LECTURE NOTES

ON

IRON & STEEL MAKING TECHNOLOGY

Illustration of ironmaking and steelmaking flowsheet

By

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COURSE CODE: MME 405  COURSE TITLE: IRON & STEEL MAKING TECHNOLOGY

COURSE CREDIT LOAD: [L-Lectures = 1; T-Tutorials = 1; P-Practical = 0; U-Credit Unit = 2]
PREREQUISITES: 1. Engineering Thermodynamics [ENG 209]
2. Introduction to Chemical Metallurgy [MME 204]

COURSE CONTENT
Application of chemical and thermodynamic principles to integrated metallurgical processes in the
- Iron blast furnace,
- Basic oxygen steel making,
- Direct reduction and electric furnace steel making, Ferro-alloy production, Slag-metal reactions.
- Refining processes including precipitation, segregation and vacuum degassing.
- Mass and heat balances in iron and steel making.

ASSESSMENT
There will be two types of assessment in this course. The first one comprises assignments and a quiz; the second is final examination at the end of the course. The assignment and quiz count for 30% of your total course mark. At the end of the course, you are required to write an examination of about two to three hours duration. This examination will count for 70% of your total course mark. The table below shows how the actual marks will be distributed.

<table>
<thead>
<tr>
<th>Assessment</th>
<th>Actual Marks</th>
<th>% of Course Marks</th>
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</thead>
<tbody>
<tr>
<td>Assignments (by U. Mark)</td>
<td>20 marks</td>
<td>30%</td>
</tr>
<tr>
<td>Quiz/Test (by J.U. Anaele)</td>
<td>10 marks</td>
<td></td>
</tr>
<tr>
<td>Final Examination (by Mark &amp; Anaele)</td>
<td>70 marks</td>
<td>70%</td>
</tr>
<tr>
<td>Total</td>
<td>100 marks</td>
<td>100%</td>
</tr>
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</table>

IRON AND STEEL: WHAT DO WE MEAN?
Ordinarily, iron is the metallic chemical element, *ferrum* (Fe). However, from commercial and industrial viewpoint, iron implies not the pure chemical element, but an alloy that is dominated by the element iron (Fe). Iron and steel are alloys of chiefly Fe and C and are known as **ferrous alloys**. They can be classified in terms of chemical composition, structure, applicability and method of production. Referring to the Fe–C (or more correctly, Fe–Fe₃C) phase diagram (Figure 1), ferrous alloys are broadly classified into **cast irons** and **steels**. Alloys of Fe and C with more than 2.11% carbon are called cast irons, whereas those with less are called steels.

Depending on composition and microstructure, the general-purpose cast irons fall into the following grades: **grey cast iron**, **white cast iron**, **malleable cast iron**, and **ductile or nodular cast iron**. Steel is not any specific product. It is rather a malleable alloy of iron and one or more of other elements like carbon (C), chromium (Cr), nickel (Ni), silicon (Si), vanadium (V), tungsten (W) or almost any active element (other than gas) from the periodic table of elements. There are as many as two thousand odd varieties of steels in use, which specifically differ in their chemical composition. However, a couple of hundred varieties are predominantly in use.
The chemical composition of steels broadly divides them into two major groups, viz. (a) plain carbon steels and, (b) alloy steels. The plain carbon steels are essentially alloys of iron and carbon only whereas, if one or more alloying elements other than carbon are added to steel in significant amounts to ensure specific better properties such as better mechanical strength, ductility, electrical and magnetic properties, and corrosion resistance and so on, it is known as an alloy steel. These specifically added elements are known as alloying additions in steels.

Steels may contain many other elements such as Al, Si, Mn, S, P, O, etc. which are not added intentionally for any specific purpose, but are inevitably present because of their association in the process of iron and steel making and cannot be totally eliminated during the known process of iron and steel making. These are known as impurities in steel and every attempt is made to minimize them during the process of steelmaking to acceptable or safe limits in the case of each element.

Plain carbon steels are broadly subdivided into four major types based on their carbon contents, viz.:
- Soft or Low Carbon Steels up to 0.15%C
- Mild Steels in the range 0.15 – 0.35%C
- Medium Carbon Steels in the range 0.35 – 0.65%C
- High Carbon Steels in the range 0.65 – 1.75%C

The alloy steels are also broadly subdivided into three groups on the basis of the total alloying elements present into:
- Low Alloy Steels up to 5% total alloying contents
- Medium Alloy Steels 5 – 10% total alloying contents
- High Alloy Steels above 10% total alloying contents

In terms of uses, steels are often classified as structural, deep-drawing, rail, forging, flats, etc. In terms of dominant microstructure, we may talk of ferritic steels, austenitic steels, martensitic steels, and even duplex steels (containing two structures, ferrite and austenite, and can be found in some special stainless steels). With regards to corrosion resistance and surface appearance, a special class of steels have been developed known as stainless steels. Gone are the days when steels were classified according to the process of manufacture, e.g. Bessemer steel, Acid Open Hearth steel, Basic Open Hearth steel, Electric steel, etc. Technology has made such classifications irrelevant.

FERROUS METALLURGY

The field of metallurgical engineering can be divided based on types of metals produced and used into ferrous metallurgy and nonferrous metallurgy. This division is traditional or historical as well as economic. Whereas ferrous metallurgy deals with iron and steel, nonferrous metallurgy concerns all other metals such as aluminium, copper, zinc, etc. This view divides all metals in the periodic table into two: iron and others. This is because iron and steel production (ferrous metallurgy) is the dominant
branch of metallurgical engineering based on volume of production, size of the industry, work force employed, and so on. For example, the production of iron and steel in one year exceeds the production of all other metals combined in ten years. Therefore, iron is economically or commercially very important.

On the basis of the principles and techniques involved (scientifically and technically), metallurgical engineering is classified into chemical metallurgy (including subdivisions like extractive metallurgy, corrosion, etc.), physical metallurgy (which though younger, matured faster than its sister science of chemical metallurgy), and mechanical metallurgy. Steel is by far the most important engineering material known to man, and its manufacture is the most important process in the field of extractive metallurgy. In this course (Ironmaking and Steelmaking Technology), we shall be dealing with ferrous extractive metallurgy.

Table 1: Relative Abundance of Elements in the Lithosphere (Earth’s Crust)

<table>
<thead>
<tr>
<th>Chemical Elements</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>46.46</td>
</tr>
<tr>
<td>Silicon</td>
<td>27.61</td>
</tr>
<tr>
<td>Aluminium</td>
<td>8.07</td>
</tr>
<tr>
<td>Iron</td>
<td>5.06</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.64</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.75</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.58</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.07</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.62</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.14</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.12</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.09</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.06</td>
</tr>
<tr>
<td>Barium</td>
<td>0.04</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.09</td>
</tr>
<tr>
<td>Fluorine</td>
<td>0.03</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.02</td>
</tr>
<tr>
<td>All other elements</td>
<td>0.50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Abundancy Range</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Over 10%</td>
<td>O (46.46); Si (27.61)</td>
</tr>
<tr>
<td>1–10%</td>
<td>Al (8.07); Fe (5.06); Ca (3.64); Na (2.75); K (2.58); Mg (2.07)</td>
</tr>
<tr>
<td>0.1–1%</td>
<td>C; H; Mn; P; Ti</td>
</tr>
<tr>
<td>0.01–0.1%</td>
<td>Ba; Cl; Cr; F; Rb; S; Sr; V; Zr</td>
</tr>
<tr>
<td>0.001–0.01%</td>
<td>Cu; Ce; Co; Ga; La; Li; Nb; Ni; Pb; Sn; Th; Zn; Yt</td>
</tr>
<tr>
<td>1–10 ppm</td>
<td>As; B; Br; Cs; Ge; Hf; Mo; Sb; Ta; U; W; and most of the rare Earths</td>
</tr>
</tbody>
</table>
IRON AND ITS ORES
About 5% of the earth’s crust (lithosphere) is the element iron, making Fe the fourth most abundant element in the lithosphere after O, Si and Al. Hence, Fe is the second most abundant metal after Al (Table 1). However, it is present as a compound, mostly as iron oxide. Major iron bearing minerals include magnetite (Fe₃O₄), haematite (Fe₂O₃), limonite (2Fe₂O₃·3H₂O), goethite (Fe₂O₃·H₂O), siderite (FeCO₃), pyrrhotite (FeS), pyrite or fool’s gold (FeS₂) and marcasite (also FeS₂ having a different crystal structure from pyrite). Haematite is the most important and most abundant iron mineral (containing 70% Fe); magnetite is the only ferromagnetic mineral (used and referred to as lodestone), and pyrrhotite is the only magnetic sulphide mineral.

THERMODYNAMICS OF OXIDE REDUCTION
a) Search for Appropriate Reducing Agents
Iron is extracted from its oxide using appropriate reducing agents. The non-oxide minerals are first converted to the oxide by calcination (in the case of the carbonate) or roasting (in the case of the sulphides). Table 2 presents the relative ease of reducing oxides at three different temperatures. According to this table, a metal may reduce any oxide that appears above it in the table; the strongest reducing agents are the metals with oxides that are low in the table, viz. Ca, Li, Al and Mg are excellent reducing agents. CaO is the most difficult oxide to reduce; therefore, Ca is the best reducing agent listed. Thus, a metal oxide may be reduced by means of another metal which has a higher oxygen affinity (i.e. by a metal which has a more stable oxide).

<table>
<thead>
<tr>
<th></th>
<th>At 399°C</th>
<th>At 982°C</th>
<th>At 1538°C (melting point of pure Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂O</td>
<td>Cu₂O</td>
<td>PbO</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>PbO</td>
<td>Cu₂O</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>NiO</td>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>SO₂</td>
<td>SnO₂</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>CoO</td>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td>SnO₂</td>
<td>CoO</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>P₂O₅</td>
<td>SO₂</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>H₂O</td>
<td>P₂O₅</td>
<td></td>
</tr>
<tr>
<td>SnO₂</td>
<td>FeO</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>CO₂</td>
<td>FeO</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>ZnO</td>
<td>CO₂</td>
<td></td>
</tr>
</tbody>
</table>
Above 982°C, carbon can reduce oxides of Fe. Since carbon is the cheapest reducing agent, **carbothermy** is employed in the extraction of iron. Where economically feasible, **metallothermy** e.g. silicothermy, aluminothermy, calciothermy, magnesiothermy, etc. may be used in the extraction of metals. Hydrogen oxide (water) is also listed on Table 2 indicating that hydrogen can be used as a reducing agent for some metals especially at high temperatures.

Another way of looking at this is via the **Ellingham diagram** (ΔG° -T plots) for oxides which shows the relative affinity of elements for oxygen to form oxides, and hence the ease or difficulty of liberating them from oxygen [i.e. oxide stability and thermodynamic reducibility with carbon]. The Ellingham diagram is based on the relation ΔG° = ΔH° – TΔS° from which straight line graphs of the form \[ y = mx + c \] can be plotted by rearranging to:

\[ ΔG° = -ΔS°(T) + ΔH° \]

We see from the Ellingham diagram that the easily reducible, noble metals occur at the top of Figure 2 and the highly reactive metals towards the bottom. This is not far from the historical order of discovery and use of the metals. The CO line has a negative slope and thus intercepts most metal oxides lines at different temperatures. This shows that carbon or CO can reduce a metal oxide only at temperature at least above the point of interception.
Figure 2: Simplified Ellingham diagram for oxides of elements in iron and steel making

b) Reduction by CO and C

The standard Gibbs free energy change ($\Delta G^\circ$) and the equilibrium constant (K) which are thermodynamic data, may be calculated for various reactions of the type:

$$\text{MeO} + \text{CO} = \text{Me} + \text{CO}_2$$

Where

$$K = \frac{a_{\text{Me}}p_{\text{CO}_2}}{a_{\text{MeO}}p_{\text{CO}}} = \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$$

if the metal and the oxide coexist as condensed phases, so as to have unit activities, i.e. $a_{\text{Me}} = a_{\text{MeO}} = 1$.

Recall that, $\Delta G^\circ = -RT \ln K = -2.303RT \log K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

$$\Rightarrow -2.303RT \log K = \Delta H^\circ - T\Delta S^\circ$$

Note that enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) are temperature dependent, but $\Delta H^\circ$ varies by 1% for every 100 degrees rise in temperature and $\Delta S^\circ$ varies by 5% for
100 degrees rise in temperature; and these variations tend to cancel rather than reinforce each other.

\[ \log K = \log \frac{P_{CO_2}}{P_{CO}} = \frac{\Delta H^o - T\Delta S^o}{-2.303RT} = -\frac{\Delta H^o}{2.303R} + \frac{\Delta S^o}{2.303R} \]

This means that the gas ratio \( K = \frac{P_{CO_2}}{P_{CO}} \) has a definite value and is a function only of temperature as long as \( a_{Me} = a_{MeO} = 1 \). Straight line graphs of the type \( \log \frac{P_{CO_2}}{P_{CO}} = -\left( \frac{\Delta H}{2.303R} \right) \frac{1}{T} + \frac{\Delta S}{2.303R} \) can be plotted using the above equation in the form. Rosenquist plotted such graphs (Figure 3a), and showed the gas ratio \( \frac{P_{CO_2}}{P_{CO}} \) for a number of metals of industrial significance.

Figure 3: Rosenquist diagrams showing: (a) equilibrium gas ratio \( \frac{P_{CO_2}}{P_{CO}} \) as function of inverse temperature for the reduction of various oxides; and (b) metastable equilibria for the formation of \( Fe_3C \) and carbon contents in austenite as given by dashed lines. It can be seen that:

- The \( \frac{P_{CO_2}}{P_{CO}} \) ratio varies between \( 10^5 \) for \( Cu_2O \) reduction to \( Cu \) and \( Fe_2O_3 \) reduction to \( Fe_3O_4 \), to less than \( 10^{-5} \) for the reduction of \( MnO \) and \( SiO_2 \) to \( Mn \) and \( Si \) respectively. Even lower gas ratios would be found for the reduction of \( Al_2O_3 \) and \( MgO \). [NB: High \( \frac{P_{CO_2}}{P_{CO}} \) ratio means that dominates \( P_{CO_2} \) or \( CO_2 \) dominates; low \( \frac{P_{CO_2}}{P_{CO}} \) ratio means that dominates \( P_{CO} \) or \( CO \) dominates in the furnace atmosphere].
- The gas ratio \( \frac{P_{CO_2}}{P_{CO}} \) for the Boudouard reaction \( [C + CO_2 = 2CO] \) is also shown. Since for this reaction \( K = K_{Boudouard} = \frac{P_{CO}^2}{P_{CO_2}} \), it means that the gas
The gas ratio is given by \( \frac{P_{CO_2}}{P_{CO}} = \frac{K_{Boudouard}}{P_{CO_2}^2/P_{CO}} = \frac{P_{CO}}{1} \times \frac{P_{CO_2}}{P_{CO}} = \frac{P_{CO_2}}{P_{CO}} \). The result shows that the gas ratio here is a function of \( P_{CO} \) or CO and consequently of the total pressure \( P_{CO} + P_{CO_2} \). The Boudouard reaction results in an increase in pressure as a result of the increase in the number of gaseous molecules as CO is formed (i.e. 1 molar volume of CO \( \text{reacts with C to yield 2 molar volumes of CO} \)). As shown in Figure 3a, the gas ratio \( P_{CO_2}/P_{CO} \) is plotted for a total pressure \( P_T = P_{CO} + P_{CO_2} = 1 \text{ atm} \). For higher or lower values of the total pressure the curve will shift upward or downward in accordance with this equilibrium expression.

For the reduction of a metal oxide with CO in the absence of solid carbon the curve for the Boudouard reaction may be ignored since the reduction of the oxide in this case takes place when the gas ratio in the atmosphere falls below the equilibrium line in question. Thus;

- CuO, PbO and NiO will be reduced at gas ratios between \( 10^5 \) and \( 10^2 \) i.e. at small concentrations of CO. Meaning that if pure CO is used all of it will be converted to CO\( _2 \) before the reaction stops.
- MnO, SiO\( _2 \), and Cr\( _2 \)O\( _3 \) reduction by CO requires a gas free of CO\( _2 \) i.e. the reduction stops as soon as CO\( _2 \) is formed. Meaning that the reduction of MnO, SiO\( _2 \), and Cr\( _2 \)O\( _3 \) by CO is in practice impossible.

If solid carbon is present in the reaction mixture the two reactions \( \text{MeO} + \text{CO} = \text{Me} + \text{CO}_2 \) and \( \text{C} + \text{CO}_2 = 2\text{CO} \) take place simultaneously, resulting to the overall reaction \( \text{MeO} + \text{C} = \text{Me} + \text{CO} \). In effect, simultaneous equilibrium between MeO, Me, and C will occur at the temperature where the curves for the two reactions \([\text{MeO} + \text{CO} = \text{Me} + \text{CO}_2 \text{ and } \text{C} + \text{CO}_2 = 2\text{CO}] \) meet.

- Thus, SnO\( _2 \), Sn and C may be in equilibrium at 610\(^\circ\)C with an atmospheric pressure of \( P_{CO} + P_{CO_2} = 1 \text{ atm} \). This means that SnO\( _2 \) may be reduced by carbon at any temperature above 610\(^\circ\)C. Similarly, Fe\( _3 \)O\( _4 \) will be reduced to FeO above 650\(^\circ\)C, FeO to Fe above 700\(^\circ\)C, and so on. MnO and SiO\( _2 \) may be reduced by carbon at temperatures above about 1400 to 1600\(^\circ\)C, all assuming 1 atm total pressure.

- If the reaction takes place at the equilibrium temperature, the equilibrium gas mixture will be given by the corresponding value at the point of intersection between the two curves; e.g. for SnO\( _2 \) reduction at 610\(^\circ\)C, \( P_{CO_2}/P_{CO} \approx 10^{0.5} \approx 3 \), and for MnO reduction at 1500\(^\circ\)C, \( P_{CO_2}/P_{CO} = 10^{-4} \).

- If the reaction occurs above the equilibrium temperature, the resulting gas mixture is the intermediate between the values for the two reactions but closest to the value for the reaction has the highest reaction rate. Therefore it is not strictly correct to assume that the reduction of metal oxide with carbon is given by the equation \([\text{MeO} + \text{C} = \text{Me} + \text{CO}] \), as is often done. This would
be the case only for the reduction of the most stable oxides where the concentration of CO$_2$ in the resulting gas mixture is extremely low.

- Notice that the curves for NiO and for oxides of the more noble metals do not intersect the carbon curve. In these cases the temperature of reduction and the composition of the reaction gas mixture is determined entirely by reaction kinetics. In fact, temperatures as high as (or even above) that of red hot carbon may be required.

- The enthalpy ($\Delta H$) for the different reactions may be deduced from the slope of the curves given by $\left[ \frac{\Delta H}{2.303 R} \right]$.

- The reduction of the oxides of the relatively noble metals (such as NiO, PbO, Cu$_2$O, Fe$_2$O$_3$, and FeO) with CO is exothermic i.e. negative $\Delta H$; while the reduction of the less noble metal oxides (such as SnO$_2$, Fe$_3$O$_4$, Cr$_2$O$_3$, MnO, and SiO$_2$) is endothermic, i.e. positive $\Delta H$.

- The reaction between C and CO$_2$ is strongly endothermic. Therefore the reduction of practically all metal oxides with carbon is endothermic, and the enthalpy of reduction increases with increasing stability of the oxide.

- It follows therefore that reduction of stable oxides with Crequires not only a high temperature but also large amounts of heat at that temperature; translating to high fuel or energy requirements.

**c) Reduction of Iron Oxides by CO and C**

Figure 3b shows in greater detail the $P_{CO}/P_{CO_2}$ ratio for reduction of the various iron oxides, as well as the Boudouard reaction for $P_{CO} + P_{CO_2} = 1$ atm. It follows that the wustite phase, Fe$_x$O or FeO, is unstable below about 570ºC and below this temperature magnetite, Fe$_3$O$_4$, reduces directly to metallic iron. It also means that for a gas mixture with $P_{CO} + P_{CO_2} = 1$ atm the area to the right of the Boudouard line represents an unstable condition, the gas having a tendency to precipitate soot until the Boudouard line is reached. The sooting reaction (graphite formation) is rather slow, however, and in practice gas mixtures with a high CO content may be preserved down to room temperature. Also, the equilibrium between Fe$_3$O$_4$, Fe, and the CO–CO$_2$ gas mixture may be established in this region, even though the gas as such is unstable. In the presence of a CO–CO$_2$ gas mixture the iron phase will pick up some carbon as is the case for $\gamma$-modification of iron resulting to the solid solution austenite which can dissolve up to almost 2 percent carbon. In the austenite phase the chemical activity of carbon increases from zero for pure iron to unity for saturation with graphite. Thus between the gas and austenite the equilibrium $CO_2 + C_{(dissolved in iron)} = 2CO$ will be established with the equilibrium constant $K = P_{CO}^2 / P_{CO_2} \cdot a_C$. For any given temperature and gas composition there will be a certain carbon activity, i.e., a certain carbon content in the austenite. As shown in Figure 3b, the curves for constant carbon
contents intersect the Boudouard line at austenite compositions which are saturated, i.e., in equilibrium with graphite.

Since the sooting reaction is very slow, gas mixtures may be established which are supersaturated with respect to graphite, corresponding to a carbon activity greater than unity. In this range the gas may react with iron to form cementite, \( \text{Fe}_3\text{C} \). In addition, cementite may form by the reduction of wustite and magnetite at temperatures below 700ºC according to the reactions

\[
3\text{FeO} + 5\text{CO} = \text{Fe}_3\text{C} + 4\text{CO}_2
\]

and

\[
\text{Fe}_3\text{C} + 5\text{CO}_2
\]

The gas ratios for these reactions which are metastable equilibria, are also shown in Figure 3b.

Finally, at high temperature and in the presence of carbon, iron will form a eutectic mixture between austenite and graphite. This mixture, with about 4.2 percent C, is responsible for the fact that in the iron blast furnace low-melting pig iron (melting point, 1150ºC) rather than pure iron (melting point, 1538ºC) is formed.

d) **Reduction by \( \text{H}_2 \)**

Hydrogen is of less industrial importance in the reduction of oxides than C and CO, but may be used under certain conditions. The generalized reduction reaction for metal oxide with hydrogen is

\[
\text{MeO} + \text{H}_2 = \text{Me} + \text{H}_2\text{O}_{(g)}
\]

with hydrogen is

\[
K = \frac{a_{\text{Me}} P_{\text{H}_2\text{O}}}{a_{\text{MeO}} P_{\text{H}_2}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}
\]

provided the activities of Me and MeO are both unity. From \( \Delta G^\circ = -RT \ln K = -2.303RT \log K \) and \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \), we have that:

\[
\log K = \log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} = \frac{\Delta H^\circ - T\Delta S^\circ}{-2.303RT} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R}
\]

Straight line graphs of the equation

\[
\log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} = -\left(\frac{\Delta H^\circ}{2.303R}\right) \frac{1}{T} + \frac{\Delta S^\circ}{2.303R}
\]

have been plotted for the reduction of important metal oxides as shown in Figure 4. The curves are similar to the ones for reduction with CO. Since the reaction \( \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}_{(g)} \) is less exothermic than the reaction \( \text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2 \), the reduction of MeO to Me with \( \text{H}_2 \) is less exothermic than the corresponding reaction with CO. This is noticeable in the slope of the curves, and \( \text{H}_2 \) at high temperature is a better reducing agent than CO, but is a poorer one at lower temperature.

Very often the reduction is carried out with mixtures of CO and \( \text{H}_2 \). In such situations the reaction will occur so that the water–gas equilibrium \([\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2]\) is satisfied. This reaction shifts to the right at low temperatures confirming again that CO is a better reducing agent than \( \text{H}_2 \) at lower temperatures.

Natural gas which consists essentially of methane (CH\(_4\)) is a reducing agent of considerable importance. Above 500ºC methane is unstable and decomposes into carbon and hydrogen. The hydrogen and carbon will reduce the metal oxide each according to its own equilibrium constant. Therefore, when natural gas is used as a reducing agent, e.g., in the production of sponge iron, it is first subjected to a partial oxidation (reforming) to give CO and \( \text{H}_2 \).
Figure 4: / Rosenquist diagrams showing equilibrium gas ratio, as function of inverse temperature for the reduction of various oxides.

IRON AND STEEL MAKING ROUTES

Steel is manufactured by the chemical reduction of iron ore in steel plants, which may be classified into two broad categories:

- **Integrated Steel Plants** (ISPs) following the BF–BOF [Blast Furnace – Basic Oxygen Furnace] route of iron and steel making, or
- **Mini Steel Plants** (MSPs) via the DRI–EAF [Direct Reduced Iron – Electric Arc Furnace] route.

In the conventional integrated steel manufacturing process, the *pig iron* or *hot metal* from the blast furnace (BF) is converted to steel in a basic oxygen furnace (BOF). ISPs are relatively large in size with individual module capacities ranging from 1 to 5 Mt (metric tonne = 1,000kg) of steel per year. The *Ajaokuta Steel Complex* of Nigeria was planned to use the BF–BOF route to make iron and steel. Steel can also be made in an electric arc furnace (EAF) from scrap steel, and, in some cases, from *direct reduced iron* (DRI) or *spongy iron*. This is the DRI–EAF route. MSPs are smaller in size with module capacities generally between 0.5 Mt and 1.0 Mt per year, and in some
cases up to 2 Mt per year. The **Delta Steel Complex, Aladja** was envisaged for this route of iron and steel making.

BOF is typically used for high-tonnage production of plain carbon steels, while the EAF is used to produce low-tonnage plain carbon steels as well as specialty (or alloy) steels. Plain carbon steels account for 90% of the world’s steel production while alloy steels account for the remaining 10%. An emerging technology, direct steel manufacturing, produces steel directly from iron ore.

In the BOF process, coke making and iron making precede steelmaking; these steps are not necessary with an EAF. Pig iron is manufactured from sintered, pelletized, or lump iron ores using coke and limestone in a blast furnace. It is then fed to a BOF in molten form along with scrap metal, fluxes, ferro-alloys, and high-purity oxygen to manufacture steel. In some integrated steel mills, sintering (heating to bond or fuse particles together without melting) is used to agglomerate fines and so recycle ironrich materials such as mill scale. **Mill scale** is the flaky surface found on hot rolled steel plates, sheets or profiles when they are being produced by rolling red hot iron or steel billets in rolling mills. It is a product corrosion/oxidation and is composed of iron oxides such as FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$.

Iron and steel making, like most metallurgical processes, are **integrated processes**. An integrated process may be defined as a coordinated sequence of unit operations and unit processes which is in some respects self-complete. It may be self-complete in that it represents all the actions in a plant, or in a section of the plant in which a particular job is done, from start to finish. It is sequential and coordinated in that materials flow from one step to the next in an orderly fashion; the product of one step serving as the feedstock for the next, and the whole sequence of activities can be represented conveniently by **flow sheets**. Integrated processes are usually carried out in integrated plants.

**THE IRON BLAST FURNACE**

The iron blast furnace is a very tall vertical **shaft furnace**, which makes use of carbon mainly in the form of coke to reduce iron from its oxide ores usually haematite (Fe$_2$O$_3$) or magnetite (Fe$_3$O$_4$). It is so named because its working involves the introduction of an air blast. The furnace (depicted in Figure 5) consists of a shaft that can be up to 60m high and 7.5m in diameter, made of steel shell lined with **refractory bricks**; and may produce from 2,000 to 10,000 tonnes of iron per day. Since a refractory lining lasts for several years, it is only at the end of this period that the blast furnace is shut down; otherwise it works a 365-day year.

The blast furnace is called a **shaft furnace** because it is tall and vertical and its raw materials are introduced from the top, and they react as they fall through the height. The furnace is charged with ore, coke, and fluxes. The ore (Fe$_2$O$_3$ or Fe$_3$O$_4$) is reduced, first to **wustite** (FeO) and then to Fe. **The actual reduction sequence is**

\[
Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe
\]

The lowest oxide of iron, **wustite**, is not a natural
mineral but is formed in the blast furnace (and found in some slags), and is stable only above 570°C. Its formula is given as Fe$_x$O where $x \approx 0,947$ on average and can range from 0.86 to 1.0. In other words, wustite is an oxygen-deficient non-stoichiometric compound of iron and oxygen. For practical purposes however, wustite formula is approximated to FeO.

The purpose of the fluxes is to make a slag of suitable composition, and they are usually lime (CaO) or limestone (CaCO$_3$), sometimes with dolomite (CaCO$_3$·MgCO$_3$) added. In the bottom of the furnace hot air blast is introduced through the tuyeres (from the French word tuyau which means pipe). The furnace gases are taken out from the top of the furnace, and molten pig iron (hot metal) and molten slag are withdrawn from the hearth in the bottom of the furnace. Thus, the blast furnace operates by the countercurrent principle, i.e. hot gases rise up in counter-motion to the falling burden (ore and fluxes) and coke. The inverted cone between the stack and the hearth is called bosh.

![Iron blast furnace, showing chemical reactions](image)

Figure 5: Iron blast furnace, showing chemical reactions

The principal objective of this furnace is to produce molten pig iron (hot metal) of uniform composition at a very high rate. The name pig iron has a history. In early days, the iron from the BF is not taken to the steelmaking stage in hot or molten form, but is cast and allowed to solidify into iron pigs according to the following story:

*The slag is drained continually into slag pits, but the iron is only cast every few hours into a ditch or trench called a trough, which leads to small runners called sows, which have numerous cavities, attached called pigs.*
This whole process takes place in the casthouse, which contains areas for iron casting and slag casting. The side for iron removal consisted of a large ditch called a trough that sloped from the front of the furnace to the casthouse floor. It then split into two runner systems. A main runner on each system ran parallel with the length of the casthouse. As this runner sloped downhill, a series of dams were made at regular intervals. At a right angle before each dam, a smaller runner called a sow was produced. Then off this sow were numerous cavities called pigs. This system looked like a series of piglets suckling their mother.

Hence, the iron that came out of the blast furnace was called pig iron [hot metal is the preferred term today, especially if in molten form] because the iron ran out into a trench dug in the ground and then into several large, shallow depressions that stuck out at right angles to the trench. Some one thought that the arrangement looked like a sow (adult female pig) suckling her pigs: hence, pig iron. These iron pigs weigh between 70 and 100 pounds (≈ 32 to 45 kg).

The liquid pig iron contains approximately 4–5% C, 0.3–0.7% Si, 0.01–0.04% S, 0.1% P and 0.1% Mn; which is suitable for subsequent refining of steel. The main critical operating parameter is the temperature of the iron and slag which must be greater than 1427°C (1700K) in order for these products to be tapped from the furnace in the molten state. Metal composition, though not that important because of its subsequent processing to steel, is however adjusted to steelmaking plant specifications by appropriate adjustments of slag composition and furnace temperature. A schematic view of a typical blast-furnace plant (furnace and accessories) is presented in Figure 6.
Figure 6: Schematic cross-section of the iron blast furnace and its auxiliary equipment; materials-handling, charging, tapping, gas-handling and hot-blast equipment.

RAW MATERIALS FOR BLAST FURNACE PROCESSES

The raw materials used in modern blast furnaces include:

1) Solids: Ore, metallurgical coke and flux which are charged into the top of the furnace;

2) Air: Which is blasted through the tuyeres near the bottom of the furnace. Oxygen gas is also introduced through the tuyeres to enrich the air.

3) Hydrocarbon additives: Which may be gas, liquid or solid are also introduced through the tuyeres (as innovation).

A description of the various raw materials is as follows:

a. **Iron Oxides (Ore):** Usually haematite (Fe₂O₃), occasionally magnetite (Fe₃O₄), which are added as:
   i. 1–2 cm diameter pellets produced from finely ground beneficiated ore [5–10% SiO₂, 4%Al₂O₃, remainder being Fe₂O₃],
   ii. 1–3 cm chunks (small lumps) of sinter produced from ore fines,
   iii. 1–5 cm direct shipping ore.

NB: The charge of a particular blast furnace may contain one, two or all three of these iron oxide forms. Again, iron oxides from steelmaking slag and *mill scale* can also be used as they also provide iron units.
b. **Metallurgical Coke**: This contains 90% C, 10% ash (mainly SiO$_2$ and Al$_2$O$_3$), 0.5–1.0% S (dry basis) and 5–10% H$_2$O. Metallurgical coke which supplies most of the reducing gas (CO) and heat for ore reduction and smelting is produced by heating mixtures of powdered coking coal (25–30 wt.% volatile content) in the absence of air. This process causes the volatiles to be distilled from the coal in order to give a porous coke, which is (i) reactive at high temperatures, and (ii) strong enough to avoid being crushed near the bottom of the blast furnace. The compressive strength and porosity of the metallurgical coke permit uniform gas flow through the burden as it softens and melts in the lower regions of the furnace. Blast furnace coke is a key material for BF ironmaking, acting as a major energy source (fuel), a reductant, a carburizing agent (for iron and steel), and a gas permeable structural support. Coke is charged to the furnace as 2–8 cm pieces.

c. **Fluxes (CaO, MgO)**: These oxides flux the silica (SiO$_2$) and alumina (Al$_2$O$_3$) impurities of ore and coke to produce a low melting point (1327°C or 1600K) fluid slag. CaO also causes part of the sulphur in the furnace charge introduced mainly as an impurity in the coke, to be removed in the slag rather than in the product – pig iron (hot metal). The fluxes, CaO and MgO, are charged as pre-flux i.e. as 2–5 cm pieces of limestone (CaCO$_3$) and dolomite (CaCO$_3$·MgCO$_3$).

d. **Hot Air-Blast**: This is usually supplied as a preheated material between 1200 and 1600K (927 - 1327°C) and in some cases enriched with oxygen to give blast containing up to 25 wt.% O$_2$. This hot blast air burns incandescent coke [white hot coke, \( \cong 1800K \)] in front of the tuyeres to provide heat which is used for:

   i. reduction of reactants, ii. heating and melting of the charge and products, and iii. keep the slag and pig iron above their melting points and thus facilitate easy removal or tapping of the product.

e. **Gas, Liquid or Solid Hydrocarbon**: These provide additional reducing gas (CO and H$_2$) for the reduction process. Fuel oil and tar are the most common additives. Natural gas and pulverized coal are also used.

**PRODUCTS FROM THE BLAST FURNACE PROCESSES**

The main product of the blast furnace, *molten pig iron or hot metal* is tapped from the furnace at regular intervals (or continuously in the case of very large furnace) through one of several holes near the bottom of the hearth. A representative analysis of molten pig iron is given in Table 3 below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt.%)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4 – 5</td>
<td>Saturated</td>
</tr>
</tbody>
</table>
Si  0.3 – 1.0
S  0.01 – 0.04
P  Up to 0.1  Depending on the ore
Mn 0.1 – 0.5  Depending on the ore
Fe  About 90  Remainder

Composition of the pig iron from a particular blast furnace is chosen to meet the requirements of the steelmaking plant to which the iron is being sent. The composition of the pig iron can be adjusted by controlling:

i. Slag composition,

ii. Furnace temperature (particularly at the lower half of the furnace).

The pig iron is transported in the molten state to the steelmaking plant where the impurity elements are reduced to lower levels by oxygen refining. In some cases, the molten pig iron is desulfurized by treatment with calcium carbide (CaC₂) or magnesium coke (MgC₂) prior to oxygen refining.

The blast furnace forms two by-products, namely: slag and flue gas or blast furnace gas or top gas.

a) Slag: Slag is a complex product formed by the chemical combination of fluxes with silicates, aluminates and other gangue constituents in iron oxide and coke ash. A typical composition and analysis of blast furnace slag is: 30–40wt.% SiO₂, 5–15wt.% Al₂O₃, 35–45wt.% CaO, 5–15wt.% MgO, 0–1wt.% (Na₂O + K₂O), and 1–2.5wt.% S. The slag contains very little iron oxide, which is indicative of the excellent reducing efficiency of the furnace. The composition of the slag is chosen to:

i. Remove SiO₂ and Al₂O₃ in a fluid slag;

ii. Absorb Na₂O and K₂O (alkalis) which otherwise tend to build up in the furnace.

Na₂O and K₂O enter through coke and ore as ash along with SiO₂ and Al₂O₃. They are partially reduced to Na and K vapour near the bottom of the furnace and this vapour subsequently rises to the cooler parts of the furnace where a portion re-oxidizes to become entrapped in solid form in the descending burden. The process becomes cyclic and it leads to the accumulation of sodium and potassium compounds in the furnace. Physical symptoms of this build up are a restriction of gas flow through the burden and an erratic descent of charge. Partial reduction of SiO₂ to SiO vapour is thought to also cause similar problems.

iii. Absorb sulphur rather than have it dissolve in the iron product, and

iv. Control the silicon content of the hot metal
A *slag basicity ratio* between 1.1 and 1.2 appears to best meet the above four slagging requirements. That is, 

$$\text{Slag Basicity} = \frac{\text{wt.% CaO} + \text{wt.% MgO}}{\text{wt.% SiO}_2 + \text{wt.% Al}_2\text{O}_3} = 1.1 \leq 1.2$$

is considered satisfactory.

Recall that *basicity* is the ratio of basic oxides to acidic (or amphoteric/neutral) oxides. Slags usually are solutions of various metallic silicates; some may consist of borates, phosphates, aluminates, and similar compounds. However, because silica and the silicates are such common minerals, usually silica constitutes the acid radical in slags. Solidified iron blast furnace slag may be used for the manufacture of Portland cement, concrete aggregate, tiles, road construction aggregates, and in the manufacture of fertilizer if rich in phosphates.

**b) Top Gas:** These gases leave the furnace through the upper chamber i.e. the gas collection system at the top of the blast furnace. A typical modern blast furnace top gas composition is roughly 23 wt.% CO, 22 wt.% CO$_2$, 3 wt.% H$_2$, 3 wt.% H$_2$O and 49 wt.% N$_2$. This is equivalent to net combustion energy of about 4000 kJ/m$^3$ (about $\frac{1}{10}$ that of natural gas). The ratio of $\frac{\text{CO}}{\text{CO}_2}$ is an important indicator of the operation of the blast furnace. After removal of *flue dust*, the top gas is burnt in *auxiliary stoves* to preheat the air blast for the furnace; thus adding *sensible heat* to improve the efficiency of combustion. The top gas can also be utilized as a fuel in the downstream and upstream facilities of any steel plant, sometimes with the addition of the richer *coke oven gas*. The blast furnace top gas and coke oven gas can also be used to raise steam for in-plant power generation. The *flue dust* (which is ore fines) is *agglomerated* by sintering or *briquetting* and recharged to the furnace or stockpiled for future use.

Figure 7 is a modern blast furnace showing direction of movement of inputs (ore, coke, flux, air blast) and outputs (hot metal, slag, flue dust, and furnace gas). Table 4 and Figure 8 show representative *materials balance* for a blast furnace.
Figure 7: A modern blast furnace showing direction of movement of input and output materials

Table 4: Representative materials balance for a blast furnace producing 2000 tonnes of pig iron per day

<table>
<thead>
<tr>
<th>CHARGE</th>
<th>AMOUNT(tonnes)</th>
<th>PRODUCTS</th>
<th>AMOUNT(tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore, say 50% Fe</td>
<td>4000</td>
<td>Pig Iron (Hot Metal)</td>
<td>2000</td>
</tr>
<tr>
<td>Limestone</td>
<td>800</td>
<td>Slag</td>
<td>1600</td>
</tr>
<tr>
<td>Coke</td>
<td>1800 8</td>
<td>Flue Dust</td>
<td>200</td>
</tr>
<tr>
<td>Air</td>
<td>000</td>
<td>Furnace Gas</td>
<td>10800</td>
</tr>
</tbody>
</table>
The materials balance or *metallurgical balance* of a system/plant when unsteady state conditions apply is:

\[
\text{Input} = \text{Output} + \text{Accumulation}
\]

For a steady state system, the equation simplifies to:

\[
\text{Input} = \text{Output}
\]

When complete and accurate stoichiometric data are available for a process, a table is easily drawn up to show the balance of materials and the balance for each important element. Such a table can be regarded as the metallurgical equivalent of the accountant’s balance sheet. A typical *metallurgical balance sheet* for an iron blast furnace is given in Table 5. The primary data are the weights (masses) and analyses (% compositions) of the materials entering and leaving the process – the other columns are calculated. Obviously, the metallurgical balance contains the most essential items of information for judging and controlling metallurgical performance, just as the balance sheet of a business is essential in determining profit or loss and in controlling the business.

Several factors operate to prevent exact balances between input and output. Accumulation or depletion of materials in process may account for large differences between input and output over a short term. Periodic inventories and clean ups,
however, furnish a direct check on accumulation and depletion. Spillages and unaccountable losses also show up when the materials balance is calculated. Often, however, consistent differences between input and output are the result of errors in the primary stoichiometric data, and it can become a serious and embarrassing problem to determine whether failure to balance is due to unexplained losses, accumulations in equipment, weighing errors, or analytical errors.

BLAST FURNACE OPERATION

The operations involved in blast furnace processes are: charging of solids through the top (via the two-bell system or modern bell-less top using a rotating distributing chute); continuous injection of hot blast with some hydrocarbons through the tuyeres; continued or periodic tapping of liquid products (hot metal and slag) from the bottom; and continuous removal of gas and dust. *NB: Iron blast furnaces are charged with alternate layers of coke and ore plus flux. The layers are normally 0.5–1 m thick, with larger diameter furnaces tending to have the thicker layers.*

Most of the operating procedures (e.g. charging, blowing, and fuel injection) are carried out mechanically under automatic control, and modern blast furnaces are extensively equipped with continuous monitoring devices. Typical continuously monitored process variables are:

- **Temperature**: of hot blast, cooling water, shaft wall, top gas;
- **Pressure**: of blast, furnace interior at several levels and top;
- **Flow rates**: of blast through each tuyere, tuyere injectants through each tuyere, and cooling water.

In addition, iron and slag temperature and composition are determined intermittently during tapping. Burdening of the furnace (e.g. ore and flux quantities being charged) and conditions at the tuyeres (blast temperature, oxygen level, tuyere injectant quantity) are decided, often by computer, based on these measurements. The only major manual manoeuvre is tapping of iron and slag.

The process never stops and a blast furnace campaign continues 5 to 8 years before refractory wear forces a shutdown. Minor perforations in the shaft can be patched without shutting down the furnace. The furnace can be ‘banked’ with an all-coke charge to keep it hot during temporary production stoppages.

The rate of pig-iron production in any given furnace is determined by the rate at which oxygen, as air or air plus pure O₂, is blown into the furnace. High blast rates lead to:

i. Rapid combustion of coke in front of the tuyeres,
ii. A rapid rate of CO production and, as a consequence,
iii. A high rate of iron reduction

About 1.3 to 2.2 tonnes of blast air are required per tonne of pig iron produced.

However, there is a maximum rate at which air can be blown into the furnace. Excessive velocities (going above this rate) lead to:
i. The air and furnace gases ascending through open ‘channels’ in the solid charge (a phenomenon called *channelling*) rather than in an evenly distributed flow pattern and this causes the reducing gases to pass through the furnace incompletely reacted, therefore resulting to inefficient use of the carbon or coke in the charge.
Table 5: Metallurgical balance for an iron blast furnace {Adapted with metrication from Schuhmann, Jr. R. (1952)}

<table>
<thead>
<tr>
<th>Materials</th>
<th>Weight</th>
<th>Fe</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>P</th>
<th>Mn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg</td>
<td>kg</td>
<td>%</td>
<td>kg</td>
<td>%</td>
<td>kg</td>
<td>%</td>
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<td>%</td>
</tr>
<tr>
<td>Ore No. 1</td>
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<td>3609.2</td>
<td>49.8</td>
<td>420.5</td>
<td>5.8</td>
<td>217.4</td>
<td>3.0</td>
<td>14.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Ore No. 2</td>
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<td>350.9</td>
<td>46.8</td>
<td>61.2</td>
<td>8.2</td>
<td>17.2</td>
<td>2.3</td>
<td>1.4</td>
<td>0.2</td>
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<tr>
<td>Ore No. 3</td>
<td>3580.2</td>
<td>1682.7</td>
<td>47.0</td>
<td>379.7</td>
<td>10.6</td>
<td>82.3</td>
<td>2.3</td>
<td>7.3</td>
<td>0.2</td>
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<tr>
<td>Ore No. 4</td>
<td>465.4</td>
<td>248.1</td>
<td>53.3</td>
<td>15.0</td>
<td>3.2</td>
<td>11.0</td>
<td>2.3</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Cinder, mill scale, scrap</td>
<td>1564.8</td>
<td>958.4</td>
<td>61.25</td>
<td>7.9</td>
<td>123.6</td>
<td>20.3</td>
<td>1.3</td>
<td>23.5</td>
<td>1.5</td>
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<tr>
<td>Coke</td>
<td>7032.9</td>
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<td></td>
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<td></td>
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<tr>
<td>Limestone</td>
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<tr>
<td><strong>TOTALS</strong></td>
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<td>1467.4</td>
<td>618.8</td>
<td>1874.7</td>
<td>89.8</td>
<td>13.53</td>
<td>98.5</td>
<td>70.77</td>
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Products (Output)
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<th>Actual</th>
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<table>
<thead>
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<table>
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<td>98.5</td>
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<tr>
<td></td>
<td>70.77</td>
<td></td>
</tr>
</tbody>
</table>

*Present in pig iron as Si; *Present in slag as MnO
ii. Preventing newly melted iron and slag from descending evenly through the bosh (this phenomenon is called flooding) which may lead to an uneven descent of solid charge and to an erratic furnace operation.

Typical operational blast rates are 40–50 Nm$^3$/min$^1$ of blast per m$^2$ of hearth area. A blast furnace can operate down to about 70% of its normal capacity without any deleterious effects. Below this rate of production, the charge begins to react unevenly. [NB: Nm$^3$ means normal cubic metres of air or gas. 1 Nm$^3$ = 1 m$^3$ of gas at 273 K, 1 atmosphere].

**IMPROVEMENTS IN PRODUCTIVITY OF THE BLAST FURNACE**

The productivity [expressed in tonnes of hot metal per day (THM/day)] of the blast furnace has continually increased from the time of its inception until today when furnaces of 12000-tonnes-per-day capacity have been built. Much of this improvement has been due to larger furnaces of improved design (better charge distribution machinery, better cooling systems, and refractories that are more resistant) but changes in the physical and chemical characteristics of the input materials and altered conditions inside the furnace have also led to greatly improved performances. The following areas of improvement are worth noting.

1) **Use of evenly sized, well distributed, sinter and pellet burdens**: The most important factor in increasing the productivity of the blast furnace has been the switch from unsized ore to evenly sized, well distributed, sinter and pellet burdens. Uniform burdens permit furnace gases to rise rapidly through the charge without causing channeling and this, in turn, allows the furnaces to be operated at high blast rates (i.e. at high production rates). In fact, the productivities of older furnaces have been almost doubled by the use of sized sinter and pellets. An added benefit has been decreased losses of ore as dust or fines in the furnace gases.

2) **Injection of hydrocarbon liquids, gases or solids through the tuyeres**: This has also led to improved furnace productivities by lowering the requirement for coke in the solid charge. This leaves more space in the stack for ore and it leads to a greater reduction capacity. [Well, if the price of coke is high relative to the prices of fuel oil and natural gas per unit of reducing capability or enthalpy, the injection of these fuels through the tuyeres will automatically result in direct cost savings]. However, recent increases in the prices of natural gas and fuel oil have lowered this direct-cost advantage.

3) **Use of hotter blast**: Hand in hand with hydrocarbon injection has come the use of hotter blast. Hot-blast air offsets cooling due to the entry of cold hydrocarbons into the tuyere zone of the furnace and also adds enthalpy to the system. Blast temperatures in modern installations are typically 1300 to 1600 K (1027 to 1327°C).

4) **Control of blast humidity**: Air constitutes almost a half of the materials entering the blast furnace. Consequently, relatively small changes in humidity are important with regard to the amount of water carried into the furnace. The endothermic
decomposition of the water vapour in the hot zone adjacent to the tuyeres absorbs considerable heat. This extra heat absorbed in the hearth of the furnace increases the amount of fuel required in the form of coke. Some fuel (and hence, cost) savings can be realized by drying the blast air either by a regenerative heat exchange cycle or by passing the air through suitable drying columns. The use of hotter blast [as in (3) above] can actually take care of humidity problem.

5) **Enrichment of the air blast with pure oxygen:** The oxygen replaces a portion of the air requirement and hence ensures the lowering of the quantity of nitrogen passing through the furnace. This partial elimination of nitrogen (a diluent in combustion) has the following advantages:

a) It increases the flame temperature in front of the tuyeres thus permitting increased injection of cold hydrocarbons;

b) It permits an increased rate of CO production (CO is the reducing gas) and consequently an increased rate of ore reduction without increasing the total rate of gas flow (channeling and flooding) through the furnace. In effect, the production rate of the furnace can be raised without causing channeling and flooding.

6) **Pressurization of the blast furnace up to 3 atmospheres gauge at the furnace top:** High-pressure operation permits an increased mass-flow rate of gas through the blast-furnace charge without an increase in gas velocity. This in turn permits a greater throughput of reducing gas without a decrease in gas/solid reaction time, leading to an increased rate of iron production. Many furnaces are now operated in this way. High furnace pressure is obtained by throttling the gas exit from the furnace. The furnace structure must be strengthened for this type of operation.

**BLAST FURNACE COSTS**

So far, we have seen that the blast furnace is a large installation with a very high production rate of molten pig iron. A single blast furnace (i.e. 5000 tonnes of iron per day) costs in the order of $100 \times 10^6$ U.S. dollars including blowers, hot-blast stoves, materials-handling equipment, dust collection and effluent control. [This is 1977 figures by Berczynski, as quoted by Peacey and Davenport (1979)]. This high capital cost per unit is the biggest disadvantage of the process. In fact, the blast furnace is economical only at large-scale (high iron tonnage) production.

The iron blast furnace is an efficient device for producing large quantities of molten iron, ready for refining to steel. Its principal advantages are its exceptional stability of operation and its high rate of iron production. Its only disadvantage is its large unit size and its consequently high initial capital cost. **The high capital cost of building and installing a blast furnace and the stringent demand for high-grade ore and metallurgical coke (which is even more costly than the ore), has led to search for alternative iron making technologies, e.g. Direct Reduced Iron (DRI) and Smelting Reduction (SR) technologies.**
ASSIGNMENT PROBLEMS A

1. A common material from which iron is produced is beneficiated and pelletized haematite ore. Calculate the quantity of haematite ore pellets (6% SiO₂) required to produce 1 tonne of pig iron (5% C, 1% Si, 1% Mn).

2. In modern blast furnaces, the carbon supply rate (from coke and tuyere injected hydrocarbons) is in the order of 420 kg per tonne of pig iron (5% C, 1% Si, 1% Mn). Express this carbon supply rate in terms of (i) kg of carbon per tonne of product Fe, (ii) kg moles of C per kg mole of product Fe.

3. A blast furnace operator wishes to increase his hearth temperature by enriching the blast to 25 vol.% oxygen. What weight and volume (Nm³) of pure oxygen must he inject per 1000 Nm³ of dry air blast.

4. Iron ore, limestone, and coke of the analyses given below are to be charged to an iron blast furnace:

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>H₂O</th>
<th>Mn</th>
<th>P</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>50.0</td>
<td>8.0</td>
<td>3.0</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone</td>
<td>4</td>
<td>50</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>86</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The furnace is operated to produce a pig iron analyzing 94% Fe, 4% C, and 1% Si, and a slag in which %CaO + %MgO = %SiO₂ + % Al₂O₃. Previous experience indicates that the coke consumption will be 900 kg per tonne of pig iron produced and that the quantity of air in the blast will be 80% of that theoretically required to burn the C in the coke to CO. Calculate the following:

a) the weights of ore and limestone to be charged per tonne of coke,
b) the volume of dry air to be supplied in m³/min. at STP [i.e. in Nm³/min] for a furnace producing 1000 tonnes of pig iron per 24 hours,
c) the composition of the blast furnace gas and the volume produced per day in a 1000-tonne furnace.

CHEMICAL REACTIONS IN THE BLAST FURNACE

The chemical reactions, which take place in the furnace, are as shown in Figures 5 and 9. The temperatures of the various zones of the furnace are also shown in Figure 9.

i. Coke in the region of the tuyeres burn completely:

\[ \text{C + O}_2 = \text{CO}_2 \]; [Exothermic]

Just above the tuyeres (the bosh region) the CO₂ is reduced by the white hot coke to CO:
On balance the overall reaction is strongly exothermic, so that the temperature remains high. Thus, at the tuyere level, air reacts with coke to give the overall reaction:

\[ \text{CO}_2 + \text{C} = 2\text{CO} ; \quad [\text{Endothermic}] \]

and this represents the main source of heat and reducing gas for the blast furnace. Figure 10 confirms that in the region of the tuyeres, there is early combustion of coke to \( \text{CO}_2 \) and subsequent reaction of \( \text{CO}_2 \) with coke to form \( \text{CO} \).
Figure 9: Schematic illustration of the iron blast furnace and its chemical equations. Notice the slow increase in temperature from 900 to 1000°C. The dotted line at the 900°C level represents the border between the indirect and direct reduction zones.

![Graph showing gas composition vs. distance from entry into furnace, with peaks for N₂, O₂, CO, and CO₂]

Figure 10: Composition of the gas directly in front of an experimental BF tuyere

ii. As the CO, which is a powerful reducing agent, rises through the charge, the ore in the upper part of the stack is reduced through the stages:

Thus, the overall reaction is:

\[
3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2
\]

\[
\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2
\]

\[
\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2
\]

or \( \text{Fe}_x\text{O} + \text{CO} = x\text{Fe} + \text{CO}_2 \)

\[
\text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2.
\]

These reactions begin when the temperature has reached a few hundred degrees Celsius, but the main reactions occur in the range 700 to 1200°C. In modern blast furnaces, the reduction of \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) to \( \text{FeO} \) is completed before the reduction to metallic iron (Fe) starts. This gives the most efficient utilization of the CO content in the gas, and is achieved by the use of highly reactive ores of small lump size, for example, pellets. For coarser and less reactive ores the reactions are apt to overlap.

The last reduction of wustite to iron occurs only after the ore has reached the lower part of the stack where the temperature has increased to above 1000°C. In this region the reaction on the coke surface is sufficiently rapid to make the wustite reduction \( \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \) and the Boudouard reaction or coke gasification
\[ \text{C} + \text{CO}_2 = 2\text{CO} \] take place simultaneously. Thus, \( \text{CO}_2 \) formed by the reduction of \( \text{FeO} \) may react with carbon to give the overall reaction:

\[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} \]

The above reaction is sometimes called \textit{direct reduction} (i.e. coke or solid carbon directly reducing iron oxide to Fe) even though it actually occurs through the gas phase. The reaction between coke and \( \text{CO}_2 \) in this case is sometimes called \textit{solution loss}, meaning that some carbon reacts (dissolves) before it reaches the tuyeres. In comparison, the reaction between CO and iron ore in the upper part of the stack, where the temperature is too low for the coke to react, is called \textit{indirect reduction}.

The reduction sequence \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \) takes place in the upper part of the furnace where the temperature is too low for the iron so formed to melt. It therefore remains as a spongy mass until it moves down into the lower part of the furnace where it melts and runs down over the white-hot coke dissolving carbon, sulphur, manganese, phosphorus, and silicon as it goes. Apart from carbon, which is absorbed from the coke; these other elements (S, Mn, P, Si) are dissolved following their reduction from compounds present as impurities in the original ore. Thus, in the lower part of the furnace – where the products are mainly molten –, the following reactions occur to some extent:

\[
\begin{align*}
\text{MnO} + \text{C} &= \underline{\text{Mn}} + \text{CO} \\
\text{SiO}_2 + 2\text{C} &= \underline{\text{Si}} + 2\text{CO} \\
\end{align*}
\]

*The underlining indicates that the element so underlined is in solution in Fe i.e. hot metal.* These reactions may also be called direct reductions since coke or C is directly acting as the reducing agent and CO is produced.

**iii.** At the same time as this reduction is taking place, the earthy waste or gangue associated with the ore combines with lime (formed by the decomposition of limestone added with the charge) to produce a fluid slag, thus:

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 \ ; \ \text{Decomposition}
\]

\[
2\text{CaO} + \text{SiO}_2 = 2\text{CaO}\cdot\text{SiO}_2 \ ; \ \text{Calcium silicate slag}
\]

The function of the lime (CaO) here is to liquify the gangue, which is composed of largely silica that would not melt at the blast furnace temperature unless attacked chemically to form a low melting point slag, which will run from the furnace. The slag produced is of low value and is used mainly for filling purposes, e.g. railway ballast, road making, concrete aggregate and for the manufacture of slag wool (thermal and acoustic insulation material). It should not be confused with the basic slag used in agriculture (fertilizer production) which is a by-product of steelmaking process. CaO can also desulphurize the hot metal by taking some sulphur (as CaS) to the slag:

\[
\text{S} + \text{CaO} + \text{C} = \underline{\text{CaS}} + \text{CO}
\]

The furnace is tapped at regular intervals, the iron generally being stored in the molten state in a mixer prior to transfer to the steelmaking plant. Some may be cast as pigs for subsequent re-melting, e.g. in foundries.
The blast furnace top gas contains considerable amounts of CO which remain unused during reduction of the ore. Since the gas has useful calorific value, the blast furnace performs a secondary role as a giant gas producer and all of this gas is utilized as fuel. After being cleaned of dust much of it is burned in the Cowper stoves which, in turn, preheat the ingoing air blast. Two such regenerator stoves are required for each blast furnace. While one is being re-heated by the burning blast furnace gas, the other is pre-heating the ingoing air; and they reverse roles in the next phase. The surplus gas is utilized in many ways in integrated steelmaking plants, e.g. for generating electric power or for firing different types of reheating furnaces used around the plant.

**HEAT AND MASS TRANSFER IN THE STACK**

The unique feature of the blast furnace is that in the countercurrent flow of gas and solids, the heat transfer from gas to solids is accompanied by oxygen transfer from solids to gas. Reichardt diagram (Figure 11) shows that as a result of heat transfer, the enthalpy of gas decreases with decreasing temperature of the ascending gas, as represented by the line ERA in Figure 11a. The line SR represents the increase in the enthalpy of the solids with increasing temperature during descent in the stack. In the lower part of the furnace, the overall heat capacity of the burden increases because of fusion, the onset of the strongly endothermic Boudouard reaction \[ \text{CO}_2 + \text{C} = 2\text{CO} \], and greater heat losses; hence the slope of line RC is greater than that of SR.

The net result is that, as shown in Figure 11b, over some distance in the stack, the temperature difference between the ascending gas and the descending burden reaches a minimum known as the thermal pinch point or thermal reserve zone where the temperature of the rising gases remains relatively constant.

**GAS–SOLID REACTIONS**

The oxygen in the air blast is entirely consumed by reaction with the coke charge within the small radius of the tuyere:

\[ \text{C} \ [s] + \text{O}_2 \ [g] = \text{CO}_2 \ [g]; \Delta G_1^0 = -394 \, 000 - 0.8T \, \text{J/mol}. \quad \text{[1]} \]

The standard free energy for this reaction as shown, is \( \Delta G_1^0 = -394 \, 000 - 0.8T \, \text{J/mol} \). where pure graphite is the standard state for carbon. \[ \text{[Recall that standard state free energy} = 0; \text{standard state activity} = 1] \]. Outside this zone (the tuyere), there is no free oxygen available, so the CO\(_2\) reacts with more coke to form CO:
Figure 11: Illustration of Reichardt diagram: (a) Enthalpy of the gas and solid as a function of temperature; (b) Temperature of the gas and solid along the furnace height

\[
\text{CO}_2[g] + \text{C} [s] = 2\text{CO}_2[g]; \Delta G^o_2 = +170000 - 174T \text{ J/mol}. \quad [2]
\]
Thereafter, the oxygen potential is controlled by the carbon–oxygen equilibria and by the temperature. These equilibria are represented by:

- Reaction [1]: i.e. $\text{C}_{[s]} + \text{O}_2{[g]} = \text{CO}_2{[g]}; \Delta G_1^o = -394\,000 - 0.8T\,\text{J/mol}$, and
- The sum of reactions [1] and [2];

$$2\text{C}_{[s]} + \text{O}_2{[g]} = 2\text{CO}_2{[g]}; \Delta G_{1+2}^o = -224\,000 - 174.8T\,\text{J/mol.} \quad ...[1+2]$$

That is, the two reactions as well as their free energies are added (Hess’ law).

By **oxygen potential**, we mean the chemical potential of oxygen, i.e.

$$\mu_i = \bar{G}_i = RT\ln a_i \quad \text{at constant } T \text{ and } P$$

where $\mu_i$ is chemical potential of component i in solution; $\bar{G}_i$ is partial molar free energy of component i in the solution (i.e. per mole of i); $T$ is temperature in kelvin ($T = t + 273$), $R$ is universal gas constant ($=8.314 \text{ J·mol}^{-1}·\text{K}^{-1}$); and $a_i$ is activity of component i (element or compound) in a solution at temperature T; noting that $a_i = p_i$, where $p_i$ is the partial pressure of component i (in atmospheres) in an ideal gas mixture. Now, ironmaking is principally a process of reduction of iron oxides in ores. On the other hand, steelmaking principally involves oxidation of impurity elements such as C, Si, Mn, present in liquid iron. For a mole of oxygen gas ($O_2$), such oxidation reactions can be represented with the generalized stoichiometric equation:

$$\frac{2x}{y} M + O_2{[g]} = \frac{2}{y} M_xO_y \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots [3]$$

Where, $M_xO_y$ is the oxide of M; and $M_xO_y$ and M may be solid, liquid, or even gaseous. The standard free energy for the formation of the oxide $M_xO_y$ per mole of $O_2$ is:

$$\Delta G = -RT\ln K, \text{ where } K \text{ is the equilibrium constant;}$$

$$\Rightarrow \Delta G = -RT\ln \left[ \frac{(a_{M_xO_y})^{\frac{2}{y}}}{(a_M)^{\frac{2x}{y}} \cdot a_{O_2}} \right]$$

where, by definition, $a_M = 1, a_{M_xO_y} = 1$

$$a_{O_2} = p_{O_2} \text{ (oxygen behaving as an ideal gas).}$$
In conclusion, the free energy ($\Delta G$) for the oxidation of an element using a mole of oxygen gas ($O_2$) can be expressed in Joules per mole of $O_2$ per kelvin and it is mathematically given as $\Delta G = RT \ln P_{O_2}$. This is the oxygen potential of the reaction since the value of $\Delta G$ depends on $P_{O_2}$.

Now, let us go back to oxygen potential. For reactions [1], [2] and [1+2], the associated oxygen potentials are shown in Figure 12 (plotted using the data in Table 6) for 1 atmosphere pressure of CO$_2$ and CO. The two lines intersect at 700°C. At all temperatures above the point of intersection, the CO line is at a lower oxygen potential than the CO$_2$ line. It implies that at higher temperatures, CO is more stable and the reaction $CO_2[g] + C[s] \rightleftharpoons 2CO[g]$ goes to the right, i.e. CO production is favoured. At lower temperatures CO$_2$ is more stable and the direction of the reaction is reversed, i.e. CO$_2$ production is favoured.

The equilibrium constant of reaction [2] is:

$$K = \frac{p_{CO}^2}{p_{CO_2} \cdot a_c} = \frac{p_{CO}^2}{p_{CO_2}} \quad \text{[1]}$$

Table 6: $\Delta G - T$ data for reactions [1], [2] and [1+2] Temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta G_1$ (kJ/mol.)</th>
<th>$\Delta G_2$ (kJ/mol.)</th>
<th>$\Delta G_{1+2}$ (kJ/mol.)</th>
<th>K (at $M - M_xO_y - O_2$ equilibrium)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>-393.782</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>400</td>
<td>1073</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>600</td>
<td>1273</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>800</td>
<td>1473</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>1000</td>
<td>1673</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>1200</td>
<td>1873</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>1400</td>
<td>2073</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>1600</td>
<td>2273</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>1800</td>
<td>2473</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
<tr>
<td>2000</td>
<td>2673</td>
<td>122.498</td>
<td>-271.72</td>
<td>0 273</td>
</tr>
</tbody>
</table>
Where the activity of carbon, $a_c = 1$, as carbon is in its standard state (i.e. pure carbon). A ratio of $P_{CO}^2 / P_{CO_2}$ as a function of temperature can be obtained using the Van’t Hoff Isotherm as follows:

$$\Delta G^o = -RT \cdot ln K = -RT \cdot ln \frac{P_{CO}^2}{P_{CO_2}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots [2]$$

Substituting for $R = 8.314$ J/mol·K and converting to common logarithm, we obtain:

$$\Delta G^o = -8.314 \times 2.303 T \cdot log \frac{P_{CO}^2}{P_{CO_2}} = -19.14T \cdot log \frac{P_{CO}^2}{P_{CO_2}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots [3]$$
On rearrangement, equation [3] becomes:

\[ \frac{\Delta G^0}{19.14T} = -\log \frac{P_{CO}^2}{P_{CO_2}} \] ...

Using \( \Delta G^0 = +170 \ 000 - 174T \) [mol. for.

\[
\text{CO}_2 + \text{C} = 2\text{CO}
\]

( ) ( ) ( ) at temperature

of 1900°C, and substituting in equation [4] yields:

\[
\frac{170 \ 000 - (174)(2173)}{19.14 \times 2173} = -\log \frac{P_{CO}^2}{P_{CO_2}}, \{\text{Recall that } T(K) = t(°C) + 273\}
\]

\[
\Rightarrow \log \frac{P_{CO}^2}{P_{CO_2}} = -\frac{170 \ 000 - (174)(2173)}{19.14 \times 2173} = \frac{208 \ 102}{41 \ 591.22} = 5 \equiv \frac{5}{1}
\]

\[
\therefore \frac{P_{CO}^2}{P_{CO_2}} = 10^5 = 100 \ 000 \equiv \frac{100 \ 000}{10^0} \text{ or } \frac{100 \ 000}{1}
\]

This result shows that at high temperatures, such as at 1900°C (2173K), the partial pressure of CO is very high while that of CO\(_2\) is negligible; hence, the production of CO is favoured. \{Recall that when \( K \) is positive (especially large positive values), \( \Delta G \) is negative, the reaction will be thermodynamically feasible or spontaneous. The more negative is the value of \( \Delta G \) (large negative values), the more favourable the reaction\}.

Now, using temperature of 300°C (573K) with the same \( \Delta G^0 = +170 \ 000 - 174T \) [mol. for. reaction [2], we obtain that:

\[
\log \frac{P_{CO}^2}{P_{CO_2}} = -\frac{170 \ 000 - (174)(573)}{19.14 \times 573} = -\frac{70 \ 298}{10 \ 967.22} = -6.4
\]

\[
\therefore \frac{P_{CO}^2}{P_{CO_2}} = 10^{-6.4} \equiv \frac{1}{10^{6.4}} = \frac{1}{2 \ 551 \ 886.432}
\]

Again, this result confirms that at low temperatures such as at 300°C (573K), the partial pressure of CO\(_2\) is very high compared to that of CO, which is negligible, hence, the production of CO\(_2\) is favoured. \{Again, recall that when \( K \) is negative, \( \Delta G \) is positive, the reaction will be thermodynamically unrealistic or impossible. The more positive is the value of \( \Delta G \) (large positive values), the more unfavourable the reaction\}.

Table 7 shows \( \log \frac{P_{CO}^2}{P_{CO_2}} \) values and \( \frac{P_{CO}^2}{P_{CO_2}} \) ratios for various temperatures for the reaction, \( \text{CO}_2[g] + \text{C}[s] = 2\text{CO}[g] \). The data confirms that as temperature increases, the value of \( \log \frac{P_{CO}^2}{P_{CO}} \) increases, as shown in Figure 13. In addition, \( P_{CO} \) ratios are low at
Table 7: Temperature vs. data for $\text{CO}_2[g] + C[s] = 2\text{CO}_2[g]$

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Temp. (K)</th>
<th>$\log \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$</th>
<th>$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>273</td>
<td>-23.44 3.63078 × 10^{-24}</td>
<td>3.63078/10^{24}  = 1/10^{23.44}</td>
</tr>
<tr>
<td>100</td>
<td>373</td>
<td>-14.72 1.90546 × 10^{-15}</td>
<td>1.90546/10^{15}  = 1/10^{14.72}</td>
</tr>
<tr>
<td>200</td>
<td>473</td>
<td>-9.68 2.0893 × 10^{-10}</td>
<td>2.0893/10^{10}   = 1/10^{9.68}</td>
</tr>
<tr>
<td>300</td>
<td>573</td>
<td>-6.40 3.98107 × 10^{-7}</td>
<td>3.98107/10^{7}   = 1/10^{6.40}</td>
</tr>
<tr>
<td>400</td>
<td>673</td>
<td>-4.10 7.94328 × 10^{-5}</td>
<td>7.94328/10^{5}   = 1/10^{4.10}</td>
</tr>
<tr>
<td>500</td>
<td>773</td>
<td>-2.39 0.004073803</td>
<td>4.073803/10^{3}  = 1/10^{2.39}</td>
</tr>
<tr>
<td>600</td>
<td>873</td>
<td>-1.08 0.083176377</td>
<td>8.3176377/10^{2} = 1/10^{1.08}</td>
</tr>
<tr>
<td>700</td>
<td>973</td>
<td>-0.03 0.933254301</td>
<td>9.33254/10       = 1/10^{0.03}</td>
</tr>
<tr>
<td>800</td>
<td>1073</td>
<td>0.81 6.456542290</td>
<td>6.45654/1        = 10^{0.81}/1</td>
</tr>
<tr>
<td>900</td>
<td>1173</td>
<td>1.51 32.35936569</td>
<td>32.35936/1       = 10^{1.51}/1</td>
</tr>
<tr>
<td>1000</td>
<td>1273</td>
<td>2.11 128.8249552</td>
<td>128.8249/1       = 10^{2.11}/1</td>
</tr>
<tr>
<td>1100</td>
<td>1373</td>
<td>2.62 416.8693835</td>
<td>416.8693/1       = 10^{2.62}/1</td>
</tr>
<tr>
<td>1200</td>
<td>1473</td>
<td>3.06 1148.153621</td>
<td>1148.1536/1      = 10^{3.06}/1</td>
</tr>
<tr>
<td>1300</td>
<td>1573</td>
<td>3.44 2754.228703</td>
<td>2754.2287/1      = 10^{3.44}/1</td>
</tr>
<tr>
<td>1400</td>
<td>1673</td>
<td>3.78 6025.595861</td>
<td>6025.5958/1      = 10^{3.78}/1</td>
</tr>
<tr>
<td>1500</td>
<td>1773</td>
<td>4.08 12022.64435</td>
<td>12022.6443/1     = 10^{4.08}/1</td>
</tr>
<tr>
<td>1600</td>
<td>1873</td>
<td>4.34 21877.61624</td>
<td>21877.6162/1     = 10^{4.34}/1</td>
</tr>
<tr>
<td>1700</td>
<td>1973</td>
<td>4.58 38018.93963</td>
<td>38018.9396/1     = 10^{4.58}/1</td>
</tr>
<tr>
<td>1800</td>
<td>2073</td>
<td>4.80 63095.73445</td>
<td>63095.7344/1     = 10^{4.80}/1</td>
</tr>
<tr>
<td>1900</td>
<td>2173</td>
<td>5.00 100000.0000</td>
<td>100000.0000/1    = 10^{5.00}/1</td>
</tr>
<tr>
<td>2000</td>
<td>2273</td>
<td>5.18 151356.1248</td>
<td>151356.1248/1    = 10^{5.18}/1</td>
</tr>
</tbody>
</table>

Note: If $\frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = 1/10^{6.4}$; then $P_{\text{CO}}/P_{\text{CO}_2} = 1^{1/2}/10^{6.4} = 1/10^{6.4} \approx 1/2,511,886$. Table 7: Temperature vs. data for.
Similarly, for $$\frac{P_{CO}^2}{P_{CO_2}} = 10^5/1; \frac{P_{CO}}{P_{CO_2}} = 10^{5\times1/2}/1 = 10^{2.5}/1 \approx 316/1$$

These examples are for temperatures of 300°C and 1900°C, respectively.

**Figure 13: Variation with temperature of log $\frac{P_{CO}^2}{P_{CO_2}}$ for $CO_2$[g] + C[\text{s}] = 2CO[\text{g}]

at total pressure of 1 atm**
ratios are high at high temperatures \([\geq 800^\circ C]\), and this favours CO\(_2\) production. This is also corroborated in Figure 14. Notice that at temperatures in excess of 1000\(^\circ\)C, the concentration of CO\(_2\) is negligible and the total pressure of the carbonaceous gases is approximately equal to the partial pressure of CO \([i.e.\ P_{CO} + P_{CO_2} \approx P_{CO}]\). Below 400\(^\circ\)C, the partial pressure of CO is negligible and the reverse applies \([i.e.\ P_{CO} + P_{CO_2} \approx P_{CO_2}]\). Between these temperature limits, the pressure of both gases are significant and if \(P_{CO} + P_{CO_2} = 1\) atmosphere pressure, it means that the partial pressure of each gas is less than atmospheric.

In practice, the furnace gas is diluted with large amount of N\(_2\) and smaller quantities of H\(_2\) and H\(_2\)O vapour from the air blast. In consequence, \(P_{CO} + P_{CO_2} < 1\) atmosphere although the gas pressure of 1.3 to 1.5 atmospheres at the tuyere level is offset by the dilution of gas. In Figure 12, this effect is judged by the reaction: \(2C_{[s]} + O_2_{[g]} = 2CO_{[g]}\) \((0.5\ atm.)\). This corresponds more closely to the partial pressure of the CO in the hearth and bosh of the blast furnace. The CO and CO\(_2\) lines (in Figure 12) now intersect at a lower temperature and the \(P_{CO}/P_{CO_2}\) ratios in the blast furnace are slightly lower than those previously tabulated.
THE HEAT BALANCE: DIRECT AND INDIRECT REDUCTIONS

From the point of view of blast furnace theory, the most important reactions are those involving wustite, e.g.

\[ \text{Fe}_{0.947}O + C = 0.947\text{Fe} + \text{CO}; \quad \Delta H = +156 \text{kJ} \]
\[ \text{Fe}_{0.947}O + \text{CO} = 0.947\text{Fe} + \text{CO}_2; \quad \Delta H = -14 \text{kJ} \]

Experimental work suggests that when the initial stages of oxidation is high [i.e. high O/Fe ratio of iron oxide], e.g. approaching Fe$_3$O$_4$ [with O/Fe = 3/2 = 1.5], the first stage of reduction is rapid but the direct reduction of wustite is much slower and decreases as reduction proceeds.

The simplest method of assessing the carbon requirements for smelting iron in the blast furnace is from the overall heat balance. One of the most important factors in considering the overall thermal balance is the proportion of direct and indirect reduction. From the point of view of maximum evolution of heat (negative $\Delta H$, exothermicity), maximum gaseous reduction using CO (i.e. indirect reduction) is to be preferred. In his —ideal working blast furnace or ideal blast furnace operation—, Gruner (a French metallurgist) postulated in 1872 that maximum efficiency of operation occurred when all the reduction was indirect. This eventually became known as Gruner’s theorem, which states that, the “ideally perfect working” of a blast furnace will be achieved when “the reduction of iron ore is made as far as possible by the transformation of CO into CO$_2$, that is, without any consumption of solid carbon”. Maximum indirect reduction however, although giving maximum evolution of heat (thermal requirement) does not necessarily mean minimum carbon consumption (chemical requirement). This is shown in Figure 15 and illustrated by the following reactions:

![Figure 15: Relationship among indirect reduction, direct reduction, solution loss and carbon rate in a Blast Furnace](image)

Figure 15: Relationship among indirect reduction, direct reduction, solution loss and carbon rate in a Blast Furnace

a) Assuming that all reduction is by the gaseous reductant CO and that the final
CO/CO\textsubscript{2} ratio is 1, then we can have the following reactions;

i. \( \text{Fe}_2\text{O}_3 + 6\text{CO} = 2\text{Fe} + 3\text{CO}_2 + 3\text{CO} ; \Delta H = +349 \text{ kJ} \) \{consuming reducing gas and energy, leaving CO/CO\textsubscript{2} ratio = 1\}

ii. \( 6\text{C} + 3\text{O}_2 = 6\text{CO} ; \Delta H = -698 \text{ kJ} \) \{producing reducing gas and energy\}

b) Assuming reduction is partially direct and partially indirect, then the following reaction can occur directly between carbon and iron oxide;

iii. \( \text{Fe}_2\text{O}_3 + 2\text{C} = 2\text{Fe} + \text{CO} + \text{CO}_2 ; \Delta H = +308 \text{ kJ} \) \{consuming carbon directly and energy\}

The enthalpies for reactions (i.), (ii.) and (iii.) are those for coke (carbon). In case (a), by comparing reactions (i.) and (ii.), it is clear that 3 moles of C [through CO] are required to reduce 1 mole of Fe [i.e. \(6\text{C}/2\text{Fe} = 3\) moles of C for every mole of Fe] and giving a thermal yield of 349 kJ [i.e. \(\text{net } \Delta H = (-698) + (+349) = -698 + 349 = -349 \text{ kJ}\)]. However, in case (b), reaction (iii.) shows that 1 mole of C is required per mole of Fe [i.e. \(2\text{C}/2\text{Fe} = 1\) mole of C for every mole of Fe], but there is a thermal deficit of 308 kJ [\(\text{net } \Delta H = +308 \text{ kJ}\)].

In other for the blast furnace process to operate, sufficient heat must be supplied by:

- Combustion of coke,
- Indirect reduction of iron oxides, and
- Sensible heat of the blast;

This is required to balance heat consumed in:

- Melting of iron and slag,
- Direct reduction, and
- Other endothermic reactions (such as decomposition of CaCO\textsubscript{3} and MgCO\textsubscript{3}, reduction of SiO\textsubscript{2}, etc.) and heat losses from the furnace

For any given condition, the proportions of indirect reduction and direct reduction must be balanced to supply the heat required for the melting process. Similar reactions can be written for different CO/CO\textsubscript{2} ratios.

The approach of using the overall thermal balance to access coke rates in the iron blast furnace is based on a calculation of thermal requirements of smelting i.e. sensible heat of metal and slag, reduction of metalloids, cooling losses and calcination of CaCO\textsubscript{3} and MgCO\textsubscript{3}. This must be balanced by heat available from:

- the amount of carbon used,
- the sensible heat in the blast,
- the degree of combustion to CO and CO\textsubscript{2},
- the amount of indirect reduction
Calculations can be made which give the available heat for different amount of carbon consumed with different degrees of conversion to CO and CO$_2$ and with differing degrees of indirect reduction. The result of this kind of calculation is shown in Figure 16. The diagram gives the overall heat available to satisfy the thermal demands of melting slag and iron, reduction of metalloids, and heat losses from the furnace as a function of the carbon used (omitting that used to carburize the iron). Data are given for various degrees of direct reduction and CO/CO$_2$ ratios. The ore is assumed to be Fe$_2$O$_3$ but similar diagrams can be constructed for ores with differing degrees of oxidation [O/Fe ratios]. In this diagram, the amount of direct reduction is expressed as the percentage of iron reduced by the reaction:

$$\text{Fe}_{0.947}O + C = 0.947\text{Fe} + \text{CO}$$

Figure 16 illustrates that the factors (amount of carbon used, sensible heat in the blast, and degree of combustion to CO and CO$_2$) are not independent variables and that if one is altered the other two are also affected. It is apparent that the greater the thermal demands [i.e. low thermal surplus] of the process, the lower must be the CO/CO$_2$ ratio and the greater the amount of indirect reduction in order to achieve a given carbon consumption. If a comparison is made at the same CO/CO$_2$ ratio (i.e. the same efficiency of conversion of carbon to CO$_2$), then the greater the thermal demands of the process,
the greater must be the proportion of indirect reduction and also the greater the carbon rate.

If the degree of direct reduction is the limiting factor, then with increase in thermal demands, the coke rate and CO/CO$_2$ ratio must increase. Variations in the thermal requirements of the process are largely dependent on the slag bulk. Hence, rich ores have lower thermal requirements for smelting than lean ores.

Figure 16 illustrates the Gruner's theorem in that the greater the amount of indirect reduction, the greater is the thermal surplus available to meet the thermal requirements of the process. Hence the degree of indirect reduction becomes more important the greater the thermal requirements of the process (i.e. in the case of lean ore burdens), but even in rich ore burdens the efficiency of the process is higher the greater the proportion of indirect reduction.

**MATHEMATICAL TREATMENT AND GRAPHICAL REPRESENTATION OF THE IRON BLAST FURNACE OPERATION [RIST DIAGRAM]**

The mass (materials or stoichiometric) balance and heat (thermal or enthalpy) balance of the iron blast furnace can be represented by model equations and graphs. A most useful geometrical method for rapidly understanding and predicting changes in blast furnace operation due to variations in blast and burden parameters was devised by Prof. Andre Rist and co-workers (in France), and they published a series of papers in 1960s, where a mathematical model based on mass and heat balances considering equilibrium conditions of chemical reactions was presented. This model was illustrated by so-called *Rist operating diagram*, which is a dual representation of the blast furnace mass, and heat balances.

**The Stoichiometric Development**

The counter-current nature of iron blast furnace avails us the opportunity to derive the following equations based on the steady-state operating conditions, i.e. conditions under which there is no accumulation of mass in the furnace. This permits balancing of the carbon, iron and oxygen inputs and outputs of the furnace and it provides the foundation for developing a stoichiometric equation for the process. For simplicity, the stoichiometric equations are developed on a molar basis.

**Elemental Balances**

Industrial observations show that (i) Fe leaves the furnace almost exclusively in the hot metal, i.e. less than 0.5% leaves in the slag, (ii) the oxygen content of the hot metal is negligibly small so that no oxygen leaves the furnace in the metal, (iii) oxides which enter the furnace in gangue, flux and coke ash leave the furnace mainly in slag. It is also pertinent to note that the loss of input materials as dust in top gas, fall between 10 to 20
kg per tonne of Fe. This is ignored in the mass balance equation because it is assumed that all dusts are eventually recycled back to the furnace after gas cleaning. Under steady-state conditions, the blast furnace must obey three basic elemental balance equations*:

\[
\begin{align*}
    n^i_{Fe} &= n^o_{Fe} \ldots \ldots \ldots [1a] \\
    n^i_C &= n^o_C \ldots \ldots \ldots [1b] \\
    n^i_O &= n^o_O \ldots \ldots \ldots [1c]
\end{align*}
\]

where \( n^i \) is the number of moles of each component entering the furnace and \( n^o \) is the number of moles leaving, \textit{all expressed in terms of a production of one mole of useful Fe in pig iron, i.e. per mole of product Fe}. [*In addition to material or elemental balance equations, the blast furnace must also obey steady-state heat balance equation, namely; \textit{heat supply} = \textit{heat demand}].

Fe, C and O enter and leave the furnace in many forms, but initially the only forms that need be considered are:

<table>
<thead>
<tr>
<th>Element Forms into furnace</th>
<th>Forms out of furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Iron oxide(s)</td>
</tr>
<tr>
<td></td>
<td>Hot metal (pig iron)</td>
</tr>
<tr>
<td>C</td>
<td>Coke</td>
</tr>
<tr>
<td></td>
<td>Top gas (CO, CO(_2)), C-in-Fe (C dissolved in hot metal)</td>
</tr>
<tr>
<td>O</td>
<td>Iron oxides, blast air</td>
</tr>
<tr>
<td></td>
<td>Top gas as CO and CO(_2)</td>
</tr>
<tr>
<td>N(_2)</td>
<td>Blast air</td>
</tr>
<tr>
<td></td>
<td>Top gas as N(_2)</td>
</tr>
</tbody>
</table>

**Composition Ratios**

Before developing the stoichiometric equation [i.e. blast furnace mass balance equation], it is useful to introduce several variables which concisely represent C, Fe and O concentrations and quantities in the furnace inputs and outputs. A useful variable for describing top gas composition is \((O/C)^g\). This variable represents concisely the mole fractions of CO and CO\(_2\) in the carbonaceous portion of the top gas

\[
(X^g_{CO}, X^g_{CO_2})
\]

Knowing that the O/C ratios for pure CO and pure CO\(_2\) are 1 and 2 respectively, Mixtures of CO and CO\(_2\) will have O/C ratios between 1 and 2. If we define \((O/C)^g\) as the molar oxygen/carbon ratio [moles of O\(_2\)/moles of C] in the top gas, the molar fractions of CO \(_2\) and CO in the top gas will then be given as:

\[
X^g_{CO_2} = (O/C)^g - 1 \ldots \ldots \ldots [2a]
\]

\[
X^g_{CO} = 2 - (O/C)^g \ldots \ldots \ldots [2a]
\]

Where

\[
X^g_{CO} + X^g_{CO_2} = 1 \ldots \ldots \ldots [2c]
\]

With \(X^g_{CO}\) and \(X^g_{CO_2}\) given or known, \((O/C)^g\) can be obtained using:

\[
(O/C)^g = X^g_{CO} + 2 \cdot X^g_{CO_2} \ldots \ldots [2d]
\]
Likewise, if we define the molar oxygen fraction in the charge of iron oxide, \((O/Fe)^x\), as being the number of moles of O per mole of Fe in iron oxides [where \(x\) designates the particular iron oxide], then the composition of the iron oxide portion of the charge may be expressed as:

\[
\begin{align*}
O & \text{ Fe } = 3 \quad 2 = 1. \\
O & \text{ Fe }^x = 4 \quad 3 = 1.33 \text{ for magnetite } \text{ Fe}_3 \text{O}_4 \\
& \text{ \(x\) lies somewhere between 1.33 and 1.50}
\end{align*}
\]

For a mixed charge of \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_3\text{O}_4\), \((O/Fe)^x\) lies somewhere between 1.33 and 1.50.

\[(O/Fe)^x = 1/0.947 = 1.05 \text{ for wustite of composition } (\text{Fe}_{0.947}\text{O})\]

Finally, the carbon content of the hot metal is designated as and defined in terms of the molar ratio of C in hot metal to Fe in hot metal.

\[(O/Fe)^x \Rightarrow \{\text{moles of oxygen entering in iron} \quad \text{per mole of Fe entering in iron}\}\]

\[(C/Fe)^m \Rightarrow \{\text{moles of C leaving hot metal} \quad \text{per mole of product Fe}\} \quad \text{oxides}\]

To sum up, these ratios can be used to concisely represent certain quantities of oxygen and carbon entering and leaving the furnace. In this context their meanings are:

\[(O/C)^g \Rightarrow \{\text{moles of oxygen leaving in top gas} \quad \text{per mole of carbon leaving in top gas}\}\]

With the foregoing in mind, then the various element balances are:

a) **Iron (Fe) Balance**

Since the only outlet for Fe is in the hot metal, and \(n^{i}_{Fe}\) and \(n^{o}_{Fe}\) are in terms of moles of Fe in hot metal, it follows that \(n^{i}_{Fe} = n^{o}_{Fe}\) and \(n^{i}_{Fe}/n^{o}_{Fe} = 1\). On the basis of one mole of product Fe, then;

\[n^{i}_{Fe} = n^{o}_{Fe} = 1 \ldots \ldots \ldots \ldots \ldots [3]\]

b) **Carbon (C) Balance**

As C leaves (i) via the top gas and (ii) in the hot metal [which is essentially liquid Fe saturated with C]; the carbon balance can be represented as follows:

\[n^{i}_{C} = n^{o}_{C} = n^{g}_{C} + (C/Fe)^m \ldots \ldots \ldots \ldots [4]\]

Where \(n^{g}_{C}\) moles of C leaving via the top gas and \((C/Fe)^m\) is moles of C leaving in hot metal, both per mole of product Fe.

c) **Oxygen (O) Balance**

Oxygen enters the furnace as blast air and in iron oxides, i.e.

\[n^{i}_{O} = n^{g}_{O} + (O/Fe)^x \ldots \ldots \ldots \ldots \ldots [5a]\]
Where \( n^B_0 \) is the moles of O brought into the furnace in blast air per mole of product Fe. \((O/Fe)^x\) is the oxygen input of the iron oxides per mole of their input Fe, but by equation \[3\] it can also be expressed per mole of product Fe.

Oxygen leaves the furnace in the top gas only. In terms of variables already considered, its quantity may be described by:

\[
 n^o_0 = n^g_c \cdot \frac{(O/C)^g}{c} \ldots \ldots \ldots \ldots [5b] \quad \{ \text{Compare: } O = C \times \frac{o}{c} \}
\]

Where \( n^g_c \) is number of moles of carbon leaving in the top gas per mole of product Fe and \((O/C)^g\) is moles of oxygen leaving in the top gas per mole of carbon leaving in the top gas. Since by equation \[1c\], \( n^i_c = n^o_0 \), it implies that equations \[5a\] and \[5b\] can be equated to each other, thus:

\[
 n^B_0 + (O/Fe)^x = n^g_c \cdot \frac{(O/C)^g}{c} \ldots \ldots \ldots [6a]
\]

On rearrangement, equation \[6a\] becomes:

\[
 (O/Fe)^x = n^g_c \cdot \frac{(O/C)^g}{c} - n^b_0 \ldots \ldots \ldots [6b]
\]

Equation \[6b\] resembles the general equation of a straight line, i.e. \([y = mx + c]\). Equation \[6b\] may be rewritten by recalling that the carbon input either (i) reacts with oxygen in the blast and iron oxides, or (ii) dissolves in the hot metal (carburizes the hot metal). The carbon, which reacts with oxygen, is known as active carbon. The carbon that goes into the molten metal is called inactive carbon and is accounted for by \((C/Fe)^m\) in equation \[4\]. If the moles of active carbon is designated as \( n^A_c \), then in equation \[4\], \( n^g_c = n^A_c \) so that equation \[6b\] becomes:

\[
 \frac{O}{Fe}^x = n^A_c \cdot \frac{(O/C)^g}{c} - n^b_0 \ldots \ldots \ldots 6c
\]

So a plot of \((O/Fe)^x\) [the molar ratio of oxygen to iron in iron oxides] against \((O/C)^g\) [the molar ratio of oxygen to carbon in the top gas] will be a straight line whose slope is \( n^g_c \) or \( n^A_c \) and the intercept on the \((O/Fe)^x\) axis is \(-n^b_0\).

Equation \[6b\] or \[6c\] is the stoichiometric equation for the blast furnace in its most direct and simplest form, as represented in Figure 17. It is also very important to note that when coke is the only source of carbon [the simplified model does not consider the use of hydrocarbon injectants], the input–output carbon balance \( (n^i_c = n^o_0) \) of equation \[4\] becomes:

\[
 n^i_c = n^o_0 = n^{coke}_c = n^A_c + (C/Fe)^m \ldots \ldots \ldots [7]
\]

By comparing equations \[6b\], \[6c\] and \[7\], the slope can also be expressed as:

\[
 \text{slope} = \frac{(O/Fe)^x}{(O/C)^g} = n^g_c = n^A_c = [n^i_c - (C/Fe)^m] = [n^o_0 - (C/Fe)^m] = [n^{coke}_c - (C/Fe)^m]
\]
Based on equation [7], we can revisit equations [2a] and [2b] and express CO and CO$_2$ in moles instead of mole fractions, thus:

\[ n_{CO}^g = n_C^A \cdot X_{CO}^g \] \[ n_{CO_2}^g = n_C^A \cdot X_{CO_2}^g \] \[8\]

d) Nitrogen (N$_2$) Balance
Nitrogen enters and leaves the furnace as molecular nitrogen (N$_2$); not participating in the reactions but acts as a diluent of air. [It contributes volume and mass, and carries the bulk of the heat leaving the furnace in the top gas. In the case of preheated air blast, N$_2$ carries the bulk of the sensible heat in the blast entering the furnace]. Since oxygen and nitrogen occupy 21% and 79% of air by volume respectively, the number of moles of N$_2$ in the top gas is:

\[ n_{N_2}^g = \frac{0.79}{0.21} \cdot \frac{1}{2} \cdot n_O^g \] \[8c\]

\[ \{ \text{It is necessary here to multiply } n_O^g \text{ by 1/2 or divide it by 2 because } n_O^g \text{ considers oxygen as atomic (i.e. O) instead of molecular (i.e. O$_2$)} \} \]

Figure 17: Simplified Inputs and outputs of the iron blast furnace for the materials and enthalpy balances used in the derivation of the Rist model and diagram
**Rist Diagram Based on Stoichiometric Balance**

The **Rist diagram**, as it is called, is a graphical and alternative way of presenting the material and heat balances of the iron blast furnace. It is based on the general principles for countercurrent reactors. The molar O/C ratio in the furnace gas \( [\text{O/C}]^g \) and the molar O/Fe ratio in the burden \( [\text{O/Fe}]^b \) are used, respectively, as abscissa (\( x \)-axis) and ordinate (\( y \)-axis), as shown in Figure 18. A plot of \( [\text{O/Fe}]^x \) against \( [\text{O/C}]^b \) will be a straight line passing through the coordinates:

\[
\begin{align*}
(x_1, y_1) & \text{ where } x_1 \text{ is for } \frac{\text{O}}{\text{C}} = 0; \text{ and } y_1 \text{ is for } \frac{\text{O}}{\text{Fe}} = -\frac{n_O}{n_Fe} \\
(x_2, y_2) & \text{ where } x_2 \text{ is for } \frac{\text{O}}{\text{C}} = \frac{\text{O}}{\text{C}}^b; \text{ and } y_2 \text{ is for } \frac{\text{O}}{\text{Fe}} = \frac{\text{O}}{\text{Fe}}^x
\end{align*}
\]

The resulting straight line is known as the **operating line**. The operating line in Figure 18 was plotted using the data in Table 8, which is for a somewhat inefficient blast furnace operation. A few things are worth noting about the Rist diagram of Figure 18:

- The O/C atomic ratio is plotted along the abscissa (\( x \)-axis), and the top gas composition is shown at the top of the diagram, i.e. 1.0 for CO and 2.0 for CO\(_2\).
- The O/Fe atomic ratio is plotted along the ordinate (\( y \)-axis), and the topmost O/Fe ratio is that of the unreduced ore, i.e. 1.5 for haematite (Fe\(_2\)O\(_3\)). As reduction progresses in stages [Fe\(_2\)O\(_3\ → \)Fe\(_3\)O\(_4\ → \)FeO → Fe], the O/Fe ratio reduces from 1.5 to 1.33 (Fe\(_3\)O\(_4\)) to 1.0 (FeO) to 0 (zero for Fe).
- The positive side of the ordinate (above zero) represents oxygen [or oxygen removed] from iron oxides while the negative side (below zero) represents oxygen from air blast [including oxygen removed from SiO\(_2\), MnO, etc. in the ore].
- The operating line is permitted to lie anywhere between O/C = 1 and O/C = 2. As it rotates anticlockwise towards O/C = 1, the slope \( n^g_C = n^A_C \) increases, leading to higher coke consumption due to low utilization of CO i.e. inefficient blast furnace operation. Alternatively, as the operating line rotates clockwise towards O/C = 2, the slope reduces, meaning lower coke rate, effective utilization of CO in reduction or more efficient blast furnace operation.

**Table 8: Data for the blast furnace operation plotted in Figure 16**

<table>
<thead>
<tr>
<th>ITEM</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Specification</td>
</tr>
<tr>
<td></td>
<td>1 000</td>
</tr>
</tbody>
</table>
### Iron oxide

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass (Kg)</th>
<th>Reaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>53</td>
<td>(O/Fe)$^x$ = 3/2 = 1.5</td>
</tr>
</tbody>
</table>

**Pig iron**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass (Kg)</th>
<th>Reaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% C (inactive carbon)</td>
<td>4.4</td>
<td>(C/Fe)$^m$ = 0.25</td>
</tr>
</tbody>
</table>

**Coke (only carbon source)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass (Kg)</th>
<th>Reaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% C [495 kg of carbon]</td>
<td>41.3</td>
<td>$n_c^A = n_c^I - (C/Fe)^m = 2.05$</td>
</tr>
</tbody>
</table>

**Active carbon**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass (Kg)</th>
<th>Reaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>442</td>
<td>36.8</td>
<td>$n_c^A = n_c^I - (C/Fe)^m = 2.05$</td>
</tr>
</tbody>
</table>

**Oxygen from Blast air**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass (Kg)</th>
<th>Reaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>25.0 (as O)</td>
<td>$n_O^B = 1.40$</td>
</tr>
</tbody>
</table>

*Note that blast furnace iron (inside the furnace) is saturated with carbon, 5 wt.% C ([C/Fe]$^m$ ≈ 0.25] at 1800 K. (C/Fe)$^m$ shall be assigned with the value of 0.25 in this course.*

Insertion of the data in Table 8 into equation [6b or 6c] will reveal the top gas compositions of the blast furnace thus:

\[(O/Fe)^x = n_c^A \cdot (O/C)^g - n_O^B \quad ... ... ... [6c]\]

\[\Rightarrow 1.5 = 2.05 \cdot (O/C)^g - 1.4\]

\[\Rightarrow 2.05 \cdot (O/C)^g = 1.5 + 1.4 = 2.9\]

\[\therefore (O/C)^g = \frac{2.90}{2.05} = 1.41\]
Figure 18: The Rist diagram based on stoichiometric balance only. The numerical values of $m_B^B n_C^A$, $(O/C)^g$ and $(O/Fe)^x$ are for the blast furnace operation described in Table 8. Physical meanings of the slope and intercepts are also described.

This O/C ratio of 1.41 is equivalent to the following CO and CO$_2$ mole fractions, using equations [2a], [2b] and [2c]:

$$= 2 - (O/C)^g \ldots \ldots \ldots \ldots [2a]$$

$$\therefore x_{CO}^g = 2 - 1.41 = 0.59$$
Confirm that \( X_{\text{CO}_2}^g = (O/C)^g - 1 \) \[2b\]
\[ X_{\text{CO}_2}^g = 1.41 - 1 = 0.41 \]

\( X_{\text{CO}}^g + X_{\text{CO}_2}^g = 0.59 + 0.41 = 1 \) \[2c\]

Confirm also that \( (O/C)^g = X_{\text{CO}}^g + 2 \cdot X_{\text{CO}_2}^g = 0.59 + 0.82 = 1.41 \) \[2d\]

For the carbonaceous portion of the top gas, this translates to 59% CO and 41% CO\(_2\).

Furthermore, from equations [8a], [8b] and [8c], we can determine the moles of CO, CO\(_2\) and N\(_2\) for the blast furnace operation:

\[ n_{\text{CO}}^g = n_C^A \cdot X_{\text{CO}}^g \quad \ldots \ldots \ldots \quad [8a] \]
\[ n_{\text{CO}_2}^g = n_C^A \cdot X_{\text{CO}_2}^g \quad \ldots \ldots \ldots \quad [8b] \]
\[ n_{\text{N}_2}^g = \frac{0.79}{0.21} \cdot \frac{1}{2} \cdot n_O^g = \frac{0.79}{0.21} \cdot \frac{1}{2} \cdot 1.4 = 2.63 \text{ moles per mole of product Fe} \]

This gives the overall top gas composition as 26% CO, 18%CO\(_2\), and 56% N\(_2\).

\{That is \( \frac{1.21}{1.21+0.84+2.63} \times 100 = \frac{1.21}{4.68} \times 100 \approx 26\% \text{ for CO, for example } \}\). For

**ASSIGNMENT PROBLEMS B**

1. Convert the following operating parameters into numerical values for their equivalent blast furnace model variables.

<table>
<thead>
<tr>
<th>SN</th>
<th>Operating parameter</th>
<th>Model variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ore charge: hematite</td>
<td>( (O/Fe)^x )</td>
</tr>
<tr>
<td>b</td>
<td>Blast: 1200 Nm(^3) of dry air per tonne of product Fe</td>
<td>( b \cdot n_O )</td>
</tr>
<tr>
<td>c</td>
<td>Pig iron: 4.9% C</td>
<td>( (C/Fe)^n )</td>
</tr>
<tr>
<td>d</td>
<td>Total carbon in charge: 460 kg of dry coke (90% C) and 50 kg of oil (85% C) per tonne of Fe</td>
<td>( n_C^i = n_C^o )</td>
</tr>
<tr>
<td>e</td>
<td>Active carbon from (c) and (d) ( f ) Carbon in top gas [from (e)]</td>
<td>( n_C^A )</td>
</tr>
<tr>
<td>g</td>
<td>Top gas composition: 23.9 vol.% CO, 20.5% CO(_2), 55.6% N(_2) ( h ) Quantity of CO and CO(_2) in the top gas [from (f) and (g)]</td>
<td>( (O/C)^g ), ( n_{\text{CO}}^g, n_{\text{CO}_2}^g )</td>
</tr>
</tbody>
</table>
2. A blast furnace is charged with hematite pellets. It produces a 5% carbon pig iron. 450 kg of carbon (as coke) and 370 kg of oxygen (as air blast) are supplied to the furnace per tonne of product Fe. Calculate analytically:
   (a) the composition (including N\textsubscript{2}) of the top gas from this furnace;
   (b) the volume of top gas per kg mole and per tonne of product Fe.

3. Plot the operating line for the operation in Problem 2 on an O/C: O/Fe graph and check graphically your answer to part (a) of Problem 2. Express your comparative answers in terms of the oxygen/carbon ratio in the top gas.

4. The Problem 2 blast furnace is switched to an acid, low SiO\textsubscript{2} sinter in which the predominant iron oxide is Fe\textsubscript{3}O\textsubscript{4}. The low SiO\textsubscript{2} content of this feed leads to a low slag production (per tonne of product Fe) which permits the operator to cut back his coke and blast supplies to 425 kg of C and 345 kg of O\textsubscript{2} (per tonne of Fe) respectively. Demonstrate graphically the effects of this change and determine the mole fractions of CO and CO\textsubscript{2} in the carbonaceous portion of the top gas \((X\textsubscript{CO}^g, X\textsubscript{CO_2}^g)\) for this new operation.

5. The operator of a small, old blast furnace wishes to check his blast-metering devices on the basis of top-gas analysis and coke-rate measurements. Determine, analytically or graphically, what his total blast volume (Nm\textsuperscript{3} of dry air) should have been for the following operating conditions:

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore: hematite (5% SiO\textsubscript{2}, all of which goes to slag)</td>
<td></td>
</tr>
<tr>
<td>Hot metal (5% C)</td>
<td>1000 tonnes</td>
</tr>
<tr>
<td>Coke (88% C, dry basis)</td>
<td>700 tonnes (a poor operation)</td>
</tr>
<tr>
<td>Top-gas composition</td>
<td>vol.% CO/vol.% CO\textsubscript{2} = 1.2</td>
</tr>
</tbody>
</table>

6. The composition of the top gas from a hematite-charged furnace is 22 vol.% CO, 20 vol.% CO\textsubscript{2}, 58 vol.% N\textsubscript{2}. The blast volume is 1400 Nm\textsuperscript{3} per tonne of product Fe. From these data, calculate graphically the quantity of carbon taking part in the blast-furnace reactions (per tonne of product Fe). Calculate also the total carbon being used by the furnace if the pig iron contains 5 wt.% C.

**Rist Diagram Based on Stoichiometric and Thermal Balances**

The Rist diagram of Figure 18 as well as the analytical and graphical solutions required in the Assignment Problems B are based on equation [6]:

\[
(O/Fe)^x = n_c^A \cdot (O/C)^B - n_o^B \ldots \ldots \ldots \ldots [6c]
\]

This equation is useful for checking the consistency of measured top-gas compositions with measured inputs to the furnace. It is not, however, powerful enough to predict [before charging and operating the furnace] the quantities of coke and blast which are necessary for a given type of blast furnace operation and furnace charge. In this section, we shall be concerned with developing a second equation for the process, based upon a steady-state enthalpy balance for the furnace.
It is useful to consider the blast furnace enthalpy balance in terms of an enthalpy demand and an enthalpy supply. Blast furnace enthalpy balance can be divided into reactions, which supply heat to the process, e.g. formation of CO and CO₂, and reactions, which require heat, e.g. dissociation of iron oxides and heating and melting of product iron. In its most simplified case, the demand is considered to be the enthalpy required to produce liquid Fe 1800 K (1527°C) from Fe₂O₃ at 298 K (25°C) and the supply is the enthalpy provided by oxidation of carbon at 298 K (25°C) to CO and CO₂.

This simplification assumes the following:
• the air blast enters the furnace at 298 K (25°C) and the top gas leaves at 298 K (25°C), i.e. neither carries sensible heat, which permits the N₂ of the blast to be ignored for the moment;
• the only charge materials are Fe₂O₃ and C, i.e. there is no gangue, flux or coke ash and thus no slag;
• the enthalpy of the carbon in the pig iron product is negligible;
• there are no convective or radiative heat losses from the furnace.

The demand/supply form of the enthalpy equation (thermal balance) is:

\[
\frac{D}{\text{per mole of product Fe}} = \frac{S}{\text{per mole of product Fe}}
\]

Where \( n_{\text{Fe}_2\text{O}_3} \cdot (-\Delta H^o_{298}^\circ)_{\text{Fe}_2\text{O}_3} + \left( H^o_{1800\text{Fe}(l)} - H^o_{298\text{Fe}(s)} \right) \) = \( n_{\text{CO}}^g \cdot (-\Delta H^o_{298}^\circ)_{\text{CO}} + n_{\text{CO}_2}^g \cdot (-\Delta H^o_{298}^\circ)_{\text{CO}_2} \) \[9\]

Where \( n_{\text{Fe}_2\text{O}_3}, n_{\text{CO}}, n_{\text{CO}_2} \) are moles of Fe₂O₃ charged to the furnace and moles of CO and CO₂ leaving the furnace all per mole of product Fe. The enthalpies of C, O₂ and N₂ are zero because they enter or leave the furnace at 298 K in accordance with the assumptions as typified by Figure 17.

This simplified form of the enthalpy equation (equation [9]) is advantageous in many ways:
• both sides of the equation contain positive numbers;
• an additional enthalpy requirement for the process, e.g. for heating and melting slag, can be included simply and clearly as an additional heat-demand term;
• an additional enthalpy supply, e.g. enthalpy in hot blast, can be incorporated as an additional supply term.

This demand/supply form also demonstrates that for a blast furnace to be operating at a steady state, its heat demand must be exactly met by its heat supply. Otherwise, the furnace will be warming or cooling and an adjustment of coke and blast inputs will eventually have to be made.
If we insert into equation [9] the numerical values [thermochemical data can be sourced from references like NIST-JANAF Thermochemical Tables] of the heats of formation of the substances, we have:

It is appropriate to express equation [9c] in the same terms as equation [6] and this can be achieved by using equations [8a] and [8b] and [2a] and [2b], thus:

\[ n^g_{CO} = n^g_{C} \cdot X^g_{CO} \quad \ldots \quad [8a] \quad \text{and} \quad X^g_{CO} = 2 - (O/C)^g \quad \ldots \quad [2a] \]

\[ \therefore \quad n^g_{CO} = n^g_{C} \cdot X^g_{CO} = n^g_{C} \cdot \{2 - (O/C)^g\} = n^A_{C} \cdot \{2 - (O/C)^g\} \]

\[ n^g_{CO_2} = n^g_{C} \cdot X^g_{CO_2} \quad \ldots \quad [8b] \quad \text{and} \quad X^g_{CO_2} = (O/C)^g - 1 \quad \ldots \quad [2b] \]

\[ \therefore \quad n^g_{CO_2} = n^g_{C} \cdot X^g_{CO_2} = n^g_{C} \cdot \{(O/C)^g - 1\} = n^A_{C} \cdot \{(O/C)^g - 1\} \]

Note also that 1 mole of product Fe requires \( \frac{1}{2} \) mole of input Fe\(_2\)O\(_3\) that is;

\[ \frac{1}{2} \text{Fe}_2\text{O}_3 \text{ yields} 1 \text{ Fe} \]

Since both sides of equation [9c]) are in terms of kJ per kg mole of product Fe;

\[ \therefore \quad n_{Fe_2O_3} = \frac{1}{2} \]

Substituting accordingly, we obtain:

\[ \frac{1}{2} \cdot 826 \ 000 + 73 \ 000 = n^A_{C} \cdot 111 \ 000 \ (2 - (O/C)^g) + n^A_{C} \cdot 394 \ 000 \ \{(O/C)^g - 1\} \]

\[ \Rightarrow \ 413 \ 000 + 73 \ 000 = n^A_{C} \cdot [111 \ 000 \cdot (2 - (O/C)^g) + 394 \ 000 \ \{(O/C)^g - 1\}] \]

\[ \Rightarrow \ 486 \ 000 = n^A_{C} \cdot [222 \ 000 - 111 \ 000 \cdot (O/C)^g + 394 \ 000 \cdot (O/C)^g - 394 \ 000] \]

\[ \therefore \ 486 \ 000 = n^A_{C} \cdot [283 \ 000 \cdot (O/C)^g - 172 \ 000] \quad \ldots \quad [9d] \]

Since D = S, it means that both D and S can be equated to the right hand side of equation [9d]:

\[ D = S = n^A_{C} \cdot [283 \ 000 \cdot (O/C)^g - 172 \ 000] \quad \ldots \quad [10a] \]

At this point, it is useful to generalize that the demand term is a variable, in which case equation [9d] becomes:

\[ D \ n^A_{C} \cdot [283 \ 000 \cdot (O/C)^g - 172 \ 000] \quad \ldots \quad [10b] \]

This can be rearranged (by dividing both sides by 283000 and opening up the bracket) to:

\[ \frac{D}{283 \ 000} = n^A_{C} \cdot \left(\frac{O}{C}\right)^g - n^A_{C} \cdot \frac{172 \ 000}{283 \ 000} \quad \ldots \quad [10c] \]
Where, $D$ is the heat demand of the process per kg mole of Fe produced by the furnace. This generalized $D$ term facilitates enthalpy calculations for different iron oxides and different molten metal temperatures and, when necessary, additional enthalpy demands are readily incorporated into it. For example, it has been shown from the foregoing that the heat demand for producing $\text{Fe}(l)$ at 1800 K from $\frac{1}{2}$ mole of $\text{Fe}_2\text{O}_3$ at 298 K is 486 000 kJ (kg mole of product Fe)$^{-1}$. Similarly, the heat demand for producing one mole of $\text{Fe}(l)$ at 1900 K from $\frac{1}{3}$ mole of $\text{Fe}_3\text{O}_4$ at 298 K is:

$$D = n_{\text{Fe}_3\text{O}_4} \cdot (-\Delta H^\circ_{\text{Fe}_3\text{O}_4}^{298}) + H^\circ_{0 \text{Fe}(l)} - H^\circ_{298 \text{Fe}(s)}$$

$$D = \frac{1}{3} \cdot (1121000) + (78000) = 373667 + 78000 \approx 452000 \text{ kJ (kg mole of product Fe)}^{-1}$$

Since $\frac{1}{3}\text{Fe}_3\text{O}_4 \rightarrow 1 \text{ Fe}$ so that $n_{\text{Fe}_3\text{O}_4} = \frac{1}{3}$

The calculations of heat demand $D$ for the two iron oxides shows that the determination of $D$ does not require the variables $n^A_C$ and $(\text{O/C})^g$, i.e. its value depends only upon the nature of the charge, the composition and temperature of the iron and slag and heat losses. Of course changes in $D$, due say to an increased slag production per tonne of product Fe, will necessitate changes in $n^A_C$ and $(\text{O/C})^g$ for the furnace to re-establish steady-state operating conditions.

We can now combine the stoichiometric (mass) balance equation [6c] and the enthalpy (heat) balance equation [10b] as follows:

$$\left( \frac{\text{O}}{\text{Fe}} \right)^x = n^A_C \cdot \left( \frac{\text{O}}{C} \right)^g - n^B_O \text{ .... ... ... [6c] }$$

$$\frac{D}{283000} = n^A_C \cdot \left( \frac{\text{O}}{C} \right)^g - n^A_C \cdot \frac{172000}{283000} \text{ .... ... [10c] }$$

Subtracting equation [10c] from equation [6c], we have:

$$\left( \frac{\text{O}}{\text{Fe}} \right)^x - \frac{D}{283000} = -n^B_O + n^A_C \cdot \frac{172000}{283000}$$

$$\therefore \left[ \left( \frac{\text{O}}{\text{Fe}} \right)^x - \frac{D}{283000} \right] = n^A_C \cdot \frac{172000}{283000} - n^B_O \text{ .... ... [11a] }$$

Or

$$\left[ \left( \frac{\text{O}}{\text{Fe}} \right)^x - \frac{D}{283000} \right] = n^g_C \cdot \frac{172000}{283000} - n^B_O \text{ .... ... [11b] }$$
This shows that once \( (O/Fe)^x \) and \( D \) are specified (i.e. from the nature of the ore and its heat demand), we are left with two unknowns in the combined model equation. This means that specification of either \( n_C^A \) (from the input carbon per mole of product Fe and the carbon content of the pig iron) or \( n_O^B \) (oxygen in dry blast air per mole of product Fe) fully defines the simplified blast furnace operation shown in Figure 17.

Equation [11] can be seen to be a single equation containing four operating variables. Two of these variables, the oxygen/iron ratio \( (O/Fe)^x \) of the iron ore and its associated heat demand \( D \), will normally be specified in any blast furnace problem, but even with these specifications, equation [11] still contains two unknown variables \( n_C^A \) and \( n_O^B \). To achieve a fully predictive blast furnace model or equation requires:

- conceptually dividing the furnace, top from bottom, at some height within the chemical reserve zone;
- carrying out stoichiometric and enthalpy balances over the two segments. Experience has shown that the most important balances are those of the bottom segment.

The position of the chemical reserve zone in the furnace is described in idealized form in Figure 19, which also shows the location of the conceptual split of the furnace into top and bottom segments.

Figure 19: Conceptual division of the blast furnace into top and bottom segments. The position of the dividing plane in relation to the chemical and thermal reserve zones is shown.
Conceptual division of the blast furnace specifically through its chemical reserve zone has the advantage that it imposes two new conditions, viz.:

- The net mass of each element leaving the top segment across the division must equal the net mass of that element crossing into the bottom segment.
- The net enthalpy in the material leaving the top segment across the division must equal the net enthalpy crossing into the bottom segment.

The above conditions, which must be described by the enthalpy and stoichiometric equations of the segments, arise from the observations that:

- There is no carbon gasification in or above the chemical reserve zone, i.e. all carbon in the charge descends through the top segment into the bottom before it takes part in any chemical reactions;
- The only iron-bearing material crossing the division is wustite, Fe$_{0.947}$O, i.e. all higher oxides have been reduced to Fe$_{0.947}$O by the time they descend into the chemical reserve but all reduction to Fe takes place below the chemical reserve.

The inputs and outputs of the two segments are shown in Figure 20.

![Figure 20](image-url)
As noted previously, conditions in and above the chemical reserve zone are such that coke does not take part in any chemical reactions in the top segment of the furnace. This means that the carbon of the charge descends unreacted into the wustite reduction zone and that, consequently, the amount of carbon entering the wustite reduction zone is the same as the amount entering the furnace, i.e.

\[ n^i_C = n^{\text{wrz}}_C \]

Similarly, because the amounts of carbon entering the furnace and the wustite reduction zone are identical, the amounts leaving must also be identical, i.e.

\[ n^o_C = n^{0\text{wrz}}_C \]

Since from equation [1b],

\[ n^i_C = n^o_C \ldots \ldots [1b] \]
\[ . \]
\[ . \]
\[ . \]
\[ n^{\text{wrz}}_C = n^{0\text{wrz}}_C \]

The abbreviation wrz refers to the bottom segment of the furnace and it is known as the wustite reduction zone because it is in this segment that final reduction occurs. This equation [12] is important because when compared with equations [4] and [7], we have that:

\[ n^g_C + (\text{C}/\text{Fe})^m = n^{g\text{wrz}}_C + (\text{C}/\text{Fe})^m \quad \text{or} \quad n^A_C + (\text{C}/\text{Fe})^m = n^{A\text{wrz}}_C + (\text{C}/\text{Fe})^m \]

That is, \( n^g_C = n^{g\text{wrz}}_C \) or \( n^A_C = n^{A\text{wrz}}_C \)

This is consistent with the assumption that in and above the chemical reserve zone there are no reactions with solid carbon to form CO or CO₂. This being the case, the amount of carbon ascending as CO and CO₂ from the bottom segment must, as the equation shows, be the same as the amount of carbon leaving the furnace in the top gas.

Accordingly, for the wustite reduction zone, equations [6b] and [6c] applies as follows:

\[ (\text{O}/\text{Fe})^{x\text{wrz}} = n^{g\text{wrz}}_C \cdot (\text{O}/\text{C})^{\text{wrz}} - n^B_O \ldots \ldots \ldots [12a] \]
\[ (\text{O}/\text{Fe})^{x\text{wrz}} = n^{A\text{wrz}}_C \cdot (\text{O}/\text{C})^{\text{wrz}} - n^B_O \ldots \ldots \ldots [12b] \]

Since the conceptual division of the blast furnace through its chemical reserve zone imposes the condition that the only iron-bearing material entering the bottom segment is wustite Fe_{0.947}O, it implies that:

\[ 1 = (\text{O}/\text{Fe})^{x\text{wrz}} = (\text{O}/\text{Fe})^{\text{Fe}_{0.947}O} = \frac{0.947}{1.056} = 1.06 \]

If we assume that the gas in the chemical reserve, i.e. the gas leaving the bottom segment, has the equilibrium composition for the reaction:

\[ \text{CO} + \text{Fe}_{0.947}O \rightleftharpoons 0.947\text{Fe} + \text{CO}_2 \]

at a thermal reserve temperature of 1200 K. From data in NIST-JANAF Thermochemical Tables, this equilibrium composition is:

\[ X^g_{\text{CO}} \approx 0.7 \quad \text{and} \quad X^g_{\text{CO}_2} \approx 0.3 \]

From equations [2a] or [2b]:

59
\[(O/C)^{wrz}_{\text{g}} = 2 - X_{CO}^{g} = 2 - 0.7 = 1.3\]

or
\[(O/C)^{wrz}_{\text{g}} = X_{CO_{2}}^{g} + 1 = 0.3 + 1 = 1.3\]

Substitution of these numerical values into equation [12b] leads to:
\[1.06 = 1.3 \cdot n_{C}^{A} - n_{O}^{B} \ldots \ldots [12c]\]

This is a single equation in terms of the two operating parameters \(n_{C}^{A}\) and \(n_{O}^{B}\), moles of blast oxygen (O) and moles of active carbon per mole of product Fe. It might also be noted here that maintenance of continuity demands that the sum of the stoichiometric equations of the segments must equal the stoichiometric equation of the whole furnace. This being the case, the stoichiometric equation for the top segment is equation [6c] minus equation [12c]; that is:

In
\[\frac{(O/Fe)^x - 1.06}{n_{C}^{A}} = [(O/C)^{g} - 1.3] \ldots \ldots [13a] \]

addition to equations or
\[(O/Fe)^x = n_{C}^{A} \cdot (O/C)^{g} - [1.3 \cdot n_{C}^{A} - 1.06] \ldots \ldots [13b]\]

we need only one further equation before the remaining operating requirements of the furnace (\(n_{C}^{A}\) and \(n_{O}^{B}\)) are fully defined. This additional equation comes from the enthalpy balance in the wustite reduction zone, as shown in the following section.

The items in the enthalpy balance of the wustite reduction zone are shown in Figure 18. \(Fe_{0.947}O\) and C enter at the thermal reserve temperature (1200 K); gas of the chemical reserve composition leaves at 1200 K, and pig iron is produced at 1800 K. Blast enters at a temperature \(T_{B}\) depending upon the particular operation.

In their —*The Iron Blast Furnace: Theory and Practice*, Peacey and Davenport (1979), showed that the demand – supply form of the enthalpy equation for the bottom segment (wustite reduction zone) of a conceptually divided furnace is:

\[D^{wrz} = S^{wrz} = n_{C}^{A} \cdot (198\ 000) + E^{B} \cdot n_{O}^{B} - \frac{1}{2} H_{1200(0_{2})}^{o}(1.3 \cdot n_{C}^{A} - n_{O}^{B} - 1.06)\]

Where,
- \(D^{wrz}\) = heat demand for reduction, heating and melting in the bottom segment (wustite reduction zone),
- \(S^{wrz}\) = enthalpy (heat) supply in the bottom segment (wustite reduction zone),
- 1.06 = \((O/Fe)^{wtrz}\) \{O/Fe ratio for wustite \((Fe_{0.947}O)\)\}
- 1.3 = \((O/C)^{g}_{wrz}\) \{CO/CO_{2}/Fe/\(Fe_{0.947}O\) equilibrium at 1200 K\}
- 198 000 = \[\{2 - (O/C)^{g}_{wrz}\} \cdot H_{1200(0_{2})}^{f} + \{(O/C)^{g}_{wrz} - 1\} \cdot H_{1200(0_{2})}^{f}\]
- \(E^{B}\) = the enthalpy which the dry blast air has in excess of that which it would have at the thermal reserve temperature. It is positive when blast temperature, \(T_{B}\) > 1200 K; zero when \(T_{B} = 1200 K\); and negative when \(T_{B} < 1200 K\.)
But we can eliminate
$$\frac{1}{2}H_{1200(\text{O}_2)}^0(1.3 \cdot n_C^A - n_O^B - 1.06)$$
as it reduces to zero when equation [12c] is considered.

$$D_{wrz} = S_{wrz} = n_C^A \cdot (198\,000) + E \cdot n_O \quad \ldots \ldots \quad [14]$$

Equations [12c] and [14] indicate that once the enthalpy of the blast, $n_O^B$, and the heat demand of the wustite reduction zone, $D_{wrz}$, are specified we have two equations with two unknowns ($n_C^A$ and $n_O^B$), which can be solved simultaneously to obtain values for $n_C^A$ and $n_O^B$. Thus the operating requirements of the process, $n_C^A$ (carbon taking part in reduction and heating per mole of product Fe), and $n_O^B$ (oxygen in blast air per mole of product Fe) are uniquely defined. Alternatively, for calculation purposes, equations [12c] and [14] may be combined by substituting $n_O^B = 1.3 \cdot n_C^A - 1.06$ from equation [12c] into equation [14] thus:

$$D_{wrz} = S_{wrz} = n_C^A \cdot (198\,000 + 1.3 \cdot E) - 1.06 \cdot E \quad \ldots \ldots \quad [15a]$$

Equation [15a] illustrates clearly how $n_C^A$ is affected by changes in $D_{wrz}$ and $E$. It provides a straightforward method for calculating $n_C^A$ from numerical values of $D_{wrz}$ and $E$. Blast oxygen, $n_O^B$, is then readily determined from $n_C^A$ by means of equation [12c].

Equation [15a] can be rewritten as follows:

$$D_{wrz} = n_C^A \cdot [1.3 \cdot (282\,000 + E) - 169\,000] - 1.06 \cdot E \quad \ldots \ldots \quad [15b]$$

Where:

$$282\,000 = H_{1200\text{co}}^f - H_{1200\text{co}_2}^f$$

The values of $D_{wrz}$ and $E$ can be calculated as follows:

$$D_{wrz} = n_{Fe_{0.947}O} \cdot \left( \Delta H_{1200}^{\text{Fe}_{0.947}O} + \left( H_1^{\text{Fe}_{0.947}O} - H_1^{\text{Fe}_{0.947}O(s)} \right) + (\text{C/Fe})^m \cdot \left( H_{1200\text{co}}^o - H_{1200\text{co}}^o \right) \right)$$

Note that since $1.06 \text{Fe}_{0.947}O \xrightarrow{\text{yields}} 1 \text{Fe}, n_{Fe_{0.947}O} = 1.06$

$$D_{wrz} = 280\,900 + 38\,000 + 11\,000 \equiv 330\,000 \text{ kJ (kg mole of product Fe)}^{-1}$$

This value of $D_{wrz}$ is for the simplest case in which the only demand is for producing a 5% carbon pig iron at 1800 K. $D_{wrz}$ will vary, of course, with the amount of gangue and slag in the furnace, the rate of radiative and convective heat loss from the bottom segment and the enthalpy demands of subsidiary reactions in the bottom segment. Other demands, e.g. for slag heating and melting, are simply added to this base value.

Recall that $E$ represents the enthalpy in the blast above that which it would have at 1200 K. Therefore, at 1400 K, we have:
Insertion of this value of $E^B$ and the specified value of 330 000 kJ for $D^{wrx}$ into equation [15] gives:

$$D^{wrx} = n_C^A \cdot (198 000 + 1.3 \cdot E^B) - 1.06 \cdot E$$

$\Rightarrow 330 000 = n_C^A \cdot (198 000 + 1.3 \times 16 667) - 1.06 \times 16 667$

\[\therefore n_C^A = \frac{n_O^B}{330 000} = \frac{330 000}{202 000} = 1.63\] moles of C per mole of product Fe.

From equation [12c], is determined as follows:

\[n_O = 1.3 \cdot n_C - 1.06 = 1.3 \times 1.63 - 1.06\]

\[\therefore n_O^B = 2.119 - 1.06 \approx 1.06\] moles of O per mole of product Fe.

We can at this point use equation [6c] to compute $(O/C)^g$ and hence the top gas composition for haematite charge;

\[
(O/C)^g = \frac{(O/Fe)^x + n_O^B}{n_C^A} = \frac{1.5 + 1.06}{1.63} = 1.57
\]

This O/C ratio of 1.57 is equivalent to the following CO and CO$_2$ mole fractions, using equations [2a], [2b] and [2c]:

\[
X_{CO}^g = 2 - 1.57 = 0.43
\]

\[
X_{CO_2}^g = 1.57 - 1 = 0.57
\]

Confirm $X_{CO}^g + X_{CO_2}^g = 0.43 + 0.57 = 1$ \hspace{1cm}$\therefore$ [2c]

That is, the carbonaceous portion of the top gas comprises 43% CO and 57% CO$_2$.

Furthermore, from equations [8a], [8b] and [8c], we can determine the moles of CO, CO$_2$ and N$_2$ for the blast furnace operation:

\[
n_{CO} = n_C \cdot X_{CO}^g = 1.63 \times 0.43 = 0.7\] moles per mole of product Fe

\[
n_{CO_2}^g = n_C^A \cdot X_{CO_2}^g = 1.63 \times 0.57 = 0.93\] moles per mole of product Fe

\[
n_{N_2}^g = 0.21 \times \frac{1}{2} \cdot n_O^B = 0.79 \times \frac{1}{2} \times 1.06 \approx 2.0\] moles per mole of product Fe
This gives the overall top gas composition as 19.3% CO, 25.6% CO\(_2\), and 55.1% N\(_2\).

For example, 
\[
\frac{0.7}{0.7+0.93+2.0} \times 100 = \frac{0.7}{3.63} \times 100 = 19.3\% \text{ for CO}
\]

**Note:** Equations [14] and [15] also show clearly that an increase in \(D^\text{WRT}\) (for minor endothermic reactions, for heating and melting of gangue and slag and for convective and radiative heat losses) inevitably leads to increased blast-furnace demands for carbon (\(n^A_C\)) and blast oxygen (\(n^B_O\)). Thus large slag falls (per tonne of Fe) and heat losses lead to high coke demands and low furnace productivities. Increases in blast temperature (i.e. increases in \(E^B\)) result in smaller requirements for carbon and blast oxygen.

**Slopes and Coordinates of the Operating Equations**

A summary of the slopes and coordinates of the operating equations derived so far is as follows:

i. \((O/Fe)^x = n^A_C \cdot (O/C)^g - n^B_O \ldots \ldots \ldots \ldots [6c]\)

Equation [6c] is the stoichiometric equation for the whole blast furnace, and it describes a straight line, which on O/C vs. O/Fe axes has the slope \(n^A_C\) and passes through the points:

\[
\frac{O/C}{\text{Intercept point on } O/Fe \text{ axis}} = \left(\frac{0}{Fe}\right)^x - \frac{D}{283 000} = n^A_C \cdot \frac{172 000}{283 000} - n^B_O \ldots \ldots \ldots [11a]
\]

\(x_1, y_1\) and \(x_2, y_2\) as follows:

ii. Similarly, equation [11a] describes a line of the same slope as that of equation [6] but in this case through the points:

\[
\frac{O/C}{\text{Intercept point on } O/Fe \text{ axis}} = 0, O/Fe = -n^B_O \quad \text{and} \quad \frac{O/C}{\text{Coordinates of one of the midpoints on the line segment}} = \left(\frac{172 000}{283 000}\right), O/Fe = \left(\frac{O}{Fe}\right) - \frac{D}{283 000}
\]

iii. \(1.06 = 1.3 \cdot n^A_C - n^B_O \ldots \ldots \ldots \ldots [12c]\)

Similarly, equation [12c] is for the bottom segment stoichiometry and describes a line of the same slope as that of equation [6] but in this case through the points:

\[
\frac{O/C}{\text{Intercept point on } O/Fe \text{ axis}} = 0, O/Fe = -n^B_O \quad \text{and} \quad \frac{O/C}{\text{The wustite reduction point of the chemical pinch point, that is, point } W \text{ in Figure 19}} = 1.3, O/Fe = 1.06
\]

iv. \((O/Fe)^x = n^A_C \cdot (O/C)^g - [1.3 \cdot n^A_C - 1.06] \ldots \ldots \ldots [13b]\)
Accordingly, equation [13b] represents the top segment stoichiometry, and describes a part or segment of the same line (same slope) but passing through the points:

\[
\begin{align*}
O/C &= 0, O/Fe = -[1.3 \cdot n_C^A - 1.06] \\
\text{Intercept point on O/Fe axis} \\
O/C &= (O/C)^B, O/Fe = (O/Fe)^X \\
\text{Top gas & Incoming iron oxide}
\end{align*}
\]

\[D^{wtrz} = n_C^A \cdot [1.3 \cdot (282 000 + E^B) - 169 000] - 1.06 \cdot E^B \ldots \ldots \ldots \ldots \ldots [15b]\]

In the same vein, equation [15b] which is the combined stoichiometric/enthalpy equation can be plotted on O/C vs. O/Fe axes. For purposes of plotting a graph, Peacey and Davenport (1979) cumbersomely rearranged equation [15b] to:

\[
1.06 - \left(1.06 - \frac{D^{wtrz} + 1.06 \cdot E^B}{282 000 + E^B}\right) = n_C^A \cdot \left[1.3 - \frac{169 000}{282 000 + E^B}\right] \ldots \ldots \ldots [15c]
\]

Equation [15c] describes a straight line with slope \(n_C^A\) passing through the points:

\[
\begin{align*}
\frac{O/C}{282 000 + E^B}, \quad O/Fe &= 1.06 - \frac{D^{wtrz} + 1.06 \cdot E^B}{282 000 + E^B}
\end{align*}
\]

The thermal pinch point around which the operating line rotates, i.e. point P in Figure 19

\[
O/C = 1.3, \quad O/Fe = 1.6
\]

The wustite reduction point or the chemical pinch point that is, point W in Figure 19

Equation [15c] may be simplified as follows. Since D or \(D^{wtrz}\) and \(E^B\) can be fixed or specified in a straightforward manner depending on the nature of the iron ore and blast temperature, the LHS is fixed, that is:

\[
\left[1.06 - \left(1.06 - \frac{D^{wtrz} + 1.06 \cdot E^B}{282 000 + E^B}\right)\right] = \left[\frac{D^{wtrz} + 1.06 \cdot E^B}{282 000 + E^B}\right] = \text{constant} = \left[\frac{O}{Fe}\right]_P
\]

Where, P is thermal pinch point (P).

Similarly, on the RHS, \(\left[1.3 - \frac{169 000}{282 000 + E^B}\right]\) is fixed and can be simplified to \(\left[\frac{O}{C}\right]_P\)

Since the intercept on O/Fe axis is always at \(n_O^B\) and some oxides other than iron oxide (e.g. SiO₂, MnO, etc.) are also reduced thereby contributing oxygen to \(n_O^B\) (say \(n_O^M\)); the simplified general operating equation may be written as:

\[
\left[\frac{O}{Fe}\right]_P = n_C^A \cdot \left[\frac{O}{C}\right]_P - \left[\frac{O}{C}\right]_P + n_O^B + n_O^M \ldots \ldots \ldots \ldots \ldots [16]
\]

Where,

- P refers to the invariant point known as thermal pinch point, whose coordinates are, in general, \((O/C)_P\) and \((O/Fe)_P\) (see Figures 21 and 22);
- \(n_O^M\) represents oxygen removed from oxides other than iron oxide (i.e. \(||OB||\) in Figure 22).

In summary;
• Each of the equations [6c], [11a], [12c], [13b] and [15b] describes a straight line of slope \( n^A_C \);
• Thus all the equations describe portions or segments of the same straight line passing through the points listed;

<table>
<thead>
<tr>
<th>O/C</th>
<th>O/Fe</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[</td>
<td>Point of Interception on O/Fe axis</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>Point of Interception on O/Fe axis</td>
</tr>
<tr>
<td>[\frac{169,000}{282,000 + E^B}]</td>
<td>[1.06 - \frac{D^{wruz} + 1.06 \cdot E^B}{282,000 + E^B}]</td>
<td>Thermal pinch point, i.e. point H in Figure 21</td>
</tr>
<tr>
<td>1.3</td>
<td>1.06</td>
<td>Che21 mica1 pinch point, i.e. point W in Figure</td>
</tr>
<tr>
<td>((O/C)^8)</td>
<td>((O/Fe) \times )</td>
<td>Top gas O/C ratio and Iron oxide O/Fe ratio,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i.e. point A in Figures 21 and 22</td>
</tr>
</tbody>
</table>

The positions of these points are slightly altered by hydrocarbon injection and/or oxygen enrichment of the blast into the furnace. However, the effects of these additions can be readily included on the Rist diagram (Figures 21 and 22).

Table 9: Data for the blast furnace operation plotted in Figure 21*

<table>
<thead>
<tr>
<th>ITEM</th>
<th>QUANTITY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specification</td>
</tr>
<tr>
<td>Fe</td>
<td>\Fe_2O_3</td>
</tr>
<tr>
<td>Input iron oxide</td>
<td>\Fe_{0.947}O</td>
</tr>
<tr>
<td>Iron oxide entering wrz</td>
<td>5%C</td>
</tr>
<tr>
<td>Pig iron</td>
<td></td>
</tr>
<tr>
<td>Blast temperature</td>
<td></td>
</tr>
<tr>
<td>Blast enthalpy</td>
<td></td>
</tr>
</tbody>
</table>

*(This value of \(D^{wruz}\) is realistic enough to cover thermal demands for decomposition of flux, heating and melting of slag, heat losses and minor endothermic reactions in the furnace, in addition to reducing iron oxide and melting the iron and dissolving 5\% C in it).*
The Rist operating diagram shown in Figure 21 was plotted using the above O/C and O/Fe relations for the points through which the line passes based on the data in Table 9. **As an assignment** plot the same graph and show how you determined the coordinates of the chemical pinch point (W), the thermal pinch point (P) and the slope \((\Pi_C^A)\). Show also how you determined \(\Pi_C^1\), \(\Pi_C^B\) and the top gas composition \((O/C)g\). Hence calculate the complete top gas analysis (% CO, % CO\(_2\), and % N\(_2\)). What is the composition of the carbonaceous portion of the top gas (i.e. \(X_{CO}^g\) and \(X_{CO_2}^g\) in percentages).

**Description of the Rist Diagram (Figure 22)**

The ordinate (O/Fe axis), in addition to oxygen combined with iron gives oxygen removed by partial reduction of SiO\(_2\), MnO, P\(_2\)O\(_5\), etc. as well as oxygen introduced through the blast, all related to the iron content of the burden. For practical reasons, the zero point for the O/Fe axis is chosen where all oxygen has been removed from the iron oxides. However, it does not imply that oxygen from SiO\(_2\), MnO, P\(_2\)O\(_5\), etc., and from the blast have negative values. Thus in Figure 22:

- \(\text{b} = \{\text{the vertical distance}|OB| = |XB|\}\) gives oxygen removed from SiO\(_2\), MnO, P\(_2\)O\(_5\), etc. and
- \(\text{z} = \{\text{the vertical distance}|BZ|\}\) gives oxygen in the blast.
- \(O/C = 1\) if the furnace gas is considered free of H\(_2\) and H\(_2\)O and all C in the top gas is present as CO.
- Similarly, an abscissa value of O/C = 2 corresponds to all C in the top gas being present as CO\(_2\).

The equilibrium line for the reduction of the iron oxides at a constant temperature of, say, 950°C is shown in the upper right quadrangle of Figure 22, i.e. the thick zig-zag line. The 950°C (1223 K) temperature level is called the thermal pinch point of the blast furnace. The equilibrium line shows breaks at the compositions of the various iron oxides.

- For O/Fe values between 1.5 and 1.33, between haematite (Fe\(_2\)O\(_3\)) and magnetite (Fe\(_3\)O\(_4\)), the equilibrium gas is almost pure CO\(_2\), corresponding to O/C = 2. This means there is full utilization of CO to produce CO\(_2\) according to the reactions:
  \[3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \quad \parallel \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2\]
Figure 21: Blast furnace operating line (Rist diagram) as fixed by enthalpy point P and wustite reduction point W. The numerical values are for the blast furnace operation described in Table 9.
For O/Fe values between 1.33 and about 1.13, i.e. for equilibrium between magnetite ($\text{Fe}_3\text{O}_4$) and wustite ($\text{Fe}_x\text{O}$), the O/C ratio at 950°C is about 1.8. In this case, CO has not been fully utilized to produce $\text{CO}_2$; the furnace top gas will contain some CO. The following reaction is typical of the process:

$$\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \parallel \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$$

For O/Fe values between 1.06 and 0, i.e. for equilibrium between wustite ($\text{Fe}_{0.947}\text{O}$) and metallic iron (Fe), the O/C ratio at 950°C is about 1.3, which is still low utilization of CO.

$$1.06\text{Fe}_{0.947}\text{O} + \text{CO} = \text{Fe} + \text{CO}_2 \parallel \text{Fe}$$

For lower temperatures, which could apply for highly reactive ores, the magnetite–wustite line would shift towards lower O/C values; it shifts leftwards
decreasing to O/C = 1. At the same time, the wustite–iron line would shift toward higher O/C values; it shifts rightwards approaching O/C = 2.

The operating line \(|ZA|, |BA^I|, |BA^II|\) or \(|X \text{A}^\text{III}|\) must run or pass through the left of the equilibrium line in order for the furnace gas to be reducing to the iron oxides. As shown (Figure 22), the operating line \(|ZA|\) touches the equilibrium line at point W and this corresponds to initial reduction of wustite at 950°C. Point W may be called the **chemical pinch point** of the furnace. In principle any operating line which touches the equilibrium line at that point, and which does not cross the equilibrium line, would satisfy the chemical requirements (i.e. mass or stoichiometric balance) for a countercurrent ironmaking shaft furnace. Lines \(|BA^I|\) and \(|BA^II|\) in Figure 22 are such alternate lines that can meet the chemical requirements.

In an iron blast furnace, however, the thermal requirements (heat or enthalpy balance) would also have to be satisfied. This is obtained by the burning of a certain amount of carbon at the tuyeres, corresponding to the operating line having also to run through point Z on the ordinate axis. The actual position of point Z is calculated from a heat balance for the lower half of the furnace, taking into account the temperature of the blast \(T_B\), the slag volume, and heat losses \(D^{\text{wrtz}}\) takes care of all these. It can be shown that for a given blast temperature and heat loss, the operating line has to run through a certain point P (the **thermal pinch point** of the furnace), whether it touches point W or not. The reason for this is can be deduced as follows:

- The vertical distance \(\{a = |AY|\}\) on the ordinate axis corresponds to the amount of oxygen removed by indirect reduction. Indirect reduction uses CO or CO\(_2\) for the reduction of iron oxides. For example, between 400 to 950°C the following reactions can take place:

\[
\text{Fe}_2\text{O}_3 + 1.5\text{CO}_2 + 3.75\text{CO} = 2\text{FeO} + 2.5\text{CO}_2 + 2.75\text{CO}
\]

and

\[
y = |YX| = |YO|
\]

\[
\text{FeO} + 0.5\text{CO} + 4.75\text{CO} = \text{Fe} + 1.5\text{CO} + 3.75\text{CO}
\]

- The vertical distance \(\{\) corresponds to the amount of oxygen removed by direct reduction. Direct reduction involves the reduction of iron oxides and/or other oxides such as SiO\(_2\), MnO, etc. by coke, C. For example, between 950 to 1400°C the following direct reductions can take place:

\[
\text{FeO} + C = \text{Fe} + \text{CO}; \quad \text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}; \quad \text{MnO} + 2\text{C} = \text{Mn} + \text{CO}
\]

Where, the underscore indicates elements dissolved in iron, the molten pig iron.

- Recall that the vertical distance \(\{b = |OB| = |XB|\}\) corresponds to the amount of oxygen removed from SiO\(_2\), MnO, etc.

- All the direct reductions (that of iron oxides as well as reduction of SiO\(_2\), MnO, etc.) are strongly endothermic. Thus, the vertical distance \(\{y + b = |YO| + |OB| = |YB|\}\) gives a measure of the endothermic load on the lower half of the
Recall also that \( z = |\text{BZ}| \) corresponds to the amount of oxygen in the blast; and it gives a measure of the exothermic contribution from the tuyere reaction, i.e.

\[
C + O_2 = CO_2 \quad \text{or} \quad 2C + O_2 = 2CO
\]

If, due to poor indirect reduction, the extent of direct reduction is increased, the energy requirement has to be compensated for by burning more carbon at the tuyeres, i.e. by increased amount of blast. Two alternative operating lines which would satisfy the thermal requirements of the furnace are shown in Figure 22, pivoting around point P (i.e. the dashed lines). However, one of the lines (the one on the right side of point W) would not satisfy the chemical requirements.

The slope of the operating line corresponds to the ratio \((C/Fe)\), that is, the number of moles of carbon needed per mole of iron produced, not including the carbon which dissolves in the hot metal i.e. \((C/Fe)^m\). In effect, the slope is related as follows:

\[
\text{Slope} = \frac{\text{Vertical Interval}}{\text{Horizontal Interval}} = \frac{O/Fe}{O/C} = \frac{0}{C} = \frac{C/Fe}{0} = n_C^A = n_C^B = [n_C^0 - (C/Fe)^m]
\]

It can be deduced easily that low \(C/Fe\) ratios imply high iron yield, that is, improved productivity of the blast furnace. Figure 22 shows that the slope of the operating line decreases (i.e. low \(C/Fe\) values are obtained) if:

- the operating line runs closer to the point W; which is achieved by using a highly reactive ore and closely countercurrent plug flow (i.e. following the sequence \(Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe\));
- less carbon is burned at the tuyeres, which is achieved by shifting the point P to the left, made possible by the use of a high blast preheat.

The \(CO_2/CO\) ratio of the top gas (which is related to the \(O/C\) values) is given by point A [points \(A^I, A^{II}, A^{III}\)], and it is seen that this increases with decreasing slope of the operating line. High \(CO_2/CO\) ratio implies high \(O/C\) value and vice versa. If \(CO_2\) dominates the top gas, \(O/C\) ratio tends towards 2.0. But if \(CO\) dominates, the \(O/C\) ratio tends towards 1.0. In between \(O/C\) values of 1.0 and 2.0, the top gas contains a mixture of \(CO\) and \(CO_2\). Maximum \(O/C\) ratio is always preferred (implying full utilization of \(CO\) for reduction).

Most modern blast furnaces operate with some hydrogen (\(H_2\)) and water vapour (\(H_2O\)) in the top gas, which derive from steam or hydrocarbons added to the blast. Even though the presence of \(H_2\) and \(H_2O\) requires some modification of the Rist diagram, it does not affect its principles. The operating line of a given blast furnace may be calculated from the concentration of \(CO_2\), \(CO\), and \(N_2\) in the top gas. \(N_2\) concentration gives a measure of the amount of blast used, and the amount of steam or hydrocarbon added to the blast. By comparing the operating line with the known equilibrium line (such as line \([ZA]\) passing through both P and W), it can be deduced how close it runs to point W, that is, how well the furnace is performing. Hence, the line \([ZA]\) passing through both P and W.
represents the best possible operating practice with a minimum coke rate (i.e. highest efficiency or productivity). This corresponds to the concept of an ideal blast furnace originally proposed by Gruner.

The principle of the Rist diagram can also apply in other ironmaking processes, such as DRI or sponge iron processes.

**OXYGEN – EXCHANGE DIAGRAM**

The countercurrent nature of the blast furnace implies that solid burden descending from the top encounters the ascending hot reducing gas, and this encounter leads to (i) *heat exchange*, i.e. heat transfer from gas to solid; (ii) *oxygen exchange*, i.e. oxygen transfer from solid (oxide ores) to gas (CO and CO₂). A metal oxide (say, MeO, Me₂O₃ or Me₃O₄) on reaction with carbon produces a gaseous mixture of CO and CO₂ as illustrated in Figure 23.

![Figure 23: Schematic illustration of the reaction of metal oxide and CO](image)

It affords us the technique to express the process thus:

\[
\begin{align*}
\text{MeO} + \text{C} &= \text{Me} + \{\text{CO}/\text{CO}_2\} \\
\text{Me}_2\text{O}_3 &\rightarrow \text{Me}_3\text{O}_4 \rightarrow \text{MeO} \rightarrow \text{Me}
\end{align*}
\]

The reaction sequence is ; e.g. for iron oxide, the sequence is Fe₂O₃ → Fe₃O₄ → FeO → Fe. In a countercurrent flow, oxygen is transferred from the solid oxide to the gaseous phase in form of CO or CO₂ or both.

**Case I:**

Consider the case where \(x\)-axis (O/C ratio) is 1.0 [i.e. for CO] and \(y\)-axis (O/Me or O/Fe ratio) is 1.5 [i.e. for Fe₂O₃] as depicted in the oxygen-exchange diagram (Figure 24). Passing CO through the shaft and assuming complete conversion to CO₂ [O/C = 2.0], i.e. we produce Me + CO₂ such that all \(\text{CO} \xrightarrow{\text{converts to}} \text{CO}_2\) as \(\text{Fe}_2\text{O}_3 \xrightarrow{\text{converts to}} \text{Fe}\).
The reaction is therefore:

\[
\text{FeO}_{1.5} + 1.5\text{CO} = \text{Fe} + 1.5\text{CO}_2
\]

or

\[
\frac{1}{2}\text{Fe}_2\text{O}_3 + \frac{3}{2}\text{CO} = \text{Fe} + \frac{3}{2}\text{CO}_2 \text{ or }
\]

\[
0.5\text{Fe}_2\text{O}_3 + 1.5\text{CO} = \text{Fe} + 1.5\text{CO}_2
\]

Figure 24: Oxygen exchange diagram for iron (or metal) oxide reduction

**Case II:**

In reality, 100% CO\(_2\) cannot be obtained. Consider the case where 50% CO and 50% CO\(_2\) are obtained and the Fe\(_2\)O\(_3\) is fully reduced to Fe / (see Figure 24); 

\[
\text{Slope} = \frac{\text{O/Fe}}{0/\text{C}} = \frac{\text{C/Fe}}{1.5 - 1.0} = 1.5 - 0 = 1.5 = 3 \text{ moles of C per mole of Fe.}
\]

It can be seen that the value of 1.5 was used for O/C ratio when the top gas composition is 50% CO and 50% CO\(_2\). The O/C ratio for 50% CO and 50% CO\(_2\) is calculated as follows:

\[
\frac{0}{\text{C}} = \frac{50}{100} \times 1.0 + \frac{50}{100} \times 2.0 = \frac{1}{2} \times 1.0 + \frac{1}{2} \times 2.0 = 0.5 + 1.0 = 1.5 \text{ or } \frac{3}{2}.
\]

Alternatively, applying \((O/C)^g = X_{CO}^g + 2 \cdot X_{CO_2}^g \ldots \ldots [2d]\)

\[
\Rightarrow (O/C)^g = 50\% + 2 \times 50\% = 0.5 + 2 \times 0.5 = 0.5 + 1 = 1.5
\]

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Notice that the slope of 3 indicates that 3 moles or grammes of C either free or in combination as CO is used per mole of Fe. Therefore, our chemical reaction must reflect it, thus:

\[
\frac{1}{2} \text{Fe}_2\text{O}_3 + 3\text{CO} = \text{Fe} + \frac{3}{2}\text{CO} + \frac{3}{2}\text{CO}_2
\]

or

\[
\frac{1}{2} \text{Fe}_2\text{O}_3 + 3\text{CO} = \text{Fe} + \frac{3}{2}\text{CO} + \frac{3}{2}\text{CO}_2
\]

In general, for any case;

\[
\frac{O}{C} = \frac{x + 2y}{x + y} = \frac{X_{\text{CO}} + 2 \cdot X_{\text{CO}_2}}{X_{\text{CO}} + X_{\text{CO}_2}} = \frac{1 + X_{\text{CO}_2}}{X_{\text{CO}} + X_{\text{CO}_2}} \quad \ldots \ldots [17a] \quad \text{[in mole fractions]}
\]

or

\[
\frac{O}{C} = \frac{x + 2y}{x + y} = \frac{n_{\text{CO}} + 2 \cdot n_{\text{CO}_2}}{n_{\text{CO}} + n_{\text{CO}_2}} \quad \ldots \ldots [17b] \quad \text{[in moles]}
\]

Where, \(x\) = molar concentration of CO (or its mole fraction) in the product;
\ny = molar concentration of CO\(_2\) (or its mole fraction) in the product.

Since we are considering a case of 50% CO and 50% CO\(_2\):

\[
\frac{5 \cdot (5)}{0.5 + (0.5)} = \frac{5}{0.5 + 0.5} = \frac{5}{1.0} = 1.5
\]

**Case III:**

Consider the case (see Figure 24) where on the \(x\)-axis we go from 0 to 2.0 (i.e. from coke with \(O/C = 0\) to CO\(_2\) with \(O/C = 2.0\)); and on the \(y\)-axis from 1.5 to 0 (i.e. from Fe\(_2\)O\(_3\) with O/Fe = 1.5 to Fe with O/Fe = 0). This is a case of direct reduction as carbon (coke) is used and not CO for the reduction, and Fe and CO\(_2\) are produced.

\[
\text{Slope} = \frac{0/\text{C}}{1.5/0} = \frac{C/\text{Fe}}{2.0-0} = \frac{1.5}{2.0} = \frac{3}{4} = 0.75 \text{ mole of C per mole of Fe.}
\]

The chemical reaction for the scenario is therefore:

\[
0.5\text{Fe}_2\text{O}_3 + 0.75\text{C} = \text{Fe} + 0.75\text{CO}_2
\]

or

\[
\text{FeO}_{1.5} + 0.75\text{C} = \text{Fe} + 0.75\text{CO}_2
\]

or

\[
\frac{1}{2} \text{Fe}_2\text{O}_3 + \frac{3}{4}\text{CO} = \text{Fe} + \frac{3}{4}\text{CO}_2
\]

**Case IV:**

Consider a more realistic case (see Figure 24) where on the \(x\)-axis we go from 0 to
1.5 (i.e. from coke with $O/C = 0$ to 50% CO and 50% CO$_2$ with $O/C = 1.5$); and on the $y$-axis from 1.5 to 0 (i.e. from Fe$_2$O$_3$ with $O/Fe = 1.5$ to Fe with $O/Fe = 0$). This is another case of direct reduction as carbon (coke) is used and not CO for the reduction; however, Fe and equal mixtures of CO and CO/Fe are produced.

The chemical reaction for this carbon rate is therefore:

\[
\frac{1.5}{0.5}Fe_2O_3 + C = Fe + 0.5CO + 0.5CO_2
\]

or

\[
FeO + C = Fe + 0.5CO + 0.5CO
\]

or

\[
\frac{1}{2}Fe_2O_3 + C = Fe + \frac{1}{2}CO + \frac{1}{2}CO_2
\]

Example:

Consider the reaction: \(MeO + CO = Me + CO_2\). Given that \(K = \frac{a_{Me}P_{CO_2}}{a_{MeO}P_{CO}} = \frac{P_{CO_2}}{P_{CO}} = 0.43\), determine \(X_{CO}\) and \(X_{CO_2}\) and O/C for the reaction.

Solution:

Assuming the sum of the partial pressures of CO and CO$_2$ is equal to 1 atmosphere. That is;

\[
P_{CO_2} + P_{CO} = 1 \text{ atm.}
\]

\[
\Rightarrow P_{CO_2} = 1 - P_{CO}
\]

\[
\therefore K = \frac{P_{CO_2}}{P_{CO}} = \frac{1 - P_{CO}}{P_{CO}} = 0.43
\]

\[
\Rightarrow 0.43P_{CO} = 1 - P_{CO}
\]

\[
\Rightarrow 0.43P_{CO} + P_{CO} = 1.43P_{CO} = 1
\]

\[
\therefore P_{CO} = \frac{1}{1.43} = 0.699 \approx 0.7
\]

\[
\therefore P_{CO_2} = 1 - P_{CO} = 1 - 0.7 = 0.3
\]

Since the partial pressure of a gas \(P_{gas}\) is proportional to its mole fraction \(X_{gas}\); then, \(P_{CO}\) is proportional to \(X_{CO}\), and \(P_{CO_2}\) is proportional to \(X_{CO_2}\).

Therefore:

\(X_{CO} = 0.7 \implies 70\% \text{ CO since } P_{CO} = 0.7 \text{ atm.}\)

\(X_{CO_2} = 0.3 \implies 30\% \text{ CO}_2 \text{ since } P_{CO_2} = 0.3 \text{ atm.}\)

\(O/C = X_{CO} + 2 \cdot X_{CO_2} = 0.7 + 2 \times 0.3 = 0.7 + 0.6 = 1.3\) [from equation [2d]]

Confirm that \(K = \frac{P_{CO_2}}{P_{CO}} = \frac{X_{CO_2}}{X_{CO}} = \frac{0.3}{0.7} = 0.43\)
Accordingly, from $\frac{X_{CO_2} + X_{CO}}{X_{CO}} = 1 \ldots \ldots [2b]$ it can be verified that:

$$K = \frac{P_{CO_2}}{P_{CO}} = \frac{X_{CO_2}}{X_{CO}} = \left[ \frac{1 - X_{CO}}{X_{CO}} \right] \quad \text{or} \quad \left[ \frac{X_{CO_2}}{1 - X_{CO_2}} \right] = \left[ \frac{1 - 0.7}{0.7} \right] \quad \text{or} \quad \left[ \frac{0.3}{1 - 0.3} \right] = 0.43$$

SLAG COMPOSITION OF THE BLAST FURNACE

There is a distribution of Si, Mn and S between metal and slag. The P content of the pig iron depends only on the P content of the ore charged, since under the conditions operating in the iron blast furnace, virtually all the phosphorus charged finds their way into the hot metal.

The primary slag results from the melting of partially reduced ore and once melting takes place tends to contain FeO, Al$_2$O$_3$ and SiO$_2$. As melting takes place and the molten slag encounters the hot coke, reduction of FeO occurs. The slag then begins to lose FeO and absorb CaO and MgO so that the secondary slag now formed changes to one based on the CaO-Al$_2$O$_3$-SiO$_2$-MgO system. The secondary slag forms before it reaches the hearth and as it moves down into the tuyere zone, C burns to give coke ash (Al$_2$O$_3$ and SiO$_2$). Coke ash joins the secondary slag in the hearth thereby increasing its Al$_2$O$_3$ and SiO$_2$ contents. Sulphur is also introduced into the slag as the coke ash is burnt. Basically, the final blast furnace slag contains 30–40 wt.% SiO$_2$, 5–15 wt.% Al$_2$O$_3$, 35–45 wt.% CaO, 5–15 wt.% MgO, 0–1 wt.% (Na$_2$O + K$_2$O), and 1–2.5 wt.% S. The MgO is added to reduce the melting temperature of slag. The blast furnace slag should have a melting temperature of 1400°C or less. In addition, the CaO/SiO$_2$ ratio should be high (about 1.1 to 1.2), in order to give good desulphurization.

SLAG – METAL EQUILIBRIA

a) Silicon Distribution

Silicon comes into the furnace in the form of silica or silicate partially in the ore (gangue) and partially in coke (coke ash) Pig iron picks up Si by the reaction:

$$\text{SiO}_2(s) + 2C = \text{Si} + 2\text{CO}; \quad \Delta G^0 = +593 \text{ 570} - 396.16T \text{ J}$$

At the bottom of the furnace, if the iron that is dripping through the slag is rich in Si, the reverse of the above reaction takes place. The equilibrium constant for the reaction is given by:

$$K = \frac{[\text{Si}] \cdot [\text{CO}]^2}{[\text{SiO}_2] \cdot [\text{C}]^2} = \frac{a_{\text{Si}} \cdot P_{\text{CO}}^2}{a_{\text{SiO}_2} \cdot a_{\text{C}}^2}$$

For the reaction to be at equilibrium, $\Delta G^0 = 0$.

$$\Rightarrow \Delta G^0 = 593 \text{ 570} - 396.16T = 0$$

$$\Rightarrow 396.16T = 593 \text{ 570}$$

$$\therefore T = \frac{593 \text{ 570}}{396.16} = 1498 \text{ K} = 1225^\circ \text{C}$$

That is, the equilibrium temperature for the reaction is 1498 K or 1225°C.
Again, at equilibrium, \( \Delta G^0 = -RT \ln K = -2.303RT \log K = 0 \).
That is, \( -2.303RT \log K = 593.570 - 396.16T \)
\[
\Rightarrow \log K = \frac{593.570 - 396.16T}{-2.303RT} = \frac{593.570 - 396.16T}{-2.303 \times 8.314T} = -\frac{593.570}{19.147T} + \frac{396.16T}{19.147T}
\]
\[
\therefore \log K = -\frac{31000}{T} + 20.7 \quad \ldots \ldots \ldots \ldots \quad [17]
\]
It can be verified that substitution of the equilibrium temperature of 1498 K into \[
[\log K = -\frac{31000}{T} + 20.7]
\] gives \( \log K = 0 \), from which \( K = 10^0 = 1 \).

At temperatures below and above the equilibrium temperature (1498 K), the values of \( \log K \) and \( K \) are as shown below:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \log K )</th>
<th>( K )</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>(K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1273</td>
<td>-3.652 0.0002</td>
<td>Forward reaction not favoured</td>
</tr>
<tr>
<td>1100</td>
<td>1373</td>
<td>-1.878 0.0132</td>
<td>Forward reaction not favoured</td>
</tr>
<tr>
<td>1200</td>
<td>1473</td>
<td>-0.345 0.4518</td>
<td>Forward reaction not favoured</td>
</tr>
<tr>
<td>1225</td>
<td>1498</td>
<td>0</td>
<td>1.0000 Forward and backward reaction at equilibrium</td>
</tr>
<tr>
<td>1300</td>
<td>1573</td>
<td>0.992</td>
<td>9.8175 Forward reaction favoured</td>
</tr>
<tr>
<td>1400</td>
<td>1673</td>
<td>2.170</td>
<td>147.91 Forward reaction favoured</td>
</tr>
<tr>
<td>1500</td>
<td>1773</td>
<td>3.215</td>
<td>1640.6 Forward reaction favoured</td>
</tr>
</tbody>
</table>

It is seen that the forward reaction \( \text{SiO}_2(s) + 2\text{C} = \text{Si} + 2\text{CO} \) is favoured by high temperatures above the equilibrium temperature of 1225°C. The Si content of hot metal is 0.3 – 1.0 wt.%.

**b) Sulphur Distribution**

Sulphur comes mostly from coke and the S content of pig iron should be less than 0.04 wt.%. The relevant reaction for sulphur removal from iron is:

\[
\text{CaO} + \text{S} + \text{C} = (\text{CaS}) + \text{CO}
\]

Where, the symbol ( ) indicates that the calcium sulphide is carried into the slag. At this point, let us take note that the symbol (\%S) implies \%S in slag, and [\%S] implies \%S in hot metal. Similarly, \( \text{S} \) and \( \text{C} \) imply sulphur and carbon embedded (dissolved) in the metal, respectively.

The modern approach is to express this equation in the ionic form using lime (CaO) as the source of \( \text{O}^{2-} \), thus:

\[
[S] + (\text{O}^{2-}) = (\text{S}^{2-}) + [\text{O}]
\]

From the point of **slag–metal partition**, the most important valuable thermodynamic properties of slags will be data on CaO and CaS. By using a gas–liquid reaction;

\[
\frac{1}{2}\text{S}_2 + \text{CaO} = \text{CaS} + \frac{1}{2}\text{O}_2
\]

or

\[
\frac{1}{2}\text{S}_2(g) + (\text{O}^{2-}) = (\text{S}^{2-}) + \frac{1}{2}\text{O}_2(g)
\]

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It is easy to control the pressure of $O_2$ and $S_2$ and measure the quantity of $S$ absorbed as sulphide capacity ($C_s$) of the slag given by:

$$C_s = \frac{p_{O_2}}{p_{S_2}^{1/2}} = \frac{P_{O_2}}{P_{S_2}^{1/2}} \vdots \vdots \vdots \vdots \vdots [18]$$

Sulphide capacity is defined as the potential capacity of a slag melt to hold sulphur as sulphide, at a given temperature. Mathematically, it is equal to (wt. % $S^2$ in slag) × $\left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2}$, where $P_{O_2}$ and $P_{S_2}$ are partial pressures of $O_2$ and $S_2$ in the gas at equilibrium with the slag. Sulphide capacity values are obtained by equilibrating liquid slag with a gas mixture of known $O_2$ and $S_2$ partial pressures. The higher the value of $C_s$, the more the slag can absorb sulphur. $C_s$ is a function of slag composition and temperature only, and its values can be tabulated or presented graphically for reference.

In blast furnace operations (i.e. ironmaking), there is high C and Si content in the pig iron and this keeps the oxygen potential in iron low. As a result, desulphurization is enhanced. In steelmaking conditions, we have high oxygen potential in the steel. To remove sulphur from the steel then, we need to make the activity of CaO in the slag to be high, i.e. by increasing the slag basicity. CaO is the most powerful desulphurizer among the basic oxides present in iron and steel making slags. CaO reacts with $S$ or FeS in hot metal and forms CaS which is soluble in the slag, and this forms the fundamentals of sulphur removal from hot metal to slag in the blast furnace. The sulphur partition coefficients (or sulphur distribution ratios) for these two pressures (ironmaking and steelmaking) are:

$$L_s = \frac{\% S}{\% S} \text{ ranges from 20 to 40 (for ironmaking slags)}$$

$$L_s = \frac{\% S}{\% S} \text{ ranges from 3 to 4 (for steelmaking slags)}$$

In contrast to the phosphorus control, the blast furnace conditions (its slag properties) are in favour of sulphur removal from hot metal to slag. Hence, desulphurization is much better in ironmaking than in steelmaking furnaces.

The main hot metal desulphurization reaction can be expressed as:

$$[FeS] + (CaO) = [FeO] + (CaS)$$

For which the equilibrium constant is:

$$K = \frac{a(FeS).a(CaO)}{a(FeO).a(CaS)}$$

The sulphur distribution ratio (partition coefficient) expressed as $L_s = (\% S)/[\% S]$ is closely linked to the equilibrium constant $K$, as shown. A lower activity of FeO and a higher activity of CaO in the slag are in favour of a higher $L_s$ at a given temperature.
Slag basicity (proportional to CaO activity in the slag) is a very important parameter for sulphur removal.

**Example:**
*Given a sulphur partition coefficient of 20, determine ($\%S$) and [%S] for the following scenario. Suppose we have coke with about 1% S and that we are using 500 kg of coke for 1 tonne (1000 kg) of iron and we are producing 250 kg of slag per tonne of iron.*

**Solution:**
Weight of coke = 500 kg
Weight of iron produced = 1000 kg
Weight of sulphur involved = 1% of 500 kg = \( \frac{1}{100} \times 500 \text{ kg} = 5 \text{ kg} \)
⇒ Weight of S per tonne of pig iron = 5 kg
Weight of slag expected = 250 kg

- If all S goes into metal (pig iron), then, [%S] = \( \frac{5 \text{ kg}}{1000 \text{ kg}} \times 100 = 0.5\% \)

Since in fact, not all the S goes into iron, but some are partitioned or distributed to slag, using a sulphur partition coefficient of 20, then:

\[ L_S = \frac{(%S)}{[%S]} = 20 \]

⇒ (%S) = 20·[%S]

- Taking a sulphur balance:
  Weight of S in slag + Weight of S in metal = 5 kg
  \[ \frac{250 \cdot (%S)}{100} + \frac{1000 \cdot [%S]}{100} = 5 \text{ kg} \]
  \[ \Rightarrow \frac{250 \cdot 20 \cdot [%S]}{100} + \frac{1000 \cdot [%S]}{100} = 5 \]
  \[ \Rightarrow 50 \cdot [%S] + 10 \cdot [%S] = 5 \]
  \[ \Rightarrow 60 \cdot [%S] = 5 \]
  \[ \Rightarrow [%S] = \frac{5}{60} = 0.083 \]

From (%S) = 20·[%S] = 20·0.083 = 1.67

**NB:** If all S were to go into the slag, then (%S) would be \( \frac{5}{250} \times 100 = 2 \)

Supposing the distribution or partition coefficient is 40 and not 20, then we will have [%S] = 0.045 and (%S) = 1.82. To achieve the high partition coefficient of 40, the slag coefficient should be increased. High (%S)/[%S] is very vital to S removal. There is an increase nowadays to treat the metal outside the furnace (i.e. in a ladle) with a desulphurizing agent. This is known as **ladle desulphurization**. One such treatment uses...
soda ash (Na$_2$CO$_3$) as a desulphurizing agent to treat a pool of molten metal and liquid slag, thus:

$$S + Na_2CO_3 + 2C = Na_2S + 3CO$$

or

$$S + Na_2CO_3 + Si = Na_2S + SiO_2 + CO$$

Other desulphurizing processes for pig iron are based on the use of solid lime (CaO), calcium carbide (CaC$_2$), or calcium cyanamide (CaCN$_2$). In all cases the reaction product is solid calcium sulphide (CaS) which goes into the slag.

c) Phosphorus Distribution

In the blast furnace, phosphorus originates from coke, iron ore, and flux in the form of P$_2$O$_5$. Silica helps in breaking of the phosphate bond and releasing free P$_2$O$_5$ gas, and thus promotes the reduction indirectly. P$_2$O$_5$ vapour will react with carbon via Boudouard reaction or be directly reduced with carbon when it passes through the coke. The reduction of P$_2$O$_5$ is almost complete, and no physical or chemical condition can influence it. More than 90% of the phosphorus load enters the iron and the rest is lost either in the slag or in the flue gas or is absorbed in the refractory linings. Therefore, production of low P hot metal is only possible by using low P-bearing coke and ore. Dephosphorization requires oxidizing conditions, and cannot be conducted in the blast furnace, which operates under reducing atmosphere. All phosphorus is therefore removed during oxygen steelmaking in most of the steelmaking operation.

d) Manganese Distribution

Manganese occurs in the burden as oxides (MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$) and carbonate (MnCO$_3$) or silicate and phosphate if converter slag is charged. Reduction of manganese oxides are also stage-wise similar to iron oxides, and until MnO the reduction reactions take place in the upper and middle zone of the blast furnace via —indirect reduction! with CO gas. MnO is more difficult to be reduced with CO, and is mostly through direct reduction in the lower zone (bosh or belly) via Boudouard reaction. Further reduction of MnO by silicon in the hearth can also take place. High Mn recovery is preferred in most cases and it is an alloying element in steelmaking. Normally about 50–70% of manganese is recovered in the blast furnace to produce hot metal for steelmaking.

The basic equations governing Mn distribution are: a)

$$Mn(s) + \frac{3}{2}O_2 \rightarrow MnO \quad \Delta G^\circ = -408,344 + 88.83T \text{ J}$$

and

$$C(s,\text{graphite}) + \frac{3}{2}O_2 \rightarrow CO \quad \Delta G^\circ = -118,050 - 84.39T \text{ J}$$

b) from which we can get the overall reaction.

Example:
Given reactions (a) and (b) as above, find the overall reaction governing Mn distribution, and hence find the $\Delta G^0$ for the overall reaction.

**Solution:**
The overall reaction is obtained by Hess’s law. First, reverse reaction (a) and change the sign of its $\Delta G^0$. That is,

\[ \text{MnO}_s = \text{Mn}_s + \frac{1}{2}\text{O}_2 (g) \quad \Delta G^0 = +408,344 - 88.83T \text{ J} \]

Second, add reaction (b) to the reversed reaction (i.e. a. ii) to obtain: c)

\[ \text{MnO}_s + \text{C}_{(s, \text{ graphite})} = \text{Mn}_s + \text{CO} (s,g) \quad \Delta G^0 = +290,294 - 173.22T \text{ J} \]

The Mn partition ratio (related to the equilibrium constant) for the overall reaction [reaction (c)] is:

\[ K = \frac{[\text{Mn}] \cdot [\text{CO}]}{[\text{MnO}] \cdot [\text{C}]} = \frac{a_{\text{Mn}} \cdot P_{\text{CO}}}{a_{\text{MnO}} \cdot a_C} \]

If $a_C = 1$ and $P_{\text{CO}} = 1$ atmosphere, then;

\[ K = \frac{a_{\text{Mn}}}{a_{\text{MnO}}} \]

The student can verify that, for this reaction,

\[ \log K = -\frac{15161}{T} + 9.05 \ldots \ldots [19] \]

The effect of an increase in temperature is to raise the partition ratio for a given carbon activity and CO pressure.

**Example:**
*Determine the partition ratio for equation [19] at unit carbon activity, unit partial pressure of CO and 1327°C. Determine also the equilibrium temperature for reaction (c) above.*

**Solution:**
\[ T = 1327°C + 273 = 1600 \text{ K} \]

\[ \therefore \log K = \log \frac{a_{\text{Mn}} \cdot P_{\text{CO}}}{a_{\text{MnO}} \cdot a_C} = \log \frac{a_{\text{Mn}}}{a_{\text{MnO}}} = -\frac{15161}{T} + 9.05 = -\frac{15161}{1600} + 9.05 \]

\[ \Rightarrow \log K = -9.475 + 9.05 = -0.425 \]

\[ \Rightarrow K = \frac{a_{\text{Mn}}}{a_{\text{MnO}}} = 10^{-0.425} = 0.376 \]

That is, at 1600 K (1327°C), $a_{\text{Mn}} = 0.376$ whereas $a_{\text{MnO}} = 1.000$
At equilibrium, 
\[ \Delta G^\circ = +290,294 - 173.22T = 0 \]
\[ \Rightarrow 173.22T = 290,294 \]
\[ \therefore T_{\text{equilibrium}} = \frac{290,294}{173.22} \approx 1676 \text{ K} = 1403^\circ \text{C} \]

Hence, above 1403°C, production of Mn will be favoured. The influence of temperature is to increase the recovery of Mn; and a 200°C rise in temperature, other factors being the same, the Mn recovery is increased eleven fold. For example, at 1800 K (1527°C = 1327°C + 200°C), if \( a_{\text{Mn}} \) and \( P_{\text{CO}} \) remain unity, then;

\[ \log K = \log \frac{a_{\text{Mn}}}{a_{\text{MnO}}} = -\frac{15,161}{T} + 9.05 = -\frac{15,161}{1800} + 9.05 = -8.423 + 9.05 = 0.627 \]
\[ \Rightarrow K = \frac{a_{\text{Mn}}}{a_{\text{MnO}}} = 10^{0.627} = 4.236 \]

Comparing, we have that \( K_{1527°C} \) is eleven times bigger than \( K_{1327°C} \). This confirms that 57°C is eleven times bigger than 7°C.

**BLAST FURNACE CHARGE CALCULATIONS (BURDENSING)**

Charge balance or material balance must be ensured in all metallurgical operations, i.e. every gramme of each element entering the system must be accounted for in the products leaving the system. Provided accurate analyses (compositions) and weights (or volumes) of all reagents and products are available, setting up a material balance is an easy matter. In many situations, however, some of the required data are unavailable and a certain amount of indirect computation is necessary to establish a material balance.

Charge calculations are done by assuming a material balance and then working backward from it to determine the exact quantities of concentrate (iron ore), flux (limestone), fuel (coke), etc., that must be supplied to the system to yield the desired products. The term _charge_ in common usage refers to the materials fed at the top and therefore includes the fuel: the ore and flux without the fuel is sometimes termed the _burden_. Burden is therefore the proportion of ore and flux to fuel, in the charge of a blast furnace. Charge calculations for the iron blast furnace is called _‘burdening’_ the furnace; the ore and flux together constitute the _burden_ on the furnace and fuel. From the economic standpoint, the hot metal produced in iron smelting is usually the most important product, but from the point of view of the blast furnace operator, the slag is the most important product. Since metals usually melt at lower temperatures than slags, there will seldom be any trouble with the metal if the slag melts easily and runs freely. Most of the difficulties encountered in the operation of smelting furnaces result from
the fact that the problem of the furnace operator is to adjust his furnace charge to produce a slag that has the required characteristics.

The first thing to be decided in charge calculation is the composition of the slag to be produced. Past experience, coupled with information about the melting points and viscosity of various slags, will usually show the operator must aim for a composition between certain definite limits. This is complicated by the fact that the operator is seldom free to choose his ores and fluxes—he must make his charge of whatever material is available and do it in such a way as to use up all the available material. In an iron blast furnace, for example, it may be necessary to use as much of a certain ore as possible, because it is cheaper than other more desirable ones. If an iron ore is high in phosphorus, it will be necessary to mix it with enough low-phosphorus ore to keep the phosphorus content of the pig iron below a certain prescribed limit.

The operator must know how much fuel will be required by the furnace in smelting a tonne of charge, which impurities will enter the hot metal and which can be held in the slag, which substances will be lost in the top gases, the amount of dust loss, etc. When all these questions have been considered, the operator is ready to calculate the composition of the furnace charge. [See Assignment Problem A4]

Example 1:
An iron blast furnace is to smelt an ore mixture having the following composition: 60% Fe, 10% SiO₂, and 4% CaO. The available flux contains 92% CaCO₃ and 8% SiO₂. The coke contains 90% C, 7% SiO₂, and 3% CaO. Determine the weight of ore, flux, and coke to be charged to yield 1000 kg of pig iron containing 95% Fe, 4% C, and 1% Si, and a slag having the ratio SiO₂:CaO = 1:2, assuming that the furnace requires 950 kg of coke per tonne of pig iron.

Solution:
- Weight of Fe in pig iron = 1000 × 0.95 = 950 kg

Since 60% of the ore is Fe and weight of Fe to be produced is 950 kg;
- \( \text{Weight of ore required} = \frac{950}{0.60} \approx 1583 \text{ kg} \)
- Weight of SiO₂ in pig iron = 1000 × 0.01 = 10 kg
- Weight of SiO₂ to be reduced to Si in pig iron = 10 × \( \frac{60}{28} \) \approx 21.4 kg {Molar mass of Si = 28 g}
- Weight of SiO₂ from ore = 1583 × 0.10 = 158.3 kg
- Weight of SiO₂ from coke = 950 × 0.07 = 66.5 kg
- Weight of CaO from ore = 1583 × 0.04 \approx 63.3 kg
- Weight of CaO from coke = 950 × 0.03 = 28.5 kg

Let \( x \) equal the weight in kg of flux required; then
• $92\% \text{ CaCO}_3 = \frac{92}{100} \times 56 \approx 51.5\% \text{ CaO}$ (Molar mass of CaO = 40 + 16 = 56 g)
• $\Rightarrow \text{ Weight of CaO in flux} = 0.515x \text{ kg}$
• $\Rightarrow \text{ Weight of SiO}_2 \text{ in flux} = 0.08x \text{ kg}$
• $\Rightarrow \text{ Weight of CaO in flux} = \text{ Weight of SiO}_2 \text{ in flux}$
  
  \[
  \frac{158.3 + 66.5 + 0.08x - 21.4}{63.3 + 28.5 + 0.515x} = \frac{1}{2}
  \]
• $\Rightarrow \frac{203.4 + 0.08x}{91.8 + 0.515x} = \frac{1}{2}$
• $\Rightarrow 91.8 + 0.515x = 406.8 + 0.16x$
• $\Rightarrow 0.355x = 315$
• $\Rightarrow x = \frac{315}{0.355} \approx 887 \text{ kg of flux}$

\[\therefore \text{ The charge will consist of 887 kg of flux, 1583 kg of ore, and 950 kg of coke.}\]

**ALTERNATIVE IRON REDUCTION PROCESSES**

Integrated steel mills incorporating sinter plants, coke ovens, BFs, BOFs, casters, and various pieces of downstream equipment have proven to be cost-effective if massive amounts of steel can be profitably sold, to a large market, but they aren’t ideal for every situation. Building a conventional integrated facility is extremely expensive, and early plants produced large amounts of pollutants. There have always been local situations where being able to make small amounts of material for a regional market, or to support a local mining industry could compete with a far-away integrated facility—even more so in periods of high transportation costs. Research and development of smaller, lower-cost, more environmentally responsible ironmaking technologies continues, even with the success of integrated steel mills.

Smelting in the iron blast furnace, unarguably, is by far the most important process for the production of iron, and may likely continue to dominate in the future. However, blast furnaces require coke, and coke plants are expensive and have many environmental problems associated with their operation. Therefore, other techniques are now available which present a challenge to the blast furnace route for ironmaking. The emerging and eventual future alternative ironmaking processes where metallurgical coke can be replaced by pulverized coal or other gaseous reducing agents are classified into *direct reduction* (DR) and *smelting reduction* (SR). Notable examples of commercial alternative ironmaking processes are MIDREX as direct reduction process and COREX as smelting reduction process.

Alternative methods may have potentialities under the following conditions:

- Lack of good coking coals
- Availability of other reducing agents such as cheap coal (non-coking), oil or natural gas, or even cheap electric power
Desirability of limited production capacity (small scale or mini production) and great flexibility

Availability of high-grade ore concentrates.

**Direct Reduction (DR)**

Direct reduction (DR) may be defined as any process in which metallic iron is produced by reduction (removal of oxygen) of iron ore or any other iron oxide by avoiding the liquid melting phase and below the melting temperature of any materials involved with use of solid, liquid or gaseous reductants. Direct reduction involves the use of appropriate reducing agents (e.g., natural gas) to produce solid iron from iron ores in suitable furnaces. The solid product is called DRI and is mainly applied as feedstock in EAF. The direct reduction process has been commercialized since the 1970s and a variety of processes have been developed. All DR processes have as their aim to reduce the ore at a temperature below the melting point of iron and produce an unmelted product, **sponge iron** or **direct-reduced iron** (DRI). Based on a high-grade iron ore concentrate, this sponge iron may be refined directly to steel in an electric arc furnace (EAF) or even used directly in **powder metallurgy**. Sometimes the production of sponge iron is called —**direct reduction**‖, the meaning being ***the conversion of iron ore to quality metallic iron in the solid state, in one-step, bypassing the blast furnace***‘; it has nothing to do with the term ***direct reduction‘ as previously applied to bosh reactions in the blast furnace. Hence, sponge iron is also called **direct-reduced iron**, DRI. It is necessary sometimes to compact DRI to reduce its porosity, resulting to a densified product called **hot briquetted iron**, HBI.

Since the mid-1970s a considerable change has taken place in worldwide iron and steel making, namely the growth of direct reduction processes, the most popular of which natural gas (mainly methane, CH₄) is used as a reductant and fuel instead of the metallurgical quality coke as used in the blast furnace. The two most popular direct reduction methods are known as the **Mildrex process** and the **HyL process (HyL I, III, and IV M)**, the latter being named after Hojalata y Lamina in Mexico, where the process originated.

These new developments have taken place despite the efficiency of the blast furnace route because:

- Metallurgical grade coke is an expensive form of energy. Therefore, any country (particularly those in the ***third world‘) having cheap natural gas and cheap noncoking coal available can produce iron much more cheaply than via the blast furnace. In Nigeria, natural gas is being wasted daily through gas flaring. The Delta Steel Company, Aladja, was planned to reduce high-grade iron ore to iron using natural gas. One major setback to the Ajaokuta Steel Plant is the lack of good coking coal in Nigeria. Hence, alternative ironmaking processes (not requiring metallurgical coke) is viable for Nigeria.
The blast furnace is only economically viable if large production tonnages (5 000 – 10 000 tonnes per day) are envisaged. This entails very high capital expenditure, thereby reducing the flexibility of production.

The direct reduction units can be of special use in the ‘third world’ for the following reasons:

- They allow small flexible units of iron production, coupled with electric arc furnace steelmaking. The material reserve problems are much reduced compared with the blast furnace.
- Scrap imports are eliminated.
- Sponge iron (DRI) and HBI have market value and can be exported.

Sponge iron processes may roughly be divided into two groups, those based on solid fuel (coal based) and those based on gaseous reducing agents (reformed natural gas or gasified coal).

**SOLID FUELS FOR DIRECT REDUCTION PROCESSES**

The fuel may be either coke breeze, cheap coals, or lignite so that in all cases, the main reducing agent is solid carbon. By coke breeze we mean fine particles of coke or coke dust not suitable for blast furnace ironmaking, except for sintering iron ore. Thermodynamics has shown that solid carbon may reduce wustite at temperatures in excess of about 700°C. The reaction on the carbon surface is very slow below 950°C. However, in practice temperatures of 1000 to 1200°C is used. The gas produced by the reduction may have a CO₂/CO ratio of about 0.2, and the overall reaction may be described by the stoichiometric equation:

\[
\frac{2}{3}\text{Fe}_2\text{O}_3 + 6\text{C} = \frac{14}{3}\text{Fe} + 5\text{CO} + \text{CO}_2 \quad \text{for which} \quad \frac{\text{CO}_2}{\text{CO}} = \frac{n_{\text{CO}_2}}{n_{\text{CO}}} = \frac{1}{5} = 0.2
\]

This reaction is strongly endothermic with an overall \( \Delta H_{298} \) of 916 kJ. In addition, about 372 kJ of heat is needed to raise the reaction products to 1000°C, giving a total heat requirement of 1288 kJ for \( \frac{14}{3} \) moles of Fe, or about 4942 kJ/kg of iron. That is,

\[
\frac{1288 \text{ kJ}}{14/3 \text{ mole}} = \frac{1288 \text{ kJ}}{14/3 \times 55.85 \text{ g}} = \frac{1288 \text{ kJ}}{14 \times 55.85 \text{ kg}} = \frac{0.2606 \text{ kg}}{1000} = 4942
\]

This extra heat may be supplied by means of electricity or by burning more fuel. The burning of additional fuel has the disadvantage, however, that the combustion of fuel requires oxidizing conditions, whereas the reduction of the ore requires reducing conditions. The combustion and reduction zones (of whichever furnace or kiln), therefore, have to be separated in such a way that heat may flow from one zone to the other, but without infiltration of the combustion gases.

A ring kiln or tunnel kiln (in case of the Swedish Hoganas process and the Italian Kinglor–Meter process) or rotary kiln (SL/RN process) has been found suitable for this process. The most critical part of rotary kiln reduction is the controlled combustion of coal and its conversion to CO. This conversion is also aided by controlled introduction
of air from the discharge end of the kiln as well as through blowers mounted on the kiln shell, which rotate with the kiln and supply air to the secondary air pipes protruding up to the centre line of the kiln. The shell-mounted blower and the secondary air pipe assembly, thus provide air at several locations in the space above the charge bed, axially along the kiln length.

In the SL-RN process (Figure 25), which has found some industrial application, the combustion air is introduced in controlled quantities along the entire length of the kiln; thus ensuring a constant temperature of about 1000ºC throughout the kiln, and also an atmosphere which becomes increasingly reducing toward the discharge end.

The coke breeze or coal used contain some sulphur. In order to prevent this from being picked up by the freshly reduced iron, some burned lime is added to the reaction mixture, where it reacts with sulphur to form calcium sulphide thereby controlling the sulphur in sponge iron. In all cases, after the products have been cooled in a protective atmosphere, the sponge iron is separated from excess coke or coal char and from the lime–sulphide mixture. Since sponge iron is magnetic in nature, it can be easily separated from the non-magnetic portion of the cooled discharge, consisting mainly of coal ash or coke char, by using magnetic separators. The coke may be returned to the process or used for other purposes within the plant, e.g. in the sintering plant.

Figure 25: Flow sheet for the SL/RN
GASEOUS REDUCING AGENTS FOR DIRECT REDUCTION PROCESSES
The fuel may be derived either from natural gas or oil or may be produced from solid carbon (coal or coke), e.g. in a gas producer. In all cases, the raw fuel is converted into mixtures of CO and H₂ by partial combustion or reforming.

Gaseous reduction has the advantage that the heat of reaction is small; reduction with CO is even slightly exothermic. It may also occur at lower temperature than reduction with carbon, even though the equilibria involved are less favourable. Thus at a temperature of, say, 850°C the equilibrium ratios CO₂/CO and H₂O/H₂ for the reduction of wustite are both around one-half (0.5), which means that only one-third (0.33) of the gas may be utilized for the reduction. The resulting gas mixture may partly be used for prereduction (Fe₂O₃ → FeO) in a countercurrent system, and by combustion with air, to supply the necessary calories to heat the ore to the reaction temperature. Still, there will be a considerable excess of reduction gas which cannot find immediate use in the process.

Where the sponge iron plant is part of an integrated iron- and steelworks the excess gas may find use for holding furnaces (soaking pits), etc. but even in this case, the supply may easily exceed the demand. In other cases, the gas may be treated to remove CO₂ and H₂O and returned to the process, or it may be burned to waste or to generate electricity. In some modern processes H₂O is first taken out by condensation to water, after which the remaining CO₂ – CO – H₂ mixture is used in the reforming of the raw fuel. In this way, a good gas economy is obtained.

We shall be concerned here with only two direct reduction processes that utilize gaseous reducing agents, namely, the MIDREX process [which is followed at Delta Steel Company, Aladja] and the HyL process. The Midrex process became a viable alternative for Nigeria because of the abundance of natural gas which has mostly been flared (burned to waste) for the past four decades. In fact, our gas reserves are said to be far greater than our oil reserves; hence the establishment of the Liquified Natural Gas (LNG) Plant at Bonny.

- The MIDREX Process
  Developed in 1967 by the Midland Ross Corporation of Cleveland, USA, the MIDREX technology has become the most important direct reduction process, and accounts for 67% of the world’s total DRI production. Its main reactor, i.e., the shaft furnace, behaves as a moving bed reactor. In the MIDREX process iron ore or pellets are reduced in a shaft furnace, Figure 26, which resembles the upper half of a blast furnace.
Figure 26: Schematic process flow sheet of a standard MIDREX process

Natural gas, which is essentially methane, is first reformed to a mixture of CO and H₂ by reaction with returned top gas from the furnace. The reforming is carried out at about 1000°C in pipes which contain a nickel catalyst. As the reforming reaction is endothermic the necessary heat is supplied by burning some natural gas as well as the remainder of the top gas in the chamber surrounding the pipes. The reformed gas, which contains about 50% H₂, 35% CO as well as minor amounts of CO₂, CH₄, and N₂ is introduced into the shaft furnace at a temperature of 800 to 900°C, at which temperature the reduction of wustite to iron takes place. In the upper part of the shaft the haematite pellets are prereduced to wustite, and the temperature of the gas drops to 300 to 400°C.

The top gas passes through a scrubber to remove dust and to condense some of the water vapour, thereafter the cleaned top gas that contains about equal amounts of CO and CO₂ together with appreciable amounts of hydrogen and some water vapour is used partly to reform the raw natural gas, partly to supply heat for the reformer. In the lower part of the MIDREX shaft the metallized product is cooled to essentially room temperature by means of a separated flow of cooling gas.

With respect to the Rist diagram of Figure 22, the operating line for the gas in the MIDREX shaft is given by the line \( \frac{X_A}{Y_H} \), and we see that if only CO and CO₂ are considered, the top gas will have a CO₂/CO ratio of about 0.67, which is more than enough to prereduce haematite to wustite. For lower temperature for the wustite reduction the CO₂/CO ratio of the top gas will be somewhat higher. [As a homework that will not be graded, the student is required to determine the O/C value of the top gas if the CO₂/CO ratio = 0.67].
The HyL/Energiron Process

The HyL I process developed in Monterrey in Mexico is in principle not much different from the MIDREX process. The main difference is that the ore is maintained in a stationary position in a number of fixed beds (about 4 or 5 of them), and the gas is made to flow from one bed to the other. As in the MIDREX process natural gas is first converted to a mixture of CO and H₂ which at a temperature of 900 to 1000°C is passed through a bed which contains partially reduced ore, which is reduced to its final metallized state. The gas from this bed is now cooled to condense most of its water vapour, and is then reheated regeneratively and introduced into a bed, which contains a less reduced ore. The same operation is repeated for the third bed which contains the fresh haematite ore, which thereby is heated to reaction temperature and prerduced. The remaining one or two beds are either being charged with fresh ore or are being cooled by cooling gas, and the metallized product removed. By keeping the ore and metallized product in a stationary position, difficulties are avoided which, in a shaft furnace, are encountered from sintering and sticking of the charge. Furthermore, the reaction may be carried out at increased pressure of a few atmospheres, with corresponding higher reaction rates.

HyL I is a batch process and its popularity has continuously dwindled even with little improvement of the process in Hyl II. There is confusion of terminology about HyL reactors in literature, where some authors call them retorts. The term retort should be reserved for reactors with external heating. A better name for HyL reactors would be fixed-bed reactors.

The HyL technology, originally developed in Mexico, is now owned by the Italian technology company Tenova, and has been re-branded as ENERGIRON. All current ENERGIRON plants utilize a single moving bed shaft furnace (instead of 4 or 5 fixed beds as in Hyl I and II), either with an external reformer (HyL III) or without (HyL IV M). The original HyL I technology was a batch process based on a series of fixed-bed reactors and is no longer offered. In basic terms, the operation of the current ENERGIRON technology with reformer is quite similar to the MIDREX process, but there are certain differences. A major difference is in the operation of the reformer. In the MIDREX process, the reformer operates on a mixture of cleaned top gas and natural gas, with no steam necessary. The reformer product gas is then modified further in temperature and/or composition, as necessary. ENERGIRON, however, only feeds fresh natural gas to their reformers, using externally generated steam in the process. The reformed natural gas must be cooled to remove water. It is then combined with top gas (from which much of the CO₂ has been removed), and the combined stream heated to temperature, also with possible adjustments to chemistry.

ENERGIRON runs at higher pressures, which requires more complex equipment at the top and bottom of the shaft, but leads to an overall smaller plant footprint. The basic process uses a steam reformer, which requires more processing to improve the quality of their reducing gas. However, by not recirculating top gas to the reducing gas feed,
they eliminate the chance of sulphur from the ore being transferred via the gas phase to poison the catalyst in the reformer. More recently, in the Hyl IV M process, ENERGIRON has utilized the well-known catalytic quality of the reduced iron in the shaft to do complete in situ reforming and avoid the need for an external reformer. A major mechanical difference between the two reactors relates to the internal configuration of the furnace. The MIDREX process incorporates —burden feeders— or —cluster breakers— to help prevent the generation of large clusters, which can cause significant operating problems. The HYL III shaft, on the other hand, —depends on furnace geometry and good temperature control to avoid burden sticking and to maintain plug flow—

One drawback of all sponge iron processes is that the product is subject to corrosion or rusting during storage and transportation. The processes should, therefore, preferably operate in direct connection with a steel plant. Most recently, technology has been developed to take advantage of the thermal content of the DRI after reduction; in those cases where the steelmaking shop is near the DRI plant, hot DRI is transported through specially designed equipment to reach the melt shop.

**Smelting Reduction (SR)**
This involves combining iron ore reduction with smelting in a reactor (furnace), without the use of coke. The product is liquid pig iron, which can be treated and refined in the same way as hot metal from the blast furnace. Today, only one variant of SR is commercially proven, namely COREX, but a number of variants are in an advanced stage of development.

❖ **COREX Process**
The COREX process is a two-stage process, as is shown in Figure 27. In the first step, iron ore is reduced to sponge iron in a shaft furnace by means of reducing gas. In the second step, the reduced iron is melted in the melter–gasifier vessel. Reducing gas (CO and H₂) used in the reduction shaft is supplied by gasification of coal by means of oxygen, forming a fixed or fluidized bed in the melter–gasifier. The partial combustion of the coal in the melter–gasifier generates the heat to melt the reduced iron. Liquid iron and slag are discharged at the bottom, by a conventional tapping procedure similar to that used in blast furnace operation.

Because of the separation of iron reduction and iron melting/coal gasifying in two steps, a high degree of flexibility is achieved and a wide variety of coals can be used. The process is designed to perform at elevated pressure, up to 5 bar. Charging of coal and iron ore is performed through a lock hopper system. The reducing gas contains 65–70% CO, 20–25% H₂, and 2–4% CO₂. After leaving the melter–gasifier, the hot gas is mixed with cooling gas to adjust the temperature to approximately 850ºC. The gas is then
cleaned in hot cyclones and fed into the shaft furnace as a reducing gas. When the gas leaves the shaft furnace, it still has a relatively high calorific value and may be used as an export gas where the opportunity exists.

Figure 27: Process flow sheet of the COREX process (left) and schematic view of the COREX reactor (right)

The COREX process, formerly known as the KR (Korf Reduction) process, was developed by Voest Alpine Industrieanlagenbau, Austria (VAI, now Siemens-VAI) and Korf Engineering, Germany in the late 1970s. The feasibility of the COREX process was confirmed during the 1980s. Following the first industrial application of a COREX 1000 THM/day plant at Iscor Pretoria, South Africa, four 2000 THM/day were subsequently put into operation at Posco/Korea, Mittal Steel/South Africa and at JSW Limited/India. In early November 2007, the first COREX 3000 THM/day plant was started up at Baosteel, China. It has a nominal production capacity of 1.5 million THM/year.

Recently a variant of COREX process, FINEX, is co-developed by VAI and Posco for the production of hot metal based on the direct use of iron ore fines and noncoking coal. Fine iron ore is charged into a series of fluidized-bed reactors together with fluxes. The iron ore fines pass in a downward direction through four reactors where they are heated and reduced to DRI by means of a reduction gas—derived from the gasification of the coal—that flows in the counter-current direction to the ore. The first commercial FINEX plant with a capacity of 1.5-million-ton/year started operation at the Pohang Works since early 2007.

 Electric Iron Smelting Process
In countries where coke is expensive, relative to the cost of electricity, as in Scandinavia (Norway, Sweden, Denmark, Finland), Italy, Yugoslavia, Venezuela, and Japan, electric iron smelting process may be an alternative to the blast furnace. In this case,
liquid hot metal similar to blast furnace pig iron is produced on a mini-scale without the blast furnace using coal, oxygen and/or electricity. A typical electric iron smelting furnace is shown in Figure 28.

The processes involved more nearly resemble blast furnace smelting except that heat is supplied by an electric arc rather than by coke combustion, though low-grade coke or pulverized coal is used as the reducing agent. The coal is mixed with the ore and fed into a reaction hearth where carbon electrodes provide the heating current (arc). Since no air is introduced (as in the blast air of the BF), the gas volume is much less than in the blast furnace, and is limited to what is produced by ‘direct reduction’, more or less according to the reaction:

$$\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO} \quad \Delta H_{298} = 482 \text{ kJ}$$

The gas leaving the reduction chamber is very rich in CO so that it is cleaned and used as an energy source in the same way as blast furnace top gas. Electric smelting of iron has the advantage that it produces less CO$_2$, whereas for every tonne of pig iron tapped from the blast furnace some 3.5 tonnes of CO$_2$ finds its way ultimately into the atmosphere. Thus a large blast furnace producing 10 000 tonnes of pig iron per day is responsible for discharging into the environment about 12 million tonnes of CO$_2$ every year – this way promoting greenhouse effect.

Referring to the Rist diagram of Figure 22, and including some reduction of SiO$_2$, MnO, etc., the operating line for the SR process would be given by line $BA^I$. We see that this
line runs far to the left of the chemical pinch point, \( W \), and from a chemical viewpoint, the electric iron smelting process is not very elegant. The coke consumption per tonne of pig iron amounts to 350 to 400 kg of poor quality coke. The electric energy consumption is about 2000 kWh/tonne of pig iron, and this can be reduced to 1000 kWh/tonne by preheating and prereduction of the burden in a rotary kiln, for example.

**STEELMAKING (REFINING PROCESSES)**

Steelmaking can be roughly defined as the refining or removal of unwanted elements or other impurities from hot metal produced in a blast furnace or similar process or the melting and refining of scrap and other forms of iron (e.g. DRI) in a melting furnace. Pig iron, as we know contains some impurities, which originate from the ore, the fluxes, or the fuel. In particular the high sulphur, phosphorus and carbon contents have embrittling effect. Sulphur forms a network of sulphide films through the metal. At forging temperatures these films melt and allow the iron grains separated by them to fall apart (*hot shortness*). Phosphorus forms a hard Fe\(_3\)P compound which embrittles the iron at ordinary temperatures (*cold shortness*). Carbon similarly forms an embrittling Fe\(_3\)C compound as in *white cast iron*. However, if the silicon content of the iron is high and the cooling rate of the casting is low, the Fe\(_3\)C is *graphitized* in the iron thus making the resulting *grey cast iron* to be fairly soft and much less brittle. Wrought iron is soft because it contains almost no carbon; and pig iron is brittle because it contains too much. Early experience showed that irons with intermediate carbon contents, i.e. *carbon steels*, could be superior to both in their combination of hardness, strength and toughness. In steelmaking unwanted impurities in iron are removed or reduced drastically while useful impurities (such as carbon) are reduced to the required steel specifications. In some cases, intentional alloying elements (e.g., V, Cr, Ni, Si, etc.) are added as required.

Ironmaking (a reduction process) produces hot metal or sponge iron with carbon, silicon, manganese, sulphur and phosphorus as the main impurities. For further use of the metal, it is usually necessary to subject it to a refining process. In steelmaking (an oxidizing process), the refining is done in order to give a product with controlled amounts of desired impurities (alloying elements). Sometimes refining is done to recover some valuable impurities (e.g. Mn).

Refining processes are always based on the principle that different elements distribute (partition) themselves differently in different phases (e.g. liquid metal and liquid slag), and that these phases may be separated physically. In metal–slag systems the preferential oxidation and slagging of less noble elements is by far the most important, and may be given the common name of *fire refining*. Steelmaking processes fall under fire refining.

Steelmaking by fire refining is based on the difference in affinity for oxygen for the different elements present in hot metal, molten sponge iron or scrap. However, it also depends on the chemical activities of the elements dissolved in the metallic phase and of the oxides dissolved in the slag. In fire refining the metal is subjected to oxidation
either by means of air or oxygen, or by means of some oxide of the metal which is to be refined. Thus pig iron may be oxidized (fire-refined) with oxygen or with iron ore (e.g. mill scale).

Figures 29 and 30 show the trend in steelmaking process routes in the USA (from 1955 to 1996) and worldwide (from 1970 to 1995). It can be seen that the BOF and EAF steelmaking have displaced the Open Hearth steelmaking which had earlier displaced the Bessemer steelmaking process. While BOF is the dominant technology, it is closely followed by EAF route.

Figure 29: US crude steel production trend by process from 1955 to 1996 [Source: International Iron and Steel Institute]

In the year 2000, about 850 million tonnes of raw or crude steel were produced around the world, representing 93% of all global metal production (Appendix V). Most of that steel was made either in BOF or EAF. Because steel can be recycled endlessly without ever losing its quality, nearly half of this number were produced/recycled from scraps, especially in the EAF (Kassinger, 2003).
As already noted, most all of the hot metal produced in the world is refined in an oxygen steelmaking process (OSM), also known as basic oxygen steelmaking (BOS), notably in the basic oxygen furnace (BOF). The major element removed is carbon which is removed by oxidation to carbon monoxide (CO). Other elements such as silicon, phosphorous, sulphur and manganese are transferred to a slag phase. In the EAF steelmaking process, the chemical reactions are similar but generally less extensive. After treating the metal in an OSM converter (BOF) or an EAF it is further refined in the ladle. This is commonly called secondary refining or ladle metallurgy. For stainless steelmaking, the liquid iron-chromium-nickel metal is refined in an argon-oxygen decarburization vessel (AOD), a vacuum oxygen decarburization vessel (VOD) or a similar type process.

**Primary Steelmaking**
This involves the conversion or refining of hot metal and steel scrap into steel (especially carbon steel) via basic oxygen steelmaking (notably in BOF), or melting and refining scrap steel and/or sponge iron (DRI) in an electric arc furnace.

**Secondary Steelmaking**
Secondary steelmaking is most commonly performed in ladles and often referred to as ladle refining or ladle metallurgy where the steel produced in BOF or EAF can be further refined or improved. Some of the operations performed in ladles include
deoxidation or killing, vacuum degassing, alloy addition, desulphurization, removal or modification of inclusion etc. to improve the chemistry and cleanliness of the steel.

**Basic Oxygen Steelmaking (BOS/BOF)**

The process of steelmaking is mainly one involving oxidation of impurities present in the original charge, so that they form a slag which floats on the surface of the molten steel or are lost as fume. In the Bessemer process, impurities were removed from the charge of molten pig iron by blowing air through it. The impurities, mainly carbon, phosphorus, silicon and manganese, acted as fuel and so the range of compositions of pig iron was limited, because sufficient impurities were necessary in order that the charge did not _blow cold_ from lack of fuel.

The oxidized impurities either volatilized or formed a slag on the surface of the charge. Since the air blast contained only 20 per cent of oxygen by volume, much valuable heat was carried away from the charge by the 80 per cent nitrogen also present. Worse still, a small amount of this nitrogen dissolved in the charge, and, in the case of mild steel destined for deep drawing operations, caused a deterioration in its mechanical properties.

The new oxygen processes produce mild steel very low in nitrogen, so that its deepdrawing properties are superior to those of the old Bessemer steel. Improvements of this type are essential if mild steel is to survive the challenge of reinforced plastics, such as ABS, in the field of automobile bodywork. The earliest of these oxygen processes was the L-D process, so called because it originated in the Austrian industrial towns of Linz and Donawit in 1952. It was made possible by the low-cost production of _tonnage oxygen_ and it is interesting to note that Bessemer had foreseen these possibilities almost a century earlier but of course did not have access to tonnage oxygen. Since 1952, a large number of variations of the original process have been developed but have become rationalized under the general heading of _basic oxygen steelmaking_ (BOS).

The BOS process is generally carried out in the _basic oxygen furnace_ (BOF), which is a pear-shaped vessel of up to 400 tonnes capacity lined with basic refractories (e.g. magnesite bricks covered with a layer of dolomite). Thus, the process is known as basic due to the chemical nature of the refractories (CaO and MgO) that line the vessel. This lining must be basic to match the basic slag which is necessary for the removal of impurities from the charge. If the lining were chemically acid (e.g. silica bricks) it would be attacked by the basic slag and would quickly disintegrate.

In this process, no heat is carried away by useless nitrogen (as was the case in the old Bessemer process) so a charge containing up to 40 per cent scrap can be used. _Recall that heat is generated autogenously in this process since the oxidation of the impurities_
carbon, phosphorus, silicon and manganese is exothermic. The scrap is loaded to the converter first, followed by lime and molten pig iron (Figure 31). Oxygen is then blown (at supersonic speed) at the surface of the molten charge from a water-cooled lance which is lowered through the mouth of the converter to within 0.5 m of the surface of the metal. At the end of the blow, this slag is run off first and any adjustments made to the carbon content of the charge which is then transferred to the ladle, preparatory to being cast as ingots, or, much more probably, fed to a continuouscasting unit which, is currently the modern practice.

Figure 31: Stages in the manufacture of steel by the BOF process. Steel scrap is added first (i), followed by molten pig iron (ii). At the end of the ’blow’ the slag is run off first (iv), before ’teeming’ the steel into a ladle.

BOS has the following major advantages over competing processes:
(i) It is rapid—the cycling time is about forty-five minutes;
(ii) Nitrogen contamination is very low so that deep-drawing quality mild steel is produced;
(iii) Thermal efficiency is high because heat is not carried away by nitrogen as in the former Bessemer process. Hence the charge may include 40%—and in some circumstances 50%—scrap. A wide variety of both scrap and pig iron can be used.

The principal chemical reactions taking place as oxygen is blown from the top into the melt are:

\[
\begin{align*}
\text{i.} & \quad [\text{Fe}] + [\text{O}] = (\text{FeO} \\
\text{ii.} & \quad [\text{C}] + [\text{O}] = (\text{CO}) \\
\text{iii.} & \quad [\text{Si}] + 2[\text{O}] = (\text{SiO}) \\
\text{iv.} & \quad [\text{Mn}] + [\text{O}] = (\text{MnO}_{2}) \\
\text{v.} & \quad 2[\text{P}] + 5[\text{O}] = (\text{P}2) \\
\text{vi.} & \quad [\text{Fe}] + [\text{O}] = (\text{FeO}) \\
\text{vii.} & \quad [\text{Fe}] + (\text{FeO}) = (\text{CO} \quad 0)
\end{align*}
\]

The heat produced due to the above chemical reactions is sufficient enough to raise the temperature of hot metal from around 1250–1300°C to molten steel tapping temperature of 1600–1650°C. All the other elements form slag except carbon which leaves as a
gaseous phase. The last reaction is useful for the recovery of manganese (an important alloying element) into the steel.

**Electric Arc Steelmaking**

This is the only alternative steelmaking process which is significant at present and its operation is complementary to BOS rather than competitive. Originally electric-arc furnaces were used for the manufacture of high-grade tool and alloy steels but are now widely employed both in the treatment of hot metal and of process scrap as well as scrap from other sources. Depending on market requirements, an EAF can be switched over easily to produce plain carbon or alloy steel. The charge can include steel scrap, hot metal and DRI. With or without hot metal, quality steel can be refined from scrap steel alone or scrap and sponge iron. The high cost of electricity is largely offset by the fact that cheap scrap can be processed economically to produce high-quality steel.

Since electricity is a perfectly ‘clean’ method of providing heat, no impurities are transmitted to the charge as was the case with producer gas used in the now extinct open-hearth process. Moreover, the chemical conditions (either oxidizing or reducing slags) within the electric-arc furnace can be varied at will to favour successive removal of the various impurities present in the charge. Sulphur, which was virtually impossible to eliminate in either the Bessemer or open-hearth processes, can be effectively reduced to extremely low limits in the electric-arc process. The furnace (Figure 32) employs carbon electrodes which strike an arc on to the charge.

![Figure 32: The principles of the EAF for steelmaking](image)

The hot carbon arc provides a slightly reducing atmosphere and high metal temperatures, e.g. 1800°C can be reached in the hearth. At this temperature CO is more stable than the alloy oxides, so that the alloy content of special scrap need not be lost. The first stage in electric steelmaking is to charge steel scrap and DRI and melt this down with the arcs. The lining is basic allowing the addition of lime and mill scale (or
iron ore) in order to produce a basic oxidizing slag which removes most of the carbon, silicon, manganese and phosphorus into the slag phase. The slag formed at this stage is run off (poured away) and is often replaced by a reducing slag made by throwing in lime and anthracite (which react to form CaC₂) which effectively removes sulphur in accordance with the following reaction:

\[
\text{FeS} + \text{C} + \text{CaO} = \text{Fe} + \text{CO} + \text{CaS}
\]

or

\[
\text{FeS} + \text{CaC} + 2\text{O} = \text{Fe} + 2\text{CO} + \text{CaS}_2
\]

Also, in this reducing environment the necessary ferro-alloys; ferro-manganese, ferrochromium, ferro-vanadium, etc. can be fed into the bath without loss due to oxidation.

Hence the main advantages of the arc process are:

i. Removal of sulphur is reliable;
ii. Conditions are chemically clean and contamination of the charge is impossible;
iii. Temperature can be accurately controlled;
iv. Carbon content can be adjusted between fine limits;
v. The addition of alloying elements can be made with precision. Electric arc furnaces are widely used for making high grade steels, especially alloy steels, from steel scrap. The main elements added to steel are Ni, Cr, Mn, V, Mo, W, Nb, Ti, mostly as ferro-alloys.
vi. High grade plain carbon steels can be made from steel scrap in large EAFs, e.g. 150 000 kg capacity.

STEELMAKING REACTIONS AND THERMODYNAMICS

In steelmaking process, the impurities in iron are lowered to the desired steel specification. The relevant reactions are as given below:

1. Phosphorus Removal

\[
\frac{2\text{P}}{\text{Fe}} + \frac{5\text{O}}{} = \frac{\text{P}_2\text{O}_5}{\text{slag}} ; \Delta H = 1200 \text{ kJ}
\]

\[
\log K_P = \log \left( \frac{[\text{P}_2\text{O}_5]^{a_{\text{P}_2\text{O}_5}}}{[\text{P}]^2 \cdot [\text{O}]^5} \right) = \frac{35700}{T} - 30.3
\]

It is assumed that the \( \text{P}_2\text{O}_5 \) in the slag is combined with lime to form the compound \( 4\text{CaO} \cdot \text{P}_2\text{O}_5 \). Thus:

\[
\frac{2\text{P}}{\text{Fe}} + \frac{5\text{O}}{} + \frac{4\text{CaO}}{\text{slag}} = \frac{4\text{CaO} \cdot \text{P}_2\text{O}_5}{\text{slag}}
\]

The experimental expression for \( \log K_P \) has been found to be

\[
\log K_P = 10.78 \log(\%\text{CaO}) - 0.00894t - 6.245 ; \text{ where } t \text{ is temperature in } ^\circ\text{C}.
\]
The preferential oxidation of P can only occur if:
\[ \Delta G_{\text{P}_2\text{O}_5} \text{ at } 1600 \, ^\circ\text{C} < \Delta G_{\text{FeO}} \text{ at } 1600 \, ^\circ\text{C} \]
- equilibrium condition;

By van’t Hoff isotherm for non
\[ \Delta G_{\text{P}_2\text{O}_5,1600 \, ^\circ\text{C}} = \Delta G_{\text{FeO,1600 \, ^\circ\text{C}}} + RT \cdot \ln \left( \frac{\text{at}_{\text{P}_2\text{O}_5}}{\text{at}_{\text{P}} \cdot \text{at}_{\text{O}}} \right)^5 \]

The above equation indicates that \( \Delta G_{\text{P}_2\text{O}_5} \text{ at } 1600 \, ^\circ\text{C} < \Delta G_{\text{FeO}} \text{ at } 1600 \, ^\circ\text{C} \) can be satisfied when \( \Delta G_{\text{P}_2\text{O}_5} \) is made highly negative by:
- Lowering (\( \text{at}_{\text{P}_2\text{O}_5} \)) by using a basic slag, i.e. \( 4\text{CaO} + \text{P}_2\text{O}_5 = \text{Ca}_3(\text{PO}_4)_2 + \text{CaO} \) excess, and
- Increasing the supply of oxygen i.e. \( \text{at}_{\text{O}} \) to the metal using iron ore or mill scale.

Removal of phosphorus from metal is favoured by low metal temperature:
\[
\frac{2\text{P}}{(\text{in Fe})} + 5\text{O} \text{ (in Fe)} \text{ injected into Fe} \text{ partitioned to slag} = \text{P}_2\text{O}_5 ; \quad \Delta G = -683,000 + 580T \text{ J} \cdot \text{mol}^{-1}
\]

2. **Sulphur Removal**

The relevant sulphur removing reaction is:
\[(\text{CaO}) + \text{S} + \text{C} = (\text{CaS}) + \{\text{CO}\}\]

Because of the difficulty in measuring the activities of the components, sulphide capacity data of liquid slags are used in estimating slag’s sulphur removing ability. The ionic form of the above equation is:
\[
\text{S}_{(\text{in Fe})} + \text{O}^{2-}_{(\text{slag})} = \text{O}_{(\text{in Fe})} + \text{S}^{2-}_{(\text{slag})} ; \quad \Delta G = 72,000 - 38T \text{ J} \cdot \text{mol}^{-1}
\]
\[
\therefore \log K = \log \left( \frac{\text{at}_{\text{S}_{2-}} \cdot \text{at}_{\text{Ca}}}{\text{at}_{\text{O}_{2-}} \cdot \text{at}_{\text{C}}} \right) = \frac{\Delta G}{2.303RT} = - \frac{3760}{T} + 1.985
\]

The conditions necessary for sulphur removal during steelmaking are:
- Basic slag formation (by CaO addition);
- Low oxygen potential (using a reducing slag containing Fe-Si or anthracite);
- High metal temperature.

Thus, since CaO favours both S and P removal, early formation of basic slag before attainment of high temperatures is crucial to aid both P removal (at low temperatures) and S removal (at high temperatures). P and S both deteriorate the mechanical properties of the steel. They are therefore maintained at maximum concentrations of 0.04%.

3. **Manganese**

The relevant reaction is:
In representing the slag-metal equilibria, it is customary to use the total iron (as oxides) in the slag as $\Sigma FeO$. The composition of most steelmaking slags are in the ranges: 50–60% CaO, 3–8% MgO, 3–8% MnO, 6–26% $\Sigma FeO$, 15–25% SiO$_2$, 1–5% P$_2$O$_5$, ~1% Al$_2$O$_3$. Where the pig iron phosphorus content is high the slag may contain up to 20% P$_2$O$_5$ or more. Manganese exchange between metal and slag may be represented by the equation:

$$\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe} \ ; \ K_{\text{Mn}} = \frac{(\%\text{MnO})}{[\%\text{Mn}] \cdot [\%\Sigma \text{FeO}]} \text{ in terms of weight percent}$$

For basic slags at steelmaking temperatures,

$$K_{\text{Mn}} = \frac{6}{B}$$

Where $B$ is the basicity which is somewhat arbitrary. If we assume that 1 mole of CaO is equivalent to 1 mole of MgO and that $\frac{1}{2}$ mole of P$_2$O$_5$ is equivalent to 1 mole of SiO$_2$, then, $B$ may be defined by the ratio:

$$B = \frac{\%\text{CaO} + 1.4(\%\text{MgO})}{\%\text{SiO}_2 + 0.84(\%\text{P}_2\text{O}_5)}$$

### 4. Silicon Removal (Desiliconization)

The relevant reaction is:

$$\text{Si} \text{(1% in Fe)} + 2\text{O} \text{(in Fe)} = \text{SiO}_2 \text{(in slag)} \ ; \ \Delta H = -745 \text{ kJ}$$

$$\log K_{\text{Si}} = \log \left( \frac{a_{\text{SiO}_2}}{[a_{\text{Si}] \cdot [a_{\text{O}}]}^2} \right) = \frac{\Delta G}{2.303RT} = \frac{29150}{T} - 11.01$$

### 5. Carbon

The relevant reaction is:

$$\text{C} \text{(1% in Fe)} + \text{O} \text{(in Fe)} = \text{CO} \text{(gas)} \ ; \ \Delta H = 1331 \text{ kJ}$$

$$\log K_C = \log \left( \frac{P_{\text{CO}}}{[a_c] \cdot [a_{\text{O}}]} \right) = \frac{\Delta G}{2.303RT} = -\frac{1045}{T} + 2.131$$

According to (Turkdogan, 2010):

$$\log K_C = \frac{1168}{T} + 2.07$$

For carbon contents below about 0.5% and at steelmaking temperatures of about 1600°C, the coefficient of carbon in iron increases while that of oxygen decreases with increasing carbon content. For the slag composition indicated previously (under manganese above), the following relationship holds:
Atomic oxygen has been used in the reactions above since the iron oxide dissociates at the slag-metal interface to release atomic oxygen into the metal, thus:

\[
\frac{\text{Fe}_2\text{O}_3}{\text{in slag}} \rightarrow \frac{2\text{FeO}}{\text{in slag}} + \frac{\text{O}}{\text{in Fe}}
\]

In practice, Mn and Si oxidize immediately but C oxidation is delayed because of the large interfacial area between CO and the liquid steel.

\[
r_c = \frac{2 \cdot \gamma \cdot T_f}{L_f \cdot \Delta T}
\]

Where; \(r_c\) = critical bubble radius required to initiate nucleation;
- \(\gamma\) = interfacial energy between the liquid steel and CO bubble
- \(T_f\) = freezing point of the liquid steel
- \(L_f\) = latent heat of fusion
- \(\Delta T\) = degree of supercooling

The \(r_c\) for homogeneous nucleation of CO is too high under normal steelmaking conditions so that CO nucleates on various materials including refractory crevices where the interfacial energy or tension is reduced.

In the catch carbon method, the steel is tapped when the carbon being oxidized attains the specific concentration. It is bad practice to go below the required carbon concentration and then to begin to adjust by adding pig iron or anthracite, as this will result to the lowering of temperature and increase of inclusions. The oxidation of carbon provides CO evolution which gives the boiling action called the carbon oil reaction. The turbulence created improves the reaction kinetics and hence the production rate in open hearth and electric arc steelmaking processes (where oxygen lancing may not be employed).

When the desired carbon level has been attained, deoxidant is added to stop further decarburization of the metal and to obtain the required structure in the solidified steel, i.e. rimmed, semi-killed or killed. Low to medium (up to about 4%) alloying additions are subsequently made in the ladle later after deoxidation to prevent their removal to the slag as oxides. Greater amounts of alloying additions cannot be made effectively in the ladle without undue cooling and loss of compositional uniformity. They must be added therefore in the initial charge and this will lead to some loss to the slag (due to oxidation) which must be therefore maximally recovered. To illustrate this, let us examine the production of high chromium alloy steel.

**Production of 18-8 Stainless Steel**

In stainless steels, low level of carbon (about 0.05%) is required to prevent intercrystalline corrosion or weld decay. During carbon oxidation by the oxidizing slag, simultaneous oxidation (i.e. loss) of chromium take place. This can be reduced by employing high temperatures or by adding of ferrosilicon (Fe-Si) to the slag to recover the oxidized chromium.
From thermodynamic considerations we can deduce a way to largely preferentially oxidize carbon \( [\text{C} + \underline{O} = \{\text{CO}\}] \), i.e. with minimal oxidation of chromium in the metal.

\[
2\text{Cr(\text{in Fe})} + 3\text{O(\text{in Fe})} = \text{Cr}_2\text{O}_3(\text{in slag}) \quad ; \quad \Delta G = -887400 + 393T \text{ J} \cdot \text{mol}^{-1}
\]

\[
\log K_{\text{Cr}} = \log \frac{[\text{Cr}_2\text{O}_3]}{[\text{Cr}]^2 \cdot [\text{O}]} = \frac{\Delta G}{2.303RT} = \frac{46346.34}{T} - 20.52
\]

Given that \( [\text{O}] = \frac{p_{\text{CO}}}{[\text{C}][\text{O}]} \), and assuming \( [\text{Cr}_2\text{O}_3] = 1 \), then \( [\text{Cr}] = K \cdot [\text{C}]^2/3 \cdot p_{\text{CO}} \)

\[
\Rightarrow [\text{O}] = \sqrt[3]{\frac{K_{\text{Cr}}}{[\text{Cr}]^2/3 \cdot [\text{O}]^3}} = \sqrt[3]{\frac{[\text{Cr}_2\text{O}_3]}{[\text{Cr}]^2 \cdot K_{\text{Cr}}}} = \frac{[\text{Cr}_2\text{O}_3]}{[\text{Cr}]^{2/3} \cdot K_{\text{Cr}}^{1/3}}
\]

Ni, Co and Mo form less stable oxides than FeO so they are not essentially lost to the slag and can be added to the melt with the charge. Mn and Si being oxidized, are corrected using ferroalloy additions. Ferroalloys are important raw materials for the manufacture of alloy steels and special carbon steels. Some of them are used as deoxidizers in steelmaking (e.g. Fe-Mn, Fe-Si, Fe-Si-Mn), and others provide the necessary elements for special steels (Table 10).

**Table 10: Percentage of elements added to steels as ferro-alloys**

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Mo</th>
<th>Others</th>
<th>Application</th>
</tr>
</thead>
</table>

This means that \( [\text{Cr}] \propto [\text{Cr}]^{2/3} \cdot p_{\text{CO}} \). The lowering of \( p_{\text{CO}} \) renders \( \Delta G_{C-CO} \) more negative than \( \Delta G_{Cr-Cr_2O_3} \), resulting in preferential oxidation of carbon. Lowering of \( p_{\text{CO}} \) is achieved by flushing the melt in AOD (argon-oxygen decarburization) converter with oxygen and argon (inert gas).
FERROALLOYS

Substances such as manganese, silicon, chromium, etc. are produced in large amounts, not as the elements themselves, but alloyed with iron, i.e. as ferroalloys, for steelmaking. The main alloys produced are ferrosilicon (15–90 % Si), ferromanganese (80% Mn, 5% C, 1% Si), spiegeleisen (~18% Mn, 5% C), silica-manganese (70% Mn, 20% Si, 1.5% C), ferrochromium (70% Cr, 5% C), ferrotungsten, ferromolybdenum, ferrovanadium and ferrotitanium.

Ferroalloys are relatively impure products which in addition to their valuable component contain considerable amounts of iron, and which are used as additives in steelmaking. The iron content may either be as a result of the iron in the ore or it may have been added deliberately in order to facilitate the reduction process or to lower the melting point of the alloy. Examples of the former are FeCr and FeMn since their ores invariably contain some Fe and since these metals are less noble (more reactive) than iron, the Fe content of the alloy will be determined by the iron content of the ore. FeCr and FeMn each contains up to 70 – 80% of the valuable metal. Example of the latter is FeSi where scrap Fe is added in order to facilitate the reduction. FeSi contains up to 45 – 90% Si.

Some ferroalloys are made in blast furnaces but the high reduction temperatures needed and the high carbon content of the product are unsatisfactory features. The other method now used is the electrothermic process. The charge is contained in a crucible and heated by a submerged arc. The charge consists of the mineral to be reduced, e.g. quartz (SiO₂) for ferrosilicon, pyrolusite (MnO₂) for ferromanganese, chromite (FeO·Cr₂O₃) for ferrochromium, ilmenite (FeO·TiO₂) for ferrotitanium, together with coke, steel scrap or iron as required, and limestone flux where necessary.

Carbon is an effective reducing agent for most of the ferroalloys at the high temperatures achieved in the electric furnace, although aluminium or ferrosilicon is used to reduce ilmenite, in the presence of iron oxide, to ferrotitanium. Most ferroalloys are produced by carbothermic reduction of oxide ores. Since the reaction takes place at well over 1000°C the partial pressure of CO₂ is low, therefore the reduction may be conveniently expressed thus:
Unfortunately, with few exceptions these metals also form very stable carbides, the order of increasing stability being Mn$_3$C, NbC, Al$_4$C$_3$, CaC$_2$, SiC, Cr$_2$C$_6$, VC, TiC, and ZrC. Thus if an oxide of one of the above metals is reduced with an excess of carbon, the product will be a carbide rather than the pure metal. If the reaction mixture had contained only enough carbon to give the pure metal, the product would be a mixture of metal carbide and unreacted metal oxide. These may react on further heating as follows:

\[ \text{MeO} + \text{C} = \text{Me} + \text{CO} \]

At 1 atm, this reaction shifts to the right with increasing temperature. Even though the carbide can be decomposed according to this reaction, the resulting metal still contains a considerable amount of dissolved C. this is the case for FeCr and FeMn (for example), which in the molten state are able to dissolve up to 10% of C. Reducing significantly the C causes the loss of oxides in the slag. Nevertheless, the combined case of vacuum and high temperature facilitates the production of low carbon ferroalloys.

Another complication in the production of reactive metals at high temperature is the formation of volatile compounds e.g. suboxides as SiO and Al$_2$O. If their partial pressures become significantly higher than CO pressure, carbothermic production of the metal will be virtually impossible.

VACUUM DEGASSING/REFINING
Apart from oxygen (the removal of which is done by deoxidation, as discussed below), other gases encountered in steelmaking are hydrogen and nitrogen. Their removal shall be dealt with in the next edition of this Lecture Note.

KILLING (DEOXIDATION) OF STEEL
Deoxidation of steel is carried out in the ladle during secondary steelmaking to reduce or completely remove the amount of dissolved oxygen in steels. Just like sucking oxygen out of a living organism implies killing the organism, the term deoxidation of steel is also referred to as killing. Depending on the level of deoxidation expected, different deoxidizing agents (deoxidizers or deoxidants) are used in required amounts. Deoxidizers are usually elements that have more affinity for oxygen than iron, and so they form stable oxides that can float on top of the molten steel and get partitioned into the slag. In some cases the oxides can remain in the steel in forms not as harmful as atomic oxygen. Examples are Ti, Al, Si and Mn.

The soundness of steel castings and ingots depends among other factors on the degree of deoxidation (Figure 33). The following degrees or types of deoxidation are commonly practiced:

i. **Killed steel** is produced when there is complete deoxidation. Killed steel is produced when powerful deoxidizers such as silicon (in form of Fe-Si) and
aluminium are used. During solidification of killed steels, little or no gas evolution takes place.

ii. **Rimming steel** is produced when partial deoxidation (e.g. using manganese and a small quantity of aluminium) is carried out. Manganese is usually added in the form of ferromanganese or spiegeleisen.

iii. **Semi-killed steel** is produced when the degree of deoxidation vary between the extremes of killing and rimming. Semi-killed steels are similar to killed steel, but insufficient deoxidant has been added so that complete deoxidation cannot be attained.

iv. **Capped steel** starts as rimmed steel but part way through the solidification the ingot is capped. This can be done by literally covering the ingot mould or by adding a deoxidizing agent. The top of the ingot then forms into a solid layer of steel, but the rim of the rest of the ingot is thinner than in a rimmed steel.

Thus the increasing order of degree of deoxidation is **rimming, semi-killing and killing**. With decreasing gas evolution during solidification, steels are classified as **rimmed, semi-killed and killed**.

Eight typical conditions of commercial ingots, cast in identical bottle-top moulds, in relation to the degree of suppression of gas evolution are shown schematically in Figure 33. The dotted line indicates the height to which originally the steel was poured in each ingot mould. Depending on the carbon content and particularly oxygen content, the ingot structures range from that of a fully killed or dead-killed ingot (No. 1) to that of a violently rimmed ingot (No. 8). Included in the series are semi-killed steel (No. 2), capped steel (No. 5), and rimmed steel (No. 7).

![Figure 33: Series of typical ingot structures vis-à-vis degree of deoxidation](image)

**Deoxidation of Ingots and Castings**

A steel ingot is a solidified product which has not attained its final size and shape. It is reduced by mechanical working or plastic deformation processes to the final desired shape and size according to the following size reduction sequence ingot→bloom→billet→slab→plate→sheet→strip→foil, or →bar→rod→wire, etc. On
the other hand, a steel casting is not a semi-finished product, but in its size and shape is the final end product of a solidification process. Hot liquid steel dissolves oxygen, but the solubility of oxygen in steel decreases with temperature. As steel cools, excess oxygen can cause blowholes or precipitate FeO. Therefore, several strategies have been developed for *deoxidation*.

Deoxidation with manganese is often reinforced by deoxidation with silicon and aluminium. These are more powerful deoxidizers than manganese and the term killing usually refers to their use. Silicon-killed steel is made by adding ferrosilicon (75 per cent Si 25 per cent Fe) together with some silicomanganese which helps to float the silica away as manganese silicate. Aluminium-killed steel is made by adding a small amount of aluminium to the steel in the ladle. Al-killed steel is tougher than Si-killed steel at low temperatures (e.g. 0°C) but Si-killed steel is stronger at high temperatures (e.g. 400°C).

Most steel is cast into ingot moulds and then rolled into bars and sheet. Ingot moulds are vertical, approximately cylindrical, shells of grey cast iron, open at the top, square or polygonal in cross-section and capable of holding a few 1000 kg of steel. The steel is *teemed*, i.e. run out from a nozzle in the bottom of the ladle, either into the top of the ingot mould below it, or down a *trumpet* and along a *runner* into the bottom of the mould. To permit easy separation of the ingot, the moulds are slightly tapered from top to bottom.

Depending on whether the ingot or mould is to be lifted off, the mould is set with either its wide or narrow end uppermost. Ingots are mainly cast with their wide ends up, to reduce the depth of pipe. When a killed steel solidifies, the contraction which the metal undergoes produces a large contraction cavity or pipe, as shown in Figure 34a.

![Figure 33](image)

*Figure 33:* Steel ingots; (a) killed steel, (b) killed steel in mould with hot top, (c) rimming steel
This unsound part of the ingot has to be cut off and returned for re-melting, so that the productivity is reduced. The effect can be minimized by delaying the solidification at the top of the mould, so that a reservoir of liquid is maintained there to feed into the ingot below as this freezes and contracts. This is done by fitting a thermally insulating refractory or even exothermically-lined hot top or feeder head, as shown in Figure 34b. Although this gives a considerable improvement, the metal discarded from the hot top and the cost of the hot top itself still add to the expense of the ingot. The alternative is to prevent the metal from shrinking by allowing a small amount of CO to form as bubbles, when it freezes. This is done in rimming steels. These are low-carbon (< 0.15 per cent C) steels usually used for sheet steel pressings. Only low-carbon steels contain enough oxygen to rim satisfactorily. Silicon and aluminium are not used but some manganese is added to the ladle. With careful control, the CO effervescence is delayed until about 0.025m of iron has solidified against the wall of the mould. The bubbles then form and compensate for the freezing contraction, so that no pipe is formed and none of the ingot has to be discarded. The CO blow-holes weld up when the ingot is afterwards forged. Another advantage is that the oxygen in the metal captures its carbon from the first layers to solidify, so that these become very ductile carbon-free iron. This soft skin gives the metal a good smooth surface when it is afterwards rolled into sheet and pressed.

Cheap steel for girders, plates, etc. is usually made by a balanced or semikilled method. It is slightly deoxidized with silicon or aluminium but not enough to require a hot top.

CONTINUOUS CASTING OF STEEL
Further adjustment of steel chemistry in the tundish and subsequent casting by means of a continuous casting machine shall be discussed in the next edition of this Lecture Note

STEEL AND INDUSTRIAL POWER OF NATIONS
Since the onset of the Industrial Revolution, the material wealth and power of a nation has depended largely upon its ability to make steel and steel products. The industrial, economic and military power of any nation depends on steel. Think of the ordinary office pin, needle, razor blade, fork and spoon, knife, hoe, shovel. Think of the bicycle, car, train, ship, and plane. According to Kassinger (2003), North American automakers and their parts suppliers used about 18 million tonnes of steel in their vehicles in 1998 alone. The average vehicle contained about 822 kg of flat-rolled sheet, bar, tubular, rod, and wire steel. Think of the sewing machine, printing press, file cabinets, refrigerators, air-conditioners, microwave ovens, and washing machines. Think of tractors, bulldozers, and the bridges across River Niger, skyscrapers, and all military hardware. You can find steel everywhere.
It is important to note that Gross Domestic Product (GDP) is not enough to measure national development. Whether the economists believe it or not, one other parameter for measuring development is the **per capita consumption of steel** in any nation. That is the total weight of steel (in kilograms) processed to finished products (e.g. from office pins and razor blades to automobiles and aircrafts, etc.) divided by the population. Thus, the consumption of iron and steel per capita basis is regarded as an accurate indicator of the economic and industrial development of any nation. It is therefore not surprising that while the steel consumption per capita for the highly industrialized nations ranges between 250 and 600 kg of crude steel, those for the under-developed countries are far less. For instance, in the year 2013, the figures for Japan and South Korea were 516.4 and 1,057.4 kg respectively, while that of Africa was 41.8 kg with South Africa and Egypt having 105.8 and 88.9 kg respectively. The other countries in Africa put together had 28.8 kg. For steel use or consumption on non-per capita basis, the 2013 figures for Japan and South Korea were 65.3 and 51.6 million tonnes of finished steel products respectively, while that of Africa was 29 million tonnes with South Africa and Egypt having 5.4 and 7.6 million tonnes of finished steel products respectively. The other countries in Africa put together produced 16 million tonnes of finished steel products. In all these data from the World Steel Association (Appendices III and IV), the giant of Africa (Nigeria) had too little an impact to receive even a mention. As shown in Appendices I, II and V, in 2013, only South Africa and Egypt were ranked (21 and 23 respectively) in Africa among the top 50 steel producing countries. Of the 1606 million tonnes of crude steel produced in 2013, these 50 nations produced 1593 (99.2%) million tonnes of crude steel while the rest of the world (including Nigeria) produced 13 (0.8%) million tonnes of crude steel. 

*If Nigeria must become like the Republic South Korea, if Nigeria must become like Japan, if Nigeria must transfer from buying and selling trade to manufacturing, then Nigeria must accept, with all its implications, that the industrial, economic, military, social and even political power of any nation is dependent on steel. To industrialize, there is the need to have a sound industrial base. This will provide the solid foundation on which the industrial super-structure will be built. This industrial base is nothing other than a well-developed iron and steel industry. According to Ohimain (2013), Nigeria is blessed with all the major raw materials needed for the production of iron and steel including 3 billion tonnes of iron ore, 3 billion tonnes of coal, and limestone in excess of 700 million tonnes and 187 billion standard cubic feet (SCF) of natural gas. Yet, Western countries had hitherto (through the World Bank and IMF) advised Nigeria to concentrate on Agriculture rather than venture into the high-tech and heavy manufacturing steel business (Mohammed, 2002). As rightly observed by Arrey (2013), —*The controversy that historical knowledge supports the truth that industrialization is marked by a fall on agricultural products and a corresponding rise in non-agricultural*
activities mostly in manufacturing industries and services, seems to be factual when juxtaposed with the truth that Nigerian’s industrialization is inextricable linked to social pathologies viz.: ineptitude of leadership, weak organizational competence, corruption, faulty policy articulation and implementation, dynamics of international politics where IMF, world bank, the Paris club etc., hold sway.

Taking cognizance of the strategic importance of iron and steel, many third world countries have been able to lift their economies away from third world poverty and starvation, and seriously threatening the developed countries of the world in economic wellbeing for their people. A few examples will suffice; India, South Korea, Pakistan, Egypt, Iran, Iraq, Algeria, Libya, Turkey, Venezuela, Indonesia, Singapore, Malaysia and Mexico. The steel projects in all these countries started as serious national projects, with their Governments taking active interest in the steel development. Pandit Nehru of India once called the giant steel structures coming up in Bhilai, Durgapur and Ruerkela in the late 1950s, as the —Temple of Modern India. Saudi Arabia, Algeria and Libya with their fabulous oil reserves also have developed viable steel industries. Other third world oil producing countries with very well developed steel industries include Indonesia, Venezuela and Mexico.

According to the World Steel Association (World Steel in Figures 2014), Steel is a cornerstone and key driver for the world’s economy. The steel industry directly employs more than two million people worldwide, plus two million contractors and four million people in supporting industries. Including industries such as construction, transport and energy, the steel industry is a source of employment for more than 50 million people.

Iron and steel industries or projects have multiplier effects on the economy because of their ability to induce other related economic and industrial activities (Mark, 2000). A cursory look at Ajaokuta Steel Company (referred to as the bedrock of Nigeria’s Industrialization) as noted by Mohammed (2002) reveals that this Company will have a multiplier linkage effect on the national economy. If Phase 1, that is, production of 1.3 million tonnes of liquid steel is completed and put to commercial use, the nation has the following direct benefits to derive:

- Employment of 10,000 workers in the Plant;
- Employment of not less than 20,000 Nigerians in the raw materials industries providing feed-stock to the plant;
- Employment of not less than another 30,000 Nigerians in the industries that use the products of the plant;
- Conservation of foreign exchange used for importation of steel products annually;
- Contribution of not less than 30% of the inputs to the automotive industry in Nigeria, in the first instance;
Ajaokuta Steel Plant has the capacity to meet most of the national requirements of Chemicals and tar (as by-products of the steel production process) and refractory bricks, using locally available raw materials and the Alumino-Silicate Refractory Plant;

Export potential to ECOWAS sub-region;

Most industries in Nigeria have problem sourcing for their machinery and spare parts. The Ajaokuta Steel Company’s well-equipped Engineering Works Complex can assist to a large extent.

The non-completion and commissioning of the Ajaokuta Steel Project implies that Nigeria is yet to produce blast furnace iron (BFI) as shown in Appendix VI. However, the completion and subsequent epileptic operation of the Delta Steel Plant brought Nigeria among the nations producing direct-reduced iron (DRI) as shown in appendix VII.

Appendix I: Major steel producing countries 2012 and 2013 (million tonnes crude steel production)

<table>
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<th>2013 Rank</th>
<th>Tonnage</th>
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<td>Techint Group (&quot;)</td>
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**Appendix II: Top 50 steel producing companies in 2013 (million tonnes crude steel production)**

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<th>Rank</th>
<th>Company</th>
<th>Tonnage</th>
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<td>Rizhao Steel</td>
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|   | Company                  | Consumption |   | Country                
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</table>

* worldsteel members
** Handan, which is part of Hebei Group, is a member of worldsteel
(1) Some Chinese companies consolidated to form Tianjin Bohai Steel in 2013
(2) Pingxiang and Jiujiang were merged with Fangda Steel at the end of 2012
(3) RIVA Fire Group was split into ILVA SpA and Riva Forni Elettrici SpA in June 2013

Appendix III: Apparent Steel Consumption/Use 2007 to 2013 (million tonnes finished steel products)

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Appendix IV: Apparent Steel Consumption/Use Per Capita 2007 To 2013 (kilograms finished steel products)

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### Appendix V: Crude steel production, 1980-2013 (In thousand tonnes)

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**Note:** MME 405 Lecture Notes; © Engr. U. Mark, Dec. 2008, Revised Dec 2014
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**Regions, definitions - only countries listed above are included**

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**European Union (12):** Austria, Belgium, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, United Kingdom

**European Union (10):** Austria, Belgium, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, United Kingdom

**Former USSR:** Armenia, Azerbaijan, Belarus, Georgia, Kazakhstan, Kyrgyzstan, Moldova, Russia, Tajikistan, Turkmenistan, Ukraine, Uzbekistan, Kyrgyz Republic

**North America:** Canada, Costa Rica, Cuba, Dominican Republic, El Salvador, Guatemala, Honduras, Mexico, Panama, Trinidad and Tobago, United States

**South America:** Argentina, Brazil, Chile, Colombia, Ecuador, Peru, Uruguay, Venezuela

**Africa:** Algeria, Angola, Congo (Kinshasa), Egypt, Ghana, Kenya, Libya, Mauritania, Morocco, Niger, Nigeria, South Africa, Tanzania, Uganda, Zimbabwe

**Middle East:** Iran, Iraq, Israel, Jordan, Qatar, Oman, Saudi Arabia, Syria, United Arab Emirates

**Asia & Oceania:** Australia, Bangladesh, China, Hong Kong, India, Indonesia, Japan, Malaysia, Mongolia, Myanmar, New Zealand, North Korea, Pakistan, Philippines, Singapore, Sri Lanka, South Korea, Taiwan, Thailand, Vietnam

**Appendix VI: Blast furnace iron (BFI) production, 1980-2013 (in thousand tonnes)**

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**Note:** The data for the years 1980 to 2020 are approximate and subject to change. The values represent the production of blast furnace iron (BFI) in thousand tonnes. The data may not be exhaustive for all regions and countries.
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European Union (25) European Union (15), Czech Republic, Hungary, Poland, Slovak Republic
European Union (27) European Union (25), Cyprus, Malta
CIS Kazakhstan, Russia, Ukraine
former USSR CIS, Estonia
North America Canada, Mexico, United States
South America Argentina, Brazil, Chile, Colombia, Paraguay, Peru, Venezuela
Africa Algeria, Egypt, Morocco, South Africa, Tunisia, Zimbabwe
Middle East Iran
Asia & Oceania Australia, China, India, Japan, Malaysia, New Zealand, North Korea, Pakistan, South Korea, Taiwan, China, Vietnam

Appendix VII: Direct reduced iron (DRI) production, 1980-2013 (in thousand tonnes)

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<td>542</td>
<td>502</td>
<td>499</td>
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</tbody>
</table>

**Note:** The table above is a representation of the data provided in the image. The columns represent different regions and years, while the rows indicate specific data points for each entry.
<table>
<thead>
<tr>
<th>Region</th>
<th>Countries Listed Above Are Included</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Union (10)</td>
<td>Germany</td>
</tr>
<tr>
<td>European Union (12)</td>
<td>European Union (10)</td>
</tr>
<tr>
<td>European Union (15)</td>
<td>European Union (12), Sweden</td>
</tr>
<tr>
<td>European Union (27)</td>
<td>European Union (15)</td>
</tr>
<tr>
<td>CIS</td>
<td>Kazakhstan</td>
</tr>
<tr>
<td>Former USSR</td>
<td>Russia</td>
</tr>
<tr>
<td>North America</td>
<td>Canada, Mexico, Trinidad and Tobago, United States</td>
</tr>
<tr>
<td>South America</td>
<td>Argentina, Brazil, Peru, Venezuela</td>
</tr>
<tr>
<td>Africa</td>
<td>Egypt, Libya, Nigeria, South Africa</td>
</tr>
<tr>
<td>Middle East</td>
<td>Bahrain, Iran, Oman, Qatar, Saudi Arabia, United Arab Emirates</td>
</tr>
<tr>
<td>Asia &amp; Oceania</td>
<td>Australia, China, India, Indonesia, Malaysia, Myanmar, New Zealand</td>
</tr>
</tbody>
</table>
REFERENCES


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World Steel Association: *Crude steel production, 1980-2013*; www.worldsteel.org

World Steel Association: *World steel in Figures 2014*; http://www.worldsteel.org