Two

Basic Chemical Calculations

2.1 INTRODUCTION

In Chapter 1, an attempt was made to present various systems of units and their conversions from one system of units to another. Before discussing material and energy balances, it is important to understand basic chemical principles.

Matter exists in three different forms, viz., solids, liquids and gases. Most of the elements and compounds can be had in all the three forms except a few, e.g., iodine and ammonium chloride, for which the liquid state is not visible and the solid state is sublimated into gaseous state. The easiest way of expressing the quantity of matter is mass. For solids and liquids, this can be done by weighing on a balance. However, a gas occupies the entire volume available to it, and hence it is customary to specify the volume along with its temperature and pressure. Very often, liquid volumes are also specified, in which case, additional information regarding its density is required to compute the mass of the liquid.

2.2 MOLE, ATOMIC WEIGHT AND MOLECULAR WEIGHT

Although measurement in terms of mass is of direct interest to the engineers, matter is basically made up of atoms and molecules. However, since the discovery of the fundamental laws of chemistry, chemists considered it significant to express quantity of matter in atoms and molecules rather than in terms of auxiliary properties, such as mass and volume. For instance, "gram atom" and "gram mole" have been used to specify amounts of chemical elements or compounds. These units have a direct relationship "with atomic weights" and "molecular weights" which are in fact relative masses.

Originally, the atomic weight of oxygen was taken as a reference base and its numerical value was fixed at 16. However, the physicists discovered different isotopes of oxygen which created a conflict between the physicists and the chemists. In 1959-60, this controversy came to an end and both the groups of scientists finally agreed on a standard based on carbon-12. The table of elements based on this scale was formulated in which atomic masses were listed. Appendix-II at the end of this book gives values of atomic masses and atomic numbers of naturally-occurring isotopes. The amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilograms of carbon-12 is defined as a mole. As noted in Chapter 1, a mole is the base unit in SI units.

Some elements are monoatomic while others are diatomic. Potassium and sodium are examples of monoatomic elements while chlorine, oxygen, nitrogen, etc. are diatomic elements. In this book, gram mole and kilogram mole will be specified as mol and kmol respectively.

For chemical compounds, a mole is defined as the amount of substance equal to its formula weight. The formula weight is called the molar mass or molecular weight. Based on this understanding, the molecular weight of a monoatomic element is its atomic mass (weight) while that of a diatomic element is double that of its atomic mass (weight).

$$1 \text{ atom Al} = 27^* \text{ g Al}$$

$$1 \text{ katom Na} = 23^* \text{ kg Na}$$

$$1 \text{ mol O} = 2 \text{ gatom } O_2 = 32^* \text{ g } O_2$$

$$1 \text{ kmol } H_2 = 2 \text{ katom } H_2 = 2^* \text{ kg } H_2$$

$$1 \text{ mol NaCl} = 23 + 35.5 = 58.5^* \text{ g NaCl}$$

$$1 \text{ kmol } CuSO_4 = 63.5 + 32 + (4 \times 16) = 159.5^* \text{ kg } CuSO_4$$

From the above discussion, it follows that

$$\frac{(1 \text{ mole of compound X})}{(1 \text{ mole of compound Y})} = \frac{(\text{molecular weight of X})}{(\text{molecular weight of Y})} \tag{2.1}$$

This expression is of considerable importance in the following chapters where the material and heat balances of chemical reactions are presented. In addition, it is also invaluable in converting the mole composition into weight composition.

Example 2.1 How many grams of NH_4Cl are there in 5 mol ?

Solution

$$\text{Molecular weight of } NH_4Cl = 14 + 4 + 35.5 = 53.5 \text{ g}$$

$$5 \text{ mol of } NH_4Cl = 5 \times 53.5 = 267.5 \text{ g } NH_4Cl \qquad \textit{Ans.}$$

Example 2.2 Convert 499 g $CuSO_4.5H_2O$ into mol. Find equivalent mol of $CuSO_4$ in the crystals.

Solution

$$\text{Molecular weight of } CuSO_4 = 159.5 \text{ g}$$

*Rounded-off value.

$$\text{Molecular weight of } CuSO_4.5H_2O = 159.5 + 5\,(1 \times 2 + 16) = 249.5 \text{ g}$$

$$\text{Moles of } CuSO_4.5H_2O = \frac{499}{249.5} = 2 \text{ mol}$$

Ans.

In the formula of $CuSO_4.5H_2O$, the moles of $CuSO_4$ are equal (one in each) and hence, the equivalent moles of $CuSO_4$ in the crystals are 2.0 mol.

Example 2.3 How many moles of K_2CO_3 will contain 117 kg K?

Solution

$$\text{Atomic weight of K} = 39$$

$$\text{Atoms of K} = \frac{117}{39} = 3 \text{ katom}$$

Each mole of K_2CO_3 contains 2 atoms of K.

$$2 \text{ atoms of K} \equiv 1 \text{ mole of } K_2CO_3$$

(The sign ≡ refers to 'equivalent to' and not 'equal to')

$$\text{Moles of } K_2CO_3 = \frac{3}{2} = 1.5 \text{ kmol}$$

Ans.

The number of atoms present in a mole can be obtained from Avogadro's number.

$$1 \text{ mol} = 6.022\,1367 \times 10^{23} \text{ atoms}$$

From this relation it is once again clear that the number of atoms present in a matter is directly proportional to the number of moles and not the mass.

Example 2.4 How many atoms are present in 416.6 g of barium chloride?

Solution

$$\text{Molecular weight of } BaCl_2 = 137.3 + 2 \times 35.5 = 208.3$$

$$\text{Moles of } BaCl_2 = 416.6/208.3 = 2 \text{ mol}$$

$$\text{Atoms present in the mass of 416.6 g } BaCl_2 = 2 \times 6.022 \times 10^{23}$$

$$= 12.044 \times 10^{23}$$

Ans.

2.3 EQUIVALENT WEIGHT

In chemical reactions, one *equivalent weight* of an element or compound has precisely the same power for chemical combination as one equivalent weight of any other element or compound. It depends strictly upon the reaction in which the molecule participates. Consider the reaction:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (2.2)$$

In this reaction, hydrogen is monovalent whereas oxygen is divalent. Two atoms of hydrogen combine with one atom of oxygen to form water.

Again

$$KOH + HNO_3 \rightarrow KNO_3 + H_2O \quad (2.3)$$

In this reaction, one equivalent weight of KOH combines with one equivalent weight of HNO_3 to produce one equivalent weight of KNO_3 and one equivalent of H_2O. Thus, it is clear that the reactivity of a molecule in a chemical reaction determines the equivalent weight of the molecule.

In simple terms, the equivalent weight of an element or a compound is equal to the atomic weight or molecular weight divided by the valence. The *valence* of an element or a compound depends on the numbers of hydrogen ions accepted or the hydroxyl ions donated for each atomic weight or molecular weight.

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{valence}} \quad (2.4)$$

$$1 \text{ g equivalent of hydrogen} = \frac{1}{1} = 1 \text{ g of hydrogen}$$

$$1 \text{ g equivalent of oxygen} = \frac{16}{2} = 8 \text{ g of oxygen}$$

$$1 \text{ g equivalent of Cu} = \frac{63.5}{2} = 31.75 \text{ g Cu}$$

$$1 \text{ g equivalent of } H_3PO_4 = \frac{98.1}{3} = 32.7 \text{ g } H_3PO_4$$

Example 2.5 Find the equivalent weights of (a) CO_3 radical and (b) Na_2CO_3.

Solution

$$\text{Molecular weight of } CO_3 \text{ radical} = 12 + 3 \times 16 = 60$$

$$\text{Valence of } CO_3 \text{ radical} = 2$$

$$\text{Equivalent weight of } CO_3 \text{ radical} = \frac{60}{2} = 30$$

Ans. (a)

$$\text{Molecular weight of } Na_2CO_3 = 2 \times 23 + 60 = 106$$

$$\text{Valence of } Na_2CO_3 = 2 \text{ equivalent weight of Na/mole} = 2$$

$$\text{Equivalent weight of } Na_2CO_3 = \frac{106}{2} = 53$$

Ans. (b)

2.4 SOLIDS

The composition of solids is chiefly expressed in weight (wt.) percentages (truly speaking, mass percentages).

In a mixture of two compounds A and B,

$$\text{Weight \% of A} = \left[\frac{\text{weight of A}}{(\text{Weight of A} + \text{weight of B})}\right] \times 100 \tag{2.5}$$

$$\text{Weight \% of B} = \left[\frac{\text{weight of B}}{(\text{weight of A} + \text{weight of B})}\right] \times 100$$

$$= 100 - \text{weight \% A} \tag{2.6}$$

Another way of expressing the composition is in mole %

$$\text{Moles of A} = \frac{\text{weight of A}}{\text{molecular weight of A}} \tag{2.7}$$

$$\text{Moles of B} = \frac{\text{weight of B}}{\text{molecular weight of B}} \tag{2.8}$$

$$\text{Moles \% A} = \left[\frac{\text{moles of A}}{(\text{moles of A} + \text{moles of B})}\right] \times 100 \tag{2.9}$$

$$\text{Moles \% B} = \left[\frac{\text{moles of B}}{(\text{moles of A} + \text{moles of B})}\right] \times 100 \tag{2.10}$$

With the help of Eqs (2.7) to (2.10), the weight % can be converted to mole %. Whenever no specific mention is made about the composition, i.e., whether it is weight % or mole %, it is taken as weight % for solids.

When the weight % and mole % are expressed as fractions, they are known as weight fraction and mole fraction respectively. Equations (2.5) to (2.10) are entirely general and can be applied to mixtures of any number of components with appropriate denominators.

Example 2.7 Sodium chloride weighing 600 kg is mixed with 200 kg potassium chloride. Find the composition of the mixture in (a) weight % (b) mole %.

Solution Basis*: 600 kg NaCl and 200 kg KCl

*It is always desirable to start by writing a definite basis which will be used in the example.

$$\text{Weight of NaCl in the mixture} = 600 \text{ kg}$$

$$\text{Weight of KCl in the mixture} = 200 \text{ kg}$$

$$\text{Total weight of the mixture} = 600 + 200 = 800 \text{ kg}$$

$$\text{Weight \% of NaCl, } w_A = \left(\frac{600}{800}\right) \times 100 = 75$$

$$\text{Weight \% of KCl, } w_B = 100 - 75 = 25 \qquad \textit{Ans. (a)}$$

$$\text{Molecular weight of NaCl, } M_A = 23 + 35.5 = 58.5$$

$$\text{Moles of NaCl} = \frac{600}{58.5}$$

$$= 10.26 \text{ kmol}$$

$$\text{Molecular weight of KCl, } M_B = 39 + 35.5 = 74.5$$

$$\text{Moles of KCl} = \frac{200}{74.5}$$

$$= 2.68 \text{ kmol}$$

$$\text{Total moles in the mixture} = 10.26 + 2.69 = 12.95 \text{ kmol}$$

$$\text{Mole \% NaCl, } x_A = \left(\frac{10.26}{12.95}\right) \times 100 = 79.23$$

$$\text{Mole \% KCl, } x_B = 100 - 79.23 = 20.77 \qquad \textit{Ans.(b)}$$

In chemical calculations, mole % is a logical expression of the composition. However, weight % is the more practical and convenient in the laboratory. Therefore, conversion of weight fraction to mole fraction and vice versa is frequently encountered in stoichiometric calculations. A simple graphical method, presented by Atallah[1], using rectangular graph paper is quite handy for the binary system.

Figure 2.1 is the graphical solution of Example 2.7. On the Y-axis, points representing molecular weights of two components are marked as P and Q. Draw lines RP and RQ. Weight fraction $w_A = 0.75$ is marked on X-axis. Draw a vertical line to intersect RQ (i.e. line representing molecular weight of B component) at C. Join CE. This intersects RP at D. Draw a vertical line passing from D which gives mole fraction of component A (x_A) on X-axis. Similar is the case with component B. It may be noted that results tally with the calculated values. For conversion of mole fraction to weight fraction, the procedure is to be reversed.