SOLUTION

Mixture

Mixture is a combination of mutually non-reactive two or more different substances. For example, combination of salt and sugar (a), combination of salt and sand (b), combination of sand and sugar (c), combination of salt, sand and sugar (d), combination of salt (e), sugar and iron dust (f), combination of salt, sand, sugar and iron dust (g), all are mixtures. If sufficient amount of water is added to above all those mixtures new one (mixture) will form for each case. The new mixture resulting from (a) is different from others. Because there is only one (single) phase in former and more than one phase in later ones. So we can say that, there are two types of mixture:

i.   Homogeneous mixture: only one phase is present here. Examples, salt and water, sugar and water.

ii. Heterogeneous mixture: more than one phase is present here. Examples, salt and sand, sand and water. tuth paste (colloid)

Solution

Solution is a homogeneous mixture of mutually non-reactive two or more different substances in molecular level. For example, when a small amount of sugar is added to a glass of water and slightly stirred with a stick, it forms a homogeneous mixture which is a solution. In this solution sugar molecules are uniformly dispersed in the molecules of water. When a small amount of sodium chloride (NaCl) salt is added to a glass of water and slightly stirred with a stick, it also forms a homogeneous mixture which is a solution. This solution of sodium chloride (NaCl) salt consists of ions of salt (Na^+ and Cl^-) uniformly dispersed in water.

Components of solution

A solution contains at least two different components. They are solvent and solute. The higher amount component in the solution is known as solvent and the lower amount component is known as solute. In the above examples, sugar and NaCl are solute and water is solvent.

Types of solution

Solutions can be classified in different ways. Depending upon the physical states of solute and solvent, there are seven types of solutions. They are listed below with examples for each type.

Sl	Physical state of solute	Physical state of solute	Example
1	Gas	Gas	Air
2	Gas	Liquid (carbonated drinks)	O_2 in water, CO_2 in water
3	Gas	Solid	Adsorption of H_2 by platinum
4	Liquid	Liquid	Alcohol in water

5	Liquid	Solid	Mercury in silver
6	Solid	Liquid	Salt and sugar in water
7	Solid	Solid	Metal alloys are solid solutions, steel

Figure 1: Solution

Composition or concentration of solution

The concentration of a solution can be defined as the amount of solute present in a given amount of solvent/solution.

$$\text{Concentration of solution} = \frac{\text{amount of solute}}{\text{amount of } \cancel{\text{solvent}}/\text{solution}}$$

Concentration of a solution can be expressed in different terms. Such as

1. Molarity
2. Molality
3. Normality
4. Mole fraction
5. Percent (generally w/w, w/v, v/v)

Molarity -----> moles per liter in solution

Molarity of a solution is defined as the number of moles of solute per litre of the solution.

1 mole solute + solvent = 1 litre solution (1 molar).

Example, 1 mole H_2SO_4 (98 g) + solvent (water) = 1 litre H_2SO_4 solution (1 molar).

$$Molarity, C = \frac{w \times 1000}{M \times V\ (ml)}$$

Here,

w = amount of the solute

M = molecular weight of the solute

V = volume of the solution in ml

Molarity = mole of solute / volume of solution

Molality -------> moles per kg in solvent

Molality of a solution is defined as the number of moles of solute per kilogram (1000 g) of solvent.

1 mole solute + 1 kilogram (1000 g) solvent = 1 molal solution (volume is inconsiderate).

1 mole H_2SO_4 (98 g) + 1 kilogram (1000 g) solvent (water) = 1 molal H_2SO_4 solution.

$$Molality, C_m = \frac{w \times 1000}{M \times W\ (g)}\ mol/kg$$

Here,

w = amount of the solute

M = molecular weight of the solute

W = amount of the solvent in g

> Molality = mass of solute / mass of solvent(kg)
>
> Relation between Molarity & Normality:
> $$N = S * e$$
>
> e = No of replacable H+ ion

Normality -------> gram-equivalent per liter in solution

Normality of a solution is defined as the number of gram-equivalents of solute per litre of solution.

1 gram-equivalents solute + solvent = 1 litre solution (1 Normal).

1 gram-equivalents H_2SO_4 (49 g) + solvent (water) = 1 litre H_2SO_4 solution (1 Normal).

$$Normality = \frac{w \times 1000}{E \times V\ (ml)}$$

Here,

w = amount of the solute,

E = gram-equivalent weight of the solute

V = volume of the solution in ml

Mole fraction

A simple solution is made of two components. One is solute and another is solvent. Mole fraction of a solute in a solution can be defined as the ratio of the number of moles of solute to the total number of moles of solute and solvent in the solution. Thus,

$$Mole\ fraction\ of\ solute = \frac{number\ of\ moles\ of\ solute}{number\ of\ moles\ of\ solute\ and\ solvent}$$

If n is moles of solute and N is moles of solvent, then the mole fraction of solute would be

$$X_{solute} = \frac{n}{n + N}$$

And the mole fraction of solute would be

Mole Fraction:
$$x\_N = n\_N / (n\_1 + n\_2 + ... + n\_N)$$

$$X_{solution} = \frac{N}{n + N}$$

Mole fraction is unitless. Total mole fraction of all the components in a solution is 1.

$$X_{solute} + X_{solvent} = 1$$

Percent by weight

It is weight of solute as a percent of the total weight of the solution. That is,

$$percent\ of\ solute\ by\ weight = \frac{weight\ of\ solute}{weight\ of\ solvent} \times 100$$

For example, if a solution of HCl contains 36 percent of HCl by weight, it has 36 g of HCl in 100 g of solution.

Problem: 2.45 g of NaCl is dissolved in 65 ml of a solution. What is the percent of NaCl by weight in the solution? (Ans 3.77)   (2.45x 10^-3 / 65 x 10^-3) x 100% = 3.77%

Problem: Calculate the mole fraction of HCl in a solution of hydrochloric acid containing 36 percent of HCl by weight. (Ans 0.218; Essentials of physical chemistry by Bahl, Bahl and Tuli, page 530)

Problem: What is the molarity of a solution prepared by dissolving 75.5 g of pure potassium hydroxide in 540 ml of solution? (Ans 2.50 M; Essentials of physical chemistry by Bahl, Bahl and Tuli, page 531)

Problem: What is the weight of HCl present in 155 ml of a 0.540 M solution? (Ans 3.06 g of HCl; Essentials of physical chemistry by Bahl, Bahl and Tuli, page 532)

Problem: 5.0 g of toluene (C_7H_8) is dissolved in 225 g of benzene. What is the molality of toluene in the solution? (Ans 0.24 m)

Problem: 5.0 g of NaCl is dissolved in 1000.0 g of water. Density of the resulting solution is 0.997 g/ml. Calculate the molality, molarity, normality and mole fraction of NaCl in the solution. (Ans 0.0855 m, 0.0847 M, 0.0847 N and 1.536×10^{-3} respectively; Essentials of physical chemistry by Bahl, Bahl and Tuli, page 533)

Factors affecting the partial solubility

It has found that, a particular solute is soluble in one solvent but insoluble in another solvent. For example NaCl is soluble in water but insoluble in benzene. The solubility of NaCl in water varies with temperature. The solubility of a solute in a solvent depends on the following three factors.

1. Nature of the components (solute and solvent)
2. Temperature and
3. Pressure

1. Nature of the components (solute and solvent): There is a saying that, *like dissolves like*. Polar substance is soluble in polar solvent and non-polar substance is soluble in non-polar solvent. For example NaCl is soluble in water and CCl_4 is soluble in benzene. In case of gas liquid system, the gases which form compound with the solvent or get ionized into the solution are more soluble. For example, NH_3 forms NH_4OH with water and HCl gets ionized (as H^+ and Cl^- ions) in water. For this reason, they are more soluble in water. CO_2 and SO_2 gases are also soluble in water but less. The solubility of O_2, N_2 and H_2 gases in water is very less.

HCl ----> H+ + Cl-
NH3 + H2O ----> NH4Cl -----> NH4+ + OH-
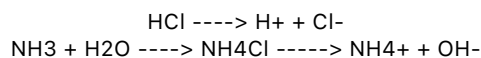
It has been found that, the solubility of a gas in pure solvent is more than that in electrolyte solution. For example, the solubility of CO_2 gas in 0.5 N KCl solution is 8.8% less than that in pure water. Because, some water molecules are used to hydrate the K^+ ion and Cl^- ion in KCl solution. These water molecules do not take part in the dissolution of gas.

Question: Solubility of a gas in pure solvent is more than that in electrolyte solution. Explain with proper example.

N.B. The volume of the solvent slightly increases for the dissolution of the gas.

Exothermic ----> produce heat
Endothermic ----> required heat

2. Temperature: Dissolution of gas in water is an exothermic process.

Gas + liquid ⇌ gas-liquid system (solution) + heat.

So, increase of temperature decreases the solubility of the gas. Therefore, in gas liquid system, the solubility of the gas decreases with increase in temperature and vice versa. If temperature increases the mobility of the gas molecules increases and escape from the solution at a time.

In case of solid-liquid system, generally solubility of a solid in water increases with increase in temperature. Because it is an endothermic process. For example, the solubility of NaCl salt in water increases with increases in temperature.

A crystal solid is dissolved in water in two steps.

Step 1	MX (s) + Energy required (lattice energy)	=	$M^+ + X^-$
			(isolated gaseous ions)
Step 2	$M^+ + x$.solvent	=	$[M(solvent)_x]^+$ + energy released (solvation energy)
	$X^- + y$.solvent	=	$[X(solvent)_y]^-$ + energy released (solvation energy)

Step 1 is endothermic and the step 2 is exothermic process. The overall process of dissolution would be either exothermic or endothermic depending on these two.

3. Pressure: When we loosen or open the cork of a cold drinks (7 up, Pepsi, sprite etc.), a turbulent flow of gas (CO_2) appears. This seems that the gas was pressurized in the liquid. If pressure is low the solubility of gas in liquid is low.

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


Gas ⇌ gas in liquid solution
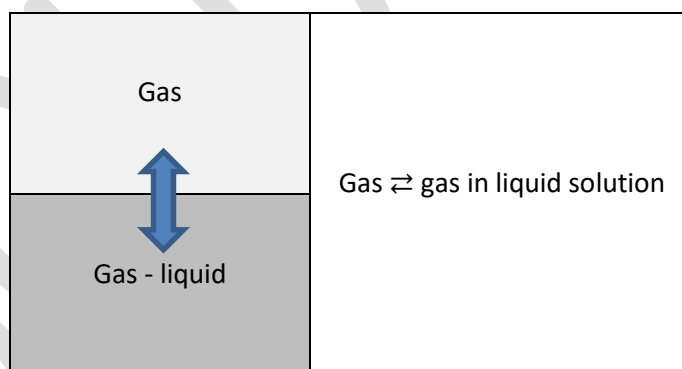
If pressure is increased on the system, the equilibrium will move in the direction which will reduce the pressure (as per Le Chatelier principle). The pressure can be reduced by dissolving more gas in the solvent. Thus solubility or concentration of a gas in a given solvent is increased with increase of pressure.

Henry's law (Solution of gas in liquid)

The relationship between pressure and solubility of a gas in a particular solvent was investigated by **William Henry (1803).** He have a generalization which is known as Henry's law. It states that, *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 applied on the solvent surface.
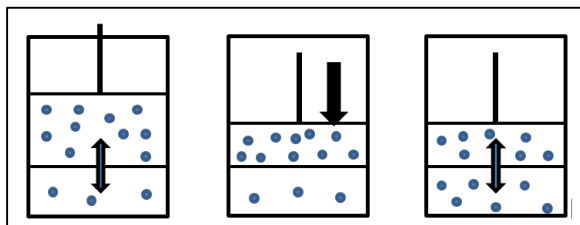
Mathematically, Henry's law may be expressed as

$C \propto P$

Or $C = k \times P$

Where,

P = pressure of the gas applied on the liquid surface

C = Concentration of the gas in the solution

K = proportionality constant known as Henry's law constant.

If concentration of gas is plotted against its pressure applied on the liquid surface, a straight line is obtained passing through the origin. The slope of the line will be equal to the Henry's law constant k.
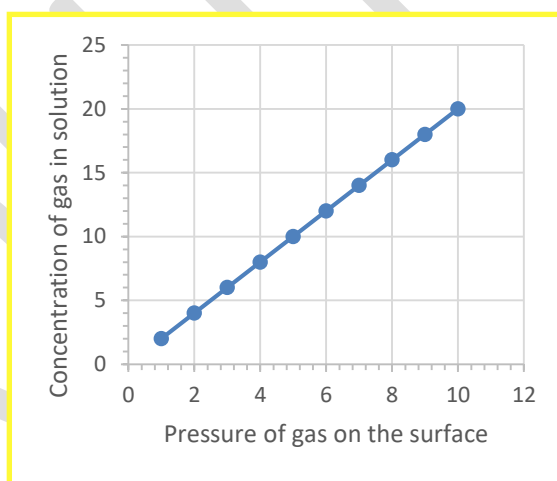
If a gas liquid system give this type of plot, that system follows the henry's law. That means Henry's law is valid for the system.

Limitations (Applicability) of Henry's law

1) It applies closely to gases with nearly ideal behavior.
2) It is applicable at moderate temperature and pressure. Not so high not so low temperature and pressure.
3) The solubility of the gas in the solution must be low. At higher concentration it is not applicable.

4) The gas should not react with the solvent to form new species. Thus ammonia and HCl react with water. They do not obey this law. $NH_3 + H_2O = NH_4OH \rightleftarrows NH_4^+ + OH^-$ HCl + H_2O = H_3O^+ + Cl^-

5) The gas does not associate or dissociate in the solvent. It should be in the same molecular form in the solution as in the gaseous phase.

Problem: The solubility of pure oxygen in water at 20 °C and 1.00 atmospheric pressure is $1.38×10^{-3}$ mole/litre. Calculate the concentration of oxygen at 20 °C and partial pressure of 0.21 atmosphere. (Ans $2.9×10^{-4}$ mole/litre) BT-535p.

Problem: The solubility of pure nitrogen in water at 20 °C is 0.0150 g/litre when partial pressure of nitrogen is 580 torr. Calculate the solubility of nitrogen at 20 °C in water when its partial pressure is 800 torr. (Ans 0.0207 g/litre) BT-536p.

Distribution law (The Nernst Distribution law), Distribution of a solute between two immiscible solvents

I f we take two immiscible solvents A and B in a beaker, they form separate layers. When a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from solvent B to A. Finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

Distribution of solute X between solvent A and B.

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = a\ constant$$
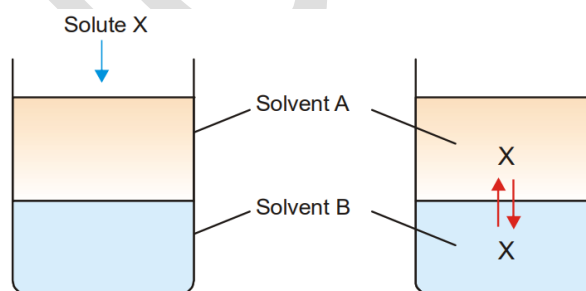
Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law (or Nernst's Partition law) or simply Distribution law or Partition law.

According to this law, *a dissolved substance, irrespective of its amount, distributes itself between two non-miscible solvents in contact with each other in such a way that at equilibrium, the ratio of the concentrations of the substance in the two layers is constant at any given temperature.*

If a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents, then

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = a\ constant.$$

If C_1 denotes the concentration of the solute X in solvent A and C_2 the concentration of the solute X in solvent B, Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D$$

The constant KD (or simply K) is called the Distribution coefficient or Partition coefficient or Distribution ratio.

The law deals with the distribution of a solid between two non-miscible or partially miscible solvents in contacts with each other. Consider, for example, the distribution of iodine between two non-moscible solvents – water and carbon tetrachloride. Iodine is soluble in both solvents. When a known volume of a solution of iodine is shaken for a period of time with carbon tetrachloride, it is found that iodine distributes or divides itself between the water and carbon tetrachloride layers in such a way that at equilibrium, the ratio of the concentrations of iodine in the two layers is constant at a given temperature and is independent of the actual amount of iodine present. If C_1 is the concentration of iodine in carbon tetrachloride layer and C_2 is the concentration of iodine in aqueous layer, then

$$\frac{C_1}{C_2} = K_D$$

Some examples of distribution law are the distribution of

1. Iodine between water and carbon disulphide or chloroform,
2. Phenol between water and amyl alcohol,
3. Bromine between water and carbon disulphide,
4. Succinic acid between water and ether etc.

PROBLEM: A solid X is added to a mixture of benzene and water. After shaking well and allowing to stand, 10 ml of the benzene layer was found to contain 0.13 g of X and 100 ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient. (Ans: 5.9)

PROBLEM: In the distribution of succinic acid between ether and water at 15ºC, 20 ml of the ethereal layer contains 0.092 g of the acid. Find out the weight of the acid present in 50 ml of the aqueous solution in equilibrium with it if the distribution coefficient for succinic acid between water and ether is 5.2. (Ans: 1.196 g)

Solubility and Distribution Law

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as,

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

Where, S_1 and S_2 are the solubilities of the solute in the two solvents. Hence knowing the value of the Distribution coefficient (K_D) and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.

PROBLEM. At 25°C an aqueous solution of iodine containing 0.0516 g litre^{-1} is in equilibrium with a carbon tetrachloride (CCl4) solution containing 4.412 g litre^{-1}. The solubility of iodine in water at 25°C is 0.34 g litre^{-1}. Find the solubility of iodine in carbon tetrachloride. (Ans 29.07 g litre^{-1})

Limitations/Applicability of Distribution Law

The conditions to be satisfied for the application of the Nernst's Distribution law are:

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1. **Constant temperature:** The temperature is kept constant throughout the experiment.
2. **Same molecular state:** The molecular state of the solute is the same in the two solvents. The law does not hold if there is association or dissociation of the solute in one of the solvents.
3. **Equilibrium concentrations:** The concentrations of the solute are noted after the equilibrium has been established.
4. **Dilute solutions:** The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high.
5. **Non-miscibility of solvents:** The two solvents are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of solute to them.

Application of Distribution

 Law

a. Determination of equilibrium constant from distribution coefficient.
b. Solvent extraction of substances with a suitable solvent. The greater the distribution ratio is in favour of the organic solvent, the greater will be the amount extracted in any one operation.
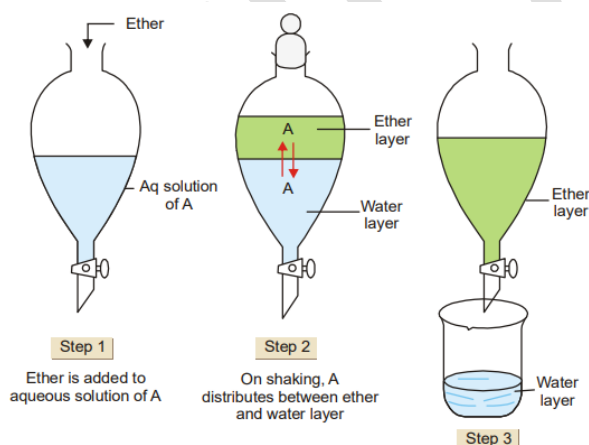

Figure: Extraction in a separatory funnel.

c. Multiple extraction: The process of extraction when carried with the total amount of the given solvent in a single operation, is referred to as simple extraction. To recover the maximum amount of the substance from aqueous solution, the extraction is made in two or more successive operations using small portions of the solvent provided. This is called multiple extraction or multi-step extraction.
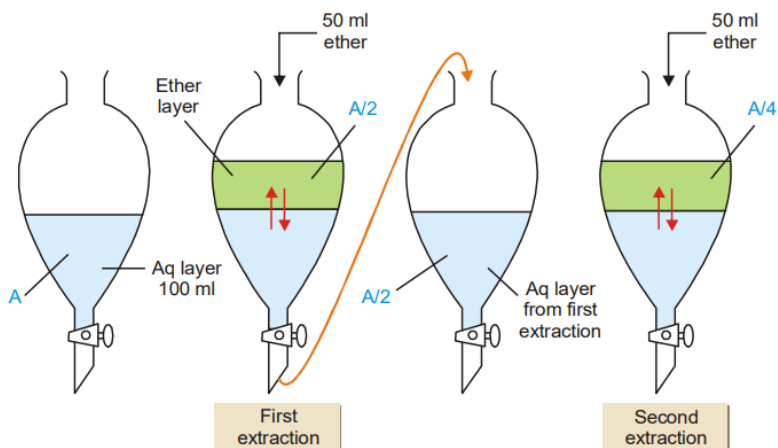
Figure: Illustration of Multiple extraction. The given solvent (ether) is used in two successive portions of 50 ml each.

d. Liquid–liquid chromatography (Partition chromatography).
e. Determination of Solubility.
f. Determination of association of solute in a solvent.
g. Determination of dissociation of solute in a solvent.