



جامعة شط العرب
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Analytical Chemistry (Theory Lectures) *First year*

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1446 A. H.

Analytical Chemistry

The science seeks ever improved means of measuring the chemical composition of natural and artificial materials by using techniques to identify the substances which may be present in a material and to determine the exact amounts of the identified substance. Analytical chemistry involves the analysis of matter to determine its composition and the quantity of each kind of matter that is present. Analytical chemists detect traces of toxic chemicals in water and air. They also develop methods to analyze human body fluids for drugs, poisons, and levels of medication.

Analytical chemistry consists of:

(A) Qualitative analysis which deals with the identification of elements, ions, or compounds present in a sample (tells us what chemicals are present in a sample).

(B) Quantitative analysis which is dealing with the determination of how much of one or more component is present (tells how much amounts of chemicals are present in a *sample*). This analysis can be divided into three branches.

(1) Volumetric analysis (Titrimetric analysis): The analyte reacts with a measured volume of reagent of known concentration, in a process called titration.

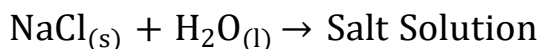
(2) Gravimetric analysis: usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

(3) Instrumental analysis: They are based on the measurement of a physical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation. Examples are spectrophotometry (ultraviolet, visible, or infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy (absorption, fluorescence).

Solutions

Solution: Homogeneous mixture of two or more substance produce from dissolved (disappeared) solute particle (ions, atoms, molecules) (lesser amount) between solvent particle (larger amount).

Solute (lesser amount) + Solvent (larger amount) → Solution



Concentrated Solution has a large amount of solute.

Dilute Solution has a small amount of solute.

Solute	Solvent		
	Gas	Liquid	Solid
Gas	O _{2(g)} in N _{2(g)} , Air	CO _{2(g)} in H ₂ O _(L) , Soda	H _{2(g)} in Pd _(s) , H ₂ catalyst
Liquid	Perfume	Alcohol _(L) in H ₂ O _(L)	Hg _(L) in Ag _(s) , Dental filling
Solid	Dust air, Smoke industry	NaCl _(s) in H ₂ O _(L) , salt water, saline sol.	Zn _(s) in Cu _(s) , Brass alloy

Classification of solutions according to amount of solute:

(1) Unsaturated solutions: if the amount of solute dissolved is less than the solubility limit, or if the amount of solute is less than capacity of solvent.

(2) Saturated solutions: is one in which no more solute can dissolve in a given amount of solvent at a given temperature, or if the amount of solute equal to capacity of solvent.

(3) Super saturated solutions: solution that contains a dissolved amount of solute that exceeds the normal solubility limit (saturated solution). Or a solution contains a larger amount of solute than capacity of solvent. This it's occurs when the solution is heated to a high temperature.

Classification of solution based on solute particle size:

(1) True solution: A homogeneous mixture of two or more substance in which substance (solute) has a particle size less than 1 nm dissolved in solvent. Particles of true solution cannot be filtered through filter paper and are not visible to naked eye (NaCl in water).

(2) Suspension solution: heterogeneous mixtures which settles on standing and its components can be separated by filtrating (Amoxicillin Antibiotics), particle of solute visible to naked eye.

(3) Colloidal solution: homogeneous mixture which does not settle on standing, nor are their components filterable, solute particle visible with electron microscope (milk).

Stoichiometric Calculations:***Gram atomic weight:***

(gAw sometime Awt): Is the weight of a specified number of atoms of that element (contains exactly the same number of atoms of that element as there are carbon atoms in exactly 12g of carbon 12 (this number is Avogadro's number = 6.022×10^{23} atoms).

Gram molecular weight:

(gMw sometimes M.wt): Defined as the sum of the atomic weight of the atoms that make up a molecular compound. Or the weight of Avogadro's number of molecules of any compound.

Gram formula weight:

(gFw some time F.wt): The sum of the atomic weight of the atoms that make up an ionic formula. (is the more accurate description for substances that do not exist as molecules but exist as ionic compounds e.g strong electrolytes-acids, bases, salts). Sometimes use the term molar mass (Molecular weight, M.wt) in place of gram formula weight, gFw).

Example (1):- Calculate the number of grams in one mole of $\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$ (calculate gram molecular or formula weight).

Solution:

One mole is the formula weight expressed in grams. The formula weight is

(Ca=40.08, S=32.06, O=16.00, H=1.01)

$$\text{CaSO}_4 \cdot 7\text{H}_2\text{O} = 40.08 + 32.06 + (16.0 \times 4) + 7[(2 \times 1.01) + 16.00] \\ = 262.28 \text{ gm/mol.}$$

Mwt of $\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$	=	Ca $\times 1$	=	40.08 $\times 1$	=	40.08
		S $\times 1$	=	32.06 $\times 1$	=	32.06
		O $\times 4$	=	16 $\times 4$	=	64.00
		H $\times 14$	=	1.01 $\times 14$	=	14.14
		O $\times 7$	=	16 $\times 7$	=	112.00

						262.28 (gm/mol)

Mole Concept: Mole

which is Avogadro's number (6.022×10^{23}) of atoms, molecules, ions or other species. Numerically: it is the atomic, molecular, or formula weight of a substance expressed in grams.

$$\text{Mole} = \frac{\text{Weight (gm)}}{\text{Formula weight (gm/mol)}} \qquad \text{mmole} = \frac{\text{Weight (mg)}}{\text{Formula weight (mg/mmol)}}$$

*(1mole = 1000 mmole)

Where formula weight represents the atomic or molecular weight of the substance.

Example (2):-Calculate the number of moles in 500 mg Na_2WO_4 .

Solution (A.wt W= 183,84 g/mole , Na = 23 g/mole, O = 16 g/mol)

$$\text{Mmole} = \frac{\text{Wt (mg)}}{\text{M.wt (mg/mmol)}} = \frac{500 \text{ (mg)}}{293.8 \text{ (mg/mmol)}} = 1.706 \text{ mmole}$$

$$\text{Mole} = \frac{\text{mmole}}{1000} = \frac{1.706}{1000} = 0.00170 \text{ mol}$$

Example (3): How many molecules are contained in 25.0 g H_2 .

Solution: (A.wt H= 1.008 g/mole)

$$\text{Moles } \text{H}_2 = \frac{\text{Wt (gm)}}{\text{F.wt}} = \frac{25 \text{ (gm)}}{2.016 \text{ (gm/mol)}} = 12.40 \text{ mole}$$

No. Molecules = No. moles $\times$ Avogadro number

$$= 12.40 \times 6.022 \times 10^{23} = 7.74 \times 10^{24} \text{ molecule}$$

Example (4):-How many milligrams are in 0.250 mmole Fe_2O_3 (ferric oxide).

Solution: (A.wt O= 16 g/mole , Fe = 56.85 g/mole)

$$\text{Mwt of } \text{Fe}_2\text{O}_3 = \text{Fe} \times 2 = 56.85 \times 2 = 113.7$$

$$\text{O} \times 3 = 16 \times 3 = 48.0$$

$$\begin{array}{r} \text{-----} \\ 159.7 \end{array}$$

$$\text{Wt (mg)} = \text{mmole} \times \text{M.wt (mg/mole)}$$

$$= 0.250 \text{ mmole} \times 159.7 \text{ mg/mole} = 39.9 \text{ mg}$$

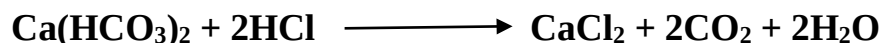
Example (5):- Calculate the number of mole of NaCl required to prepare 1Kg of AgCl according to the equation: (Na=23, Cl=35.5, N=14 , Ag =107.86, O = 16 g/mole)



$$\text{No. of moles AgCl} = \frac{W_t}{M.wt} = \frac{1000\text{gm}}{143.36 \text{ gm/mol}} = 6.98 \text{ mol}$$

according to the balance equation the mole ratio between NaCl & AgCl equal 1:1 therefore we need 6.98 mol of NaCl.

Example (6): Calculate the number of moles of Ca (HCO₃)₂ required to prepare 1.5 mol of CO₂ according to the equation.



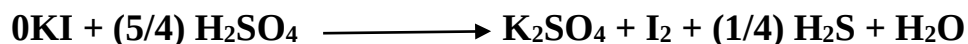
solution: No. of mol of Ca (HCO₃)₂ = No. of mol of CO₂ × 0.5

$$= 1.5 \times 0.5 = 0.75 \text{ mol of Ca (HCO}_3)_2$$

Example (7): What mass of KI is needed to produce 69.6 gm of K₂SO₄ by the reaction :
(Mwt, K= 39.1 , S = 32 , O = 16 , I = 127)



We divide the equation by 4



solution :

$$\text{No. of mol of K}_2\text{SO}_4 = \text{wt} / \text{M.wt} \longrightarrow 69.6 \text{ gm} / 174 \text{ (gm /mol)} = 0.4 \text{ mol}$$

$$\text{No. of mol of KI} = 2 \times 0.4 = 0.8 \text{ mol}$$

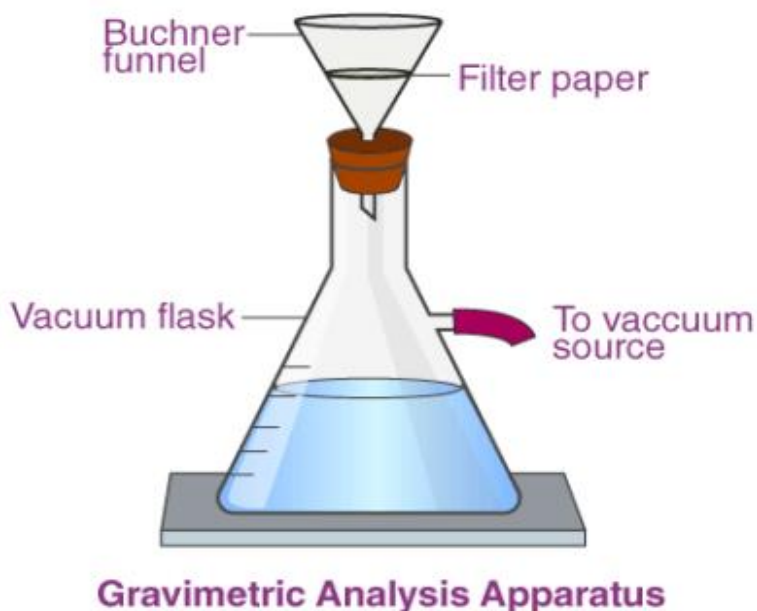
$$\text{wt of KI} = \text{mol} \times \text{M.wt} = 0.8 \times 166 = 133\text{gm}$$

Gravimetric Analysis

Gravimetric analysis is a method in analytical chemistry to determine the quantity of an analyte based on the mass of a solid. Example: Measuring the solids suspended in the water sample – Once a known volume of water is filtered, the collected solids are weighed.

The principle of Gravimetric Analysis:

The principle behind the gravimetric analysis is that the mass of an ion in a pure compound can be determined. Later, used to find the mass percent of the same ion in a known quantity of an impure compound.



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Gravimetric Analysis Apparatus

Steps followed in the Gravimetric Analysis

1. Preparation of a solution containing a known weight of the sample.
2. Separation of the desired constituent.
3. Weighing the isolated constituent.
4. Computation of the amount of the particular constituent in the sample from the observed weight of the isolated substance.

Types of Gravimetric Analysis:

There are 4 fundamental types of gravimetric analysis. Of which, there are 2 common types involving changes in the phase of the analyte to separate it from the rest of a mixture, resulting in a change in mass.

Volatilization gravimetric

- Volatilization Gravimetric involves separating components of our mixture by heating or chemically decomposing the sample.

Precipitation gravimetric

- Precipitation Gravimetric uses a precipitation reaction to separate one or more parts of a solution by incorporating it into a solid.

Electro gravimetric

- Electro gravimetric is a method used to separate and quantify ions of a substance, usually a metal.

Thermo gravimetric

- Thermo gravimetric is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time.

Advantages of Gravimetric Analysis:

If the methods are followed carefully, it provides exceedingly precise analysis. It is used to determine the atomic masses of many elements to six-figure accuracy. It provides little room for instrumental error and does not require a series of standards for calculation of an unknown

Disadvantages of Gravimetric Analysis:

It usually provides only for the analysis of a single element, or a limited group of elements, at a time. Comparing modern dynamic flash combustion coupled with gas chromatography with traditional combustion analysis.

Examples of Gravimetric Analysis:**Q1/ What is the principle of gravimetric analysis?**

Gravimetric analysis relies on the contrast of the masses of two analyte-containing compounds. The idea behind gravimetric analysis is that it is possible to calculate the mass of an ion in a pure compound and then use it to calculate the mass percentage of the same ion in a specified volume of an impure compound.

Q2/ What are the applications of gravimetric analysis?

In analytical chemistry, gravimetric analysis is a way of determining the analyte quantity based on the density of a solid. Example: Measuring the solids suspended in the water sample. The collected solids are weighed until a known water volume is purified.

Q3/ What is the difference between gravimetric and volumetric analysis?

A gravimetric feeder is a self-calibrating, speed-based dosing device based on weight. On the other hand, a volumetric feeder does this depending on the velocity of volume. Using loss-in-weight technique, which calculates the decreased weight during dosing, weight is estimated.

Q4/ How does volumetric titration work?

A widely-used quantitative computational methodology is volumetric analysis. This approach requires the calculation of the volume of a solution of known concentration that is used to assess the analyte concentration, as the name suggests. The end point of the titration is the point at which the colour alteration takes place.

Q5/ What are the advantages of gravimetric analysis?

Gravimetric analysis allows for highly detailed analysis if procedures are practised closely. In fact, to calculate the atomic masses of several elements in the periodic table to six figure precision, gravimetric analysis was used.

concentration

It is one of the properties of solutions of all kinds; It is the ratio of the presence of solute to the solvent or to the total solution, and this ratio is measured in several ways: Before that, one must define the solute and the solvent.

❖ **Solute:** It is the substance that is dissolved and may be solid, liquid or gaseous.

❖ **Solvent:** It is the liquid substance that receives a solute.

❖ **Solvent and solute:** Together they are called solution.

There are several ways to express concentration, including:

Molarity (M)

The number of moles of solute in one liter of the solution.
Its units (mole/l).

$$M = \frac{\text{Number of moles of a}}{\text{Volume of the solution (L)}} \quad \text{No. of moles} = \frac{\text{wt. (gm)}}{\text{M.Wt}}$$

Wt. = weight of a solute

M. Wt = Molecular weight

Molecular weight :-

The total of the atomic weights of the components of a substance.

Example1:

Calculate the molecular weight of sodium hydroxide NaOH, noting that the atomic weights are: Na= 23, O= 16, H= 1 ?

Solution:

$$\text{M.Wt. (NaOH)} = [(1 \times 23) + (1 \times 16) + (1 \times 1)] = 40 \text{ gm/mol}$$

Example2:

Calculate the molecular weight of sodium Carbonate Na_2CO_3 , noting that the atomic weights are: Na= 23, O= 16, C= 12 ?

Solution:

$$\text{M.Wt. (Na}_2\text{CO}_3) = [(2 \times 23) + (1 \times 12) + (3 \times 16)] = 106 \text{ gm/mol}$$

Molar concentrations can be calculated from the following equations:-

1- For solid material:

$$M = \frac{\text{wt. (gm)}}{\text{M.Wt}} * \frac{1000}{V \text{ (ml)}}$$

M : Molar concentration (mol/l)
 Wt. : weight of a solute (gm)
 M.Wt. : Molecular weight (gm/mol)
 V : Volume of solution (ml)

Example

Calculate the molarity of a solution that contains 10.6 g of sodium carbonate Na_2CO_3 in one liter of aqueous solution?

Solution:

$$M = \frac{\text{wt. (gm)}}{\text{M.Wt}} * \frac{1000}{V \text{ (ml)}} \longrightarrow M = \frac{10.6}{106} * \frac{1000}{1000}$$

$$M = 0.1 \text{ mol/l}$$

2- For liquid material:

$$M = \frac{\text{Sp. Gr} * \% * 1000}{\text{M. Wt}}$$

M : Molar concentration (mol/l)
 Wt. : weight of a solute (gm)
 M.Wt. : Molecular weight (gm/mol)
 % = purity of solution
 Sp.Gr. = specific gravity (gm/ml)

Example

Calculate the molar concentration of the sulfuric acid H₂SO₄ (20%), if the specific gravity is equal 1.14 (gm/ml), noting that the atomic weights are: S= 32, O= 16, H= 1 ?

Solution:

$$\text{M.Wt.}(\text{H}_2\text{SO}_4) = [(2 \times 1) + (1 \times 32) + (4 \times 16)] = 96 \text{ gm/mol}$$

$$M = \frac{\text{Sp. Gr} \times \% \times 1000}{\text{M. Wt}} \longrightarrow M = \frac{1.14 \times 0.20 \times 1000}{96}$$

$$M = 2.375 \text{ mol/l}$$

Dilution law

$$M \times V(\text{Conc.}) = M \times V(\text{dilute})$$

Example

Prepare (0.1 M) sulfuric acid H₂SO₄ (20%) in 100 ml, if the specific gravity is equal 1.14 (gm/ml), noting that the atomic weights are: S= 32, O= 16, H= 1 ?

Solution:

$$\text{M.Wt.}(\text{H}_2\text{SO}_4) = [(2 \times 1) + (1 \times 32) + (4 \times 16)] = 96 \text{ gm/mol}$$

$$M = \frac{\text{Sp. Gr} \times \% \times 1000}{\text{M. Wt}} \longrightarrow M = \frac{1.14 \times 0.20 \times 1000}{96}$$

$$M = 2.375 \text{ mol/l}$$

$$M \times V(\text{Conc.}) = M \times V(\text{dilute}) \longrightarrow 2.375 \times V = 0.1 \times 100$$

$$V = 4.21 \text{ ml}$$

Normality (N)

The number of gram equivalent of a solute in one liter of the solution. Its units (eq/l).

$$M = \frac{\text{Number of gm equivalent of a solute}}{\text{Volume of the solution (L)}}$$

Wt. = weight of a solute

Eq.Wt. = Equivalent weight

$$\text{Number of gm equivalent} = \text{wt. (gm)} / \text{Eq.wt}$$

Equivalent weight :-

$$\text{Eq. wt.} = M.Wt. / n$$

$$M.Wt. = \text{Eq. wt.} * n$$

Calculating the value of **n** depends on the type of substance whose concentration is to be calculated as follows :-

1. Acids: **n** it represents the no. of hydrogen ions ready to be substituted.

	HCl	H ₂ SO ₄	H ₂	H ₃ P
n	1	2	2	3
M. Wt	36.5	98	36	98
Eq. wt.	36.5	49	18	38.3

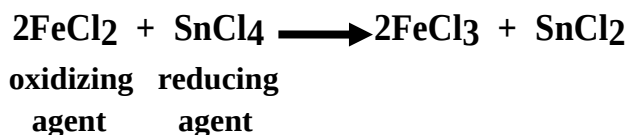
2. Bases: **n** it represents the no. of hydroxyl ions ready to be substituted.

	NaO	Ca(OH) ₂	Mg(OH) ₂	Al(OH) ₃
n	1	2	2	3
M. Wt	40	74	58	78
Eq. wt.	40	37	29	26

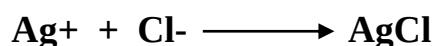
3. salts : A value n is calculated from multiplying of the no. of metal and oxidation no. of the metal.

	NaCl	Na ₂ SO	CaSO	Al ₂ (SO ₄) ₃
Oxidation no. of the metal	+1	+1	+2	+3
No.of metal	1	2	1	2
n	1	2	2	6
M. Wt	58.5	142	136	342
Eq. wt.	58.5	71	68	57

4. Oxidation - Reduction reactions : n It represents the no. of electrons lost or gained per molecule.



5. Precipitation reactions : A value n is calculated from multiplying of the no. of cations and oxidation no. of the cations.



$$n = 1 \times 1^+ \quad n=1$$

6. Complex Formation reactions: n it represents the number of electrons gifted by the Ligand.

Normal concentrations can be calculated from the following equations:-

1- For solid material:

$$N = \frac{\text{wt. (gm)}}{\text{Eq. Wt.}} * \frac{1000}{V \text{ (ml)}}$$

N : Normal concentration (eq/l)

Wt. : weight of a solute (gm)

Eq.Wt. : Equivalent weight (g/eq)

V : Volume of solution (ml)

Example

Normality of sodium carbonate solution Na_2CO_3 is 0.2N, calculate the number of grams dissolved in 250 ml, noting that the atomic weights are: Na= 23, O= 16, C= 12 ?

Solution:

$$\text{M.Wt. (Na}_2\text{CO}_3) = [(2 \times 23) + (1 \times 12) + (3 \times 16)] = 106 \text{ gm/mol}$$

$$\text{Eq. wt.} = \text{M.Wt.} / n \longrightarrow \text{Eq. Wt.} = 106/2 = 53 \text{ g/ eq}$$

$$N = \frac{\text{wt. (gm)}}{\text{Eq. Wt.}} * \frac{1000}{V \text{ (ml)}} \longrightarrow 0.2 = \frac{\text{wt. (gm)}}{53} * \frac{1000}{250}$$

$$\text{Wt} = 2.65 \text{ gm}$$

2- For liquid material:

$$N = \frac{\text{Sp. Gr} * \% * 1000}{\text{Eq. Wt.}}$$

N : Normal concentration (eq/l)

Wt. : weight of a solute (gm)

Eq.Wt. : Equivalent weight (g/eq)

% = purity of solution

Sp.Gr. = specific gravity (gm/ml)

Example

Calculate the normal concentration of the sulfuric acid H_2SO_4 (20%), if the specific gravity is equal 1.14 (gm/ml), noting that the atomic weights are: S= 32, O= 16, H= 1 ?

Solution:

$$\text{M.Wt. (H}_2\text{SO}_4) = [(2 \times 1) + (1 \times 32) + (4 \times 16)] = 96 \text{ gm/mol}$$

$$\text{Eq. wt.} = \text{M.Wt.} / n \longrightarrow \text{Eq. Wt.} = 96/2 = 48 \text{ g/ eq}$$

$$N = \frac{\text{Sp. Gr} * \% * 1000}{\text{Eq. Wt.}} \longrightarrow N = \frac{1.14 * 0.29 * 1000}{48}$$

$$N = 4.75 \text{ eq/l}$$

Example

Prepare (0.1 N) sulfuric acid H_2SO_4 (20%) in 100 ml, if the specific gravity is equal 1.14 (gm/ml), noting that the atomic weights are: S= 32, O= 16, H= 1 ?

Solution: M.Wt.(H_2SO_4)= $[(2 \times 1) + (1 \times 32) + (4 \times 16)] = 96 \text{ gm/mol}$

$$N = 4.75 \text{ eq/l}$$

$$M * V(\text{Conc.}) = M * V(\text{dilute}) \longrightarrow 4.75 * V = 0.1 * 100 \quad V = 2.10 \text{ ml}$$

Relation between normality and molarity:

$$N = M \times \text{number of equivalents}$$

Ex. Calculate the molarity of the solution $\text{Al}_2(\text{SO}_4)_3$ (0.3N) ?

Q/ What are the Differences Between Normality and Molarity ?

Solution:

No.	Molarity	Normality
1.	It is defined as the number of moles per liter of solution.	It is defined as the number of gram equivalent per liter of solution.
2.	It is used in measuring the ratio between the number of moles in the total volume of the solution.	It is used in measuring the gram equivalent in relation to the total volume of the solution.
3.	known as molar concentration.	Known as equivalent concentration.
4.	The units are M or Mol/l	The units are N or eq/l

Calculations in Gravimetric Analysis:

The results of a gravimetric analysis are generally computed from two experimental measurements: the weight of sample and the weight of a known composition precipitate. The precipitate we weigh is usually in a different form than the analyte whose weight we wish to find. The principles of converting the weight of one substance to that of another depend on using the stoichiometric mole relationships. We introduced the gravimetric factor (GF), which represents the weight of analyte per unit weight of precipitate. It is obtained from the ratio of the formula weight of the analyte to that of the precipitate, multiplied by the moles of analyte per mole of precipitate obtained from each mole of analyte, that is:

$$GF = \frac{\text{M.Wt. of analyte (g/mol)}}{\text{M.Wt. of precipitate (g/mol)}} \times \frac{a}{b}$$

M.Wt. : Molecular weight (gm/mol)

a : No. of moles of analyte

b : No. of moles of precipitate

Example:

Calculate GF for the conversions in the table on your right :

No.	Analyte	M.Wt. or A.Wt.	precipitate	M.Wt.
1	P	31	Ag ₃ PO ₄	419
2	K ₂ HPO ₄	174	Ag ₃ PO ₄	419
3	Bi ₂ S ₃	514	BaSO ₄	233.4
4	Al	27	Al ₂ S ₃	150

Solution:

$$GF = \frac{\text{M.Wt. of analyte (g/mol)}}{\text{M.Wt. of precipitate (g/mol)}} \times \frac{a}{b}$$

$$1) \text{ GF} = \frac{31 \text{ (g/mol)}}{419 \text{ (g/mol)}} \times 1 = 0.074$$

$$2) \text{ GF} = \frac{174 \text{ (g/mol)}}{419 \text{ (g/mol)}} \times 1 = 0.415$$

$$3) \text{ GF} = \frac{514 \text{ (g/mol)}}{233.4 \text{ (g/mol)}} \times \frac{1}{3} = 0.734$$

$$4) \text{ GF} = \frac{27 \text{ (g/mol)}}{150 \text{ (g/mol)}} \times \frac{2}{1} = 0.54$$

In gravimetric analysis, we are generally interested in the percent composition by weight of the analyte in the sample, that is:

$$\% \text{ analyte} = \frac{\text{Wt. of analyte (g)}}{\text{Wt. of sample (g)}} \times 100$$

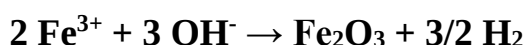
$$\text{GF} = \frac{\text{Wt. of analyte (g)}}{\text{Wt. of precipitate(g)}}$$

$$\text{Wt. of analyte (g)} = \text{Wt. of precipitate(g)} \times \text{GF}$$

$$\% \text{ analyte} = \frac{\text{Wt. of precipitate(g)} \times \text{GF}}{\text{Wt. of sample (g)}} \times 100$$

Example:

A 0.5962 g sample of iron ore is dissolved in perchloric acid (HClO_4). All iron present is oxidized to Fe^{3+} . The solution is filtered to remove solid matrix materials and made basic with addition of ammonium hydroxide. The iron precipitates as the $\text{Fe}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ gel. The precipitate is collected in a cistern crucible and ignited to produce Fe_2O_3 . What is the wt. % of iron in the sample if the analysis produced 0.3210 g Fe_2O_3 ?

Solution:

$$\text{GF} = \frac{\text{M.Wt. of analyte (g/mol)}}{\text{M.Wt. of precipitate (g/mol)}} \times \frac{a}{b}$$

$$\text{GF} = \frac{55.85 \text{ (g/mol)}}{159.69 \text{ (g/mol)}} \times 2 = 0.6995$$

$$\begin{aligned} \text{Wt. of analyte (g)} &= \text{Wt. of precipitate} \times \text{GF} \\ &= 0.3210 \times 0.6995 \\ &= 0.2245 \text{ g} \end{aligned}$$

$$\% \text{ analyte} = \frac{\text{Wt. of precipitate} \times \text{GF}}{\text{Wt. of sample}} \times 100$$

$$\% \text{ iron in the ore} = \frac{0.2245}{0.5962} \times 100$$

$$\% \text{ iron in the ore} = 37.66$$

Example:

A certain barium halide exists as the hydrated salt $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 mL) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate, M.Wt. = 233.3 g/mol) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.

Solution:

Number of moles of Ba = Wt. of BaSO_4 ppt. / M.Wt. of BaSO_4

$$= 0.2533 / 233.3$$

$$= 1.09 \times 10^{-3}$$

M.Wt. of $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$ = wt. of $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$ / No. of moles of Ba in $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$

$$= 0.2650 / 1.09 \times 10^{-3}$$

$$= 243.11 \text{ g/mol}$$

Atomic wt. of Ba $\times 2$ + M.Wt. of H_2O = $137.327 + 2 \times 18$

$$= 173.327 \text{ g/mol}$$

Atomic wt. of 2X = $243.11 - 173.327$

$$= 69.783 \text{ g/mol}$$

Atomic wt. of X = $69.783 / 2$

$$= 34.8915 \text{ g/mol}$$

The Atomic weight of chlorine is 35.45 g/mol, which is in good agreement with the result obtained and hence the halide salt is hydrated barium chloride and X = Chlorine.

H.W:

1) A 0.4960 g sample of a CaCO_3 (M.Wt. = 100 g/mol) is dissolved in an acidic solution. The calcium is precipitated as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (M.Wt. = 146 g/mol) and the dry precipitate is found to weigh 0.6186 g. What is the percentage of CaO (M.Wt. = 56 g/mol) in the sample?

2) 0.8 g sample contains sulfur S (A.Wt.= 32 g/mol) has been dissolved. The sulfur is precipitated as BaSO_4 (M.Wt. = 233 g/mol) . If the weight of the precipitate is 0.3 g calculate the percentage of sulfur in the sample?

Formality (F):

The number of gram formula weight of the solute per one liter of the solution. Its units (g. FW./l).

$$F = \frac{\text{Number of formula weight of a solute}}{\text{Volume of the solution (L)}}$$

$$\text{Number of formula weight} = \frac{\text{wt. (gm)}}{\text{formula weight}}$$

$$F = \frac{\text{wt. (gm)}}{F.Wt} * \frac{1000}{v(ml)}$$

F : Formula concentration (FW./l)

Wt. : weight of a solute (gm)

F.Wt : formula weight (gm/ FW)

V : Volume of solution (ml)

Example:

Calculate the formality of sodium chloride (NaCl) solution, 5.85g of which have been dissolved to form 250mL of the given solution.

Step 1: Given,

- Weight of solute (NaCl)=5.85g
- Molecular weight of solute (NaCl)=58.5gmol⁻¹
- Volume of solution =250mL=0.250L(∵1L=1000ml)

Step 2: To determine the formality of NaCl solution.

Formality = $\frac{\text{Given weight of solute}}{\text{Molecular weight of solute} \times \text{Volume of solution in litre}}$

- Formality = $\frac{5.85\text{g}}{58.5\text{g/mol} \times 0.250\text{L}}$
- Formality = 0.4F

Therefore, the formality of NaCl solution is 0.4F.

Molality (m):

Molal concentration (Molality) m:-The solution concentration produced from dissolved solute (mole) in solvent (kg), molality does not change with temperature and is used for physicochemical measurements.

The number of moles of solute in 1000 gram of the solvent. Its units (mole/kg).

$$m = \frac{\text{Number of moles of a solute}}{1000 \text{ gram of the solvent}} \quad \text{Number of moles} = \frac{\text{wt. (gm)}}{M.Wt.}$$

$$m = \frac{\text{wt. (gm)}}{M.Wt} \times \frac{1000}{Wt \text{ (gm)}}$$

Example:

Calculate the molal concentration for solution prepared from mixing 4 g NaOH with 500 g water.

Solution:

$$m = \frac{\text{wt. (gm)}}{M.Wt} \times \frac{1000}{Wt \text{ (gm)}}$$

$$m = \frac{4 \text{ (gm)}}{40} \times \frac{1000}{500 \text{ (gm)}}$$

$$m = 0.2$$

Mole Fraction (X):

It is the ratio between number of solute or solvent moles and the total number of solute and solvent moles.

$$X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \quad X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$X_{\text{solute}} + X_{\text{solvent}} = 1$$

Example:

Calculate the mole fraction for the components of the resulting solution by dissolving 20gm NaOH in 500 ml water?

Solution:

$$n_{\text{NaOH}} = \frac{Wt}{M.Wt} = \frac{20}{40} = 0.5 \quad X_{\text{NaOH}} = \frac{0.5}{0.5 + 27.8} = 0.0178$$

$$n_{\text{H}_2\text{O}} = \frac{Wt}{M.Wt} = \frac{500}{18} = 27.8 \quad X_{\text{solute}} + X_{\text{solvent}} = 1$$

$$X_{\text{H}_2\text{O}} = 1 - 0.0178 = 0.983$$

Weight percentage concentration (W/W%):

Number of grams of solute in 100 gm of solution.

$$W/W \% = \frac{Wt. \text{ of solute}(gm) * 100}{Wt. \text{ of solution}}$$

Volume percentage concentration (V/V%):

Number of milliliters of solute in 100 milliliters of solution.

$$V/V \% = \frac{V \text{ of solute}(ml) * 100}{V \text{ of solution } (ml)}$$

Weight/Volume percentage concentration (W/V%):

Number of grams of solute in 100 milliliters of solution.

$$W/V \% = \frac{Wt. \text{ of solute}(gm) * 100}{V \text{ of solution } (ml)}$$

Example:

Calculate the volume percentage concentration of a solution prepared from 50 ml of methyl alcohol to 200 ml of distilled water?

Solution:

$$V/V \% = \frac{V \text{ of solute}(ml) * 100}{V \text{ of solution } (ml)} = \frac{50}{(50 + 200)} * 100 = 20\%$$

Example:

Calculate the weight percentage of a solution prepared by dissolving 5.0 gm of Silver nitrate in 100 ml of water, Assume that the density of water is equal to (1 gm/ cm³).

Solution:

$$W/W \% = \frac{Wt. \text{ of solute}(gm) * 100}{Wt. \text{ of solution}} = \frac{5}{(5 \text{ gm} + 100 \text{ ml} * 1 \text{ gm/ml})} * 100 = 4.76\%$$

Example:

Calculate the molarity of NaCl a solution if the percentage weight/ volume is equal 0.85% ?

Solution:

$$W/V \% = \frac{Wt. \text{ of solute}(gm) * 100}{V \text{ of solution } (ml)}$$

$$0.85 = \frac{\text{Wt. of solute(gm)}}{100 \text{ ml}} * 100$$

$$\diamond \text{ Wt. of solute} = 0.85 \text{ gm}$$

$$M = \frac{\text{wt. (gm)}}{\text{M.Wt}} * \frac{1000}{v(\text{ml})} = \frac{0.85}{58.5} * \frac{1000}{100} \quad \text{M} = 0.145$$

Parts per million (ppm):

Number of milligrams of solute in kilogram of solution.

$$\diamond \text{ ppm} = \frac{\text{Wt. of solute(mg)}}{\text{Wt. of solution(kg)}}$$

Or :

Number of milligrams of solute in one liter of solution.

$$\diamond \text{ ppm} = \frac{\text{Wt. of solute(mg)}}{V \text{ of solution(L)}}$$

Example:

Prepare 100 ppm from CuSO_4 solution in 1L of distilled water.?

Solution:

$$1 \text{ ppm} = 1 \text{ mg/L}$$

$$\text{ppm} = 100 \text{ mg/L}$$

$$= 0.1 \text{ gm/L}$$

Example:

Prepare 100 ppm from Ca^{+2} solution using CaSO_4 in 1L , 0.5L of distilled water?

Solution:

1. In 1 L.

1 ppm = 1 mg/L 100

ppm = 100 mg/L

= 0.1 g/L

	Ca+2	CaSO ₄
M.Wt	40	136
Wt	0.1	x

X = 0.34 gm

2. In 0.5 L.

Wt(gm)	V(ml)
0.34	1000
x	500

X = 0.17 gm

Chemical equilibrium

To understand the chemistry of seawater it is necessary to have some understanding of physical chemistry. Only a few basic concepts are required. The material in this lecture comes from the field of chemical thermodynamics. A rigorous presentation is included in an appendix for those interested. For the purpose of this class there are only a few basic concepts you need to know in order to conduct equilibrium calculations. With these calculations we can predict chemical composition using chemical models.

The main questions we ask are:

1. Is a geochemical system at chemical equilibrium?
2. If not, what reaction(s) are most likely to occur? Here are some examples of the types of problems where equilibrium calculations are useful.

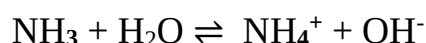
Example: Solubility - Diatoms exist in surface seawater. The solubility of diatom shell material (called opal) is written as: $\text{SiO}_2 \cdot 2\text{H}_2\text{O} (\text{Opal}) \leftrightarrow \text{H}_4\text{SiO}_4$ (diatom shell material) (silicic acid). There are two chemical problems here:

- 1) The surface ocean is everywhere undersaturated with respect to Opal, yet diatoms grow. And furthermore they are preserved in sediments over long time periods (millions of years).
- 2) There are two mineral forms of $\text{SiO}_2(\text{s})$ which are called opal and quartz. The most stable form of solid $\text{SiO}_2(\text{s})$ at earth surface conditions is quartz not opal! Why do diatoms make opal instead of quartz? The reaction between these two solid phases is written as: $\text{SiO}_2 (\text{Opal}) \leftrightarrow \text{SiO}_2 (\text{quartz})$

Chemical and ionic equilibrium:

There are two types of reactions:

- 1) **Reversible reaction**, $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$



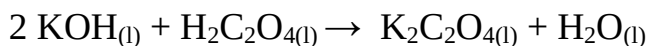
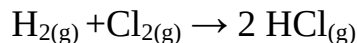
- 2) **Irreversible reaction**, $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$



Generally, most of the chemical reactions are considered as reversible reactions.

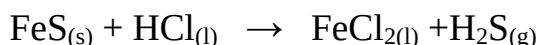
There are two kinds of systems :

a) **Homogenous reactions** : chemical reactions in which the reactants and products are in the same phase (solid , liquid or gas)



b) **Heterogeneous reactions** :

Chemical reactions in which the reactants and products have more than one phase.

**Equilibrium constant (K) :**

A numerical quantity that relate the concentration of reactants and products in a chemical reaction to one another.

For the chemical reaction : $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

According to **mass action law** which states that (The rate of chemical reaction is directly proportional with formula concentration of reaction substances each raise to the power indicated by the number of ion or molecule appearing in the balanced equation of the reaction). Then:

$$V_f \propto [\text{A}]^a, [\text{B}]^b \text{ (f= forward)}$$

$$V_f = K_f [\text{A}]^a [\text{B}]^b$$

$$V_b \propto [\text{C}]^c, [\text{D}]^d \text{ (b= backward)}$$

$$V_b = K_b [\text{C}]^c [\text{D}]^d$$

At equilibrium state : ($V_f = V_b$)

$$K_f [\text{A}]^a [\text{B}]^b = K_b [\text{C}]^c [\text{D}]^d$$

$$\underline{K_f} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$K_b = K = [\text{A}]^a [\text{B}]^b$$

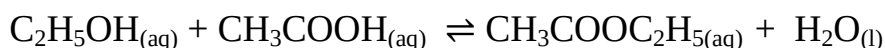
K = equilibrium constant

Lechatelier principle :

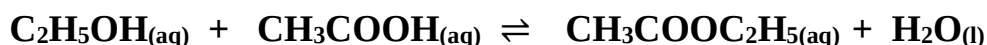
The position of chemical equilibrium will always shift in a direction that tends to remove the effect of the applied stress .

Example:

Consider the reaction between ethanol and ethanoic (acetic) acid:



In an experiment, 0.1 mole of ethanol and 0.2 mole of acetic acid were mixed together forming 1 liter solution and the mixture was allowed to reach equilibrium. The number of moles of acetic acid present at equilibrium were 0.115 mole . Calculate the equilibrium constant value (K_c).



At Start 0.1 mole 0.2 mole 0.0 mole 0.0mole

At Equilibrium

moles $[\text{CH}_3\text{COOH}]$ reacted = Original – remain = 0.2 - 0.115 = 0.085 mole

moles $[\text{CH}_3\text{COOH}]$ reacted = $[\text{CH}_3\text{COOC}_2\text{H}_5]$ produced = $[\text{H}_2\text{O}]$ produced = 0.085 mole

moles $[\text{C}_2\text{H}_5\text{OH}]$ remain = Original – reacted = 0.1 – 0.085 = 0.015 mole

$$\text{Molarity} = \frac{\text{No. of mole}}{V(L)}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5]_{\text{eq}} = 0.085 \text{ M} \quad [\text{H}_2\text{O}]_{\text{eq}} = 0.085 \text{ M}$$

$$[\text{CH}_3\text{COOH}]_{\text{eq}} = 0.115 \text{ M} \quad [\text{C}_2\text{H}_5\text{OH}]_{\text{eq}} = 0.015 \text{ M}$$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5_{(\text{aq})}] [\text{H}_2\text{O}_{(\text{l})}]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}_{(\text{aq})}]} = \frac{[0.085] [0.085]}{[0.015] [0.115]} = 4.19$$

Factors effecting the reactions at equilibrium :

- 1) Nature of reactants.
- 2) Temperature.
- 3) Concentration.
- 4) Pressure (in gas reactions).

Some familiar equilibrium constant expressions :

K_w = ion product (or ionization) constant for water .

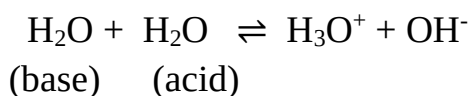
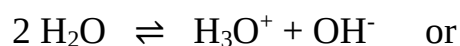
K_{sp} = solubility product constant.

K_a = ionization (or dissociation) constant of a weak acid.

K_b = ionization (or dissociation) constant of a weak base.

Ion product constant for water (K_w) :

Aqueous solutions contains small amount of hydronium ions $[H_3O^+]$ and hydroxide $[OH^-]$ ions as a consequence of the dissociation reaction:



H_2O acid molecule gives H^+ to H_2O base molecule to produce H_3O^+ ions

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K [H_2O]^2 = [H_3O^+][OH^-] = K_w$$

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ mol}^2 / \text{L}^2 \text{ at } 25^\circ\text{C}$$

K_w is **temperature dependant** it increases with temperature rise , and decreases with its decrease.

Variation of K_w with temperature :

Temperature $^{\circ}\text{C}$	K_w
0.0	1.14×10^{-15}
25	1.01×10^{-14}
37	2.6×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
70	2.30×10^{-13}
100	4.9×10^{-13}

K_w is used only for water.

Example :

Calculate the hydronium $[\text{H}_3\text{O}^+]$ and hydroxide ion $[\text{OH}^-]$ concentrations of pure water at 25°C and 100°C ($K_w = 4.9 \times 10^{-13}$) ?

Answer:

Because OH^- and H_3O^+ are formed from the dissociation of water only, then their concentrations are equal,



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

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

Substitution in the above equation gives :

$$K_w = [\text{H}_3\text{O}^+]^2 \quad \text{also} \quad K_w = [\text{OH}^-]^2$$

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

$$\text{At } 25^{\circ}\text{C} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.01 \times 10^{-14}} = 1.01 \times 10^{-7}$$

$$\text{pH} = -\log(1.01 \times 10^{-7}) = 7.00$$

At 100 °C

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{4.9 \times 10^{-13}} = 7.0 \times 10^{-7}$$

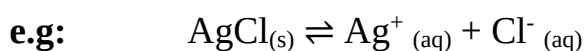
$$\text{pH} = -\log(7 \times 10^{-7}) = 6.15$$

Exercise:

Calculate the change in pH of pure water on heating from 25°C to 50°C ($K_w = 5.47 \times 10^{-14}$).

Equilibrium involving sparingly soluble ionic solids:

Most sparingly soluble salts are dissociated in saturated aqueous solution.



$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]}$$

$$K [\text{AgCl}_{(s)}] = K_{sp} = [\text{Ag}^+_{aq}] [\text{Cl}^-_{aq}]$$

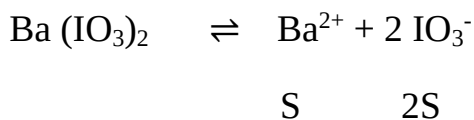
Where

K_{sp} = solubility product constant (applied only for saturated solution) .

Example :

How many grams of $\text{Ba}(\text{IO}_3)_2$ (M.wt = 487 gm / mol) can be dissolved in 500 mL of water at 25°C ? K_{sp} for $\text{Ba}(\text{IO}_3)_2 = 1.57 \times 10^{-9}$.

Solution:



$$K_{sp} = [\text{Ba}^{2+}] [\text{IO}_3^-]^2$$

$$K_{sp} = (\text{S})(2\text{S})^2 = 1.57 \times 10^{-9} = 4\text{S}^3$$

$$\text{S} = \sqrt[3]{\frac{1.57 \times 10^{-9}}{4}} = 7.32 \times 10^{-4} \text{ mole/L} \quad \text{or (M) = Solubility}$$

$$\text{No. of moles} = \text{Weight (g)} / \text{Molar mass (g / mol)}$$

Weight = No. of moles x Molar mass (g / mol)

As Molarity (M) = *No. of moles / Volume(liters)*

Then No. of moles = Molarity x Volume (liters)

Substituting for the No. of moles gives:

Weight (g) Molar mass (g / mol) = Molarity x Volume (liters)

Weight (g) = Molarity x Volume (liters) x Molar mass (g / mol)

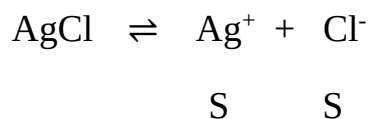
Weight in grams of $\text{Ba}(\text{IO}_3)_2 = 7.32 \times 10^{-4} \text{ mol/liter} \times 500 \text{ 1000 Liter} \times 487 \text{ g/mol} = 0.178 \text{ g}$

Then weight in grams of $\text{Ba}(\text{IO}_3)_2$ that is dissolved in 500 mL water = 0.178 g

Example :

Calculate the weight in grams of AgCl (143.3 g / mol) that can be dissolved in 600 mL of water? K_{sp} for AgCl = 1.8×10^{-10} .

Solution:



$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{sp} = (\text{S})(\text{S}) = 1.8 \times 10^{-10} = \text{S}^2$$

$$\text{S} = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ mole/L or (M) = solubility}$$

Weight(g) = Molarity x Volume (liters) x Molar mass (g / mol)

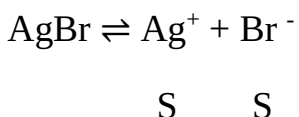
Weight in grams of AgCl = $1.34 \times 10^{-5} \text{ mol/liter} \times 600/1000 \text{ Liter} \times 143.32 \text{ g/mol} = 1.15 \times 10^{-3} \text{ g} = 1.15 \text{ mg}$

Calculating Solubility Product Constant (Ksp) From Solubility:

Example :

The weight of the sparingly soluble substance AgBr (187.8 g/mol) that dissolves in 500 mL of water to form a saturated solution is 6.65×10^{-5} gm. Calculate the Ksp of AgBr.

Solution:



$S = \text{molar solubility} = \text{Molarity}$

Molarity of AgBr (M) =

$$\text{Molarity of AgBr (M)} = \frac{6.65 \times 10^{-5} \times 1000}{187.8 \times 500} = 7.08 \times 10^{-7} = S$$

$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

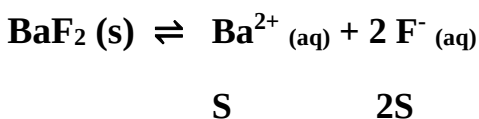
$$K_{sp} = (S)(S) = S^2$$

$$K_{sp} = (7.08 \times 10^{-7})^2 = 5.01 \times 10^{-13}$$

Example:

The solubility of barium fluoride, BaF₂, is 7.94×10^{-3} M at 25 °C. Calculate its solubility product constant, Ksp.

Solution:



$$\text{Solubility} = [\text{Ba}^{2+}] = (S) = 7.94 \times 10^{-3} \text{ M}$$

$$[\text{F}^-] = (2S)$$

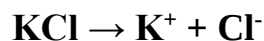
$$K_{sp} = [\text{Ba}^{2+}][\text{F}^-]^2$$

$$K_{sp} = (S)(2S)^2 = 4S^3$$

$$K_{sp} = 4(7.94 \times 10^{-3} \text{ M})^3 = 4(5 \times 10^{-7}) \longrightarrow K_{sp} = 2 \times 10^{-6}$$

Estimation of precipitate formation:**Example:**

Show if a precipitate of AgCl will form on mixing equal quantities of a solution of 1×10^{-5} M of silver nitrate AgNO_3 and a solution of 1×10^{-3} M potassium chloride KCl . The K_{sp} of AgCl = 1.8×10^{-10} .

Solution:

On mixing equal quantities of the two solutions, each concentration is halved.

$$M_1V_1(\text{before mixing}) = M_2V_2(\text{after mixing})$$

$$[\text{Ag}^+_{(\text{aq})}] = M_1V_1 / V_2 = (1 \times 10^{-5} \text{M})(1 \text{mL}) / (2) \text{mL} = 5 \times 10^{-6} \text{M}$$

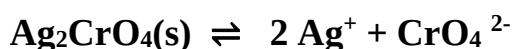
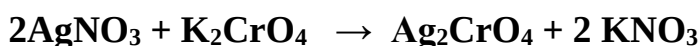
$$[\text{Cl}^-_{(\text{aq})}] = M_1V_1 / V_2 = (1 \times 10^{-3} \text{M})(1 \text{mL}) / (2) \text{mL} = 5 \times 10^{-4} \text{M}$$

$$\text{I.P} = [\text{Ag}^+_{(\text{aq})}][\text{Cl}^-_{(\text{aq})}] = (5.0 \times 10^{-6}) \times (5.0 \times 10^{-4}) = 2.5 \times 10^{-9}$$

As ionic product (I.P) > K_{sp} then a precipitate (AgCl) will form.

Example:

Will a precipitate form when 20.0 mL of 0.01 M AgNO_3 solution is mixed with 2.00 Liter of 0.002 M K_2CrO_4 . the K_{sp} for Ag_2CrO_4 is 1.1×10^{-12} .

Solution:

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

Having AgNO_3 gives Ag^+ and K_2CrO_4 gives CrO_4^{2-}

To calculate the ionic product (I.P) of $[\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$ after mixing

$$M_1V_1(\text{before mixing}) = M_2V_2(\text{after mixing})$$

$$[\text{Ag}^+] = M_1V_1 / V_2 = (0.01 \text{M})(20 \text{mL}) / (2000+20) \text{mL} = 9.9 \times 10^{-5} \text{M}$$

$$[\text{CrO}_4^{2-}] = M_1V_1 / V_2 = (0.002 \text{M})(2000 \text{mL}) / (2000+20) \text{mL} = 0.002 \text{M}$$

$$I.P = [Ag^+]^2 [CrO_4^{2-}] = (9.9 \times 10^{-5})^2 (0.002) = 2.0 \times 10^{-11}$$

As $I.P > K_{sp}$ then precipitate will form.

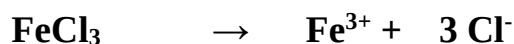
Notes:

1. If ionic product (I.P) < K_{sp} (dissolution Occurs).
2. If ionic product (I.P) = K_{sp} (equilibrium state).
3. If ionic product (I.P) > K_{sp} (precipitation Occurs).

Example:

What pH is required to just precipitate $Fe(OH)_3$ ($K_{sp} = 4 \times 10^{-38}$) from 0.10 M $FeCl_3$ solution?

Solution:



0.10 mole 0.10 mole

$$K_{sp} = [Fe^{3+}][OH^-]^3 = 4 \times 10^{-38} [0.1][OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}$$

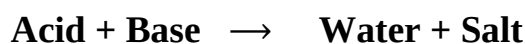
$$pOH = -\log(7 \times 10^{-13}) = 12.2$$

$$pH = 14 - 12.2 = 1.8$$

Reactions of Acid - Base

An **acid-base reaction** is one in which a hydrogen ion, H^+ , is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion.

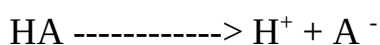
The reaction between an acid and a base is called an acid-base reaction or a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base cancel each other's chemistry to produce a rather innocuous substance—water. In fact, the **general acid-base reaction** is



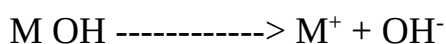
Arrhenius Theory

The Swedish chemist Svante Arrhenius published his theory of acids and bases in 1887. It can be simply explained by these two points: Arrhenius Acids and Bases

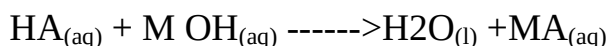
1. An acid is a substance which dissociates in water to produce one or more hydrogen ions (H^+).
2. A base is a substance which dissociates in water to produce one or more hydroxide ions (OH^-).
3. Based on this definition, Arrhenius acids must be soluble in water. Arrhenius acid-base reactions can be summarized with three generic equations:



An acid will dissociate in water producing hydrogen ions.



A base (usually containing a metal) will dissociate in water to produce hydroxide ions.



Acids and bases will neutralize each other when mixed. They produce water and an ionic salt, neither of which are acidic or basic.

The Arrhenius theory is simple and useful. It explains many properties and reactions of acids and bases. For instance, mixing hydrochloric acid (HCl) with sodium hydroxide (NaOH) results in a neutral solution containing table salt (NaCl).

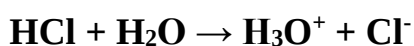
However, the Arrhenius theory is not without flaws. There are many well known bases, such as ammonia (NH₃) that do not contain the hydroxide ion. Furthermore, acid-base reactions are observed in solutions that do not contain water. To resolve these problems, there is a more advanced acidbase theory.

Brønsted-Lowry Theory

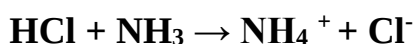
The Brønsted-Lowry theory was proposed in 1923. It is more general than the Arrhenius theory—all Arrhenius acids/bases are also BrønstedLowry acids/bases.

Brønsted-Lowry Acids and Bases

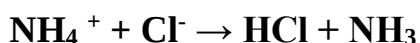
1. An acid is a substance from which a proton (H⁺ ion) can be removed. Essentially, an acid donates protons to bases.
2. A base is a substance to which a proton (H⁺) can be added. Essentially, a base accepts protons from acids.
3. Acids that can donate only one proton are **monoprotic**, and acids that can donate more than one proton are **polyprotic**.
4. These reactions demonstrate the behavior of Brønsted-Lowry acids and bases:



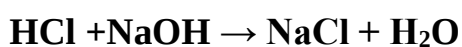
An acid (in this case, hydrochloric acid) will donate a proton to a base (in this case, water is the base). The acid loses its proton and the base gains it.



Water is not necessary. In this case, hydrochloric acid is still the acid, but ammonia acts as the base.



The same reaction is happening, but now in reverse. What was once an acid is now a base (HCl → Cl⁻) and what was once a base is now an acid (NH₃ → NH₄⁺). This concept is called conjugates.



Two examples of acids (HCl and H₃O⁺) mixing with bases (NaOH and OH⁻) to form neutral substances (NaCl and H₂O).





A base (sodium hydroxide) will accept a proton from an acid (ammonia). A neutral substance is produced (water), which is not necessarily a part of every reaction. Compare this reaction to the second one. Ammonia was a base, and now it is

Strong and Weak Acids/Bases

A **strong acid** is an acid which dissociates completely in water. That is, all the acid molecules break up into ions and solvate (attach) to water molecules. Therefore, the concentration of hydronium ions in a strong acid solution is equal to the concentration of the acid.

The majority of acids exist as **weak acids**, an acid which dissociates only partially. On average, only about 1% of a weak acid solution dissociates in water in a 0.1 mol/L solution. Therefore, the concentration of hydronium ions in a weak acid solution is always less than the concentration of the dissolved acid.

Strong bases and **weak bases** do not require additional explanation; the concept is the same.

*The conjugate of a **strong acid/base** is very weak. The conjugate of a **weak acid/base** is not necessarily strong.

This explains why, in all of the above example reactions, the reverse chemical reaction does not occur. The stronger acid/base will prevail, and the weaker one will not contribute to the overall acidity/basicity. For example, hydrochloric acid is strong, and upon dissociation chloride ions are formed. Chloride ions are a weak base, but the solution is not basic because the acidity of HCl is over stronger than basicity of Cl^- . Most acids and bases are weak.

Strong Acid	Formula
Perchloric acid	HClO_4
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Hydrohalic acids	HCl, HBr, HI

Although the other halogens make strong acids, **hydrofluoric acid** (HF) is a weak acid. Despite being weak, it is incredibly corrosive—hydrofluoric acid dissolves glass and metal.

Within a series of **oxyacids**, the ions with the greatest number of oxygen molecules are the strongest. For example, nitric acid (HNO_3) is strong, but nitrous acid (HNO_2) is weak. Perchloric acid (HClO_4) is stronger than chloric acid (HClO_3), which is stronger than the weak chlorous acid (HClO_2). Hypochlorous acid (HClO) is the weakest of the four.

Common strong bases are the hydroxides of Group 1 and most Group 2 metals. For example, potassium hydroxide and calcium hydroxide are some of the strongest bases. Can be assume that any other bases (including ammonia and ammonium hydroxide) are weak.

Formula	Strong Base
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
Ca(OH)_2	Calcium hydroxide
Sr(OH)_2	Strontium hydroxide
Ba(OH)_2	Barium hydroxide

Acids and bases that are strong are not necessarily concentrated, and weak acids/bases are not necessarily dilute. Concentration has nothing to do with the ability of a substance to dissociate. Furthermore, **polyprotic acids** are not necessarily stronger than **monoprotic acids**.

Equilibrium Constant for Conjugate Acids and Bases

Stage one: Calculation of Hydrogen ion concentration

1. Strong acids:



$$[\text{H}^+] = [\text{HCl}]$$

Example:

Calculate $[H^+]$ of 0.01 M HCl solution and the pH solution?

Solution:

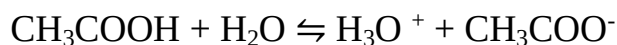
$$[H^+] = [HCl] = 0.01 \text{ M}$$



$$\begin{array}{ccc} 0.01 & 0 & 0 \\ 0 & 0.01 & 0.01 \end{array} \longrightarrow pH = -\log [H^+] = -\log 0.01 = 2$$

2. Weak acids:

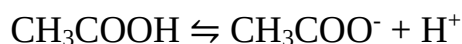
Ionic equilibrium in weak acids is occurring since the ionization is partial.



$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]} \quad K_a : \text{acid ionization constant}$$

Example:

Calculate $[H^+]$ of 0.1 M CH_3COOH at 25 °C if $K_a = 1.85 \times 10^{-5}$?

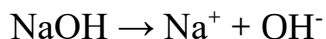
Solution:

$$\begin{array}{ccc} 0.1 & 0 & 0 \\ 0.1-X & X & X \end{array} \begin{array}{l} \text{before ionization} \\ \text{after ionization} \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.85 \times 10^{-5} = \frac{X \cdot X}{0.1-X} \longrightarrow 1.85 \times 10^{-5} = \frac{X \cdot X}{0.1}$$

$$X^2 = 1.85 \times 10^{-6} \longrightarrow X = 1.35 \times 10^{-3} \text{ mole/L}$$

Stage two : Calculation of Hydroxide ion concentration**1. Strong bases:**

$$[\text{OH}^-] = [\text{NaOH}]$$

Example:

Calculate concentration of NaOH if the pH = 12?

Solution:

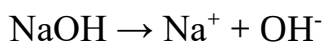
$$\text{pH} = 12$$

$$\text{pOH} = 14 - 12$$

$$\text{pOH} = 2$$

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

$$[\text{OH}^-] = 10^{-2} \longrightarrow [\text{OH}^-] = 0.01$$



$$[\text{OH}^-] = [\text{NaOH}] \longrightarrow [\text{NaOH}] = 0.01 \text{ M}$$

2. Weak bases:

Ionic equilibrium in weak bases is occurring since the ionization is partial.



$$\text{Kb} = \frac{[\text{NH}_4]^+ [\text{OH}]^-}{[\text{NH}_4\text{OH}]}$$

Kb : base ionization constant

Example:

Calculate $[\text{OH}^-]$ of 0.1 M ammonia solution if $K_b = 1.8 \times 10^{-5}$, Calculate pH and pOH?

Solution:

0.1 0 0 before ionization

0.1-X X X after ionization

$$K_b = \frac{[\text{NH}_4]^+ [\text{OH}]^-}{[\text{NH}_4\text{OH}]}$$

$$1.8 \times 10^{-5} = \frac{X * X}{0.1-X} \longrightarrow 1.8 \times 10^{-5} = \frac{X * X}{0.1}$$

$$X^2 = 1.8 \times 10^{-6} \longrightarrow X = 1.34 \times 10^{-3} \text{ mole/L}$$

$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] \\ &= -\log 1.34 \times 10^{-3} \\ &= -\log 1.34 - (-3) \\ &= ? \end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 - ? = ?$$

**H.W **

1. Calculate pH and pOH of 0.01 M ammonium hydroxide solution if The degree of ionization = 0.125?
2. Calculate pH of 0.5 gm Sodium hydroxide in 150 ml distilled water?

Ionization Constants of Acids and Bases

Strong acids are more completely ionized in solution than are weak acids. The degree of ionization of any acid is given by its **ionization constant, K_a** . Ionization constant can be expressed on a logarithmic scale. These values are called pK_a , and they defined as follows:

$$pK_a = -\log K_a$$

For bases, the same thing : K_b and pK_b , $pK_b = -\log K_b$

Properties of Acids and Bases

Acids and bases have very different properties, allowing them to be distinguished by observation.

Indicators



Bromothymol blue is an indicator that turns blue in a base, or yellow in acid. Made with special chemical compounds that react slightly with an acid or base, **indicators** will change color in the presence of an acid or base. A common indicator is **litmus paper**. Litmus paper turns red in acidic conditions and blue in basic conditions. **Phenolphthalein purple** is colorless in acidic and neutral solutions, but it turns purple once the solution becomes basic. It is useful when attempting to neutralize an acidic solution; once the indicator turns purple, enough base has been added.

Physical properties

The following is for informative purposes only. **Do not sniff, touch, or taste any acids or bases** as they may result in injury or death.

The physical properties of acids and bases are opposites.

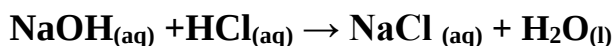
	Acids	Bases
Taste	sour	bitter
Feel	stinging	slippery
Odor	sharp	odorless

These properties are very general; they may not be true for every single acid or base. Another warning: if an acid or base is spilled, it must be cleaned up immediately and properly (according to the procedures of the lab you are working in). If, for example, sodium hydroxide is spilled, the water will begin to evaporate. Sodium hydroxide does not evaporate, so the concentration of the base steadily increases until it becomes damaging to its surrounding surfaces.

Chemical Reactions

Neutralization

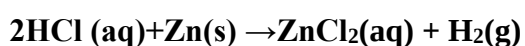
Acids will react with bases to form a **salt** and **water**. This is a **neutralization reaction**. The products of a neutralization reaction are much less acidic or basic than the reactants were. For example, sodium hydroxide (a base) is added to hydrochloric acid.



hydrochloric acid + sodium hydroxide $\rightarrow$ sodium chloride + water

This is a double replacement reaction.

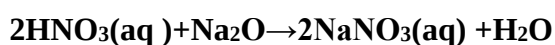
Acids



Acids react with metal to produce a metal salt and hydrogen gas bubbles.



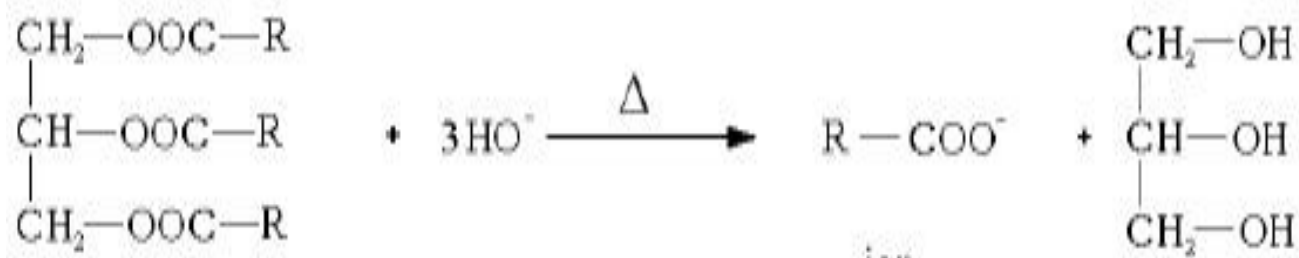
Acids react with metal carbonates to produce water, CO_2 gas bubbles, and a salt.



Acids react with metal oxides to produce water and a salt.

Bases

Bases are typically less reactive and violent than acids. They do still undergo many chemical reactions, especially with organic compounds. A common reactions is **saponification**: the reaction of a base with fat or oil to create soap.



Saponification converts an "ester" into an "alcohol" and salt.

Salts

Salts are ionic compounds composed of cations and anions held together by ionic bonds, they are solid at room temperature. Salts are formed by the reaction of an acid and a base. Some salts are quite soluble in water. Others are classified as slightly soluble or insoluble.

Buffer Solution

is **define** as a solution that resists change in pH as a result of either dilution or small additions of strong acids or strong bases. The most efficient buffer solution contains large and approximately equal concentration of a conjugate acid and base pair.

If solution of acetic acid is mixed with a solution of sodium acetate, a buffer solution of certain pH value is formed. When dilute HCl is added then its H^+ ions will react with acetate ion and acetic acid is formed which is sparingly ionized and hence will not change pH value. The same applies for NaOH solution, then OH^- ions will react with H^+ ions of acetic acid to form water and again pH will not increase only little.

Types of Buffer Solution

1. Buffer Solutions of weak acid and its salt.



$$K_a = \frac{[CN^-][H^+]}{[HCN]}$$

$$[H] = K_a \times \frac{\text{Acid}}{\text{Salt}}$$

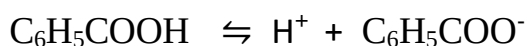
calculate pH of this Buffer solution by following law:

$$pH = pK_a + \log \frac{\text{Salt}}{\text{Acid}}$$

Example:

Calculate pH of solution that is 0.5 M benzoic acid solution (C_6H_5COOH) and sodium benzoate solution (concentration = 10gm/L) if pK_a $C_6H_5COOH = 4.1$?

Solution:



$$M \text{ of } (\text{C}_6\text{H}_5\text{COONa}) = \frac{10\text{gm}}{134 \text{ gm/mol}} = 0.074 \text{ mol/L}$$

$$\text{pH} = \text{pK}_a + \log \frac{\text{Salt}}{\text{Acid}}$$

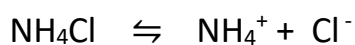
$$\text{pH} = 4.1 + \log \frac{0.07}{0.5}$$

$$\text{pH} = 4.1 + \log 0.14$$

$$= 4.1 - 0.85$$

$$= 3.25$$

2. Buffer Solutions of weak base and its salt.



$$[\text{OH}] = K_b \times \frac{\text{base}}{\text{Salt}}$$

calculate pH of this Buffer solution by following law:

$$\text{pOH} = \text{pK}_b + \log \frac{\text{Salt}}{\text{base}}$$

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

Example:

Calculate pH of solution that is 0.5 M NH_4OH solution and 0.3 M NH_4Cl solution, if $\text{pK}_b \text{ NH}_4\text{OH} = 4.74$?

Solution:



$$\text{pOH} = \text{pK}_b + \log \frac{\text{Salt}}{\text{base}}$$

$$\text{pOH} = 4.74 + \log \frac{0.3}{0.5} = 4.74 - 0.22 \quad \text{pOH} = 4.52 \quad \text{pH} = 14 - 4.52 \rightarrow \text{pH} = 9.48$$

Mechanism of action of buffer solution to resist change in acidic function

A. Common ion:

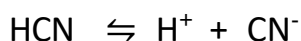
The process of reducing the dissociation of the weak electrolyte when a strong electrolyte is present containing the same weak electrolyte ions.

Types of Common ion:

1. Common ion of weak acid and its salt.
2. Common ion of weak base and its salt.

Common ion effect:

1. It reduces the acidity of the weak acid and increases pH numerical value.



2. It reduces the alkaline of the weak base and increases pOH numerical value.

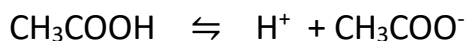
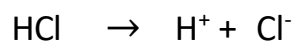


3. It increases the precipitation of salt sparingly soluble.



B. Addition Strong acid or Strong base:

1. Addition a few amounts of Strong acid to buffer Solutions of week acid and its salt.



Calculate pH of solution by following law:

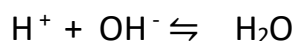
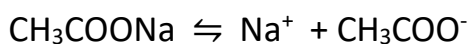
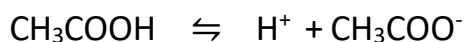
$$\text{pH} = \text{pK}_a + \log \frac{[\text{C}_s] - [\text{H}^+]}{[\text{C}_a] + [\text{H}^+]}$$

C_s = Molar concentration of salt

C_a = Molar concentration of week acid

$[\text{H}^+]$ = Molar concentration of the added strong acid

2. Addition a few amounts of Strong base to buffer Solution of week acid and its salt.



Calculate pH of solution by following law:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{C}_s] + [\text{OH}^-]}{[\text{C}_a] - [\text{OH}^-]}$$

C_s = Molar concentration of salt

C_a = Molar concentration of week acid

$[\text{OH}^-]$ = Molar concentration of the added strong base

3. Addition a few amounts of Strong acid to buffer Solutions of week base and its salt.



calculate pH of solution by following law:

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{C}_s] + [\text{H}^+]}{[\text{C}_b] - [\text{H}^+]}$$

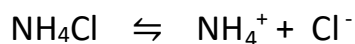
C_s = Molar concentration of salt

C_b = Molar concentration of week base

$[\text{H}^+]$ = Molar concentration of the added strong acid

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

4. Addition a few amounts of Strong base to buffer Solutions of week base and its salt.



Calculate pH of solution by following law:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{C}_s] - [\text{OH}^-]}{[\text{C}_b] + [\text{OH}^-]}$$

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

C_s = Molar concentration of salt

C_b = Molar concentration of week base

$[\text{OH}^-]$ = Molar concentration of the added strong base

Capacity of buffer solution

Each buffer solution certain capacity to withstand amounts of strong acid or strong base that is without changing (or cause little change) pH value of the solution. This ability is called capacity of the buffer solution.

buffer solution also may be formed during titration of week acid like acetic acid with strong base as NaOH. The solution will contain a mixture of acetic acid not titrate and Sodium acetate that formed by the addition of NaOH and therefore the pH value is slightly changed. If all the acid is neutralized and the solution contain CH_3COONa then pH value will rise suddenly at the end point of the reaction (equivalent point).

Buffer solution capacity depended on two factors:

- 1. Week acid to salt ratio or Week base to salt ratio of molecular concentration degree:**

The capacity will be at maximum when the concentration of the salt equal to the concentration of the acid. This occur at the middle of titration ($\text{pH} = \text{p}K_a$), and the capacity will be at maximum when the concentration of the salt equal to the concentration of the base. This occur at the middle of titration ($\text{pH} = \text{p}K_b$).

- 2. The concentration of (acid and salt) or (base and salt):**

The capacity buffer solution is increasing with the increase in the acid and salt concentration, and The capacity buffer solution is increasing with the increase in the base and salt concentration.

Example:

Calculate concentration of NH_4Cl in 0.1 M ammonium solution, To be the pH of solution = 9, if $K_b \text{ NH}_4\text{OH} = 1.8 \times 10^{-5}$?

Solution:

$$\text{pH} = 14 - \text{pOH} \longrightarrow \text{pOH} = 14 - 9 = 5$$

$$\text{pOH} = \text{p}K_b + \log \frac{\text{Salt}}{\text{base}}$$

$$5 = -\log (1.8 \times 10^{-5}) + \log \frac{[\text{C}_s]}{[0.1]}$$

$$5 = 4.74 + \log [\text{C}_s] - \log [0.1]$$

$$-0.74 = \log [\text{C}_s]$$

$$[\text{C}_s] = 10^{-0.74} \longrightarrow [\text{C}_s] = 0.18 \text{ M}$$

Example:

Find the amount of change in the acidic function for a buffer solution (1L) of acetic acid and sodium acetate a concentration 0.1 M for both of them, when 2 mL of 5 M NaOH solution were added to it, if $K_a = 1.8 \times 10^{-5}$?

Solution:

$$\text{pH} = \text{p}K_a + \log \frac{\text{Salt}}{\text{Acid}} \longrightarrow \text{pH} = -\log (1.8 \times 10^{-5}) + \log \frac{0.1}{0.1} = 4.74$$

$$M_1 \times V_1 = M_2 \times V_2 \longrightarrow 2 \times 5 = M_2 \times 1000 \longrightarrow M_2 = 0.01 \text{ M}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_s] + [\text{OH}^-]}{[\text{C}_a] - [\text{OH}^-]}$$

$$\text{pH} = -\log (1.8 \times 10^{-5}) + \log \frac{0.1 + 0.01}{0.1 - 0.01} \longrightarrow \text{pH} = 4.83$$

$$\Delta \text{pH} = 4.83 - 4.74$$

$$\Delta \text{pH} = 0.09$$

Volumetric Analysis

1. Neutralization titrations (Acid-Base)

Indicators of Neutralization: they are weak organic acids or weak organic bases show color change or emit luminescence at certain pH value when an acid or base are added. Its action can be explained by two theories:

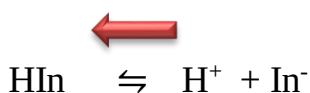
A. Ionic theory

This theory assumes that the Indicators are weak acids or weak bases, and therefore that they are molecularly ionized and have a color in the ionized part differs from its color in the non-ionized part. When the Indicator is added to the water, it is in a state of equilibrium, as in the following equation:



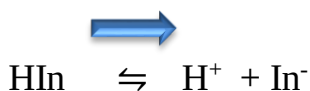
1. When adding strong acid such as HCl to a solution contains Indicator

The acid ionizes to give hydrogen ions (H^+) which reacts with the negative ion In^- . The reaction turns to the left and more (HIn) is formed according to the Lee-Chatelet rule, the color of the Indicator for the acid medium appears.



2. When adding strong base such as NaOH to a solution contains Indicator

The base ionizes to give hydroxide ions (OH^-) which reacts with the hydrogen ion (H^+) and pull it out of the solution. The reaction turns to the right and more (HIn) is formed according to the Lee-Chatelet rule, the color of the indicator for the base medium appears.



The dissociation constant of Indicator can be calculated from the following equation:

$$K_a = \frac{[H^+][In^-]}{[HIn]} \text{ ----- } 1$$

$$[H^+] = K_a \frac{[HIn]}{[In^-]} \text{ ----- } 2$$

$$pH = pK_a + \log \frac{[HIn]}{[In^-]} \text{ ----- } 3$$

The human eye does not distinguish between two colors unless the two colors differ by at least ten times, meaning that:

The **acid** color does not appear unless it is: $\frac{[HIn]}{[In^-]} \geq \frac{10}{1} = 10$

The **base** color does not appear unless it is: $\frac{[HIn]}{[In^-]} \leq \frac{1}{10} = 0.1$

We substitute into equation 3 :

$$pH \text{ (acidic)} = pK_a + \log 10 = pK_a + 1$$

$$pH \text{ (basic)} = pK_a + \log 0.1 = pK_a - 1$$

$$= pK_a \pm 1$$

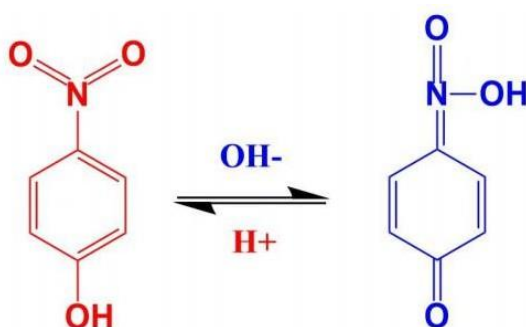
$$\Delta pH = pH \text{ (acidic)} - pH \text{ (basic)}$$

$$\Delta pH = pK_a + 1 - (pK_a - 1) = 2$$

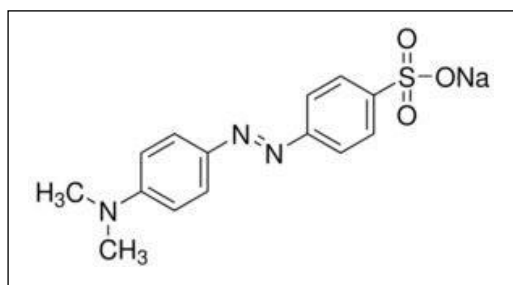
This range of pH is known as the range of indicator, it represents an average as some of the indicators have a wider range or less than that. the change in the pH of the solution by two units at the equivalence point is sufficient to change the concentration (color intensity) of the indicator ten times and characterize it by the human eye.

B. Chromophore theory:

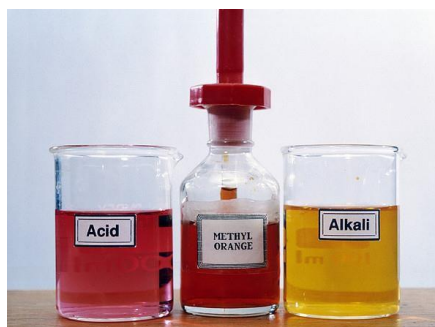
This theory assumes that an isomeric change occurs in the indicator molecule composition during the addition of the acid or the base, such that a change occurs in the composition of the active groups and atoms. These isomers differ in their chemical structure and thus they differ in color.

**The most important Indicators used in Neutralization titrations**

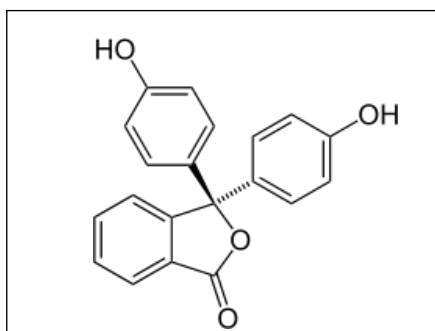
Methyl Orange: It is an unstable organic compound, a weak base ROH, Its color changes in the pH range (3.2 - 4.4). The red color takes on the values of the pH range less or equal 3.2 (The non-ionized acidic form), and the yellow color at the values of the pH range greater or equal 4.4 (The non-ionized base form), and the orange color in the pH range between (3.2 - 4.4).



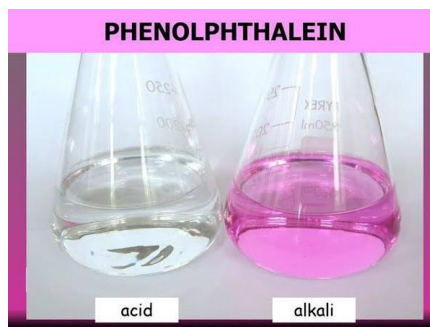
Methyl Orange structure



Phenolphthalein: It is an organic compound, a weak acid RH, its color changes in the pH range (8.2 - 10). The colorless form takes on the values of the pH range less than or equal to 8.2 (The non-ionized acidic form), and the pink color at the values of the pH range greater than or equal to 10 (The non-ionized base form) .



Phenolphthalein structure



Some common indicators and the extent of their work

Name of indicator	Color at lower pH	pH range	End-point	Color at higher pH
methyl violet	yellow	0.0 - 1.6	0.8	blue
thymol blue	red	1.2 - 2.8	2.8	yellow
methyl orange	red	3.2 - 4.4	3.7	yellow
bromophenol blue	yellow	2.8 - 4.6	4.0	blue
bromocresol green	yellow	3.8 - 5.4	4.7	blue
methyl red	red	4.2 - 6.3	5.1	yellow
bromothymol blue	yellow	6.0 - 7.6	7.0	blue
thymol blue	yellow	8.0 - 9.6	8.1	blue
phenolphthalein	colorless	8.2 - 10.0	9.3	pink/violet
alizarin yellow	yellow	10.1 - 13.0	12.5	orange/red