



Physical Chemistry (2)

For first Year Students

Physical Chemistry (General Chemistry II)

First term

1-State of Matter, Gaseous State

General characteristics of gases - General physical properties of gases - General gas laws (*Boyle's Law - Charles and Gay-Lussac's Law - Amonton's Law - Avogadro's Law*) - The Molar volume - (P - n) Relationship - (n - T) Relationship - State equation of gases - The values of the constant (R) - Student exercises.

2-Liquid State

Properties of liquids - Vapour pressure - Effect of temperature on vapour pressure - Determination of vapour Pressure - Barometric method - Experimental determination of vapour pressure of the liquid - The direct (Static) method - The dynamic method - Effect of vapour pressure on boiling points- Determination of boiling points - Surface tension - Determination of surface tension - Drop Formation Method - Viscosity - Units of Viscosity - Measurement of Viscosity - The Ostwald Method - Measuring the liquid viscosity using the falling ball method (*Stokes Equation*) - Students exercises.

3-Thermochemistry

Heat of the reaction under constant volume, ΔE - Heat of reaction under constant pressure, ΔH - Different types of heat (Enthalpy) of reaction - Heat of formation - Standard heat formation - Heat of combustion - Heat of neutralization - Heat of hydrogenation - Heat of solution - Heat of dilution - Laws of thermochemistry - First law - Lavoisier and *Laplace Law* - Second Law - *Hess's Law* of constant heat summation - Student Exercises.

Second term

4-Solutions

Types of Solutions - Ways of Expressing Solution Concentration - Weight or mass percent - Mole fraction - Molarity and Formality - Molality - Normality - Mole Fraction percent - Part per million (ppm) and part per billion (ppb) - Solution of gases in Gases - Complete miscibility - *Dalton's law* of partial pressures - Solution of Gases in liquids - Completely soluble (easy soluble) - Miserly soluble gases - *Henry's Law* - Limitations of *Henry's Law* - General Distribution law and *Henry's Law* - Application of *Henry's Law* - Factors affecting gas solubility in liquids - Nature of the dissolved gas Nature of the solvent liquid - Solutions of gases in liquids - Solutions of liquids in liquids - Completely miscible liquids - (i) Ideal solutions - B- Non-ideal solution Positive deviation - Negative deviation - Composition of the vapour phase and the solution - Distillation of completely miscible solution - Distillation of completely miscible liquids - Students exercises.

5-Chemical Equilibrium

Chemical equilibrium is dynamic equilibrium - Reversible and irreversible Reactions - The $\text{N}_2\text{O}_4\text{-NO}_2$ equilibrium system - Factors affecting the chemical equilibrium - Temperature effect - Catalyst effect - Concentration

effect - Pressure effect-Law of mass action - Equilibrium Constant K_C -
The relation between K_P and K_C - Students exercises.

6-IONIC EQUILIBRIA

1- Application of Law of mass action to solutions of electrolytes
(*Ostwald* Law of dilution) - Ionization of polybasic Acids - Solubility
Product - Effect of common ion on solubility product - Ionization of
water - The hydrogen- Ion exponent value - Buffer solutions - Theory
of buffer Action - Student exercises.

Second term

2-4. Solutions

A solution is a homogeneous mixture of two or more substances on molecular level. The constituent of the mixture present in a smaller amount is called the Solute and the one present in a larger amount is called the Solvent. For example, when a smaller amount of sugar (solute) is mixed with water (solvent), a homogeneous solution in water is obtained.

Concentration of a Solution: The concentration of a solution is defined as: **the amount of Concentration is generally expressed as the quantity of solute present in a given amount of solution.**

Concentration is generally expressed as the quantity of solute in a unit volume of solution. $\text{Concentration} = \frac{\text{Quantity of solute}}{\text{Volume of solution}}$

A solution containing a relatively low concentration of solute is called dilute solution. A solution of high concentration is *called concentrated solution*.

4.1. Types of Solutions

The common solutions that we come across are those where the solute is a solid and the solvent is a liquid. In fact, substance in any three states of matter (solid, liquid, gas) can act as solute or solvent. Thus, there are **seven types of solutions** whose examples are listed in Table (4.1).

Table (4.1): Type and Examples of Solutions		
State of Solute	State of Solvent	Example
Gas	Gas	Air
Gas	Liquid	Oxygen and CO ₂ in water
Gas	Solid	Adsorption of H ₂ by palladium
Liquid	Gas	Water vapour in air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Benzene in Iodine
Solid	Gas	Camphor vapour in air
Solid	Liquid	Salt and sugar
Solid	Solid	Metal alloys

Of the ninth types of solutions mentioned in Table (4.1), we will discuss only the important ones in detail; the most important one is the solution that the solvent is liquid.

4.2. Ways of Expressing Solution Concentration

If we considered a solution consisting of a solute (B) and a solvent (A) and their weight by grams are w_B and w_A , and their number of moles are n_B and n_A , and their volumes are V_B and V_A respectively. The total solution volume by liter is V .

There are several different ways of expressing concentration of a solution are summarized in table (4.2) for Common Units for Reporting Concentration, as following:

- (1) Weight or Mass percent
- (2) Mole fraction
- (3) Molarity and Formality
- (4) Molality
- (5) Normality
- (6) Mole Fraction percent
- (7) Part per million (ppm) and part per billion (ppb)

4.2.1. Weight or Mass percent:

It is the weight of the solute as a percent of the total weight of the solution (or the dissolved weight of solute in grams present in (100 g) of solution. That is,

$$W_{\text{solute}} \% = \frac{\text{w.of solute}}{\text{weight of solution}} \times 100 = \frac{w_B}{w_A + w_B} \times 100 \quad (4.1)$$

✎ **Notable**, the solution weight can be calculated from the solution density if the solution volume is known as following:

$$d_{(\text{solution})} = \frac{W_{(\text{solution})}}{V_{(\text{solution})}} \quad (4.2)$$

Whereas:

$d_{(\text{solution})}$ the solution density with units (g/L) , (g/mL) or (kg/L).

$W_{(\text{solution})}$ the solution weight by grams unit

$V_{(\text{solution})}$ the solution volume with milliliter (mL), cubic centimeter (cm^3), cubic decimeter (dm^3), liter (L) or cubic meter (m^3).

Also the relation between the volume units as following:

$$1.0 \text{ m}^3 = 1000 \text{ L} = 1000 \text{ dm}^3 = 1.0 \times 10^{-6} \text{ cm}^3$$

$$1.0 \text{ dm}^3 = 1.0 \text{ L}$$

$$1.0 \text{ cm}^3 = 1.0 \text{ mL}$$

Example 4.1: How much the weight percent ratio of sodium chloride (NaCl), when 55 g is dissolved in 98 g water?

- (a) 33.74% (b) 35.94% (c) 37.76% (d) 39.58%

View Answer

Answer: [b]

Hint and Solution: [B] $w_B = w_{\text{NaCl}} = 55 \text{ g}$ and $w_A = w_{\text{H}_2\text{O}} = 98 \text{ g}$

$$w_B\% = \frac{w_B}{w_A + w_B} \times 100$$

$$w_{\text{NaCl}} \% = \frac{55 \text{ g}}{(98 + 55) \text{ g}} \times 100 = \frac{55 \text{ g}}{153 \text{ g}} \times 100 = 35.94\%$$

4.2.2. Mole Fraction

A simple solution is made of two substances: one is the solute and the other solvent. Mole fraction, X , of solute is defined as **the ratio of the number of moles of solute and the total number of moles of solute and solvent**. Thus,

$$X_{B \text{ (solute)}} \% = \frac{n_B}{n_A + n_B} \quad (4.3)$$

$$X_{A \text{ (solvent)}} \% = \frac{n_A}{n_A + n_B} \quad (4.4)$$

$$X_A + X_B = 1 \quad (4.5)$$

i.e.; the summation of mole fractions for all components is equal to unit.

Example 4.2: Calculate the mole fraction of water in solution containing 0.524 mol of sodium chloride and 5 mol of water.

- (a) 0.905 (b) 0.823 (c) 0.803 (d) 0.786

View Answer

Answer: [a]

Hint and Solution: [a] $n_{\text{total}} = n_A + n_B = (0.524 + 5) \text{ mol} = 5.524 \text{ mol}$

$$X_A = \frac{n_A}{n_A + n_B} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{NaCl}}} = \frac{5}{5.524} = 0.905$$

Example 4.3: Calculate the mole fraction of sodium chloride in solution of sodium chloride in water, whereas the mole fraction of water is 0.89.

- (a) 0.32 (b) 0.21 (c) 0.18 (d) 0.11

View Answer

Answer: [d]

Hint and Solution: [d] $X_A + X_B = 1$

$$X_{\text{H}_2\text{O}} + X_{\text{NaCl}} = 1 \quad \Rightarrow \quad 0.89 + X_{\text{NaCl}} = 1$$

$$X_{\text{NaCl}} = 1 - 0.89 = 0.11$$

4.2.3. Molarity (M) and Formality (F)

Both molarity and formality express concentration as moles of solute per liter of solution. There is, however, a subtle difference between molarity and formality. **Molarity** is the concentration of a particular chemical species in solution. **Formality**, on the other hand, is a substance's total

concentration in solution without regard to its specific chemical form. There is no difference between a substance's molarity and formality if it dissolves without dissociating into ions. The molar concentration of a solution of glucose, for example, is the same as its formality.

For substances that ionize in solution, such as NaCl, molarity and formality are different. For example, dissolving 0.1 mole of NaCl in 1.0 L of water gives a solution containing 0.1 mole of Na⁺ and 0.1 mole of Cl⁻. The molarity of NaCl, therefore, is zero since there is essentially no undissociated NaCl in solution. The solution, instead, is 0.1 M in Na⁺ and 0.1 M in Cl⁻. The formality of NaCl, however, is 0.1 F because it represents the total amount of NaCl in solution. The rigorous definition of molarity, for better or worse is largely ignored in the current literature, as it is in this text. When we state that a solution is 0.1 M NaCl we understand it to consist of Na⁺ and Cl⁻ anions. The unit of formality is used only when it provides a clearer description of solution chemistry.

Molar concentrations are used so frequently that a symbolic notation is often used to simplify its expression in equations and writing. The use of square brackets around a species indicates that we are referring to that species' molar concentration. Thus, [Na⁺] is read as the "molar concentration of sodium ions."

Molarity: The number of moles of solute per liter of solution (M).

Formality: The number of moles of solute, regardless of chemical form, per liter of solution (F).

In current practice, concentration is most often expressed as molarity. Molarity (symbol **M**) is defined as **the number of moles of solute per liter of solution**. If n is the number of moles of solute and V liters the volume of solution,

$$\text{Molarity} = \frac{\text{No Moles of Solute}}{\text{Volume of Solvent in liters}} = \text{mol/L} \quad (4.6)$$

For one mole of solute dissolved in one liter of solution $M = 1$ i.e., molarity is one. Such a solution is called 1M (read "1 molar"). A solution containing two moles of solute in one liter is 2M ("two molar"); and so on. As evident from expression (1), **unit of molarity is mol liter⁻¹**.

Example 4.4: Calculate the molarity of solution of sodium chloride in water, if 0.735 mol is dissolved in quantity of water until the volume of the solution becomes 650 mL.

(a) 1.13 M (b) 1.33 M (c) 1.41 M (d) 1.47 M

View Answer

Answer: [a]

Hint and Solution: [a] To calculate the sodium chloride solution, the number of moles of dissolved sodium chloride must be known and the solution volume V:

$$n_2 = 0.735 \text{ mol} \quad \& \quad V = \frac{650 \text{ mL}}{1000 \text{ mL L}^{-1}} = 0.65 \text{ L}$$

$$\therefore M = (\text{mol/L}) = \frac{n_2}{V} = \frac{0.735 \text{ mol}}{0.65 \text{ L}} = 1.13 \text{ mol L}^{-1}$$

4.2.4. Molality

Molality of a solution (symbol *m*) is defined as the number of moles of solute per kilogram of solvent:

$$\text{Molality} = \frac{\text{Moles of Solute}}{\text{Mass of solvent in kilograms}} = \text{mol/1 kg of solvent} \quad (4.7)$$

A solution obtained by dissolving one mole of the solute in 1000 g of solvent is called **one molal** or **1 m solution**.

Notice that: the difference between molality and molarity. Molality is defined in terms of mass of solvent while molarity is defined in terms of volume of solution.

Example 4.5: Calculate the molality of sodium chloride solution if 39 g of it is dissolved in 126 g of water.

(a) ~ 5.538 m (b) ~ 5.462 m (c) ~ 5.286 m (d) ~ 4.846 m

View Answer

Answer: [c]

Hint and Solution: [c] To calculate the mole fraction, it must be know the number of moles of both solute and solvent.

$$\text{Molality (mol/1 kg)} = \frac{\frac{w \text{ g}}{1000 \text{ g}} \text{ kg}}{\frac{\text{M.wt. g mol}^{-1}}{1000 \text{ g}} \text{ kg}} = \frac{\frac{39 \text{ g}}{58.5 \text{ g mole}^{-1}}}{\frac{126 \text{ g}}{1000 \text{ g}} \text{ 1 kg}} = 5.2857 \text{ m}$$

$$\text{molality (m)} = \frac{n_{\text{NaCl}}}{w_{\text{H}_2\text{O}}} = \frac{0.666 \text{ mol}}{0.126 \text{ kg}} = 5.2857 \text{ mol kg}^{-1}$$

$$M_{\text{NaCl}} = 5.2857 \text{ molal} = 5.2857 \text{ m}$$

4.2.5. Normality

Normality of a solution (symbol N) is defined as number of equivalents of solute per liter of the solution:

$$\text{Normality (N)} = \frac{\text{Equivalent of solute}}{\text{Volume of solution in liters}} \quad (4.8)$$

Thus, if 40 g of NaOH (eq. wt. = 40) be dissolved in one liter of solution, normality of the solution is one and the solution is called 1N (one-normal). A solution containing 4.0 g of NaOH is

$\frac{1}{10}$ N or 0.1 N or decinormal. The following ways must be followed to get the equivalent weight for bases, acids and their salts:

First: The equivalent weight of solute from the following relations: The calculation of the equivalent weight of material depends on its nature and the reaction intermediate.

For acids:

$$\text{Equivalent weight of acid} = \frac{\text{Molecular weight of the acid (g/mol)}}{\text{number of substituted hydrogen}}$$

$$\text{Equivalent weight of HCl} = \frac{\text{The molecular weight of HCl acid (g/mol)}}{1 \text{ (equivalent/mol)}}$$

$$\text{Equivalent weight of H}_2\text{SO}_4 = \frac{\text{The molecular weight of H}_2\text{SO}_4 \text{ acid (g/mol)}}{2 \text{ (equivalent/mol)}}$$

$$\text{Equivalent weight of H}_3\text{PO}_4 = \frac{\text{The molecular weight of H}_3\text{PO}_4 \text{ acid (g/mol)}}{3 \text{ (equivalent/mol)}}$$

The same calculation for base,

$$\text{The equivalent weight of base} = \frac{\text{The molecular weight of the base (g/mol)}}{\text{number of substituted hydroxyl}}$$

$$\text{Equivalent weight of NaOH} = \frac{\text{The molecular weight of NaOH (g/mol)}}{1}$$

$$\text{Equivalent weight of Ca(OH)}_2 = \frac{\text{The molecular weight of Ca(OH)}_2 \text{ (g/mol)}}{2}$$

The salts are calculated as following:

$$\text{Equivalent of salt} = \frac{\text{Molecular weight of solute (g/mol)}}{\text{No of acidic or basic radicals} \times \text{equivalent of the radical}}$$

$$\text{Equivalent weight of H}_2\text{SO}_4 = \frac{\text{molecular weight of solute Na}_2\text{SO}_4^{2-} \text{ (g/mol)}}{\text{No of acidic radical (10} \times \text{radical equivalent (2))}}$$

4.2.6. Mole Fraction percent

It is the number of moles of solute in 100 moles of solution and equal to the multiplication of the mole fraction of the solute $\times$ 100, as following:

$$X_B \% = \frac{n_B}{n_A + n_B} \times 100 \quad (4.9)$$

$$X_B \% = X_B \times 100 \quad (4.9)$$

Example 4.6: 150 g of silver nitrate (AgNO_3) is dissolved in 350 g water (H_2O) at 20°C , the solution volume is 379 mL. Calculate the following:

- (i) Solution density (ii) Molality (iii) Molarity
- (iv) The mole fraction of solute and solvent
- (v) The molecular percentage ratio of the solute
- (vi) The weight percent (vii) The normality
- (viii) The solution strength ($\text{Ag} = 108, \text{O} = 16, \text{N} = 14$)

Solution: The weight of the solute is 150 g, the weight of the solvent is 350 g and the solution volume is 379 mL.

The molecular weight of water = 18 g/mol

The molecular weight of silver nitrate = 170 g/mol

$$(i) \quad d = \frac{w}{V} = \frac{w_{H_2O} + w_{AgNO_3}}{V_{total}} = \frac{350 \text{ g} + 150 \text{ g}}{379 \text{ cm}^3} = 1.32 \text{ g/mL}$$

$$(ii) \text{ Molality} = \text{mol/1 kg}$$

$$\text{molality (m)} = \frac{\frac{w \text{ g}}{\frac{M.wt. \text{ g mol}^{-1}}{1000 \text{ g}} \text{ kg}}}{\frac{150 \text{ g}}{\frac{170 \text{ g mol}^{-1}}{1000 \text{ g}} \text{ 1 kg}}} = \frac{170 \text{ g mol}^{-1}}{350 \text{ g}} = 2.52 \text{ mol kg}^{-1}$$

$$(iii) \text{ Molarity} = \text{mol/L}$$

$$\text{molarity (M)} = \frac{\frac{w \text{ g}}{\frac{M.wt. \text{ g mol}^{-1}}{1000 \text{ ml}} \text{ 1 L}}}{\frac{150 \text{ g}}{\frac{170 \text{ g mol}^{-1}}{1000 \text{ ml}} \text{ 1 L}}} = \frac{170 \text{ g mol}^{-1}}{379 \text{ mL}} = 2.33 \text{ mol L}^{-1}$$

$$(iv) \text{ The mole fraction of the solute:}$$

$$\therefore X_B = \frac{n_B}{n_A + n_B} = \frac{\frac{150 \text{ g}}{170 \text{ g mol}^{-1}}}{\frac{350 \text{ g}}{18 \text{ g mol}^{-1}} + \frac{150 \text{ g}}{170 \text{ g mol}^{-1}}} = \frac{0.88}{19.44 + 0.88} = 0.043$$

The mole fraction of the solvent X_A can be deduced as following:

$$X_A = 1.0 - X_B = 1.0 - 0.043 = 0.957$$

$$(v) \text{ Mole percentage of the solvent (B)} = \text{solvent mole fraction} \times 100$$

$$X_B \% = 0.043 \times 100 = 4.3\%$$

$$(vi) \text{ The weight percent ratio of the solvent} = \frac{150 \text{ g}}{350 \text{ g} + 150 \text{ g}} \times 100 = 30\%$$

$$(vii) \text{ The normality} = \frac{\text{No gram equivalent of the solute}}{\text{Solution volume in liters}}$$

$$\text{The normality (N)} = \frac{\frac{150 \text{ g}}{170 \text{ g mol}^{-1}}}{0.379 \text{ L}} = 2.33 \text{ g equivalent/L}$$

$$(viii) \text{ Solution strength} = \text{Normality} \times \text{equivalent weight}$$

$$\text{Solution strength} = 2.33 \times 170 = 395.8 \text{ g/L}$$

4.2.7. Part per trillion, Part per billion and Part per million:

We have to know some common units for weight and volume in metric system. The gram is considered as the basic unit of mass and is the unit, which is often, be used in micron analysis. In the samples of very low concentration, some small units are used:

$$1.0 \text{ g} = 10^3 \text{ mg} = 10^6 \text{ } \mu\text{g} = 10^9 \text{ ng}$$

The basic unit of volume is liter (L)

$$1.0 \text{ L} = 10^3 \text{ mL} = 10^6 \text{ } \mu\text{L} = 10^9 \text{ nL}$$

4.2.7.1. The Solid Samples

The calculation of concentration of solid samples depends on weight. The common method to express the results in analytical chemistry is given as percentage of the sample (weight/weight) but both of the units of material and the sample should be the

same. As an example a sample of lime its weight is 1.267 g contains 0.3684 g of iron will contain iron percentage:

$$\frac{0.3684 \text{ g}}{1.267 \text{ g}} \times 100 = 29.08\% \text{ Fe}$$

The general expression of calculation of the percentage (w/w), which is equal to a part of hundred as following:

$$\% \text{wt/wt} = \left[\frac{\text{Solute weight by grams}}{\text{Sample weight by grams}} \right] \times 100 \quad (4.10)$$

Table: The Common Units of Concentration				
Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	μL/L
(1 ppm = 10 ⁻⁴ %)		μg/g	μg/mL	nL/mL
Parts per billion	ppb	μg/kg	μL/L	nL/L
(1 ppb = 10 ⁻⁷ % = 10 ⁻³ ppm)		ng/g	ng/mL	pL/mL*
Milligram percent	mg %	mg/100g	mg/100mL	
*pL = Picoliter = 10 ⁻¹² Liter				

Example 4.7: A plant sample its weight is 2.6 g is be analyzed. It was found that it contains 3.6 μg of zinc. What is the zinc concentration with part per million?

- (a) 1.5 ppm (b) 1.4 ppm (c) 1.3 ppm (d) 1.2 ppm

View Answer

Answer: [b]

Hint and Solution: [b] Zinc conc. = $\frac{3.6 \text{ μg}}{2.6 \text{ g}} = 1.4 \text{ μg/g} = 1.4 \text{ ppm}$

Example 4.8: A plant sample its weight is 2.6 g is be analyzed. It was found that it contains 3.6 μg of zinc. What is the zinc concentration with part per billion?

- (a) 1600 ppb (b) 1500 ppb (c) 1400 ppb (d) 1300 ppb

View Answer

Answer: [c]

Hint and Solution: [c]

$$\text{Zinc conc.} = \frac{3.6 \times 10^3 \text{ ng}}{2.6 \text{ g}} = 1.4 \times 10^3 \text{ ng/g} = 1400 \text{ ppb}$$

In medical analysis, the milligram percent (mg%) is preferred to be used more than part per million (ppm) for the little concentration. The expression (mg %) means that for mg of material for 100 g of the sample. In the last example:

$$\begin{aligned} \text{zinc conc. (mg \%)} &= \frac{3.6 \text{ μg} \times \frac{10^{-3} \text{ mg}}{\text{μg}}}{2.6 \text{ g}} \times 100 \text{ mg \%} \\ \text{zinc conc. (mg \%)} &= 0.13846 \text{ mg \% of Zn} \end{aligned}$$

4.3. Different types of Solutions

4.3.1. Solution of Gases in Gases

When a gas is mixed with another gas a completely homogeneous solution results provided of course they do not react chemically. It is obvious that such gaseous solutions will have the following characteristic properties:

4.3.1.1. Complete miscibility: According to the Kinetic Theory, a gas consists of tiny molecules moving about in vacant space and thus when one gas is dissolved in another gas they form a homogeneous solution quite readily. In such a gaseous mixture, the components can be present to an unlimited extent.

4.3.1.2. Dalton's law of Partial pressures: Since in a gaseous mixture the constituent molecules exist separately, it is obvious that the properties of the mixture will be the sum of properties of the components. Thus Dalton (1842) was the first to show that the total pressure exerted by a gaseous mixture is the sum of the individual or partial pressures of the component gases. If $P_1, P_2, P_3 \dots$ be the partial pressures of the constituents, the total pressure P_{total} of the mixture is given the expression:

$$P_{\text{total}} = P_1 + P_2 + P_3 \quad (4.11)$$

Like other gas laws, Dalton's law holds strictly only when the partial pressures are not too high. This law can be experimentally tested by comparing the total pressure of a gaseous mixture with the sum of the individual pressure of each gas before mixing.

Example 4.9: At constant temperature, 250 mL of nitrogen under 720 mm Hg and 380 mL oxygen under 650 mm Hg, were put into a one-liter flask. What will be the final pressure of the mixture?

(a) 543 mm Hg (b) 521 mm Hg (c) 4 mm Hg (d) 427 mm Hg

View Answer

Answer: [d]

Hint and Solution: [d]

Since $P_1 V_1 = P_2 V_2$ at constant temperature (Boyle's Law)

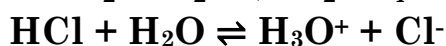
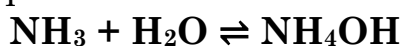
$$\begin{aligned} P_{\text{N}_2} \times 1.0 \text{ L} &= 720 \text{ mm Hg} \times 0.250 \text{ L} \\ P_{\text{N}_2} &= \frac{720 \text{ mm Hg} \times 0.25 \text{ L}}{1.0 \text{ L}} = 180 \text{ mm Hg} \\ P_{\text{O}_2} \times 1.0 \text{ L} &= 380 \text{ mm Hg} \times 0.650 \text{ L} \\ P_{\text{O}_2} &= \frac{720 \text{ mm Hg} \times 0.25 \text{ L}}{1.0 \text{ L}} = 247 \text{ mm Hg} \end{aligned}$$

$$\text{Total pressure } P = P_{\text{N}_2} + P_{\text{O}_2} = 180 + 247 = 427 \text{ mm Hg} \\ (\text{Dalton's Law})$$

4.3.2. Solution of Gases in liquids

The gases are dissolved with different degrees forming real solutions. The solution of gases in liquid is classified into classes according to their solubilities:

4.3.2.1. Completely soluble (easy soluble): These gases are completely soluble in liquids and mix completely with all ratios according to their chemical reactions (do not forming real solution). For example, the following gases react with water ammonia (NH₃), hydrogen chloride (HCl) and sulfur dioxide (SO₂) and do not forming real solution of gases in liquids because of forming their compounds with water as illustrated from the following equations:

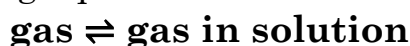


4.3.2.2. Miserly soluble gases

These gases are partially miscible in liquids without any chemical reaction, forming real solutions. Whereas the solution do not contain a large quantity of the gas and the gas can be totally expelled by raising the solution temperature. For example oxygen and nitrogen gases are dissolved in water and can be totally expelled from the solution.

4.3.2.1.1. Henry's Law

The solubility of a gas in a solvent depends on the pressure and the temperature. When a gas is enclosed over its saturated solution, the following equilibrium exists.



If pressure is increased on the system, the equilibrium will move in the direction which will reduce the pressure (*Le Chatelier's* Principle). The pressure can be reduced by more gas dissolving in solvent. Thus solubility or concentration of a gas in a given solvent is increased with increase of pressure. The relationship between pressure and solubility of a gas in a particular solvent was investigated by *William Henry* (1803). He gave a generalization which is known as Henry's Law. It may be stated as: for a gas in contact with a solvent at constant temperature, concentration of the gas that dissolves in the solvent is directly proportional to the pressure of the gas.

Mathematically, Henry's Law may be expressed as:

$$\begin{aligned} C &\propto P \\ C_{(g)} &= k_{(g)} P_{(g)} \end{aligned} \quad (4.12)$$

where, P = pressure of the gas; C = concentration of the gas in solution; and k = proportionality constant known as **Henry's Law Constant**. The value of k depends on the nature of the gas and solvent, and the units of P and C used.

Example 4.10: The solubility of pure oxygen in water at 20°C and 1.00 atmosphere pressures is 1.38×10^{-3} mole/liter. Calculate the concentration of oxygen at 20°C.

(a) $\sim 2.9 \times 10^{-5} \text{ mol L}^{-1}$ (b) $\sim 2.6 \times 10^{-6} \text{ mol L}^{-1}$

(c) $\sim 2.4 \times 10^{-8} \text{ mol L}^{-1}$ (d) $\sim 2.3 \times 10^{-9} \text{ mol L}^{-1}$

View Answer

Answer: [a]

Hint and Solution: [a] Calculation of k : $C = kP$

$$k = \frac{C}{P} = \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{1.0 \text{ atm}} = 1.38 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$$

Calculation of Concentration of O_2 at given pressure

Concentration of $O_2 = kP = 1.38 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1} \times 0.21 \text{ atm}$

$$\text{Concentration of } O_2 = 2.898 \times 10^{-5} \text{ mol L}^{-1}$$

4.3.2.3. Application of Henry's Law

Example 12: The solubility of oxygen (O_2) in water at 25°C and pressure is $1.38 \times 10^{-3} \text{ mol/L}$. Calculate the concentration of oxygen in saturated solution with air knowing that the mole fraction of oxygen in air is 21. That is at pressure 740 mm Hg and temperature 20°C.

(a) $\sim 3.82 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}$ (b) $\sim 2.34 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}$

(c) $\sim 2.82 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}$ (d) $\sim 2.53 \times 10^{-1} \text{ mol L}^{-1} \text{ atm}$

View Answer

Answer: [c]

Hint and Solution: [c] We calculate the partial pressure of oxygen using the following equation: $P_{O_2} = X_{O_2} \cdot P_{\text{total}}$

$$P_{O_2} = 21 \times \frac{740 \text{ mm Hg} \times 1 \text{ atm}}{760 \text{ mm Hg}} = 20.447 \text{ atm}$$

$$\text{Oxygen solubility} = \frac{C_{O_2}}{P_{O_2}} = 1.38 \times 10^{-3} \text{ mol L}^{-1}$$

$$C_{O_2} = 1.38 \times 10^{-3} \text{ mol L}^{-1} \times P_{O_2}$$

$$C_{O_2} = 1.38 \times 10^{-3} \text{ mol L}^{-1} \times 20.447 \text{ atm} = 2.82 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}$$

Example 13: 1.3 g of oxygen gas is dissolved in water at pressure 1.0 atm. Calculate the quantity of dissolved oxygen at pressure .9 atm.

(a) 3.98 g (b) 3.89 g (c) 3.77 g (d) 3.53 g

View Answer

Answer: [c]

Hint and Solution: [c] $\frac{C_1}{C_2} = \frac{P_1}{P_2} \Rightarrow \frac{1.3 \text{ g}}{C_2} = \frac{1.0 \text{ atm}}{2.9 \text{ atm}}$

$$C_2 = \frac{2.9 \text{ atm} \times 1.3 \text{ g}}{1.0 \text{ atm}} = 3.77 \text{ g}$$

4.3.2. SOLUTIONS OF LIQUIDS IN LIQUIDS

When two liquids are mixed together one of the following cases may arise:

- (a) Two liquids mix with each other in all-proportions, i.e.; they are completely miscible, e.g., alcohol and water.
- (b) The two liquids dissolve in each other in limited proportions only, i.e.; they are partially miscible, e.g. ether and water.
- (c) The two liquids show practically too tendency to dissolve in each other, i.e.; they are immiscible, e.g., chloro-benzene and water.

4.3.2.1. Completely miscible liquid

When a binary mixture of completely miscible liquids is confined in closed container, the space will be occupied by vapour of both liquids. The partial vapour pressure of each liquid depends on its concentration in solution. The total vapour pressure of the solution is equal to the summation of the partial vapour pressure of the two liquids. Regarding the variation of vapour pressure with the nature of the components; ideal and non-ideal solution are known.

4.3.2.2. Ideal solutions

An ideal binary solution is a mixture of two completely miscible liquids in which:

- 1- The attraction forces between molecules of one liquid are uninfluenced by the presence of the other molecules. Consequently, the tendency of molecules of both liquids to escape from the solution into the surrounding space to form vapour, or their escaping tendency, will be the same as in the pure liquid. If this conditions is fulfilled, then.
- 2- No heat is evolved or absorbed when the constituents of the solution are mixed.
- 3- The volume of the resulting solution is equal to the sum of separate volumes of the constituent's liquids.
- 4- The physical properties of the solution, e.g. "vapour pressure, density, boiling point... etc., are intermediate between those of the pure liquids.
- 5- The solution obeys Raoult's Law which states "***At constant temperature the partial vapour pressure of any volatile***

constituent of solutions proportional to the mole fraction of this constituent in solution, i.e.,

If two A and B liquids completely miscible are mixed, the total vapour pressure at certain temperature is equal to the total vapour pressure of both liquids. The partial pressure of any liquid of the two liquids is dependent on its ratio in the solution according to **“At constant temperature the partial vapour pressure of any volatile constituent of solutions proportional to the mole fraction of this constituent in solution”**.

$$\begin{aligned} P_A \propto X_A &\Rightarrow P_A \propto \frac{n_A}{n_A + n_B} \Rightarrow P_A = \text{const. } X_A \\ P_A &= \text{const. } \frac{n_A}{n_B + n_A} \end{aligned} \quad (4.13)$$

If the solution is containing the liquid (A) only, i.e.; ($n_B = 0.0$) the constant should be equal to the saturated vapour pressure of pure liquid, P_A^0 , therefore the above equation becomes:

$$P_A = P_A^0 X_A \quad (4.14)$$

Similarly:

$$P_B = P_B^0 X_B \quad (4.15)$$

i.e.; the partial vapour pressure of any volatile liquid constituent in solution is equal to the saturated vapour pressure of pure constituent multiplied with mole fraction of this constituents in the solution, this another statement of Raoult,s Law.

The total vapour pressure (P) over the solution is equal to the summation of the partial pressure of the two liquids constituents (A) and (B) that according to Dalton's Law of partial pressures considering the vapors behaves as gases.

$$\therefore P = P_A + P_B \quad (4.16)$$

$$P = P_A^0 X_A + P_B^0 X_B \quad (4.17)$$

Whereas, the total number of mole fractions is equal to one.

$$\begin{aligned} X_A + X_B &= 1 \quad \text{or} \quad \frac{n_B}{n_A + n_B} + \frac{n_A}{n_A + n_B} \\ \therefore X_A &= 1 - X_B \end{aligned} \quad (4.18)$$

The equation (5) can be rewritten as following:

$$P = P_A^0 (1 - X_B) + P_B^0 X_B \quad (4.19)$$

$$P = P_A^0 - P_A^0 X_B + P_B^0 X_B \quad (4.20)$$

$$P = (P_B^0 - P_A^0) X_B + P_A^0 \quad (4.21)$$

Similarly, we can get the following formula:

$$P = (P_A^0 - P_B^0) X_A + P_B^0 \quad (4.22)$$

A plot of P_A or P_B versus the mole fractions X_A and X_B for a solution gives a linear plot as shown in Fig. 4.1. These dotted lines pass through the points for which X_A and X_B are equal to unity. Similarly, the plot of P_{total} versus X_B is also linear (Fig. 4.1). The minimum value of P_{total} is and the maximum value is P_A^0 , assuming that component A is less volatile than component B, i.e., $P_A^0 < P_B^0$.

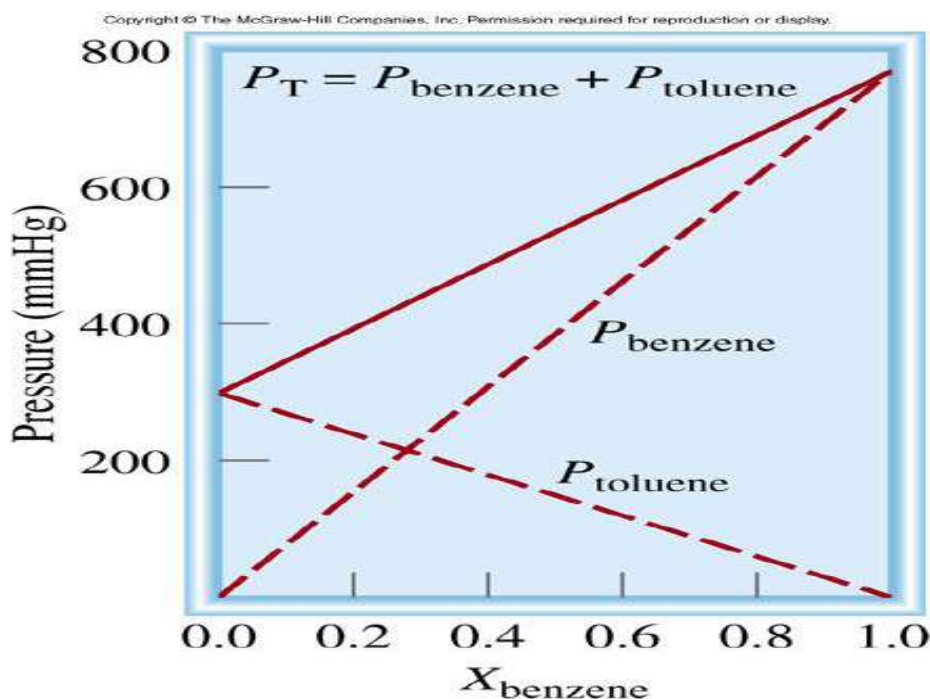


Figure (4.1) Ideal solution

4.3.2.3. Non-ideal solution

Most binary liquid mixtures deviates from Raoult's law this takes place when the attraction of molecules of a for B differs from the A-A attractions between molecules of pure A, and B-B attractions between those of pure B. two types of deviation are observed:

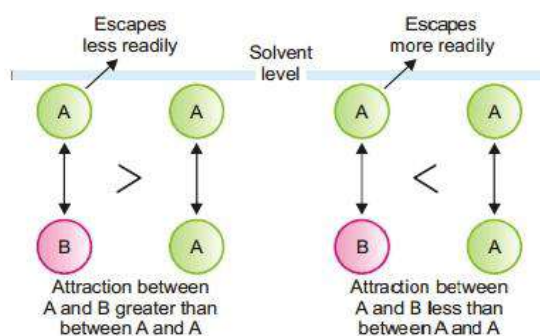


Figure (4.2) Negative deviation and Positive deviation

4.3.2.2. 1. Positive Deviation

When the attraction of molecules of A for B is less than the attraction A-A or B-b attraction, i.e.; $A-A > A-B$ or $B-B > A-B$, then the molecules of A or B tend to escape from the solution relatively easier than from pure A or pure B. In this case, the vapour pressure of the solution will be greater than that given by Raoult's Law and positive deviation is obtained as illustrated in Figure (4.3 a). The watching partial vapour pressures of the liquids are highly than their theoretical values according to Raoult's Law, therefore the curved of the partial vapour pressure are higher than the ideal curve and also, the curve of the total vapour pressure is higher than the ideal one.

4.3.2.2.2. Negative Deviation

This occurs when the A-B attraction is greater than the A-A or the B-B ($A-B > A-A$ or $B-B$). Especially when there is a sort of combination between the two liquids. In this case, the escaping tendency of the molecules of both liquids will be less than when the behaviour id ideal as shown in figure (4.3 b).

Examples of this type of solution are liquid pairs: chloroform-acetone, water-hydrochloric acid and water-nitric acid.

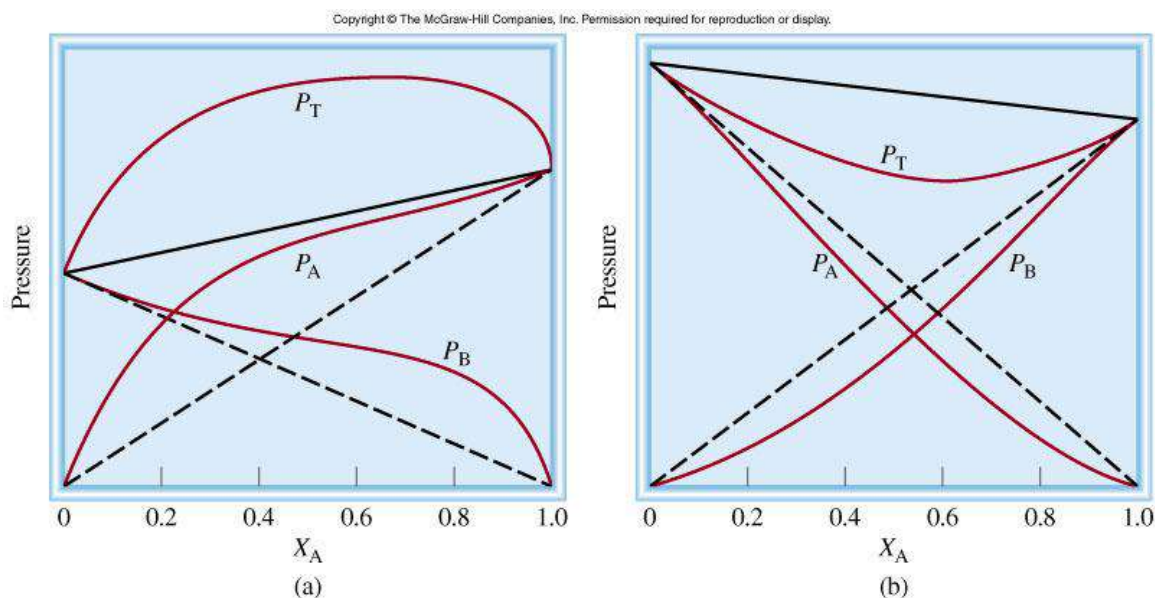


**Figure (4.3) (a) liquid-vapour equilibrium with positive deviation
(b) liquid-vapour equilibrium with negative deviation**

Composition of the vapour phase and the solution:

It is known that the ideal solution concentration is controlled by Raoult's law, and Dalton's law of partial vapour pressure

control the vapour concentration over the solution assuming that the vapors like gases.

Consider a miscible binary liquid mixture of A and B. The solution containing X_A and X_B of A and b. If X_A^V and X_B^V are the mole fractions of the vapour pressure above the mixture.

According to Dalton's law, the vapour pressure of the constituent a is:

$$P_A = P X_A^V \quad (4.23)$$

$$X_A^V = \frac{P_A}{P} \quad (4.24)$$

According to Raoult's Law:

$$P_A = P_A^0 X_A \quad (4.25)$$

$$P = P_A + P_B = P_A^0 X_A + P_B^0 X_B \quad (4.26)$$

Compensating equation (3 & 4) to equation (2), we get the following:

$$X_A^V = \frac{P_A^0 X_A}{P_A^0 X_A + P_B^0 X_B} \quad (4.27)$$

Dividing both sides of equation (5) to X_A , as following:

$$\frac{X_A^V}{X_A} = \frac{P_A^0}{P_A^0 X_A + P_B^0 X_B} \quad (4.28)$$

Dividing the right side both numerator and denominator with P_A^0 :

$$\frac{X_A^V}{X_A} = \frac{1}{X_A + \frac{P_B^0}{P_A^0} X_B} \quad (4.29)$$

From the equation (4.29), we can deduce that if $P_A^0 > P_B^0$, i.e.; the liquid (A) is more volatile than the other liquid (B), the denominator will be less than one, therefore the ratio $\frac{X_A^V}{X_A}$ is more than one which means that the concentration of liquid A in the vapour state is more than its concentration in the solution.

The general deduction for ideal solutions which obey Raoult's Law is the composition of vapour state is different than the origin solution, in the vapour state; there is the more volatile liquid than its ratio in the solution. The vapour composition is only equal to solution composition if the vapour pressure of both pure liquids is equal, i.e.; $P_A^0 = P_B^0$.

Distillation of completely miscible solution:

It is well known that the solution is boiling when its vapour pressure becomes equal to the external pressure and the

composition of solution vapour is different than the origin solution as illustrated in the following example.

Example 14: Calculate the mole fraction of acetone in the liquid and vapour state in ideal solution (obeys Raoult's law) consists of 100 g water and 322 g of acetone (CH_3COCH_3), if the boiling point of the solution is 60°C and the saturated vapour pressure of water and acetone at 60°C is 150 mm Hg and 860 mm Hg respectively.

(a) 0.64 (b) 0.73 (c) 0.79 (d) 0.85

View Answer

Answer: [d]

Hint and Solution: [d]

The molecular weight of water (A) = 18 g/mol

The molecular weight of acetone (B) = 56 g/mol

$$X_{\text{water}} = \frac{n_A}{n_A + n_B} = \frac{\frac{100 \text{ g}}{18 \text{ g mol}^{-1}}}{\frac{100 \text{ g}}{18 \text{ g mol}^{-1}} + \frac{322 \text{ g}}{58 \text{ g mol}^{-1}}} = 0.5$$

$$X_{\text{Acetone}} = \frac{n_B}{n_A + n_B} = \frac{\frac{322 \text{ g}}{58 \text{ g mol}^{-1}}}{\frac{100 \text{ g}}{18 \text{ g mol}^{-1}} + \frac{322 \text{ g}}{58 \text{ g mol}^{-1}}} = 0.5$$

The partial pressure of the water: $P_A = P_A^0 X_A$

$$\therefore P_A = 150 \text{ mm Hg} \times 0.5 = 75 \text{ mm Hg}$$

The partial pressure of acetone: $P_B = P_B^0 X_B$

$$\therefore P_B = 860 \text{ mm Hg} \times 0.5 = 430 \text{ mm Hg}$$

$$P_{\text{total}} = P_A + P_B = 75 + 430 = 505 \text{ mm Hg}$$

By application of Dalton's law of partial pressures to the vapours:

$$P_A = P_{\text{total}} \bar{X}_A$$

$\therefore$ The mole fraction of acetone in vapour ($\bar{X}_A$) is:

$$\therefore \bar{X}_{\text{Acetone}} = \frac{P_{\text{(acetone)}}}{P_{\text{total}}} = \frac{430 \text{ mm Hg}}{505 \text{ mm Hg}} = 0.85 \quad \text{or } 85\%$$

It is clear that the composition of the produced vapour is different than the origin solution composition. In vapour, the ratio of the more volatile liquid is much higher than in the origin solution. Therefore the composition of the residual solution is changed during the distillation process and the boiling temperature is changed gradually.

Example 15: What are the partial and total vapour pressure at 25°C above a solution with equal numbers of moles of benzene (C_6H_6) and toluene (C_7H_8) molecules? The saturated vapour pressures of benzene and toluene at 25°C are 95.1 and 28.4 mm Hg respectively. What is the composition of the vapour in equilibrium with the benzene?

(a) 0.71 (b) 0.73 (c) 0.75 (d) 0.77

View Answer

Answer: [d]

Hint and Solution: [d]

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{\circ} = 0.50 \times 95.2 \text{ mmHg} = 47.6 \text{ mm Hg}$$

$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^{\circ} = 0.50 \times 28.4 \text{ mmHg} = 14.2 \text{ mm Hg}$$

$$P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 47.6 + 14.2 = 61.8 \text{ mm Hg}$$

$$X_{\text{benzene}} = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{47.6 \text{ mm Hg}}{61.8 \text{ mmHg}} = 0.77$$

Example 1d: What are the partial and total vapour pressure at 25°C above a solution with equal numbers of moles of benzene (C₆H₆) and toluene (C₇H₈) molecules? The saturated vapour pressures of benzene and toluene at 25°C are 95.1 and 28.4 mm Hg respectively. What is the composition of the vapour in equilibrium with the toluene?

(a) 0.27 (b) 0.25 (c) 0.23 (d) 0.21

View Answer

Answer: [c]

Hint and Solution: [c]

$$P_{\text{benzene}} = X_{\text{benzene}} P_{\text{benzene}}^{\circ} = 0.50 \times 95.2 \text{ mmHg} = 47.6 \text{ mm Hg}$$

$$P_{\text{toluene}} = X_{\text{toluene}} P_{\text{toluene}}^{\circ} = 0.50 \times 28.4 \text{ mmHg} = 14.2 \text{ mm Hg}$$

$$P_{\text{total}} = P_{\text{benzene}} + P_{\text{toluene}} = 47.6 + 14.2 = 61.8 \text{ mm Hg}$$

$$X_{\text{toluene}} = \frac{P_{\text{toluene}}}{P_{\text{total}}} = \frac{14.2 \text{ mm Hg}}{61.8 \text{ mmHg}} = 0.23$$

4.4. Student Exercise

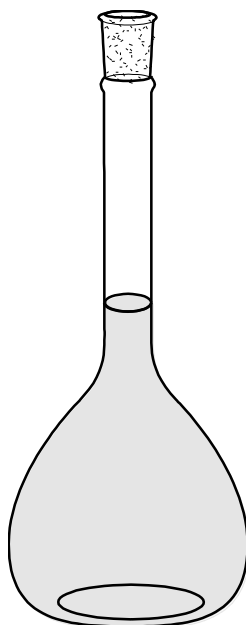
1. How much the mass of sodium chloride present in 143 g in solution its concentration is (26.7%) by weight from sodium chloride.
2. A solution is prepared of 1.46 g methanol (CH₃OH) with 13.8 g of water (H₂O). What is the mass percent of methanol?
3. How much the weight of potassium hydroxide (KOH) presents in 270 g of solution its concentration is 26.4%?
4. One kilogram of aqueous solution of glucose was prepared with concentration 17% by weight. How much grams are used from glucose?
5. Calculate the number of moles of HCl present in 5 cm³ of concentrated hydrochloric acid of density 1.19 g/cm³ and contains 37.23% by weight.
6. The purity of concentrated sulphuric acid 98% by weight and its density is 1.84 kg/L. How much the volume of concentrated sulphuric acid which contains 40 g of pure sulphuric acid?

7. Preparation of aqueous solution of sucrose of concentration value 24% by weight is needed. How many grams of sucrose must be used to get 1.0 kg of the solution?
8. Calculate the mole fraction of a solution contains 6 mol of sodium chloride dissolved in 900 g of water.
9. Calculate the mole fraction of phosphoric acid (H_3PO_4) in solution containing 12.25 g of phosphoric acid dissolved in 90 g of water.
10. Calculate the mole fractions of solute of solution of sodium hydroxide in water of concentration 32% by weight.
11. Calculate the mass percentage w% if the mole fraction of sodium chloride in solution is 0.3.
12. What is the molarity of solution contains 630 g of glucose sugar $\text{C}_6\text{H}_{12}\text{O}_6$ is dissolved in quantity of water whereas the solution volume becomes 700 mL?
14. Calculate the molarity of solution of sugar cane $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which contains 20 g of sugar dissolved in 125 g water knowing that the solution density is 1.2 g/mL.
15. At dissolving 22 g of sodium chloride (NaCl) in quantity of water, whereas the solution mass is 93 g. What is the solution molality?
16. Calculate the concentration by molality of solution is prepared by dissolving 0.1 mol of a material in one liter of water (knowing that the water density is equal to 1g/cm^3 at temperature 20°C).
17. Calculate the concentration by molality of solution is prepared by dissolving 12 g of sodium sulphate Na_2SO_4 in 139 g of water.
18. How many grams of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is necessary to be dissolved in 150 g of water to prepare a solution of concentration 0.2 molal?
19. Calculate the molarity of concentrated hydrochloric acid if its purity is 37.0% by weight, its density is 1.18 kg/L and the molecular weight of the acid is 36.5 g/mol.
20. How much mL is needed to prepare 500 mL measuring flask its molarity is 0.5 M from the following bottle filled of concentrated hydrochloric acid if its purity is 37.0% by weight, its density is 1.18 kg/L and the molecular weight of the acid is 36.5 g/mol.
21. How much mL is needed to prepare 250 cm^3 measuring flask its molarity is 1.0 M from the following bottle filled of

concentrated hydrochloric acid if its purity is 96.0% by weight, its density is 1.84 g/cm^3 and the molecular weight of the acid is 98.07 g/mol .

22. Calculate the molarity of the following chemicals using the table (4):

Table (3)					
Chemical material	Molecular formula	Molecular weight g/mol	Purity	Density (kg/L or g/mL)	Molarity
Acetic acid	CH_3COOH	60.06	100	1.05	17.4
Hydrochloric acid	HCl	36.46	37	1.18	12.0
Nitric acid	HNO_3	63.01	70	1.42	15.8
Sulphuric acid	H_2SO_4	98.07	96	1.84	18.0
Ammonium hydroxide	NH_3	17.03	28	0.90	14.8



23. At 20°C the solubility of nitrogen gas in water is 0.0150 g/liter when the partial pressure of N_2 is 580 torr. Find the solubility of N_2 in H_2O at 20°C when its partial pressure is 800 torr.

24. The solubility of oxygen gas is 0.015 g/L at temperature 20°C and pressure 580 torr. How much the solubility of nitrogen gas in water at the same temperature and pressure 800 torr.

25. The solubility of oxygen gas is 2.7×10^{-4} at temperature 20°C . Calculate the partial pressure of oxygen gas knowing

- that the Henry's constant is $1.3 \times 10^{-3} \text{ g L}^{-1} \text{ atm}$ at the same conditions.
26. The saturated vapour pressure of chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) at temperature 140°C is 939.4 mmHg, and for bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) is 939.4 mmHg assuming the two liquids are forming an ideal solution. Calculate the mole fraction of chlorobenzene in vapour state for solution of them is boiling at 140°C under pressure 1.0 atm.
 27. An ideal solution containing 58% mole of benzene and 42% mole of toluene is boiling at 90°C and pressure 1.0 atm ($1.01 \times 10^5 \text{ Nm}^{-2}$). At the mentioned temperature and composition, the vapour contains 77% mol benzene in equilibrium with the solution. Calculate the vapour pressure of pure benzene at 90°C .
 28. An ideal solution containing 58% mole of benzene and 42% mole of toluene is boiling at 90°C and pressure 1.0 atm ($1.01 \times 10^5 \text{ Nm}^{-2}$). At the mentioned temperature and composition, the vapour contains 77% mol benzene in equilibrium with the solution. Calculate the vapour pressure of pure toluene at 90°C .
 29. An ideal solution consists of 23 g ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) and 32 g methyl alcohol (CH_3OH), the saturated vapour pressure of both of them are 49 and 105.6 mm Hg respectively.
 - (i) Calculate the mole fraction for both of them in the solution.
 - (ii) Calculate the partial pressure of both of ethanol and methanol and the total vapour pressure.
 - (iii) Calculate the mole fraction of ethanol in the vapour state.
 30. Write Raoult's law for ideal solution. Two pure liquids A and B completely miscible, they have a vapour pressure of 200 and 500 mm Hg respectively at 300 K. Calculate the mole fraction of liquid A in the vapour state for a mixture of the has a pressure 35 mm Hg at the same temperature.
 31. Organic liquid immiscible with water is boiling at 90°C and pressure 734 mm Hg, the distilled liquid contains 73% by weight organic liquid. Calculate the molecular weight of the organic liquid if the partial pressure of the water at 90°C is 526 mm Hg.
 32. By distillation of a immiscible mixture of water (H_2O) and 1-bromobutane ($\text{C}_4\text{H}_9\text{Br}$) at 90°C and pressure $1.101 \times 10^5 \text{ Nm}^{-2}$. If the saturated vapour pressure for both of 1-bromobutan

and water at 90°C are $1.7 \times 10^4 \text{ Nm}^{-2}$ and $8.4 \times 10^4 \text{ Nm}^{-2}$ respectively. Calculate the weight of distilled 1-bromobutane for each one gram water. (H = 1, C = 12, Br = 80)

2-5. Chemical Equilibrium

When a chemical reaction is occurred, it is necessary to new materials are appeared not present at reaction starting, consequently, the reactant materials are decreased, and it is noticeable the appearance of new materials or disappearance of a part from the materials at start of the reaction with time passing. The rate or velocity of the reaction by the change value in concentration (expressed generally by number of moles per liter) which is happened in time unit for the both reactants and products materials.

In general, the chemical reactions are occurred with different velocities dependent on nature of reactant materials, temperature and presence of catalyst agents or impediment. Some reactions are occurred so fast and huge to be appeared as instantaneous like the neutralization of strong acid with strong base, while other reactions are preceded so strong slowness like the combination of oxygen and hydrogen forming water at normal temperatures. In-between these two reactions, there are many reactions are occurred with velocities can be measured in suitable temperatures which is related to chemical kinetics to study the different factors affecting on it.

5.1. Chemical Equilibrium is Dynamic Equilibrium

We have shown above that as the reaction " $A+B \rightleftharpoons C + D$ " attains equilibrium, the concentrations of A and B, as also of C and D remain constant with time. Apparently it appears that the equilibrium is dead. But it is not so. The equilibrium is dynamic. Actually, the forward and the reverse reactions are taking place at equilibrium but the concentrations remain unchanged.

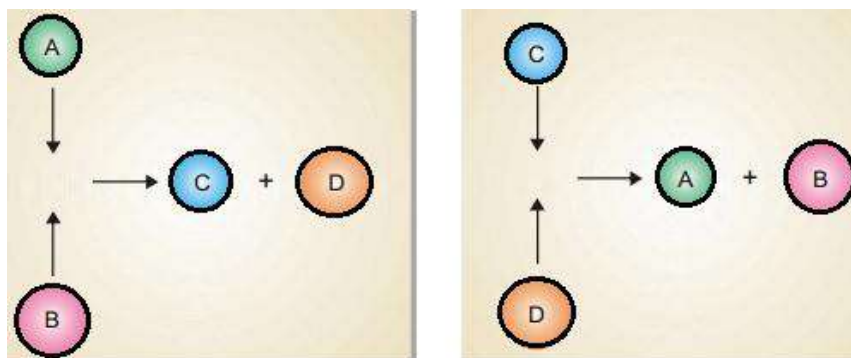
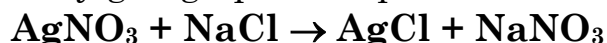


Figure (1) Molecules of A and B colliding to give C and D, and those of C and D colliding to give A and B.

The dynamic nature of chemical equilibrium can be easily understood on the basis of the kinetic molecular model. The molecules of A and B in the equilibrium mixture collide with each other to form C and D. Likewise C and D collide to give back A and B. The collisions of molecules in a closed system are a ceaseless phenomenon. Therefore collisions of A and B giving C and D (Forward reaction) and collisions of C and D giving back A and B (reverse reaction) continue to occur even at equilibrium, while concentrations remain unchanged.

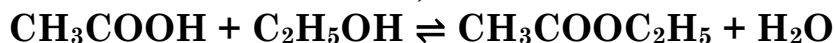
5.2. Reversible and Irreversible Reactions

Many inorganic reactions which take place between ions in solution are usually going up to completion. Thus,



This reaction takes place in one direction as indicated by the arrow and at the end of the reaction; there is no detectable residue of the reacting substances. This type of reaction takes place to completion is known as *irreversible reactions*.

The other type of reactions is known as "reversible reactions". Here the conditions are such that forward and backward reactions can occur to a noticeable extent examples of these, are most organic reactions and some inorganic ones. The interaction between acetic acid and ethyl alcohol. Is a typical example of a reversible reaction, thus?



If we start with one gram molecules of acetic acid and one gram molecule of ethyl alcohol, we obtain $\frac{2}{3}$ gram molecule of ethyl acetate and $\frac{2}{3}$ gram molecule of water and their remain $\frac{1}{3}$ gram molecule of each of acetic acid and ethyl alcohol, both reactions in equilibrium with resultants.

Similarly, a mixture of hydrogen and iodine heated in closed vessel at 450°C will not unite completely to form hydrogen iodide, since the latter decomposes to an appreciable extent into constituent elements.

5.3. The $\text{N}_2\text{O}_4\text{-NO}_2$ equilibrium system

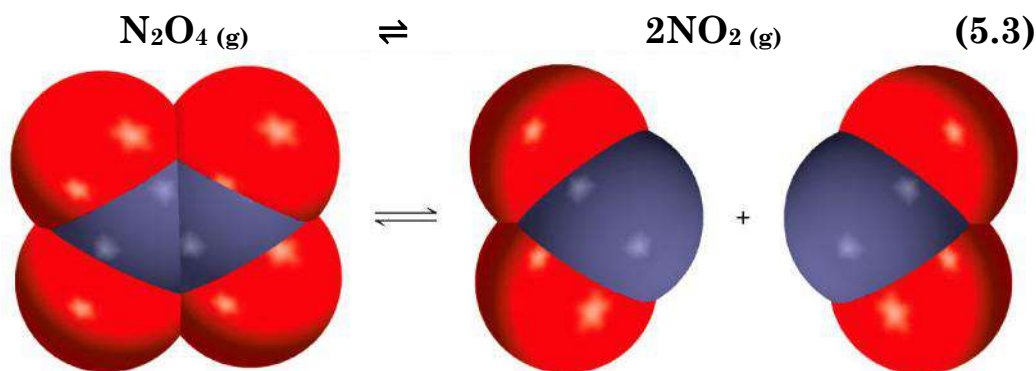
When a sample of N_2O_4 (a colorless gas) is placed in a closed, evacuated container at 100°C. Instantly, a reddish-brown color develops. This color is due to nitrogen oxide, NO_2 , formed by decomposition of a part of the N_2O_4 .



At first, this the only reaction taking place. As soon as NO_2 is formed however, the reverse reaction can occur:



As time passes, reaction (1 a) slows down and reaction (1 b) speeds up. Soon, their rates become equal. A dynamic equilibrium has been established:



At equilibrium, appreciable amounts of both gases are present. From that point on their concentration are constant, as long as the volume of the container and the temperature remain unchanged.

The approach to equilibrium in this system is illustrated by the data in Table (5.1), and plotted Figure (5.1). We start with 1.00 mole N_2O_4 in a 1.0-liter container at 100°C. The original concentration of N_2O_4 is thus 0.10 mol/L. Since there is no NO_2 present at the beginning of the experiment, its original concentration is zero. As equilibrium is approached, the net reaction is taking place that the forward direction (equation 5.1). The concentration of N_2O_4 drops rapidly at first and then more slowly. The concentration of NO_2 increases. Finally, both

concentrations level of them become constant. This indicates that we are at equilibrium. From Table (5.1) or Figure (5.1).

$$[\text{N}_2\text{O}_4] = 0.040 \text{ mol/L}$$

$$[\text{NO}_2] = 0.120 \text{ mol/L}$$

The square brackets represent equilibrium concentration in moles per liter. It is important that these be distinguished from original or other nonequilibrium concentrations.

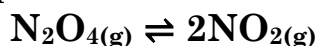


Table (5.1): Establishment of equilibrium at 100°C in the system						
Time (s)	0.0	20	40	60	80	100
Conc. N_2O_4 (mol/L)	0.100	0.070	0.050	0.04*	0.040	0.040
Conc. NO_2 (mol/L)	0.000	0.060	0.100	0.120*	0.120	0.120
*Equilibrium concentrations are bold type.						

On feature of the data in Table (5.1) deserves further comment. Notice that, over any time interval, the increase in concentration of NO_2 is exactly twice the decrease in concentration of N_2O_4 . Consider, for example, what happens in the 60 s required to reach equilibrium. The concentration of N_2O_4 decreases by 0.060 mol/L.

$$\Delta \text{ conc. } \text{N}_2\text{O}_4 = \text{final conc. } \text{N}_2\text{O}_4 - \text{org. conc. } \text{N}_2\text{O}_4$$

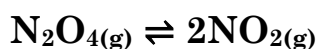
$$\Delta \text{ conc. } \text{N}_2\text{O}_4 = 0.040 \text{ mol/L} - 0.100 \text{ mol/L} = -0.060 \text{ mol/L}$$

The concentration of NO_2 increases by twice this amount, 0.120 mol/L.

$$\Delta \text{ conc. } \text{NO}_2 = 0.120 \text{ mol/L} - 0.000 \text{ mol/L} = 0.120 \text{ mol/L}$$

This relationship is explained quite simply. As equilibrium is approached, N_2O_4 decomposes:

****Negative sign indicate that concentration N_2O_4 is decreased.***



From the coefficient of the balanced equation, we see that two moles of NO_2 are formed for every one mole of N_2O_4 that decomposes. Hence, if x moles of N_2O_4 breaks down, 2x moles of NO_2 must be formed. If the concentration of N_2O_4 decrease by x mol/L, that of NO_2 must increase by twice that amount, 2x mol/L.

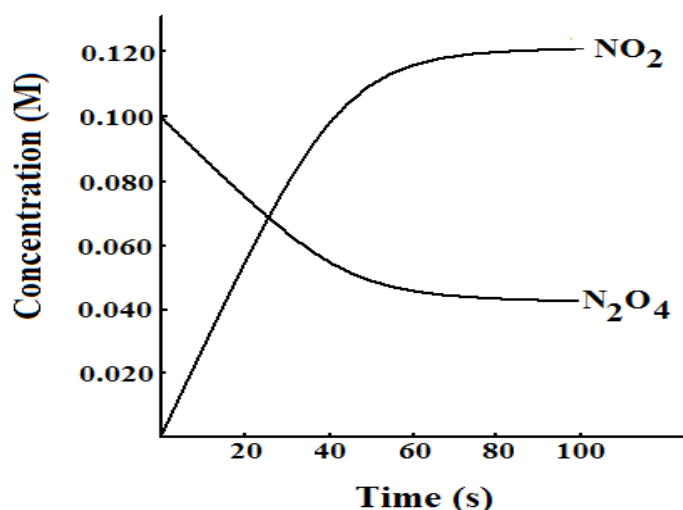


Figure (5.1) Approach to equilibrium in the N_2O_4 - NO_2 system

5.4. Factors Affecting the Chemical Equilibrium

5.4.1. Temperature Effect

Generally speaking, rise of temperature increase the reaction rates, and it has been found that the latter is doubled or trebled for every 10°C rise of temperature. For a reversible reaction the effect of temperature must be one of the following three cases:

Temperature increases the rate of the forward and backward reactions to the same, extent. Under such cases, the effect is restricted to shortening the time necessary to reach the equilibrium state; this is illustrated by Figure (5.2a), where the same proportion of resultants is obtained at high temperature as at the low temperature.

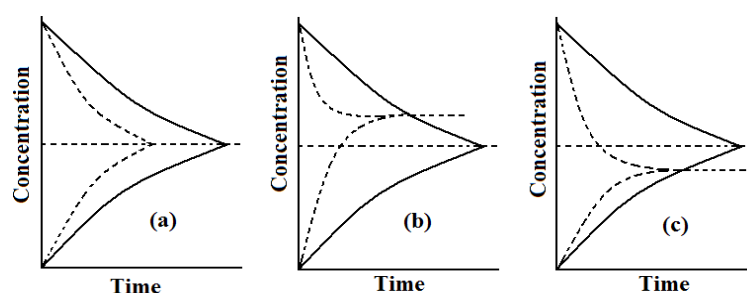


Figure (5.2) Temperature Influence on Chemical Equilibrium

(b) Temperature has an effect on the equilibrium state besides its effect on the reaction rate, this is in accordance with *Le Chatelier's Principle** which describes the quantitative effect of temperature on chemical equilibrium for example the formation of hydrogen iodide from hydrogen (H_2) and iodine (I_2) in an endothermic reaction.



Therefore, temperature rise helps the formation process. On the other hand, the decomposition of hydrogen iodide (HI) according to:



is an exothermic reaction and delayed by heating combining the effect of temperature on both directions of the above reaction, we find that the equilibrium of hydrogen iodide at higher temperature, i.e. the concentration of HI, is greater than 78 % at temperature higher than 425°C. This is illustrated by Figure (5. 2b).

For an exothermic reaction, e.g.,



The effect of temperature is to decrease the concentration of the resultants in the equilibrium mixture, besides shortening the necessary time to reach equilibrium; this is illustrated by Figure (5. 2c).

5.4.2. Catalyst Effect

Catalysis is applied to case in which the rate of a chemical reaction is accelerated by the presence of a substance which itself unchanged chemically in the process. The substance causing the acceleration is called a catalyst. Catalysis can be defined as "**The acceleration or retardation**" of chemical reactions by addition of small quantities of foreign substances to reacting system.

The effect of catalyst on chemical equilibrium may confine to one of the following cases:

(a) The catalyst accelerates both the forward and backward reactions to the same extent; the net result is to shorten the necessary time to reach the equilibrium. This is illustrated in Figure (5. 3a).

(b) The catalyst accelerates the forward reaction only without affecting the backward reaction. The catalyst is said to be positive catalyst. This is illustrated in Figure (5. 3b).

The catalyst may accelerate the backward reaction only, and is said to be negative catalyst. This effect is illustrated in Figure (5. 3c)

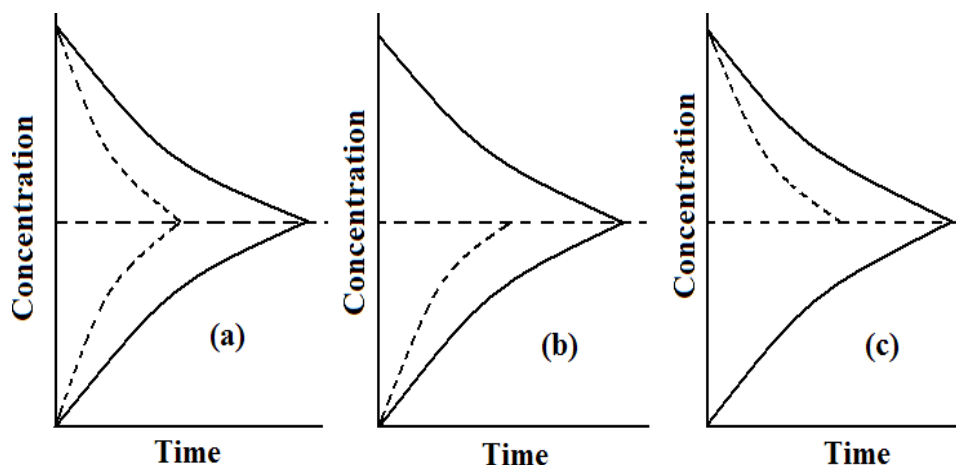
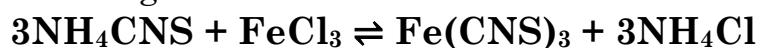


Figure (5.3) Catalyst Influence on Chemical Equilibrium

5.4.3. Concentration Effect:

In order to know the concentration effect of the reactants and resultants on the equilibrium of a reversible reaction let us study the following reaction:



Ammonium thiocyanate reacts with ferric chloride and blood red ferric thiocyanate is obtained. By experiment, it has been found that the addition of excess ammonium thiocyanate or ferric chloride results in an increase in intensity of the red color attributed to ferric thiocyanate, where ammonium chloride causes the color to become paler. From the above experiment it clear that increase of concentration of one of the reactants helps the forward reaction, while increase of the resultants help the backward reaction.

5-4-4-Effect of Pressure on Gas

When a system at equilibrium undergoes a change in pressure, the equilibrium of the system will shift to offset the change and establish a new equilibrium. The system can shift in one of two ways:

- Toward the products (i.e. in favor of the forward reaction)
- Toward the reactants (i.e. in favor of the backward reaction)

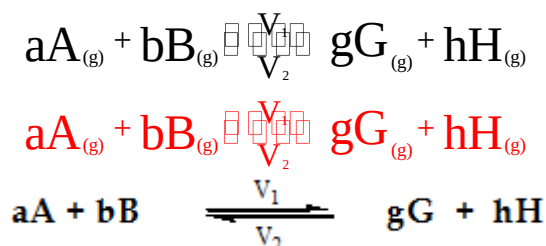
The effects of changes in pressure can be described as follows

- When there is an increase in pressure, the equilibrium will shift towards the side of the reaction with fewer moles of gas.
- When there is a decrease in pressure, the equilibrium will shift towards the side of the reaction with more moles of gas.

5.5. Law of Mass Action:

5.5.1. Equilibrium Constant K_c :

Consider a typical reversible reaction, e.g.,



V_1 represents the forward reaction and V_2 the rate of backward reaction. Therefore according to law of mass action:

Rate of forward reaction: $V_1 \propto [A]^a \cdot [B]^b$

$$V_1 = k_1 [A]^a \cdot [B]^b \quad (5.4)$$

Where: k_1 is the specific rate constant.

Similarly the rate of backward reaction: $V_2 \propto [G]^g \cdot [H]^h$

$$V_2 = k_2 [G]^g \cdot [H]^h \quad (5.5)$$

where k_2 is the specific rate constant for the reverse reaction.

When equilibrium is attained the rate of forward and backward reaction are equal. Hence: $V_1 = V_2$

Therefore: $k_1 [A]^a \cdot [B]^b = k_2 [G]^g \cdot [H]^h$

$$\text{and} \quad K_C = \frac{k_1}{k_2} = \frac{[G]^g \cdot [H]^h}{[A]^a \cdot [B]^b} \quad (5.6)$$

The constant K_C is being called the equilibrium constant of the reaction, i.e., the rate of the reaction is proportional to the molar concentration of each reaction substance raised to the power of the number of its molecules taking part in the reaction. Therefore, product of active masses of resultants raised to the power of their respective number of molecules divided by the product of active masses of reactants raised to the power of their respective number of molecules is constant.

This is an alternative expression of **law of mass action**.

If the above reaction is in the gaseous state and all gases obey ideal gas laws, the equilibrium constant is:

$$K_P = \frac{P_G^g \cdot P_H^h}{P_A^a \cdot P_B^b} \quad (5.7)$$

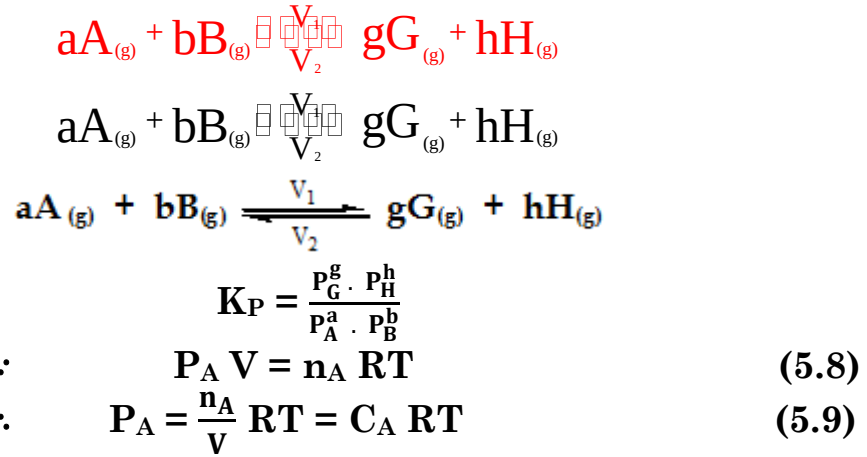
Where, K_P is the equilibrium constant expressed in partial pressure. The pressure is generally given in atmospheres.

Example 1: write expression for K_C for;

5.5.2. The Relation between K_P and K_C :

We can deduce the relation between K_P and K_C as following:

The gas equation is applicable for a mixture of gases and also applicable for any of these constituents. If we have a gaseous reaction as:



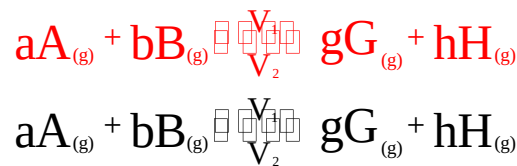
While, the quantity $\frac{n_A}{V}$ is equal to the concentration of A, which can be replaced as [A] in the last equation as following:

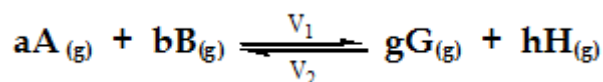
$$\begin{array}{c}
 \therefore P_A = [A] RT \quad (5.10) \\
 K_P = \frac{P_G^g \cdot P_H^h}{P_A^a \cdot P_B^b} = \frac{[G]^g \cdot (RT)^g \times [H]^h \cdot (RT)^h}{[A]^a \cdot (RT)^a \times [B]^b \cdot (RT)^b} \\
 K_P = \frac{[G]^g \cdot [H]^h \times (RT)^g \cdot (RT)^h}{[A]^a \cdot [B]^b \times (RT)^a \cdot (RT)^b} \\
 K_C = \frac{[G]^g \cdot [H]^h}{[A]^a \cdot [B]^b} \\
 K_P = K_C \cdot \frac{(RT)^g \cdot (RT)^h}{(RT)^a \cdot (RT)^b} = K_C (RT)^{(g+h)-(a+b)} \\
 \Delta n = (g+h) - (a+b) \\
 \therefore K_P = K_C (RT)^{\Delta n} \quad (5.11)
 \end{array}$$

Where: Δn is the change in the number of moles according to the reaction (number of moles of the products – number of moles of the reactants).

5.5.2. The Relation between K_P and K_C

We can deduce the relation between K_P and K_C as following:
The gas equation is applicable for a mixture of gases and also applicable for any of these constituents. If we have a gaseous reaction as:





$$K_C = \frac{[G]^g \cdot [H]^h}{[A]^a \cdot [B]^b}$$

$\therefore PV = RT$ for one mole of the gas

$$\therefore V = \frac{RT}{P}$$

$$\therefore C = \frac{1}{V} = \frac{P}{RT}$$

where, C is the concentration and we know that the concentration is the number of moles divided to the volume.

$$\therefore C_A = \left[\frac{P_A}{RT} \right]$$

By compensating in equation of K_C :

$$K_C = \frac{\left[\frac{P_G}{RT} \right]^g \cdot \left[\frac{P_H}{RT} \right]^h}{\left[\frac{P_A}{RT} \right]^a \cdot \left[\frac{P_B}{RT} \right]^b} = \frac{[P_G]^g \cdot [P_H]^h}{[P_A]^a \cdot [P_B]^b} \cdot \left[\frac{1}{RT} \right]^{\{(g+h)-(a+b)\}}$$

$$K_C = K_P \cdot \left[\frac{1}{RT} \right]^{\{(g+h)-(a+b)\}}$$

$$\Delta n = (g + h) - (a + b)$$

$$\therefore K_P = K_C (RT)^{\Delta n}$$

where, Δn is the change in the number of moles according to the reaction (number of moles of the products – number of moles of the reactants).

$$\Delta G = - nRT \ln K$$

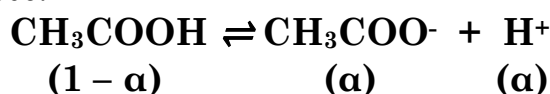
Where, ΔG is the free energy change, n is number of gas moles, R is gas constant, T is absolute temperature and K is equilibrium constant.

2-6. IONIC EQUILIBRIA

6.1. Application of Law of Mass Action to Solutions of Electrolytes (Ostwald Law of Dilution)

Weak electrolytes such as acetic acid and ammonium hydroxide undergo reversible dissociation when dissolved in water. The equilibrium between the undissociated molecules and ions for such electrolytes can be investigated by the law of mass action. The law cannot be applied to strong electrolytes since the dissociation is complete.

Consider one mole of a weak electrolyte such as acetic acid. In solution there is partial dissociation and the following equilibrium exists:



where (α) is the dissociation degree

Applying law of mass action then,

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad (6.1)$$

K_a is the ionization constant or the dissociation constant; in case of a weak acid it is designated as K_a and in case of a weak base we use K_b .

If we start with 1 gram equivalent of the electrolyte dissolved in "V" liters of solution ($V = \frac{1}{C}$), where "C" is the concentration in gram equivalent/liter of solution and let α be the dissociation degree at equilibrium, then the amount of unionized electrolytes will be $(1 - \alpha)$ g equivalent, and the amount of each of the ions will be α gram-equivalent.

The concentration (gram-equivalent per liter) of unionized acetic acid will therefore be $\frac{(1 - \alpha)}{V}$, and the concentration of each of the ions will be $\frac{\alpha}{V}$. By substituting in the above equation we obtain:

$$K_a = \frac{\left(\frac{\alpha}{V}\right) \cdot \left(\frac{\alpha}{V}\right)}{\left(\frac{1 - \alpha}{V}\right)}$$

or

$$K_a = \frac{\alpha^2}{(1 - \alpha)V} \quad (6.2)$$

This mathematical relation between the dissociation degree and the volume of solution is known as "**Ostwald** Law of Dilution"

It is clear from the above equation that α "the dissociation degree" increases with dilution. The results agree quite satisfactorily with those obtained from conductivity measurements.

In the above equation, if (α) is small, it can be neglected with respect to "1" in the denominator and the equation reduces to:

$$\begin{aligned} \alpha^2 &= K_a V \\ \therefore \alpha &= \sqrt[2]{K_a V} \end{aligned} \quad (6.3)$$

This simplified form can be used for comparing the dissociation degree of two weak electrolytes at the same dilution:

$$\begin{aligned} \alpha_1 &= \sqrt[2]{K_1 V} \\ \alpha_2 &= \sqrt[2]{K_2 V} \\ \frac{\alpha_1}{\alpha_2} &= \sqrt[2]{\frac{K_1}{K_2}} \end{aligned} \quad (6.4)$$

Or for comparing the dissociation degree of one electrolyte at two different dilutions:

$$\begin{aligned} \alpha_1 &= \sqrt[2]{K V_1} \\ \alpha_2 &= \sqrt[2]{K V_2} \\ \frac{\alpha_1}{\alpha_2} &= \sqrt[2]{\frac{V_1}{V_2}} \end{aligned} \quad (6.5)$$

6.2. Ionization of Polybasic Acids:

When a polybasic acid is dissolved in water, the various hydrogen atoms undergo ionization can be represented as following:

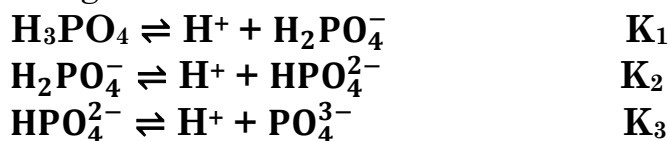


If the dibasic acid is a weak electrolyte, the law of mass action may be applied:

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \quad \text{and} \quad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]} \quad (6.8)$$

K_1 and K_2 are known as the primary and secondary dissociation constant respectively. Each stage of dissociation process has its ionization constant, and the magnitude of these constants give a measure of the extent to which each ionization has proceeded at any given concentration. The greater the value of K_1 relative to K_2 , the smaller will be the secondary dissociation and the greater must be the dilution before the later becomes appreciable. Therefore, it is possible that a dibasic acid (or polybasic acid may behave, from the point of view of dissociation, as a monobasic acid.

A tribasic constant K_1 , K_2 and K_3 (taking phosphoric acid as an example H_3PO_4) according to:



6.3. Common Ion Effect

When a soluble salt (say A^+C^+) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is suppressed.

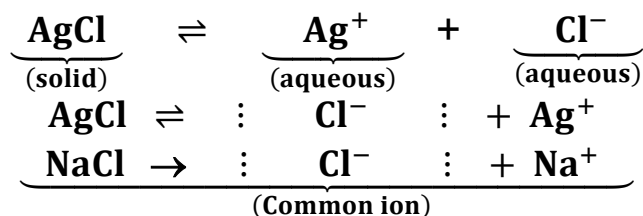


By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to **Le Chatelier's** principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ anions. Or that, the degree of dissociation of AB will be reduced.

The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the Common-ion effect.

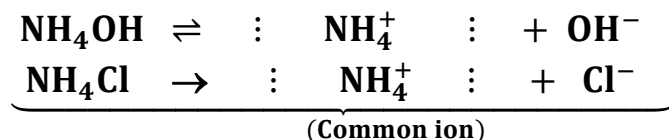
Let us consider a few examples to illustrate the common-ion effect:

Example 6.1: In a saturated solution of silver chloride, we have the equilibrium:



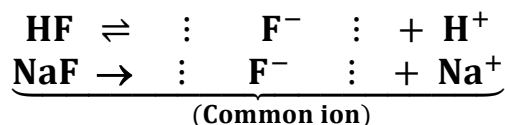
When sodium chloride is added to the solution, the concentration of Cl^- ions will increase. The equilibrium shown above will be shifted to the left to form more of solid $AgCl$. Thus the solubility of $AgCl$, a typical sparingly soluble salt, will decrease.

Example 6.2: When solid NH_4Cl is added to NH_4OH solution, the equilibrium:



shifts to the left. Thereby the equilibrium concentration of OH^- decreases. This procedure of reducing the concentration of OH^- ions is used in qualitative analysis.

Example 6.3: The common-ion effect can also be applied to the ionic equilibrium of a weak acid as HF.



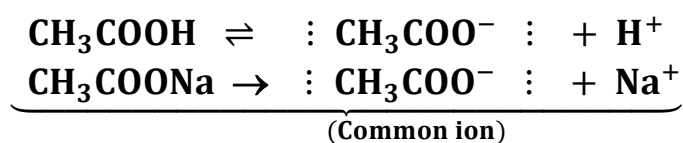
NaF is added to the equilibrium mixture. The concentration of F^-

(common ion) is increased. Thus the equilibrium shifts to the left. In other words, the degree of dissociation of HF decreases. It was found by experiment that the degree of dissociation of HF in 1M solution is 2.7, while the value reduces to 7.2×10^{-4} after the addition of 1 M NaF.

Consider a weak electrolyte such as acetic acid. In solution the following equilibrium exists:

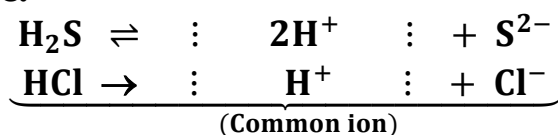


On addition of strong electrolyte having an ion in common to this solution, e.g. sodium acetate, the new equilibrium will be attained:



The acetate ion is called the common ion. The result is that the equilibrium of acetic acid is shifted to the left, i.e.; the ionization degree is decreased.

Another example:



Rule: Addition of strong electrolyte to a weak electrolyte having a common ion, results in decrease of concentration of the common and uncommon ion for the latter electrolyte. The common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

Example 6.4: 0.1 N of sodium acetate is added to 0.1 N of acetic acid at equilibrium. Calculate the hydrogen ion concentration if we assume that sodium acetate is completely dissociated $K_a = 1.8 \times 10^{-5}$ for acetic acid.

(a) 1.8×10^{-4} mol/L

(b) 1.8×10^{-5} mol/L

(c) 1.8×10^{-6} mol/L

(d) 1.8×10^{-7} mol/L

View answer

Answer: [b]

Hint and Explanation: [b]

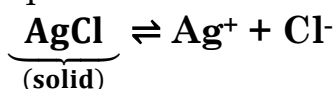
$$\begin{aligned}
 &\underbrace{\text{CH}_3\text{COOH}}_{(0.1 - x)} \rightleftharpoons \underbrace{\text{CH}_3\text{COO}^-}_x + \underbrace{\text{H}^+}_x \\
 &\underbrace{\text{CH}_3\text{COONa}}_{0.1} \rightarrow \underbrace{\text{CH}_3\text{COO}^-}_{0.1} + \underbrace{\text{Na}^+}_{0.1} \\
 K_a &= \frac{[\text{CH}_3\text{COO}^-]_{\text{total}} [\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(0.1 + x) \text{ mol L}^{-1} + x \text{ mol L}^{-1}}{(0.1 - x) \text{ mol L}^{-1}} \\
 K_a &= \frac{(0.1 + x) \text{ mol L}^{-1} + x \text{ mol L}^{-1}}{(0.1 - x) \text{ mol L}^{-1}} = 1.8 \times 10^{-5} \\
 K_a &= \frac{0.1x + x^2}{(0.1 - x)} = 1.8 \times 10^{-5}
 \end{aligned}$$

Since x is too small quantity in comparison with 0.1 value and so x^2 , can be neglected. $\therefore x = 1.8 \times 10^{-5} \text{ mol/L}$

6.4. Solubility Product

Consider a sparingly soluble electrolyte, e.g., silver chloride. When is shaken up with water, some of it (an exceedingly small quantity passes in the solution to form a saturated solution of the salt. The following equilibrium exists between the insoluble (AgCl) and ions in solution:

When an ionic solid substance dissolves in water, it dissociates to give separate cations and anions. As the concentration of the ions in solution increases, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phase and the cations and anions in solution. For example, for a sparingly soluble salt, say AgCl, we can write the equilibrium equations as follows



At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of solute from the solution. Now the solution is said to be saturated.

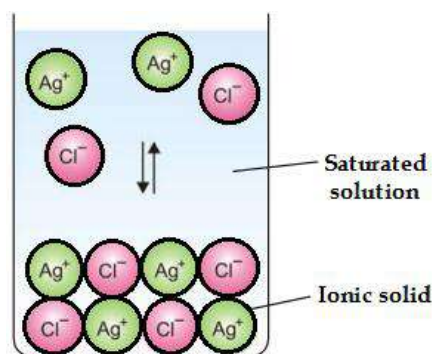


Figure (6.1) Equilibrium between an ionic solid and ions in a saturated solution.

A Saturated solution is a solution in which the dissolved and undissolved solute is in equilibrium.

A saturated solution represents the limit of a solute's ability to dissolve in a given solvent. This is a measure of the "solubility" of the solute.

The Solubility (S) of a substance in a solvent is the concentration in the saturated solution. Solubility of a solute may be represented in grams per 100 ml of solution. It can also be expressed in moles per liter.

Molar Solubility is defined as the number of moles of the substance per one liter (l) of the solution.

The value of solubility of a substance depends on the solvent and the temperature. Applying the Law of Mass Action to the above equilibrium for AgCl, we have

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$
$$[Ag^+][Cl^-] = K [AgCl]$$

Since the silver chloride is present in the solid state, its active mass may be taken as unity. Therefore, the above equation reduces to:

$$[Ag^+][Cl^-] = K_{sp} \quad (6.9)$$

Where $[Ag^+]$ and $[Cl^-]$ are expressed in mol/L. The equilibrium constant in the new context is called the **Solubility Product Constant** (or simply the Solubility Product) and is denoted by K_{sp} . The value of K_{sp} for particular solubility equilibrium is constant at a given temperature. The product $[Ag^+][Cl^-]$ in the K_{sp} expression above is also called the Ionic Product or Ion Product. This new constant K_s is known as the solubility product of silver chloride.

Therefore the solubility product is defined as the product of concentration of ions present in equilibrium with the undissolved substance.

Sparingly soluble substances such as (AgCl), $PbSO_4$... etc., possess small solubility product and can therefore be easily precipitated in solution. On the other hand, substances possessing higher solubility have high solubility products and cannot be precipitated easily from solution.

In general any substance cannot be precipitated except if the product of its ions in solution exceeds the solubility product of its sparingly soluble compound.

For any electrolyte having the general formula A_aB_b in contact with saturated solution, the equilibrium between the solid and ions in solution is:



And the solubility product is given by:

$$K_S = [A^+]^a [B^-]^b \quad (6.10)$$

The solubility product of sparingly soluble substance may be derived from knowledge of the solubility of the substance in pure water.

For example, if the solubility of silver chloride in water is "s" g *mol/Liter*, then since this salt is completely dissolved, even in the saturated solution, the concentration of both silver and chloride ions is "s" gm. Ion per liter, therefore:

$$K_{SP} = [Ag^+] [Cl^-]$$

or solubility ($s^2 = K_s$ solubility product)

In case of salt having more than two ions in solution, e.g., Ag_2CrO_4 .

$$\begin{aligned} \underbrace{Ag_2CrO_4}_{(solid)} &\rightleftharpoons 2Ag^+ + CrO_4^{2-} \\ K_S &= \underbrace{[Ag^+]^2}_{(2s)^2} \underbrace{[CrO_4^{2-}]}_{(s)} = 4s^3 \\ \therefore \text{Solubility (s)} &= \sqrt[3]{\frac{K_S}{4}} \end{aligned}$$

Example 6.5: The solubility of silver chloride is 0.0018 g/L. Calculate the solubility product knowing that the molecular weight of silver chloride ($AgCl$) is equal to 143.3?

- (a) 1.56×10^{-10} (b) 1.65×10^{-10} (c) 1.73×10^{-10} (d) 1.85×10^{-10}

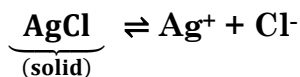
View answer

Answer: [a]

Hint and Explanation: [a]

$$\text{The solubility in gram mole/liter} = \frac{0.0018 \text{ g L}^{-1}}{143.3 \text{ g mol}^{-1}} = 1.25 \times 10^{-5}$$

Therefore in a liter of solution the concentration of silver ions is equal to 1.25×10^{-5} and concentration of chloride ions = 1.25×10^{-5} g ions and since:



$$K_{SP} = [Ag^+] [Cl^-] = (1.25 \times 10^{-5}) \times (1.25 \times 10^{-5}) = 1.56 \times 10^{-10}$$

Example 6.6: Calculate the solubility product of silver chromate, given that its solubility is 2.5×10^{-2} g/liter (M.wt. of $Ag_2CrO_4 = 322$ g/mol).

- (a) 7.5×10^{-9} (b) 7.5×10^{-10} (c) 7.5×10^{-11} (d) 7.5×10^{-12}

View answer

Answer: [d]

Hint and Explanation: [d] $\underbrace{\text{Ag}_2\text{CrO}_4}_{(\text{solid})} \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$

$$\text{Solubility in g mol L}^{-1} = \frac{\text{Solubility}}{\text{M.wt.}} = \frac{2.5 \times 10^{-2}}{322} = 7.5 \times 10^{-5}$$

$$K_S (\text{Ag}_2\text{CrO}_4) = (2 \times 7.5 \times 10^{-5})^2 \times (7.5 \times 10^{-5}) = 7.5 \times 10^{-12}$$

Example 6.7: Calculate the solubility of magnesium hydroxide in g/L at 26°C, if its solubility product is 5×10^{-12} and it's M.wt. = 58.3 g/mol?

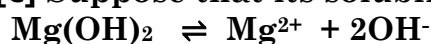
(a) 4.4×10^{-3} g/L (b) 5.4×10^{-3} g/L

(c) 6.4×10^{-3} g/L (d) 7.4×10^{-3} g/L

View answer

Answer: [c]

Hint and Explanation: [c] Suppose that its solubility is x then:



$$K_S (\text{Mg}(\text{OH})_2) = (\text{Mg}^{2+}) (\text{OH}^-)^2 = (x) \cdot (2x)^2 = 4x^3$$

$$4x^3 = 5 \times 10^{-12}$$

$$x = \sqrt[3]{\frac{5 \times 10^{-12}}{4}} = 1.1 \times 10^{-4} \text{ mol/liter}$$

$$s = x \cdot \text{M.wt.} = (1.1 \times 10^{-4} \text{ mol L}^{-1}) \times (58.3 \text{ g mol}^{-1}) = 6.4 \times 10^{-3} \text{ g liter}^{-1}$$

6.5. Ionization of water

It was found by **Kohlrausch** and others that water possesses small but definite conductivity. Water must therefore be slightly ionized in accordance with the equation:

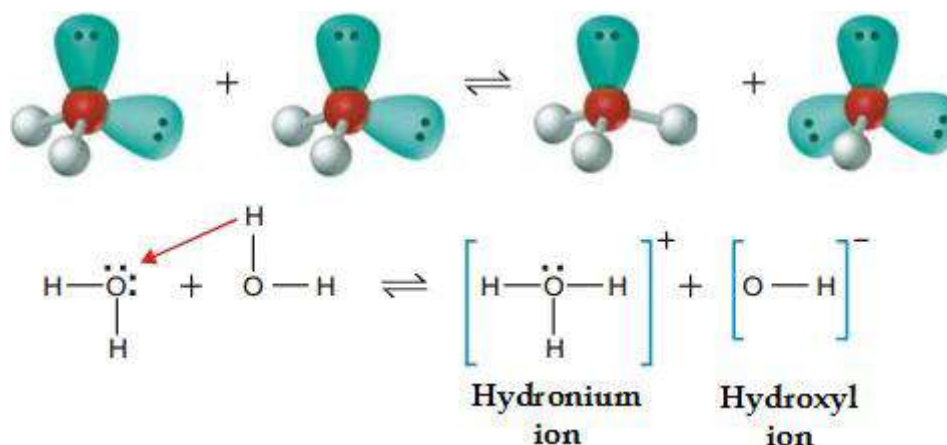
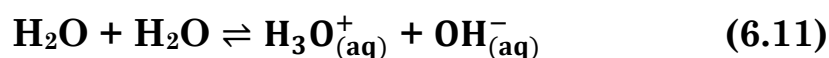


Figure (6.2) Auto-ionization of water



The reaction is called autoionization because there are two water molecules are reacting and forming anions. Writing the

equilibrium expression by applying the law of mass action to such equilibrium, we obtain:

$$K_e = \frac{[H_3O^+] \cdot [OH^-]}{[H_2O]^2} \quad (6.12)$$

$$K_e [H_2O] = [H_3O^+]^2 + [OH^-] \quad (6.13)$$

$\therefore K_e$ at temperature 25°C is considered constant and equal to 3.26×10^{-18} and water concentration is 55.389.

$\therefore$ Equation (3) can be written as following:

$$K_w = [H_3O^+] [OH^-] \quad (6.14)$$

Where, K_w is ionization constant of water or dissociation constant of water. At temperature 25°C is:

$$K_w = 1.0 \times 10^{-14} \quad (6.15)$$

For simplicity, equation (1) water ionization can be written as following:



The ionization constant of water:

$$K_w = [H^+] [OH^-] = 1.0 \times 10^{-14} \text{ g ion/L}$$

The concentration of both hydrogen and hydroxyl anions for pure water are equal or in any neutral solution:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ g ion/L} \quad (6.17)$$

In acid solution: $[H^+] > [OH^-] > 10^{-7} \text{ g ion/liter}$

e.g., 10^{-6} , 10^{-5} and $10^{-4} \text{ g, ion/liter}$

Where in alkaline or basic solution, $[H^+] < [OH^-] < 10^{-7} \text{ g, ion/liter}$

$$[H^+] < [OH^-] < 10^{-7} \text{ g, ion/liter}$$

e.g., 10^{-8} , 10^{-9} and $10^{-10} \text{ g, ion/liter}$ Etc.

In all cases: $[H^+] [OH^-] = 10^{-14} \text{ at } 25^\circ\text{C}$

The ionic product of water varies to some extent with temperature.

6.5.1. The Hydrogen-Ion Exponent Value

Value pH scale is a convenient scale for expressing the hydrogen ion concentration, especially when dealing with small concentrations. Instead of expressing the concentrations of hydrogen and hydroxyl ions in term of gram equivalent per liter, we expose them in terms of pH units, where:

$$\text{pH} = -\log [H^+] \quad (6.18)$$

Therefore, the quantity pH is the negative logarithm of hydrogen ion concentration. It takes values between "0.0 – 14"

a) $\text{pH} = 7$ the solution is neutral $[OH^-] = [H^+] = 10^{-7}$

b) $\text{pH} < 7$ the solution is acidic $[H^+] > 10^{-7}$

c) $\text{pH} > 7$ the solution is alkaline $[H^+] < 10^{-7}$

Similarly the hydroxyl ion concentration can be expressed and is called the logarithm of hydroxyl ion pOH, and equal to:

$$\text{pOH} = -\log [\text{OH}^-] \quad (6.19)$$

We know that: $[\text{H}^+] \cdot [\text{OH}^-] = K_w = 10^{-14}$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} \quad \text{and also} \quad [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} \quad (6.20)$$

Taking the logarithm of equation (x), we get:

$$\log [\text{H}^+] + \log [\text{OH}^-] = \log K_w = \log 10^{-14} \quad (6.21)$$

By multiplication last equation with the negative sign:

$$-\log [\text{H}^+] - \log [\text{OH}^-] = -\log K_w = -\log 10^{-14} \quad (6.22)$$

By substitution of equations (6.18) and (6.19) in equation (6.22):

$$\text{pOH} + \text{pH} = \text{p}K_w = 14 \quad (6.23)$$

This is important relation which means the in neutral solutions:

$$\text{pOH} = \text{pH} = 7 \quad (6.24)$$

Example 6.8: In a 0.1 N HCl solution which is completely dissociated, the concentration of H^+ is 0.1 or 10^{-1} g ion/liter.

Example 6.9: Arrange the following solution according to increasing in its acidity:

- | | | |
|---------------|---------------|--------------|
| (a) pH = 8.28 | (b) pH = 3.5 | (c) pH = 9.5 |
| (d) pH = 7.0 | (e) pOH = 3.0 | (f) pOH = 10 |

Example 6.10: Calculate the concentration of OH^- for the 0.005 M HNO_3 electrolyte.

Example 6.11: Calculate the concentration of H^+ for the 0.005 M KOH electrolyte.

6.5.2. Buffer Solutions

A liter of water has a pH value = 7, by addition of 1 mL of 0.1 N hydrochloric acid, the pH value of water is altered to 4; and the addition of 1 mL of 0.1 N NaOH alters the pH value to 10. Therefore, water changes its pH values greatly by the addition of slight amounts of dilute acids or dilute bases and is said to be not a buffer solution. An aqueous solution of NaCl behaves in a similar manner and changes its pH value greatly by the addition of minute quantities of acids or bases; hence NaCl solution is not a buffer solution. Aqueous solution of ammonium acetate, on the other-hand, does not change its pH value except to a very small extent by the addition of slight amounts of acid and bases. *The resistance of a solution to changes in hydrogen ion concentration upon the addition of small amounts of acid or alkali is termed buffer action; and a*

solution which possesses such properties, e.g., ammonium acetate solution, is known as a buffer solution.

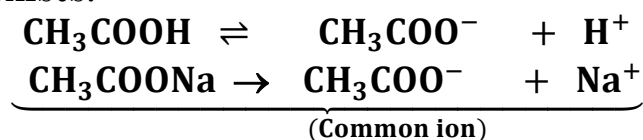
Buffer solutions are said to contain "reverse acidity" and reverse alkalinity.

It was found that equimolar mixtures of: Weak acids + their salts e.g., Acetic acid + sodium acetate or citric acid + sodium citrate. Weak base + their salts e.g., $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

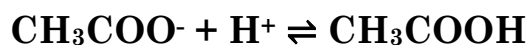
From buffer mixtures, i.e. mixtures which resist the changes in pH upon the addition of acids and alkalis.

6.5.2.1. Theory of Buffer Action

In order to understand the buffer action, let us study the equilibrium between a weak acid, e.g., acetic acid and its highly ionizable salt, e.g., sodium acetate. In solution, the following equilibrium exists:



Therefore, the ionization of acetic acid is repressed by the common ion effect. Let us now consider the addition of small amounts of H^+ ions to such a solution. The acetate ions (from sodium acetate) will combine with the added hydrogen ions of the acid to form undissociated acetic acid according to:



Therefore, the free hydrogen ions "captured" or "imprisoned" in the slightly ionized acetic acid molecules. Therefore, the hydrogen ions are no longer free and they cannot affect the pH value of the solution.

Similarly, If a small concentration of hydroxyl ions is added, the latter will combine with the hydrogen ions arising from the dissociation of the acetic acid and from unionized water; the equilibrium will be disturbed, and more acetic acid will dissociate to replace the hydrogen ions remained in this way and the pH value of the solution is not, therefore, materially changed.

One can explain in similar way the buffer action of a mixture of NH_4OH and NH_4Cl .

