Analytical Chemistry

References :

1- Skoog A. Douglas ,"Fundamental of Analytical Chemistry ",8 th edition ,Canada (2004)

2-Daniel C .Harris ,"Quantitative chemical Analysis", 6 th edition , U.S. (2003).

3- Raymond chang ,"Essential chemistry ", 2nd edition, Mc Graw –Hill (2000).

4-المبادئ الاساسية في الكيمياء التحليلية، د.نجاة جمعة صالح ، الجامعة التكنولوجية ،بغداد 1991.

Chapter one

Introduction to Analytical Chemistry :

Everything is made of chemicals. Analytical chemistry determine what and how much. In other words analytical chemistry is concerned with the separation, identification, and determination of the relative amounts of the components making up a sample.

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions what is it (qualitative) and how much is it (quantitative).

Analytical chemistry answering for basic questions about a material sample:

- What?
- Where?
- How much?
- What arrangement, structure or form?

Qualitative analysis: An analysis in which we determine the identity of the constituent species (the elements and compounds) in a sample.

Quantitative analysis: An analysis in which we determine how much of a constituent species is present in a sample.

Analytes: Are the components of a sample that are to be determined.

1.1 Classifying Analytical Techniques

A- Classical techniques

Mass, volume, and charge are the most common signals for classical techniques, and the corresponding techniques are:

1- Gravimetric techniques.

2- Volumetric techniques.

3- Coulometeric techniques.

B- Instrumental techniques

1- Spectroscopic methods - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

2- Electroanalytic methods - measure an electrical property (i.e., potential, current, resistance, amperes,etc.) chemically related to the amount of analyte.

1.2 Quantitative Analytical Methods

We compute the results of a typical quantitative analysis from two measurements.One is the mass or the volume of samole being analyzed. The second is the measurement of some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge. This second measurement usually completes the analysis, and we classify analytical methods according to the nature of this final measurement. Gravimetric methods determine the mass of analyte or some compound chemically related to it. In a volumetric method, the volume of a solution containing sufficient reagent to react completely with the analyte is measured.

1.3 Applications of Analytical Chemistry

Analytical chemistry used in many fields:

1, In **medicine**, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.

2. In **industry**, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical.Many household products, fuels, paints,Pharmaceutical, etc. are analysed

by the procedures developed by analytical chemists before being sold to the consumer.

3. **Environmental quality** is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

4. **The nutritional value of food** is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in a food are often calculated from the chemical analysis.

5. **Forensic analysis** - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.

6. **Bioanalytical chemistry and analysis** - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).

Atomic weight : It is the mass of an atom of that element based on a mass of exactly 12 to the carbon isotope C^{12}.

Molecular or Formula weight(M.wt): It is the sum of the atomic weights of the elements that constitute a molecule of the substance.

Examples :

M.wt of water (H_2O) =2x(1.008)+1x16=18.02 g/gmole

Note: it is possible to express the molecular weights in any unit of mass for example M.wt of H_2=2.016 g/gmole ,Ib/Ib mole , ton /ton mole.

the mole unit (n) : the mole (or g.mole) can be defined as the amount of the substance that contains number of molecules equal to that in exactly 12 gram of C^{12} .Hence number of moles is computed as

No .of moles $= \frac{\boldsymbol{Mass\ in\ g}}{\boldsymbol{M.wt\ g/gmole}}$

the term of g.atom can be defined as the amount of an element that contain the same number of atoms equal to that of carbon atoms in exactly 12 gm of C^{12} .Hence number of g.atoms is computed as

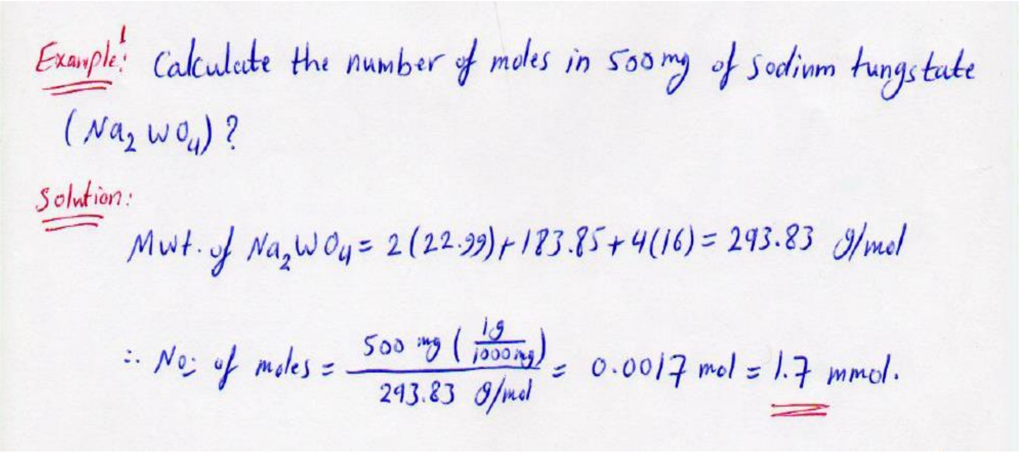
No. of g.atoms $= \frac{Mass\ of\ the\ element\ in\ g}{atomic\ weight}$

Note .Since we usually work in millimole,hence

No. of mmol $= \frac{\boldsymbol{Mass\ in\ mg}}{\boldsymbol{M.wt}}$

Calculating the Amount of a Substance in Moles or Millimoles

The two examples that follow illustrate how the number of moles or millimoles of a species can be determined from its mass in grams or from the mass of a chemically related species

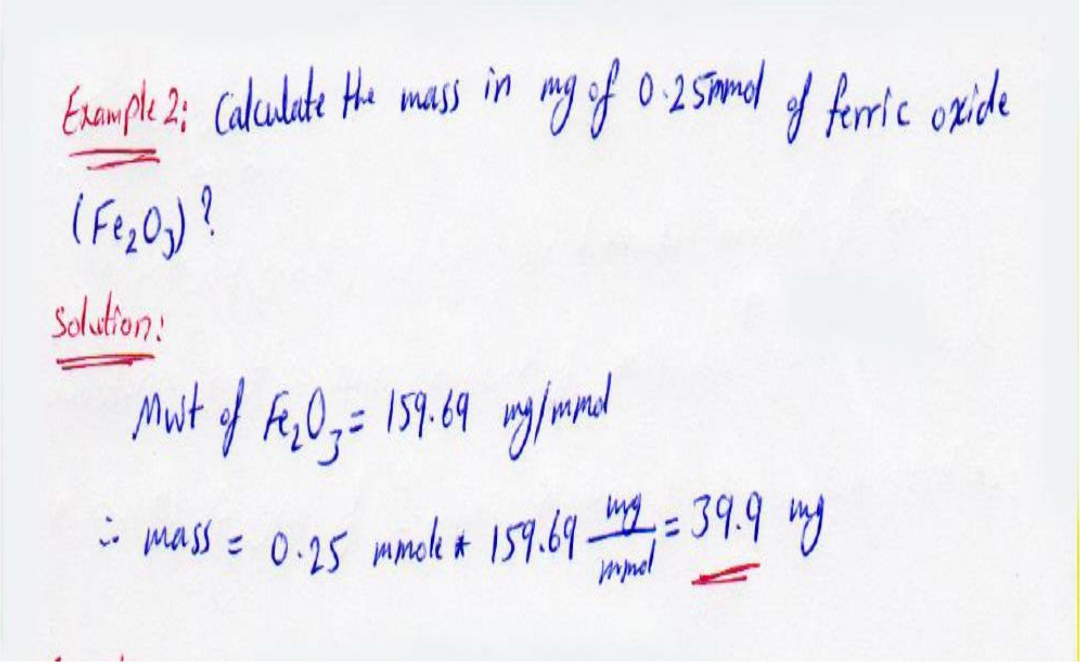


Example 1: Calculate the number of moles in 500 mg of Sodium tungstate (Na_2WO_4) ?

Solution:

$$M.wt.\ of\ Na_2WO_4 = 2(22.99) + 183.85 + 4(16) = 293.83\ g/mol$$

$$\therefore No.\ of\ moles = \frac{500\ mg\left(\frac{1g}{1000\,mg}\right)}{293.83\ g/mol} = 0.0017\ mol = 1.7\ mmol.$$

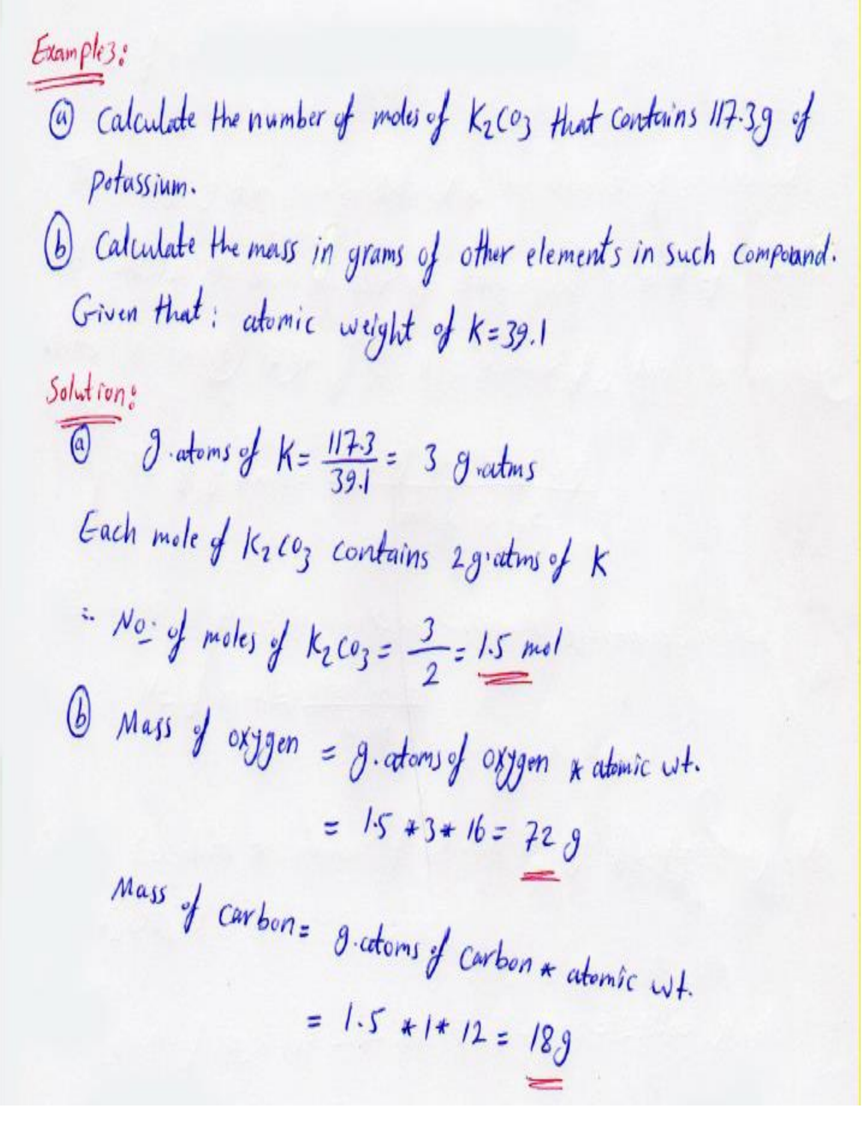


Example 2: Calculate the mass in mg of 0.25mmol of ferric oxide (Fe_2O_3)?

Solution:

Mwt of Fe_2O_3 = 159.69 mg/mmol

$\therefore$ mass = 0.25 mmole * 159.69 $\frac{mg}{mmol}$ = 39.9 mg



Example3:

ⓐ Calculate the number of moles of K_2CO_3 that contains 117.3g of potassium.

ⓑ Calculate the mass in grams of other elements in such compound.

Given that: atomic weight of K = 39.1

Solution:

ⓐ g.atoms of K = $\frac{117.3}{39.1}$ = 3 g.atms

Each mole of K_2CO_3 contains 2g.atms of K

$\therefore$ No. of moles of K_2CO_3 = $\frac{3}{2}$ = 1.5 mol

ⓑ Mass of oxygen = g.atoms of oxygen * atomic wt.

= 1.5 * 3 * 16 = 72 g

Mass of carbon = g.atoms of carbon * atomic wt.

= 1.5 * 1 * 12 = 18g

Example 5

Find the number of moles and millimoles of benzoic acid (M = 122.1 g/mol) that are contained in 2.00 g of the pure acid.

Solution

If we use HBz to represent benzoic acid, we can write that 1 mole of HBz has a mass of 122.1 g. Therefore,

$$\text{Amount HBz} = n_{\text{HBz}} = 2\text{gHBz x} \frac{1\ mol\ HBz}{122.1 gHBZ}$$

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

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

$$\text{Amount HBz} = n_{\text{HBz}} = 2\text{gHBz x} \frac{1\ mol\ HBz}{0.1221 gHBZ}$$

$$= 16.4 \text{ mmol HBz}$$

Example 6

What is the mass in grams of Na^+ (22.99 g/mol) in 25.0 g of Na_2SO_4 (142.0 g/mol)?

Solution

The chemical formula tells us that 1 mole of Na_2SO_4 contains 2 moles of Na+, that is,

$$\text{Amount } Na^+ = n_{Na+} = \text{mol } Na_2SO_4 \text{ x} \frac{2\ mol\ Na+}{\text{mol Na2SO4}}$$

To find the number of moles of Na_2SO_4, we proceed as in Example 1-1:

$$\text{Amount } Na_2SO_4 = n_{\text{ Na2SO4}} = 25\text{ g } Na_2SO_4 \text{ x} \frac{1\ mol \text{ Na2SO4}}{142\text{ g}}$$

$$= 0.176 \text{ mol}$$

$$\text{Amount Na+} = 2*0.176 = 0.352 \text{ mol}$$

$$\text{Mass } Na^+ = m_{Na+} = \text{mol } Na^+ \text{ x} \frac{22.99\ g}{\text{mol Na+}}$$

$$= 8.1\text{g}$$

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

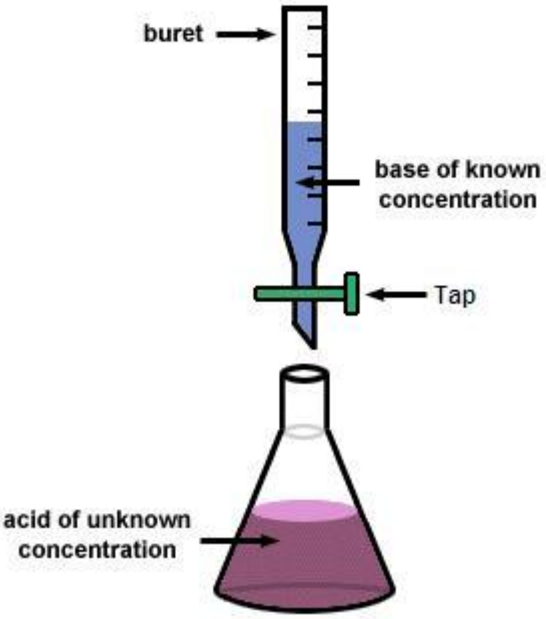
Molarity of solution : The number of moles of solute per liter of solution.

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

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

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 /

$$[C2H5OH] = \frac{number\ of\ moles}{liter\ of\ solution}$$

$$\text{No.mol C2H5OH} = 2.30\text{ gm } C_2H_5OH \times \frac{1\ mol\ C2H5OH}{96.07\ gm\ C2H5OH}$$

$$= 0.0499\text{ mol } C_2H_5OH$$

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

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

Solution/ $Cl_3CCOOH \equiv HA$

$$\text{No. mol HA} = 285.0\ \cancel{\text{mg HA}} \times \frac{1\cancel{gm\ HA}}{1000\cancel{mgHA}}\ X\ \frac{1mol\ HA}{163.4\ \cancel{gm\ HA}}$$

$$= 1.744\ X\ 10^{-3}\ \text{mol HA}$$

$$[HA] = \frac{1.744\ \ X\ 1000\ molHA}{10.0\ ml}\ x\ \frac{1000ml}{L}$$

$$= 0.174\ \text{mol HA / L} = 0.174\ M$$

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

Solution/

$$M = \frac{wt}{M.wt}\ X\ \frac{1000}{Vml}$$

$$Wt = \frac{M\ X\ M.wt\ x\ Vml}{1000}$$

$$= \frac{0.125\cancel{mmol}/\cancel{ml}\ x\ 169.9mg/\cancel{mmol}\ x\ 500\cancel{ml}}{1000} =$$

10.62mg

Equivalent Methods:

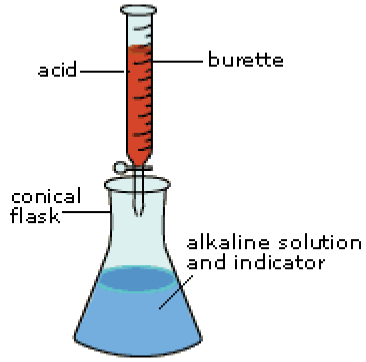
The equivalent weight (eq) is defind , for neutralization reactions , as the weight in grams that will furnish or react with one gram-atomic weight of hydrogen ion.

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

n = no.H^+ for acid

= no.OH^- for base

= no. electrons in the reaction.



Titration

A) Equivalent weight of atoms of element :

Eq. wt = = $\frac{\textit{atomic weight}}{\text{valency}}$

A) Equivalent weight of compounds:

1. Equivalent weight of Acids;

Equivalent weight of acid which contains one replaceable hydrogen

Eq .wt of acid = $\frac{\textit{molecular weight}}{\text{no.of hydrogen atom}}$

2 Equivalent weight of a base;

Equivalent weight of base which contains one replaceable hydroxyl group

Eq .wt of a base = $\frac{\textit{molecular weight}}{\text{no.of hydroxyl groups}}$

3 Equivalent weight of a salt;

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

4 Equivalent weight of Reducing and Oxidizing agent

Eq .wt. of reducing agent = $\frac{\textit{molecular weight}}{\text{no.of electrons losses in the reaction}}$

Eq .wt of oxidizing agent = $\frac{\textit{molecular weight}}{\text{no.of electrons gains in the reaction}}$

Example /

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

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

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

For eq.wt H_3PO_4

$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- = \frac{97}{1}$ =97

$H_3PO_4 \leftrightarrow 2H^+ + HPO_4^{-2} = \frac{96}{2}$ =48

$H_3PO_4 \leftrightarrow 3\ H^+ + PO_4^{-3} = \frac{95}{3}$ = 31.7

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

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

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

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?

Solution/ $NaOH \longrightarrow Na^+ + OH^-$

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

Equivalents of solute = normality x volume in liters

= 0.100 eq / ~~liter~~ x 0.500 ~~liter~~

= 0.0500 eq

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

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

Wt = 2.00 gm

طريقة اخرى للحل

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

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

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

Wt = 2.00 gm

Ex/What is the normality of a solution prepared by dissolving 25.20 gm oxalic acid ($H_2C_2O_4.2H_2O$)(126.1gm/mol) in sufficient water to give 1.200 liters of solution ?What is the molarity of this solution?

Solution/ $H2C_2O_4.2H_2O \longrightarrow 2H^+ + C_2O_4^-$

2

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

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

$$= \frac{25.20\cancel{gm}}{\frac{126.1\cancel{gm}/\cancel{mol}}{2eq/\cancel{mol}}} = 0.3996\ eq$$

The Normality is :

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

The Molarity is:

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

Relation between Molarity and Normality:

$$M = \frac{wt_1}{Mwt} * \frac{1}{L} \Rightarrow wt_1 = M * Mwt * L$$

$$N = \frac{wt_2}{eq.wt} * \frac{1}{L} \Rightarrow wt_2 = N * eq.wt * L$$

$$wt_1 = wt_2$$

$$M * Mwt * \cancel{L} = N * eq.wt * \cancel{L}$$

$$M * \cancel{Mwt} = N * \frac{\cancel{Mwt}}{n}$$

$$\therefore \quad \boxed{N = nM}$$

where:

n : no. of H^+, OH^- & cation valency.

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/ $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{-2}$

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

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

Wt = 7.1 gm

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

Solution/

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

Moles of solute = M X V

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

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

$$= 53.00 \text{ gm } Na_2CO_3$$

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

Ex/

Astandard 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/ $\mathbf{Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{-2}}$

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

$$\text{Moles of } Na_2CO_3 = 5 \cancel{mmol\ Na^+} \text{ x } \frac{1\ mmolNa2CO3}{2\ \cancel{mmolNa+}} = 2.5 \text{ mmol}$$

Grams of Na_2CO_3 = 2.5 ~~mmol~~ x 0.10599 gm/~~mmol~~ = 0.265 gm

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

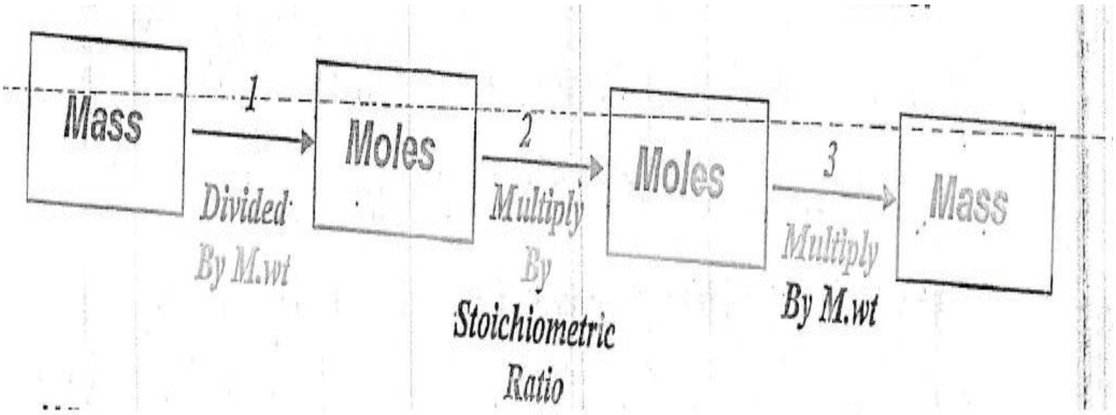
Density and specific gravityof solution

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

Chemical Stoichiometry :

The Stoichiometry of reaction is the quantitative relationship among the number of moles of reactants and products as shown by a balanced equation .

Flow diagram for making Stoichiometric Calculations



When the mass of reactant or product is given , the mass is first converted to the number of moles using molecular weight .

The stoichiometry ratio given by chemical equation for the reaction is then used to find the number of mole of another reactant. Finally ,the mass of the other reactant or the product is computed by multiply by molecular weight .

Example 8 : what mass of $AgNO_3$ is needed to convert 2.33 gm of Na_2CO_3 to Ag_2CO_3? What mass of Ag_2CO_3 will be formed ?

Solution: The chemical reaction eq. is:

$$Na_2CO_3 + 2\,AgNO_3 \longrightarrow Ag_2CO_3 + 2\,NaNO_3$$

MWt. $(Na_2CO_3) = 106\ \frac{gm}{mol}$, MWt. $(AgNo_3) = 169.9\ \frac{gm}{mol}$, MWt. $(Ag_2CO_3) = 275.7\ \frac{gm}{mol}$

no. moles of $Na_2CO_3 = \frac{wt.}{MWt.} = \frac{2.33\ gm}{106\ \frac{gm}{mol}} = 0.02198\ mol$

$\therefore$ no. mol $AgNO_3 = 0.02198 * \frac{2\ mol\ AgNO_3}{1\ mol\ Na_2CO_3} = 0.04396\ mol$

mass of $AgNO_3$ = mole * MWt. = $0.04396 * 169.9 = \underline{\underline{7.47\ g}}$ $AgNO_3$

no. moles of Ag_2CO_3 = no. moles of $Na_2CO_3 = 0.02198\ mol$

$\therefore$ mass of $Ag_2CO_3 = 0.02198 * 275.7 = \underline{\underline{6.06\ gm}}$ Ag_2CO_3

Example 2: Calcium carbide, CaC_2 reacts with water to form acetylene.

ⓐ How many grams of CaC_2 required to produce 23.6 gm acetylene.

ⓑ If 55.3 grams of $Ca(OH)_2$ are formed, how many grams of water reacted.

Solution: The chemical eq. reaction is:

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

MWt. $CaC_2 = 64$ g/mol , MWt. $C_2H_2 = 26$ g/mol , MWt. $Ca(OH)_2 = 74$

$n_{C_2H_2}$ formed $= \frac{23.6\ g}{26\ \frac{g}{mol}} = 0.908\ mol$

n_{CaC_2} reacted $= n_{C_2H_2}$ produced $= 0.908\ mol$

∴ mass of CaC_2 = $n * Mwt = 0.908 * 64 = \underline{\underline{58.1\ gm}}$

$n_{Ca(OH)_2}$ formed $= \frac{55.3\ gr}{74\ g/mol} = 0.747$ mol

∴ n_{H_2O} reacted $= 2 * n_{Ca(OH)_2} = 2 * 0.747 = 1.494$ mol

∴ mass of H_2O req. $= n * Mwt = 1.494 * 18 = \underline{\underline{26.89\ gm}}$

Example 3: An impure sample of $CaCl_2$ is dissolved and titrated with a solution of $AgNO_3$. The reaction is:

$$CaCl_2 + 2\,AgNO_3 \rightarrow Ca(NO_3)_2 + 2\,AgCl$$

It is found that 46.35 ml, 0.1034 M $AgNO_3$ titrates a 0.2843 gm sample of $CaCl_2$. Compute the percentage of $CaCl_2$ in the sample?

Solution:

mmoles of $AgNO_3$ $= 46.35\ ml * 0.1034\ \frac{mmol}{ml} = 4.793\ mmol$

The equation shows that 2 moles $AgNO_3$ reacts with 1 mole $CaCl_2$

∴ mmoles $CaCl_2$ $= 4.793 * \frac{1\ mole\ CaCl_2}{2\ mole\ AgNO_3} = 2.397\ mmol$

wt. $CaCl_2$ $= 2.397 * \underset{Mwt_{CaCl_2}}{111} = 266.1\ mg$

% $CaCl_2$ $= \frac{266.1\ mg}{284.3\ mg} * 100 = 93.6\ \%$

Calculation based on Molarity:

$$aA + bB \longrightarrow \text{product}$$

where: $R = \frac{b}{a}$

mmole of $A = M_A * V_A$

mmole of $B =$ mmole of $A * R \Rightarrow$ mmole of $B = M_A * V_A * R$ $[* Mwt_B]$

$$\therefore \boxed{\text{wt of } B \text{ in mg} = \text{mmole of } A * R * Mwt_B}$$

Example: Exactly 50 ml of HCl required 29.71 ml of 0.01963 M of $Ba(OH)_2$ to reach end point as afollowing eq.:

$$2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$$

What is the molarity of HCl?

Solution:

mmole of $Ba(OH)_2 = 0.01963 * 29.71 = 0.5832$ mmole.

mmole of $HCl = 2 *$ mmole of $Ba(OH)_2 = 2 * 0.5832 = 1.1664$ mmole.

$$\therefore M_{HCl} = \frac{1.1664}{50} = \underline{\underline{0.0233}} \text{ mmole/ml.}$$

calculation based on Normality:

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

If A reacts with B

$$eq._A = eq._B$$

$$meq._A = meq._B$$

$$N = \frac{wt.}{eq.wt} * \frac{1}{L} \Rightarrow \frac{wt}{eq.} = N * L$$

$$\therefore \quad \boxed{\frac{mg}{meq.} = N * V}$$

Example: 25 ml of HCl sol. is required to react with 0.1854 gm of pure Na_2CO_3. what is the normality of acid ? if 32.16 ml of acid reacts with 29.65 ml of NaOH. What is the normality of NaOH sol. ?

Solution:

$$meq._{HCl} = meq._{Na_2CO_3}$$

$$N_{acid} * 25\ ml = \frac{0.1854\ \cancel{gm} * \frac{1000\ mg}{1\ \cancel{gm}}}{\frac{106}{2}\ mg/meq.} \Rightarrow N_{acid} = \underline{0.1394}\ meq./ml$$

$$N_{acid} * V_{acid} = N_{base(NaOH)} * V_{base(NaOH)}$$

$$0.1394 * 32.16 = N_{NaOH} * 29.65 \Rightarrow N_{NaOH} = \underline{0.1515}\ meq/ml.$$

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 it is expressed as (g/mL) or (gm/cm^3) , where as its specific gravity (Spg)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.

$$\textbf{Density} = \frac{mass\ in}{volume}$$

$$\textbf{Specific gravity} = \frac{density\ of\ substance}{density\ of\ water}$$

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

(Normality * volume) conc =(Normality * volume)dilute

(N x V)conc = (N x V)dil

Or for concentration

(Molarity * volume) conc =(Molarlity * volume)dilute

(C x V)conc = (C x V)dil

Percentage methods:

$$\textbf{a - Weight percent (\%wt)} = \frac{\text{weight of solute}}{\text{weight of solution}} \textbf{x100}$$

$$\textbf{b - volume percent (\%vol) \%} = \frac{\text{volume of solute}}{\text{volume of solution}} \textbf{x100}$$

c – Weight/volume percent

$$\textbf{(\%wt/vol)} = \frac{\text{weight of solute}}{\text{volume of solution}}\textbf{x100}$$

d- Part per million (ppm):

$$\textbf{ppm} = \frac{\text{weight of solute in (gm)}}{\text{volume of solution in (L)}}\textbf{x10}^{\mathbf{6}}$$

Ex/A 0.2011gm sample of an organic compound was burned in a stream of oxygen , and CO_2 produced in a solution of barium hydroxide.

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

$$Co_2 + Ba(OH)_2 \longrightarrow BaCo_3 + H_2o$$

Solution/

$$1 \text{ mol } BaCo_3 \equiv 197.0gm$$

No . mol $BaCo_3$ = 0.500 gm $BaCo_3$ × $\frac{1\ mol\ BaCo3}{197gm\ BaCo3}$ $=2.538\times10^{-3}$ mol $BaCo_3$

1 mol $BaCo_3 \equiv$ 1 mol Co_2 = 2.538×10^{-3} mol

1 mol $Co_2 \equiv$ 44.0gm

Mass Co_2 = 2.538×10^{-3} $\cancel{\text{mol } Co_2}$ × $\frac{44.0gm}{\cancel{1\ mol\ CO2}}$

= 0.1116 gm Co_2

M $Co_2\%$ = $\frac{m\ CO2}{m\ comp} \times 100$

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

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 H_3po_4. The phosphate was precipitated as $MgNH_4Po_4.6H_2o$ by addition of Mg^{+2} followed by aqueous NH_3 . after being filtered and washed. The precipitate was converted to $Mg_2p_2o_7$(222.57gm mol) by ignition at 1000 C^0 this residue weighed 0.2161gm.Calculate the percent P(30.974gm mol) in the sample.

Solution/

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

1 mol MP ≡ 2 mol P

No . mol P = 30.774 gm

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

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

Ex/A 0.7151 gm sample of impure $Al_2(Co_3)_3$ 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 Co_2 ≈ 44.0 gm

No . mol Co_2 = 0.0621 $\cancel{gm\ Co_2} \times \frac{1\ mol\ CO2}{44.0\ \cancel{gm\ CO2}}$ = 1.411×10^{-3} mol

1 mol $Al_2(Co_3)_3$ ≡ 3 mol(Co_2)

1 mol $Al_2(Co_3)_3$ ≡ 2 mol (Al)

No . mol Al = 1.411×10^{-3} $\cancel{mol\ Co_2} \times \frac{2\ mol\ Al}{3\ \cancel{mol\ CO2}}$ =0.941×10^{-3} mol Al

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

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

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

$$5Hg^{+2} + 2H_5IO_6 \rightarrow Hg_5(IO_6)_2 + 10H^+$$

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 /

1 mol $Hg_5(IO_6)_2$ ≡ 1451.0 gm

No.mol $Hg_5(IO_6)_2$ = 0.4114gm $Hg_5(IO_6)_2$ x $\frac{1\ \mathrm{mol\ Hg5(IO6)2}}{1451\ gm\ \mathrm{Hg5(IO6)2}}$

= 2.84 x 10^{-4} mol

2 mol $Hg_5(IO_6)_2$ ≡ 5 mol Hg_2Cl_2

No.mol Hg_2Cl_2 = 2.84 x 10^{-4} ~~mol $Hg_5(IO_6)_2$~~ x $\frac{5\ mol\mathrm{Hg2Cl2}}{2\ \cancel{mol\mathrm{Hg5(IO6)}}2}$

= 7.10 x 10^{-4} mol

1 mol Hg_2Cl_2 ≡ 473.0 gm

Mass of Hg_2Cl_2 = 7.10 x 10^{-4} ~~mol~~ x 473.0 gm / ~~mol~~ = 0.3358 gm

% Hg_2Cl_2 = $\frac{0.3358\ gm}{0.8142\ gm}$ x 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.

Solution / $KCl + AgNO_3 \rightarrow AgCl + KNO_3$

1 mol KCl ≡ 1 mol AgCl

1mol AgCl ≡ 143.5 gm

No.mol AgCl = 0.2191 gm AgCl x 1 mol AgCl / 143.5 gm AgCl

= 1.53 x10^{-3} mol AgCl

Stoichiometric factor = 1 mol KCl / 1mol AgCl

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

1 mol KCl ≡ 74.5 gm KCl

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

% KCl = 0.114 gm / 0.2500 gm x 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 $Fe(OH)_3$. The precipitate is ignited to Fe_2O_3, giving a weighet of 1.485 gm .Calculate the percentage of Fe_3o_4 in the sample .

$$\text{No.mol } Fe_2O_3 = 1.485\text{mol } \cancel{\text{gm } Fe_2O_3} \times \frac{mol\text{Fe2O3}}{159.7\ \cancel{gm\ \text{Fe2O3}}}$$

$$= 0.00930\ \text{mol } Fe_2O_3$$

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 moles Fe_{34} ≡ 3 moles Fe_2O_3

$$\text{No.mol}Fe_3O_4 = 0.00930\ \cancel{\text{mole}Fe_2O_3} \times \frac{2\ mole\text{Fe3O4}}{3\ \cancel{mole\text{Fe2O3}}} = 0.00620\ \text{moles } Fe_3o_4$$

Weight Fe_3O_4 in sample = 0.00620 mole x 231.55 gm / mole

= 1.437 gm Fe_3O_4

Percentage Fe_3O_4 = 1.437 gm / 1.542 gm x 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.

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

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

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

Ex/Express the concentration with weight percent of the solution weighting 200.0gm and contained in 25.0gm of sodium sulphate Na_2So_4.

Solution/

$$\%(w/w) = \frac{weight\ of\ solute}{weight\ of\ solution} \times 100$$

$$= \frac{25.0gm\ solute}{200.0gm\ solution} \times 100 = 12.5\%$$

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

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

Weight (H_2o) = density × volume

$$= \frac{1gm}{cm3} \times 1L \times \frac{1000\ cm3}{L}$$

Weight = weight + weight

(solution) (solute) (solvent)

= 3gm + 1000gm = 1003gm

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

Ex/Use the volume percent, calculate the concentration of the solution is prepared by addition 50.0ml methanol (CH_3OH) to 200.0ml water?

Solution/

Volume(solution) = 50.0ml + 200.0ml = 250.0ml

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

$$\text{ppm (wt/wt)} = \frac{\text{mass of solute (g)}}{\text{mass of Sample (g)}} * 10^6$$

Example 1: A sample with mass of 2.6 g contains 3.6 μg of Zinc. Calculate the concentration of Zinc in ppm.

Solution:

$$\text{ppm(wt/wt)} = \frac{\text{mass of Zinc}}{\text{mass of sample}} * 10^6$$

$$\text{Conc. of Zinc} = \frac{3.6 * 10^{-6}\,g}{2.6\,g} * 10^6 = 1.4 \text{ ppm}$$

Example 2: A 25 μL serum sample was analyzed for glucose content and found to contain 26.7 μg. Calculate the concentration of glucose in ppm and in mg/dL.

Solution:

$$\text{ppm (wt/vol)} = \frac{\text{mass of glucose (g)}}{\text{vol. of sample (ml)}} * 10^6$$

$$\text{Conc. of glucose} = \frac{26.7 * 10^{-6}\,g}{25\,\mu L * \frac{ml}{10^3\,\mu L}} * 10^6 = 1068 \text{ ppm}$$

$$\text{Conc. of glucose} = \frac{\text{mass of glucose (mg)}}{\text{vol. of sample dL}}$$

$$= \frac{26.7\,\mu g * \frac{mg}{10^3\,\mu g}}{25\,\mu L * \frac{L}{10^6\,\mu L} * \frac{10\,dL}{L}} = 106.8 \text{ mg/dL}$$

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

$$\mathbf{HA=H^+ + A^-}$$

And a base MOH dissociates to give M^+ $^-OH_-$ ions. The reaction of HA with MOH is

$$\mathbf{MOH=M^+ + OH^-}$$

And a base MOH dissociates to give M_+ +OH_- ions. The reaction of HA with MOH is

$$\mathbf{HA + MOH = MA + H_2O}$$

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

$\mathbf{aA + bB \leftrightarrow cC + dD}$

We have the relation

$\mathbf{Ke = [D]^d [C]^c / [A]_a [B]_b}$

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 Ke 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 Ke.

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

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

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 :

$$Ke = [H_3O^+] [OH^-] / [H_2O]^2$$

Since $[H_2O]$ is constant, we have

$$[H_2O^+] [OH^-] = Kw$$

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

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

This is the value for the constant at 25 ^{0}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

$$pH = - \log [H_3O^+]$$

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

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

It will be noted that the sum pH +pOH is always 14 when the solution is at room temperature

$$pH + pOH = 14$$

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

Solution / $[H_3O^+] = M = 2 X 10^{-4}$

$pH =- \log [H_3O^+]$

$= -\log (2 x 10^{-4}) = - \log 2 + 4 \log 10$

$= -0.30 + 4$

$= 3.7$

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

Solution /

$pH = 5.40$

$pH = - \log [H_3O^+]$

$[H_3O^+] = 10^{-Ph} = 10^{- 5.4} = 10^{-6} x 10^{+0.6}$

$= 3.98 x 10^{-6} \approx 4 x 10^{-6}$

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 / $Kw = [H^+] [OH^-]$

$1 X 10^{-14} = (0.001)[OH^-]$

$[OH^-] = 1 X 10^{-14} / 1 X 10^{-3} = 1 x 10^{-11}M$

$H_2O \leftrightarrow H^+ + OH^-$

$[OH^-] = [H^+] = 1 X 10^{-11}$

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

Solution /

$Ba(OH)_2 \rightarrow Ba^{+2} + 2OH^-$

$Kw = [OH^-] [H^+]$

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

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

$[OH^-] 2 X 0.003 = 6 X 10^{-3}$

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

Solution / $pH= - \log [H^+]$

$3.8 = - \log [H^+]$

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

$= 10^{-4} X 10^{+0.2} =1.58 X 10^{-4}$

$= 1.6 X 10^{-4}$

$[H^+] [OH^-] = 1 X 10^{-14}$

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

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 25ºC ?

Solution / $HCl \rightarrow H^+ + Cl^-$

$[H^+] = 0.005 M = 5 X 10^{-3}M$

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

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

$= - 0.7 + 3$

$pH = 2.7$

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

Solution / $HNO_3 \rightarrow H^+ + NO_3^-$

$[H^+] = 2 X 10^{-4}M$

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

$= - [\log2 + \log 10^{-4}]$

$= - 0.3 + 4 = 3.7$

$pH + pOH = pKw = 14$

$pOH = 14 – pH = 14 – 3.7 = 10.3$

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

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

$$Ka = [H_3O^+] [A^-] / [HA] [H_2O]$$

$[H_2O]$ = constant

$$HA \leftrightarrow H^+ + A^-$$

$$Ka = [H^+] [A^-] / [HA]$$

Ka = acid dissociation constant for weak acid

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

Solution /

$$HF \leftrightarrow H^+ + F^-$$

$$Ka = [H^+] [F^-] / [HF]$$

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

Solution / $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

0.02 0 0

$0.02 - X \qquad X \qquad X$

$Ka = [CH_3COO^-]\,[H^+] / [CH_3COOH]$

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

Neglects

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

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

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

ملاحظة : يهمل (×) في الحالة التي يكون فيها ثابت تفكك الحامض الضعيف (Ka) يساوي

$10^{-5}, 10^{-6}$......فما دون

طريقة اخرى للحل

$pH = 1/2\ (pKa - \log Ma)$

$pKa = -\log Ka \qquad , Ma = [H^+] = [\ Acid]$

$pH\ = 1/2\ (-\log Ka - \log Ma)$

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

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

Example 1: Calculate the PH of a $2*10^{-3}M$ of hydrochloric acid solution.

Solution:

since Hcl is astrong electrolyte and it is completely ionized.

$[H^+] = 2*10^{-3} M$

$PH = -Log[H^+] = -Log(2*10^{-3}) = \underline{\underline{2.7}}$

Example 2: Calculate the POH and the PH of a $5*10^{-2}M$ solution of NaOH.

Solution:

$[OH^-] = 5*10^{-2} M$

$POH = -Log[OH^-] = -Log(5*10^{-2}) = \underline{\underline{1.3}}$

$PH + POH = 14$

$\therefore \; PH = 14 - 1.3 = \underline{\underline{12.7}}$

Example 3: Calculate the hydrogen ion concentration of a solution with pH = 9.67.

Solution:

$PH = -Log[H^+] = 9.67$

$[H^+] = 10^{-9.67} = \underline{\underline{2.14*10^{-10}}} M$

Acid - Base strength:

When an acid or base is dissolved in water, it will dissociate or ionize. The degree of ionization depends on the strength of the acid. A "strong" electrolyte is completely dissociated, while a "weak" electrolyte is partially dissociated. Hence, a weak acid has arelatively smell dissociation constant (Ka), whereas astrong of an acid has aLarge dissociation constant.

similarly, astrong base has aLarg (K_b) and a weak base has small (K_b).

Alist of some common strong and weak electrolytes are shown in the following table.

strong Electrolytes	Weak Electrolytes
HCl, HI	acetic acid CH_3COOH, $HCOOH$ formic acid
$HClO_4$, HBr	HF, HNO_2, HCN hydrocyanic acid
H_2SO_4	H_2S, H_2SO_3
HNO_3	NH_3, C_6H_5OH phenol
$NaOH$, KOH	$C_6H_5NH_2$ aniline
$Ba(OH)_2$, $LiOH$	N_2H_4CO Urea

Example 1: calculate the PH of a 0.05 M solution of acetic acid? $Ka=1.8*10^{-5}$

Solution:

The acetic acid dissociates according to the equation:

$$\underset{0.05-x}{HOAC} = \underset{x}{H^+} + \underset{x}{OAC^-}$$

$$Ka = \frac{[H^+][OAC^-]}{[HOAC]}$$

Let concentration of $H^+ = x$

conc. of $OAC^- = x$

conc. of HOAC undissociation $= 0.05-x$

$$\frac{x^2}{0.05-x} = 1.8*10^{-5}$$

$0.05-x \simeq 0.05$ [that x is negligible in comparison with 0.05)

$$\frac{x^2}{0.05} = 1.8*10^{-5} \Rightarrow x^2 = 9*10^{-7} \Rightarrow x = 9.49*10^{-4}\ M = [H^+]$$

$$PH = -Log[H^+] = -Log[9.49*10^{-4}] = \underline{\underline{3.02}}$$

The generalized approximate equation for the dissociation of aweak acid is:

$$\boxed{[H^+] = \sqrt{Ka \cdot C}}$$

where:

C: is the Concentration of the weak acid.

Example 2: what is the pH of a 0.1 M NH_3 Solution ?

$K_b = 1.75 * 10^{-5}$

Solution:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$\begin{array}{cccc} 0.1-x & & x & x \end{array}$$

$$\frac{x^2}{0.1-\underset{\text{negligible}}{x}} = 1.75*10^{-5} \Rightarrow x^2 = 1.75*10^{-6} \Rightarrow x = 1.32*10^{-3} M = [OH^-]$$

$$POH = -Log[OH^-] = -Log(1.32*10^{-3}) = 2.87$$

$$PH = 14 - POH = \underline{11.12}$$

The generalized approximate equation for the dissociation of a weak base is:

$$\boxed{[OH^-] = \sqrt{Kb.C}}$$

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:

$$B + H_2O \leftrightarrow HB^+ + OH^-$$

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

Ex/ What is the pH of a 0.0005 M solution of NaOH at 25 ^oC ?

Solution / $NaOH \rightarrow Na^+ + OH^-$

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

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

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

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

$= -0.699 + 4$

$=3.301$

$pH = 14 – 3.401 = 10.7$

Ex/ What is the pH of a 0.1 M NH_3 solution ? K_b 1.8 x 10^{-5}

Solution / $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

0.1 0 0

0.1 – X X X

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

$1.8 X 10^{-5} = (X)(X) / 0.1 –X$

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

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

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

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

$pOH + pH = 14$

$pH\ 14 - 2.87 = 11.12$

طريقة اخرى للحل

$pOH\ 1/2 [pKb - \log Mb]$

$pKb = -\log Kb$, $Mb = [OH^-] = [Base]$

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

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

$=2.87$

$pH = 14 - 2.87 = 11.12$

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

$$NaOH + HCl \rightarrow NaCl + H_2O$$

No.mmol HCl = 75 ~~ml~~ x 0.1 mmol / ~~ml~~ = 7.5 mmol

No.mmol NaOH = 50 ml x o.1 mmol / ml = 5.0 mmol

No.mmol HCl remaining = 7.5 – 5.0 = 2.5 mmol

(unneutralized)

Total volume = 75 ml + 50 ml = 125 ml

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

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

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

Solution /

No.mmol HCl = 75 ml x 0.1 mmol / ml = 7.5 mmol

No.mmol NaOH = 85 ml x o.1 mmol / ml = 8.5 mmol

No.mmol NaOH an excess =8.5 - 7.5 = 1.0 mmol

Total volume = 75 ml + 85 ml = 160 ml

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

pOH = -log [OH^-] = - log 6.25 X 10^{-3}= 2.21

pH = 14 – 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, increase 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 85 ml 0.15 M NaOH have been added to 50 ml 0.1 M HOAc ?Ka = 1.8 x 10^{-5} , pKa = 4.74

Solution / $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

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

No.mmol NaOH = 30 ~~ml~~ x o.15 mmol / ~~ml~~ = 4.5 mmol

No.mmol HOAc remaining = 5.0 – 4.5 = 0.5 mmol

pH = pKa – log mmoles acid remaining + log mmoles salt

pH = 4.74 – log 0.5 +log 4.5

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 containing0.535 gm NH_4Cl in 50ml 0.1M NH_3 ? Kb = 1.8×10^{-3}

Solution / $NH_3 + H2O \leftrightarrow NH_4^+ + OH^-$

No.mol NH_4Cl = 0.535 gm x 1mol/53.5 gm = 0.01mol

No.mmol = 0.01 ~~mol~~ x 1000 mmol / ~~mol~~ = 10 mmol NH_4Cl

No.mmol NH_3 =50 ~~ml~~ x o.1 mmol / ~~ml~~ = 5.0 mmol

pOH = pKb – log mmoles base + log mmoles salt

pOH = 4.74 – log 5.0 +log 10

pOH = 4.74 -0.699 +1.0 = 5.04

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 competin g 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 NaOH ?Ka = 1.8×10^{-5}

Solution /

pH = 1/2 (pKw + pKa + log Ms)

pKw = - log Kw = - log 1×10^{-14} = 14

pKa = - log Ka = -log 1.8×10^{-5} 4.74

Ms = [salt] = no of moles salt / 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

Ms = 5.0 mmol / 100 ml = 0.05 M

pH = 1/2 (pKw + pKa + log Ms)

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

= 8.71

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

$$[OH^-] = \sqrt{\frac{Cs\ Kw}{Ka}}$$

$$[H^+]= \sqrt{\frac{Kw\ Ka}{Cs}}$$

Where Cs 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 aweak acid

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

Solution /

pH = 1/2 (pKw - pKb - log Ms)

Ms = [salt] = no.moles salt / total volume = 10 mmol / 100 ml = 0.1 M

pH = 1/2(14-4.74 +1)=5.13

$[H^+] = \sqrt{[Cs]\frac{Kw}{Kb}}$

$= \sqrt{\frac{0.1\ x\ 10^{-14}}{1.8\ x\ 10^{-5}}} = \sqrt{\frac{1\ x\ 10^{-10}}{1.8}}$

$= 0.7 \times 10^{-5}$

pH $= -\log [H^+] = -\log [0.7 \times 10^{-5}]$

$= -\log 0.7 + 5\log 1$

$= -(-0.127 - 5) = 5.127$

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 un buffered 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:

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

$$pOH = pKb + \log \frac{[salt]}{[base]}$$

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 ? Kb = 1.8×10^{-4}

Solution / $HCOOH + H_2O \longrightarrow H_3O^+ + HCOO^-$

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

$pKa = -\log 1.8 \times 10^{-4} = 3.75$

$pH = 3.75 + \log 1.00 / 0.40$

$= 3.75 + 0.39 = 4.14$

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? Ka=1.8 x 10^{-5}

Solution / <u>Befor addation</u>

$$pH_1 = pKa + \log\frac{[salt]}{[acid]}$$

$$= 4.74 + \log 5.0 / 5.0$$

$$= 4.74$$

After addation HCl

$$pH_2 = pKa + \log \frac{salt-[\overset{+}{H}]}{acid+[\overset{+}{H}]}$$

$$= 4.74 + \log \frac{5-1}{5+1} = 4.58$$

$$\Delta pH = pH_2 - pH_1$$

$$= 4.58 - 4.74 = -0.16$$

Ex / Amixture 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 , Kb = 1.8 x 10^{-5}

Solution / $pH + pOH = 14$

$$pOH = 14 - pH = 14 - 9.0 = 5$$

$$[OH^-] = 10^{-Poh} = 10^{-5}$$

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

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

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

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

nb = 1.0 mmol / ml x 100 ml = 100 mmol

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

Weight = 180 mmol x 53.5 mg / mmol = 9600 mg = 9.6 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 NH_3 ? pKb = 4.74 , Kb = 1.8 x 10^{-5}

Solution / before add.

$$pOH = pKb + \log\frac{[\,salt]}{[bast]}$$

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

pH_1 = 14 – 4.92 = 9.08

After addation 0.0500 M NaOH

[NH3] = (0.20×400+0.0500×100)/500 = 85.0/500 = 0.170 M

[NH4Cl] = (0.30×400-0.0500×100)/500 = 115.0/500 = 0.230 M

pOH = 4.74 + log 0.230/0.170

= 4.74 + 0.13 = 4.87

pH2 = 14 – 4.87 = 9.12

ΔpH =pH2 – pH1 = 9.12 – 9.08 = 0.04

b- After addation 0.0500M Hcl

[NH3] = (0.20×400-0.0500×100)/500 = 75.0/500 = 0.150 M

[NH4Cl] = (0.30×400+0.0500×100)/500 = 125.0/500 = 0.250 M

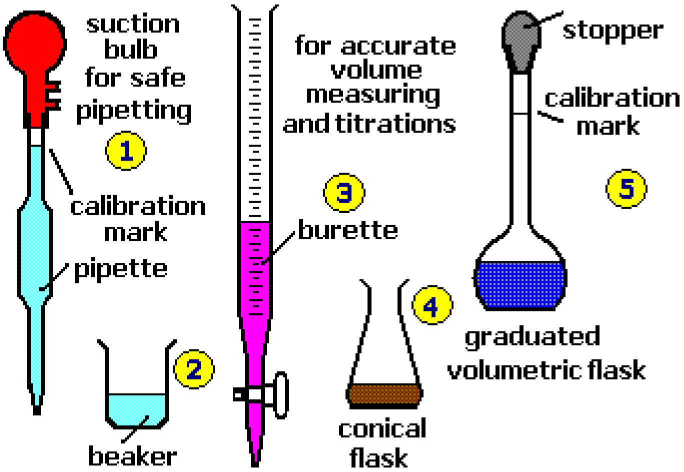
pOH = 4.74 + log 0.250/0.150

=4.74 + 0.22 = 4.96

pH2 = 14 – 4.96 =9.04

ΔpH = pH2 – pH1 = 9.04 – 9.08 = -0.04

Dilution of solutions



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

$$N_{conced} \text{ x } V_{conced} = N_{dil.} \text{ X } V_{dil.}$$

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

Solution/

$$N_{conced} \text{ x } V_{conced} = N_{dil}. \text{ X } V_{dil}$$

$$V_{conced} = \frac{Ndil\ x\ Vdil}{Nconced} = \frac{0.100\cancel{N}\ X\ 500.0\ ml}{0.1500\cancel{N}} = 333.3 \text{ ml}$$

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/

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

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

M = 12.0 mol/L = 12.0 M

No.mol HCl = 100 ~~ml~~ x 6.0 mmol/ ~~ml~~

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

$$V_{\text{conced}}\ \text{reagent} = 0.6\ \cancel{\text{mol}}\ \text{x}\ \frac{1\ l\ reagent}{12.0\ \cancel{mol}} = 0.05\ \cancel{\text{L}}\ \text{X}\ 1000\text{ml}/\cancel{\text{L}}$$

$$= 50\ \text{ml}$$

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

طريقة اخرى للحل

$$M_{\text{conced}}\ \text{x}\ V_{\text{conced}} = M_{\text{dil.}}\ \text{X}\ V_{\text{dil.}}$$

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

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

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/

$$[H_2SO_4] = \frac{1.84\ X\ 1000\cancel{gm\ reagent}\ x\ 98\cancel{gm\ H2SO4}\ X\ 1eq\ H2SO4}{L\ reagent\ x\ 100\ \cancel{gm\ reagent}\ x\ 49.0\ \cancel{gm\ H2SO4}}$$

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

$$\text{No.eq}\ H_2SO_4 = 200.0\ \cancel{\text{ml}}\ \text{x}\ 0.3\ \text{meq}\ /\cancel{\text{ml}}$$

$$= 60.0\ \text{meq}$$

$$V_{\text{conced}}\text{reagent} = 60.0\ \cancel{\text{meq}}\ \text{x}\ \frac{1\ ml}{36.8\cancel{meq}\ H2SO4} = 1.63\ \text{ml}$$

Dilute 1.63 ml of the concentrated reagent to 200.0ml

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.

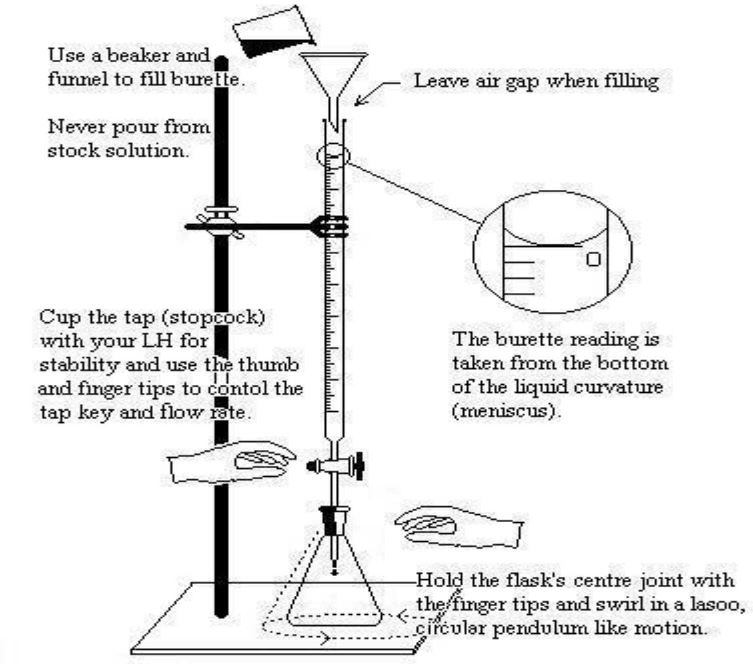
Acid and base samples are analyzed by titration with a standard solution.A weighed portion of sample is dissolved in water and standard acid or base is added to the proper end point. From the volume of reagent used and the weight of sample, the percentage putity of the sample is computed.

The basis for all computions 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 reacteat thus

A reacts with B

Equivalents A = Equivalents B

Milliequivalents A = Milliequivalents B



Place white paper underneath flask to view pink colour more clearly.

Monash Scientific 03 9791 4442

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 ≡ 0.005300 gm Na_2CO_3

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

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

$$= 44.49\text{ml}$$

Milliequivalents acid = Milliequivalents $CaCO_3$

= 44.49 ~~ml~~ x 0.100 meq / ~~ml~~ = 4.449 meq

Milliequivalents $CaCO_3$ = $\frac{weight\ of\ solute}{eq.wt}$

Weight $CaCO_3$ = Milliequivalents X eq.wt

= 4.449 ~~meq~~ x $\frac{100.1\ mg/\cancel{mmol}}{2\cancel{meq}\ /\cancel{mmol}}$

= 222.7 mg

Percentage $CaCO_3$ in sample = $\frac{222.7}{495.0}$ x 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 eq acid ≡ 1eq base

1 ml of NaOH ≡ 0.5 gm % acetic acid

1 ml of NaOH ≡ $\frac{0.5gm\ x\ 1000mg/gm}{100}$

1 ml of NaOH ≡ 5.00 mg acetic acid

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

N of NaOH = $\frac{5.00\cancel{mg}\ /ml}{40\ 60.05\ \cancel{mg}\ /meq}$ = 0.0833 meq /ml

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

Solution/

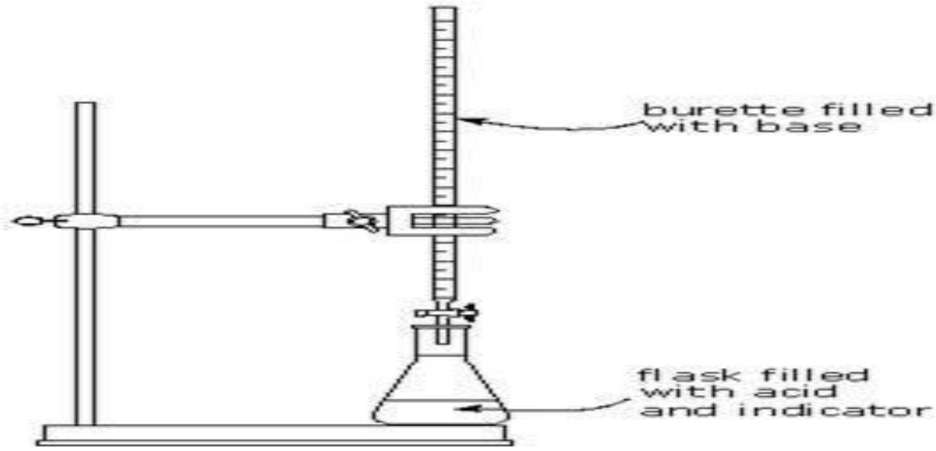
N of base ≡ N ofacid

I ml of acid ≡ 5 mg Na_2CO_3

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

$$N = \frac{50\,\cancel{mg}}{\frac{106\,\cancel{mg}/\cancel{mmol}}{2\,meq\,/\,\cancel{mmol}}} \text{ x } \frac{1}{1ml} = 0.094 \text{ meq / ml}$$

Titrations 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:

$Ba(OH)_2 + 2Hcl \longrightarrow BaCl_2 + 2H_2O$

1mmole of $Ba(OH)_2 \equiv$ 2mmole of Hcl

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

No.moles $Ba(OH)_2$ = 29.71 ~~ml~~ x 0.01963 mmol / ~~ml~~

=0.583 mmol

No.mmoles HCl = 0.583~~mmol $Ba(OH)_2$~~ x $\frac{2mmol\ HCl}{1\cancel{mmol\ Ba(OH)2}}$

= 1.166 mmol HCl

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

Ex/Ttration of a sample of an drug was analyzed for aspirin amonoprotic acid ($HC_9H_7O_4$) 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?

Solution/ $HC_9H_7O_4 + NaOH \longrightarrow NaC_9H_7O_4 + H_2O$

1mmol of $HC_9H_7O_4 \equiv$ 1mmol of NaOH

No.mmoles NaOH = 21.50 ~~ml~~ x 0.100 mmol / ~~ml~~

= 2.15 ~~mmol~~ x 10^{-3} mol/~~mmol~~ = 2.15 x 10^{-3} mol

1 mol of $HC_9H_7O_4$ ≡ 1 mol NaOH

1 mol $HC_9H_7O_4$ ≡ 180 gm

Mass of aspirin = 2.15 x 10^{-3} ~~mol~~ x 180 gm / ~~mol~~

=0.387 gm

% Aspirin = $\frac{0.387\ \cancel{gm}}{0.500\ \cancel{gm}}$ x 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 H_2SO_4.

Solution/ $H_2SO_4 + Ba(OH)_2 \longrightarrow BaSO_4 + 2H_2O$

$$1 \text{ mmol } H_2SO_4 \equiv 1\text{mmol } Ba(OH)_2$$

$$\text{Stoichiometric ratio} = \frac{1\ mmol\ Ba(OH)2}{1\ mmol\ H2SO4}$$

No.mmoles H_2SO_4 = 46.24 ~~ml H_2SO_4~~ X 0.1280 1mmol H_2SO_4 / ~~ml H_2SO_4~~

= 5.92 mmol H_2SO_4

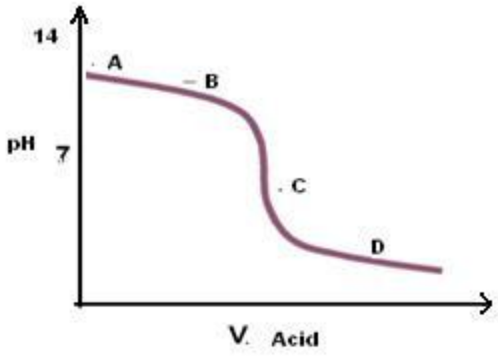
$$\text{No.mmoles } Ba(OH)_2 = 5.92\ \cancel{\text{mmol } H_2SO_4} \times \frac{1\ mmol\ Ba(OH)2}{1\cancel{mmol\ H2SO4}}$$

= 5.92 mmol $Ba(OH)_2$

$$M_{Ba(OH)2} = \frac{5.92\ mmol}{31.76\ ml} = 0.1864 \text{ mmol / ml} = 0.1864 \text{ M}$$

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 [acid] = -log [H+] = -log 0.025= -(-1.6) = 1.6

2-After addition of 10.0ml of NaOH

No.mmols acid = 0.025 mmol/ml × 100 ml =2.5 mmol

No.mmols acid(reacted)=n.moles NaoH =10.0 ml × 0.1 mmole/ml=1.0 mmol

No.mmols acid (unreacted) =2.5 – 1.0 = 1.5 mmol

Volume (solution) =100+10 = 110 ml

[acid] unreacted =$[H^+]$ = 1.5mmol/110mmol =0.0136 M

pH = -log $[H^+]$ = -log 0.0136

= -(-1.866) = 1.866

3- At equivalence point after addition 25 ml of NaoH

At the equivalence point:

$[H_3O]^+ = [OH^-] = 10^{-7}$

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

PH=7 → Bromothymol blue

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

no.mmols NaOH (react) = no.mmols acid = 2.5 mmol

no.mmols NaOH (added) = 30.0 ml ×0.1 mmol/ml = 3.0 mmol

no.mmols(NaOH) unreacted (excess) =3.0 -2.5 = 0.5 mmol

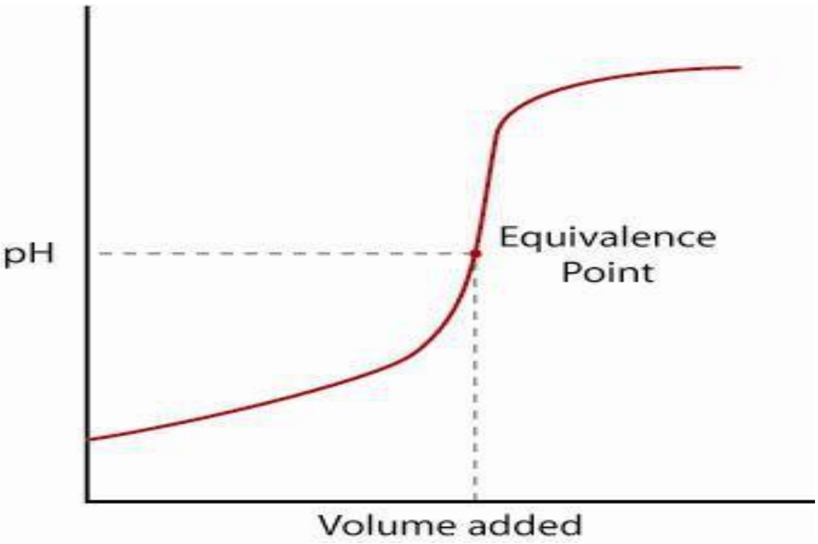
volume of solution = 100 +30 =130 ml

[base]excess =$[OH^-]$ = 0.5mmol/130ml = 0.0038

pOH = -log [OH-] = -log 0.0038

= -(-2.415) =2.415

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 ? ka =1.8× 10^{-5} , pka =4.76

Solution /

1-before added any NaOH or initial pH

pH= 1/2 (pka –log Ma)

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 = pka – log mmoles acid (unreacted) + log mmoles salt/NaOH

No.mmoles HCl = 25.0 ml ×0.1 mmol/ml =2.5 mmol

No.mmoles NaOH = 5.0 ml × 0.1 mmol/ml = 0.5 mmol

No.mmoles HCl (unreacted) = 2.5 – 0.5 = 2.0 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

No.mmoles HCl = 25 ml × 0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH (salt) = 12.5 ml × 0.1 mmol/ml = 1.25 mmol

No.mmol HCl (unreacted) =2.5 – 1.25 = =1.25 mmol

pH = pka – log mmoles acid unreacted + log 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)

No.mmoles acid = 2.5 mmol

No.mmoles NaOH = 25.0 ml × 0.1 mmol/ml = 2.5 mmol

No .mmoles acid (unreacted) = 2.5 – 2.5 = 0 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 خلات الصوديوم فقط لذلك يمكن حساب pH بالشكل التالي :

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

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

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

Ms = [salt] = (no.mmols NaOH)/(total volume) = (25.0ml ×0.1 M)/ 25+25

= 2.5 / 50 = 0.05 M

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

= 1/2 (14 +4.76 – 1.30)

= 8.73 → phenolphthalein

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

No.mmoles HCl = 25 ml × 0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH = 25.1 ml × 0.1 mmol/ml = 2.51 mmol

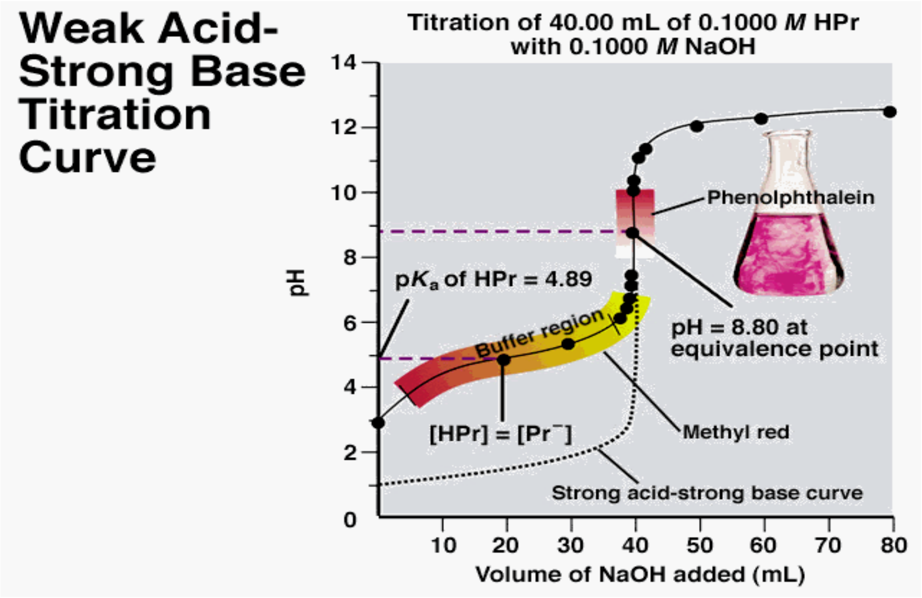
No.mmol NaOH excess =2.51 – 2.5 = 0.01 mmol

Volume =(25 + 25.1)ml = 50.1ml

$[OH^-]$ = 0.01 mmol /50.1 ml = 0.0001996M

pOH = - log $[OH^-]$ = - log 1.996×10^{-4} = 3.7

pH = 14 – 3.7 = 10.3



Gravimetric analysis

Gravimetric analysis describes a set of methods used in analytical chemistry for the quantitative determination of an analyte (the ion being analyzed) based on its mass. The principle of this type of analysis is that once an ion's mass has been determined as a unique compound, that known measurement can then be used to determine the same analyte's mass in a mixture, as long as the relative quantities of the other constituents are known.

The four main types of this method of analysis are

1-precipitation

2- volatilization

3-electro-analytical

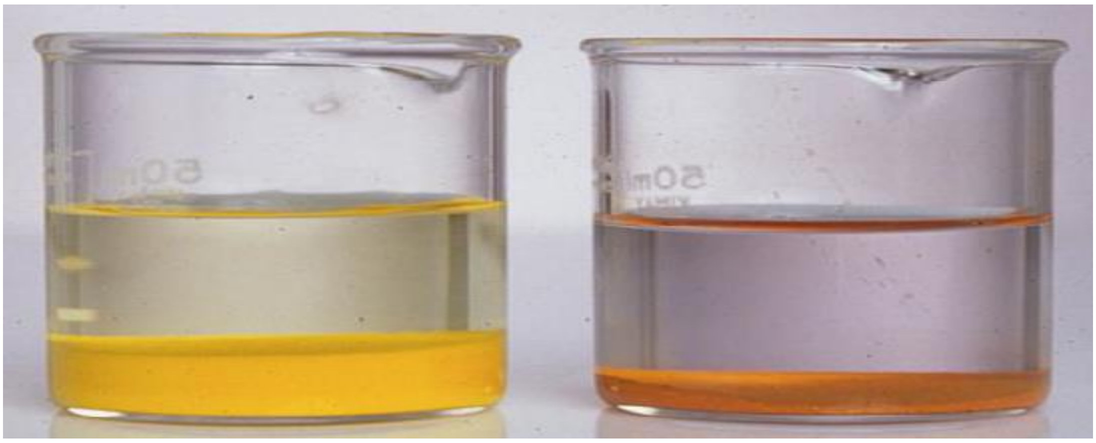
4- miscellaneous physical method.

The methods involve changing the phase of the analyte to separate it in its pure form from the original mixture and are quantitative measurements.

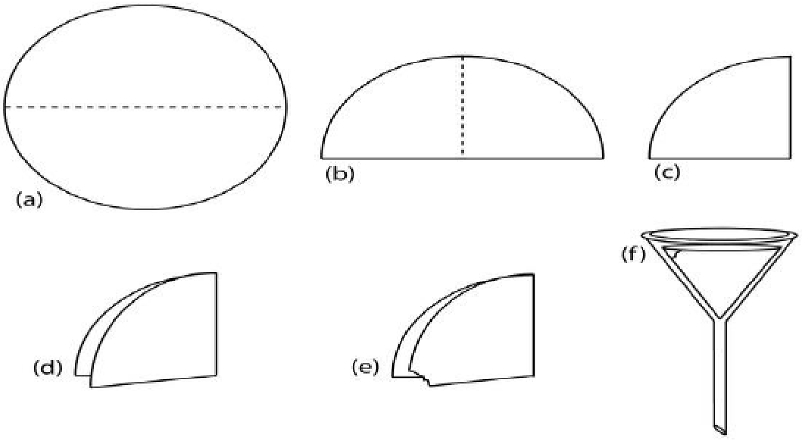
Step of gravimetric analysis

1. The sample is dissolved (water ,acid and base), if it is not already in solution.

2. The solution may be treated to adjust the pH (so that the proper precipitate is formed, or to suppress the formation of other precipitates).



3. The precipitating reagent is added at a concentration that favors the formation of a "good" precipitate . This may require low concentration, extensive heating, or careful control of the pH. Digestion can help reduce the amount of coprecipitation.
4. After the precipitate has formed and been allowed to "digest", the solution is carefully filtered. The filter is used to collect the precipitate; smaller particles are more difficult to filter.



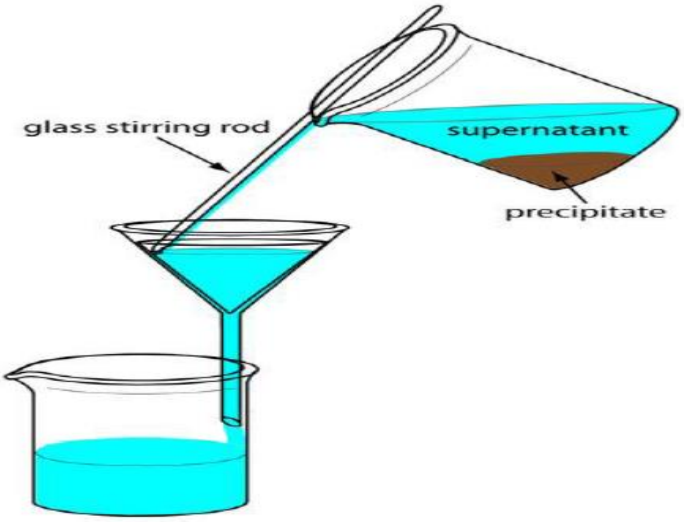


Figure 2 Proper procedure for transferring the supernatant to the filter paper cone.

5. After filtration, the precipitate – including the filter paper or crucible – is heated, or charred. This accomplishes the following:
6. After the precipitate is allowed to cool (preferably in a desiccator to keep it from absorbing moisture), it is weighed (in the crucible). To calculate the final mass of the analyte, the starting mass of the empty crucible is subtracted from the final mass of the crucible containing the sample. Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample.

$$\%\ \text{analyte} = \frac{weight\ of\ analyte}{weight\ of\ sample}\ \text{X100}$$

Gravimetric Factor(G.F)

$$\textbf{G.F} = \frac{\textbf{equivelent weight of unknown substance}}{\textbf{equivelent weight of known substance}} \textbf{X} \frac{\boldsymbol{a}}{\boldsymbol{b}}$$

Where a/b : is the stoichiometric ratio between the element and the precipitate

For example ,if is required to determine the percentage of chloride in sample ,then chloride ion is converted by precipitating reagent to AgCl

cl^- = Agcl

cl_2 = 2Agcl

a b

$$\frac{gCl2}{gAgCl} = \frac{M.wt\ CL2}{M.wt\ AgCl} \text{X} \frac{1\ mole\ Cl2}{2\ mole\ AgCl}$$

Similarity cl_2 = $pbcl_2$:

$$\frac{gCl2}{gpbCl2} = \frac{M.wt\ CL2}{M.wtpbCl2} \text{X} \frac{1\ mole\ Cl2}{1\ mole\ pbCl2}$$

% substance A= $\frac{\text{G.F} * \text{wt.of substance B}}{\text{wt.of sample}}$**X100**

The following some some common examples of the gravimetric factor

Sought sub.	weighted ppt.	G.F.
SO_4^{-2}	$BaSO_4$	$\frac{Mwt.\ SO_4}{Mwt.\ BaSO_4}$
Fe	Fe_2O_3	$\frac{2Mwt.\ Fe}{Mwt.\ Fe_2O_3}$
CO_3^{-2}	$CaCO_3$	$\frac{Mwt.\ CO_3}{Mwt.\ CaCO_3}$
P	$Mg_2P_2O_7$	$\frac{2\,Mwt.\ P}{Mwt.\ Mg_2P_2O_7}$

Example2: The phosphate in a 0.68 gm mineral sample was precipitated as $MgNH_4PO_4$. This yield 0.435 gm of $Mg_2P_2O_7$ by ignition, Calculate the percentage of P in the sample?

Solution:

$$\%P = \frac{wt.\ of\ P}{wt.\ of\ sample} * 100$$

$$wt.\ of\ P = wt.\ of\ Mg_2P_2O_7 * G.F. \rightarrow \left(\frac{2\,Mwt.\ P}{Mg_2P_2O_7} \right)$$

$$= 0.435 * \frac{2 * 30.9}{222.4}$$

$$= 0.1209\ gm$$

$$\%P = \frac{0.1209\ gm}{0.68\ gm} * 100 = 17.8\%$$

Example 1: 1.5 gm sample contain Cl^-. If we added $AgNO_3$ to solution produced precipitate from silver chloride weighted 0.9214 gm. compute percentage of chloride in the sample?

Solution:

$$G.F = \frac{Mwt.\ Cl^-}{Mwt.\ AgCl}$$

$$wt.\ of\ Cl^- = wt.\ of\ AgCl * G.F$$

$$= 0.9214 * \frac{35.5}{143.4} = 0.2282\ gm\ Cl^-$$

$$\%\ Cl = \frac{0.2282\ g}{1.5\ g} * 100 = \underline{15.2\%}$$