

## Acidimetry and Alkalimetry Demand

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### # Equivalent weight:-

The Equivalent weight of an atom of an element is defined as the number of parts by weight of that element which can combine or displace directly or indirectly 1.008 parts by weight of Hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

$$\text{Equivalent weight (E)} = \frac{\text{Atomic weight (A)}}{\text{Valency (V)}}$$

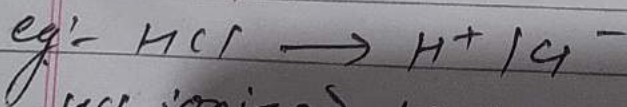
### # Equivalent weight of acid and base:-

$$\text{Equivalent weight of acid} = \frac{\text{molecular weight}}{\text{basicity}}$$

$$\text{Equivalent weight of base} = \frac{\text{molecular weight}}{\text{acidity}}$$

# The no. of replaceable  $H^+$  ion are called ~~acid~~ basicity.

# The no. of replaceable  $OH^-$  ion are called acidity.



HCl ionized to give one  $H^+$  so, it is mono basic acid (basicity 1)

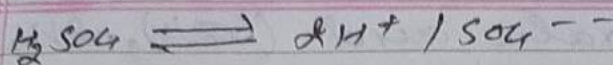
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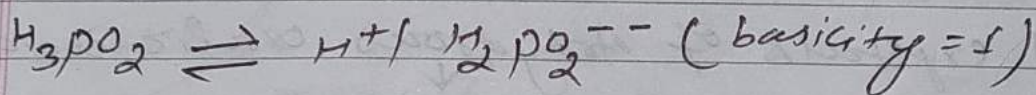
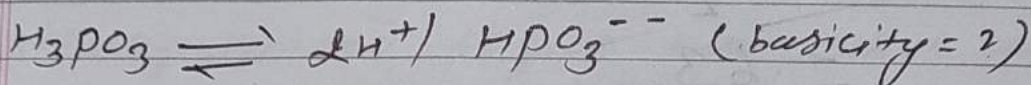
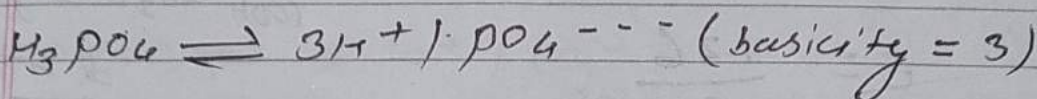
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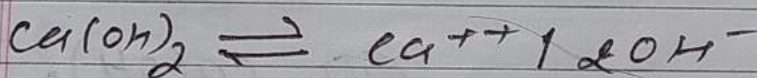
$\text{H}_2\text{SO}_4$  ionized to give two  $\text{H}^+$  ion. so, it is dibasic acid. (basicity = 2)



# eg:-



$\text{NaOH}$  ionized to give one  $\text{OH}^-$  ion. so, it is monoacidic base (acidity = 1)



$\text{Ca(OH)}_2$  ionized to give two  $\text{OH}^-$  ion. so, it is di-acidic base (acidity = 2)

Example of Equivalent weight:-

eg (1)

HCl

$$E = \frac{\text{mol. weight}}{\text{basicity}}$$

$$= \frac{36.5}{1} = 36.5$$

" H<sub>2</sub>SO<sub>4</sub>

$$E = \frac{\text{mol. wt}}{\text{basicity}}$$

$$= \frac{98}{2} = 49$$

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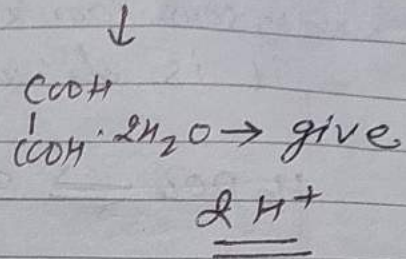
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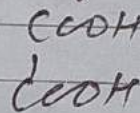
(ii) crystals of oxalic acid  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ .

$$E = \frac{\text{mol. wt}}{\text{basicity}}$$

$$E = \frac{126}{2} = 63$$



(iii) crystals of anhydrous oxalic acid



$$E = \frac{\text{mol wt}}{\text{basicity}} = \frac{90}{2} = 45.$$

Base:

(i) NaOH

$$E = \frac{\text{mol. wt}}{\text{basicity}} = \frac{40}{1} = 40$$

(ii)  $\text{Ca}(\text{OH})_2$

$$E = \frac{\text{mol. wt}}{\text{acidity}} = \frac{74}{2} = 37$$

(iii) CaO (dianhydrous)

$$E = \frac{56}{2} = 28$$

$$= 37$$

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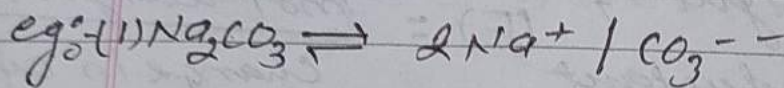
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Equivalent weight of simple salt

$$\text{Eq. wt. of simple salt} = \frac{\text{mol. wt. of salt}}{\text{total positive or negative charge.}}$$



$\text{Na}_2\text{CO}_3$  ionized to give two positive and two negative charge. So, Equivalent weight

$$E = \frac{\text{mol. wt}}{2}$$

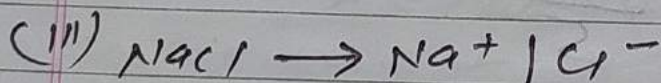
$$= \frac{106}{2}$$

$$= 53$$



$$E = \frac{100}{2}$$

$$= 50.$$

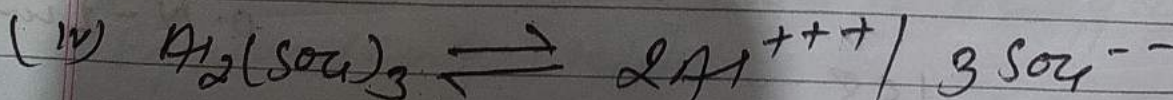


$$E = \frac{58.5}{1}$$

$$= 58.5$$

+ve  $\rightarrow$  ⑥

-ve  $\rightarrow$  ⑥



$$E = \frac{342}{6} = 57.$$



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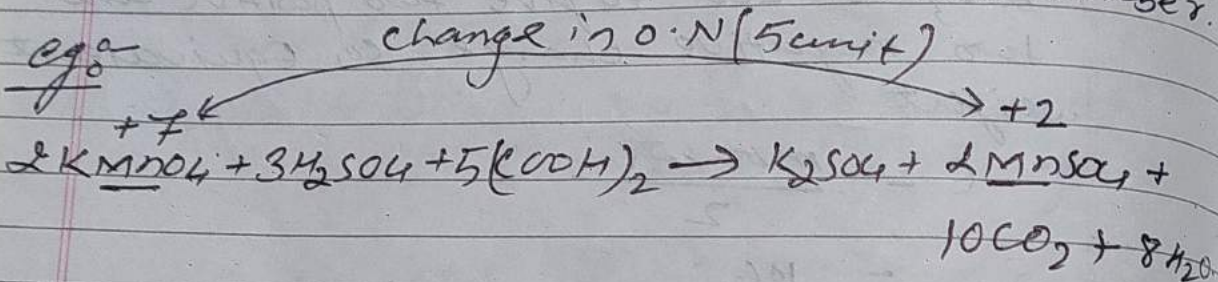
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# Equivalent weight of oxidizing and reducing agent. (oxidant and reductant)

Equivalent weight of oxidant or reductant (E) =  $\frac{\text{mol. weight}}{\text{change in oxidation number}}$



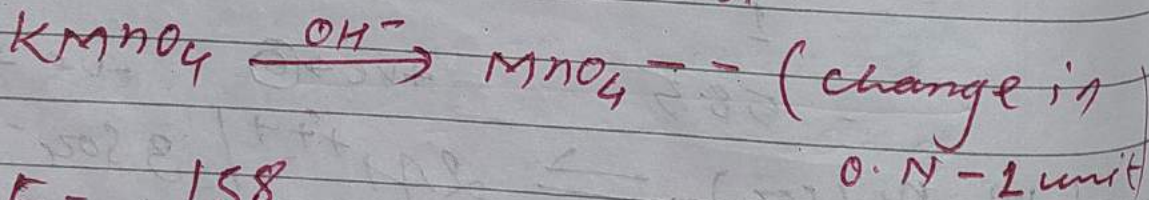
$$E \text{ of } \text{KMnO}_4 = \frac{\text{mol. wt.}}{\text{change in O.N}}$$

$$= \frac{39(4) + 55(\text{Mn}) + 16(16) \times 4}{5}$$

$$= \frac{158}{5}$$

$$= 31.6$$

#  $\text{KMnO}_4$  in basic medium:



$$E = \frac{158}{1} = 158$$

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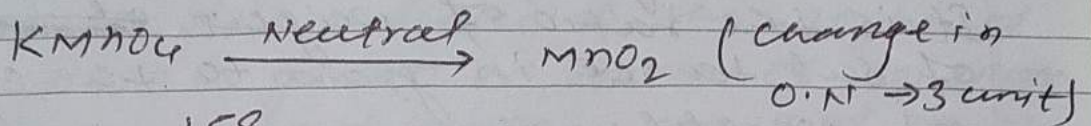
eg:-

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#  $KMnO_4$  in Neutral medium:



$$E = \frac{158}{3} = 52.6$$

# Equivalent weight of reducing agent.

Mohr's salt, oxalic acid,  $FeSO_4$ ,  $H_2O_2$  etc are reducing agent.

eg:- Mohr's salt:  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ .

$$\text{mol. weight} = 392$$

$$\text{oxidation no. change} = 1$$

$$E = \frac{\text{mol. wt}}{\text{change in } 0.N}$$

$$= \frac{392}{1}$$

$$= 392$$

# Gram Equivalent weight:

If Equivalent weight is expressed in gram, then it is said to be gram Equivalent weight.

eg:- 1-gram eq. of hydrogen = 1.008 g.

1-gram eq. of HCl = 36.5 g.

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Number of gram Equivalent:-

It is the ratio of weight of substance in gram to the equivalent weight.

$$\text{No. of gram Equivalent} = \frac{\text{weight of substance in gram}}{\text{Equivalent weight}}$$

For example:-

20 gm of NaOH contains  $\frac{20}{40} = 0.5$  gram Equivalent of NaOH.

□ concentration or strength of solution:-

It measures quantity of solute present in given volume of solution.

① gram per litre (g/l):-

gram per litre of a solution is defined as the weight of solute in gram present in one litre of solution.

$$\text{Gram/litre} = \frac{\text{weight of solute in gram}}{\text{Vol. of solution in litre}}$$

$$= \frac{\text{weight of solute in gram}}{\text{Vol. of solution in ml}} \times 1000$$

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(b) percentage solution:-

% solution is defined as the weight of solute in gram or volume of solute in ml present in either 100ml of solution or 100gm of solution.

$$\% \text{ solution } \left( \frac{w}{W} \right) = \frac{\text{wt. of solute in gram}}{\text{vol. of soln in gram}} \times 100\%$$

$$\% \text{ solution } \left( \frac{v}{V} \right) = \frac{\text{weight of solute in ml}}{\text{vol. of soln in ml}} \times 100\%$$

$$\% \text{ solution } \left( \frac{w}{V} \right) = \frac{\text{weight of solute in gram}}{\text{vol. of solution in ml}} \times 100\%$$

(c) Normality:-

Normality of a solution is defined as the number of gram-equivalent of solute present in one litre of a solution.

It is denoted by N. It can be change with temp, as it depends upon the volume of solution.

$$\text{Normality} = \frac{\text{no. of gram Equivalent of solute}}{\text{vol. of soln. in litre.}}$$

$$\left( \text{No. of gram Eq.} = \frac{\text{wt of solute}}{\text{Eq. weight}} \right)$$

$$\text{Normality} = \frac{\text{wt. of solute}}{\text{Eq. wt} \times \text{vol. of soln in litre.}} \quad \text{in g/l.}$$



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$$\text{Normality} = \frac{\text{gram/litre}}{\text{Eq. weight}}$$

$$\boxed{\text{Normality} \times \text{Eq. weight} = \text{gram/litre}}$$

Normal solution: (1N)

The solution in which one gram-equivalence of solute present in one litre of solution.

eg:- 1N solution of HCl means 36.5 gm (1-gram equivalent) of it present in one litre of solution.

Semi-normal solution: ( $\frac{1}{2}$ N or 0.5N)

The solution in which half-gram equivalence of solute present in one litre of solution.

eg:- 0.5N NaOH solution means 20 gm (half gram equivalence) of it present in one litre of solution.

Deci-normal solution ( $\frac{1}{10}$ N or 0.1N)

The solution in which one tenth gram equivalent of solute present in one litre of soln.

eg:-  $\frac{1}{10}$ N NaOH solution contain 4 gm in one litre of NaOH soln.

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# Molarity (M) :-

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molarity of a solution is defined as the number of gram moles of solute present in one litre of a solution. It is denoted by M. It decrease with temp<sup>r</sup>, as it depends upon volume of solution.

$$\text{molarity} = \frac{\text{number of gram moles of solute}}{\text{vol. of solution in litre}}$$

$$\left( \text{no. of moles} = \frac{\text{weight of solute}}{\text{molecular weight}} \right)$$

$$\text{molarity} = \frac{\text{weight of solute in gram}}{\text{molecular weight} \times \text{vol. of sol}^{\text{n}} \text{ in litre}}$$

$$\text{molarity} = \text{gram/litre} \times \frac{1}{\text{molecular wt.}}$$

$$\text{gram/litre} = \text{molarity} \times \text{molecular wt.}$$

Molar solution: of one litre of solution contains one gram mole of a solute.  
eg: - 1M  $\text{H}_2\text{SO}_4$  means 98 gm  $\text{H}_2\text{SO}_4$  present in one litre of solution.

Decimolar: - eg: -  $\frac{M}{10}$   $\text{H}_2\text{SO}_4$  means 9.8 gm of  $\text{H}_2\text{SO}_4$  present in 1 litre of solution.

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### # Molality (m) :-

molality of a solution is defined as the number of gram moles of solute present in 1000g (1K.g) of solvent.

$$\begin{aligned} \text{Molality (m)} &= \frac{\text{no. of gram moles of solute}}{\text{weight of solvent in K.g}} \\ &= \frac{\text{no. of gram moles of solute}}{\text{wt. of solvent in gram} \times 1000} \end{aligned}$$

### # Mole Fraction :-

mole fraction of a solution is defined as the ratio of number of moles of either solute or solvent to the total number of moles of solute and solvent present in solution. It depends on weight.

$$\text{mole fraction of solute} = \frac{n}{n+N}$$

$$\text{mole fraction of solvent} = \frac{N}{n+N}$$

where,

$n$  = no. of moles of solute.

$N$  = no. of moles of solvent

$n+N$  = no. of moles of solute and solvent. Signature

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The sum of mole fraction is always unity.

$$\frac{n}{n+N} + \frac{N}{n+N} = \frac{n+N}{n+N} = 1$$

# Formality (F)°

Formality of a solution is defined as the solution in which number of gram formula weight of solute present in one litre of a solution.

$$\text{Formality (F)} = \frac{\text{no. of gram formula weight}}{\text{Vol. of soln in litre.}}$$

formality is used for the expressing the concentration of ionic solid which doesn't exist in molecule.

# Relation between Normality and Molarity:-

~~Normality~~ =

$$\text{gram/litre} = \text{Normality} \times \text{Eq. wt.} \quad \text{--- (I)}$$

$$\text{gram/litre} = \text{Molarity} \times \text{mol. wt.} \quad \text{--- (II)}$$

from eqn (I) and (II)

$$\text{Normality} \times \text{Eq. wt.} = \text{molarity} \times \text{mol. wt.}$$

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But,

$$\text{Equivalent wt} = \frac{\text{mol. wt}}{\text{basicity or acidity}}$$

$$\text{mol. weight} = \text{Equivalent weight} \times \text{basicity or acidity.} \quad \text{--- (10)}$$

from eq'n (10) and (10)

$$\text{Normality} \times \text{eq/wt} = \text{molarity} \times \text{eq. wt} \times \text{basicity or acidity.}$$

$$\text{Normality} = \text{molarity} \times \text{acidity or basicity}$$

For simple salt:-

$$\text{Normality} = \text{molarity} \times \text{no. of +ve or -ve charge.}$$

For oxidizing and reducing salt:-

$$\text{Normality} = \text{molarity} \times \text{change in oxidation number.}$$

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Special formulae:-

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(i)  $\% = \text{gram/litre} / 10$

(ii)  $\text{gram/litre} = N \times \text{Eq. wt.}$

$$\% \times 10 = N \times \text{Eq. wt.}$$

$$N = \frac{\% \times 10}{\text{Eq. wt.}}$$

(iii) Molarity

$$M = \frac{\% \times 10}{\text{mol. wt.}}$$

(iv) Relation with density:-

$$N = \frac{\% \times 10 \times \text{specific gravity (density)}}{\text{Eq. wt.}}$$

$$M = \frac{\% \times 10 \times \text{specific gravity}}{\text{molecular weight}}$$

(v)  $W = \frac{V \times N}{1000}$

(vi)  $W = \frac{V \times \text{Mol. wt.} \times M}{1000}$

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Principle of volumetric analysis :-

(1) Equal volume of one solution neutralized with equal volume of another solution when their concentration is same.

eg:

1 ml of 1 N HCl = 1 ml of 1 N NaOH.

10 ml of 1 N  $KMnO_4$  = 10 ml of 1 N oxalic acid.

1000 ml of 1 N NaOH = 1000 ml of 1 N  $H_2SO_4$ .

(2) Equivalent volume and normality for same solution are reciprocal to each other.

eg:-

100 ml of 1 N HCl = 10 ml of 10 N HCl.

= 1000 ml of 0.1 N HCl.

= 1 ml of 100 N HCl.

So, a ml of b N sol<sup>n</sup> = (a x b) ml of 1 N solution.

3) when acid neutralized by base then it follows the following relation.

$$V_1 N_1 = V_2 N_2$$

where,

$V_1$  = vol. of acid

$N_1$  = Normality of acid

$V_2$  = vol. of base.

$N_2$  = Normality of base.

This eq<sup>n</sup> is called law of chemical equivalence or normality equation.

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≡ Derivation of Normality Equation:-

From law of chemical Equivalence,

No. of gram equivalence of acid = No. of gram Equivalence of base — (i)

gram/litre = Normality  $\times$  Equivalent weight

$$N \times \text{Eq. wt} = \frac{\text{wt in gram}}{\text{Vol. of sol}^n \text{ in litre}}$$

$$N \times \text{Vol. of sol}^n \text{ in litre} = \frac{\text{wt in gram}}{\text{Eq. wt}}$$

(since, no. of gram equivalence =  $\frac{\text{wt in gram}}{\text{eq. wt}}$ )

$N \times \text{Vol. of sol}^n \text{ in litre} = \text{no. of gram equivalence.}$

— (ii)

from (i) and (ii)

Vol. of sol<sup>n</sup> in litre  $\times$  Normality of acid =  
Vol. of sol<sup>n</sup> in litre  $\times$  Normality of base.

$$N_A \times \text{Vol. in ml} = N_B \times \text{Vol. in ml}$$

$$N_A \times V_A = N_B \times V_B$$

$$S_1 V_1 = S_2 V_2$$

$S_1 = N_A = \text{normality of acid}$

$S_2 = N_B = \text{normality of base}$

$V_A = V_1 = \text{Vol. of acid}$  Signature

$V_B = V_2 = \text{Vol. of base}$



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Normality factor (f):

Normality factor is defined as the ratio of weight taken and weight to be taken. It is denoted by f.

$$\text{Normality factor (f)} = \frac{\text{weight taken}}{\text{weight to be taken}}$$

The actual normality of prepared solution is the product of normality factor and given normality.

$$\text{Actual normality} = \text{given normality} \times f$$

eg:-

To prepare  $\frac{N}{10}$  oxalic acid solution in 250 ml we have to take 1.325 g. But if we take 1.320 g. Then strength may be varied.

$$f = \frac{\text{wt. taken}}{\text{wt to be taken}}$$

$$f = \frac{1.320}{1.325} \\ = 0.996$$

$$W = \frac{V \times N}{1000}$$

$$\text{Actual strength} = f \times \text{Normality}$$

$$= 0.996 \times 0.1 \text{ N}$$

$$= 0.0996 \text{ N}$$

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# # CHEMICAL ANALYSIS

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(1) Qualitative analysis:-

It involve the detection or identification of the constituents of chemical compound as radical.

(2) Quantitative analysis:

It involve the accurate estimation of particular constituent's present in given compound.

**Quantitative analysis:-**

(1) **Gravimetric analysis:-** In gravimetric analysis, the amount of constituents present in solution is determined by precipitating the species from the sol<sup>n</sup> and taking the weight of precipitate.

**# volumetric analysis:-**

"The process of determination of concentration of unknown solution by finding the exact volume of it required to neutralized with known volume of another solution having known concentration in the presence of suitable indicator is called volumetric analysis and process from which this analysis is done is called titration or titrimetric method."

The process of determination of concentration of unknown solution by gradual addition of one solution to another solution by determining the end point is called titration.

### Acidimetry Acid-base titration

#### ▣ Acidimetry:-

The process of determination of the strength of acid by finding the exact volume of it, by neutralizing it with known volume of standard alkali solution in the presence of suitable indicator is known as acidimetry.

#### ▣ Alkalimetry:-

The process of determining the strength of ~~an~~ alkali by finding exact volume of it, by neutralizing it with known volume of standard acid solution in the presence of suitable indicator is known as alkalimetry.

#### # Redox titration (Oxidation-reduction titration):-

The titration in which oxidation and reduction occur is called redox titration.

In such a titration, one species loses electron and another gains the electron. Therefore, there is change in colour of the chemical

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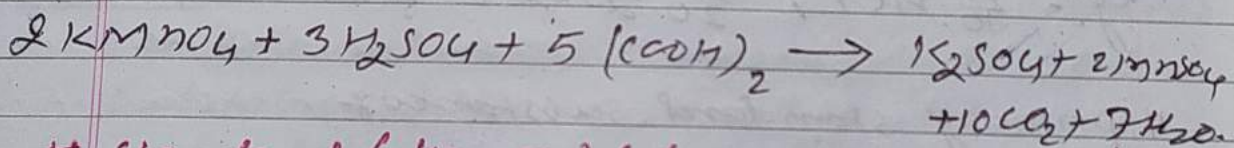
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species at the end point. In redox reaction chemical species themselves indicate the end point are called self indicators.

eg:- The titration between acidified  $\text{KMnO}_4$  solution and oxalic acid solution is redox titration in which  $\text{KMnO}_4$  acts as self indicator. At end point colour of  $\text{KMnO}_4$  get persist.



### # Standard (Known) Solution:-

The solution having known concentration is called standard solution.

(2) **primary standard solution**:- The solution prepared by dissolving suitable weight of the primary standard substance in solvent and making definite volume is called primary standard solution.

eg:-  $\frac{N}{10}$  oxalic acid solution.

$\frac{N}{5}$  Mohr's salt.

$\frac{N}{20}$   $\text{Na}_2\text{CO}_3$  solution.



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### (2L) Secondary standard solution:-

The solution which act as a standard solution only when it's concentration known with the help of another standard solution is called secondary standard solution. This process of knowing the concentration of unknown solution with the help of primary standard solution is called standardization.

eg:-  $\frac{N}{10}$  HCl,  $\frac{N}{20}$   $H_2SO_4$ ,  $\frac{N}{5}$   $KMnO_4$ , etc.

### # primary standard substance:-

The chemical substance whose exact amount can be taken in order to prepare the primary standard solution is called primary standard substance.

The requisites of primary standard substance is:

- (i) It should be pure found in pure and dry state.
- (ii) It should not be hygroscopic and deliquescent.
- (iii) It should have high equivalent weight.
- (iv) concentration of solution should not be altered after a storage of long period.

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### # secondary standard substance

The chemical substances which have not above all characteristics are called secondary standard substance.

### Different terms involve in Titration:-

Titrant:- The solution which is taken in burette is called titrant or the sol<sup>n</sup> whose concentration is known is called titrant.

Titrant:- The solution which is to be titrated or the solution which contains the substance to be estimated is called titrand or titrate.

End point:- End point is that point at which completion of the reaction is shown by the indicator by changing its colour. It is also called Neutralization point.

Equivalent point:- Equivalent point is the theoretical end point at which the number of gram equivalent of one substance is equal to number of gram equivalent of another substance.

Titration error:- The difference between end point and Equivalent point is called titration error.

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## # Indicators:-

Indicators are the chemical substances that indicate the completion of the chemical reaction by changing their own colour at the end point.

### Types of indicators:-

(i) Internal indicators:- The indicators which is used in the reaction mixture is known as internal indicators.

eg:- methyl orange, phenolphthalein, etc.

(ii) Self-indicators:- when one of the reactants can itself act as indicator, then it is known as self indicator. eg:  $KMnO_4$ .

(iii) External indicators:- these are not added in reaction mixture but are used externally. For eg:-  $K_3[Fe(CN)_6]$  act as external indicator in the titration of  $Fe^{2+}$  with  $K_2Cr_2O_7$ .

### # Characteristics of good indicators:-

- (i) It should have narrow working pH range.
- (ii) The colour change should be sharp and stable.
- (iii) Small drops of indicators should have capacity to signal end point.

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### Some common indicators and pH range:-

Indicators	colour in acidic medium	colour in basic medium	pH range
metan orange	Red	yellow	3.1 - 4.4
metan red	Red	yellow	4.2 - 6.3
phenolphthaleine	Colourless	pink	8.2 - 10.
Litmus paper	Red	Blue	5.5 - 8.

### # pH-curve and selection of indicators in acid base titration:-

In acid base titration, if alkali is taken in burette and acid is taken in conical flask, then the pH of the resulting solution is gradually increased while adding alkali in acid. If the pH of the resulting solution is plotted against the volume of alkali added, then the plots obtained are called pH-curve or titration curves. The nature of pH curve or sharpness in the pH curves help to select the suitable indicator.



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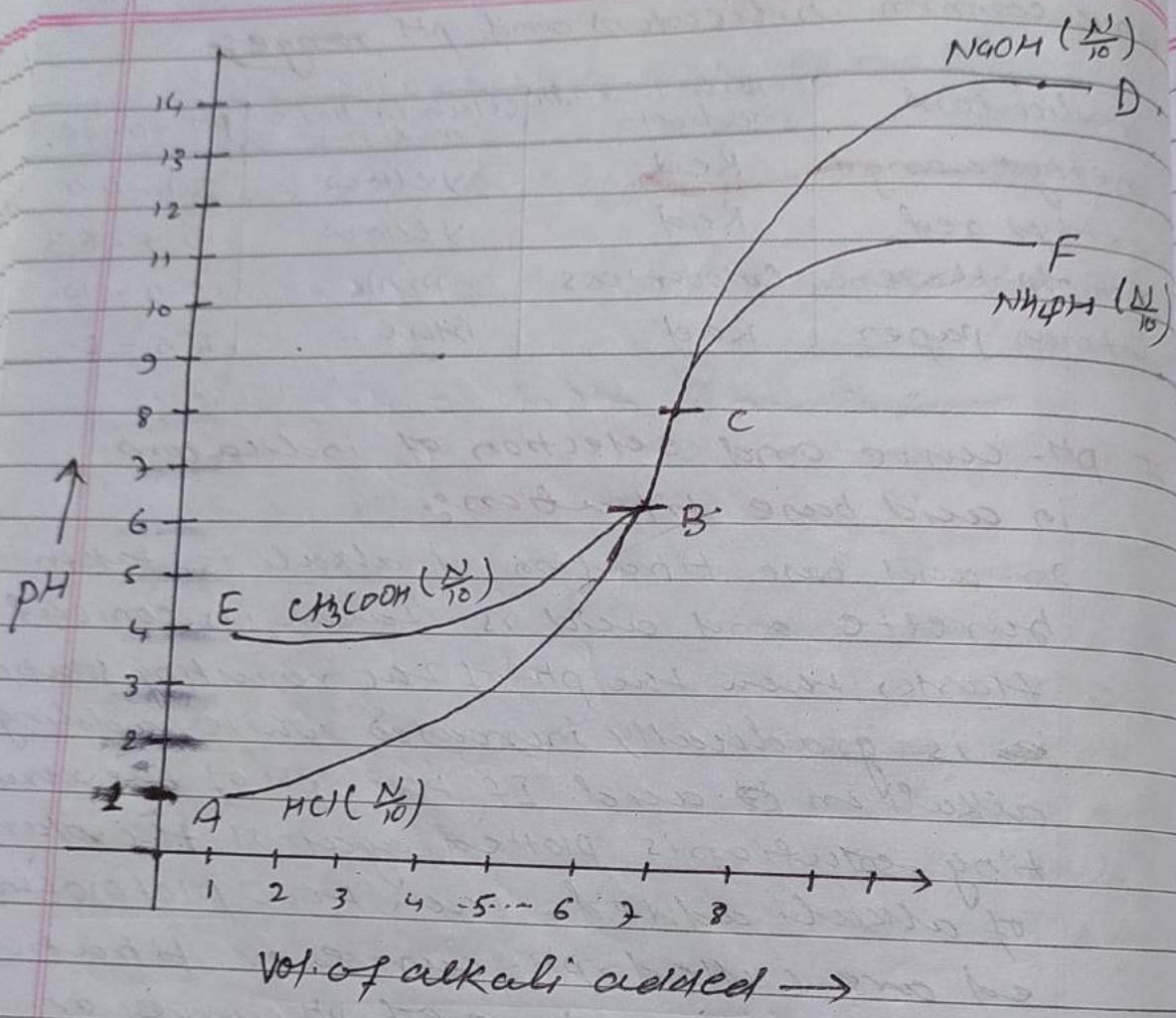


Fig:- Titration curves or pH-curves.

(i) Titration between strong acid and strong base:-  
 when strong acid is titrated against strong base, the nature of pH curve like ABCD is obtained. There is sudden pH change from 3 to 11. Therefore indicators like phenolphthalein having pH range 8.2-10, methyl orange (3.1-4.4), litmus (5-8)

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can be used as suitable indicator.

(ii) Titration between weak acid and strong base:-

When weak acid is titrated against strong base the curve like EBCD is obtained. There is sudden change in pH from ~~8.2-10.6~~ 8.2-10.6 to 11. Therefore phenolphthalein (8.2-10) is only suitable indicator.

(iii) Titration between ~~weak~~<sup>strong</sup> acid and weak base:-  
When strong acid is titrated against weak base, then curve like ABCF is obtained. There is sudden change in pH from ~~3 to 8~~ 3 to 8. Therefore methyl orange (3.1-4.4) is suitable.

(iv) Titration between weak acid and weak base:-  
When weak acid is titrated against weak base the curve like EBCF is obtained. ~~There is sudden change in pH from~~  
There is no sharpness in the curve and none of the indicator can be chosen. So, titration between weak acid and weak base is not carried out.

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molarity of mixture (for same solute)

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_m V_m \quad \text{--- (1)}$$

Normality of mixture:

$$V_1 N_1 + V_2 N_2 = V_m N_m \quad (\text{acid + acid mix})$$

$$V_1 N_1 - V_2 N_2 = V_m N_m \quad (\text{acid + base mix})$$

(acid - base)

$$N_m = +ve \quad (\text{acidic})$$

$$N_m = -ve \quad (\text{basic})$$

$$N_m = 0 \quad (\text{Neutral})$$

# ppm

$$\text{ppm} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 10^6$$

# ppb

$$\text{ppb} = \frac{\text{mass of solute (gm)}}{\text{mass of solvent (gm)}} \times 10^9$$

# milli mole (m mol)

$$\frac{1 \text{ mole}}{1000} = 1 \text{ m mole.}$$

