MATERIAL AND HEAT BALANCE OF PROCESSES

The product output of any process depends on the amount of materials consumed as raw materials and the chemical reactions taking place. Similarly, the energy requirements are related to that required for heating of material to sufficiently high temperatures and sustaining the chemical reactions. Material and heat balance calculations aim at estimating inflow and outflow of mass and energy respectively. These are essential plant records and routine calculations for plant operation.

Before attempting to calculate the raw material or energy requirements of a process, it is desirable to first obtain a clear picture of the process. The best way to do this is to draw a **flow diagram**, sometimes also called **flowsheet**.

3.1 FLOW DIAGRAMS

A flow diagram is a line diagram showing successive steps of a process by indicating the pieces of equipment in which they occur and the material streams entering and leaving each piece of equipment. Flow diagrams are very important for saving time and eliminating mistakes. The following guidelines should be observed.

1. The flow diagram should show the unit operations/process by simple rectangles.

2. In a flow diagram each arrow should represent an actual stream of material in a single phase. Thus a gaseous mixture of carbon dioxide, oxygen, carbon monoxide, nitrogen and water vapour, coming out of a combustion chamber should be shown as a single stream of gas and not as five separate streams. On the other hand, slag and metal produced by a blast furnace should be shown by two separate streams, the blast furnace itself being indicated by a simple rectangle.

A typical flow diagram is shown in Fig. 3.1 The diagram describes extraction of copper from a low grade ore.

3.2 MATERIAL BALANCE PROCEDURE

Material balance is essentially an application of the law of conservation of mass. The following equation describes in words the principle of general material balance applicable to processes both with and without chemical reactions.

$$\begin{bmatrix} \text{Accumulation of mass} \\ \text{within the system} \end{bmatrix} = \begin{bmatrix} \text{Input through system} \\ \text{boundaries} \end{bmatrix} = \begin{bmatrix} \text{Output through} \\ \text{system boundaries} \end{bmatrix} \quad (3.1)$$

Depending on the magnitudes of the last two terms of Eq. 3.1, the accumulation may be positive or negative. The equation, written simply as

Composition of materials:
Ore from mine = 1% Cu, 3% Fe, 3% S
Flotation concentrate = 25% Cu, 25% Fe, 35% S, 5% SiO_2
Tailing from flotation = 0.1% Cu, 2.2% Fe, 1.8% S
Flux for smelting = 65% SiO_2, 15% FeO
Matte = 35% Cu, 35% Fe, 25% S
Slag from matte smelting = 0.5% Cu, 45% FeO, 36% SiO_2
Slag from converter = 3% Cu, 60% FeO, 25% SiO_2

```
                        Ore from mine
                              │
                              ▼
                      ┌─────────────────┐
                      │  Comminution    │
                      └─────────────────┘
                              │
                              ▼
                      ┌─────────────────┐
                      │   Floatation    ├──────────────┐
                      └─────────────────┘              │
                              │                         ▼
                         Cocentrate                  Tailing
                              │
                              ▼
                      ┌─────────────────┐
           Flux       │    Roasting     │◄── Air
            │         └─────────────────┘
            │                 │                 Gases to waste
            │                 ▼                      ▲
            │         ┌─────────────────┐            │
            └────────►│     Matte       ├────────────┘
                      │    smelting     │
                      └─────────────────┘
                              │                      │
                              │                      ▼
                              │                 Slag to waste
                              ▼
                            Matte
                              │           ── Flux
                              │          │
            Air ──────────►┌─────────────────┐
                           │   Converting    ├──► Gases to waste
           Slag ◄──────────└─────────────────┘
                              │
                              ▼
                     Blister copper (99% Cu)
                              │
                              ▼
                      ┌─────────────────┐
                      │  Fire refining  │
                      └─────────────────┘
                              │
                              ▼
                      ┌──────────┐
                      │ Casting  │ (Anodes)
                      └──────────┘
                              │
                              ▼
                      ┌──────────────────────┐
                      │ Electrolytic refining │
                      └──────────────────────┘
                              │
                              ▼
                      ┌─────────────────┐
                      │  Fire refining  │
                      └─────────────────┘
                              │
                              ▼
                      ┌──────────┐
                      │ Casting  │
                      └──────────┘
                              │
                              ▼
                       99·95% Copper
```
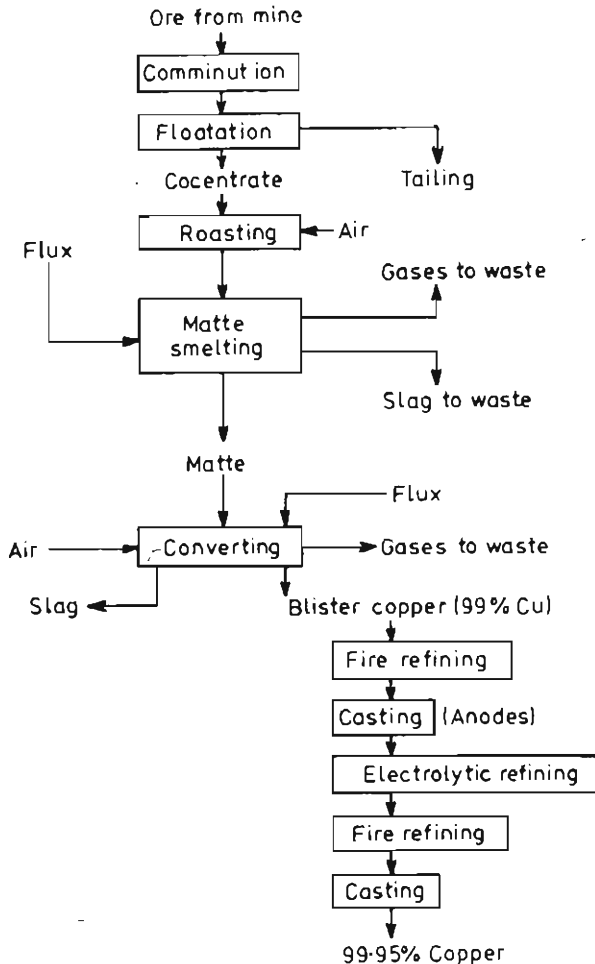
Fig. 3.1 Flow diagram for extraction of copper from a low grade ore

$$accumulation = input - output$$

reduces further when there is no accumulation within the system. In that case one has

$$input = output \qquad (3.2)$$

This is applicable to a **batch process** which involves treatment of a given mass of materials in a process after which the products are taken out.

If a process is operated such that, over long periods, continuous streams of materials enter into the processing unit and continuous streams leave the same then it is called a **continuous process**. In such a process one is concerned with the **rate of input** and **rate of output** of materials. If the continuous process runs at **steady state**, then the chemical compositions of the input materials and output materials remain unchanged and there can be no accumulation within the system either. In such a situation, the material balance equation is written as

$$\text{Rate of input of materials into the system}$$
$$= \text{Rate of output of materials from the system} \qquad (3.3)$$

In other words, for both batch process and continuous process, what goes in must come out.

In processes in which chemical reactions take place resulting in formation, consumption and/or transformation of compounds, one must apply the principles of **stoichiometry** as well as those of material balance. It should be noted that material balance holds on the total mass of materials but not on moles. Thus while one mole each of hydrogen and chlorine react to give two moles of hydrochloric acid gas, one mole of nitrogen reacts with three moles of hydrogen to produce two moles of ammonia. One mole of limestone decomposes to produce one mole of carbon dioxide and one mole of CaO. In every case, however, the total mass before and after the reaction remains the same.

For material balance, a convenient basis of calculation is to be chosen. In continuous processes, it is either unit time (an hour in a day) or unit mass of product (say, one tonne of hot metal for the blast furnace). For batch processes, it is either the entire batch or unit mass of product.

3.2.1 Stoichiometry

Imagine a process shown in Fig. 3.2 and assume it to be a steady state one.
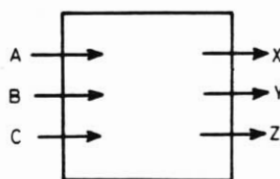
Fig 3.2 A steady-state process

A, B, C are rates of input (mass/time) of different feed materials and X, Y, Z are rates of output of different products. Let 1, 2, 3, 4 ...n denote the various chemical elements and $a_1, b_1, c_1,$ denote the weight percentages of element in A, B, C. Then the balances of chemical elements yield the following equations:

$$\left.\begin{array}{l} a_1A + b_1B + c_1C - x_1X - y_1Y - z_1Z = 0 \\ a_2A + b_2B + c_2C - x_2X - y_2Y - z_2Z = 0 \\ \cdots\cdots \qquad\qquad \cdots\cdots \qquad\qquad \cdots\cdots \\ \cdots\cdots \qquad\qquad \cdots\cdots \qquad\qquad \cdots\cdots \\ a_nA + b_nB + c_nC - x_nX - y_nY - z_nZ = 0 \end{array}\right\} \qquad (3.4)$$

Also from Eq. (3.3), $A + B + C - X - Y - Z = 0$ (3.5)

Altogether 6 $(n + 1)$ quantities are involved in these equations. Only $(n + 1)$ of them can be solved from these $(n + 1)$ simultaneous equations. The value for others must be given.

The preceding equations are based on the law of conservation of mass applied to individual chemical elements. During any chemical and physical processing (other than nuclear reactions), elements are preserved though their states of combination may change.

Mathematically the problem appears to be straight forward. However, obtaining accurate solution may be difficult. Also, some errors occur when a quantity is calculated by taking the difference between two large quantities. If some of the feed and/or product materials are gases then Gas Laws may be employed in order to convert volume percentages into weight percentages. If all the necessary information is not available then appropriate assumption should be made.

3.2.2 Steps in Material Balance Calculation

The generally recommended procedure for material balance is as follows:
  (a) Represent each process by a rectangle and indicate each feed or product material by an arrow. Write complete flow diagram.
  (b) Gather all known data in a table accompanying the sketch or, if there are not too many data, put the data on the flow diagram itself.
  (c) Make suitable assumptions if necessary.
  (d) Choose a convenient basis for calculation.
  (e) Write the overall chemical reactions that take place in the process.
  (f) Write the element balance equations.
  (g) Solve the equations.
  (h) Make up the material balance table.
  (i) Check by an independent method that the calculations are correct.

Example 3.1

A lead sinter to be smelted in a blast furnace analyses 8% CaO, 25% SiO_2, and 15% Fe. In smelting this sinter, a slag is desired with CaO, FeO and SiO_2 in the proportions.

$$CaO : FeO : SiO_2 = 4 : 6 : 7$$
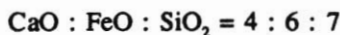
To obtain this slag, iron ore and limestone of the following analyses are added to the charge :

|	Wt% Fe	Wt% CaO	Wt% SiO_2
Iron Ore	45.0	0.5	15.0
Limestone	2.0	46.0	8.0

In addition, coke is to be added to the charge as a fuel in an amount equal to 12 percent of the weight of (sinter + iron ore + limestone). The coke contains 2.5% Fe_2O_3 and 12% SiO_2.

Assuming that all the lime, iron and silica enter the slag as CaO, FeO and SiO_2, calculate the weights of iron ore, limestone and coke to be used per metric tonne of lead sinter.

Solution

(a) The process of smelting lead sinter is represented by the rectangular block diagram in Fig. Ex. 3.1. All the known data have been shown there itself. Values to be calculated are also indicated by question marks (W_i denotes weight of species i).
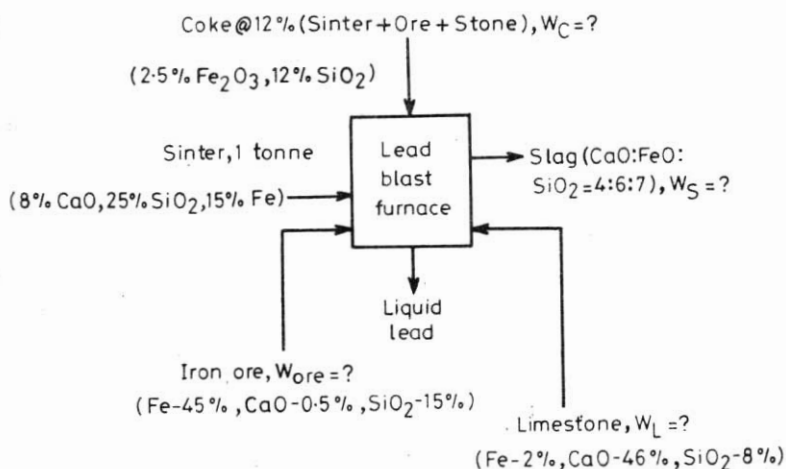
BASIS: METRIC TONNE OF LEAD SINTER

Fig. Ex. 3.1 Rectangluar block diagram for melting in lead blast furnace

(b) Basis of calculation is 1 tonne of lead sinter.

(c) There are several chemical reactions. These have not been identified. Also, the exact natures of some of the compounds have not been given. For example, it is stated that the lead sinter contains 15% Fe. As we know, iron ought to be present as some oxide and not as elemental iron. Therefore, it is neither possible, nor necessary to write down the various chemical reactions.

(d) The various element (or compound) balance equations (per tonne of lead sinter) are as follows. W_o, W_c, W_L, W_s, are weights of iron ore, coke, limestone and slage, respectively, per ton of lead sinter.

FeO balance

$$1 \times 0.15 \times \frac{72}{56} + W_o \times 0.45 \times \frac{72}{56} + W_c \times 0.025 \times \frac{144}{56}$$

(FeO in sinter) (FeO in iron ore) (FeO in coke)

$$+ W_L \times 0.02 \times \frac{72}{56} = W_s \times \frac{6}{17} \qquad \text{(Ex. 3.1)}$$

(FeO in limestone) (FeO in slag)

CaO balance

$$1 \times 0.08 \quad + \quad W_o \times 0.005 \quad + \quad W_L \times 0.46$$

(CaO in sinter) (CaO in iron ore) (CaO in limestone)

$$= W_s \times \frac{4}{17} \tag{Ex. 3.2}$$

SiO$_2$ balance

$$1 \times 0.25 \quad + \quad W_o \times 0.15 \quad + \quad W_c \times 0.12$$

(SiO$_2$ in sinter)   (SiO$_2$ in iron ore)   (SiO$_2$ in coke)

$$+ \; W_L \times 0.08 \quad = \quad W_s \times \frac{7}{17} \tag{Ex. 3.3}$$

(SiO$_2$ in limestone)   (SiO$_2$in slag)

The preceding equations are based on the assumption that all the lime, iron and silica enter the slag phase.

(e) From overall material balance

$$W_C = 0.12 \; (\; 1 + W_o + W_L) \tag{Ex. 3.4}$$

There are 4 unknowns, viz. W_o, W_c, W_L and W_s. They can be determined by solving the 4 simultaneous equations (Ex. 3.1 — Ex. 3.4)

Answer: $W_O = 93$ kg, $W_L = 195$ kg, $W_C = 155$ kg per tonne of lead sinter.

Example 3.2

Steel is being made in an L.D. converter. The metallic charge consists of hot metal and scrap in the ratio of 4 : 1. The hot metal contains 4% C, 1% Si, 1% Mn, 0.3% P and rest Fe. Oxygen of 99.5% purity is blown for refining. Lime, analysing 2% SiO$_2$, 3% MgO and rest CaO is added as flux. The gas leaving the converter has a p_{CO}/p_{CO_2} ratio of 1 : 1. 2% of total Fe charged is lost in the slag as FeO and Fe$_2$O$_3$, the ratio of ferrous to ferric ion in slag being 1 : 1. The steel may be assumed to contain 0.2% C, 0.2% Mn and rest Fe. Assume that the slag is to contain 50% CaO. Also assume that the efficiency of oxygen utilization is 90%.
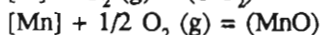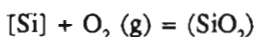
Calculate the following per tonne steel:
   (a) Weights of hot metal and scrap to be charged
   (b) Oxygen to be blown in m^3 (STP)
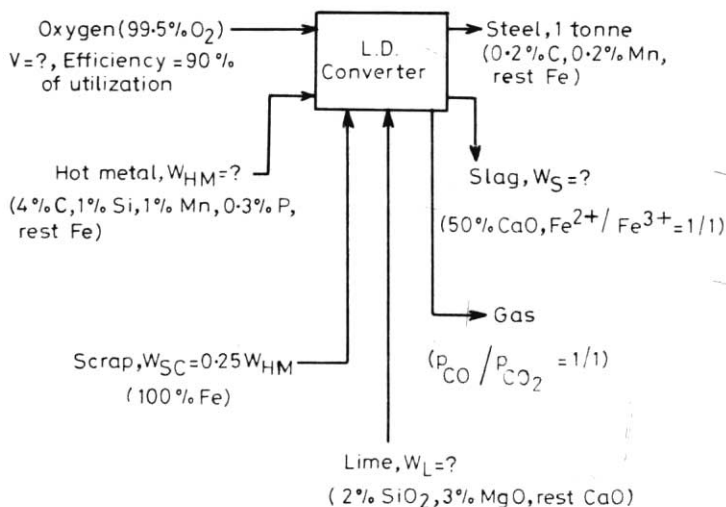   (c) Weight of lime to be charged
   (d) Weight of slag produced.

Solution

(a) The process of refining hot metal into steel is represented by the rectangular block diagram in Fig. Ex. 3.2. All the known data have been shown there including the assumptions. Values to be calculated are indicated by question mark.
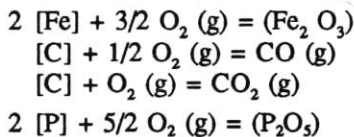
(b) Basis of calculation is 1 tonne of steel.

(c) Chemical reactions are :

[Si] + O$_2$ (g) = (SiO$_2$)
[Mn] + 1/2 O$_2$ (g) = (MnO)
[Fe] + 1/2 O$_2$ (g) = (FeO)

Oxygen$(99.5\% O_2)$ ——→ | L.D. Converter | ——→ Steel, 1 tonne
V=?, Efficiency =90 % of utilization

$(0.2\% C, 0.2\% Mn,$ rest Fe)

Hot metal, W_{HM}=?
$(4\% C, 1\% Si, 1\% Mn, 0.3\% P,$ rest Fe)

Slag, W_S=?
$(50\% CaO, Fe^{2+}/Fe^{3+} = 1/1)$

——→ Gas

Scrap, $W_{SC} = 0.25 W_{HM}$
(100 % Fe)

$(P_{CO}/P_{CO_2} = 1/1)$

Lime, W_L=?
(2 % SiO_2, 3 % MgO, rest CaO)
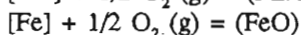
BASIS : 1 TONNE OF STEEL

Fig. Ex. 3.2 Rectangular block diagram for refining of hot metal in L.D. converter

$$2 \, [Fe] + 3/2 \, O_2 \, (g) = (Fe_2 O_3)$$
$$[C] + 1/2 \, O_2 \, (g) = CO \, (g)$$
$$[C] + O_2 \, (g) = CO_2 \, (g)$$
$$2 \, [P] + 5/2 \, O_2 \, (g) = (P_2O_5)$$

where [ ] denotes metal phase and ( ) denotes the slag phase.

(d) Calculation of weight of hot metal (W_{HM}) and weight of scrap (W_{SC}) per tonne of steel:

Fe balance

$$\left[\begin{array}{cc} (W_{SC} \times 1.00 + W_{HM} \times 0.937 \\ \text{Fe in scrap} \quad \text{Fe in hot metal)} \end{array} \right] \times (1-0.02)$$

$$= 1 \times 0.996$$
(Fe in steel)

The factor $(1 - 0.02)$ takes account of 2% loss of total Fe into the slag. Again.

$$\frac{W_{HM}}{W_{SC}} = 4 \qquad \text{(Ex. 3.6)}$$

Combining Eqs. Ex. 3.5 and Ex. 3.6

$$W_{HM} = 0.857 \text{ tonne} = 857 \text{ kg}$$

and $W_{SC} = 0.214$ tonne $= 214$ kg

(e) Calculation of volume of oxygen to be blown per tonne of steel:

Table Ex. 3.1 presents the calculations based on the stoichiometry of chemical reactions noted previously. Si, Mn, C, and P come from the hot metal only. Since

CO and CO_2 are produced in equal volumes, half of C is oxidized to CO. Similarly, since Fe^{2+}/Fe^{3+} ratio in the slag is 1 : 1, half of Fe is oxidized to FeO and the other half to Fe_2O_3. It is also recognised that 0.2% C and 0.2% Mn (i.e. 2 kg each) remain in steel.

Noting that;

      (i) 32 kg oxygen occupies 22.4 m^3 at STP,

     (ii) purity of oxygen is 99.5% and

    (iii) efficiency of oxygen utilization is 90%,

        total volume of oxygen required per tonne of steel

$$= \frac{86.67}{32} \times 22.4 \times \frac{100}{99.5} \times \frac{100}{90}$$

$$= 67.8 \ m^3 \ (STP)$$

Let weight of lime to be charged per tonne of steel be W_L in kg. Noting that slag is to contain 50% CaO and that SiO_2 and MgO of lime would also join the slag, we can do the CaO balance.

CaO balance

$$W_L \times 0.95 = W_s \times 0.5 \tag{Ex. 3.7}$$

where W_s is weight of slag in kg.

Again, $W_s = W_L + 59.73$ (Ex. 3.8)

TABLE Ex. 3.1 Results of stoichiometric calculations

Elements	Weights to be oxidised, kg	Nature of oxides	Weight of oxygen reqd., kg	Weight of slag forming oxides, kg
C	16.14	CO	21.52	—
	16.14	CO_2	43.04	—
Si	8.57	SiO_2	9.79	18.36
Mn	6.57	MnO	1.91	8.48
P	2.57	P_2O_5	3.32	5.89
Fe	9.95	FeO	2.86	12.79
	9.95	Fe_2O_3	4.26	14.21
		Total	86.70	59.73

since 59.73 kg of slag forming oxides originate from oxidation of hot metal. Solving Eqs. Ex. 3.7 and Ex. 3.8, we obtain

    $W_L = 66.37$ kg

    $W_s = 126.7$ kg

Answer : Per tonne of steel,

    (a) Weight of hot metal = 857 kg

        Weight of scrap charged = 214 kg

    (b) Total volume of oxygen to be blown = 67.8 m^3 (STP),

    (c) Weight of lime to be charged = 66.37 kg

    (d) Weight of slag formed = 126.7 kg

3.3 A NOTE IN CHEMICAL ANALYSIS AND SAMPLING

Material balance calculations require compositions of some of the inputs or outputs and hence the need of chemical analysis. Moreover, analysis of raw materials, intermediate and final products is a necessity for evaluation and control of product quality. Therefore, plants engaged in extraction and refining of metals usually have extensive analytical facilities.

The natural materials as well as industrial products very often contain a significant percentage of moisture. Therefore, the moisture content must be known. For solids, it is determined by measuring the weight loss of a sample upon drying at 105—120°C. For gases there are various methods. The moisture may be absorbed in a desiccant and weighed. Indirect methods, such as those based on dew points may also be employed. The moisture content of a gas may be expressed in various ways : percent by volume, gm per cubic meter, relative humidity etc.

One definite trend in industrial chemical analysis is the large scale use of instrumental methods. This requires more capital outlay no doubt, but is amply rewarded by the speed, labour-saving, and better automation it allows. The instruments are capable of providing inputs directly into the recorders, controller and computers through proper devices. The high speed of analysis makes the results available to the operator while there is still time to control the process. Spectroscopes of various types are the most widely used analytical instruments.

A typical chemical analysis is done on a small sample, which is assumed to have the same composition as the average of the material in question. How do we make sure that such an assumption is correct? This is an important question and all the precautionary measures in sampling are primarily aimed at satisfying this assumption as best as possible without getting involved in too lengthy a procedure. Since some numerical results are obtained in good as well as poor samples, the role of proper sampling is not appreciated by many. However, it goes without saying that poor sampling will give rise to erroneous data and may be quite critical sometimes.

Compositions of materials moving in a process are characteristically non-uniform, except in certain special cases. This is true even in continuous processes. The composition may vary with time or with position or both. For proper sampling, we must have a prior knowledge of the extent of variations.

The sampling error, i.e. the difference in composition between the sample and the average of the material, is of two kinds: systematic and random. A systematic error arises from the characteristics of the process. If a rock consists of two minerals, the more friable one would be found in larger percentage in the dusts and the less friable one would tend to concentrate in the coarser particles. In a bed of granular solids, the denser and larger particles would tend to go more to the bottom layers. In a mine, the composition of the ore changes as we go down deeper and deeper from the surface. There are physical and chemical reasons for such systematic variations. The sampler has to be aware of the pattern of variation and only then the error can be minimized. For example, in the first instance cited, he should take samples both from the finer size fractions as well as the coarser size fractions.

In contrast to the above, no physical reason can be attributed to random errors.

Neither does it show any pattern. Therefore, the only way to minimize it is to have a randomly collected large sample size. Theoretically, if the entire material is taken as the sample then there is no error. In terms of statistics, this is equivalent to an infinitely large sample or an infinite number of small sized samples. If the number of samples is finite (say n), then an error results. The error, again be predicted with certainty. We can only talk about probable errors. From statistical analysis, it can be concluded that the probable error should decrease by a factor of $n^{1/2}$ if we compare the two cases of single and n number of equal sized samples.

For granular solids, every particle tends to have a little different composition as compared to the others. The probable error decreases if more particles are included in each sample. This means that, for the same probable error, the sample size should be larger for larger particle size. A typically recommended relationship is

$$M = K \, D^a \qquad (3.6)$$

where M is the sample mass for the same probable error, D is the maximum particle size, K is an empirical constant, and 'a' usually lies between 2 and 3.

Finally, it should be noted that non-uniformity is usually not much in liquids and gases because of the mixing effects. Non-uniformity tends to be serious only for solids, especially in granular solids of natural origin. Even then in liquids where the conversion is taking place fast, as in the L.D. process of steelmaking, considerable composition differences have been found in the liquid bath.

3.4 THEORETICAL BASIS OF HEAT BALANCE

Considerable quantities of heat are required in order to carry out pyrometallurgical processes. The cost of energy is always a significant fraction of the total cost and may even become as high as 30%. A better heat economy, therefore, cuts down the production cost and it can be achieved only if a careful **heat balance** is maintained. Just as mass balance is an account of input and output of mass, heat balance is an account of input and output of heat in a process. The effort to cut down the cost of heating has resulted in many new processes. In fact there is a universal move to replace processes which involve frequent intermediate heating and cooling of materials by continuous processes. Continuous casting of ferrous alloys and continuous smelting of copper are exmples of developments in this direction. Such continuous processes eliminate intermediate heating and cooling of materials and reduce requirements of material handling operations and space. They are also amenable to better process control. The present day techniques of computer simulation and control of pyrometallurgical processes are based on material and heat balance. Other considerations such as chemical equilibria, reaction rates etc. are incorporated but they are optional depending on their utility.

A complete heat balance for a process lists the contributions of energy from various sources and the consumption of energy by various sinks, i.e. it lists input and output of energy. Figure 3.3 presents diagramatically the energy balance of a typical blast furnace. The same data can also be presented in tabular form.
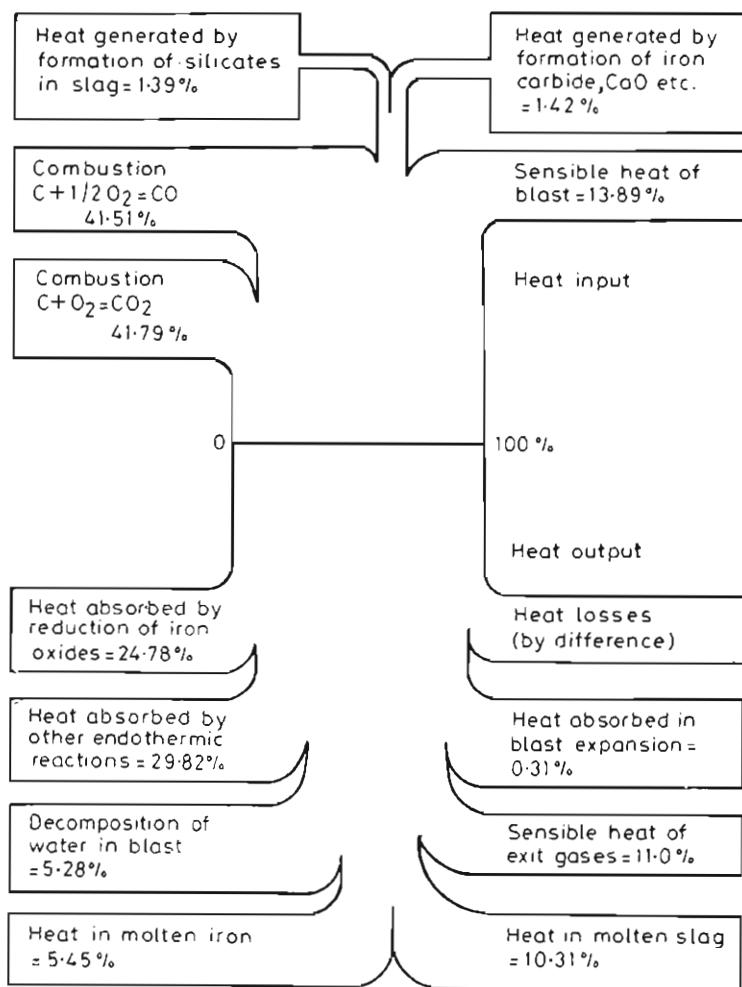
Fig. 3.3 Energy balance for a typical blast furnace

3.4.1 First Law of Thermodynamics

Just as the principle of conservation of elements affords a simple, straightforward approach in setting up materials balance equation, the **principle of conservation of energy**, specially the **First Law of Thermodynamics**, affords a sound basis for setting up an energy or heat balance. In both cases, a relatively complete accounting can be made from a knowledge of what goes into the system and what comes out with little or no need to consider the complexities and mechanisms of the processes within the system.

The First Law of Thermodynamics for a process occurring in a system states

$$E_2 - E_1 = Q - W \tag{3.7}$$

where E_1 and E_2 are the energy contents (i.e. **internal energies**) of the system in state 1 and state 2, respectively, Q is the heat absorbed by the system from the surroundings and W is the work done by the system on the surroundings.

The **heat content** or **enthalpy** of a system (H) is a thermodynamic property defined as

$$H = E + PV \tag{3.8}$$

where P and V denote, respectively, total pressure and volume. Combining with Eq. 3.7 one obtains, for a constant pressure process. ·

$$H_2 - H_1 = Q - W + P (V_2 - V_1) \tag{3.9}$$

Again, if the work done by the system on the surroundings is the work of expansion then

$$W = \int_1^2 P \, dV = P \ (V_2 - V_1) \tag{3.10}$$

provided the pressure remains constant.
Combining Eq. 3.9 with Eq. 3.10

$$H_2 - H_1 = \Delta H = Q_P \tag{3.11}$$

where Q_P is the heat absorbed by the system in changing from state 1 to state 2 by a path of constant pressure in which only expansion work is done on the surroundings. A change under a constant pressure is called an **isobaric process.**

If an isobaric process involves work other than expansion work, then

$$\Delta H = Q_P - W' \tag{3.12}$$

where W' is the work done by the system on the surroundings in the constant pressure process but does not include expansion work. For example, in an electric furnace process at constant pressure, $- W'$ equals the input of electrical work to the system.

Since most metallurgical processes follow paths of substantially constant pressure, these observations prove very useful. Their importance and usefulness lie in the fact that they relate in a simple manner a quantity of great practical significance, the heat effect for a process (Q_P), to a state property of the system, H. The change in heat content depends only on the initial and final states and not on the path of the process. Thus, the heat absorbed or evolved in practical processes can be evaluated from data on the properties of the practical system at the beginning and the end of the process.

3.4.2 Various Heat Effects

Changes in heat content may be classified into four categories as follows.

1. Changes due to temperature changes in pure substances : A substance contains some heat (i.e. it has a heat content) due to its temperature alone. One need not be concerned with the absolute magnitude of this heat content. What is important and relevant is the change that results from change in temperature. The universally accepted **Reference Temperature,** to which all changes are

referred to, is 298 K (25°C). Thus, thermodynamic tables list values of $(H_T - H_{298})$ and this quantity is commonly referred to as the heat content, meaning by implication, that H_{298} (the heat content of substance at 298 K) has been arbitrarily assumed to be zero.

The heat contents of common inorganic materials upto fairly high temperature are given in thermodynamic literature and reference books. The data is generally tabulated or presented analytically according to the following general equation.

$$H_T - H_{298} = aT + bT^2 + cT^{-1} + d \qquad (3.13)$$

where a, b, c and d are constants and T is temperature in K. The parameters a, b etc. remian constant only in the temperature ranges where there is no change in the state of aggregation.

2. Changes in heat content due to changes in state of aggregation in pure substances (melting, allotropic transformation and vaporization). These data are also given in the reference books on thermochemical data. Here the changes in heat content are designated as ΔH_m for melting, ΔH_v for vapourization etc.

3. Changes in heat content due to chemical reactions in the system. For these calculations, we proceed from the data on **Heats of Formation** (ΔH_f) of compounds. This data for common inorganic compounds have been compiled in several monographs and reference books.

The heat of formation of compound AX, at a given temperature, is the heat of the following reaction at that temperature.

$$A + X = AX \qquad (3.14)$$

where A and Y are the two elements.

Suppose that the real chemical reaction in a system is

$$AX + B = BX + A; \; \Delta H_r \qquad (3.15)$$

where ΔH_r is the heat of reaction. This reaction can be looked upon as a combination of the following two reactions.

$$A + X = AX; \quad \Delta H_f(AX) \qquad (3.16)$$
$$B + X = BX; \quad \Delta H_f(BX) \qquad (3.17)$$

we have, obviously,

$$\Delta H_r = \Delta H_f(BX) - \Delta H_f(AX) \qquad (3.18)$$

This is the Hess' Law and it allows us to calculate the heat of any reaction from the heats of formation of the compounds involved in it.

The heats of reactions depend on the reaction temperature and, therefore, reference books tabulate the heats of formation reactions at various temperatures. Even if data are not available at the required temperature it is possible to easily calculate the value of heat of reaction at an arbitrary temperature T_2 from the value of the same available at another temperature T_1 by using **Kirchoff's equation** which is written as:

$$(\Delta H_r)_{T_2} = (\Delta H_r)_{T_1} + \Sigma(\Delta H_{T_2} - H_{T_1})_{products} - \Sigma(\Delta H_{T_2} - H_{T_1})_{reactants} \qquad (3.19)$$

It is, however, necessary to have heat content data on products and reactants so that the second and third terms of Eq. 3.19 can be evaluated.

4. Change of heat content due to mixing and dilution in solutions. These values are generally not well known and sometimes appropriate assumption is made

regarding their magnitude. Most often they can be ignored altogether because the magnitudes are small.

Example 3.3

Calculate the heat of the following reaction per g. mol at 1400 K.

$$ZnO(s) + C(s) = Zn(g) + CO(g) \qquad \text{(Ex. 3.9)}$$

Given : (i) Heats of formation (ΔH_f)

of $ZnO(g)$ is	$-$ 348,570 J/mol,
and of CO (g) is	$-$ 110,537 J/mol at 296 K.
(ii) Compound/element	$H_{1400} - H_{298}$, J/mol
ZnO (s)	56,315
Zn(g)	153,454
CO(g)	35,045
C(s)	20,642

Solution: According to Hess' Law, i.e. Eq. 3.18

ΔH_r for reaction Ex. 3.9

$= \Delta H_f(CO) - \Delta H_f(ZnO)$

$= 238,033$ J/mol at 298 K.

According to the Kirchhoff's equation, i.e. Eq. 3.19

$(\Delta H_r)_{1400} = (\Delta H_r)_{298} + \Sigma(H_{1400} - H_{298})_{products} - \Sigma(H_{1400} - H_{298})_{reactants}$

$= 238,033 + 153,454 + 35,045 - (56,315 + 20,642)$

$= 249,575$ J/mol (**Answer**)

3.5 PROCEDURE FOR HEAT BALANCE

The reference or basis temperature with respect to which the heat contents (sensible heats) of the materials are measured, has to be selected first. As stated in the previous section, 298 K is the universal reference. However, we have to fix the reference state as well. The reference state of a substance is usually taken as its stablest state of aggregation (solid, liquid or gas) at the reference temperature. However, there is nothing wrong in taking a metastable state as the reference one. The basic equation is

Heat input = Heat output + Heat accumulation   (3.20)

For many processes, the accumulation term is negligible. Hence we may simply write

Heat input = Heat output   (3.21)

This equation is appropriate for a batch process. For continuous processes, the equation will be

Rate of heat input = Rate of heat output   (3.22)

Again,

Heat input = Sensible heats (heat contents) of input materials (including ΔH for changes in the states of aggregation) + Heat evolved due to exothermic reactions (measured at the reference temprature and states) + Heat supplied from outside the system   (3.23)

and, Heat output = Sensible heats of output materials (including ΔH for changes in the states of aggregation) + heat absorbed in endothermic reactions (measured at the reference temprature and states) + heats absorbed in bringing input materials to the reference temperature and states + heat loss to the surroundings

(3.24)

This equation is consistent with the First Law of Thermodynamics, this is further illustrated in Fig. 3.4.
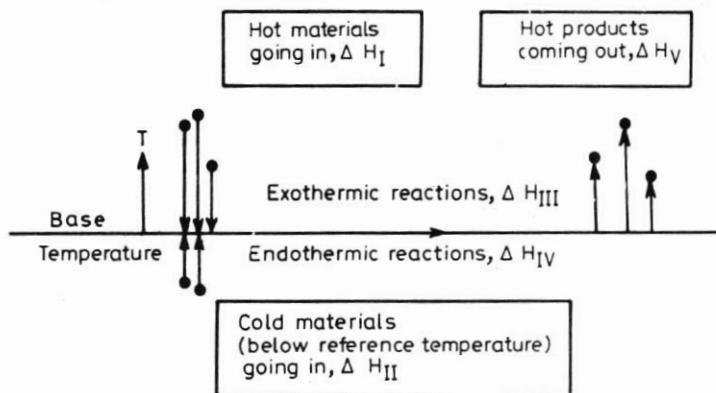
Fig. 3.4 Heat balance for a constant pressure process

STATEMENT OF
FIRST LAW OF
THERMODYNAMICS : $\Delta H_{TOTAL} = Q_P - W' = \Delta H_I + \Delta H_{II} + \Delta H_{III} + \Delta H_{IV} + \Delta H_V$

Heat Balance

INPUT	OUTPUT
1. SENSIBLE HEATS OF INPUT MATERIALS, $- \Delta H_I$	4. SENSIBLE HEATS OF OUTPUT MATERIALS, ΔH_V
2. HEATS EVOLVED IN EXOTHERMIC REACTIONS, $- \Delta H_{III}$	5. HEATS ABSORBED IN EDNOTHERMIC REACTIONS, ΔH_{IV}
3. HEAT SUPPLIED ELECTRICALLY, $- W'$	6. HEATS ABSORBED IN BRINGING INPUT MATERIALS TO REFERNCE TEMPERATURE, ΔH_{II}
	7. HEAT LOSS TO SURROUNDINGS. $- \Delta Q_p$

TOTAL : $\Delta H_I - \Delta H_{III} - W' = \Delta H_V + \Delta H_{IV} + \Delta H_{II} - \Delta Q_p$

For actual heat balance calculation, the following well defined steps should be followed.

Step 1 : Work out the complete material balance.
Step 2 : Select the reference temperature and reference states.
Step 3 : Write the process equation and the chemical reactions.
Step 4 : Perform the energy balance, calculating $\Sigma H_{(Reactants)}$ and $\Sigma H_{(Products)}$ for the left and right sides, respectively, of the process equation and ΣH_r values for the chemical reactions.
Step 5 : Perform all additional calculations called for.

Table 3.1 shows the heat balance for a typical open-hearth process of steelmaking. These data as well as those shown in Fig. 3.3 indicate the way heat is contributed and consumed in two industrially important processes.

TABLE 3.1 Typical heat balance of the open hearth process of steelmaking.

Heat input (Heat received), percent		Heat output (Heat distributed i.e. consumed), percent	
Sensible heat of gas	= 14.10	Heat content of waste gas	= 30.00
Chemically combined		Heat content of steel	= 15.00
heat of the gas	= 61.30	Heat content of slag	= 6.00
Heat of the pig iron	= 8.50	Reduction of iron oxides	= 8.90
Heat of air for combustion	= 0.02	Reduction of manganese oxides	= 0.08
Heat content of ore,		Reduction of sulphides	= 0.02
limestone, scrap	= 0.01	Heat losses (by difference)	= 40.00
Oxidation of [Si]	= 0.60		
Oxidation of [P]	= 4.00		
Oxidation of [C]	= 10.00		
Oxidation of [Mn]	= 0.87		
Oxidation of [Fe]	= 0.50		
Oxidation of [S]	= 0.10		
Total	= 100.00	Total	= 100.00

Example 3.4

An open-hearth steelmaking furnace uses a fuel gas consisting of 30% H_2, 18% CO, 17% CH_4, 29% N_2 and 6% CO_2 for heating. The primary combustion air is preheated to 1000° C. The leakage of cold air through openings may be assumed to be 20% of primary air. The flue gas contains 30% O_2. The temperature of processing of molten steel is 1600°C.

Calculate : (a) Theoretical air
(b) Excess air (in %)
(c) Adiabatic flame temperature
(d) Gross available heat

Solution :

Material Balance

(a) Basis of calculation : 100 mols of fuel gas; assumption for material balance is that air contains 21% O_2 and 79% N_2 by volume.

(b) The combustion process is shown by the rectangular block diagram in Fig. Ex. 3.4 with all known data and assumptions. n indicates number of g. moles. The question marks denote the quantities to be calculated.

(c) The combustion reactions are indicated in Table Ex. 3.4 (a). Stoichiometric calculations also have been presented.

(d) Theoretical air = no. of mols of oxygen required theoretically $\times \dfrac{100}{21}$

$$= 58 \times \frac{100}{21} = 276 \text{ mols.}$$

(e) Calculation of excess air, total air etc.: Let N_{f_1} be the total no. of mols of gas in flue. Molar balance of flue gas (per 100 mols fuel) yields

$$n_{f_1} = 134 + \text{no. of mols of nitrogen in theoretical air} + \text{excess air} = 134 +$$

$$(276 - 58) + 0.03 \times \frac{100}{21} \times n_{f_1} \qquad \text{(Ex. 3.10)}$$

since the fuel gas contains 3% O_2.

Solving Eq. (Ex. 3.10), $n_{f_1} = 410.7$ mols and it contains:
64 mols H_2O, 41 mols CO_2, 12.3 mols O_2, 293.4 mols N_2.
Excess air = 58.7 mols

$$\text{Excess air (in \%)} = \frac{\text{Excess air}}{\text{Theoretical air}} \times 100 = 21.3.\%$$

Total air = 276 + 58.7 = 334.7 mols

$$\text{Primary combustion air} = 334.7 \times \frac{1}{1.2} = 278.9 \text{ mols.}$$

Heat Balance

(f) Reference temperature = 298 K, reference state for H_2O is liquid, basis = 100 mols of fuel gas.

(g) Assumptions are that the fuel gas as well as leakage air enter the furnace at 298 K.

Fuel gas, $n = 100$ moles
(30 % H_2, 18 % CO,
17 % CH_4, 29 % N_2 and
6 % CO_2) at 298 K

Combustion chamber of O.H. furnace

Flue gas, $n_{fl} = ?$
(3 % O_2, rest CO_2,
H_2O and N_2)

Primary combustion air,
$n_a = ?$
(21 % O_2, 79 % N_2)
at 1273 K

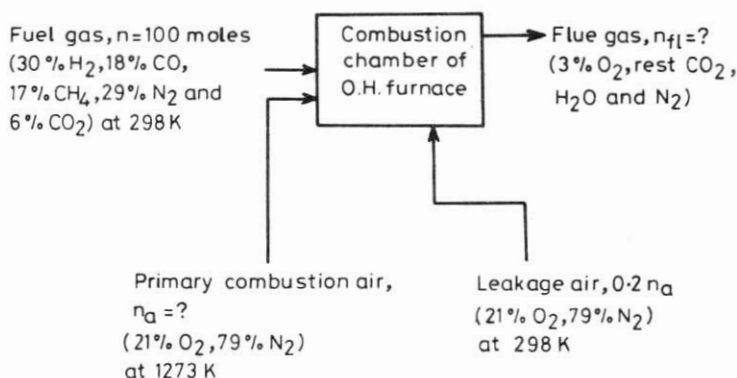Leakage air, $0.2 n_a$
(21 % O_2, 79 % N_2)
at 298 K

Fig. Ex. 3.4 Rectangular block diagram for combustion of fuel in the open–hearth steelmaking furnace

TABLE Ex. 3.4 (a) Stoichiometric calculations for combustion reactions

Species	Combustion reactions	No. of mols in fuel gas	Theoretical no. of mols of oxygen required	No. of mols of product in flue gas
H_2	$H_2 + \frac{1}{2} O_2 = H_2 O$	30	15	30
CO	$CO + \frac{1}{2} O_2 = CO_2$	18	9	18
CH_4	$CH_4 + 2O_2 + H_2O$	17	34	17 (CO_2) 34 (H_2O)
CO_2	–	6	–	6
N_2	–	29	–	29
O_2	–	0	–	0
Total :		100	58	134

(h) Heat balance :

From Eqs. 3.23 and 3.24, the heat balance equation can be written as:
Sensible heat of fuel gas (ΔH_I)
+ sensible heat of leakage air (ΔH_{II})
+ sensible heat of preheated primary air (ΔH_{III})
+ heat evolved in combustion reactions at 298 K (ΔH_{IV})
= sensible heat of flue gas at adiabatic flame temperature at T (ΔH_V) (Ex. 3.11)

This follows from the definition of adiabatic flame temperature, which is obtained if there is no heat loss from the flame, i.e. if the combustion takes place adiabatically.

From assumptions made in (g) above,
$\Delta H_I = 0$ and ΔH_{II} 0. For calculation of other heat effects, heats of formation (ΔH_f) of combustion products and heat contents of various species ($H_T - H_{298}$) are compiled in Table Ex. 3.4(b).

(i) Calculation of ΔH_{III} :
$$\Delta H_{III} = (n_{O_2} \text{ in primary air}) (\Delta H_{1273} - H_{298}) o_2$$

$$= (n_{N_2} \text{ in primary air}) (H_{1273} - H_{298})_{N_2} \qquad \text{(Ex. 3.12)}$$

Now from (f) above, $n_{O_2} = 278.9 \times \dfrac{21}{100} = 58.6$ mols

$$n_{N_2} = 278.9 \times \frac{79}{100} = 220.6 \text{ mols}$$

Again from Table 3.4 (b),

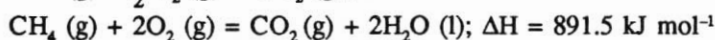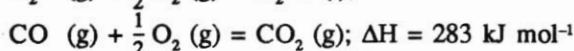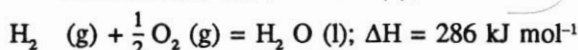$(H_{1723} - H_{298})$ per mole O_2 = 32 kJ

$(H_{1723} - H_{298})$ per mole N_2 = 30.5 kJ

Therefore, $\Delta H_{III} = 58.6 \times 32 + 220.3 \times 30.5 = 8,594$ kJ

(j) Calculation of ΔH_{IV} :

From data in Table Ex. 3.4 (b), we obtain at 298 K:

H_2 (g) $+ \frac{1}{2}O_2$ (g) $= H_2O$ (l); $\Delta H = 286$ kJ mol^{-1}

CO (g) $+ \frac{1}{2}O_2$ (g) $= CO_2$ (g); $\Delta H = 283$ kJ mol^{-1}

CH_4 (g) $+ 2O_2$ (g) $= CO_2$ (g) $+ 2H_2O$ (l); $\Delta H = 891.5$ kJ mol^{-1}

$\Delta H_{IV} = 286 \times$ no. of mols of $H_2 + 283 \times$ no. of mols

$CO + 891.5 \times$ no. of mols of CH_4 in fuel gas   (Ex. 3.13)

TABLE Ex. 3.4 (b) Values of heat contents and heats of formation*

| Species | $H_T - H_{298} = aT + bT^2 + cT^{-1} + d$, J mole^{-1} | | | | ΔH_f, J mol^{-1}, |
	a	$b, \times 10^{-4}$	$c, \times 10^{-6}$	$d, \times 10^{-5}$	$\times 10^5$ at 298 K
CO	—	—	—	—	1.11
CH$_2$	—	—	—	—	0.745
H$_2$O	− 12.18	2.68	− 0.67	− 2.38	2.86
CO$_2$	− 2.97	2.93	− 1.92	− 3.92	3.94
O$_2$	30.3	20.9	1.67	− 0.0969	—
N$_2$	27.9	21.4	0	− 0.085	—

*C.K. Wick and F.E. Block: Thermodynamic properties of 65 elements – their oxides, halides, carbides and nitrides, Bulletin 605, U.S. Bureau of Mines, Washington D.C., USA, 1969)

$= 286 \times 30 + 283 \times 18 + 891.5 \times 17$ kJ

$= 28,830$ kJ

(k) Calculation of ΔH_V

$$\Delta H_V = \Sigma n_i (H_T - H_{298})_i = T \Sigma n_i a_i + T^2 \Sigma n_i b_i + \frac{\Sigma n_i c_i}{T} + \Sigma n_i d_i \qquad (Ex.\ 3.14)$$

where the summation is to be done for all the flue gas constituents. We note from (f) that in flue gas : $n_{H_2O} = 64$, $n_{CO_2} = 41$, $n_{O_2} = 12.3$, $n_{N_2} = 293.4$, Values of a, b, c, and d for various species are listed in Table Ex. 3.4 (b). Calculations performed at different values of T are presented in Table Ex. 3.4 (c).

TABLE Ex. 3.4 (c) Calculation of $(H_T - H_{298})$ (all values in Joules)

T, K	$T \sum n_i a_i$	$T^2 \sum n_i a_i$	$\frac{1}{T} \sum n_i c_i$	$\sum n_i d_i$	$H_T - H_{298}$
1873	23,000	4,146	18	339	27,503
2100	25,800	5,212	17	339	31,368
2300	28,258	6,252	15	339	34,864
2500	30,715	7,387	14	339	38,455

(1) Calculation of adiabatic flame temperature:
   From the heat balance, i.e. Eq. Ex. 3.11, and values of
   ΔH_{III}, ΔH_{IV}, and ΔH_V, calculated in (i), (j) and (k) above,

   $\Delta H_V = \Delta H_{III} + \Delta H_{IV}$ $= 8,594 + 28,830 = 37,424$ kJ   (Ex. 3.15)

Graphical solution based on Table Ex. 3.4 (c) yields a value of $T = 2443$ K = 2170°C.

(m) Calculation of Gross Available Heat (GAH):
   By definition,
   GAH = Sensible heat contained in flue gas at adiabatic flame temperature – sensible heat contained in flue gas at critical process temperature   (Ex. 3.16)

Here the critical process temperature is the temperature at which steel is being processed, i.e. 1600°C (1873 K)

Hence, $GAH = (\Delta H_V)_{2443K} - (\Delta H_V)_{1873K}$

$= 37,424 - 27,503$

$= 9,921$ kJ per 100 mole of fuel gas.

Answer

(a) Theoretical air = 276 mols per 100 mols of fuel gas
(b) Excess air = 21.3% of theoretical air
(c) Adiabatic flame temperature = 2170°C
(d) Gross available heat = 9,921 kJ per 100 mol of fuel gas.

Problems

   3.1 A mixture of Chalcopyrite $CuFeS_2$, Pyrite (FeS_2), and Chalcocite (Cu_2S) analyzes 30% Cu, 30% Fe and 40% S. Calculate the mineralogical analysis.

   3.2 100 tonnes of a flotation concentrate is roasted per day continuously with dry air. The concentrate contains 75% ZnS, 5% PbS, 5% FeS_2 and the rest inert gangue materials. Assume that roasting converts the ZnS to ZnO, PbS to PbO and FeS_2 to FeS_3O_4 and all the sulphur of the sulphides form gaseous SO_2 and SO_3. The gases leaving the system analyze 6% SO_2 and 2% SO_3. Calculate (a) rate of blowing of air (Nm^3. s^{-1}), (b) the excess air, as percent of the quantity theoretically required for the reactions, (c) the complete analysis of the gases leaving the roaster and (d) the quantity of K_2SO_4 which can be manufactured from the sulphur in the exit gas in t day^{-1}.

   3.3 A basic open-hearth furnace treats a charge composed of the following :

Charge	Quantity, t	Chemical analysis, %
Hot metal	120	C-4, Si-0.5, Mn-1.0, P-0.3
Scrap	80	C-0.1, Si-0.05, Mn-0.5, P-0.03
Ore	6	Fe_2O_3–90, SiO_2–5, Al_2O_3–5
Limestone	12	$CaCO_3$–95, SiO_2–5

Composition of the steel tapped from the furnace is:
   C-0.1%, Mn – 0.2% P-0.03% The slag contains 50% CaO, 15% iron oxide (reported as FeO), and 4.5% MgO, rest SiO_2, MnO and Al_2O_3 , P_2O_5. The furnace is lined with burnt dolomite. Calculate (a) the weight of slag made, (b)

weights CaO and MgO picked up by the slag from the dolomite lining, (c) weight of steel made and (d) percent SiO_2, MnO and P_2O_5 in slag.

Assume single slag practice.

3.4 A copper converter blows copper matte into blister copper. The following data are provided.

	Chemical analysis, %
Matte charged	Cu-40, rest Fe and S
Flux charged	SiO_2-80, Cu_2S-4, FeS-16
Slag produced	SiO_2-30, FeO-70
Blister produced	Cu-98.5

The weight of matte charged is 50 t. Rate of blowing of air is 3 Nm^3s^{-1}. Assuming that both matte and flux are charged at the beginning, calculate (a) weight of flux charged, (b) weight of slag produced, (c) weight of blister produced, (d) blowing time for the first stage and (e) blowing time for the second stage.

3.5 A Parkes desilverizing kettle receives a charge of 40 tonnes of softened lead containing 8.5 kg of silver per tonne. The first zinc crust is formed by adding unsaturated zinc crust from treatment of a previous charge. This unsaturated crust carries 1.2 kg Ag per tonne and 70% Pb, the balance being Zn. This addition is enough to give 1 kg of Zn per 0.5 kg of Ag in the kettle.

The lead takes up in solution 0.52% of its weight of zinc; the rest of the zinc forms the compound Ag_2Zn_3 which is removed in a crust containing 70% Pb. Pure Zn is now added in an amount sufficient to remove all the remaining Ag as Ag_2Zn_3 along with some Pb. Calculate (a) the weight of unsaturated crust to be added first, (b) the weight of the first crust removed and (c) the weight of pure zinc to be added.

3.6 A blast furnace makes pig iron containing : 3.6% C, 1.4% Si, and 95% Fe. The ore is 80% Fe_2O_3, 12% SiO_2, 8% Al_2O_3. The coke (1 kg per kg of pig iron) carries 10% SiO_2, 90% C. The flux (0.4 kg per kg of pig iron) is pure $CaCO_3$. The blast furnace gas has 28% CO and 12% CO_2.

Calculate: Per tonne of pig iron made,

(i) The weight of ore used.
(ii) The weight of slag made.
(iii) The volume of the blast-furnace gas.

3.7 Pure alumina for aluminium production is produced by the Bayer process, using Bauxite of the following composition: Al_2O_3 – 58%, Fe_2O_3 – 6%, SiO_2 –4%, TiO_2 – 2%, H_2O – 30%. The ore is dired, ground and digested with NaOH forming a solution of $NaAlO_2$. The red mud filtered from this solution carries 26% Fe_2O_3, 21% FeO_3, and 14% Na_2O. Assume that it contains all the Fe_2O_3 and SiO_2 that were in the Bauxite and that the SiO_2 is present in the form of the insoluble compound Al_2O_3. Na_2O. $3SiO_2$. $9H_2O$. It is desired to have the filtered solution contain 1.5 mol of Na_2O to 1 mole of Al_2O_3.

Calculate (a) the weight of red mud for each 1,000 kg of original Bauxite, (b) the weight of Al_2O_3 lost in the insoluble compound, per kg of SiO_2, and percentage this represents of the Al_2O_3 content of the Bauxite (c) the total loss of Al_2O_3 content of the Bauxite, (d) the weight of NaOH used in forming the insoluble compound per kg of SiO_2, and the total loss of NaOH represented

by the Na_2O in the red mud and (e) the weight of NaOH used in the process per 1,000 kg of Bauxite, and the percentage of it lost in the red mud.
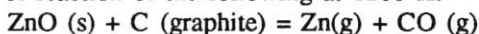
3.8 Iron ore, limestone and coke of the following analysis given below are to be charged into an iron blast furnace:

Material	Chemical analysis, %
Iron ore	Fe–50, SiO_2-8, Al_2O_3 – 3, H_2O–10, Mn–2, and P–0.05
Limestone	SiO_2–4, CaO – 50, MgO–2, Al_2O_3–1, H_2O – 1
Coke	Fe–1, SiO_2–5, Al_2O_3–3, H_2O–2, C–86, S–1.

The furnace is operated to produce pig iron analyzing 94% Fe, 4% C and 1% Si with a slag basicity (CaO/SiO_2) of 1.6. 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 coke to CO.

Calculate (a) the weight of ore and limestone to be charged per tonne of pig iron, (b) the volume of dry air to be blown in $Nm^3 s^{-1}$ for a furnace producing 1000 t pig iron per day.

3.9 Find the heat of reaction of the following at 1200 K.
$$ZnO\ (s) + C\ (graphite) = Zn(g) + CO\ (g)$$
Given the following data (in J mol^{-1} or J mol^{-1} K^{-1})
ΔH_f (ZnO) at 298 K = – 348.36 × 10^{-3}
ΔH_f (CO) at 298 K = – 110.54 × 10^3
C_p (ZnO) = 49.03 + 5.11 × 10^{-3} T – 9.13 × $10^5 T^{-2}$
C_p (graphite) = 16.87 + 4.77 × 10^{-3} T – 8.54 × $10^{-5} T^{-2}$
C_p (CO) = 28.43 + 4.1 × 10^{-3} T – 0.46 × $10^5 T^{-2}$
C_p [Zn(s)] = 22.40 + 10.05 × 10^{-3} T, 298 – 692K
C_p [Zn(l)] = 31.40, 692 – 1180 K
C_p [Zn(g)] = 20.81, 1180 K

3.10 Calculate the adiabatic flame temperature of combustion of a blast furnace gas analyzing 25% CO, 12.5% CO_2 and rest N_2 by volume. Theoretical amount of air is being used.

Given : C_p (CO_2) : 44.17 + 9.04 × 10^{-3} T J mol^{-1} K^{-1}
$\quad\quad\quad\quad C_p$ (N_2) : 27.89 + 4.27 × 10^{-3} T J mol^{-1} K^{-1}
$\quad\quad\quad\quad \Delta H_f$ (CO_2) at 298 K: – 393.79 kJ mol^{-1}

Other heat data are to be found in Prob. 3.9.

3.11 A fuel gas, consisting of CO and H_2, is being manufactured continuously by passing a mixture of oxygen and steam through a reactor containing a fluidized bed of coke, which may be assumed to be pure carbon. The coke and oxygen are fed at 298 K and the steam (at around atmospheric pressure) at 400 K. The temperature inside the reactor is being maintained at 1300 K by controlling the steam/oxygen ratio. The fuel gas also leaves the reactor at 1300 K. Assuming that 10% of heat input gets lost by conduction through the reactor wall, calculate (a) the weight ratio of steam to oxygen for operation under the conditions described and (b) the chemical analysis of the fuel gas.

Given (in J mol^{-1}): ΔH_f (H$_2$O) at 298 K = -286.04×10^3

$$H_T - H_{298} (O_2) = 29.98\ T + 2.09 \times 10^{-3}\ T^2 + 1.67 \times 10^5\ T^{-1}$$
$$- 9684$$

$$H_T - H_{298}[H_2O(l)] = 75.53\ T - 2.25 \times 10^4\ (298\text{--}373\ K)$$
$$H_T - H_{298}[H_2O(g)] = 30.57\ T - 5.15 \times 10^{-3}\ T^2 - 9571$$
$$H_T - H_{298} (H_2) = 27.30\ T + 1.63 \times 10^{-3}\ T^2 - 0.50 \times 10^5\ T^{-1} - 8114$$

Other heat data are to be found from Probs. 3.9 and 3.10

3.12   A copper converter is charged with 35 tonnes of matte, 10 tonnes of flux and makes 21.4 tonnes slag. With the help of the following data, prepare a heat balance of the converter at the end of the slagging period and at the end of the blow.

Data :

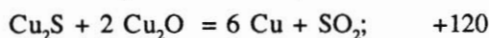| (i) Material	Chemical analysis, %	point, °C	Melting of liquid at M.P., Jg^{-1}	C_p of liquid Jg^{-1}K^{-1}
Flux	C$_2$–8%, Fe-16%, S-8% SiO$_2$-60% (Fe in flux, not as CuFeS$_2$, is Fe$_2$O$_3$	—	—	—
Matte	Cu-48%, rest Fe and S	1000	858	0.587
Slag	SiO$_2$-28%, FeO-63%, CuO-4%	1120	1256	1.045
Blister Copper	Cu-98%, S-0.5%	1083	666	0.495

(ii) Slagging period = 231 min; blister forming period = 110 min; total amount of air blast = 2.47×10^4 Nm^3. Air is enriched with O$_2$, and it contains 37% O$_2$.

(iii) Matte introduced at 1050°C flux at 25°C and blast at 25°C.

(iv) Heats of formation data:

ΔH_f for formation of slag from constituent oxides at 298 K is 1580 Joules g^{-1} of SiO$_2$

(v) ΔH at 298 K in kJ mol^{-1} of the following reactions are:

$$FeS + 3/2\ O_2 \quad = FeO + SO_2; \quad -469.0$$
$$2\ Cu + O_2 \quad = 2CuO; \quad -320.7$$
$$Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2; \quad +120$$

(vi) During blow, temperature of matte, slag and product gases are at 1300°C.

(vii) Other heat data are in the previous problems.

3.13 A continuous smelting furnace is heated with water gas 20% CO, 50% H$_2$. Fuel an air enter at 25°C Excess air is 20% of theoretical air. The operation proceeds satisfactorily and at the desired rate with the temperature of the fuel gases leaving the furnace at 1200°C. What would be the percentage increase in fuel

consumption if the excess air were increased to 50% of the theoretical air? All necessary heat data have already been provided in the previous problems.

General Reading

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4. D.M. Himmelblau, **Basic Principles and Calculations in Chemical Engineering**, Second Ed., Prentice Hall Inc., Englewood Cliffe, New Jersey (1962) Ch. 5.
5. L. Bryce Anderson and Leonard. A. Wenzel, **Introduction to Chemical Engineering**, McGraw Hill Book. Co. Inc., New York (1961) Ch. 5.
6. R. Schuhman, Jr, **Metallurgical Engineering Vol. 1 Engineering Principles**, Addison Wesley Publishing Co. Inc., Lond. (1952) Ch.3.