

Tikrit University
College of Engineering
Department of environmental Engineering
Analytical Chemistry

Lecturer: Ahmed Khaleel Al-Hadidi

: Lecture 1

Analytical chemistry:

Analytical chemistry involves separating, identifying, and determining the relative amounts of the components in a sample of matter.

Can be classified the analytical chemistry to the Qualitative analytical chemistry and Quantitative analytical chemistry.

- 1- Qualitative analysis: Reveals the chemical identity of the species in the sample.
- 2- Quantitative analysis: Provides numerical information about the amount of some species(the analyte) that is contained in a measured quantity of matter (the sample).

The results of a quantitative analysis are ordinarily expressed in relative terms.

Quantitative analysis classified in to

- 1- Gravimetric analysis: such as precipitation methods and volatilization methods
- 2- Volumetric analysis :classified to the
 - 1- Acid-Base Titrations
 - 2- Oxidation-Reduction Titrations
 - 3- precipitation Titration
- 4- Instrumental analysis:

This methods dependent on measurement one or some properties of matter that relationship with concentration of that matter

Measurement of density, colour, concentration ,potential, current

- 1-HPLC
- 2-UV
- 3-IR
- 4-GC
- 5- Atomic absorption

Gravimetric Methods Of Analysis

Gravimetric methods which are based upon the measurement of mass are two major types:

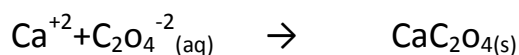


1-Precipitation methods

The analysis is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, and converted to a product of known composition by suitable heat treatment. This product is then weighed.

For example, in a precipitation method for determining calcium in natural waters recommended by an excess of oxalic acid $H_2C_2O_4$, is added to a carefully measured volume of the sample. The addition of ammonia causes essentially all of the calcium in the sample to

precipitate as calcium oxalate, The reaction is



The precipitate is collected in a weighed filtering crucible, dried, and ignited at a red heat.

This process converts the precipitate entirely to calcium oxide. The reaction is



The crucible and precipitate are cooled, weighed and the mass of calcium oxide determined by difference.

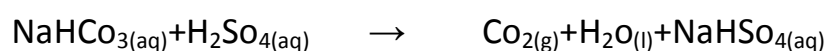


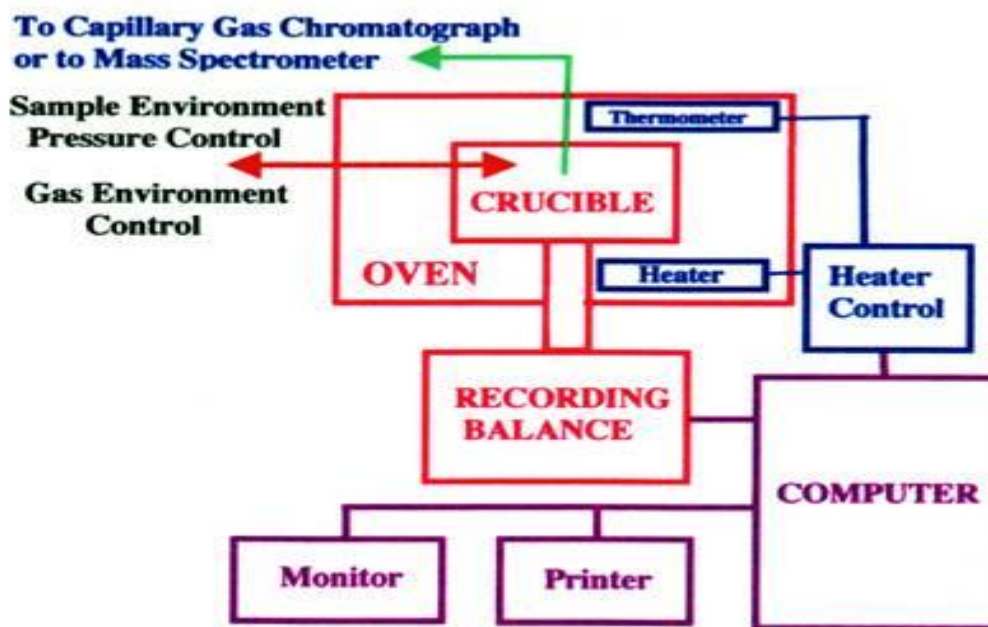
2- Volatilization methods

The analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, or alternatively the mass of the product is determined indirectly from the loss in mass of the sample.

An example of a gravimetric volatilization procedure is the determination of the sodium hydrogen carbonate content of antacid tablets.

Here a weighed sample of the finely ground tablets is treated with dilute sulfuric acid to convert the sodium hydrogen carbonate to carbon dioxide:





Gravimetric calculations of chemical analysis:

wt = weight

m.wt = molecular weight

n = number of moles

$$n = \frac{\text{weight}}{\text{molecular weight}} = \frac{wt}{m.wt}$$

Weight = mass

Molar mass:

The molar mass (m) of a substance is the mass in grams of (1)mole of that substance .

Molar masses of compounds are derived by summing the masses of all the atoms appearing in a chemical formula.

For example, the molar mass of formaldehyde, CH_2O , is

$$M_{\text{CH}_2\text{O}} = \frac{1 \text{ mol C}}{\text{mol CH}_2\text{O}} * \frac{12.00 \text{ g C}}{1 \text{ mol C}} + \frac{2 \text{ mol H}}{\text{mol CH}_2\text{O}} * \frac{1.00 \text{ g H}}{1 \text{ mol H}} + \frac{1 \text{ mol O}}{\text{mol CH}_2\text{O}} * \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 30.00 \text{ g/mol CH}_2\text{O}$$

ex/ how many moles and millimoles are contained in (2.00g) of pure benzoic acid (122.1g /mol) ?

solution/

$$1 \text{ mol HBZ} \equiv 122.1 \text{ g}$$

$$N \text{ of HBZ} = 2.00 \text{ g HBZ} \times \frac{1 \text{ mol HBZ}}{122.1 \text{ g HBZ}}$$

$$= 0.0164 \text{ mol HBZ}$$

To obtain the number of millimoles, we divide by the millimolar mass (0.1221g 1mmol). that is

$$N \text{ of HBZ} = 2.00 \text{ g HBZ} \times \frac{1 \text{ mmol HBZ}}{0.1221 \text{ g HBZ}} = 16.4 \text{ mmol HBZ}$$

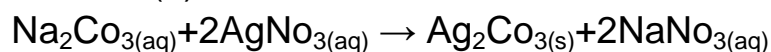
Stoichiometric calculations:

Stoichiometry is defined as the mass relationship among reacting chemical species.

Ex/a) what mass of AgNO_3 (169.9g 1mol) is needed to convert 2.33g of Na_2CO_3 (106.0g 1mol) to Ag_2CO_3 ?

b) what mass of Ag_2CO_3 (275.7g 1 mol) will be formed ?

solution/(a)



$$1\text{-no. mol Na}_2\text{CO}_3 = 2.33\text{g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0\text{g Na}_2\text{CO}_3}$$

$$= 0.02198 \text{ mol Na}_2\text{CO}_3$$

2- the balanced equation reveals that 1 mol $\text{Na}_2\text{CO}_3 \equiv 2 \text{ mol AgNO}_3$

$$\text{No. mol AgNO}_3 = 0.02198 \text{ mol Na}_2\text{CO}_3 \times \frac{2 \text{ mol AgNO}_3}{1 \text{ mol Na}_2\text{CO}_3}$$

$$= 0.04396 \text{ mol AgNO}_3$$

Here the stoichiometric factor is (2 mol AgNO_3 / 1 mol Na_2CO_3)

$$3\text{- mass AgNO}_3 = 0.04396 \text{ mol AgNO}_3 \times \frac{169.9\text{g AgNO}_3}{\text{mol AgNO}_3}$$

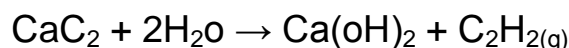
$$= 7.47\text{g AgNO}_3$$

B) no. mol $\text{Ag}_2\text{CO}_3 = \text{no. mol Na}_2\text{CO}_3 = 0.02198 \text{ mol}$

$$\text{Mass Ag}_2\text{CO}_3 = 0.02198 \text{ mol Ag}_2\text{CO}_3 \times \frac{275.7\text{g Ag}_2\text{CO}_3}{\text{mol Ag}_2\text{CO}_3}$$

$$= 6.06\text{g Ag}_2\text{CO}_3$$

Ex / Acetylene, which is used as a fuel in welding torches, is produced in a reaction between calcium carbide and water.



1) How many moles of C_2H_2 would be produced from 2.50 mol of CaC_2 ?

2) How many grams of C_2H_2 would be formed from 0.5 mol of H_2O ?

3) How many grams of Ca(OH)_2 are produced when 26.0g of C_2H_2 is formed ?

Solution/

1) 1 mol $\text{CaC}_2 \equiv 1 \text{ mol C}_2\text{H}_2$

$$\text{No. mol C}_2\text{H}_2 = 2.50 \text{ mol CaC}_2 \times \frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol CaC}_2}$$

$$= 2.50 \text{ mol C}_2\text{H}_2$$

$$2) \quad 2 \text{ mol H}_2\text{O} \equiv 1 \text{ mol C}_2\text{H}_2$$

$$\text{No. mol C}_2\text{H}_2 = 0.5 \text{ mol H}_2\text{O} \times \frac{1 \text{ mol C}_2\text{H}_2}{2 \text{ mol H}_2\text{O}}$$

$$= 0.25 \text{ mol C}_2\text{H}_2$$

$$1 \text{ mol C}_2\text{H}_2 \equiv 26.0 \text{ g}$$

$$\text{Weight C}_2\text{H}_2 = 0.25 \text{ mol C}_2\text{H}_2 \times \frac{26.0 \text{ g C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} = 6.5 \text{ g C}_2\text{H}_2$$

$$3) \quad 1 \text{ mol C}_2\text{H}_2 \equiv 1 \text{ mol Ca(OH)}_2$$

$$\text{No. mol C}_2\text{H}_2 = \frac{26.0 \text{ g C}_2\text{H}_2}{26.0 \text{ g C}_2\text{H}_2} \times \frac{1 \text{ mol C}_2\text{H}_2}{1 \text{ mol C}_2\text{H}_2} = 1 \text{ mol C}_2\text{H}_2$$

$$\text{No. mol Ca(OH)}_2 = 1 \text{ mol C}_2\text{H}_2 \times \frac{1 \text{ mol Ca(OH)}_2}{1 \text{ mol C}_2\text{H}_2} = 1 \text{ mol Ca(OH)}_2$$

$$1 \text{ mol Ca(OH)}_2 \equiv 74.0 \text{ g}$$

$$\text{Weight of Ca(OH)}_2 = 1 \text{ mol Ca(OH)}_2 \times \frac{74.0 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} = 74.0 \text{ g}$$

Ex/ What mass of AgCl can produce from 0.615 gm sample that assays 30.1% AlCl₃ ?

Solution/

$$1 \text{ mol AlCl}_3 \equiv 132 \text{ gm}$$

$$\text{No. mol AlCl}_3 = 0.615 \text{ gm AlCl}_3 \times \frac{1 \text{ mol AlCl}_3}{132 \text{ gm AlCl}_3}$$

$$= 4.66 \times 10^{-3} \text{ mol AlCl}_3$$

The amount of AlCl₃ in the sample is :

$$4.66 \times 10^{-3} \text{ mol} \times 0.301 = 1.402 \times 10^{-3} \text{ mol}$$

$$1 \text{ mol AlCl}_3 \equiv 3 \text{ mol AgCl}$$

$$\text{No. mol AgCl} = 1.402 \times 10^{-3} \text{ mol AlCl}_3 \times \frac{3 \text{ mol AgCl}}{1 \text{ mol AlCl}_3}$$

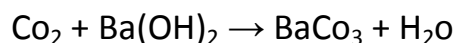
$$= 4.206 \times 10^{-3} \text{ mol AgCl}$$

$$1 \text{ mol AgCl} \equiv 143 \text{ gm}$$

$$\text{Mass AgCl} = 4.206 \times 10^{-3} \text{ mol} \times \frac{143 \text{ gm}}{1 \text{ mol}} = 0.601 \text{ gm AgCl}$$

Ex/A 0.2011gm sample of an organic compound was burned in a stream of oxygen , and CO₂ produced in a solution of barium hydroxide.

Calculate the percentage of carbon in the sample if 0.500gm BaCo₃ was formed .



Solution/

$$1 \text{ mol BaCO}_3 \equiv 197.0\text{gm}$$

$$\text{No . mol BaCO}_3 = 0.500 \text{ gm BaCO}_3 \times \frac{1 \text{ mol BaCO}_3}{197 \text{ gm BaCO}_3} = 2.538 \times 10^{-3}$$

mol BaCO₃

$$1 \text{ mol BaCO}_3 \equiv 1 \text{ mol CO}_2 = 2.538 \times 10^{-3} \text{ mol}$$

$$1 \text{ mol CO}_2 \equiv 44.0\text{gm}$$

$$\text{Mass CO}_2 = 2.538 \times 10^{-3} \text{ mol CO}_2 \times \frac{44.0 \text{ gm}}{1 \text{ mol CO}_2}$$

$$= 0.1116 \text{ gm CO}_2$$

$$\text{M CO}_2\% = \frac{m \text{ CO}_2}{m \text{ comp}} \times 100$$

$$\% = \frac{0.1116}{0.2011} \times 100 = 55.49 \%$$

Ex/A 0.3516 gm sample of a commercial phosphate detergent was ignited at a red heat to destroy the organic matter . the residue was then taken up in hot HCl, which converted the P to H₃po₄. The phosphate was precipitated as MgNH₄Po₄.6H₂o by addition of Mg⁺² followed by aqueous NH₃ . after being filtered and washed. The precipitate was converted to Mg₂p₂o₇(222.57gm mol) by ignition at 1000 C⁰ this residue weighed 0.2161gm. Calculate the percent P(30.974gm mol) in the sample.

Solution/

$$\text{No. mol MP} = 0.2161 \text{ gm MP} \times \frac{1 \text{ mol MP}}{222.57 \text{ gm MP}} = 19.418 \times 10^{-4} \text{ mol P}$$

1 mol MP \equiv 2 mol P

No. mol P = 30.774 gm

$$\text{Mass P} = 19.418 \times 10^{-4} \text{ mol} \times \frac{30.974 \text{ gm}}{\text{mol}} = 0.06015 \text{ gm P}$$

$$\text{Percent P\%} = \frac{0.06015}{0.3516} \times 100 = 17.107 = 17.11\%$$

Ex/A 0.7151 gm sample of impure $\text{Al}_2(\text{CO}_3)_3$ decomposed with HCl. The liberated CO_2 was collected on calcium oxide and found to weight 0.0621 gm the percentage of (Al) in the sample ?

Solution/

1 mol $\text{CO}_2 \approx 44.0 \text{ gm}$

$$\text{No. mol } \text{CO}_2 = 0.0621 \text{ gm } \text{CO}_2 \times \frac{1 \text{ mol } \text{CO}_2}{44.0 \text{ gm } \text{CO}_2} = 1.411 \times 10^{-3} \text{ mol}$$

1 mol $\text{Al}_2(\text{CO}_3)_3 \equiv 3 \text{ mol}(\text{CO}_2)$

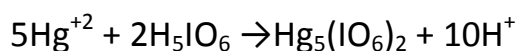
1 mol $\text{Al}_2(\text{CO}_3)_3 \equiv 2 \text{ mol}(\text{Al})$

$$\text{No. mol Al} = 1.411 \times 10^{-3} \text{ mol } \text{CO}_2 \times \frac{2 \text{ mol Al}}{3 \text{ mol } \text{CO}_2} = 0.941 \times 10^{-3} \text{ mol Al}$$

$$\text{Mass. Al} = 0.041 \times 10^{-3} \text{ mol} \times \frac{234 \text{ gm}}{1 \text{ mol}} = 0.22 \text{ gm Al}$$

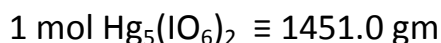
$$\% \text{ Al} = \frac{0.22 \text{ gm}}{0.7151 \text{ gm}} \times 100 = 30.76 \%$$

Ex / the mercury in a 0.8142 gm sample was precipitated with an excess of paraper iodic acid H_2IO_6



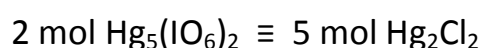
The precipitate was filtered free of precipitating agent, dried and weighed 0.4114 gm was recovered. Calculate the percentage of Hg_2Cl_2 in the sample.

Solution /



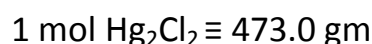
$$\text{No. mol Hg}_5(\text{IO}_6)_2 = 0.4114 \text{ gm Hg}_5(\text{IO}_6)_2 \times \frac{1 \text{ mol Hg}_5(\text{IO}_6)_2}{1451 \text{ gm Hg}_5(\text{IO}_6)_2}$$

$$= 2.84 \times 10^{-4} \text{ mol}$$



$$\text{No. mol Hg}_2\text{Cl}_2 = 2.84 \times 10^{-4} \text{ mol Hg}_5(\text{IO}_6)_2 \times \frac{5 \text{ mol Hg}_2\text{Cl}_2}{2 \text{ mol Hg}_5(\text{IO}_6)_2}$$

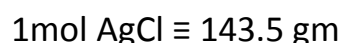
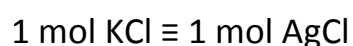
$$= 7.10 \times 10^{-4} \text{ mol}$$



$$\text{Mass of Hg}_2\text{Cl}_2 = 7.10 \times 10^{-4} \text{ mol} \times 473.0 \text{ gm / mol} = 0.3358 \text{ gm}$$

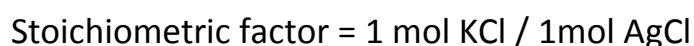
$$\% \text{ Hg}_2\text{Cl}_2 = \frac{0.3358 \text{ gm}}{0.8142 \text{ gm}} \times 100 = 41.24 \%$$

Ex / treatment of a 0.2500 gm sample of impure potassium chloride with an excess of AgNO_3 resulted in the formation of 0.2191 gm of AgCl . Calculate the percentage of KCl in the sample.



$$\text{No. mol AgCl} = 0.2191 \text{ gm AgCl} \times 1 \text{ mol AgCl} / 143.5 \text{ gm AgCl}$$

$$= 1.53 \times 10^{-3} \text{ mol AgCl}$$



$$\text{No. mol KCl} = 1.53 \times 10^{-3} \text{ mol AgCl} \times \frac{1 \text{ mol KCl}}{1 \text{ mol AgCl}} = 1.53 \times 10^{-3} \text{ mol KCl}$$

$$1 \text{ mol KCl} \equiv 74.5 \text{ gm KCl}$$

$$\text{Mass KCl} = 1.53 \times 10^{-3} \text{ mol KCl} \times 74.5 \text{ gm / mol KCl} = 0.114 \text{ gm KCl}$$

$$\% \text{ KCl} = 0.114 \text{ gm} / 0.2500 \text{ gm} \times 100 = 45.6 \%$$

Ex/ A sample of impure magnetite , Fe_3O_4 , weighing 1.542 gm is dissolved ; the iron is oxidized to Fe^+ and precipitated as $\text{Fe}(\text{OH})_3$. The precipitate is ignited to Fe_2O_3 , giving a weight of 1.485 gm .Calculate the percentage of Fe_3O_4 in the sample .

$$\text{No. mol Fe}_2\text{O}_3 = 1.485 \text{ gm Fe}_2\text{O}_3 \times \frac{\text{mol Fe}_2\text{O}_3}{159.7 \text{ gm Fe}_2\text{O}_3}$$

$$= 0.00930 \text{ mol Fe}_2\text{O}_3$$

This is equivalent to 2 / 3 as many moles of Fe_3O_4 , since 2 moles Fe_3O_4 will yield 3 moles Fe_2O_3 when oxidized.

$$2 \text{ moles Fe}_3\text{O}_4 \equiv 3 \text{ moles Fe}_2\text{O}_3$$

$$\text{No. mol Fe}_3\text{O}_4 = 0.00930 \text{ mole Fe}_2\text{O}_3 \times \frac{2 \text{ mole Fe}_3\text{O}_4}{3 \text{ mole Fe}_2\text{O}_3} = 0.00620 \text{ moles Fe}_3\text{O}_4$$

$$\text{Weight Fe}_3\text{O}_4 \text{ in sample} = 0.00620 \text{ mole} \times 231.55 \text{ gm / mole}$$

$$= 1.437 \text{ gm Fe}_3\text{O}_4$$

$$\text{Percentage Fe}_3\text{O}_4 = 1.437 \text{ gm} / 1.542 \text{ gm} \times 100 = 93.1 \%$$

Calculations involving concentrations of solutions

- 1- Physical methods :- the simplest ways of expressing the strength of a solution are in terms of the amount of solute present per unit amount of solvent or solution. Such methods are known as physical methods because they are based only on physical measurements of weight or volume and do not take into account the chemical reactions of the solute.

The more widely used physical methods are :

- 1- Grams solute per liter (or 1000ml) solution gm/L(solution)
gm/1000ml(solution).
- 2- Grams solute per liter (or 1000ml) solvent.
gm/L(solvent) gm/1000ml (solution).
- 3- Grams solute per unit weight of solution gm/gm (solution)
- 4- Grams solute per unit weight of solvent gm/gm(solvent)

1- Percentage methods.

$$\text{Weight percent (w/w)} = \frac{\text{mass solute}}{\text{mass solution}} \times 100\%$$

$$\text{Volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{Weight / volume percent (w/v)} = \frac{\text{mass solute,g}}{\text{volume solution,ml}} \times 100\%$$

Ex/Express the concentration with weight percent of the solution weighting 25.0gm and contained in 200.0gm of sodium sulphate Na_2SO_4 .
Solution/

$$\begin{aligned} \%(w/w) &= \frac{\text{weight of solute}}{\text{weight of solution}} \times 100 \\ &= \frac{25.0\text{gm solute}}{200.0\text{gm solution}} \times 100 = 12.5\% \end{aligned}$$

Ex/Use the weight percent, calculate the concentration of the solution when 3gm AgNO_3 dissolve in 1L distilled water ?

Solution/1L H_2O → weight H_2O

$$\text{Density} = \frac{\text{weight}}{\text{volume}}$$

$$\text{Weight (H}_2\text{O)} = \text{density} \times \text{volume}$$

$$= \frac{1\text{gm}}{\text{cm}^3} \times 1\text{L} \times \frac{1000\text{ cm}^3}{\text{L}}$$

$$\text{Weight} = \text{weight} + \text{weight}$$

$$\text{(solution)} \quad \text{(solute)} \quad \text{(solvent)}$$

$$= 3\text{gm} + 1000\text{gm} = 1003\text{gm}$$

$$(w/w)\% = \frac{3\text{gm}}{1003\text{gm}} \times 100 = 0.299\% \rightarrow 0.3\%$$

Ex/Use the volume percent, calculate the concentration of the solution is prepared by addition 50.0ml methanol (CH₃OH) to 200.0ml water?

Solution/

$$\text{Volume(solution)} = 50.0\text{ml} + 200.0\text{ml} = 250.0\text{ml}$$

$$V/V \% = \frac{50 \text{ ml}}{250 \text{ ml}} \times 100 = 20.0 \%$$

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

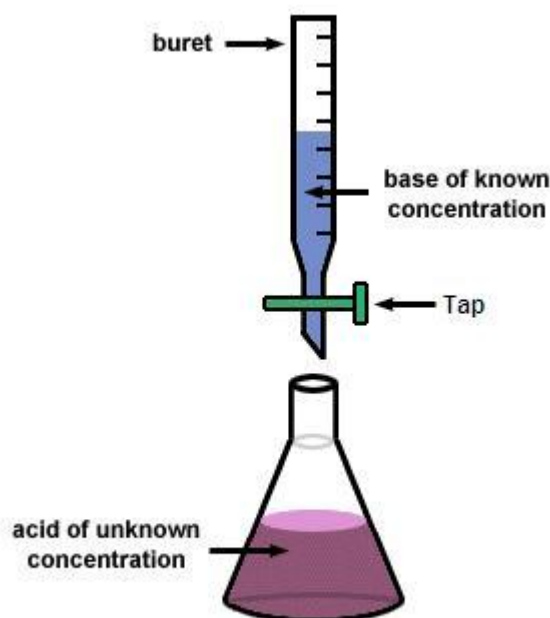
Molarity of solution : The number of moles of solute per liter of solution.

$$\text{Molarity}[M] = \frac{\text{number of moles solute}}{\text{liters of solution}}$$

$$\text{Molarity}[M] = \frac{\text{grams of solute}}{\text{molecular weight}} \times \frac{1}{\text{liters of solution}}$$

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 C_2H_5OH (46.07 gm /mole) in 3.50 L of solution.

Solution /

$$[C_2H_5OH] = \frac{\text{number of moles}}{\text{liter of solution}}$$

$$\begin{aligned} \text{No. mol } C_2H_5OH &= 2.30 \text{ gm } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ gm } C_2H_5OH} \\ &= 0.0499 \text{ mol } C_2H_5OH \end{aligned}$$

$$[C_2H_5OH] = \frac{0.0499 \text{ mol}}{3.5L} = 0.0143 \text{ mol / L} = 0.0143 \text{ M}$$

EX/Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contains 285.0 mg of trichloroacetic acid , Cl_3CCOOH (163.4gm / mol) , in 10.0ml.

Solution/



$$\begin{aligned} \text{No. mol HA} &= 285.0 \text{ mg HA} \times \frac{1 \text{ gm HA}}{1000 \text{ mg HA}} \times \frac{1 \text{ mol HA}}{163.4 \text{ gm HA}} \\ &= 1.744 \times 10^{-3} \text{ mol HA} \\ [\text{HA}] &= \frac{1.744 \times 10^{-3} \text{ mol HA}}{10.0 \text{ ml}} \times \frac{1000 \text{ ml}}{1 \text{ L}} \\ &= 0.174 \text{ mol HA / L} = 0.174 \text{ M} \end{aligned}$$

EX/ How many grams of AgNO_3 (169.9 gm/mol) must be used to prepared 500.0 ml of 0.125 M?

Solution/

$$\begin{aligned} M &= \frac{\text{wt}}{M.\text{wt}} \times \frac{1000}{V\text{ml}} \\ \text{Wt} &= \frac{M \times M.\text{wt} \times V\text{ml}}{1000} \\ &= \frac{0.125 \text{ mmol/ml} \times 169.9 \text{ mg/mmol} \times 500 \text{ ml}}{1000} = \\ &10.62 \text{ mg} \end{aligned}$$

Equivalent Methods:

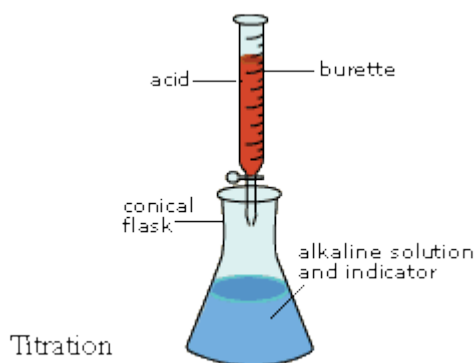
The equivalent weight (eq) is defined, for neutralization reactions, as the weight in grams that will furnish or react with one gram-atomic weight of hydrogen ion.

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{n} = \frac{M.Wt}{n}$$

$n = \text{no. H}^+$ for acid

$= \text{no. OH}^-$ for base

$= \text{no. electrons in the reaction.}$



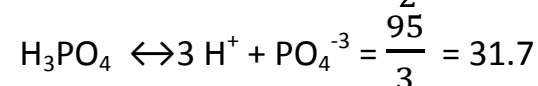
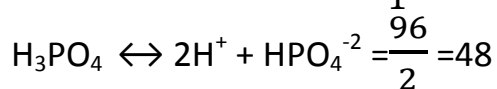
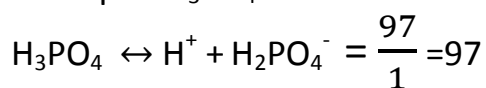
Example /

$$\text{Equivalent weight of HCl} = \frac{MHCl}{n} = \frac{36.5}{1} = 36.5$$

$$\text{For eq.wt NaOH} = \frac{MNaOH}{n} = \frac{40}{1} = 40$$

$$\text{For eq.wt Ba (OH)}_2 = \frac{MBa(OH)_2}{n} = \frac{171}{2} = 85.5$$

For eq.wt H₃PO₄



$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{no. of valency}} = \frac{M.wt}{n}$$

$$\text{Normality(N)} = \frac{\text{Equivalent Solute}}{\text{liters of solution}}$$

$$\text{Normality(N)} = \frac{\frac{\text{grams solute}}{\text{molecular weight}}}{\text{hydrogen equivalents per mole}} \times \frac{1}{\text{liters of solution}}$$

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 40.0g/mol) are needed for preparation of 500.0 ml 0.100N solution?



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

Equivalents of solute = normality x volume in liters
 = 0.100 eq / liter x 0.500 liter
 = 0.0500 eq

Equivalents of solute = $\frac{\text{weight in grams}}{\frac{\text{molecular weight}}{\text{no. of valency}}}$

$$0.0500 \text{ eq} = \frac{Wt}{\frac{40.0 \text{ g/mol}}{1 \text{ eq/mol}}}$$

Wt = 2.00 gm

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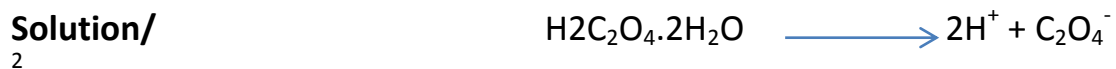
$$N = \frac{Wt}{\text{eq.wt}} \times \frac{1000}{Vml}$$

$$0.100 \text{ eq/L} = \frac{wt}{\frac{M.wt}{n}} \times \frac{1000}{500 \text{ ml}}$$

$$0.100 \text{ eq/L} = \frac{wt}{\frac{40.0 \text{ gm/mol}}{1 \text{ eq/mol}}} \times \frac{1000 \text{ ml/L}}{500 \text{ ml}}$$

Wt = 2.00 gm

Ex/What is the normality of a solution prepared by dissolving 25.20 gm oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (126.1 gm/mol) in sufficient water to give 1.200 liters of solution ? What is the molarity of this solution?



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

Number of equivalents = $\frac{\text{weight of solute}}{\frac{\text{molecular weight}}{\text{no. of valency}}}$
 = $\frac{25.20 \text{ gm}}{\frac{126.1 \text{ gm/mol}}{2 \text{ eq/mol}}} = 0.3996 \text{ eq}$

The Normality is :

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

The Molarity is:

$$M = \frac{N}{n} = \frac{0.3330 \text{ eq/liter}}{2 \text{ eq/mol}} = 0.1665 \text{ mol/liter}$$

Ex/How many grams of pure sodium sulfate Na_2SO_4 (M.wt 142.0g/mol) are needed for preparation of 200.0 ml 0.500N solution?

Solution/ $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{-2}$

$$N = \frac{wt}{eq.wt} \times \frac{1000}{Vml}$$

$$0.500eq/L = \frac{wt}{\frac{142gm/mol}{2eq/mol}} \times \frac{1000ml/L}{200ml}$$

$$Wt = 7.1 \text{ gm}$$

Ex/Describe the preparation of 5.000 L of 0.1000M Na_2CO_3 (105.99g/mol) from the primary standard solid?

Solution/

$$\text{Molarity} = \frac{\text{number of moles solute}}{\text{liters of solution}}$$

$$\text{Moles of solute} = M \times V$$

$$= 0.1000\text{mol/L} \times 5.000\text{L} = 0.5000\text{mol}$$

$$\text{Grams of solute} = 0.500\text{mol} \times \frac{105.999\text{gm}}{\text{mol}}$$

$$= 53.00 \text{ gm Na}_2\text{CO}_3$$

Therefore the solution is prepared by dissolving 53.00 gm of Na_2CO_3 in water and diluting to exactly 5.00 L.

Ex/

A standard 0.0100 M solution of 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 Na_2CO_3 ?

Solution/ $\text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}^+ + \text{CO}_3^{-2}$

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

$$\text{Moles of Na}_2\text{CO}_3 = 5 \text{ mmol Na}^+ \times \frac{1 \text{ mmol Na}_2\text{CO}_3}{2 \text{ mmol Na}^+} = 2.5 \text{ mmol}$$

$$\text{Grams of Na}_2\text{CO}_3 = 2.5 \text{ mmol} \times 0.10599 \text{ gm/mmol} = 0.265 \text{ gm}$$

The solution is therefore prepared by dissolving 0.265 gm of Na_2CO_3 in water and diluting to 500.0ml.

Density and specific gravity of 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 gravity is 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.

Ex/ Calculate the molar concentration of HNO₃ (63.0gm/mol) in a solution that has a specific gravity of 1.42 and is 70% HNO₃(W/W).

Solution/

$$M = \frac{SP.gr \times \% \times 1000}{M.wt}$$

$$M = \frac{1.42 \times 1000 \cancel{gm \ reagent} \times 70 \cancel{gm \ HNO_3} \times 1 \ mol \ HNO_3}{L \ reagent \times 100 \cancel{gm \ reagent} \times 63 \ gm \ HNO_3}$$

$$= 15.8 \text{ mol/L} = 15.8 \text{ M}$$

Ex/ Calculate the Normality of H₂SO₄ (98.08gm/mol) in a solution has a specific gravity of 1.84 and is 98% H₂SO₄(W/W).

Solution/

$$N = \frac{SP.gr \times \% \times 1000}{eq.wt}$$

$$N = \frac{1.84 \times 1000 \cancel{gm \ reagent} \times 98 \cancel{gm \ H_2SO_4} \times 1 \ eq \ H_2SO_4}{L \ reagent \times 100 \cancel{gm \ reagent} \times 49.04 \ gm \ H_2SO_4}$$

$$N = 36.8 \text{ eq/L} = 36.8 \text{ N}$$

Ex/ Sulfuric acid of density 1.3028gm per milliliter, 40.0 percent H₂SO₄ By weight. Compute the normality and molarity of the solution?

Solution/

$$N = \frac{SP.gr \times \% \times 1000}{eq.wt}$$

$$N = \frac{1.3028 \times 1000 \cancel{gm \ reagent} \times 40.0 \cancel{gm \ H_2SO_4} \times 1 \ eq \ H_2SO_4}{L \ reagent \times 100 \cancel{gm \ reagent} \times 49.04 \ gm \ H_2SO_4}$$

$$N = 10.63 \text{ eq/L} = 10.63 \text{ N}$$

$$M = \frac{N}{Valency} = \frac{10.63 \text{ eq/L}}{2 \text{ eq/mol}} = 5.31 \text{ mol/L} = 5.31 \text{ M}$$

Ex/ A sample of impure oxalic acid (H₂C₂O₄.2H₂O)(126.1gm/mol) which weighs 0.4750 gm requires 35.60 ml 0.2000N solution hydroxide for its titration. Calculate the percentage of oxalic acid in the sample.

Solution/ H₂C₂O₄.2H₂O + 2NaOH → Na₂C₂O₄ + 4H₂O

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

Equivalent Base = Equivalent Acid

Equivalent NaOH = Equivalent H₂C₂O₄

Milliequivalent NaOH = N x liter of solution

$$= 0.200 \text{ meq/ml} \times 35.60 \text{ ml}$$

$$= 7.12 \text{ meq} \times \text{eq/1000meq}$$

$$= 7.12 \times 10^{-3} \text{ eq}$$

Weight($\text{H}_2\text{C}_2\text{O}_4$) = equivalent of acid x equivalent weight

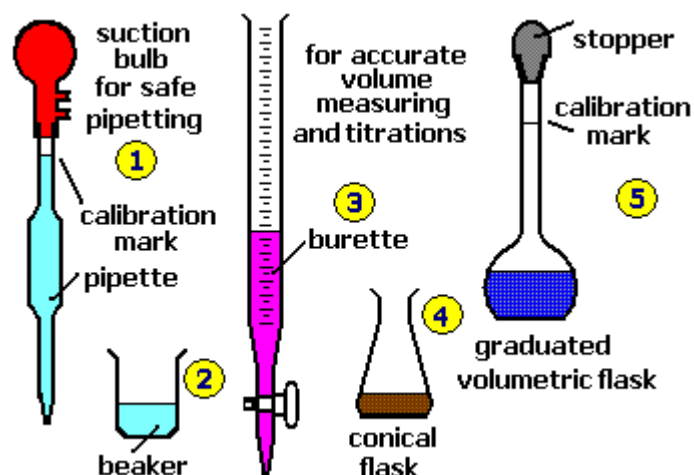
$$= 7.12 \times 10^{-3} \text{ eq} \times \frac{126.1 \text{ gm/mol}}{2 \text{ eq/mol}}$$

$$= 0.4489 \text{ gm}$$

Percentage = $\frac{\text{grams of oxalic acid}}{\text{weight of sample}} \times 100$

$$= \frac{0.4489 \text{ gm}}{0.4750 \text{ gm}} \times 100 = 94.51 \%$$

Dilution of solutions



A solution of known normality is frequently prepared from a more concentrated one of known strength by quantitative dilution.

$$N_{\text{conced}} \times V_{\text{conced}} = N_{\text{dil.}} \times V_{\text{dil.}}$$

Ex/What volume of 0.1500 N reagent is needed for the preparation of 500.0 ml ,0.100 N solution?

Solution/

$$N_{\text{conced}} \times V_{\text{conced}} = N_{\text{dil.}} \times V_{\text{dil}}$$

$$V_{\text{conced}} = \frac{N_{\text{dil}} \times V_{\text{dil}}}{N_{\text{conced}}} = \frac{0.100N \times 500.0 \text{ ml}}{0.1500N} = 333.3 \text{ ml}$$

Ex/ Describe the preparation of 100 ml 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37%(w/w)HCl?

Solution/

$$[\text{HCl}] = \frac{\text{sp.gr} \times \% \times 1000}{M.wt}$$

$$= \frac{1.18 \times 1000 \text{ gm reagent} \times 37 \text{ gm HCl} \times 1 \text{ mol HCl}}{L \text{ reagent} \times 100 \text{ gm reagent} \times 36.5 \text{ gm HCl}}$$

$$M = 12.0 \text{ mol/L} = 12.0 \text{ M}$$

$$\text{No.mol HCl} = 100 \text{ ml} \times 6.0 \text{ mmol/ml}$$

$$= 600.0 \text{ mmol} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} = 0.6 \text{ mol}$$

$$V_{\text{conced reagent}} = 0.6 \text{ mol} \times \frac{1 \text{ l reagent}}{12.0 \text{ mol}} = 0.05 \text{ l} \times 1000 \text{ ml/l} \\ = 50 \text{ ml}$$

Thus dilute 50 ml of the concentrated reagent to 100 ml.

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$$M_{\text{conced}} \times V_{\text{conced}} = M_{\text{dil.}} \times V_{\text{dil.}}$$

$$12.0 \text{ M} \times V_{\text{conced}} = 6.0 \text{ M} \times 100 \text{ ml}$$

$$V_{\text{conced}} = \frac{6.0 \text{ M} \times 100 \text{ ml}}{12.0 \text{ M}} = 50 \text{ ml}$$

Ex/ What volume of H_2SO_4 reagent is needed for the preparation of 200.0 ml, 0.3 N solution that has a specific gravity of 1.84 and is 98% (w/w) H_2SO_4 ?

Solution/

$$[\text{H}_2\text{SO}_4] = \frac{1.84 \times 1000 \text{ gm reagent} \times 98 \text{ gm H}_2\text{SO}_4 \times 1 \text{ eq H}_2\text{SO}_4}{\text{L reagent} \times 100 \text{ gm reagent} \times 49.0 \text{ gm H}_2\text{SO}_4} \\ = 36.8 \text{ eq / L} = 36.8 \text{ N}$$

$$\text{No. eq H}_2\text{SO}_4 = 200.0 \text{ ml} \times 0.3 \text{ meq / ml} \\ = 60.0 \text{ meq}$$

$$V_{\text{conced reagent}} = 60.0 \text{ meq} \times \frac{1 \text{ ml}}{36.8 \text{ meq H}_2\text{SO}_4} = 1.63 \text{ ml}$$

Dilute 1.63 ml of the concentrated reagent to 200.0 ml

Analysis of samples by titration with standard solution

Titrimetric methods include a large and powerful group of quantitative procedures that are based upon measuring the amount of a reagent of known concentration that is consumed by the analyte.

Volumetric titrimetry involves measuring the volume of a solution of known concentration that is needed to react essentially completely with the analyte.

Standard solution (standard titrant) : is a reagent of known concentration that is used to carry out a titrimetric analysis.

The equivalence point in titration is reached the amount of added titrant is chemically equivalent to the amount of analyte in the sample.

For example: the equivalence point in the titration of sodium chloride with silver nitrate occurs after exactly 1 mol of silver ion has been added for each mol of chloride ion in the sample.

The equivalence point in the titration of sulfuric acid with sodium hydroxide is reached after introduction of 2 mol of base for each mol of acid.

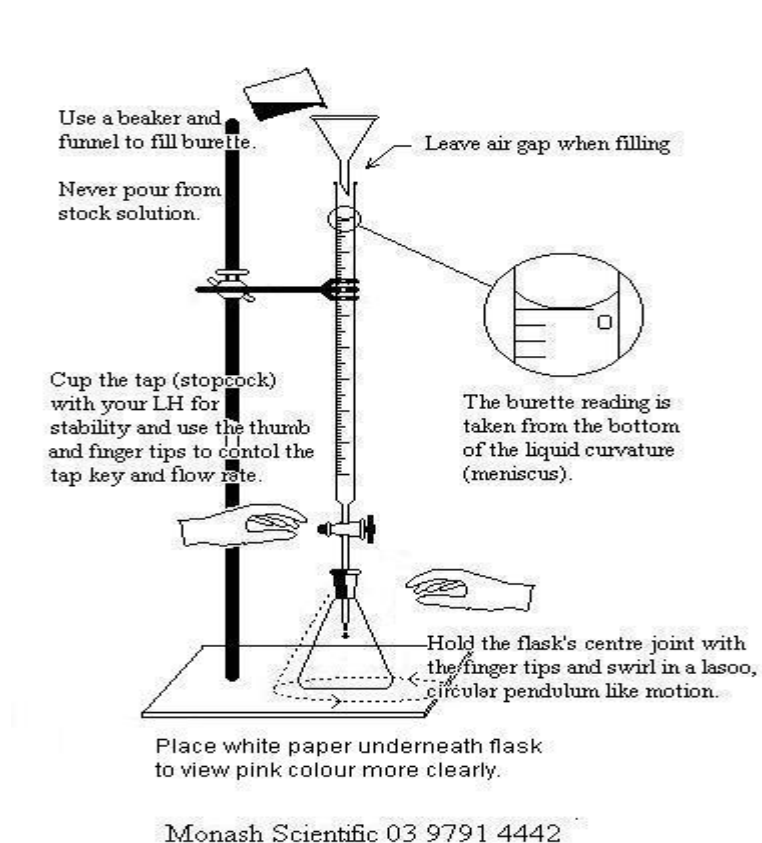
Acid and base samples are analyzed by titration with a standard solution. A weighed portion of sample is dissolved in water and standard acid or base is added to the proper end point. From the volume of reagent used and the weight of sample, the percentage purity of the sample is computed.

The basis for all computations dealing with normalities of solutions is the simple relation that the number of equivalents or milliequivalents of one reaction is equal to the number for the other reactant thus

A reacts with B

Equivalents A = Equivalents B

Milliequivalents A = Milliequivalents B



Ex/A sample of impure calcite (CaCO_3)(100.1 gm /mol) which weighs 0.4950 gm is dissolved in 50.00 ml of standard acid and the excess acid is titrated with 5.25 ml standard base; 1.00 ml of acid is equivalent to 0.005300 gm sodium carbonate; 1.050 ml acid = 1.00 ml base. Calculate the percentage of calcium carbonate in the sample.

Solution/

1 ml of acid \equiv 0.005300 gm Na_2CO_3

$$\text{N of acid} = \frac{5.300 \text{ mg}}{53.00 \text{ mg / meq}} \times \frac{1}{1 \text{ ml}} = 0.1000 \text{ meq / ml}$$

$$\begin{aligned} \text{Net volume acid required for titration of sample} &= 50.00 - \left(5.25 \times \frac{1.050}{1.000} \right) \\ &= 44.49 \text{ ml} \end{aligned}$$

$$\begin{aligned} \text{Milliequivalents acid} &= \text{Milliequivalents CaCO}_3 \\ &= 44.49 \text{ ml} \times 0.100 \text{ meq / ml} = 4.449 \text{ meq} \end{aligned}$$

$$\text{Milliequivalents CaCO}_3 = \frac{\text{weight of solute}}{\text{eq.wt}}$$

$$\begin{aligned} \text{Weight CaCO}_3 &= \text{Milliequivalents} \times \text{eq.wt} \\ &= 4.449 \text{ meq} \times \frac{100.1 \text{ mg/mmol}}{2 \text{ meq / mmol}} \\ &= 222.7 \text{ mg} \end{aligned}$$

$$\text{Percentage CaCO}_3 \text{ in sample} = \frac{222.7}{495.0} \times 100 = 44.99\%$$

Ex/ What must be the normality of sodium hydroxide solution if the volume in milliliters used for the titration of a 0.500 gm sample represents that percentage of acetic acid in the sample?

Solution/

$$1 \text{ eq acid} \equiv 1 \text{ eq base}$$

$$1 \text{ ml of NaOH} \equiv 0.5 \text{ gm \% acetic acid}$$

$$1 \text{ ml of NaOH} \equiv \frac{0.5 \text{ gm} \times 1000 \text{ mg/gm}}{100}$$

$$1 \text{ ml of NaOH} \equiv 5.00 \text{ mg acetic acid}$$



$$\text{N of NaOH} = \frac{5.00 \text{ mg/ml}}{60.05 \text{ mg/meq}} = 0.0833 \text{ meq/ml}$$

Ex/ What is the normality of hydrochloric acid solution having a sodium carbonate titer of a 5.00 mg per milliliter?

Solution/

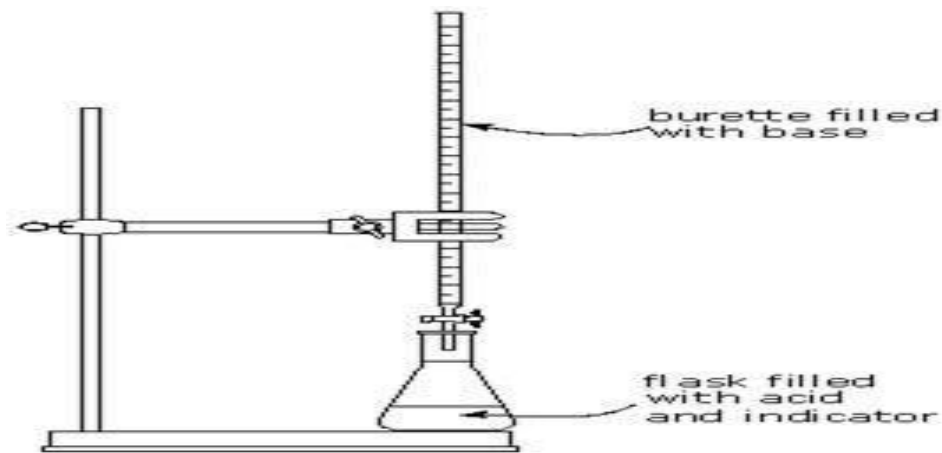
$$\text{N of base} \equiv \text{N of acid}$$

$$1 \text{ ml of acid} \equiv 5 \text{ mg Na}_2\text{CO}_3$$

$$N = \frac{wt}{eq.wt} \times \frac{1}{volume(ml)}$$

$$N = \frac{50\text{-}mg}{\frac{106\text{ }mg/mmol}{2\text{ }meq/mmol}} \times \frac{1}{1ml} = 0.094\text{ }meq/ml$$

Titration in the volumetric analysis



Titration : is an analytical procedure that allows us to measure the amount of a solution reagent of known concentration that is consumed by the analyte.

Titrant : is the solution reagent in buret.

Titrand : is the analyte in beaker.

End point : is the point in which the color of the indicator changes.

Indicator : is a substance (acid or base organic compound) that has one

Calculation of molarities from neutralization reaction (acid-base)

Ex/ Exactly 50.00 ml of an HCl solution required 29.71 ml of 0.0193M Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCL.

Solution:



1mmole of $\text{Ba(OH)}_2 \equiv 2\text{mmole of HCl}$

$$\text{Stoichiometric ratio} = \frac{2\text{mmole HCl}}{1\text{mmol Ba(OH)}_2}$$

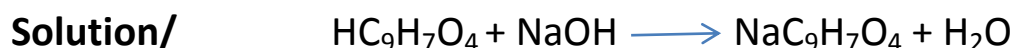
$$\begin{aligned} \text{No. moles Ba(OH)}_2 &= 29.71 \cancel{\text{ml}} \times 0.01963 \text{ mmol} / \cancel{\text{ml}} \\ &= 0.583 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{No. mmoles HCl} &= 0.583 \cancel{\text{mmol Ba(OH)}_2} \times \frac{2\text{mmol HCl}}{1\text{mmol Ba(OH)}_2} \\ &= 1.166 \text{ mmol HCl} \end{aligned}$$

$$M_{\text{HCl}} = \frac{1.166\text{mmol HCl}}{50.0 \text{ ml HCl}} = 0.0233 \text{ mmol} / \text{ml} = 0.0233 \text{ M}$$

Ex/ Titration of a sample of a drug was analyzed for aspirin a monoprotic acid ($\text{HC}_9\text{H}_7\text{O}_4$) of 0.500 gm sample of the drug required 21.50 ml of 0.100M NaOH for complete neutralization.

What percentage by mass of the drug was aspirin?



1mmol of $\text{HC}_9\text{H}_7\text{O}_4 \equiv 1\text{mmol of NaOH}$

$$\begin{aligned} \text{No. mmoles NaOH} &= 21.50 \cancel{\text{ml}} \times 0.100 \text{ mmol} / \cancel{\text{ml}} \\ &= 2.15 \cancel{\text{mmol}} \times 10^{-3} \text{ mol} / \cancel{\text{mmol}} = 2.15 \times 10^{-3} \end{aligned}$$

mol

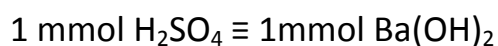
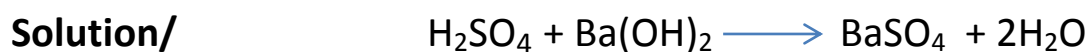
$$1 \text{ mol of HC}_9\text{H}_7\text{O}_4 \equiv 1 \text{ mol NaOH}$$

$$1 \text{ mol HC}_9\text{H}_7\text{O}_4 \equiv 180 \text{ gm}$$

$$\begin{aligned} \text{Mass of aspirin} &= 2.15 \times 10^{-3} \cancel{\text{mol}} \times 180 \text{ gm} / \cancel{\text{mol}} \\ &= 0.387 \text{ gm} \end{aligned}$$

$$\% \text{ Aspirin} = \frac{0.387 \text{ gm}}{0.500 \text{ gm}} \times 100 = 77.4 \%$$

Ex/ Calculate the molarity of the Ba(OH)₂ solution if 31.76 ml were needed to neutralize 46.25 ml of 0.1280 M H₂SO₄.



$$\text{Stoichiometric ratio} = \frac{1 \text{ mmol Ba}(\text{OH})_2}{1 \text{ mmol H}_2\text{SO}_4}$$

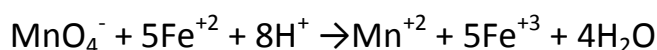
$$\begin{aligned} \text{No. mmoles H}_2\text{SO}_4 &= 46.25 \text{ ml H}_2\text{SO}_4 \times 0.1280 \text{ mmol H}_2\text{SO}_4 / \text{ml H}_2\text{SO}_4 \\ &= 5.92 \text{ mmol H}_2\text{SO}_4 \end{aligned}$$

$$\begin{aligned} \text{No. mmoles Ba}(\text{OH})_2 &= 5.92 \text{ mmol H}_2\text{SO}_4 \times \frac{1 \text{ mmol Ba}(\text{OH})_2}{1 \text{ mmol H}_2\text{SO}_4} \\ &= 5.92 \text{ mmol Ba}(\text{OH})_2 \end{aligned}$$

$$M_{\text{Ba}(\text{OH})_2} = \frac{5.92 \text{ mmol}}{31.76 \text{ ml}} = 0.1864 \text{ mmol / ml} = 0.1864 \text{ M}$$

Calculation of Oxidation – Reduction titration

EX/A 0.8040 gm sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{+2} and titrated with 47.22 ml of 0.022242 M KMnO_4 solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 gm/mol) and (b) % Fe_3O_4 (231.51 gm/mol). The reaction of the analyte with the reagent is described by the equation:



Solution/

(a) Stoichiometric ratio = 5 mmol Fe^{+2} / 1mmol KMnO_4

$$\begin{aligned} \text{Amount } \text{KMnO}_4 &= 47.22 \text{ ml } \text{KMnO}_4 \times 0.022242 \text{ mmol } \text{KMnO}_4 / \text{ml} \\ &\text{KMnO}_4 \end{aligned}$$

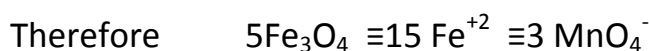
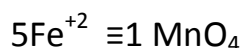
$$= 1.0587 \text{ mmol } \text{KMnO}_4$$

$$\begin{aligned} \text{Amount } \text{Fe}^{+2} &= 1.0587 \text{ mmol } \text{KMnO}_4 \times 5 \text{ mmol } \text{Fe}^{+2} / 1 \text{ mmol } \text{KMnO}_4 \\ &= 5.2935 \text{ mmol } \text{Fe}^{+2} \end{aligned}$$

$$\begin{aligned} \text{Mass } \text{Fe}^{+2} &= 5.2935 \text{ mmol } \text{Fe}^{+2} \times 0.055847 \text{ gm } \text{Fe}^{+2} / \text{mmol } \text{Fe}^{+2} \\ &= 0.2956 \text{ gm } \text{Fe}^{+2} \end{aligned}$$

$$\begin{aligned} \% \text{Fe}^{+2} &= 0.2956 \text{ gm } \text{Fe}^{+2} / 0.8040 \text{ gm sample} \times 100 \\ &= 36.77 \% \end{aligned}$$

(b) in order to derive a stoichiometric ratio, we note that



$$\text{Stoichiometric ratio} = 5 \text{ mmol } \text{Fe}_3\text{O}_4 / 3 \text{ mmol } \text{KMnO}_4$$

$$\begin{aligned} \text{Amount } \text{KMnO}_4 &= 47.22 \text{ ml } \text{KMnO}_4 \times 0.022242 \text{ mmol } \text{KMnO}_4 / \text{ml} \\ &\text{KMnO}_4 \end{aligned}$$

$$= 1.0587 \text{ mmol } \text{KMnO}_4$$

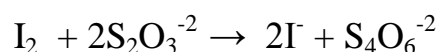
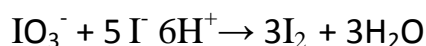
$$\begin{aligned} \text{Amount } \text{Fe}_3\text{O}_4 &= 1.0587 \text{ mmol } \text{KMnO}_4 \times 5 \text{ mmol } \text{Fe}_3\text{O}_4 / 3 \text{ mmol } \text{KMnO}_4 \\ &= 1.7644 \text{ mmol } \text{Fe}_3\text{O}_4 \end{aligned}$$

$$\text{Mass Fe}_3\text{O}_4 = 1.7644 \text{ mmol} \times 0.23154 \text{ gm / mmol}$$

$$= 0.4086 \text{ gm}$$

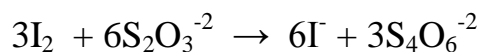
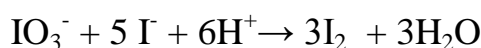
$$\% \text{Fe}_3\text{O}_4 = 0.4086 \text{ gm} / 0.8040 \text{ gm} \times 100 = 50.81 \%$$

Ex/ Titration of the I_2 produced from 0.1238 gm of primary – standard KIO_3 required 41.27ml of sodium thiosue :



Calculate the concentration of the $\text{Na}_2\text{S}_2\text{O}_3$.

Solution /



$$\text{No. mol KIO}_3 = 0.1238 \text{ gm} \times 1 \text{ mol} / 214.00 \text{ gm}$$

$$= 5.785 \times 10^{-4} \text{ mol} \times 10^3 \text{ mmol} / \text{mol}$$

$$= 0.5785 \text{ mmol KIO}_3$$

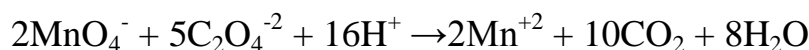
$$\text{No. mmol Na}_2\text{S}_2\text{O}_3 = 0.5785 \text{ mmol KIO}_3 \times 6 \text{ mmol Na}_2\text{S}_2\text{O}_3 / 1 \text{ mmol KIO}_3$$

$$= 3.471 \text{ mmol Na}_2\text{S}_2\text{O}_3$$

$$\text{M} = 3.471 \text{ mmol} / 41.27 \text{ ml} = 0.0841 \text{ M}$$

Ex / Titration of 0.2121 gm of pure $\text{Na}_2\text{C}_2\text{O}_4$ (134.00 gm / mol) required 43.31ml of KMnO_4 . What is the molarity of the KMnO_4 solution?

The chemical reaction is :



Solution /

$$\text{stoichiometric ratio} = 2 \text{ mmol KMnO}_4 / 5 \text{ mmol Na}_2\text{C}_2\text{O}_4$$

$$\text{Amount Na}_2\text{C}_2\text{O}_4 = 0.2121 \text{ gm} \times 1 \text{ mmol} / 0.13400 \text{ gm}$$

$$= 1.5828 \text{ mmol}$$

$$\text{Amount KMnO}_4 = 1.5828 \text{ mmol Na}_2\text{C}_2\text{O}_4 \times 2 \text{ mmol KMnO}_4 / 5 \text{ mmol}$$

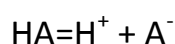
$$\text{Na}_2\text{C}_2\text{O}_4$$

$$= 0.6332 \text{ mmol KMnO}_4$$

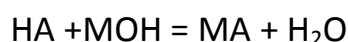
$$M = 0.6332 \text{ mmol KMnO}_4 / 43.31 \text{ ml KMnO}_4 = 0.01462 \text{ mmol/ml} = 0.01462 \text{ M}$$

Acid – base equilibria and PH of solutions

An acid is a substance that furnishes protons or H^+ ions and a base a substance that accepts protons. In classical terminology the acid HA dissociates in aqueous solution according to the equation



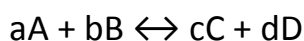
And a base MOH dissociates to give $\text{M}^+ + \text{OH}^-$ ions. The reaction of HA with MOH is



This reaction goes more or less to completion because the H_2O molecule is only slightly dissociated. To understand the limitations of acid-base titrations and the selection of proper indicators for such titrations, the student must understand the equilibrium relations involved in neutralization reactions.

Equilibrium constant :

A chemical reaction is at equilibrium when the rates of the forward and the concentrations of the reacting components are related by the equilibrium constant equation. For the reaction



We have the relation

$$K_e = [\text{D}]^d [\text{E}]^e / [\text{A}]^a [\text{B}]^b$$

In which the square brackets indicate the molar concentrations of the reacting species, and each molar concentration is raised to a power that is the coefficient of that substance in the chemical equation. The constant K_e is known as the equilibrium constant. Conventionally the products of the reaction are written in the numerator of the expression.

The equilibrium constant is experimentally determined for every reaction by measuring the concentrations of the reacting species after a condition of equilibrium has been attained. The constant is valid only at the temperature at which the determination is made, a change in temperature will change the equilibrium concentrations, there by changing the numerical value of K_e .

Factors effecting the equilibrium state:

Temperature , Pressure , Concentration, Time, Volume and Catalyst.

pH and Hydrogen ion concentration

Pure water dissociates slightly, forming equivalent amounts of hydronium and hydroxide ions , according to the equation



The H^+ ion formed by dissociation of one H_2O molecule unites with another H_2O molecule to form an hydronium ion. At room temperature the concentration of H_3O^+ and OH^- ions in pure water are each 1×10^{-7} molar.

The equilibrium expression for dissociation of water is :

$$K_e = [\text{H}_3\text{O}^+] [\text{OH}^-] / [\text{H}_2\text{O}]^2$$

Since $[\text{H}_2\text{O}]$ is constant, we have

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = K_w$$

The constant K_w is evaluated by substituting known numerical values for the concentrations of the ions and solving this gives

$$K_w = (1 \times 10^{-7}) (1 \times 10^{-7}) = 1 \times 10^{-14}$$

This is the value for the constant at 25 °C .

The obvious simple solution is to use a related function , known as pH, to express hydronium ion concentrations .The function pH is defined by the equation

$$\text{pH} = - \log [\text{H}_3\text{O}^+]$$

which also gives corresponding values for the concentration of OH^- ion pOH, defined by

$$\text{pOH} = -\log [\text{OH}^-]$$

It will be noted that the sum $\text{pH} + \text{pOH}$ is always 14 when the solution is at room temperature

$$\text{pH} + \text{pOH} = 14$$

Ex/ What is the pH of a solution in which the hydronium ion concentration is 0.0002 M ?

Solution / $[\text{H}_3\text{O}^+] = \text{M} = 2 \times 10^{-4}$

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (2 \times 10^{-4}) = -\log 2 + 4 \log 10 \\ &= -0.30 + 4 \\ &= 3.7\end{aligned}$$

Ex/The pH of a solution is 5.40. What is the concentration hydronium ion?

Solution /

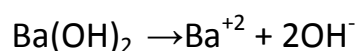
$$\begin{aligned}\text{pH} &= 5.40 \\ \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-5.4} = 10^{-6} \times 10^{+0.6} \\ &= 3.98 \times 10^{-6} \approx 4 \times 10^{-6}\end{aligned}$$

Ex/ What is the OH^- concentration in 0.001 M of HCl solution? What is the H^+ concentration derived from the dissociates of the solvent ?

Solution /

$$\begin{aligned}K_w &= [\text{H}^+] [\text{OH}^-] \\ 1 \times 10^{-14} &= (0.001)[\text{OH}^-] \\ [\text{OH}^-] &= 1 \times 10^{-14} / 1 \times 10^{-3} = 1 \times 10^{-11} \text{M} \\ \text{H}_2\text{O} &\leftrightarrow \text{H}^+ + \text{OH}^- \\ [\text{OH}^-] &= [\text{H}^+] = 1 \times 10^{-11}\end{aligned}$$

Ex/ What are the concentration of H^+ and OH^- in 0.0030 M solution of $\text{Ba}(\text{OH})_2$?

Solution /

$$K_w = [\text{OH}^-] [\text{H}^+]$$

$$1 \times 10^{-14} = (2 \times 0.003) [\text{H}^+]$$

$$[\text{H}^+] = 1 \times 10^{-14} / 6 \times 10^{-3} = 1.6 \times 10^{-12}$$

$$[\text{OH}^-] 2 \times 0.003 = 6 \times 10^{-3}$$

Ex / A sample of blood found to have a pH 3.80. What were the H^+ and OH^- concentration in the blood?

Solution /

$$\text{pH} = -\log [\text{H}^+]$$

$$3.8 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-3.8}$$

$$= 10^{-4} \times 10^{+0.2} = 1.58 \times 10^{-4}$$

$$= 1.6 \times 10^{-4}$$

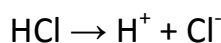
$$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 1.6 \times 10^{-4} = 6.25 \times 10^{-11}$$

Expression of equilibrium constant in acidic medium

For strong acid, such as HCl, we never need to write law of chemical equilibrium because the dissociation almost completely. However, is a weak acid and its reaction with water is an equilibrium law.

Ex / What is the pH of a 0.005 M solution of HCl at 25°C ?

Solution /

$$[\text{H}^+] = 0.005 \text{ M} = 5 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 5 \times 10^{-3}$$

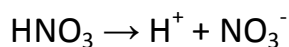
$$\text{pH} = -[\log 5 + \log 10^{-3}]$$

$$= -0.7 + 3$$

$$\text{pH} = 2.7$$

Ex / What is the pOH of a 2×10^{-4} M solution of HNO_3 ?

Solution /



$$[\text{H}^+] = 2 \times 10^{-4} \text{M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 2 \times 10^{-4}$$

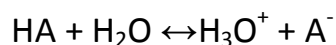
$$= -[\log 2 + \log 10^{-4}]$$

$$= -0.3 + 4 = 3.7$$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14$$

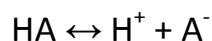
$$\text{pOH} = 14 - \text{pH} = 14 - 3.7 = 10.3$$

Expression of equilibrium constant for a weak acid in aqueous solution in the general equation:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

$[\text{H}_2\text{O}] = \text{constant}$

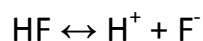


$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

K_a = acid dissociation constant for weak acid

Ex / Express the acid dissociation constant for weak acid HF is dissolved in water ?

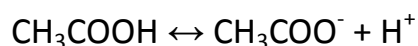
Solution /



$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

Ex / / What is the pH of 0.02M solution of acetic acid ? $K_a = 1.8 \times 10^{-5}$

Solution /



$$0.02 \quad 0 \quad 0$$

$$0.02 - X \quad X \quad X$$

$$K_a = [\text{CH}_3\text{COO}^-] [\text{H}^+] / [\text{CH}_3\text{COOH}]$$

$$1.8 \times 10^{-5} = (X)(X) / (0.02 - X)$$

Neglects

$$X^2 = 36 \times 10^{-8}$$

$$X = 6 \times 10^{-4} \text{ M} = [\text{H}^+]$$

$$\text{pH} - \log [\text{H}^+] = -\log 6 \times 10^{-4} = -0.78 + 4 = 3.22$$

ملاحظة : يهمل (x) في الحالة التي يكون فيها ثابت تفكك الحامض الضعيف (K_a) يساوي

10⁻⁵ , 10⁻⁶.....فما دون

طريقة اخرى للحل

$$\text{pH} = 1/2 (\text{pK}_a - \log M_a)$$

$$\text{pK}_a = -\log K_a \quad , \quad M_a = [\text{H}^+] = [\text{Acid}]$$

$$\text{pH} = 1/2 (-\log K_a - \log M_a)$$

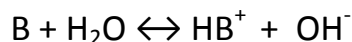
$$= 1/2 (-\log 1.8 \times 10^{-5} - \log 0.02)$$

$$= 1/2(4.47 + 1.7) = 3.22$$

Expression of equilibrium constant in basic medium

For strong base, such as , NaOH , we never need to write law of chemical equilibrium because the dissociation almost completely. However, is a weak base and its reaction with water is an equilibrium law.

in the general quation:



$$K_a = [HB^+] [OH^-] / [B]$$

Ex/ What is the pH of a 0.0005 M solution of NaOH at 25 °C ?

Solution /



$$[OH^-] = 0.0005 \text{ M} = 5 \times 10^{-4} \text{ M}$$

$$pOH = -\log [OH^-]$$

$$= -\log 5 \times 10^{-4}$$

$$= -\log 5 + 4 \log 10$$

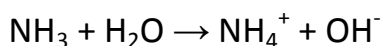
$$= -0.699 + 4$$

$$= 3.301$$

$$pH = 14 - 3.401 = 10.7$$

Ex/ What is the pH of a 0.1 M NH₃ solution ? K_b 1.8 x 10⁻⁵

Solution /



$$0.1 \qquad \qquad 0 \qquad 0$$

$$0.1 - X \qquad \qquad X \qquad X$$

$$K_b = [NH_4^+] [OH^-] / [NH_3]$$

$$1.8 \times 10^{-5} = (X)(X) / 0.1 - X$$

$$1.8 \times 10^{-5} = X^2 / 0.1$$

$$X^2 = 1.8 \times 10^{-6}$$

$$X = 1.34 \times 10^{-3} = [OH^-]$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 1.34 \times 10^{-3} = 2.87$$

$$\text{pOH} + \text{pH} = 14$$

$$\text{pH} = 14 - 2.87 = 11.12$$

طريقة اخرى للحل

$$\text{pOH} = 1/2 [\text{pKb} - \log \text{Mb}]$$

$$\text{pKb} = -\log \text{Kb} \quad , \quad \text{Mb} = [\text{OH}^-] = [\text{Base}]$$

$$\text{pOH} = 1/2 [\text{pKb} - \log \text{Mb}]$$

$$= 1/2 [-\log 1.8 \times 10^{-5} - \log 0.1]$$

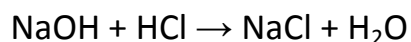
$$= 2.87$$

$$\text{pH} = 14 - 2.87 = 11.12$$

Calculation of pH of aqueous solution

Ex/ What is the pH of the resulting solution when 50 ml 0.1 M NaOH has been added to 75 ml 0.1 M HCl ?

Solution / Each mol of NaOH added neutralizes mole of HCl



$$\text{No. mmol HCl} = 75 \text{ ml} \times 0.1 \text{ mmol / ml} = 7.5 \text{ mmol}$$

$$\text{No. mmol NaOH} = 50 \text{ ml} \times 0.1 \text{ mmol / ml} = 5.0 \text{ mmol}$$

$$\text{No. mmol HCl remaining} = 7.5 - 5.0 = 2.5 \text{ mmol}$$

(unneutralized)

$$\text{Total volume} = 75 \text{ ml} + 50 \text{ ml} = 125 \text{ ml}$$

$$[\text{HCl}] = [\text{H}^+] = \text{no. mmol} / \text{volume ml} = 2.5 \text{ mmol} / 125 \text{ ml} = 0.02 \text{ M}$$

$$\text{pH} = -\log 0.02 = -\log 2 \times 10^{-2} = 1.7$$

Ex/ What is the pH of solution obtained by adding 85 ml 0.1 M NaOH to 75 ml 0.1 M HCl ?

Solution /

$$\text{No. mmol HCl} = 75 \text{ ml} \times 0.1 \text{ mmol / ml} = 7.5 \text{ mmol}$$

$$\text{No. mmol NaOH} = 85 \text{ ml} \times 0.1 \text{ mmol / ml} = 8.5 \text{ mmol}$$

$$\text{No. mmol NaOH an excess} = 8.5 - 7.5 = 1.0 \text{ mmol}$$

$$\text{Total volume} = 75 \text{ ml} + 85 \text{ ml} = 160 \text{ ml}$$

$$[\text{NaOH}] = [\text{OH}^-] = \text{no. mmol} / \text{volume ml} = 1.0 \text{ mmol} / 160 \text{ ml} = 6.25 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 6.25 \times 10^{-3} = 2.21$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.21 = 11.79$$

Weak acid plus its salt

If a salt that contains the same anion is added to solution of a weak acid, the effect is to decrease the concentration of hydronium ion. The salt, completely ionized, increases the concentration of the anion, thereby displacing the chemical equilibrium.

In the titration of a weak acid by a strong base, each mole of base added gives a mole of salt. The effect of this salt must be considered in computing the pH of the solution.

Ex/ What is the pH of an acetic acid solution when 30 ml 0.15 M NaOH have been added to 50 ml 0.1 M HOAc? $K_a = 1.8 \times 10^{-5}$, $\text{p}K_a = 4.74$



$$\text{No. mmol HOAc} = 50 \text{ ml} \times 0.1 \text{ mmol / ml} = 5.0 \text{ mmol}$$

$$\text{No. mmol NaOH} = 30 \text{ ml} \times 0.15 \text{ mmol / ml} = 4.5 \text{ mmol}$$

$$\text{No. mmol HOAc remaining} = 5.0 - 4.5 = 0.5 \text{ mmol}$$

$$\text{pH} = \text{p}K_a - \log \text{mmoles acid remaining} + \log \text{mmoles salt}$$

$$\text{pH} = 4.74 - \log 0.5 + \log 4.5$$

$$\text{pH} = 4.74 - (-0.3) + 0.65 = 5.7$$

Weak base plus salt with common ion

The treatment is similar to that for the weak acid.

Ex / What is the pH of a solution containing 0.535 gm NH_4Cl in 50ml 0.1M NH_3 ? $K_b = 1.8 \times 10^{-3}$

Solution / $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$

No. mol $\text{NH}_4\text{Cl} = 0.535 \text{ gm} \times 1 \text{ mol} / 53.5 \text{ gm} = 0.01 \text{ mol}$

No. mmol = $0.01 \text{ mol} \times 1000 \text{ mmol} / \text{mol} = 10 \text{ mmol } \text{NH}_4\text{Cl}$

No. mmol $\text{NH}_3 = 50 \text{ ml} \times 0.1 \text{ mmol} / \text{ml} = 5.0 \text{ mmol}$

$\text{pOH} = \text{pK}_b - \log \text{ mmoles base} + \log \text{ mmoles salt}$

$\text{pOH} = 4.74 - \log 5.0 + \log 10$

$\text{pOH} = 4.74 - 0.699 + 1.0 = 5.04$

$\text{pH} = 14 - 5.04 = 8.96$

salt of weak acid and strong base

when an equivalent amount of NaOH has been added to a solution of a weak acid (such as HOAc), the solution is not neutral, as it is when an equivalent amount of strong base has been added to a strong acid. The reason is that two bases, the OAc^- and the OH^- ions, are competing for the protons. At the equivalence point we have added a mole of OH^- ion for each mole of HOAc originally present. But, since a small fraction of the total number of protons is still held by the OAc^- ion, as undissociated HOAc molecules, we have an excess of OH^- ions present.

The pH of the solution is computed from the equilibrium constant of the two competing reaction.

Ex / What is the pH at the equivalence point when 50 ml 0.1 M NaOH is titrated with 0.1 M HOAc ? $K_a = 1.8 \times 10^{-5}$

Solution /

$\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log M_s)$

$\text{pK}_w = - \log K_w = - \log 1 \times 10^{-14} = 14$

$\text{pK}_a = - \log K_a = - \log 1.8 \times 10^{-5} = 4.74$

$M_s = [\text{salt}] = \text{no of moles salt} / \text{total volume}$

No.mmol HOAc = 50 ml x 0.1 mmol / ml = 5.0 mmol

At equivalent point:

mmoles of acid = mmols of base

no.mmolNaOH = 50 ml x 0.1 mmol / ml = 5.0 mmol

Total volume = (50 + 50)ml = 100 ml

$M_s = 5.0 \text{ mmol} / 100 \text{ ml} = 0.05 \text{ M}$

$\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log M_s)$

$= 1/2(14 + 4.74 + \log 0.05)$

$= 8.71$

The general expression for the concentration of OH^- ion in a solution of a salt of a weak acid and strong base is

$$[\text{OH}^-] = \sqrt{\frac{C_s K_w}{K_a}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w K_a}{C_s}}$$

Where C_s is the salt concentration , neglecting the small amount which **reacts**.

Salt of weak base with strong acid

The equilibrium expression is treated exactly the same as for a weak acid

Ex / What is the pH of a solution containing 10mmol NH_4Cl in a volume of 100ml ? $K_b = 1.8 \times 10^{-5}$

Solution /

$\text{pH} = 1/2 (\text{pK}_w - \text{pK}_b - \log M_s)$

$M_s = [\text{salt}] = \text{no.moles salt} / \text{total volume} = 10 \text{ mmol} / 100 \text{ ml} = 0.1 \text{ M}$

$\text{pH} = 1/2(14-4.74 +1)=5.13$

$$\begin{aligned}
[\text{H}^+] &= \sqrt{[\text{CS}] \frac{K_w}{K_b}} \\
&= \sqrt{\frac{0.1 \times 10^{-14}}{1.8 \times 10^{-5}}} = \sqrt{\frac{1 \times 10^{-10}}{1.8}} \\
&= 0.7 \times 10^{-5}
\end{aligned}$$

$$\begin{aligned}
\text{pH} &= -\log [\text{H}^+] = -\log [0.7 \times 10^{-5}] \\
&= -\log 0.7 + 5\log 1 \\
&= -(-0.127 - 5) = 5.127
\end{aligned}$$

Buffers solution

A buffer solution is one that contains a weak acid and its salt or a weak base and its salt. The name is based on the fact that an acid or base added to a buffer solution causes less change in pH than an acid or base added to pure water or to an unbuffered solution. To illustrate the buffer effect, we shall consider a solution containing acetic acid and a salt, sodium acetate or ammonium hydroxide and ammonium chloride.

Expression of the general equation for buffer solution is:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

calculation of the pH of buffer solution

Ex / What is the pH of a solution that is 0.40 M in formic acid and 1.00 M in sodium formate? $K_b = 1.8 \times 10^{-4}$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pK}_a = -\log 1.8 \times 10^{-4} = 3.75$$

$$\text{pH} = 3.75 + \log 1.00 / 0.40$$

$$= 3.75 + 0.39 = 4.14$$

Ex / Calculate the pH change that takes place when a 1.0 mole of HCl is added to 5.0 m each of acetic acid and sodium acetate? $K_a = 1.8 \times 10^{-5}$

Solution / Befor addation

$$\begin{aligned} \text{pH}_1 &= \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.74 + \log 5.0 / 5.0 \\ &= 4.74 \end{aligned}$$

After addation HCl

$$\begin{aligned} \text{pH}_2 &= \text{pK}_a + \log \frac{\text{salt} - [\text{H}^+]}{\text{acid} + [\text{H}^+]} \\ &= 4.74 + \log \frac{5-1}{5+1} = 4.58 \end{aligned}$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1$$

$$= 4.58 - 4.74 = -0.16$$

Ex / A mixture of NH_3Cl and 1.0 M NH_3 solution is prepared to give a buffer of pH 9.0. What quantities of each are required? if we use 100 ml NH_3 solution, $K_b = 1.8 \times 10^{-5}$

Solution / $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 14 - \text{pH} = 14 - 9.0 = 5$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5}$$

$$[\text{OH}^-] = K_b \times \frac{nb}{ns}$$

$$10^{-5} = 1.8 \times 10^{-5} \times \frac{nb}{ns}$$

$$\frac{nb}{ns} = \frac{10^{-5}}{1.8 \times 10^{-5}}$$

$$\frac{nb}{ns} = \frac{1}{1.8} \Rightarrow \frac{ns}{nb} = 1.8$$

$$nb = 1.0 \text{ mmol / ml} \times 100 \text{ ml} = 100 \text{ mmol}$$

$$\frac{ns}{100 \text{ mmol}} = 1.8 \Rightarrow ns = 1.8 \times 100 \text{ mmol} = 180 \text{ mmol}$$

$$\text{Weight} = 180 \text{ mmol} \times 53.5 \text{ mg / mmol} = 9600 \text{ mg} = 9.6 \text{ gm}$$

Ex / Calculate the pH change that takes place when a 100.0 ml portion
 (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400.0 ml of
 the buffer solution that contains 0.3M ammonium chloride and 0.2 M
 NH₃ ? pK_b = 4.74 , K_b = 1.8 x 10⁻⁵

Solution / before add.

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = 4.74 + \log \frac{0.3}{0.2} = 4.92$$

$$\text{pH}_1 = 14 - 4.92 = 9.08$$

After addition 0.0500 M NaOH

$$[\text{NH}_3] = (0.20 \times 400 + 0.0500 \times 100) / 500 = 85.0 / 500 = 0.170 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = (0.30 \times 400 - 0.0500 \times 100) / 500 = 115.0 / 500 = 0.230 \text{ M}$$

$$\text{pOH} = 4.74 + \log 0.230 / 0.170$$

$$= 4.74 + 0.13 = 4.87$$

$$\text{pH}_2 = 14 - 4.87 = 9.12$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1 = 9.12 - 9.08 = 0.04$$

b- After addition 0.0500M HCl

$$[\text{NH}_3] = (0.20 \times 400 - 0.0500 \times 100) / 500 = 75.0 / 500 = 0.150 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = (0.30 \times 400 + 0.0500 \times 100) / 500 = 125.0 / 500 = 0.250 \text{ M}$$

$$\text{pOH} = 4.74 + \log 0.250 / 0.150$$

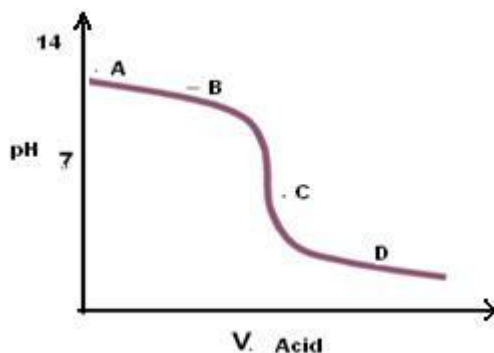
$$= 4.74 + 0.22 = 4.96$$

$$\text{pH}_2 = 14 - 4.96 = 9.04$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1 = 9.04 - 9.08 = -0.04$$

Titration curves

Graphs of PH versus the volume of reagent added in a titration are known as titration curves.



Strong acid- strong base:

Note the following features of the titration:

1-The PH changes slowly at first ,until the equivalence point is approached.

2-In the region of the equivalence point there is a rapid change in PH. There is a nearly vertical rise in the region from pH 4 to 10.

3- After the equivalence point is passed, the curve flattens out, as excess of NaOH is added.

The curve will become as :

EX/ compute the pH for additions of 0,10,20, and 30ml 0.1M NaOH to 100 ml 0.025 M HCl . Use the computed values and the pH of 7.00 at the equivalence point to plot the titration curve.

Solution /

1-Before any NaoH added or initial pH

[acid] = 0.025 M

pH = $-\log [\text{acid}] = -\log [\text{H}^+] = -\log 0.025 = -(-1.6) = 1.6$

2-After addition of 10.0ml of NaOH

$$\text{No. mmols acid} = 0.025 \text{ mmol/ml} \times 100 \text{ ml} = 2.5 \text{ mmol}$$

$$\text{No. mmols acid (reacted)} = n. \text{ moles NaOH} = 10.0 \text{ ml} \times 0.1 \text{ mmole/ml} = 1.0 \text{ mmol}$$

$$\text{No. mmols acid (unreacted)} = 2.5 - 1.0 = 1.5 \text{ mmol}$$

$$\text{Volume (solution)} = 100 + 10 = 110 \text{ ml}$$

$$[\text{acid}] \text{ unreacted} = [\text{H}^+] = 1.5 \text{ mmol} / 110 \text{ mmol} = 0.0136 \text{ M}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] = -\log 0.0136 \\ &= -(-1.866) = 1.866 \end{aligned}$$

3- At equivalence point after addition 25 ml of NaOH

At the equivalence point:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}$$

$$n_{\text{HCl}} - n_{\text{NaOH}} = 0 \rightarrow \text{eq. point}$$

pH=7 → Bromothymol blue

4- After addition excess of NaOH , 30 ml NaOH added

$$\text{no. mmols NaOH (react)} = \text{no. mmols acid} = 2.5 \text{ mmol}$$

$$\text{no. mmols NaOH (added)} = 30.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 3.0 \text{ mmol}$$

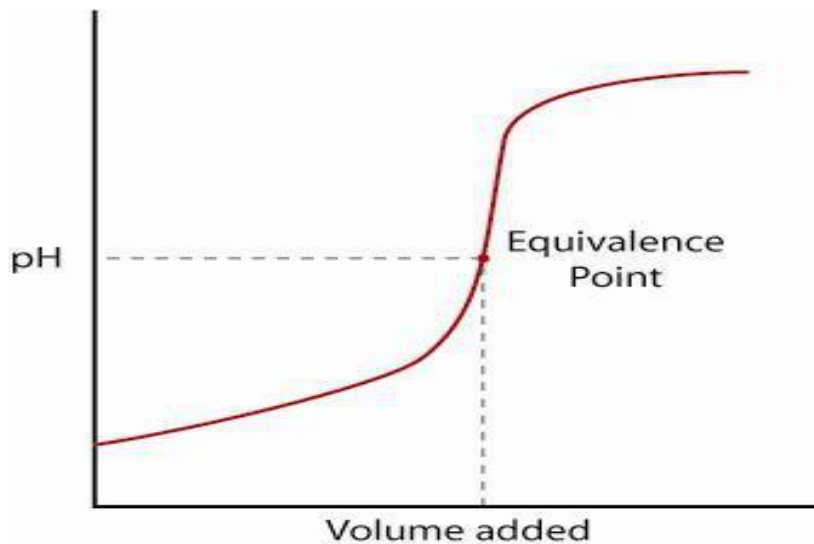
$$\text{no. mmols (NaOH) unreacted (excess)} = 3.0 - 2.5 = 0.5 \text{ mmol}$$

$$\text{volume of solution} = 100 + 30 = 130 \text{ ml}$$

$$[\text{base}] \text{ excess} = [\text{OH}^-] = 0.5 \text{ mmol} / 130 \text{ ml} = 0.0038$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] = -\log 0.0038 \\ &= -(-2.415) = 2.415 \end{aligned}$$

$$\text{pH} = 14 - 2.415 = 11.585$$



Weak acid – strong base

The curve will be become as :

EX/ compute the pH of 25.0 ml 0.1 M acetic acid at addition of 0,5,10,12.5,20,25,and 30 ml 0.1 M NaOH ? $K_a = 1.8 \times 10^{-5}$, $pK_a = 4.76$

Solution /

1-before added any NaOH or initial pH

$$pH = 1/2 (pK_a - \log M_a)$$

$$pH = 1/2 (4.76 - \log 0.1)$$

$$pH = 1/2 (4.76 + 1) = 1/2 (5.76)$$

$$= 2.88$$

2-After addition 5.0 ml NaOH

$$pH = pK_a - \log \text{mmoles acid (unreacted)} + \log \text{mmoles salt/NaOH}$$

$$\text{No. mmoles HCl} = 25.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH} = 5.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 0.5 \text{ mmol}$$

$$\text{No. mmoles HCl (unreacted)} = 2.5 - 0.5 = 2.0 \text{ mmol}$$

$$pH = 4.76 - \log 2.0 + \log 0.5$$

$$= 4.76 - 0.30 - 0.30 = 4.16$$

3- After addition of 12.5 ml of NaOH

في هذه الحالة يتم معادلة نصف الحامض وان تركيز الحامض يصبح مساويا الى تركيز الملح لذلك فان :

$$pH = pka$$

$$pH = 4.76$$

$$\text{No. mmoles HCl} = 25 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH (salt)} = 12.5 \text{ ml} \times 0.1 \text{ mmol/ml} = 1.25 \text{ mmol}$$

$$\text{No. mmol HCl (unreacted)} = 2.5 - 1.25 = 1.25 \text{ mmol}$$

$$pH = pka - \log \text{ mmoles acid unreacted} + \log \text{ mmoles salt (NaOH)}$$

$$= 4.76 - \log 1.25 + \log 1.25$$

$$pH = 4.76$$

4- At eq .point (after addition of 25.0 ml of NaOH)

$$\text{No. mmoles acid} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH} = 25.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No .mmoles acid (unreacted)} = 2.5 - 2.5 = 0 \quad \text{this is eq . point}$$

ملاحظة:- عندما يكون عدد مولات القاعدة المضافة مساوية لعدد مولات الحامض الاصلي فان تلك هي نقطة التكافؤ ، والمحلول في هذه الحالة يحتوي على خلاص الصوديوم فقط لذلك يمكن حساب pH بالشكل التالي :

$$pH = 1/2 (pkw + pka + \log Ms)$$

$$pkw = 14 \quad \text{from } kw = 1 \times 10^{-14}$$

$$pka = 4.76 \quad \text{from } ka = 1.8 \times 10^{-5}$$

$$Ms = [\text{salt}] = (\text{no. mmols NaOH}) / (\text{total volume}) = (25.0 \text{ ml} \times 0.1 \text{ M}) / 25 + 25$$

$$= 2.5 / 50 = 0.05 \text{ M}$$

$$pH = 1/2 (14 + 4.76 + \log 0.05)$$

$$= 1/2 (14 + 4.76 - 1.30)$$

$$= 8.73 \rightarrow \text{phenolphthalein}$$

5- After eq . point (excess of NaOH) addition of 25.1 of NaOH

No.mmoles HCl = 25 ml \times 0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH = 25.1 ml \times 0.1 mmol/ml = 2.51 mmol

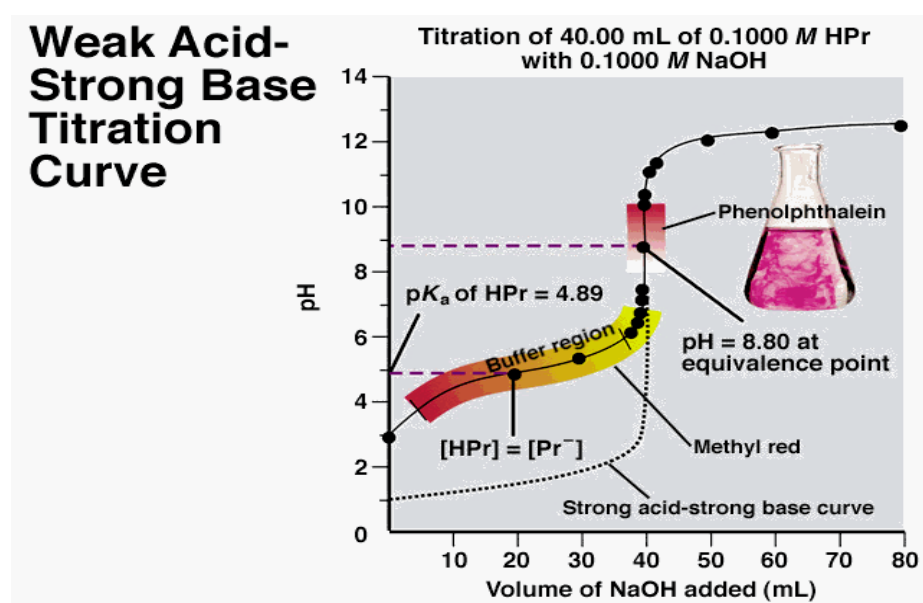
No.mmol NaOH excess = 2.51 – 2.5 = 0.01 mmol

Volume =(25 + 25.1)ml = 50.1ml

$[\text{OH}^-] = 0.01 \text{ mmol} / 50.1 \text{ ml} = 0.0001996\text{M}$

$\text{pOH} = -\log [\text{OH}^-] = -\log 1.996 \times 10^{-4} = 3.7$

$\text{pH} = 14 - 3.7 = 10.3$



strong acid – weak base

Ex /Calculate the pH during the titration of 25.00 ml of 0.1 M NH_4OH with 0.1 M HCl after the addition of the following volumes of reagent: 0, 5.25 and 30 ml ? $\text{pK}_b = 4.74$

Solution /

1- Befor addition

$$\text{pOH} = 1/2(\text{pK}_b - \log M_b)$$

$$\text{pOH} = 1/2 (4.74 - \log 0.1)$$

$$= 1/2 (4.74 + 1) = 2.87$$

$$\text{pH} = 14 - 2.87 = 11.13$$

2- After addition 5 ml of HCl

$$\text{No. mmoles } \text{NH}_4\text{OH} = 25 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No. mmoles HCl} = 5 \text{ ml} \times 0.1 \text{ mmol/ml} = 0.5 \text{ mmol}$$

$$\text{No. mmol } \text{NH}_4\text{OH (unreacted)} = 2.5 - 0.5 = 2.0 \text{ mmol}$$

$$\text{pOH} = \text{pK}_b - \log \text{ mmoles base} + \log \text{ mmoles salt(acid)}$$

$$\text{pOH} = 4.74 - \log 2.0 + \log 0.5$$

$$= 4.74 - 0.3 - 0.3 = 4.74 - 0.6 = 4.14$$

$$\text{pH} = 14 - 4.14 = 9.86$$

3- At eq point (after addition 25 ml of HCl)

$$\text{pH} = 1/2 (\text{pK}_w - \text{pK}_b - \log M_s)$$

$$M_s = \text{mmoles HCl} / \text{total volume} = 25 \text{ ml} \times 0.1\text{M} / (25 + 25) \text{ ml} = 0.05\text{M}$$

$$\text{pH} = 1/2 (14 - 4.74 - \log 5 \times 10^{-2})$$

$$= 1/2 (9.26 + 1.3) = 5.28 \quad \text{methyl red (orange)}$$

4- After addition 30 ml of HCl

$$\text{No. mmoles HCl added} = 30 \text{ ml} \times 0.1 \text{ mmol/ml} = 3.0 \text{ mmol}$$

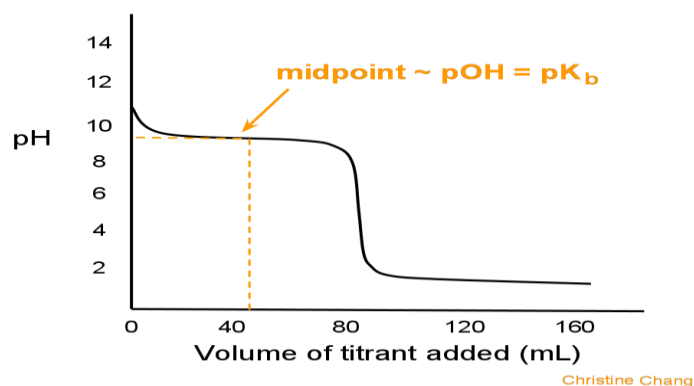
$$\text{No. mmol } \text{NH}_4\text{OH (reacted)} = 25 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

No. mmol HCl (unreacted) = 3.0 – 2.5 = 0.5 mmol

Total volume = (30 + 25)ml = 55 ml

$[H^+] = \text{no. mmol HCl} / \text{total volume} = 0.5 \text{ mmol} / 55 \text{ ml} = 0.009 \text{ M}$

$\text{pH} = -\log [H^+] = -\log 9 \times 10^{-3} = 2.05$



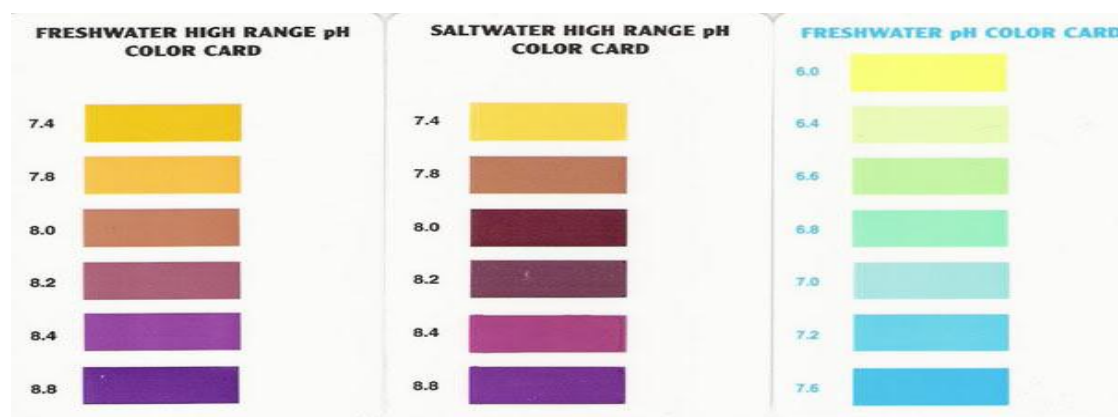
weak acid – weak base

Can not make such titration because it's very difficult which gives the values of pH line connected, to it does not appear sharp change near or at the equivalent point so it can not use any indicator for such titration.

Acid – Base indicator

Acid – Base indicators are highly colored organic dyes which exhibit a change in color when the pH of a solution is changed between certain limits. The pH at which this color change occurs differs for various indicators, this is fortunate for the analyst, since he thereby is enabled to select the indicator whose color change most nearly corresponds to the pH of the equivalence point for a given titration.

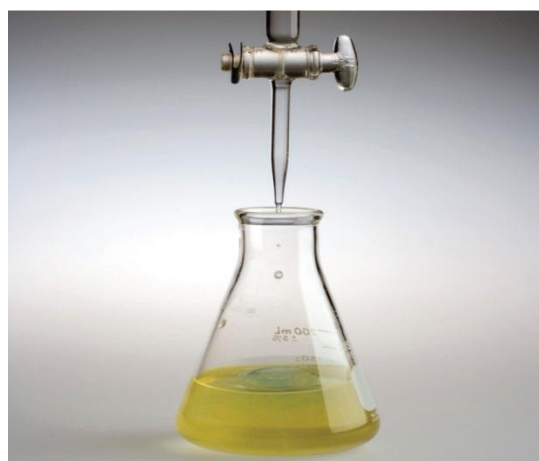
Chemistry of indicators



The amount of indicator required to give the necessary intensity of color is so small that a negligible amount of reagent is required for reaction with the indicator. At most, less than 10^{-3} mmol of indicator is employed, and not more than 0.01ml 0.1N acid or base is required to neutralize the indicator .

The mechanism of indicator color change has been widely investigated . The generally accepted theory is that the formation of an indicator ion is attended by a molecular rearrangement which gives rise to chromophoric, or color – forming, group. Para nitro phenol may be cited as an example. In acid solution this is colorless, but in basic solution it is yellow. The structural formulas for the colorless molecule and colored ion .

Selection of indicator for titration



Ascorbic acid



Sodium ascorbate

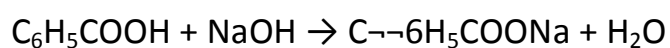
One of the following methods is used to select the indicator for a given titration.

1-If the titration curve is known, we select that indicator whose end point most closely corresponds to the pH of the equivalence point

2-If the ionization constant for the acid or base we wish to titrate is approximately the same as the constant for the acid or base of a known titration, we choose the indicator that is suitable for this known titration. This, when titrating an acid whose K_a is 10^{-4} or 10^{-5} , we can safely use phenolphthalein indicator for experience has shown it to work for acetic acid whose ionization constant is 1.8×10^{-5} .

3-If the titration is one for which where no prior experience, we compute the pH at the equivalence point the computed pH is the basis for selection of the indicator.

Ex/ Compute the pH at the equivalence point for titration of 50ml 0.01M benzoic acid with 0.01M NaOH and select the proper indicator from table (1-1)? $K_a = 7 \times 10^{-5}$.



Solution /

$$\text{No. m mols acid} = 0.01 \text{ m mol / ml} \times 50 \text{ ml} = 0.5 \text{ m mol}$$

$$\text{No. m mols base} = 0.01 \text{ m mol / ml} \times 50 \text{ ml} = 0.05 \text{ m mol}$$

$$\text{pH} = 1/2 (\text{p}K_w + \text{p}K_a + \log M_s)$$

$$\begin{aligned} M_s &= [\text{salt}] = (\text{no mmol NaOH}) / (\text{Total volum}) = (0.5 \text{ mmol}) / (50+50) \text{ ml} \\ &= (0.5 \text{ mmol}) / (100 \text{ ml}) = 0.005 \text{ m} \end{aligned}$$

$$\text{pH} = 1/2 (14 + 4.15 - 2.3) = 7.93$$

Reference to table(1 – 1) shows we can use either

pH range (6.8 – 8.4) ← phenol red

pH range (7.2 – 8.7) ← cresol red.

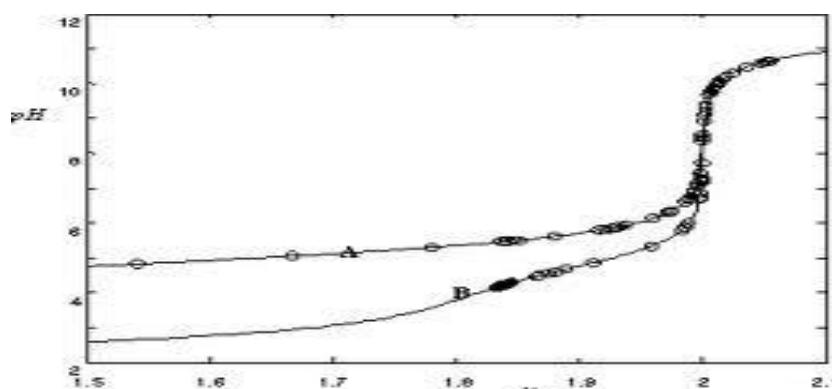
Table (1 – 1) acid – base indicator

Common name	pH range	Color change Acid – base
Cresol red	0.2 – 1.8	Red – yellow
Methyl violet	0.5 – 1.5	Yellow – blue
Thymol blue	1.2 – 2.8	Red – yellow
Methyl yellow	2.8 – 4.0	Red - yellow
Bromophenol blue	3.0 – 4.6	Yellow – blue
Methyl orange	3.1 – 4.4	(red – orange) – yellow
Bromo cresol green	4.0 – 5.6	Yellow – blue
Methyl red	4.2 – 6.2	Red – yellow
Chlorphenol red	4.8 – 6.4	Yellow – red
Bromo thymol blue	6.0 – 7.6	Yellow – blue
Phenol red	6.8 – 8.4	Yellow – red
Cresol red	7.2 – 8.7	Yellow – red
Thymol blue	8.0 – 9.6	Yellow – blue
Phenol phthalein	8.0 – 9.8	Colorless – red
Thymol phthalein	9.3 – 10.5	Colorless – blue

Feasibility of titrations

A pH change of about 2 unit is required to cause a color change in an acid – base indicator. This color change must be abrupt (occurring with addition of not more than 0.1 – 0.2 ml of reagent) if the analyst is to observe a sharp end point. Otherwise he will see a gradual fading of one color and appearance of another and he will not be able to say at exactly what volume of reagent the titration is completed.

In the titration of a very weak acid or base the pH change at the equivalence point is gradual. This effect is shown in the titration curve for boric acid, Fig (1)



The pH at the equivalence point is about 11, but the pH change is so gradual at this point that about 5 ml of base is needed to cause a pH change of one unit. This titration, therefore; is not feasible and should not be attempted with an internal acid – base indicator. (it could be done by electrometric titration).

After selecting the proper indicator for a titration , we should evaluate the feasibility before attempting to carry out the operations . The feasibility may be evaluated by one of the following methods:

- 1- By inspection of the titration curve, if this is available for the concentration of solutions we plan to use. We see in fig (1-1) an example of a feasible titration acetic acid .
- 2- By analogy to titrations that are known to be feasible. We know, for example , that solutions whose concentrations when the ionization constant of the weak acid or base is 10^{-5} or greater, since we have had experience with titrations of acetic acid and ammonia. The titrations of other acids or bases of strengths comparable to these two are therefore known to be feasible , provided the concentrations of the solutions are also comparable to those we have employed.
- 3- By computation of the pH change caused by addition of 0.1 ml of reagent , at the equivalence point. That is , we compute the pH at the equivalence point and the pH for the further addition of 0.1 ml of reagent. If the change is of the order 1 pH unit or greater, we may expect the end point to be sufficiently sharp to permit accurate observation.

Ex / Is the titration of 0.01M benzoic acid by 0.01 M NaOH ?

Solution /

In a previous calculation it was shown that the pH at the equivalence point for this titration is 7.93.

We now compute the pH when an additional 0.1 ml NaOH is added.

No. mmoles acid = $50 \text{ ml} \times 0.01 \text{ mmol/ml} = 0.5 \text{ mmol}$

No. mmoles NaOH = $50.1 \text{ ml} \times 0.01 \text{ mmol/ml} = 0.501 \text{ mmol}$

No. mmol NaOH excess = $0.501 - 0.5 = 0.001 \text{ mmol}$

total Volume = $(50 + 50.1) \text{ ml} = 100.1 \text{ ml}$

compute the $[\text{OH}^-]$ of this excess

$[\text{OH}^-] = [\text{NaOH}] = 0.001 \text{ mmol} / 100.1 \text{ ml} = 10^{-5} \text{ M}$

$\text{pOH} = -\log [\text{OH}^-] = -\log 10^{-5} = 5.0$

$\text{pH} = 14 - 5.0 = 9.0$

$$\Delta\text{pH } 9.0 - 7.93 = 1.07 > 1.0$$

We expect the titration to be feasible.

In practice it has been found that the end point is sufficiently sharp.

- 4- As a rough guide to feasibility of titration, we can generalize that when the solutions are 0.1 M or stronger, the titration of a weak acid or base of ionization constant 10^{-5} or greater is always feasible. It is not feasible to titrate a weak acid with a weak base or vice versa. When acids or bases whose K_i is 10^{-5} or greater are titrated in very dilute solution, a computation should be made of the rate of change of pH with volume of reagent, when K_i approaches 10^{-6} , the titration may or may not be feasible, depending on the particular indicator available. When K_i is less than 10^{-6} , the titration is generally not feasible.