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# Introduction to Analytical Chemistry

**Class- F.Y.B.Sc.**


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## 1. Introduction to Analytical Chemistry

### What is Analytical Chemistry:-

Analytical chemistry is a branch of chemistry which deals with study of instruments and methods used to separate, identify, and quantify matter. In practice, separation, identification or quantification may constitute the entire analysis or be combined with another method.

There are of two types.

1. Qualitative analysis

2. Quantitative analysis

**1. Qualitative Analysis:-** Qualitative chemical analysis is a branch of chemistry that deals with the identification of elements or grouping of elements or compound present in a sample.

The techniques employed in qualitative analysis vary in complexity, depending on the nature of the sample. In some cases it is necessary only to verify the presence of certain elements or groups for which specific tests applicable directly to the sample (*e.g.*, flame tests, spot tests) may be available.

More often the sample is a complex mixture, and a systematic analysis must be made in order that all the constituents may be identified. It is customary to classify the methods into two classes: qualitative inorganic analysis and qualitative organic analysis.

Classical qualitative methods use separations such as precipitation, extraction and distillation. Identification may be based on differences in color, odour, melting point, boiling point, solubility, radioactivity or reactivity.

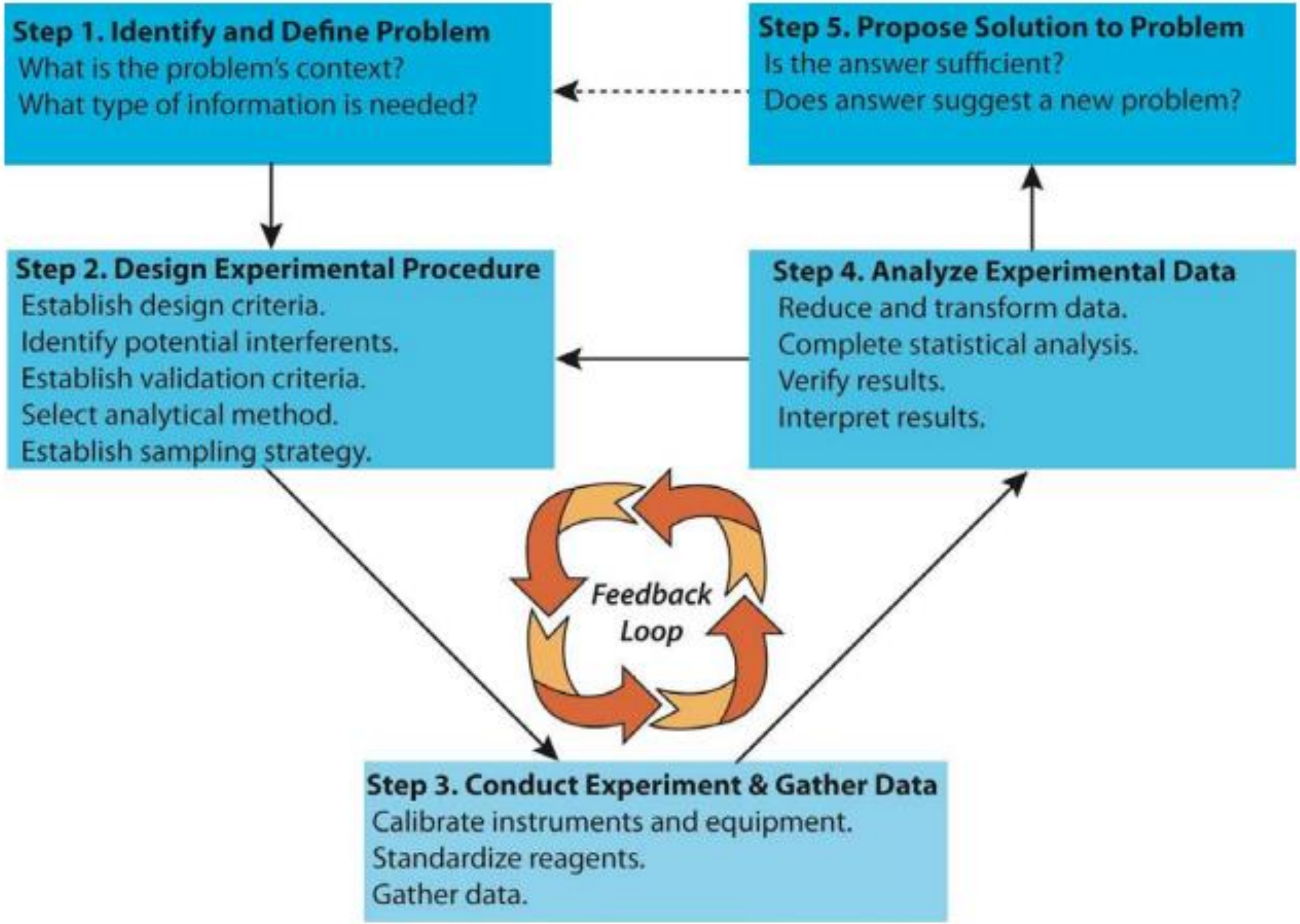
**2. Quantitative Analysis:-** Quantitative analysis is the measurement of the quantities of particular chemical constituents present in a substance. Quantitative Analysis refers to analyses in which the amount or concentration of an analyte may be determined (estimated) and expressed as a numerical value in appropriate units. Classical quantitative analysis uses mass or volume changes to quantify amount. Quantitative analysis involves gravimetric and volumetric analysis.

**Gravimetric analysis:-** Gravimetric analysis involves determining the amount of material present by weighing the sample before and/or after some transformation. The determination of the amount of water in a hydrate by heating the sample to remove the water such that the difference in weight is due to the loss of water.

**Volumetric analysis:-** Titration involves the addition of a reactant to a solution being analyzed until some equivalence point is reached. Often the amount of material in the solution being analyzed may be determined. Most familiar example is the acid-base titration involving a colour changing indicator. There are many other types of titrations, for example potentiometric titrations. These titrations may use different types of indicators to reach some equivalence point.

**Analytical perspectives:-** Having noted that each field of chemistry brings a unique perspective to the study of chemistry, we now ask a second deceptively simple question. What is the analytical perspective?

Many analytical chemists describe this perspective as an analytical approach to solving problems. Although there are probably as many descriptions of the analytical approach as there are analytical chemists, it is convenient for our purpose to define it as the five-step process shown in Figure.


Step 1. Identify and Define Problem
What is the problem's context?
What type of information is needed?
Step 5. Propose Solution to Problem
Is the answer sufficient?
Does answer suggest a new problem?
Step 2. Design Experimental Procedure
Establish design criteria.
Identify potential interferents.
Establish validation criteria.
Select analytical method.
Establish sampling strategy.
Step 4. Analyze Experimental Data
Reduce and transform data.
Complete statistical analysis.
Verify results.
Interpret results.
Feedback
Loop
Step 3. Conduct Experiment & Gather Data
Calibrate instruments and equipment.
Standardize reagents.
Gather data.

Three general features of this approach deserve our attention. First, in steps 1 and 5 analytical chemists may collaborate with individuals outside the realm of analytical chemistry.

In fact, many problems on which analytical chemists work originate in other fields. Second, the analytical approach includes a feedback loop (steps 2, 3, and 4) in which the result of one step may require reevaluating the other steps. Finally, the solution to one problem often suggests a new problem.

**Common Analytical Problems :-** Analytical chemistry begins with a problem, examples of which include evaluating the amount of dust and soil ingested by children as an indicator of environmental exposure to particulate based pollutants, resolving contradictory evidence regarding the toxicity of perfluoro polymers during combustion, and developing rapid and sensitive detectors for chemical and biological weapons. At this point the analytical approach may involve a collaboration between the analytical chemist and the individual or agency working on the problem. Together they determine what information is needed. It also is important for the analytical chemist to understand how the problem relates to broader research goals or policy issues. The type of information needed and the problem's context are essential to designing an appropriate experimental procedure.

To design the experimental procedure the analytical chemist considers criteria such as the desired accuracy, precision, sensitivity, and detection limits; the urgency with which results are needed; the cost of a single analysis; the number of samples to be analyzed; and the amount of sample available for analysis. Finding an appropriate balance between these parameters is frequently complicated by their interdependence. For example, improving precision may require a larger amount of sample. Consideration is also given to collecting, storing, and preparing samples, and to whether chemical or physical interferences will affect the analysis. Finally a good experimental procedure may still yield useless information if there is no method for validating the results.

The most visible part of the analytical approach occurs in the laboratory. As part of the validation process, appropriate chemical and physical standards are used to calibrate any equipment and to standardize any reagents. The data collected during the experiment are then analyzed. Frequently the data is reduced or transformed to a more readily analyzable form. A statistical treatment of the data is used to evaluate accuracy and precision, and to validate the procedure. Results are compared to the original design criteria and the experimental design is reconsidered, additional trials are run, or a solution to the problem is proposed. When a solution is proposed, the results are subject to an external evaluation that may result in a new problem and the beginning of a new cycle.

Many problems in analytical chemistry begin with the need to identify what is present in a sample. This is the scope of a qualitative analysis, examples of which include identifying the products of a chemical reaction, screening an athlete's urine for a performance-enhancing drug, or determining the spatial distribution of Pb on the surface of an airborne particulate. An early challenge for analytical chemists was developing simple chemical tests to identify inorganic ions and organic functional groups.

Modern methods for qualitative analysis rely on instrumental techniques, such as infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (MS).

Perhaps the most common analytical problem is a quantitative analysis, examples of which include the elemental analysis of a newly synthesized compound, measuring the concentration of glucose in blood, or determining the difference between the bulk and the surface concentrations of Cr in steel. Much of the analytical work in clinical, pharmaceutical, environmental, and industrial labs involves developing new quantitative methods to detect trace amounts of chemical species in complex samples. Most of the examples in this text are of quantitative analyses.

Another important area of analytical chemistry, which receives some attention in this text, are methods for characterizing physical and chemical properties. The determination of chemical structure, of equilibrium constants, of particle size, and of surface structure are examples of a characterization analysis.

The purpose of a qualitative, a quantitative, or a characterization analysis is to solve a problem associated with a particular sample. The purpose of a fundamental analysis, on the other hand, is to improve our understanding of the theory that supports an analytical method and to understand better an analytical method’s limitations.

# Calculations Used in Analytical Chemistry

A several analytical results obtained from quantitative analysis. Mostly S.I. unit relates with the mass and weight of any chemical substance. Number of ways are used to express the concentration of solutions.

**Units of measurements:-**

**S. I. Units:-**

The international system of units(SI) is based on some fundamental units. All scientists all over the world adopted a standardized system of units called as International system of Units(S.I Units).The fundamental base units is shown in table 2.1

# Table 2.1 SI base units of physical quantity

| Physical Parameter(Quantity) | Name of units | Abbreviations |
| --- | --- | --- |
| Mass. | kilogram. | kg |
| Length | Meter | m |
| Time | second | s |
| Temperature | Kelvin | K |
| Amount of substance. | mole | Mol |
| Electric current. | ampere | A |
| Luminous intensity | candela | cd |

The additional common physical quantities derived from SI units. In analytical chemistry determined the quantity of chemical substances from mass measurement like metric units of kilograms(kg),grams (g),milligrams (mg),and micrograms(μg)are generally used. Similarly volumes are measured in units of liters(L),milliliters(ml),and micro liters(μL). The SI unit of volume stated as $10^{-3}$ $m^3$. and milliliter as$10^{-6} m^3$.

## Distinction between mass and weight:-

To understand the difference between mass and weight is very important. Mass measures the amount of matter in an object.

Weight is the force of attraction between an object and surrounding on the earth. The gravitational force of attraction varies with geographical area and location. The weight of an object also depends on latitude. The mass of an object however remains constant regardless of where weight is measure.

## Table 2.2 Prefixes for Units

| Prefix parameter | Abbreviations | Multiplier in power |
|---|---|---|
| yotta | Y | $10^{24}$ |
| zetta | Z | $10^{21}$ |
| exa | E | $10^{18}$ |
| peta | P | $10^{15}$ |
| tera | T | $10^{12}$ |
| giga | G | $10^{9}$ |

| | | |
|---|---|---|
| mega | M | $10^{6}$ |
| kilo | k | $10^{3}$ |
| hecto. | h | $10^{2}$ |
| deca. | da | $10^{1}$ |
| deci. | d | $10^{-1}$ |
| centi. | c | $10^{-2}$ |
| milli | m | $10^{-3}$ |
| micro | µ | $10^{-6}$ |
| nano | n | $10^{-9}$ |
| pico | p | $10^{-12}$ |
| femto | f | $10^{-15}$ |
| atto | a | $10^{-18}$ |
| zepto | z | $10^{-21}$ |
| yocto | y | $10^{-24}$ |

The weight *w and mass m and g is the acceleration due to gravity the relation put forth as,* w=mg

Chemical analysis is based on mass but not always locality. A balance is used for comparison of mass of an object of one or more standard masses, because of *g affects known and unknown equally, the mass of an object is identical to the standard masses with which compared with each other.*

The distinction between mass and weight is often lost in our common usage. The process of comparing masses is called to be weighing. The object of known mass as well as the results of weighing are frequently called weights. Always keep in mind that, analytical data are based on mass rather than weight. In other words ,we will use weigh for determining the mass of an any object. We will say about weight means standard masses used in weighing.

## Comparison between mass and weight:-

### Mass:

1.Mass is measured by using balance comparing with the identical masses.

2.Mass measures the amount of matter.

3.Mass doesn't change with location.

### Weight:

1.Weight is measured using a scale.

2.Weighing of mass called weights.

3.Weight of an object changes with location.

## The mole:

The measurement of chemical substance by using S.I unit is mole. The mole is associated with a chemical formula and it is represented by Avogadro's number 6.022 X$10^{23}$ of particles. The molecular weight of a compound expressed in grams is called gram mole or mole. Molar masses are calculated by taking sum of the atomic masses of all atoms in the chemical formula.

For example.

One mole of nitrogen atoms has atomic weight =14gms.=6.022 x$10^{23}$ atoms.

Another example, the molar mass of acetaldehyde $CH_3CHO$,is

Molar mass of $CH_3CHO$=(2 x Atomic mass of C)+(4 x Atomic mass of H)+(1 x Atomic mass of O)

= (2 x 12)+(4 x 1)+(1 x 16) g/mol = 44 g/mol.

Thus,1 mole of acetaldehyde has a mass 44 g.

**Problem 1.Calculate the molar mass of glucose,**

**Solution:**

Molar mass of $C_6H_{12}O_6$=(6 x Atomic mass of C)+(12 x Atomic mass of H)+(6 x Atomic mass of O)

= (6 x 12)+(12 x 1)+(6 x 16) g/mol = 180 g/mol.

Thus,1 mole of glucose has a mass 180 g.

## Millimole:-

The mole is very large unit ,hence a smaller unit which is 1000 times smaller of it, known as millimole. Analytical calculations are more convenient with millimoles (mmol) than moles .The millimoles is 1/1000 moles. The mass in grams of millimole or milli molar mass (mM) is same as 1/1000 of the molar mass.

Thus, 1mole = 1000 millimoles.

For example. one millimole of NaOH = 40 milligrams.

## Calculating the amount of a substance in moles and millimoles:-

The number of moles and mllimoles of a chemical compound or atoms can be calculated from its mass in grams.

**Problem 2. How many moles, millimoles of benzoic acid are contained in 4.00g of benzoic acid?**

**(Given: Molar mass of benzoic acid is122.1 g/mole)**

**Solution:**

$$\text{Number of moles} = \frac{\text{mass(g)}}{\text{molar mass}(\frac{g}{mol})}$$

$$K = \frac{[H+][OH-]}{[H2O]}$$

$$= \frac{4.00\,g}{122.1g/mol}$$

Number of moles of benzoic acid =0.03276 mole

$$\text{Number of millimoles of benzoic acid} = \frac{\text{Number of moles(g)}}{(\frac{1}{1000})}$$

$$= 0.0327 \text{x} 1000$$

$$= 32.7 \text{mmol}$$

Number of millimoles of benzoic acid = 32.7mmol

**Problem 3.How many grams of $Na^{+}$(22.99g/mol) are contained in 50.00 g of $Na_2SO_4$?**

**(Given-molar mass of $Na_2SO_4$ is 142.0 g/mol)**

**Solution:** 1mol of $Na_2SO_4$ contains 2 mol of $Na^{+}$.

$$\text{Amount of } Na^{+} = \text{Number of mol of } Na_2SO_4 \times \frac{2 \text{ mole of } Na^{+}}{\text{mol of Na2SO4}}$$

Combining above equations we get,

$$\text{No.of mol of } Na_2SO_4 = 50.00\text{g of } Na_2SO_4 \times \frac{1 \text{ mole of Na2SO4}}{142.0 \text{ g of Na2SO4}} = 0.3521 \text{ mol of } Na_2SO_4$$

$$\text{Mass of } Na^{+} = \text{No.of mol of } Na_2SO_4 \times 22.99 \text{ mole of } Na^{+}$$

$$\text{Mass of } Na^{+} = 8.09 \text{ g}$$

**Problem 4: How many number of moles and millimoles of 2g solute of calcium carbonate($CaCO_3$)?**

**(Given: Atomic mass of calcium=40 g/mol,C=12 g/mol,O=16 g/mol)**

Solution:

i)Molar mass of Calcium carbonate=Atomic mass of (1 x Ca + 1 x C + 3 x O)g/mol

= 1 x 40 + 1 x 12 + 3 x 16

= 100 g/mol

$$\text{Number of moles of calcium carbonate} = \frac{\text{Mass of calcium carbonate in g}}{\text{molar mass}}$$

$$\text{Number of moles of calcium carbonate} = \frac{2\text{ g}}{100\text{ g/mol}}$$

$$= 0.02\text{ mol}$$

ii) Number of millimoles of $CaCO_3$ $= \frac{\text{Number of moles of} CaCO3}{1/1000}$

$$= \frac{0.02}{1/1000} \text{ mmol.}$$

$$= 0.02x1000$$

$$= 20 \text{ mmol}$$

Number of millimoles of $CaCO_3$ = 20 mmol.

**Problem 5:** How many number of millimoles of solute in 5.0 liter of 0.1 M of oxalic acid?

Solution:

0.1 M of oxalic acid = 0.1 mol of solute per liter of solution

$$\text{Number of millimoles/liter} = \frac{\text{Number of moles}}{1/1000}$$

$$= 0.1x1000$$

$$=100 \text{ mmol/L}$$

Number of millimoles of solute in 5 liters = 5L x 100

$$= 500 \text{ mmol.}$$

## Significant figures:-

The digit or number in a measured quantity, including all digits known exactly and single last digit whose quantity is uncertain called significant figures.

Suppose by taking a weight of chemical substance (sample) on balance the record noted as 3.3459 g, the last digit in this figure exactly known. It is assume that last digit has uncertainty at least value ±1,the absolute uncertainty at least is ± 0.0001 g.

The significant figures are important in various calculations .It is useful for analysis to report any type of measurement.

In the addition and subtraction operation carried out to the last digit is significant for all numbers in calculation mechanism.

Take a example having different decimal points in the digits. The sum of 0.44, 555.24, 11.5479 figures is 567.23,the last digit is significant for all last three numbers in the second decimal position.

$0.44+11.5479+555.24 = 567.2279$

The figure is rounded to be 567.23.

In case of multiplication and dividing the calculation contains the same number of significant figures, the number in the calculation is lowest significant figures as,

$$\frac{37.04 \times 0.246}{41.027}$$

$= 0.222093$

$= 0.222$

These digits are significant figures

After complete calculation final answer should be rounded up with the number to significant figures.

**Problem 6: Make the rounded up the following to three significant figures.**

1) 0.54397

2) 0.35278

3) 0.24099

4) 0.44395

**Solution: Rounded up the numbers into three significant figures as**

1) 0.544

2) 0.353

3) 0.241

4) 0.444

## Problem 7: How many significant figures of the followings.

1) 0.067547

2) 0.02301

3) 0.776

4) 563

Solution: the significant figures of the above figures as

1) 5

2) 4

3) 3

4) 3

## Solutions and their concentrations:-

The concept of concentration is frequently used as a general term referring to a quantity of substance in a defined volume of solution. Different methods of expressing the concentration of solutions. Chemist used a number of fundamental ways to determine concentration of solution these are percent concentration, molar concentration, solution diluents volume ratio and p-functions.

## Molar Concentrations:-

A molar concentration is one which is prepared by dissolving one mole of solute in one liter of the solution. Molar concentration of a solute is also called as molarity. Therefore,

$$\text{Molar concentration (M)} = \frac{\text{Number of moles of solute(n)}}{\text{Volume of solution in liters(L)}}$$

OR

$$\text{Molar concentration (M)} = \frac{\text{Number of millimoles of solute(n)}}{\text{Volume of solution in milliliters(mL)}}$$

The unit of molar concentration is molar and it is denoted by 'M', expressed as mol/liter or mmol/mL.

Thus, 1 M solution of oxalic acid means the solution prepared by dissolving one mole of the oxalic acid (126 g) in one liter of solvent. The molarity of a solution is always fixed since the molecular weight of the compound does not change. Molar concentration are expressed by two ways molar analytical concentration and molar equilibrium concentration. These concentration of solute undergo chemical change in solution or not.

**Molar analytical concentration:-**

The molar analytical concentration of a solution gives the total number of moles of a solute in 1 liter of the solution or the total number of millimoles in 1 mL.

For example, $H_2SO_4$ solution has 1.0 M concentration can be prepared by dissolving 98 g or 1.0 mol of $H_2SO_4$ in water and make dilute to 1.0 L. The $H_2SO_4$ does not undergo any chemical change in water solvent.

**Molar equilibrium concentration:-**

The molar equilibrium concentration is expressed in molar concentration of a particular species in a solution at equilibrium. It is necessary to know how the solute behaves when it is dissolved in a particular solvent.

For example, The molarity of $H_2SO_4$ in a solution with an analytical concentration of 1.0 M is actually 0.0 M because the $H_2SO_4$ is entirely dissociated into a mixture of $H^+$, $HSO_4^-$ and $SO_4^{2-}$ ions, actually no $H_2SO_4$ molecules present in this solution.

The equilibrium concentrations are represented by using square brackets around the chemical formula. thus $H_2SO_4$ with an analytical concentration is of 1.0 M then,

$[H_2SO_4] = 0.00$ M. $[H^+] = 1.01$ M

$[HSO_4^-] = 0.99$ M. $[SO_4^{2-}] = 0.01$ M

**Problem 8: Calculate the molar analytical concentration of ethanol in an aqueous solution it contains 3.30 g of $C_2H_5OH$ in 5.50 L of solution.**

(Given: molar mass of ethanol = 46.07 g/mol )

Solution:

$$\text{Amount of } C_2H_5OH = \frac{3.30 \text{ g C2H5OH}}{46.07 \text{ g C2H5OH}}$$

$$= 0.07163 \text{ mol}$$

For molar concentration divide by volume of solution.

$$\text{Concentration } C_2H_5OH = \frac{0.07163 \text{ mol}}{5.50 \text{ L}}$$

$$= 0.0130 \text{ mol/L}$$

$$= 0.0130 \text{ M}$$

**Problem 9: Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contain 300 mg of trichloroacetic acid, in 50.0 mL, the acid is 70% ionized in water.**

(Given: molar mass of trichloroacetic acid is 163.4 g/mol)

Solution:

Mass of trichloroacetic acid = 300 mg = 0.300 g

Volume of solution = 50.0 mL = 0.050 L

1) Number of moles of $CCl_3COOH = \dfrac{\text{Mass in g}}{\text{Molar mass in}\frac{\text{g}}{\text{mol}}}$

$$= \frac{0.300\ \text{g}}{163.4\ \text{g/mol}}$$

$$= 0.0018\ \text{mol}$$

2) The molar analytical concentration (M) = $\frac{\text{Number of moles (n)}}{\text{Volume in liters (L)}}$

$$= \frac{0.0018 \text{ mol}}{0.05 \text{ L}}$$

$$= 0.037 \text{ M}$$

In this solution 70% acid dissociates as $H^+$ and $CCl_3COO^-$ ions.

The molarity of acid is 30%.

Thus,

$$[CCl_3COOH] = \text{molar concentration x } \frac{\text{percent undissociated}}{100}$$

$$= 0.037 \text{ M x } \frac{30}{100}$$

$$= 0.0111 \text{ M}$$

3) The equilibrium concentration = 70% of analytical concentration.

$$\text{Thus, } [H^+] = \text{molar concentration x } \frac{\text{percent dissociated}}{100}$$

$$= 0.037 \text{ x } \frac{70}{100}$$

$$= 0.0259 \text{ M}$$

## Percent concentration:-

Chemist expresses solution concentration in terms of percent or parts per hundred. The percent composition of a solution can be expressed by many ways as

$$\text{Weight percent(w/w)} = \frac{\text{weight of solute(g)}}{\text{weight of solution (g)}} \text{ x } 100\%$$

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

$$\text{Weight/Volume percent(w/v)} = \frac{\text{weight of solute(g)}}{\text{volume of solution (g)}} \text{ x } 100\%$$

**a) Weight percent (w/w) :-** It is frequently used to express the concentration of commercial aqueous reagent.

For example, $HNO_3$ is sold as a 70% solution, it means that the reagent contains 70 g $HNO_3$ per 100 g of solution.

**b) Volume percent (v/v) :-** It is also frequently used to specify the concentration of the solution prepared by the dilution of pure liquid with another liquid compound.

For example, 5% aqueous solution of ethanol usually 5 mL dissolve in 100 mL of water.

**c) Weight to volume percent (w/v) :-** It is often used to indicate the composition of dilute aqueous solutions of solid reagent.

For example, 10% aqueous $AgNO_3$, it is prepared by dissolving 10 g of $AgNO_3$ of 100 mL of water in solution.

## Parts Per Million(ppm):-

A Parts Per Million (PPM) solution is one which is prepared by dissolving one gram of solute in $10^6$ grams of solution.

$$\text{ppm} = \frac{\text{Mass of solute in gms}}{\text{Mass of solvent n grams}} \times 10^6$$

Thus 1 p.p.m. solution is the solution containing 1 gm of solute in $10^6$ gm of solution means 1 mg of solute per liter of solution.

For example 1 milligram per liter of KCl is equivalent to 1ppm of KCl. This method of expression generally used for dilute solutions. Concentrations of environmental samples are expressed in ppm.

## Parts per billion (ppb):-

It is the number of parts of solute per billion ($10^9$) parts of solution.

Thus,

$$ppb = \frac{\text{Mass of solute in (g)}}{\text{Mass of solution in (g)}} \times 10^9$$

It is also defined as 1 ppb means 1 μg of solute in 1 L of solution.

## Parts per thousand (ppt):-

It is the number of part of solute per thousand ($10^3$) parts of solution.

Thus,

$$ppt = \frac{\text{Mass of solute in (g)}}{\text{Mass of solution (g)}} \times 10^3$$

## Problem 11: What is the molar equilibrium concentration of $K^+$ ion in a solution containing 75 ppm of $K_3[Fe(CN)_6]$.

(Given: molar mass of $K_3[Fe(CN)_6]$ = 329.3 g/mol)

Solution :

The solution is dilute to its density 1.0 g/mL,

75 ppm = 75 mg/L

$$= \frac{75 \text{ mg K3[Fe(CN)6]}}{1000 \text{ mg K3[Fe(CN)6]}} \times \frac{1 \text{ mol K3[Fe(CN)6]}}{329.3 \text{ g K3[Fe(CN)6]}}$$

$= 2.277 \times 10^{-4}$ mol/L $= 2.277 \times 10^{-4}$ M

1 mol of $K_3[Fe(CN)_6]$ = 3 mol of $K^+$ ions

$[K^+]$ = 3 x molar concentration of $K_3[Fe(CN)_6]$.

$= 3 \times 2.277 \times 10^{-4}$

$= 6.83 \times 10^{-4}$ M

**Problem 12: Calculate the concentration of given solute in weight to volume percent, ppm and ppb of 500 mL aqueous solution contains 75 mg of solute.**

Solution:

500 mL = 0.500 L

75 mg = 0.075 g = 75 x $10^3$ μg

1) weight to volume percent (w/v) = $\frac{\text{weight of solute(g)}}{\text{volume of solution (g)}}$ x 100%

$$= \frac{0.075\ \text{g}}{500\ \text{mL}} \times 100\%$$

$$= 0.015\ \%$$

$$2)\ \text{ppm} = \frac{\text{Mass of solute (mg)}}{\text{Mass of solution (L)}}$$

$$= \frac{75\ \text{mg}}{0.500\ \text{L}}$$

$$= 150\ \text{mg/L} = 150\ \text{ppm}$$

$$3)\ \text{ppb} = \frac{\text{Mass of solute }(\mu\text{g})}{\text{Mass of solution (L)}}$$

$$= \frac{75 \times 10{-}3\ \mu\text{g}}{0.500\ \text{L}}$$

$$= 150 \times 10^{-3}\ \text{ppb}$$

## Solution-diluents volume ratios:-

The volume of dilute solution is specified in terms of the volume of more concentrated solution and the specific amount of solvent used in diluting it.

**p-functions:-**

Chemists/scientists always express the concentration of a species in terms of p-value or p-function. This value is negative logarithm to base 10 of the molar concentration of that particular species.

The mathematical representation as follows,

$p^{X} = -\log_{10}[X]$

The advantage of p-values is the allowing concentration that vary over 10 or more orders of magnitude to be expressed in terms of positive number or value.

**Problem 13:** Calculate the p-function for the following solutions

i) $2.0 \times 10^{-3}$M in NaCl.

ii) $5.0 \times 10^{-3}$M in KCl

iii) $4.0 \times 10^{-2}$M in KCl

**Solution:**

i) $pNa = -\log(2.0 \times 10^{-3})M$

$= 2.699$

ii) $pK = -\log(5.0 \times 10^{-3})M$

$= 2.30$

iii) $pK = -\log(4 \times 10^{-2})M$

$= 1.40$

**Problem 14:** Calculate the $[H^+]$ ion in a solution has p-value/pH of 7.19.

**Solution:**

The standard relation as,

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

$$= 7.19$$

$$\log[H^+] = -7.19$$

The concentration of $H^+$ as,

$$[H^+] = \text{antilog}(-7.19)$$

$$= 6.45 \times 10^{-8} M$$

**Problem 15:** Calculate the $[Ag^+]$ ion in a solution has p-value/pAg of 6.372.

**Solution:**

By using standard relation as,

$$pAg = -\log[Ag^+]$$

$$= 6.372$$

$$\log[Ag^+] = -6.372$$

$$[Ag^+] = 4.246 \times 10^{-7}$$

$$= 4.25 \times 10^{-7}$$

## Density and specific gravity of solutions:-

Density is defined as the mass per unit volume of solution.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

It is expressed in kilogram per liter ( kg/lit) or gram per milliliter (g/ml).

The specific gravity is the ratio of density of substance to the density of water at $4^0$C .Specific gravity is dimensionless and not tie with any system of unit. The numerical value is same as that of density of the substance. The density of water is approximately 1.00 g/mL. If density % composition and equivalent weight are known then normality can be calculated easily.

Let x be the density and y be the specific gravity and E is the equivalent weight.

Thus,

$$\text{Normality} = \frac{y \times 1000\,x}{100E}$$

$$\text{Molarity} = \frac{y \times 1000x}{100M}$$

'M' represents molaritiy.

Table3.Specific gravities of some commercially used concentrated acids and bases

| **Reagent** | **Formula** | **Concentration% (w/w)** | **Specific Gravity** |
|---|---|---|---|
| Acetic acid | $CH_3COOH$ | 99.7 | 1.05 |
| Ammonia | $NH_3$ | 29.0 | 0.90 |
| Hydrochloric acid | $HCl$ | 37.2 | 1.19 |
| Hydrofluoric acid | $HF$ | 49.5 | 1.15 |
| Nitric acid | $HNO_3$ | 70.5 | 1.42 |
| Perchloric acid | $HClO_4$ | 71.0 | 1.67 |
| Phosphoric acid | $H_3PO_4$ | 86.0 | 1.71 |
| Sulphuric acid | $H_2SO_4$ | 96.5 | 1.84 |

## Chemical Stoichiometry:-

Stoichiometry (Greek word stoichion means element) is branch of chemistry which deals with the calculation of combining masses of elements. Stoichiometry is defined as the quantitative aspect dealing with mass and volume relationship between the reactants and products.

The symbols of the elements and formulae of the compounds stand for quantitative aspects of chemical reactions. The stoichiometry provides brief applications to some chemical calculations.

## Empirical formulas:-

An empirical formula gives the simplest whole number ratio of atoms in a chemical compound. The empirical formula of $C_2H_4O_2$, $C_3H_6O_3$ and $C_6H_{12}O_6$ have same empirical formula $CH_2O$. The empirical formula is obtained from the percent composition of a compound.

It is the ratio of atoms of different elements in the molecule of a compound.

It is based on following points

1.The ratio of each element to the atomic weight of the substance.

2.It is expressed by whole number.

3.The whole number shown below the symbol of the element to get empirical formula.

**Molecular Formula:-**

Molecular formula of a compound is indicates actual number of atoms of each element present in the molecule. It may be same as that of empirical formula.

The relation is expressed as,

Molecular formula= n x Empirical formula

Where n represents integer as 1,2,3,4,........etc.

'n' may be calculated by taking the ratio of Molecular weight to Empirical weight.

Molecular formula indicates the different element present in the number and number of atoms of each elements, molecular formula requires the information of molar mass of the species. Molecular formula weight or molar mass of a compound can be calculated by the addition of atomic weights present in the molecular formula.

Thus,

Molar mass or molecular weight of $SO_2$=1 x 32+2 x 16=64 g/mol

The structural formula gives additional information about the compound. For example, chemically different dimethyl ether and ethanol have the same molecular formula $C_2H_6O$. Their structural formula is $CH_3OCH_3$ and $C_2H_5OH$ respectively.

The steps are used to determine the empirical formula and molecular formula-

1) A percentage composition of chemical compound is determined quantitatively.

2)The percentage of every element is divided by atomic weight gives atomic ratio.

3) This atomic ratio of each element is divided by minimum value of atomic ratio to get simplest ratio.

4) The fractional ratio if present then values of simplest ratio of each element multiply by smallest integer to get the whole number.

5) For empirical formula, symbols of elements are written with whole number ratio by subscript.

6) Molecular formula is determined from empirical formula.

**Problem 16:** An organic compound contains 52.06% carbon, 34.71% oxygen and 13.02% hydrogen, calculate the empirical formula and empirical formula mass of the compound.

(Given: molar mass of C = 12 g/mol, H = 1 g/mol, O = 16 g/mol)

Solution:

1) Carbon

$$\text{Relative number of carbon} = \frac{\%\ \text{weight}}{\text{molar mass}}$$

$$= \frac{52.06}{12}$$

$$= 4.34$$

2) Oxygen

$$\text{Relative number of Oxygen} = \frac{\%\ \text{weight}}{\text{molar mass}}$$

$$= \frac{34.71}{16}$$

$$= 2.169$$

3) Hydrogen

$$\text{Relative number of Hydrogen} = \frac{\%\ \text{weight}}{\text{molar mass}}$$

$$= \frac{13.02}{1}$$

$$= 13.02$$

Therefore, Oxygen gives simplest ratio = 2.169

$$\text{Number of element of carbon} = \frac{\text{Atomic ratio}}{\text{simplest ratio}}$$

$$= \frac{4.34}{2.169}$$

$$= 2.000$$

$$\text{Number of element of Hydrogen} = \frac{\text{Atomic ratio}}{\text{simplest ratio}}$$

$$= \frac{13.02}{2.169}$$

$$= 6.00$$

$$\text{Number of element of oxygen} = \frac{\text{Atomic ratio}}{\text{simplest ratio}}$$

$$= \frac{2.169}{2.169}$$

$$=. \quad 1$$

Hence, empirical formula = $C_2H_6O$

Empirical formula mass = (2x12)+(6x1)+(1x16)

= 46 g/mol

## Stoichiometric Calculations:-

The balance chemical equation gives the stoichiometry or combining ratio of reactants and products in the units of moles the relationship explains different stoichiometric calculations.

The calculation of stoichiometry involves three step process-

1) The transformation of the known mass of chemical substance in grams into number of moles.

2) The multiplication by factor that gives stoichiometry.

3) The reconversion of the calculated data in moles back to metric units.

For example, the balanced equation gives its stoichiometry in moles of reactants and products.

$$2NaI_{(aq)} + Ba(NO_3)_{2(aq)} \longrightarrow BaI_{2(S)} + 2NaNO_{3(aq)}$$

The above equation indicates that 2 mol of aqueous sodium iodide combine with 1 mol of aqueous solution of barium nitrate to produce 1 mol of solid barium iodide and 2 mol aqueous sodium nitrate.

Problem 17: What is the mass of $AgNO_3$ needed to convert 3.44 g of $Na_2CO_3$ to $Ag_2CO_3$?

(Given: molar mass of $AgNO_3$ = 169.9 g/mol, $Na_2CO_3$ = 106.0 g/mol )

Solution: The balanced stoichiometric chemical equation as

$$Na_2CO_{3(aq)} + 2Ag(NO_3)_{2(aq)} \longrightarrow Ag_2CO_{3(S)} + 2NaNO_{3(aq)}$$

**Step1**: Number of mole of $Na_2CO_3$ = 3.44 gm $Na_2CO_3 \times \frac{1 \text{ mol Na2CO3}}{106.0 \text{ g Na2CO3}}$

$= 0.03245$ mol $Na_2CO_3$

**Step2**: Multiply the number of moles by factor that accounts stoichiometry. It means that 1 mol $Na_2CO_3$ reacts with 2 mol of $AgNO_3$

Thus, number of mole of $AgNO_3$ = 0.03245 mol $Na_2CO_3$ $\times \frac{2 \text{ mol } AgNO3}{1 \text{ mol } Na2CO3}$

= 0.0649 mol $AgNO_3$

**Step3**: To convert number of mole back to metric units

Mass of $AgNO_3$ = mole of $AgNO_3$ $\times$ molar mass of $AgNO_3$

= 0.0649 mol X 169.9 g/mol

Mass of $AgNO_3$ = 11.03 g

**Problem 18:** What will be the analytical molar $Na_2CO_3$ concentration in the solution produced when 25.0 mL of 0.200 M $AgNO_3$ mixed with 100.0 mL of 0.0800 M $Na_2CO_3$ ?

Solution:

The mole of $AgNO_3$ = 25.0 mL $AgNO_3$ X $\frac{0.200 \text{ mol } AgNO3}{1000 \text{ mL } AgNO3}$

$= 5.00 \text{ X } 10^{-3}$ mol

The mole of $Na_2CO_3$ = 100.0 mL $Na_2CO_3$ X $\frac{0.0800 \text{ mol } Na2NO3}{1000 \text{ mL } Na2NO3}$

$= 8.00 \text{ X } 10^{-3}$ mol

The number of moles of unreacted $Na_2CO_3$ is given by

$= [8.00 \text{ X } 10^{-3} \text{ mol } Na_2CO_3] - [5.00 \text{ X } 10^{-3} \text{ mol } AgNO_3 \text{ X } \frac{1 \text{ mol } Na2NO3}{2 \text{ mol } AgNO3}]$

$= 5.5 \text{ X } 10^{-3}$ mol $Na_2CO_3$

The molarity is the number of moles of $Na_2CO_3$/L

Therefore, molar concentration = $\frac{5.5 \text{ X } 10^{-3} \text{ mol } Na2NO3}{(100.0+25.0) \text{ mL}}$

= 0.0440 M $Na_2CO_3$


Thank you!