

# 8

## CHAPTER

# Solutions and Partial Molar Quantities

### 8.1 SOLUTIONS

*Solution* may be defined as a homogeneous phase composed of different chemical substances. Nearly all chemical substances of metallurgical interest (i.e. solid, liquid, or gas; dilute or concentrated) are regarded as solutions. e.g. pure copper, brass, molten metal, molten slag, flue gases etc. A solution is assumed as a homogeneous one.

Solutions are mainly classified into two types:

- *Aqueous solutions*: These are used in inorganic and physical chemistry, mostly at room temperature or low temperatures. e.g. NaCl in water to make NaCl solution. It is a solution prepared with water as a base.
- *Nonaqueous solution*: Metallurgical processes are mostly carried out at high temperature. So all metallurgical solutions are nonaqueous and inorganic solution. Hence metallurgical solution means inorganic, nonaqueous solutions for high temperature system.

Metallurgical solution can be further classified:

1. *Metallic solution*: Single phase alloys (e.g. Ag – Cu, Fe – Ni etc) are metallic solutions.
2. *Non-metallic solution*: A molten slag is an oxide solution, may contain compounds like  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{FeO}$ , and  $\text{Al}_2\text{O}_3$  etc or sulphide solution which contain  $\text{FeS}$ ,  $\text{Cu}_2\text{S}$  etc.

No material (either element or compound) is absolutely pure. It will have some impurities, may be in very small quantities. Even at such low concentrations they may affect some properties significantly. e.g.

- (i) Liquid steel dissolves hydrogen gas to the extent of few parts per million ( ppm; 1 ppm = 0.0001 %). Even this low concentration of hydrogen causes fine cracks on the surface of solid steel.
- (ii) Liquid copper dissolves some oxygen during processing; even a concentration less than 0.1 % decreases ductility and electrical conductivity of Cu. Hence for high conductivity Cu, oxygen should be removed to a very low level to get OFHC copper.
- (iii) In semi-conductors even traces of impurities of the order of parts per billion ( $1 / 10^9$ ) may affect their performance.

For all practical purposes the *composition of a solution* is expressed in terms of percentage by weight, and for theoretical purposes, it is convenient to express composition in mol or gram atomic basis; i.e., mol fraction or atom fraction. *Atom fraction* is used for solid or liquid metals and *mol fraction* is used for oxides, slags and other compounds.

#### 8.1.1 Atom Fraction

Atom fraction of a component in a solution is defined as the ratio of total number of gram atoms of that component, and total number of gram atoms of all components present in a given amount of solution.

Hence, atom fraction ( $N_1$ ) of component 1 in a solution will be:

$$N_1 = \left( \frac{n_1}{\sum_i n_i} \right) \quad \dots (8.1)$$

Where  $n_1$  = total number of gram atoms of component 1.

$\sum_i n_i$  = total summation of gram atoms of total  $I$  components present in the solution.

$$\text{Gram atom (n)} = \left( \frac{\text{Weight of a component in gms}}{\text{Atomic weight of that component in gms}} \right) \quad \dots (8.2)$$

### Conversion (weight % to atom % or vice-versa)

To convert given composition in weight % to atom fraction, it is convenient to consider a total mass = 100 gms. So that the number of gm atoms of each component ( $n_1, n_2$  etc) contained in that is:

$$n_1 = \left( \frac{\% 1}{A_1} \right), \quad n_2 = \left( \frac{\% 2}{A_2} \right) \text{ etc} \quad \dots (8.3)$$

where % 1, % 2 etc are the weight % of component 1, 2 etc and  $A_1, A_2$  etc are the atomic weights of component 1, 2 etc.

$$\text{Hence, atom fraction of component 1: } N_1 = \left[ \frac{\left( \frac{\% 1}{A_1} \right)}{\sum_i \left( \frac{\% i}{A_i} \right)} \right] \quad \dots (8.4)$$

e.g. in case of binary solution of A and B, the weight % and atom % are given as follows:

$$\text{Weight \% A} = \left[ \frac{(\text{atom \% A} \times \text{At wt of A}) \times 100}{(\text{atom \% A} \times \text{At wt of A} + \text{atom \% B} \times \text{At wt of B})} \right] \quad \dots (8.5)$$

$$\text{Atom \% A} = \left[ \frac{\left( \frac{\text{wt \% A}}{\text{At wt of A}} \right)}{\left( \frac{\text{wt \% A}}{\text{At wt of A}} \right) + \left( \frac{\text{wt \% B}}{\text{At wt of B}} \right)} \right] \times 100 \quad \dots (8.6)$$

### 8.1.2 Mol Fraction

Similar to atom fraction, mol fraction of a component in a solution is defined as the ratio of number of gm mol of that component, and total number of mol of all components present in a solution. i.e.,

$$X_1 = \left( \frac{n_1}{\sum_i n_i} \right) \quad \dots (8.7)$$

Where  $n_1$  = total number of gm mol of component 1,

$\sum_i n_i$  = total number of gm mol of total  $i$  components present in a solution i.e., solutes plus solvent.

Other composition units used in analytical work for aqueous solution are:

(i) Molality: number of mol of solute per 1000 gms of solvent,

## Converting Atomic % to wt %.

- For each element listed in the compound, multiply the atomic % of that element by its atomic weight.

For each element, let's call this value  $p$

- Add all values of  $p$  together, & let's call this value  $p(\text{total})$

- Now, each value of  $p$ , divided it by  $p(\text{total})$ , to obtain  $w$

- Multiplying the resulting value of  $w$  by 100 gives us wt % values for each respective element in the compound.

e.g. Neodymium-based permanent magnet materials whose composition listed below, in atomic %. terms as being 15 %. Nd, 77 %. Fe, 8 %. B

Step 1

Atomic wt of each element  
 Nd - 144.24, Fe - 55.85

B - 10.81

$$p(\text{Nd}) = 144.24 \times 15 = 2163.60$$

$$p(\text{Fe}) = 55.85 \times 77 = 4300.05$$

$$p(\text{B}) = 10.81 \times 8 = 86.49$$

Step 2

$$p(\text{total}) = \frac{2163.60 + 4300.05 + 86.49}{15 + 77 + 8} = 6550.15$$

Step - 3

$$\frac{\text{Each (P)}}{\text{Total (P)}}$$

$$\text{Step: 4}$$

$$\frac{\text{Each (P)}}{\text{Total (P)}} \times 100$$

$$\omega(\text{Md}) = \frac{2163.60}{6550.15} = 0.33 \Rightarrow 0.33 \times 100 = 33\% \text{ (M_d)}$$

$$\omega(\text{Fe}) = \frac{4300.07}{6550.15} = 0.65 \Rightarrow 0.65 \times 100 = 65\% \text{ (F_e)}$$

$$\omega(\text{B}) = \frac{86.49}{6550.15} = 0.013 \Rightarrow 0.013 \times 100 = 1.3\% \text{ (B)}$$

\* In case of Uninary soln (A component)

$$\text{wt \% A} = \left[ \frac{\text{atom \% A} \times \text{At. wt of A}}{\text{atom \% A} \times \text{At. wt of A}} \right] \times 100\%.$$

$$= 100\%.$$

\* In case of Binary soln (A &amp; B component)

$$\text{wt \% A} = \left[ \frac{\text{Atom \% A} \times \text{At. wt of A}}{(\text{Atom \% A} \times \text{At. wt of A}) + (\text{Atom \% B} \times \text{At. wt of B})} \right] \times 100\%$$

$$\text{wt \% B} = \left[ \frac{\text{Atom \% B} \times \text{At. wt of B}}{(\text{Atom \% A} \times \text{At. wt of A}) + (\text{Atom \% B} \times \text{At. wt of B})} \right] \times 100\%$$

\* In case of Ternary soln [A, B &amp; C component]

$$\text{wt \% A} = \left[ \frac{\text{Atom \% A} \times \text{At. wt of A}}{(\text{Atom \% A} \times \text{At. wt of A}) + (\text{Atom \% B} \times \text{At. wt of B}) + (\text{Atom \% C} \times \text{At. wt of C})} \right] \times 100\%$$

$$\text{wt \% B} = \left[ \frac{\text{Atom \% B} \times \text{At. wt of B}}{(\text{Atom \% A} \times \text{At. wt of A}) + (\text{Atom \% B} \times \text{At. wt of B}) + (\text{Atom \% C} \times \text{At. wt of C})} \right] \times 100\%$$

$$\text{wt \% C} = \left[ \frac{\text{Atom \% C} \times \text{At. wt of C}}{(\text{Atom \% A} \times \text{At. wt of A}) + (\text{Atom \% B} \times \text{At. wt of B}) + (\text{Atom \% C} \times \text{At. wt of C})} \right] \times 100\%$$



## Partial Pressure:

In mixture of gases, each constituent gas has a partial pressure which is the fractional (molar) pressure of that constituent gas if it alone occupied the entire volume of original mixture at the same temperature.

- The total gas pressure of an ideal gas mixture is the sum of the partial pressure of the gases in the mixture.
- The partial pressure of a gas is a measure of thermodynamic activity of gas's molecule.
- Gases dissolve, diffuse & react according to their partial pressure and not according to their concentration in gas mixture or liquid.

$$\star P = P_{H_2} + P_{H_2} + P_{NH_3}$$

→ In ideal gas, the molecules are so far apart, they do not interact with each other.

→ Most actual real gas comes very close to this ideal.

→ In Ideal gas mixture

ideally the ratio of partial pressure equal to ratio of the number of molecules.

i.e.

Mole fraction  $x_i$  of an individual gas component in an ideal gas mixture can be expressed in terms of component's partial pressure or the moles of components.

$$x_i = \frac{P_i}{P} = \frac{n_i}{n}$$

$$\Rightarrow P_A = x_A \cdot P$$

$x_i$  = Mole fraction of any individual gas component in a gas mixture

$P_i$  = Partial Pressure of any individual gas component in a gas mixture

$n_i$  = Moles of any individual gas component in gas mixture

$n$  = total moles of gas mixture

$P$  = total pressure of gas mixture

Converting wt. % to atomic %.

1. For each element listed in compound, divide the wt. % of the element by its atomic wt.  
For each element, let's call these value m
2. Add the all the values of m together, and let's call them m<sub>(total)</sub>
3. Now, for each value of m, divide it by m<sub>(total)</sub>, to obtain a
4. Multiplying the resulting value of a by 100 gives us the atomic percent values, for each respective element in the starting compound.

\* For Uninay soln b (only A component)

$$\text{Atom.}\% \text{ A} = \left[ \frac{\frac{\text{wt.}\% \text{ A}}{\text{At. wt. of A}}}{\frac{\text{wt.}\% \text{ A}}{\text{At. wt. of A}}} \right] \times 100$$

\* For Binary soln b (A & B component)

$$\text{Atom.}\% \text{ A} = \left[ \frac{\frac{\text{wt.}\% \text{ A}}{\text{At. wt. of A}}}{\left( \frac{\text{wt.}\% \text{ A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt.}\% \text{ B}}{\text{At. wt. of B}} \right)} \right] \times 100$$

Atom % B =

$$\left[ \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right] \times 100$$

$$\left[ \frac{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right)}{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)} \right] \times 100$$

x 100

For Ternary Soln (A, B &amp; C compounds)

$$\text{Atom \% A} = \left[ \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right] \times 100$$

$$\left[ \frac{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)}{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)} \right] \times 100$$

$$\text{Atom \% B} = \left[ \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right] \times 100$$

$$\left[ \frac{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)}{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)} \right] \times 100$$

$$\text{Atom \% C} = \left[ \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right] \times 100$$

$$\left[ \frac{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)}{\left( \frac{\text{wt. \% A}}{\text{At. wt. of A}} \right) + \left( \frac{\text{wt. \% B}}{\text{At. wt. of B}} \right) + \left( \frac{\text{wt. \% C}}{\text{At. wt. of C}} \right)} \right] \times 100$$

Example:  
 Samarium-Based permanent magnet material whose composition is listed in wt %. terms.

34 %. Sm

66 %. Co

Atomic wt of Sm = 150.35

Atomic wt of Co = 58.9 g

$$\text{Atom \% Sm} = \left[ \frac{\text{wt. \% of Sm}}{\text{At. wt. of Sm}} \right] \times 100$$

$$\left[ \frac{\left( \frac{\text{wt. \% of Sm}}{\text{At. wt. of Sm}} \right) + \left( \frac{\text{wt. \% of Co}}{\text{At. wt. of Co}} \right)}{\left( \frac{\text{wt. \% of Sm}}{\text{At. wt. of Sm}} \right) + \left( \frac{\text{wt. \% of Co}}{\text{At. wt. of Co}} \right)} \right] \times 100$$

x 100

$$m(Sm) = \frac{34}{150.35} = 0.23$$

$$m(Co) = \frac{66}{58.93} = 1.12$$

$$m(\text{total}) = 0.23 + 1.12 = 1.35$$

$$\text{Atomic wt of In} = \left[ \frac{0.23}{1.35} \right] \times 110 = 0.17 \times 110 = 18.7$$

$$\text{Atomic wt of Co} = \left[ \frac{1.12}{1.35} \right] \times 110 = 0.83 \times 110 = 83.7$$

- (ii) Molarity: number of mol of solute per one litre of solution.
- (iii) Normality: gm equivalents of solute per one litre of solution.  
i.e., equivalent wt in gms = (atomic wt / valency)

## 8.2 IDEAL AND NON-IDEAL SOLUTIONS

### 8.2.1 Raoult's Law

There are two statements of *Raoult's law* as follows:

I. The original empirical statement of Raoult's law, which is obeyed by limited number of binary solutions is that the partial pressure of the vapour of any component of an ideal solution is equal to the product of its mol fraction and the vapour pressure of the pure component at the same temperature as that of ideal solution.

Hence,

$$P_A = X_A \cdot P_A^0 \quad \dots(8.8)$$

where,  $P_A$  is the partial pressure of the vapour of any component, A of an ideal solution,  
 $X_A$  is its mol fraction, and  $P_A^0$  is the vapour pressure of the pure component.

However, as studied earlier, if the vapour behaves as an ideal gas,

Then  $P_A = f_A$  and  $P_A^0 = f_A^0$  where  $f$  is the fugacity of vapour.

Therefore,  $f_A = X_A \cdot f_A^0$

$\dots(8.9)$

Now by definition,  $\left( \frac{f_A}{f_A^0} \right) = a_A$ . where  $a_A$  is the activity of component A.

Therefore,

$$a_A = X_A$$

$\dots(8.10)$

II) Another statement of Raoult's law is the activity of a component equal to the mol fraction of that component, i.e.,  $a_A = X_A$  (as shown in Figure 8.1).

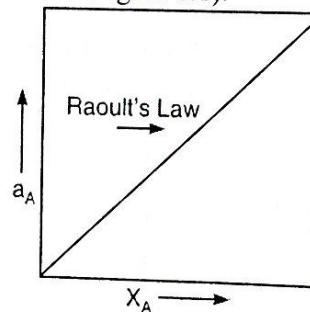


Fig 8.1. Raoult's law curve

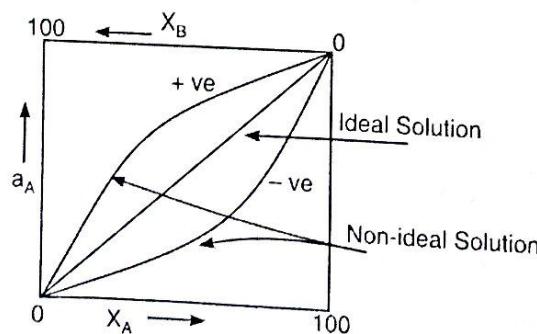


Fig 8.2. Ideal and non-ideal solutions

An *ideal solution* is one which obeys Raoult's law over all temperatures and pressures. Figure 8.2 shows the activity vs mol fraction plot for binary system of A and B components. i) Since ideal solution obeys Raoult's law and hence lines for component A and B are diagonal. ii) For non-ideal

solution the activity ( $a$ ) vs mol fraction ( $X$ ) curve is above or below the diagonal i.e., departure from Raoult's law may be + ve or - ve.

### 8.2.2 Henry's Law

*Henry's law* states that the activity of a component (i.e., solute) is proportional to its mol fraction. e.g.  $a_A \propto X_A$  (as shown in Figure 8.3).

Therefore,

$$a_A = \gamma X_A \quad \dots (8.12)$$

where  $\gamma$  is called activity coefficient or activity quotient.

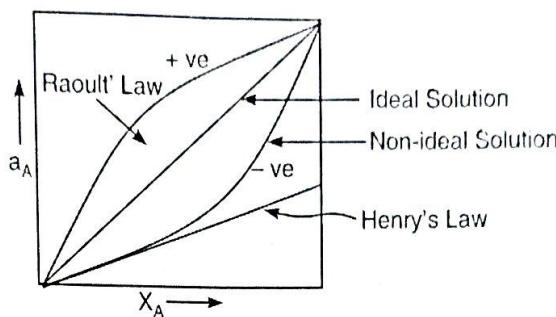


Fig 8.3: Henry's law curve

Hence,  $\gamma_i$  is defined as the ratio of activity of  $i$  to its mol fraction i.e.,  $\gamma_i = \left( \frac{a_i}{X_i} \right)$ .

(i) For ideal solution:  $\gamma_i = 1$ .

(ii) For non-ideal solution:  $\gamma_i > 1 \rightarrow +ve$  deviation

$\gamma_i < 1 \rightarrow -ve$  deviation. (as shown in Figures 8.2 and 8.3).

*Non-ideal solution* is one that does not obey Raoult's law. Non-ideal solutions do not have any general relation between activity and mol fraction for solutes, but many dilute solutions are non-ideal solutions and hence they obey Henry's law.

### 8.3 SIEVERT'S LAW

One of the important groups of solution is the solutions of gases in metals. Gases dissolve in metals in the atomic condition and their solubility in metal at a given temperature depends on the pressure of the gas.

If the hydrogen gas at a pressure ( $P_{H_2}$ ) in equilibrium with a molten metal will form a system represented by:

$$H_2(g) = 2\bar{H} \quad \dots (8.13)$$

where  $\bar{H}$  is atomic hydrogen in molten metal.

$$\text{Hence, equilibrium constant, } k = \left( \frac{(a_H)^2}{P_{H_2}} \right) \quad \dots (8.14)$$

Considering that the solution of gases in metals obeys Raoult's law, so we take activity equal to mass concentration i.e.,

$$\underline{\underline{a_H}} = [H] \quad \text{what relation with } X_H? \dots (8.15)$$

(i) Hence, for a diatomic gas like hydrogen,  $k = [[H]^2 / P_{H_2}]$

Therefore, the solubility of hydrogen in metal:

$$[H] = \sqrt{(k \cdot P_{H_2})} = k' \cdot \sqrt{P_{H_2}} \quad \dots (8.16)$$

Where  $k'$  is solubility constant =  $\sqrt{k}$  and  $P_{H_2}$  is partial pressure of hydrogen gas.

(ii) For monatomic gas like carbon monoxide, the solubility will be proportional to partial pressure:

$$[CO] = k \cdot P_{CO} \quad \dots (8.17)$$

(iii) For multiaatomic gas i.e., each gas molecule of n atoms:

$$\text{Solubility} = k' \cdot (P_G)^{1/n} \quad \dots(8.18)$$

Hence, *Sievert's law* states that the solubility of a diatomic gas in a molten metal at a given temperature is proportional to the square root of its partial pressure.

Effect of temperature: the solubility of a gas in molten metal increases with increase in temperature at constant pressure.