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## Solutions-1

PART-1: Introduction, Methods of expressing concentration

## 1. Solution

Homogeneous mixture of two or more substances whose composition vary within certain limits is known as Solution or a True Solution.

Eg: Salt in water, sugar in water.
In a homogeneous mixture composition is same throughout the mixture.
A solution contains only two components is called a binary solution. The two components are solute and solvent.

The component present in lesser proportion (or) dissolved state is solute and the component present in greater proportion (or) dissolving medium is a solvent.

## 2. Characteristics of a solution

i. It is a homogeneous mixture.
ii. Formation of solution is a physical change but not a chemical change.
iii. Solute cannot be separated from solution by filtration.
iv. Solute can be separated from solution by distillation, absorption (or) Crystallization.

If the solute is non-volatile and solvent is volatile then they are separated by evaporation
(Or) distillation
v . The properties of a solution like density, vapour pressure, boiling point depend on relative amount of solute and solvent.

## 3. Solubility

i. Solubility (s) is the number of grams of the solute that dissolves in 100 grams of a solvent at a given temperature to make a saturated solution.
$S=w X 100 / \mathrm{m}$, where $\underline{\mathrm{w}}$ is wt of solute and $\underline{\mathrm{m}}$ is wt of solvent.
ii if Solubility, $S>1 \mathrm{~g} / \mathrm{ml} \quad, \quad \mathrm{S}<0.001 \mathrm{~g} / \mathrm{ml} \quad, \mathrm{S}=0.001-1 \mathrm{~g} / \mathrm{ml}$
Soluble Insoluble sparingly soluble
iii. Solubility depends on the nature of solute, solvent, temperature and pressure. It has no units.

It is related to Molarity as , $\mathrm{m}=\mathrm{SX10} / \mathrm{GMW}$
4. Solubility of a solid in a liquid depends on Lattice and Hydration energies. The heat liberated or absorbed when one mole of solute is dissolved in excess solvent is known as Heat of solution. It is the algebraic sum of lattice and hydration energies.
i. If lattice energy > hydration energy, endothermic change takes place. The vessel becomes cool.
eg. $\mathrm{NH}_{4} \mathrm{Cl}, \mathrm{AgNO}_{3}$, Нуро.
The solubility of these substances increases with temperature.
ii. If hydration energy > lattice energy, exothermic change takes place. The vessel becomes warm,
eg. $\mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{NaOH}, \mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{Na}_{2} \mathrm{SO}_{4}$. Etc.,
The solubility of these substances decreases with temperature.
iii. If hydration energy = lattice energy, heat is neither evolved nor absorbed.
eg. NaCl
The solubility of these substances independent of temperature
5. The solubility of a solid or liquid in a liquid follows the principle 'Like dissolves

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like', the. Solubility of a gas in water generally decreases with increase in temperature and increases with increase in pressure.
6. Solubility of a gas in a liquid is expressed in terms of absorption coefficient.

The volume of the gas at NTP dissolved in a unit volume of solvent at a temperature and

1 atm pressure is called absorption coefficient.
Factors influencing the solubility of a gas in a liquid are:
I) Nature of gas and liquid
Ii) Temperature
iii) Pressure of the gas

With an increase in the pressure, the number of gaseous molecules per unit volume over the solution increases. Thus solubility of gas increases.

Conditions for high solubility of gas in a liquid are
i) High pressure
ii) Low temperature
(For the dissolution of gases in liquids, Heat of solution is always negative, because lattice energy is zero)
7. Henry's law: At a given temperature, the mass of a gas (m) dissolved per unit volume of a solvent is proportional to the pressure of the gas (p)."

At constant temperature,
$m \alpha p$ or $m=k p$ ( $k$ is constant)
The partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction

Of gas $(\mathrm{X})$ in the solution $\mathrm{p}=\mathrm{K}_{\mathrm{H}} \mathrm{X}$, where $\mathrm{K}_{\mathrm{H}}$ is Henry's law constant.
It is to be noted that the higher the value of Henry's law constant, the lower is the solubility of the gas in the liquid.
Henry's law is not applicable to the gases which react with solvent.
Eg. $\mathrm{NH}_{3} \& \mathrm{HCl}$ react with water.

## 8. Applications of Henry's Law

i) Increase in the solubility of $\mathrm{CO}_{2}$ in soda water is due to high pressure of the gas
ii) At higher altitudes the partial pressure of oxygen is less. This leads to lower concentration of oxygen in blood and tissues of mountain climbers and people living at higher altitudes. Due to lower pressure of oxygen Persons become weak and unable to think properly. These symptoms are called 'anoxia'.

## 9. Types of Solution: (Based on Nature of Solvent)

1. Aqueous Solutions (Solvent is water)
2. Non-Aqueous Solutions (Solvent is other than $\mathrm{H}_{2} \mathrm{O}$ )
i Solutions with alcohol as solvent are called alcoholic solutions.
ii. Solutions with Ether as solvent are called ethereal solutions.
iii. Solutions with liq. Ammonia as solvent are called Ammoniacal solutions.
iv. In Amalgams - mercury is one of the components.

The commonly used Solvents in non-aqueous Solutions are
liq. $\mathrm{NH}_{3}$, liq. $\mathrm{SO}_{2}, \mathrm{CHCl}_{3}, \mathrm{C}_{6} \mathrm{H}_{6}, \mathrm{CS}_{2}$, acetic acid etc.

## 10. Types of solutions and common examples

| Type of solution | Solute | Solvent | Common example |
| :--- | :---: | :---: | :--- |
| Solid solutions | Solid | Solid | Copper dissolved in gold |
|  | Liquid | Solid | Amalgam of mercury with sodium |
|  | Gas | Solid | Solution of hydrogen in palladium |
| Liquid solutions | Solid | Liquid | Sugar dissolved in water |
|  | Liquid | Liquid | Ethyl alcohol dissolved in water |
|  | Gas | Liquid | Carbondioxide dissolved in water |
| Gaseous solutions | Solid | Gas | Camphor in air |

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Liquid Gas Moisture in air
Gas Gas Mixture of any two gases.[CO+ $\left.\mathrm{H}_{2}\right]$

## 11. Methods of Expressing Concentrations

The quantity of solute present in definite quantity of the solution relative to the solvent is known as Concentration of solution or strength of solution.
i. The solution with known concentration is called a STANDARD SOLUTION
ii The solution containing relatively smaller quantity of solute compared to that of solvent is called a DILUTE SOLUTION.
iii The solution which contain excess solute, in a definite quantity of the solution is called a CONCENTRATED SOLUTION:
iv The ratio between density of solution and density of water at the given temperature is known as relative density or specific gravity of solution.

Specific gravity $=$ density of solution $/$ density of water
Specific gravity has no units.

## 1.2: Physical methods

1 Weight Fraction: It is amount of solute in grams present in 100 g solution
Weight Fraction $=$ yt of solute/wt of solution
Weight $\%=$ [wt of solute/wt of solution] X100
2. Volume fraction $=$ Vol. of solute $/ \mathrm{vol}$. of solution

Volume $\%=[$ Vol. of solute $/$ vol. of solution $]$ X100
3. mass/volume percentage: It is mass of solute dissolved in 100 ml of solution.
$\mathbf{w} / \mathbf{v} \%=[\mathrm{wt}$. of solute/vol. of solution] X100
4. PPM (PARTS PER MILLION): It is the mass of the solute present in million parts by mass of the solution

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*Molarity, mole fraction and wt. fraction do not change with temperature

## 1.3: Chemical Methods

I. Molarity: - (M) It is number of gram moles of solute dissolved per litre of solution.
Unit = Moles/litre

Molarity decreases with increase in temperature.
$M=\frac{n}{\mathrm{~V}_{\mathrm{Lit}}}$
$\mathrm{n}=$ number of moles of solute
$\mathrm{V}=$ Volume of Solution in litres.
$\mathrm{M}=\frac{\mathrm{w}}{\text { GMW }} \times \frac{1000}{\mathrm{~V}} \quad \because \mathrm{n}=\frac{\mathrm{w}}{\text { GMW }}$
$\mathrm{w}=$ weight of the solute in grams
$\mathrm{v}=$ volume of the solution in millilitres
GMW = molecular weight of the solute in grams

1) Number of millimoles of the solute present in V ml . of the solution $=$ Volume of solution in ml.X Molarity $=\mathrm{VM}$
2) Number of moles of solute present in Vml. of the solution $=\mathrm{VXM} / 1000$
3) Number of moles of solute present in V litres of solution $=\mathrm{M} \mathrm{V}$
4) When a solution is diluted its molarity decreases, but number of moles of solute before \& after dilution remains constant.
$\mathrm{V}_{1} \mathrm{M}_{1}=\mathrm{V}_{2} \mathrm{M}_{2}$
$\mathrm{V}_{1}=$ Volume of the solution before dilution.
$\mathrm{M}_{1}=$ Molarity of the solution before dilution.
$\mathrm{V}_{2}=$ Volume of the solution after dilution.
$\mathrm{M}_{2}=$ Molarity of the solution after dilution .
5) Volume of water added to get a solution of known molarity $=\mathrm{V}_{2}-\mathrm{V}_{1}$ or $\left(\mathrm{M}_{1}-\right.$ $\left.\mathrm{M}_{2}\right) \mathrm{V}_{1} \mathrm{M}_{2}$
6) When weight/volume percentage is given,

$$
\mathrm{M}=\frac{10 \times(\mathrm{w} / \mathrm{v}) \%}{\mathrm{GMW}}
$$

7) When weight percentage of solution and specific gravity or density are given then

$$
\mathrm{M}=\frac{10 \times \mathrm{d} \times(\mathrm{w} / \mathrm{w}) \%}{\text { GMW }}
$$

Where $\mathrm{w} / \mathrm{w} \%=$ percentage by weight
$\mathrm{d}=$ Density in gram $/ \mathrm{ml}$
8) For a mixture of two solutions of different molarities, the molarity of the resulting solution is given by

$$
\mathrm{M}=\left[\frac{\mathrm{V}_{1} \mathrm{M}_{1}+\mathrm{V}_{2} \mathrm{M}_{2}}{\mathrm{~V}_{1}+\mathrm{V}_{2}}\right]
$$

9) When two solutions are titrated against each other as per the following equation $n_{1} A+n_{2} B \rightarrow m_{1} C+m_{2} D$, The molarities of the two solutions are related as
$\frac{M_{1} V_{1}}{n_{1}}=\frac{M_{2} V_{2}}{n_{2}}$
II. Normality: It is number of gram equivalents of solute dissolved per litre of solution.

Unit $=$ gm. equivalents $/$ litre
Normality decreases as temperature increases.

$$
\mathrm{N}=\frac{\text { number of equivalents of solute }}{\text { volume of solution in litres }} \text { (or) } \quad \mathrm{N}=\frac{\text { wt of solute }}{\text { Gram equivalent weight }} \times \frac{1000}{\text { Vol of solution in } \mathrm{ml}}
$$

a) Equivalent weight of an Acid

$$
\mathrm{E}_{\text {Acid }}=\frac{\frac{\text { Formula weight of acid }}{\text { Basicity of acid }}}{\text { a }}
$$

Number of replaceable hydrogen's present in one molecule of acid is called its basicity.

Equivalent weights of some acids

| Acid | Formula | Formula <br> Weight | Basicity | Equivalent <br> weight |
| :--- | :--- | :--- | :---: | :---: |
| Hydrochloric acid | HCl | 36.5 | 1 | 36.5 |
| Sulphuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 98 | 2 | 49 |
| Nitric acid | $\mathrm{HNO}_{3}$ | 63 | 1 | 63 |
| Acetic acid | $\mathrm{CH}_{3} \mathrm{COOH}$ | 60 | 1 | 60 |
| Oxalic acid | $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | 126 | 2 | 63 |
| Phosphoric acid | $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 98 | 3 | 32.67 |
| Phosphorous acid | $\mathrm{H}_{3} \mathrm{PO}_{3}$ | 82 | 2 | 41 |
| Hypophosphorus acid | $\mathrm{H}_{3} \mathrm{PO}_{2}$ | 66 | 1 | 66 |

Formula weight of base
b. Equivalent weight of base $=$ Acidity of base

Equivalent weights of some bases

| base | Formula | Formula <br> weight | Acidity | Equivalent <br> weight |
| :--- | :--- | :--- | :---: | :---: |
| Sodium hydroxide | NaOH | 40 | 1 | 40 |
| Potassium hydroxide | KOH | 56 | 1 | 56 |
| Calcium hydroxide | $\mathrm{Ca}(\mathrm{OH})_{2}$ | 74 | 2 | 37 |
| Aluminium hydroxide | $\mathrm{Al}(\mathrm{OH})_{3}$ | 78 | 3 | 26 |


| Ferrous hydroxide | $\mathrm{Fe}(\mathrm{OH})_{2}$ | 90 | 2 | 45 |
| :--- | :--- | :--- | :--- | :--- |
| Ferric hydroxide | $\mathrm{Fe}(\mathrm{OH})_{3}$ | 107 | 3 | 35.67 |
| Ammonium hydroxide | $\mathrm{NH}_{4} \mathrm{OH}$ | 35 | 1 | 35 |
| Chromic hydroxide | $\mathrm{Cr}(\mathrm{OH})_{3}$ | 103 | 3 |  |
| 34.33 |  |  |  |  |

d.Equivalent weight of Ion $=\quad \frac{\text { Formula weight }}{\text { Charge } / \text { Valency }}, \quad \mathrm{E}_{\mathrm{Fe}^{+2}}=\frac{56}{2}=28$

Formula weight of oxidant
e.Equivalent weight of oxidising agent Electrons gained by one molecule of oxidant
eg: $\mathrm{KMnO}_{4}$ acts as oxidant in acidic, basic and also in neutral medium.

1. In acidic medium : $\mathrm{KMnO}_{4}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightarrow \mathrm{K}^{+}+\mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$

One molecule of $\mathrm{KMnO}_{4}$ gains five electrons. Hence, the equivalent weight of $\mathrm{KMnO}_{4}$

$$
=\frac{\text { Mol.wt.of } \mathrm{KMnO}_{4}}{5}=\frac{158.04}{5}=31.608
$$

2. In neutral as well as weakly basic medium
$\mathrm{KMnO}_{4}+\mathbf{2 H}_{2} \mathrm{O}+3 \mathrm{e}^{-} \rightarrow \mathrm{K}^{+}+\mathbf{4 \mathrm { OH } ^ { - }}+\mathrm{MnO}_{2}$
One molecule of $\mathrm{KMnO4}$ gains three electrons.
Hence The equivalent weight of
$\mathbf{K M n O}_{4}=\frac{\text { Mol.wt.of } \mathrm{KMnO}_{4}}{3}=\frac{158.04}{3}=\mathbf{5 2 . 6 8}$
3. In strongly alkaline medium: $\mathrm{MnO}_{4}^{-}+\mathrm{e}^{-} \rightarrow \mathrm{MnO}_{4}{ }^{2-}$

Then the equivalent weight of $\mathrm{KMnO}_{\mathbf{4}}=\left\{\frac{\text { Mol.wt.of } \mathrm{KMnO}_{4}}{1}\right\}=\mathbf{1 5 8 . 0 4}$
f.Equivalent weight of reducing agent
$\mathrm{E}_{\text {reductant }}=\frac{\text { Formula weight of reductant }}{\text { Electrons lost ty one molecule of reductant }}$
Mohr's salt is ferrous ammonium sulphate
Formula $=\mathrm{FeSO}_{4}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4} .6 \mathrm{H}_{2} \mathrm{O}$
Formula weight $=392$

$$
\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+}+\mathrm{e}^{-}
$$

The equivalent weight of Mohr's salt is $392 / 1=392$
Some useful relations
i) $\quad$ Number of equivalents of solute $=\mathrm{V} \times \mathrm{N}$, volume V is in litres.
ii) Number of mill equivalents of solute $=V \times N$, volume $V$ is in millilitres.
iii) The mass of a solute ( w ) in grams, present in V litres of a solution, can be calculated from normality of the solution $(\mathrm{N})$ as,
$w=N \times V \times G E W$
Here GEW is the gram equivalent weight of solute.
iv) Normality of the mixture when two solutions of same solute are mixed
$N=\frac{N_{1} V_{1}+N_{2} V_{2}}{V_{1}+V_{2}}$
v) When $\mathrm{V}_{\mathrm{a}} \mathrm{ml}$ of a strong acid of normality $\mathrm{N}_{\mathrm{a}}$ is mixed with $\mathrm{V}_{\mathrm{b}} \mathrm{ml}$ of a strong base of normality $\mathrm{N}_{\mathrm{b}}$,
i) If $\mathrm{N}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}=\mathrm{N}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}$ the solution is neutral
ii) If $\mathrm{N}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}>\mathrm{N}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}$, the solution is acidic. Normality w.r.t $\mathrm{H}^{+}$

$$
=\frac{\mathrm{N}_{\mathrm{a}} \mathrm{~V}_{\mathrm{a}}-\mathrm{N}_{\mathrm{b}} \mathrm{~V}_{\mathrm{b}}}{\mathrm{~V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}}
$$

iii) If $\mathrm{N}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}<\mathrm{N}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}$, the solution is basic Normality w.r.t $\mathrm{OH}^{-}=\frac{\mathrm{N}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}-\mathrm{N}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}}{\mathrm{V}_{\mathrm{a}}+\mathrm{V}_{\mathrm{b}}}$
vi) Normality, Molarity interrelation:
i) For acids: Normality $=$ Molarity X Basicity of acid
ii) For bases: Normality $=$ Molarity X Acidity of base
iii) For salts: Normality $=$ Molarity $X$ total + ve or - ve charge of the salt
iv) For oxidising (or) reducing agents :

Normality $=$ Molarity $X$ total change in oxidation state per mole of oxidant or reductant
vii) For exact neutralisation of acid with base

$$
\frac{\text { wt of base }}{\text { GEW of base }}=\frac{\mathrm{N}_{\mathrm{a}} \mathrm{~V}_{\mathrm{a}}(\mathrm{ml})}{1000} ; \quad \frac{\mathrm{wt} \text { of acid }}{\text { GEW of acid }}=\frac{\mathrm{N}_{\mathrm{b}} \mathrm{~V}_{\mathrm{b}}(\mathrm{ml})}{1000}
$$

viii) In case of dilution: $\mathrm{V}_{1} \mathrm{~N}_{1}=\mathrm{V}_{2} \mathrm{~N}_{2}$, The volume of the solution before and after dilution are $\mathrm{V}_{1}$ and $\mathrm{V}_{2}$ and normalities are $\mathrm{N}_{1}$ and $\mathrm{N}_{2}$ respectively.

## III. Molality

It is defined as the number of gram moles of the solute present in one kilogram of solvent. It is denoted by ' $m$ '. Units of molality are $\mathbf{m o l} \mathbf{~ k g}^{\mathbf{- 1}}$. It is independent of temperature. Molality is the most accurate and theoretically the best method of expressing concentration.
Molality (m) is given as

$$
\mathrm{m}=\frac{\text { number of moles ofsolute }(\mathrm{n})}{\text { number of } \mathrm{kg} \text { ofsolvent }(\mathrm{W})}(\text { Or }) \quad \mathrm{m}=\frac{\mathrm{w}}{\text { GMW }} \times \frac{1000}{\mathrm{~W}}
$$

Here w and W are masses of solute and solvent respectively in grams.GMW is the gram molecular mass of solute.

Some useful relations
i. $\mathrm{m}=\frac{10 \times \text { Solubility }}{\text { Gram molecular weight }}$
ii. $\quad \mathrm{m}=\frac{\text { Molarity } \times \text { Vol in lit }}{\text { weight of solvent in } \mathrm{kg}}$
iii. $\mathrm{m}=\frac{1000 \times \text { Molarity }}{(1000 \times \text { specific gravity })-\mathrm{M} \times \mathrm{GMW}}$
iv. Mole fraction of solute $=$

$$
\frac{\mathrm{m}}{\mathrm{~m}+\left(\frac{1000}{\mathrm{MW} \text { of solvent }}\right)}
$$

## IV: Mole fraction

It is the ratio of number of moles of a component to the total number of moles of the solution. It is denoted by the symbol ' X '. If number of moles of component substances $A$ and $B$ in a solution are respectively $n_{A}$ and $n_{B}$,

Mole fraction of component $A=n_{A}=n_{A} / n_{A}+n_{B}$
Mole fraction of component $B=n_{B}=n_{B} / n_{A}+n_{B}$

The sum of the mole-fractions of all components in a solution is unity. Mole fraction is very useful in calculations involving gas mixtures and also in relating some physical properties like vapour pressure.

One hundred times mole fraction is called mole percentage. Mole fraction and mole percentage have no units. They do not vary with a change in temperature of solution.

