Volumetric Calculation

Introduction :-

When several non-reacting substance are mixed, then there are three possible type of mixtures:

a.) Coarse mixture (sand + salt) & (sugar + salt).

b.) Colloidal dispersion (Gum + water) & (fine clay + water)

c.) True solution (salt + water)

In the coarse mixture there exist heterogeneity where as in true solution there is complete homogeneity. In colloidal dispersion, the heterogeneity is not readily apparent & it is not homogeneous.

Distinction between solute & solvent:

I.) Phase method.

Let there be a substance 'A' in solid phase & 'B' in liquid phase then if the phase of the resulting mixture is-:

a.) solid, then solute = B, solvent = A.

b.) liquid, then solute = A, solvent = B

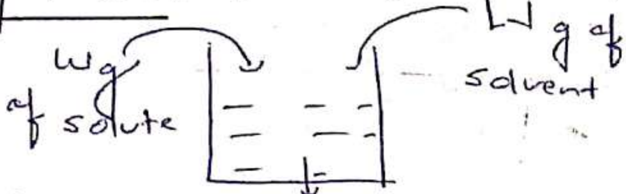
II.) Amount Method:

According to this method, the substance which is in larger porpportion by mass is solvent while the one in lesser porp-oration is solute.

eg: A solid mixture of A & B. if $W_A > W_B$ then solute is B & solvent is A.

Method of Expressing the concentration of solution;

<u>1.) Mass Percentage or Percent by Mass:</u> $(\% w/w)$



~~Mass percentage~~

Mass Percentage of solute $(\% w/w)_{solute}$

$$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$(\% w/w)_{solute} = \frac{w\,g}{(w+W)\,g} \times 100.$$

Similarly, Mass percentage of solvent $(\% W/w)_{solvent}$.

$$= \frac{\text{Mass of solvent}}{\text{Mass of solution}} \times 100$$

$$(\% w/w)_{solvent} = \frac{W\,g}{(w+W)\,g} \times 100.$$

Mass percentage is unitless.

Also, $(\% w/w)_{solute} + (\% w/w)_{solvent} = 100.$

<u>Proof</u>: $\frac{w\,g}{(w+W)\,g} \times 100 + \frac{W\,g}{(w+W)\,g} \times 100$

$$\frac{(w+W)\,g}{(w+W)\,g} \times 100 = 100.$$

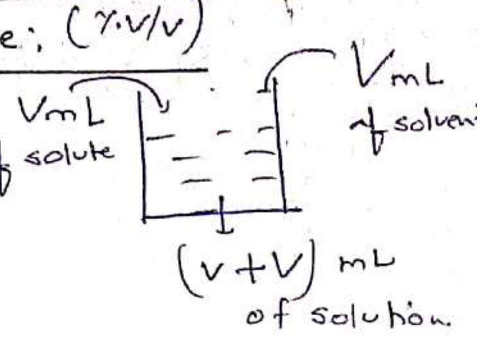
<u>Q.)</u> A solution of NaOH 40% (w/w) of NaOH in 10 litre of solution. Calculate (take solvent = water)

a) Mass of NaOH & solvent.

b.) Moles of NaOH & solvent.

c) Given density of solution is 1.5 g/mL.

2.) Volume Percentage or Percentage by volume; (%v/v)



Volume percentage of solvent $(\%V/v)_{solvent}$

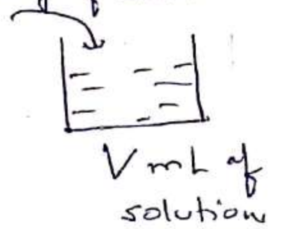
$$= \frac{V\,mL}{(v+V)\,mL} \times 100$$

Volume Percentage of solute $(\%v/v)_{solute}$

$$= \frac{v\,mL}{(v+V)\,mL} \times 100.$$

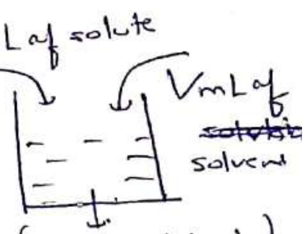
Like Mass percentage, Volume percentage, is unitless quantity.

(3.) Mass by Volume Percentage $(\%w/v)_{solute}$



$$= \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

$$= \frac{W\,g}{V\,mL} \times 100.$$



Let us suppose, (1) Expressing $(\%V/v)_{solute}$ to $(\%w/v)_{solute}$.

Given, ρ_{solute} = density of solute. (in g/mL)

$\rho_{solvent}$ = density of solvent. (in g/mL)

V_{solute} = Volume of solute. (in mL)

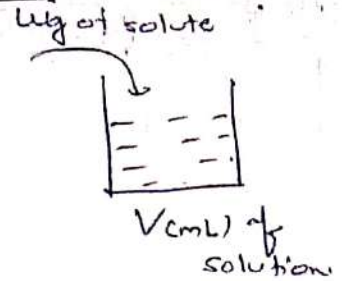
$V_{solvent}$ = Volume of solvent (in mL)

M_{solute} = Mass of solute (in g) = $V_{solute} \times \rho_{solute}$.

$$(\%w/v)_{solute} = \frac{V_{solute} \times \rho_{solute}}{(V_{solute} + V_{solvent})} \times 100.$$

Expressing $(\%w/w)_{solute}$ from $(\%V/v)_{solute}$:

$$(\%w/w)_{solute} = \left(\frac{\rho_{solute} \times V_{solute}}{\rho_{solute} \times V_{solute} + \rho_{solvent} \times V_{solvent}}\right) \times 100$$



4) Molarity (M) :

$$\text{Molarity (M)} = \frac{\text{no. of moles of solute}}{\text{Volume of solution in (L)}}$$

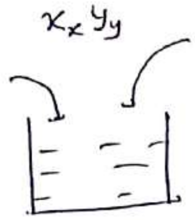
$= \text{Wg} / \cancel{\text{M}}\ \text{mol}$

Let M_{solute} = Molecular wt. of solute (g/mole)

then, no. of moles of solute = $Wg / M (g/mol)$

$$\text{Volume of solution} = \frac{V\,mL}{1000 (mL/L)}$$

so, $$\boxed{\text{Molarity} = \left(\frac{W/M}{V/1000}\right) \text{mol}/l}$$



case - I)

Molarity of ionic compound.

Suppose, an ionic compound $X_x Y_y$ dissolved in $V (L)$ of solution, then,

$$X_x Y_y \rightleftharpoons xX^{y+} + yY^{x-}$$

In case of complete dissociation.

$$X_x Y_y \rightleftharpoons xX^{y+} + yY^{x-}$$

	$X_x Y_y$	X^{y+}	Y^{x-}
Initial	1	0	0
Eq^m	0	x	y

so, $$\text{Molarity (of cation)} = \frac{x \text{ mole}}{V \text{ L}}.$$

$$\text{Molarity (of anion)} = \left(\frac{y}{V}\right) \text{mol}/l.$$

In case of partial dissociation,

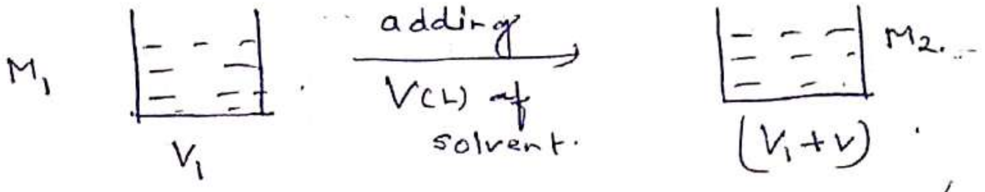
$$X_x Y_y \rightleftharpoons xX^{y+} + yY^{x-}$$

	$X_x Y_y$	X^{y+}	Y^{x-}
Initial	1	0	0
Eq^m	$(1-\alpha)$	$x\alpha$	$y\alpha$.

$$\text{Molarity (of cation)} = \frac{x\alpha}{V} \text{ mol}/l.$$

$$\text{Molarity (of anion)} = \left(\frac{y\alpha}{V}\right) \text{mol}/L.$$

Case-2: Molarity of dilution.



In both solution, mass of solute / moles of solute remains constant.

In 1st solution, $M_1 = \dfrac{n_1}{V_1}$ $\quad \therefore n_1$ = no. of moles of solute in soln. 1

$$n_1 = M_1 V_1 \quad \text{——— (1)}$$

2nd solution, $M_2 = \dfrac{n_2}{V_2}$ $\quad \therefore n_2$ = no. of moles of solute in soln. 2, after dilution

$$n_2 = M_2 V_2 \quad \text{——— (2)}$$

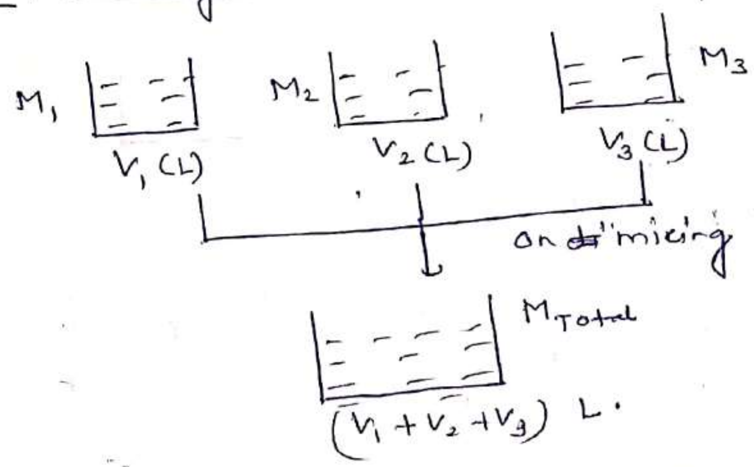
During dilution, no. of moles remain constant,

$$n_1 = n_2$$

$$M_1 V_1 = M_2 V_2$$

$$\boxed{M_2 = \frac{M_1 V_1}{V_2} = \left(\frac{M_1 V_1}{V_1 + V}\right)}$$

Case-3: Mixing of two solution:

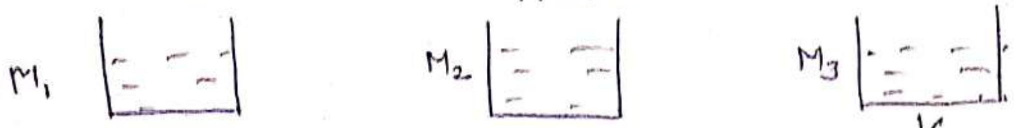


$$M_{Total}(V_1+V_2+V_3) = M_1V_1 + M_2V_2 + M_3V_3$$

$$\boxed{M_{Total} = \frac{(M_1V_1 + M_2V_2 + M_3V_3)}{(V_1+V_2+V)}}$$

Case-4.) Molarity of Mixing of two or more acid with different basicity:

Acid 1. Acid 2 Acid 3.



V_1 V_2 V_3

Basicity: x_1 x_2 x_3.

M_1 ($H^{\oplus}$ from Acid 1) $= \dfrac{x_1 n_1}{V_1}$ —(1) where, n_1 = no. of moles of Acid 1.

M_2 ($H^{\oplus}$ from Acid 2) $= \dfrac{x_2 n_2}{V_2}$ —(2) n_2 = no. of moles of Acid 2.

M_3 ($H^{\oplus}$ from Acid 3) $= \dfrac{x_3 n_3}{V_3}$ —(3) n_3 = no. of moles of Acid 3.

Upon Mixing three solutions,

Resulting Molarity will be M_{Total}.

$$M_{Total}(H^+) = \frac{M_1V_1 + M_2V_2 + M_3V_3}{V_1 + V_2 + V_3}.$$

From eq (1), (2) & (3)

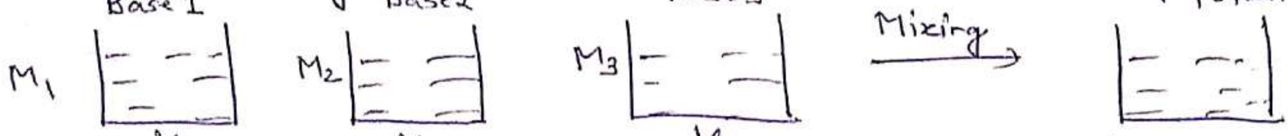
$$M_{Total} = \frac{(x_1n_1 + x_2n_2 + x_3n_3)}{V_1 + V_2 + V_3}$$

Generalize:

$$M_{Total} = \frac{\sum_{i=1}^{n} (\text{basicity})_i \times n_i}{\sum_{i=1}^{n} V_i}$$

Case-5: Molarity of Mixing two or more base with different Acidity.

Base 1 Base 2 Base 3 Mixing M_{Total}.



V_1. V_2 V_3 $(V_1+V_2+V_3)$

Basicity: y_1 y_2 y_3.

$$M_{Total}(OH^{\ominus}) = \left(\frac{y_1n_1 + y_2n_2 + y_3n_3}{V_1 + V_2 + V_3}\right)$$

Generalize:

Generalize,

$$M_{Total} = \frac{\sum_{i=1}^{n} (\text{acidity})_i \times n_i}{\sum_{i=1}^{n} V_i}$$

Molality:

It is defined as the number of moles of solute present in 1kg of the solvent. It is denoted by 'm'.

$$\text{Molality} = \left(\frac{W_B/M_B}{W_A/1000}\right) \text{mol/kg}$$

Where,
W_B = weight of solute (in g)
M_B = Molecular wt. of solute. (in g/mole)
W_A = weight of solvent (in g).

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Molecular mass of solute}}$$

where, 'solubility' $= \frac{\text{mass of solute in (gram)}}{\text{Mass of solvent in (g)}} \times 100$.

Relation between Molarity & Molality:

$$\frac{1}{m} = \frac{\rho}{M} - \frac{m_B}{1000}$$

where, ρ = density of solution.
m = molality
M = Molarity
m_B = molecular mass of so[lute]

Mole fraction:

It is defined as the ratio of number of moles of one component to total no. of moles of the solution. It

Mole ~~of~~ fraction of component (X_i)

$$X_1 = \frac{n_i}{\sum_{i=1}^{n} n_i} = \frac{n_1}{n_1 + n_2 + n_3 \cdots n_n}$$

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Also, $x_i = \dfrac{w_i / M_i}{\sum_{i=1} w_i / M_i}$ where, w_i = mass of each component (i)
M_i = Molecular wt. of component (i)

$$x_1 = \left(\frac{w_1 / M_1}{\frac{w_1}{M_1} + \frac{w_2}{M_2} + \frac{w_3}{M_3} --- \frac{w_n}{M_n}} \right)$$

Also, sum of Mole feaction of each component = 1.

$$\sum_{i=1}^{n} x_i = 1$$

$$x_1 + x_2 + x_3 --- x_n = 1.$$

Relation between Mole feaction & Molasity:

$$M = \frac{x_B \times 1000 \times d}{x_A M_A + x_B M_B}$$

where, x_B = mole feaction of solute
x_A = mole feaction of solvent.
d = density.
M_A = molecular wt. of solvent A.
M_B = molecular wt. of solute B.

Relation between Mole feaction & Molality:

$$\frac{x_B \times 1000}{(1 - x_B)\, m_A} = m.$$

Where, x_B = Mole feaction of solute B.
M_A = Molecular weight of solvent A.

Q1 Example 1; The density of a 3M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole feaction of sodium thiosulphate (iii) The molalities of $Na^{\oplus}$ & $S_2O_3^{2-}$ ion?

<u>Soln.</u> (i) Molarity = $\frac{x \times density \times 10}{m_A}$ where x = % mass of solute, m_A = molecular wt.

$3 = \frac{x \times 1.25 \times 10}{158}$

$x = 37.92\ \%$

(ii) No. of moles of $Na_2S_2O_3 = \frac{474}{158} = 3$

Mass of water = $(1250 - 474) = 776g$

No. of moles of water = $\frac{776g}{18\ g/mol} = 43.1$

Mole fraction of $Na_2S_2O_3 = \frac{3}{43.1+3} = 0.065$

(iii) No. of moles of $Na^{\oplus}$ ion = $2 \times 3 = 6$ mole

Molality of $Na^{\oplus}$ ions = $\frac{\text{No. of moles of } Na^{\oplus} \text{ ions}}{\text{Mass of water in (kg)}}$

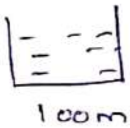
$= \frac{6}{776} \times 1000 = 7.73m.$

<u>Example:2</u> ; What would be molality of a solution made by mixing equal volume of 30% by mass of H_2SO_4 ($\rho = 1.218\ g/cm^3$) & 70% by mass of H_2SO_4 (density = $1.610\ g/cm^3$).

<u>Soln</u>:

100mL
solution1

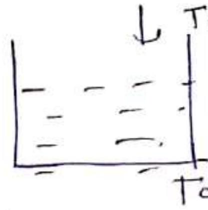
Mass of solution = 121.8g
Mass of H_2SO_4 = 36.54g
Mass of water = 85.26g



100mL
Solution 2.

Mass of solution = 161g.
Mass of H_2SO_4 = 112.7g
mass of water = 48.3g

↓ Total H_2SO_4 = 149.24g



Total water = 133.56g

$$\text{Molality} = \frac{(149.24g / 98\ g/mole)}{133.56\ g / 1000\ g/kg} = 11.4m.$$

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Example 3 : The mole fraction of CH_3OH in an aqueous solution is 0.02 & its density is $0.994 g/cm^3$. Determine its molarity & Molality ?

Soln: let x mole of CH_3OH & y mole of water be present in solution.

Mole fraction of $CH_3OH = \left(\frac{x}{x+y}\right) = 0.02$

$$\frac{y}{x} = 49$$

$$\text{Molality} = \frac{x}{18 \times y} \times 1000 = \frac{1000}{18 \times 49} = 1.13\ m$$

$$\text{volume of solution} = \frac{\text{Total mass}}{\text{density}} = \frac{32x + 18y}{0.994}\ mL = \frac{32x+18y}{994}\ L$$

$$\text{Molarity} = \frac{x}{32x + 18y} \times 994$$

$$= \frac{994}{32 + 18\left(\frac{y}{x}\right)} = 1.0875\ M$$

Normality: It is defined as no. of equivalent of solute present in one litre of solution is known as Normality (N).

$$\text{Normality (N)} = \frac{\text{No. of equivalent of solute}}{\text{Volume of solution in (Litre)}}$$

$$= \frac{\text{wt of solute / Equivalent weight of solute}}{\text{volume of solution in litre}}$$

No. of equivalent of solute = (Volume of solution (in litre) × Normality of solution)

No. of milli equivalent of solute = (Normality of solution × vol. of solution in millilitre)

$$\text{Equivalent weight} = \left(\frac{\text{Atomic weight}}{n\text{-factor}}\right)$$