Chapter 2

Fundamentals of Iron and Steelmaking

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There have been tremendous improvements in iron and steelmaking processes in the past twenty years. Productivity and coke rates in the blast furnace and the ability to refine steel to demanding specifications have been improved significantly. Much of this improvement is based on the application of fundamental principles and thermodynamic and kinetic parameters which have been determined. Whereas, many future improvements will be forthcoming in steelmaking equipment, process improvements resulting from the application of fundamental principles and data will likewise continue.

In this chapter the basic principles of thermodynamics and kinetics are reviewed and the relevant thermodynamic data and properties of gases, metals and slags relevant to iron and steelmaking are presented. These principles and data are then applied to ironmaking, steelmaking and secondary refining processes. These principles and data are also used in subsequent chapters in this volume.

In writing this chapter, an attempt has been made to limit the discussion to an average level suitable for the students of metallurgy pursuing graduate or post-graduate education as well as for those with some scientific background engaged in the iron and steel industry. It is assumed that the reader has some basic knowledge of chemistry, physics and mathematics, so that the chapter can be devoted solely to the discussion of the chemistry of the processes.

2.1 Thermodynamics

2.1.1 Ideal Gas

A gas which obeys the simple gas laws is called an ideal gas satisfying the following relation:

$$PV = nRT \qquad (2.1.1)$$

where n is the number of mols and R the universal molar gas constant.

For one mol of an ideal gas at 273.16K and l atm pressure, the value of the molar gas constant is:

$$R = \frac{1 \times 22414}{273.16} = 0.08205 \, \text{l atm mol}^{-1} \, \text{K}^{-1}$$

For pressure in Pa ($\equiv \text{Nm}^{-2} \equiv \text{Jm}^{-3}$) and volume in m^3,

$$R = \frac{1.01325 \times 10^5 \times 22.414 \times 10^{-3}}{273.16} = 8.314 \, \text{J mol}^{-1} \text{K}^{-1}$$

In a gas mixture containing n_1, n_2, n_3... number of mols of gases occupying a volume V at a total pressure P, the partial pressures of the constituent gaseous species are as given below.

$$p_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots} \times P \qquad (2.1.2)$$

$$P = p_1 + p_2 + p_3 + \dots \qquad (2.1.3)$$

The following equations are for a given mass of gas at constant pressure, volume and temperature:

Constant pressure (isobaric) $\qquad \dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} = \dfrac{V_3}{T_3} \dots \qquad (2.1.4)$

Constant volume (isochoric) $\qquad \dfrac{P_1}{T_1} = \dfrac{P_2}{T_2} = \dfrac{P_3}{T_3} \dots \qquad (2.1.5)$

Constant temperature (isothermal) $\qquad P_1 V_1 = P_2 V_2 = P_3 V_3 \dots \qquad (2.1.6)$

Generally speaking, deviation from the ideal gas equation becomes noticeable with easily liquefiable gases and at low temperatures and high pressures. The behavior of gases becomes more ideal with decreasing pressure and increasing temperature. The nonideality of gases, the extent of which depends on the nature of the gas, temperature and pressure, is attributed to two major causes: (1) van der Waals' forces and (2) chemical interaction between the different species of gas molecules or atoms.

2.1.2 Thermodynamic Laws

2.1.2.1 The First Law

The first law of thermodynamics is based on the concept of conservation of energy. When there is interaction between systems, the gain of energy of one of the systems is equal to the loss of the other system. For example, the quantity of heat required to decompose a compound into its elements is equal to the heat generated when that compound is formed from its elements.

2.1.2.1.1 Enthalpy (heat content)   The internal energy of a system includes all forms of energy other than the kinetic energy. Any exchange of energy between a system and its surroundings, resulting from a change of state, is manifested as heat and work.

When a system expands against a constant external pressure P, resulting in an increase of volume ΔV, the work done by the system is

$$w = P\Delta V = P(V_B - V_A)$$

Since this work is done by the system against the surroundings, the system absorbs a quantity of heat q and the energy E of the system increases in passing from state A to state B.

$$\Delta E = E_B - E_A = q - P\Delta V = q - P(V_B - V_A)$$

Upon re-arranging this equation, we have

$$(E_B + PV_B) - (E_A + PV_A) = q$$

The quantity $E + PV$ is represented by a single symbol H, thus

$$\Delta H = q = (E_B + PV_B) - (E_A + PV_A) \qquad (2.1.7)$$

The function H is known as enthalpy or heat content.

There are two fundamental thermochemical laws which express the first law specifically in terms of enthalpy. The first principle derived by Lavoisier and Laplace (1780) states that "the quantity of heat required to decompose a compound into its elements is equal to the heat evolved when that compound is formed from its elements"; i.e. the heat of decomposition of a compound is numerically

equal to its heat of formation, but of opposite sign. The second principle is that discovered by Hess (1840); it states that "the heat of reaction depends only on the initial and final states, and not on the intermediate states through which the system may pass."

2.1.2.1.2 Heat Capacity   The heat capacity of a substance is defined as the quantity of heat required to raise the temperature by one degree. The heat capacity of 1 g of a substance is called the specific heat. The heat capacity of 1 g-molecule (abbreviated as mol) is called the molar heat capacity.

The variation of energy, at constant volume, and of enthalpy, at constant pressure, with temperature gives the heat capacity of the system, thus

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{2.1.8}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{2.1.9}$$

For an ideal gas the difference between the molar heat capacities at constant pressure, C_p, and constant volume, C_V, is equal to the molar gas constant.

$$C_p - C_V = R \tag{2.1.10}$$

Because of experimental convenience, the heat capacity is determined under conditions of constant pressure (usually atmospheric).

From the temperature dependence of heat capacity at constant pressure, the enthalpy change is obtained by integrating equation 2.1.9.

$$H^\circ_{T_2} - H^\circ_{T_1} = \int_{T_1}^{T_2} C_p dT \tag{2.1.11}$$

Above 298 K, the temperature dependence of C_p is represented by:

$$C_p = a + bT - cT^{-2} \tag{2.1.12}$$

$$\Delta H = \int_{298}^{T} \left(a + bT - cT^{-2}\right) dT \tag{2.1.13}$$

where the coefficients, a, b and c are derived from C_p calorimetric measurements at different temperatures.

In recent compilations of thermochemical data, the H values are tabulated at 100 K intervals for the convenience of users.

2.1.2.1.3 Standard State   The enthalpy is an extensive property of the system, and only the change in heat content with change of state can be measured. A standard reference state is chosen for each element so that any change in the heat content of the element is referred to its standard state, and this change is denoted by ΔH°.

The natural state of elements at 25°C and 1 atm pressure is by convention taken to be the reference state. On this definition, the elements in their standard states have zero heat contents.

The heat of formation of a compound is the heat absorbed or evolved in the formation of 1 g-mol of the compound from its constituent elements in their standard states, denoted by ΔH°_{298}.

2.1.2.1.4 Enthalpy of Reaction   The change of enthalpy accompanying a reaction is given by the difference between the enthalpies of the products and those of the reactants.

For an isobaric and isothermal reaction,

$$A + B = C + D \qquad (2.1.14)$$

the enthalpy change is given by:

$$\Delta H = (\Delta H°C + \Delta H°D) - (\Delta H°A + \Delta H°B) \qquad (2.1.15)$$

By convention, H is positive (+) for endothermic reactions, i.e. heat absorption, and H is negative (−) for exothermic reactions, i.e. heat evolution.

Temperature effect:

$$\Delta H_T° = \Sigma \Delta H_{298}°\big(\text{products}\big) - \Sigma \Delta H_{298}°\big(\text{reactants}\big) + \int_{298}^{T} \Big[\Sigma C_p\big(\text{products}\big) - \Sigma C_p\big(\text{reactants}\big)\Big] dT \quad (2.1.16)$$
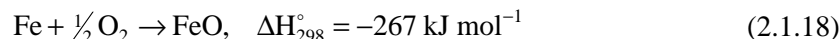
$$\Delta H_T° = \Delta H_{298}° + \int_{298}^{T} \big(\Delta C_p\big)\, dT \qquad (2.1.17)$$

The following are some examples of the special terms of the heat of reaction.

Enthalpy or heat of formation	$Fe + \tfrac{1}{2}O_2$	$\rightarrow$	FeO
Heat of combustion	$C + O_2$	$\rightarrow$	CO_2
Heat of decomposition	$2CO$	$\rightarrow$	$C + CO_2$
Heat of calcination	$CaCO_3$	$\rightarrow$	$CaO + CO_2$
Heat of fusion (melting)	Solid	$\rightarrow$	Liquid
Heat of sublimation	Solid	$\rightarrow$	Vapor
Heat of vaporization	Liquid	$\rightarrow$	Vapor
Heat of solution	$Si(l)$	$\rightarrow$	$[Si]$ (dissolved in Fe)

2.1.2.1.5 Adiabatic Reactions When a reaction occurs in a thermally insulated system, i.e. no heat exchange between the system and its surroundings, the temperature of the system will change in accordance with the heat of reaction.

As an example, let us consider the internal oxidation of unpassivated direct reduced iron (DRI) in a stockpile, initially at 25°C. The enthalpy of reaction at 298K is

$$Fe + \tfrac{1}{2} O_2 \rightarrow FeO, \quad \Delta H_{298}° = -267 \text{ kJ mol}^{-1} \qquad (2.1.18)$$

The heat balance calculation is made for 1000 kg Fe in the stockpile with 150 kg FeO formed in oxidation. The heat absorbed by the stockpile is $150 \times 10^3/72 \times 267$ kJ and the temperature rise is calculated as follows:

$$
\begin{aligned}
Q &= [n_{Fe}(C_p)_{Fe} + n_{FeO}(C_p)_{FeO}](T - 298) \\
n_{Fe} &= 17,905 \text{ g-mol for 1000 kg Fe} \\
n_{FeO} &= 2087.7 \text{ g-mol for 150 kg FeO} \\
C_p(Fe) &= 0.042 \text{ kJ mol}^{-1}K^{-1} \\
C_p(FeO) &= 0.059 \text{ kJ mol}^{-1}K^{-1} \\
\therefore Q &= 557,416 = (752 + 123)(T - 298)
\end{aligned}
$$

With this adiabatic reaction, the stockpile temperature increases to T = 935K (662°C).

The moisture in the stockpile will react with iron and generate H_2 which will ignite at the elevated stockpile temperature. This has been known to happen when DRI briquettes were not adequately passivated against oxidation.

2.1.2.2 The Second Law

The law of dissipation of energy states that all natural processes occurring without external interference are spontaneous (irreversible processes). For example, heat conduction from a hot to a cold