

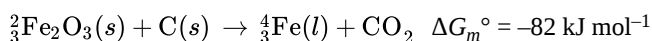
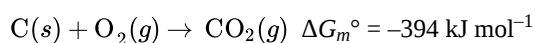
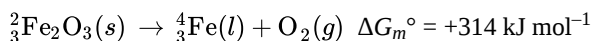
## 22.5: Reduction of Metals

The ease with which a metal may be obtained from its ore varies considerably from one metal to another. Since the majority of ores are oxides or can be converted to oxides by roasting, the free-energy change accompanying the decomposition of the oxide forms a convenient measure of how readily a metal may be obtained from its ore. Values of the free energy change per mol  $O_2$  produced are given in the table for a representative sample of metals at 298 and 2000 K. A high positive value of  $\Delta G_m^\circ$  in this table indicates a very stable oxide from which it is difficult to remove the oxygen and obtain the metal, while a negative value of  $\Delta G_m^\circ$  indicates an oxide which will spontaneously decompose into its elements. Note how the value of  $\Delta G_m^\circ$  decreases with temperature in each case. This is because a gas (oxygen) is produced by the decomposition, and  $\Delta S$  is accordingly positive.

Table 22.5.1: Free-Energy Changes for the Decomposition of Various Oxides at 298 and 2000 K.

Reaction	$\Delta G_m^\circ$ (298 K)/kJ mol <sup>-1</sup>	$\Delta G_m^\circ$ (2000 K)/kJ mol <sup>-1</sup>
$\frac{2}{3} Al_2O_3 \rightarrow \frac{4}{3} Al + O_2$	+1054	+691
$2 MgO \rightarrow 2 Mg + O_2$	+1138	+643
$\frac{2}{3} Fe_2O_3 \rightarrow \frac{4}{3} Fe + O_2$	+744	+314
$SnO_2 \rightarrow Sn + O_2$	+520	+42
$2 HgO \rightarrow 2 Hg + O_2$	+118	-381
$2 Ag_2O \rightarrow 4 Ag + O_2$	+22	-331
<b>Formation of CO<sub>2</sub></b>		
$C(s) + O_2(g) \rightarrow CO_2(g)$	-394	-396

The two metals in the table which are easiest to obtain from their oxide ores are Hg and Ag. Since the  $\Delta G_m^\circ$  value for the decomposition of these oxides becomes negative when the temperature is raised, simple heating will cause them to break up into  $O_2$  and the metal. The next easiest metals to obtain are Sn and Fe. These can be reduced by coke, an impure form of C obtained by heating coal. Coke is the cheapest readily obtainable reducing agent which can be used in metallurgy. When C is oxidized to  $CO_2$ , the free-energy change is close to  $-395 \text{ kJ mol}^{-1}$  over a wide range of temperatures. This fall in free energy is not quite enough to offset the free-energy rise when  $Fe_2O_3$  and  $SnO_2$  are decomposed at 298 K, but is more than enough if the temperature is 2000 K. Thus, for example, if  $Fe_2O_3$  is reduced by C at 2000 K, we have, from Hess' law,



Thus  $\Delta G_m^\circ$  for the reduction is negative, and the reaction is spontaneous.

The two metals in the table which are most difficult to obtain from their ores are Mg and Al. Since they cannot be reduced by C or any other readily available cheap reducing agent, they must be reduced electrolytically. The electrolytic reduction of bauxite to yield Al (the Hall process) is used to [produce aluminum](#).

### Reduction of Iron

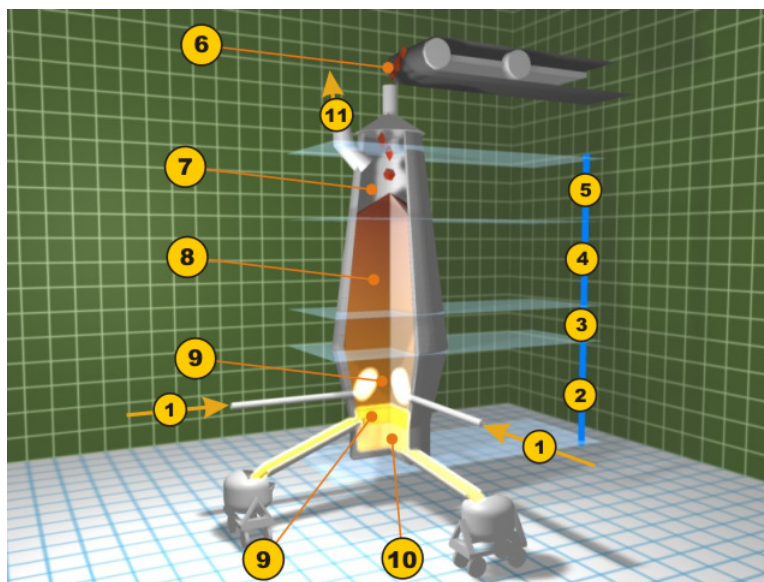
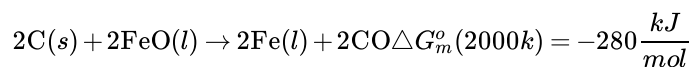


Figure 22.5.1 Schematic Diagram of a Blast Furnace for Smelting Iron 1. Hot blast from Cowper stoves 2. Melting zone 3. Reduction zone of ferrous oxide 4. Reduction zone of ferric oxide 5. Pre-heating zone 6. Feed of ore, limestone and coke 7. Exhaust gases 8. Column of ore, coke and limestone 9. Removal of slag 10. Tapping of molten pig iron 11. Collection of waste gases.

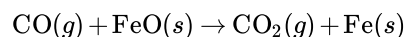
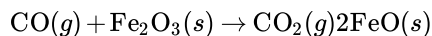
Since iron is the most important metal in our industrial civilization, its reduction from iron ore in a blast furnace (Figure 22.5.1) deserves a detailed description. The oxides present in most iron ores are  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . These oxides are reduced stepwise: first to  $\text{FeO}$  and then to  $\text{Fe}$ . Ore, coke, and limestone are charged to the furnace through an airlock-type pair of valves at the top. Near the bottom a blast of air, preheated to 900 to 1000 K, enters through blowpipes called tuyères. Oxygen from the air blast reacts with carbon in the coke to form carbon monoxide and carbon dioxide, releasing considerable heat. The blast carries these gases up through the ore, coke, and limestone, and they exit from the top of the furnace.

By the time the ore works its way to the lower part of the furnace, most of the  $\text{Fe}_2\text{O}_3$  has already been reduced to  $\text{FeO}$ . In this region, temperatures reach 1600 to 2000 K, high enough to melt  $\text{FeO}$  and bring it into close contact with the coke. Most of the  $\text{FeO}$  is reduced by direct reaction with carbon, the latter being oxidized to carbon monoxide:



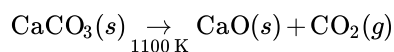
The molten iron produced by this reaction drips to the bottom of the furnace where it is collected and occasionally tapped off.

Higher in the furnace, temperatures fall below the melting points of the iron oxides. Because there is little contact between solid chunks of ore and of coke, direct reduction by solid carbon is rather slow. Gaseous carbon monoxide contacts all parts of the ore, however, and reacts much more rapidly:

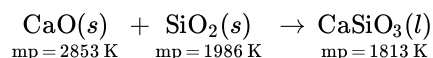


Thus much of the “carbon reduction” in ironmaking is actually carried out by carbon monoxide.

The gangue in iron ore consists mainly of silicates and silica,  $\text{SiO}_2$ . These impurities are removed in slag. Limestone added with coke and ore is calcined (decomposed to the oxide) by the high temperatures of the blast furnace:



Lime ( $\text{CaO}$ ) serves as a flux, reducing the melting points (mp) of silica ( $\text{SiO}_2$ ) and silicates:



The liquid silicates flow rapidly down through the hottest part of the furnace. This helps to prevent reduction of silica to silicon, hence yielding purer iron. The slag is less dense than molten iron and immiscible with it. Therefore the slag floats on the surface of

the iron and can easily be tapped off.

Although most blast-furnace iron now goes directly to a steelmaking furnace in molten form, much of it used to be run into molds where it hardened into small ingots called pigs because of their shape. Consequently blast-furnace iron is still referred to as pig iron. A single large blast furnace may produce more than  $10^6$  kg iron per day. For each kilogram of iron, 2 kg iron ore, 1 kg coke, 0.3 kg limestone, 4 kg air, 63 kg water, and 19 MJ of fossil-fuel energy are required. The furnace produces 0.6 kg slag and 5.7 kg, flue gas per kg iron. Nearly 5 percent of the iron ore is lost in the form of small particles suspended in the flue gas unless, as in the furnace shown in Figure 1, air-pollution controls are installed. The latter trap FeO particles for recycling to the furnace and also make the flue gas (which contains about 12% CO and 1% H<sub>2</sub>) suitable as a fuel for preheating air fed to the tuyères. Thus control of blast-furnace air pollution (a major contributor to the one-time “smoky city” reputations of Pittsburgh, Pennsylvania and Gary, Indiana) also conserves ore supplies and energy resources.

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