when the activity of FeO in the slag reaches its maximum value, which is typically about 0.6 in a slag saturated with $2CaO.SiO_2$.

Bibliography

Ellingham H J T 1944 Reducibility of oxides and sulfides in metallurgical processes. *J. Soc. Chem. Ind.* **63**, 125

D. R. Gaskell

Encyclopedia of Materials: Science and Technology
ISBN: 0-08-0431526
pp. 5481–5486