Molar Methods : A solution containing 1 mole of solute per liter of solution is defined as a (Molar solution).
Molarity of solution : The number of moles of solute per liter of solution.

$$
\begin{gathered}
\text { Molarity }[\mathrm{M}]=\frac{\text { number of moles solute }}{\text { liters of solution }} \\
\text { Molarity }[\mathrm{M}]=\frac{\text { grams of solute }}{\text { molecular weight }} \times \frac{1}{\text { litersof solution }}
\end{gathered}
$$

Moles of solute $=$ molarity x liters of solution
Grams of solute = molarity x literes of solution x molecular weight.


Ex / Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 gm of $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(46.07 \mathrm{gm} / \mathrm{mole})$ in 3.50 L of solution. Solution /
$[\mathrm{C} 2 \mathrm{H} 5 \mathrm{OH}]=\frac{\text { number of moles }}{\text { liter of solution }}$
No.mol $\begin{aligned} \mathrm{C} 2 \mathrm{H} 5 \mathrm{OH} & =2.30 \mathrm{gm} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \times \frac{1 \mathrm{~mol} \mathrm{C2H5OH}}{96.07 \mathrm{gm} \mathrm{C} 2 \mathrm{H} 5 \mathrm{OH}} \\ & =0.0499 \mathrm{~mol} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\end{aligned}$
$\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right.$ ] $=\frac{0.0499 \mathrm{~mol}}{3.5 \mathrm{~L}}=0.0143 \mathrm{~mol} / \mathrm{L}=0.0143 \mathrm{M}$
EX/Calculate the analytical and equilibrium molar concentration of the solute species in an aqeous solution that contains 285.0 mg of trichloroacetic acid, $\mathrm{Cl}_{3} \mathrm{CCOOH}(163.4 \mathrm{gm} / \mathrm{mol})$, in 10.0 ml .

Solution/
$\mathrm{Cl}_{3} \mathrm{CCOOH} \equiv \mathrm{HA}$
No. $\mathrm{mol} H A=285.0 \mathrm{mg} \mathrm{HA} \times \frac{1 \mathrm{gm} \mathrm{HA}}{1000 \mathrm{mgHA}} \times \frac{1 \mathrm{~mol} \mathrm{HA}}{163.4 \mathrm{gm} \mathrm{HA}}$

$$
=1.744 \times 10^{-3} \mathrm{~mol} \mathrm{HA}
$$

$[H A]=\frac{1.744 \times 1000 \mathrm{molHA}}{10.0 \mathrm{ml}} \times \frac{1000 \mathrm{ml}}{\mathrm{L}}$

$$
=0.174 \mathrm{~mol} \mathrm{HA} / \mathrm{L}=0.174 \mathrm{M}
$$

EX/ How many grams of $\mathrm{AgNO}_{3}(169.9 \mathrm{gm} / \mathrm{mol})$ must be used to prepared 500.0 ml of 0.125 M ?
Solution/

$$
\begin{aligned}
& \mathrm{M}=\frac{w t}{M \cdot w t} \times \frac{1000}{V m l} \\
& \mathrm{Wt}=\frac{M X M . w t \times \mathrm{Vml}}{1000} \\
& =\quad \frac{0.125 \mathrm{mmol} / \mathrm{ml} \times 169.9 \mathrm{mg} / \mathrm{mmol} \times 500 \mathrm{ml}}{1000}=
\end{aligned}
$$

10.62 mg

## Equivalent Methods:

The equivalent weight (eq) is defind, for neutralization reactions, as the weight in grams that will furnish or react with one gram-atomic weight of hydrogen ion.
Equivalent weight $=\frac{\text { molecular weight }}{n}=\frac{M \cdot W t}{n}$
$\mathrm{n}=$ no. $\mathrm{H}^{+}$for acid
$=n o . \mathrm{OH}^{-}$for base
= no. electrons in the reaction.

A) Equivalent weight of atoms of element :

Eq. $w t=\frac{\text { atomicweight }}{\text { valency }}$
A) Equivalent weight of compounds:

1. Equivalent weight of Acids;

Equivalent weight of acid which contains one replaceable hydrogen
Eq . wt of acid $=\frac{\text { molecular weight }}{\text { no.of hydrogen atom }}$
2 Equivalent weight of a base;
Equivalent weight of base which contains one replaceable hydroxyl group

Eq .Wt of a base $=\frac{\text { molecular weight }}{\text { no.ofhydroxylgroups }}$

3 Equivalent weight of a salt;
Equivalent weight of a salt in grams which contains one weight of cat ion can react or replaced by one gram of hydrogen

Equivalent weight of Reducing and Oxidizing agent
Eq .wt. of reducing agent $=\frac{\text { molecular weight }}{\text { no.ofelectrons losses in the reaction }}$
Eq .wt of oxidizing agent $=\frac{\text { molecular weight }}{\text { no.of electrons gains in the reaction }}$

## Example /

Equivalent weight of $\mathrm{HCl}=\frac{M H C l}{n}=\frac{36.5}{1}=36.5$
For eq.wt $\mathrm{NaOH}=\frac{M N a O H}{n}=\frac{40}{1}=40$
For eq.wt $\mathrm{Ba}(\mathrm{OH})_{2}=\frac{M B a(O H) 2}{n}=\frac{171}{2}=85.5$
For eq.wt $\mathrm{H}_{3} \mathrm{PO}_{4}$
$\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightarrow \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}=\frac{97}{1}=97$
$\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightarrow 2 \mathrm{H}^{+}+\mathrm{HPO}_{4}^{-2}=\frac{96}{2}=48$
$\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightarrow 3 \mathrm{H}^{+}+\mathrm{PO}_{4}^{-3}=\frac{95}{3}=31.7$
Equivalent weight $=\frac{\text { molecular weight }}{\text { no.of valency }}=\frac{M . w t}{n}$
Normality $(\mathrm{N})=\frac{\text { EquivalentS Solute }}{\text { liters ofsolution }}$
$\operatorname{Normality}(\mathrm{N})=\frac{\text { grams solute }}{\frac{\text { molecular weight }}{\text { hydrogen equivalents per mole }}} \times \frac{1}{\text { liters of solution }}$
liters of solution $x$ normality $=$ Equivalents of solute
liters of solution $x$ normality $x$ equivalent weight $=$ grams solute

## Preparation of solution

Most solution are prepared by dissolving a weighed amount of solid and adding sufficient water to make the desired volume.


Calculation of the Normality and Molarity of standard solution
Ex/How many grams of pure sodium hydroxide (M.wt $40.0 \mathrm{~g} / \mathrm{mol}$ ) are needed for preparation of 500.0 ml 0.100 N solution?

Solution/
$\mathrm{NaOH} \longrightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$

$$
\mathrm{N}=\frac{\text { Equivalents of solute }}{\text { liters of solution }}
$$

Equivalents of solute $=$ normality $x$ volume in liters

$$
\begin{aligned}
& =0.100 \mathrm{eq} / \text { litef } \times 0.500 \text { liter } \\
& =0.0500 \mathrm{eq}
\end{aligned}
$$

Equivalents of solute $=\frac{\text { weight in grams }}{\frac{\text { molecular weight }}{\text { no.of valency }}}$
$0.0500 \mathrm{eq}=\frac{W t}{\frac{40.0 \mathrm{~g} / \mathrm{mol}}{1 \mathrm{eq} / \mathrm{mol}}}$
$W \mathrm{t}=2.00 \mathrm{gm}$
طريقة اخرى للحل
$\mathrm{N}=\frac{W t}{e q \cdot w t} \times \frac{1000}{V m l}$
$0.100 \mathrm{eq} / \mathrm{L}=\frac{w t}{\frac{M \cdot w t}{n}} \times \frac{1000}{500 \mathrm{ml}}$
$0.100 \mathrm{eq} / \mathrm{t}=\frac{w t}{\frac{40.0 \mathrm{gm} / \mathrm{mol}}{1 \mathrm{eq} / \mathrm{mol}}} \times \frac{1000 \mathrm{ml} / \mathrm{t}}{500 \mathrm{ml}}$
$\mathrm{Wt}=2.00 \mathrm{gm}$
Ex/What is the normality of a solution prepared by dissolving 25.20 gm oxalic acid $\left(\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} .2 \mathrm{H}_{2} \mathrm{O}\right)(126.1 \mathrm{gm} / \mathrm{mol})$ in sufficient water to give 1.200 liters of solution ?What is the molarity of this solution?

## Solution/

$$
\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{H}^{+}+\mathrm{C}_{2} \mathrm{O}_{4}^{-}
$$

2

$$
\mathrm{N}=\frac{\text { Equivalents of solute }}{\text { liters of solution }}
$$

Number of equivalents $=\frac{\text { weight of solute }}{\frac{\text { molecular weight }}{\text { no.of valency }}}$

$$
=\frac{25.20 \mathrm{gm}}{\frac{126.1 \mathrm{gm} / \mathrm{mol}}{2 e q / \mathrm{mol}}}=0.3996 \mathrm{eq}
$$

The Normality is :

$$
N=\frac{0.3996 \mathrm{eq}}{1.200 L}=0.3330 \mathrm{eq} / \text { liter }
$$

The Molarity is:

$$
\mathrm{M}=\frac{N}{n}=\frac{0.3330 \mathrm{eq} / \mathrm{liter}}{2 e q / \mathrm{mol}}=0.1665 \mathrm{~mol} / \mathrm{liter}
$$

Relation between Molarity and Normality:

$$
\begin{aligned}
& M=\frac{w t_{1}}{M w t} * \frac{1}{L} \Rightarrow \omega t_{1}=M * M_{w t} * L \\
& N=\frac{\omega t_{2}}{\text { eq.wt }} * \frac{1}{L} \Rightarrow \omega t_{2}=N * \text { eq. wt } * L \\
& \omega t_{1}=\omega t_{2} \\
& M * M w t * L=N * \text { eq. wt * } 6 \\
& M * M \omega t=N * \frac{M w t}{n} \\
& \therefore N=n M
\end{aligned}
$$

Where:
$n$ : no. of $\mathrm{H}_{1}^{+} \mathrm{OH}$ \& cation valency.

Ex/How many grams of pure sodium sulfate $\mathrm{Na}_{2} \mathrm{SO}_{4}$ (M.wt $142.0 \mathrm{~g} / \mathrm{mol}$ ) are needed for preparation of 200.0 ml 0.500 N solution?
Solution/ $\mathrm{Na}_{2} \mathrm{SO}_{4} \longrightarrow 2 \mathrm{Na}^{+}+\mathrm{SO}_{4}^{-2}$

$$
\begin{gathered}
\mathrm{N}=\frac{w t}{e q \cdot w t} \times \frac{1000}{V m l} \\
0.500 \mathrm{eq} / \mathrm{t}=\frac{w t}{\frac{142 \mathrm{gm} / \mathrm{mot}}{2 e q / \mathrm{mol}}} \times \frac{1000 \mathrm{ml} / \mathrm{t}}{200 \mathrm{mt}} \\
\mathrm{Wt}=7.1 \mathrm{gm}
\end{gathered}
$$

Ex/Describe the preparation of 5.000 L of $0.1000 \mathrm{M} \mathrm{Na} \mathrm{NO}_{3}$ $(105.99 \mathrm{~g} / \mathrm{mol})$ from the primary standard solid?

## Solution/

$$
\begin{aligned}
& \text { Molarity }=\frac{\text { number of moles solute }}{\text { liters of solution }} \\
& \begin{aligned}
\text { Moles of solute } & =M \times \mathrm{V} \\
& =0.1000 \mathrm{~mol} / \mathrm{t} \times 5.000 \mathrm{t}=0.5000 \mathrm{~mol}
\end{aligned}
\end{aligned}
$$

$$
\begin{aligned}
\text { Grams of solute } & =0.500 \mathrm{~mol} \times \frac{105.999 \mathrm{gm}}{\mathrm{~mol}} \\
& =53.00 \mathrm{gm} \mathrm{Na}_{2} \mathrm{CO}_{3}
\end{aligned}
$$

Therefore the solution is prepared by dissolving $53.00 \mathrm{gm}^{2}$ of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ in water and diluting to exactly 5.00 L .

## Ex/

Astandard 0.0100 M solution of $\mathrm{Na}^{+}$is required for calibrating a flame photometric method for determining the element. Describe how 500.0 ml of this solution can be prepared from primary standard $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ?
Solution/ $\mathrm{Na}_{2} \mathrm{CO}_{3} \longrightarrow \mathrm{Na}^{+}+\mathrm{CO}_{3}{ }^{-2}$

$$
\text { No. } \mathrm{mol} \mathrm{Na}=500.0 \mathrm{ml} \times \frac{0.01 \mathrm{mmol}}{\mathrm{ml}}=5 \mathrm{mmol}
$$

Moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}=5 \mathrm{mmol} \mathrm{Na}{ }^{+} \times \frac{1 \mathrm{mmolNa} 2 \mathrm{CO} 3}{2 \mathrm{mmolNa}}=2.5 \mathrm{mmol}$
Grams of $\mathrm{Na}_{2} \mathrm{CO}_{3}=2.5 \mathrm{mmot} \times 0.10599 \mathrm{gm} / \mathrm{mmol}=0.265 \mathrm{gm}$
The solution is therefore prepared by dissolving $0.265 \mathrm{gm}^{2}$ of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ in water and diluting to 500.0 ml .

## Density and specific gravityof solution

Density and specific gravity are terms of encountered in the analytical literature. The density of a substance is its mass per unit volume, where as its specific gravityis the ratio of its mass to the mass of an equal volume of water. Density has units of kilograms per liter or grams per milliliter in the metric system.

