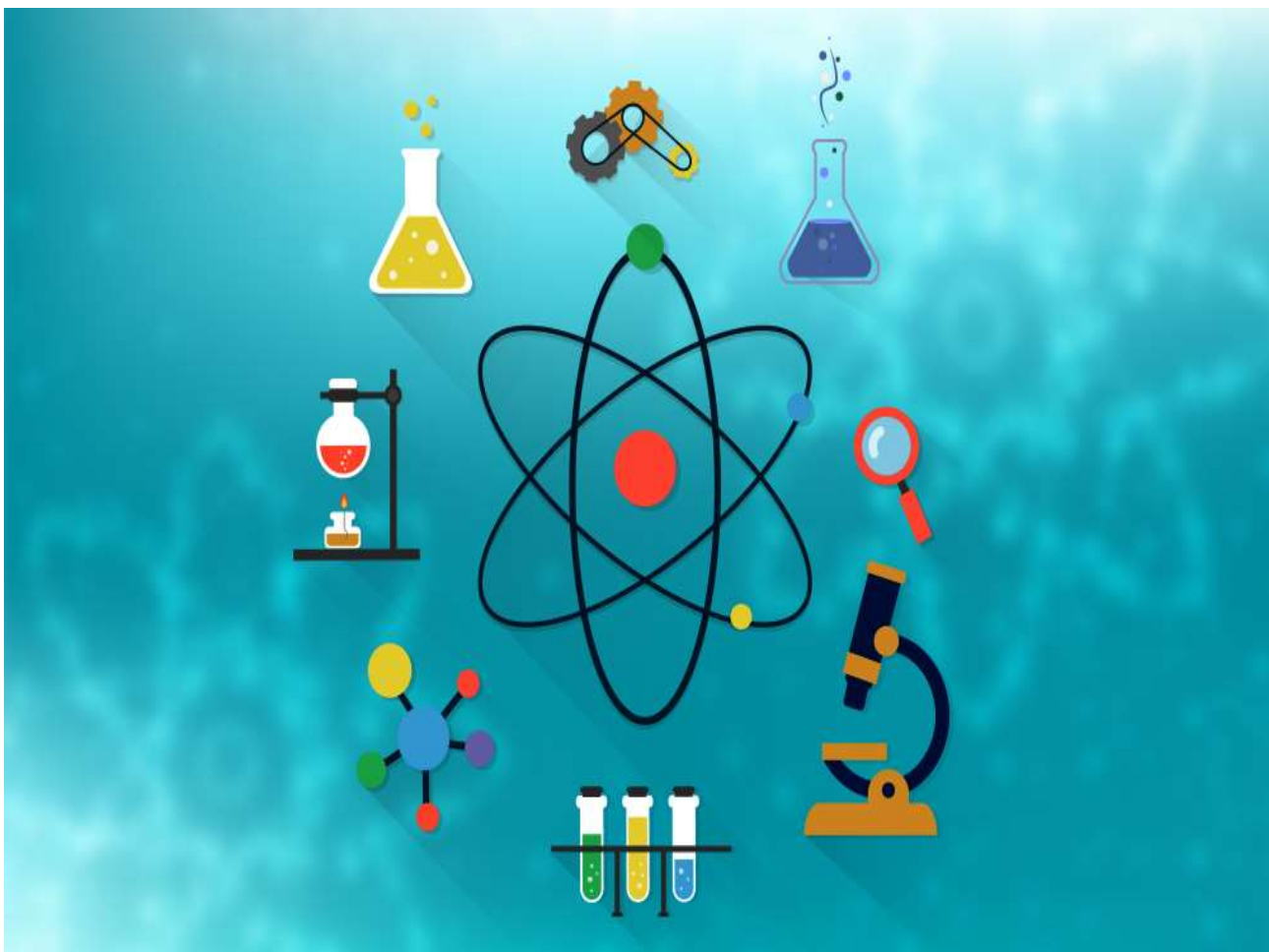


Analytical Chemistry



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➤ **Analytical chemistry:**

Analytical chemistry is a branch of chemistry that explores what the chemical and biochemical world around us is made of. This includes three main processes; separation, identification, and quantification of chemical compounds. Chemical analyses can be qualitative, as in identifying the chemical components in a sample, or quantitative, as in determining the numerical amount of a certain component in the sample or concentration. So, Qualitative analysis tells 'what' is present in a sample, while quantitative analysis is used to tell 'how much' is present in a sample. This makes it a very practical branch of chemistry with many important uses in fields as diverse as medicine, industry, astronomy, science, engineering, and police investigations (forensic analysis) making it an exciting and enjoyable subject to learn.

1. Qualitative chemical analysis:

In chemistry, Qualitative chemical analysis is a method of identification of the chemical composition of a sample. It does not measure the numerical information about a specimen but rather tells us whether an ion, atom, functional group or compound is present or absent in a sample. The analyzed sample vary in complexity depending on the sample nature. Therefore, before the qualitative analysis of any given compound, the analyte should be identified as either organic or inorganic. Organic compounds consist of carbon compounds, whereas inorganic compounds primarily contain elements other than carbon. Sugar ($C_{12}H_{22}O_{11}$) is an example of an organic compound, while table salt (NaCl) is inorganic.

➤ **Methods and Tools**

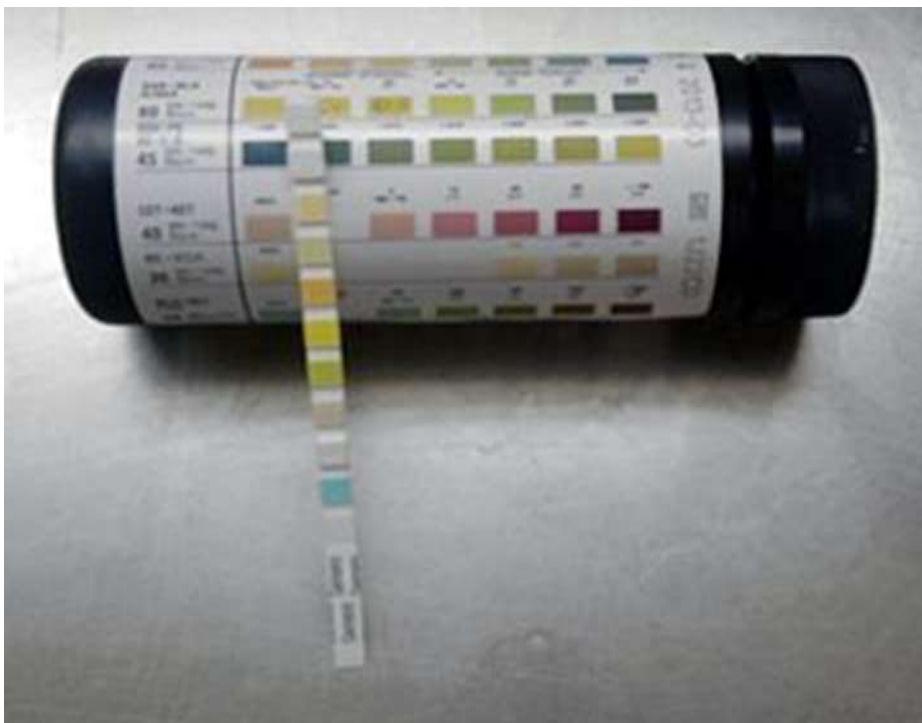
The simple qualitative analysis is performed without using expensive and complex tools or reagents. Identification may be based on differences in colour, odour, melting point, boiling point, texture, atomic structure, and the substance's ability to conduct electricity which can be observed without mechanical assistance.

This can be performed by the addition of one or a series of a chemical reagents to the sample and the target analyte can be detected and identified by observing the chemical reaction and their product. The reagents are usually chosen to react selectively with one or a single chemical compound to form the desired product. Usually, the resulted product is either a coloured complex or a precipitate.

Urine test includes the change in colour when adding the sample, resulting in a qualitative analysis without giving the concentration of the analysis in a urine sample. As an example, glucose content (concentration) which is a biomarker for diabetes can be visually observed in general urine tests and in case of high glucose concentration, a blood glucose test will be required to identify the patient case (quantitative analysis). Another example includes the precipitation process; copper (II), which reacts with ammonia to form a copper-ammonia complex that is characteristically with deep blue colour.

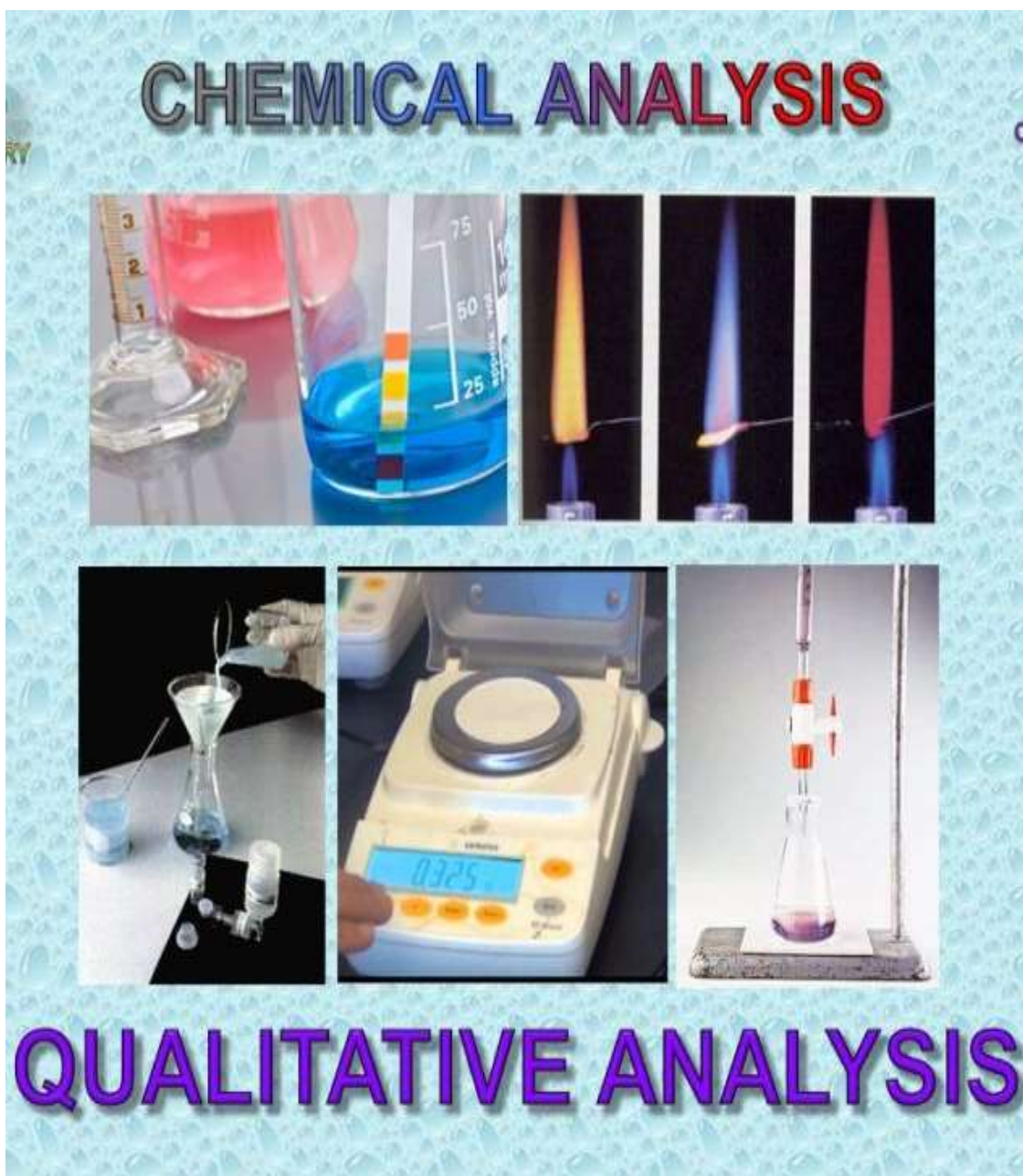
In general; classical qualitative analysis usually involves chemical reactions between added chemical reagents and functional groups of molecules. As a consequence, the result of the assay provides information about a portion of the molecule but usually does

not yield sufficient information to identify it completely. Other measurements, including those of boiling points, melting points, and densities are used in conjunction with a functional group analysis to identify the entire molecule.



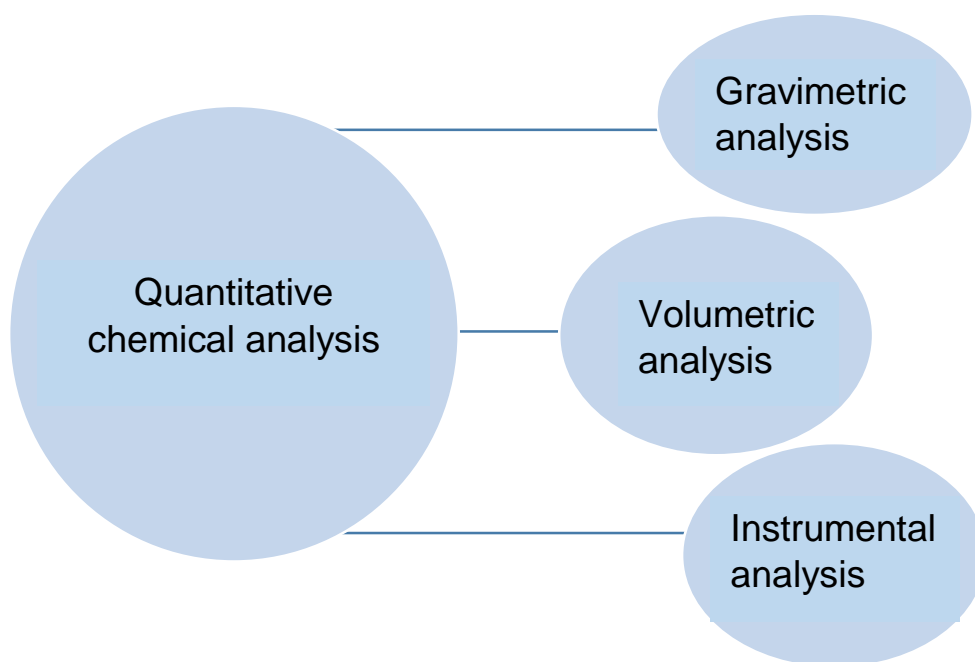
➤ Applications

Qualitative chemical analysis has its main application in the medical and criminology fields. Doctors may use qualitative chemical analysis in tests and procedures to treat and diagnose patients. Forensic scientists may use qualitative chemical analysis to identify substances left at crime scenes which can be vital in convicting criminals. Also, qualitative chemical analysis can be used at home. For instance, a person might tell the difference between margarine and butter in how quickly they melt.



2. Quantitative chemical analysis

Quantitative chemical analysis refers to analyses in which the concentration, percentage or amount of an analyte can be determined and expressed as a numerical value in appropriate units. Classical quantitative analysis can be divided into gravimetric analysis, volumetric analysis, and instrumental analysis.



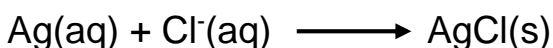
Classification of quantitative chemical analysis

A. Gravimetric analysis

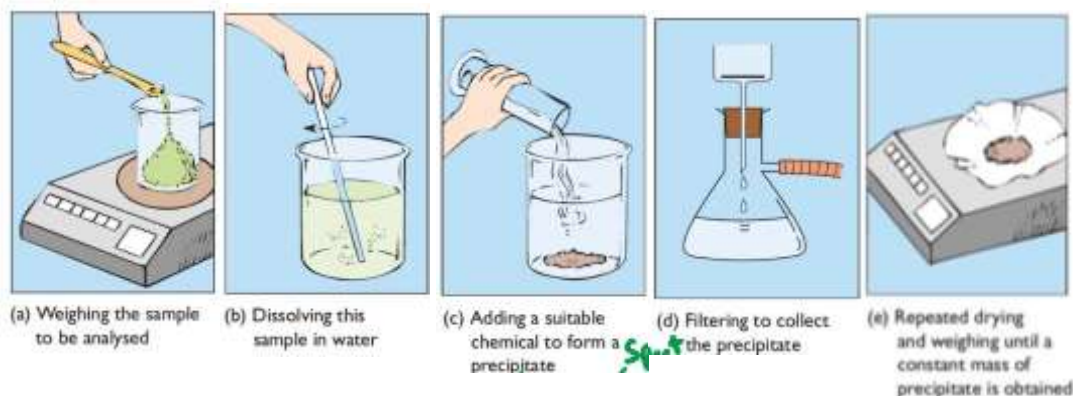
The principles behind the gravimetric analysis are that; once an excess of reagent is added to the aqueous solution containing the analyte, a precipitate is formed. The precipitate is then filtered, washed, dried, and weighed. The resulted mass is used to calculate the concentration or amount of the analyte using appropriate stoichiometric ratios.

In general, gravimetric analysis refers to a set of methods used in analytical chemistry for the quantitative determination of an analyte based on its mass.

For example, to determine the chloride ion content in drinking water, Silver Nitrate (AgNO_3) will be added to the sample solution, resulting in the precipitation of silver chloride (AgCl), as below equation:



Then the precipitate is filtered, washed, dried and it's mass determined. From the mass of the Silver Chloride, the mass of Chloride in the solution can be determined.



B. Volumetric analysis

Volumetric analysis is also known as titrimetric analysis. The reagent of a known concentration (standard solution or titrant) is added gradually or stepwise to the analyte (whose concentration is unknown) from a burette. This process is called the titration process.

* A primary standard solution is a highly purified compound that serves as reference material in all volumetric (titrimetric) analyses such as sodium carbonate (Na_2CO_3) for acids titrations and potassium hydrogen iodate ($\text{KH}(\text{IO}_3)$) for base titration. Important requirements for a primary standard solution are:

- 1-High purify.
- 2-Stability toward air.
- 3-Absence of hydrate water.
- 4-Ready availability and inexpensive.
- 5-Reasonable solubility in the titration medium.
- 6-Reasonable large molar mass so that the relative error associated with weighing the standard is minimized.

While a secondary standard solution is prepared in the laboratory for a specific analysis and standardized against a primary standard. Sodium hydroxide is an example of a secondary standard solution as commercial NaOH contains impurities of NaCl , and Na_2CO_3 and adsorb H_2O from the atmosphere. The key to perform a successful titrimetric analysis is to recognize the equivalence point of the titration (the point at which the number of moles of titrant and the analyte is equivalent), typically observed as colour change. If no spontaneous colour change occurs during the titration, a small amount of a chemical

indicator (a substance that undergoes a colour change when a reaction approaches completion) is added to the analyte before the titration. The volume of added titrant corresponding to the indicator colour change is the endpoint of the titration. The endpoint is used as an approximation of the equivalence point and is employed with the known concentration of the titrant to calculate the amount or concentration of the analyte.

As an example of biological titration, the production of viral vaccines requires virus quantification to monitor the process to optimize production yields and respond to ever-changing demands and applications. Virus quantification involves counting the number of viruses in a specific volume to determine the virus concentration in an assay called biological titration. Serial dilutions are performed on a sample in a fixed ratio (such as 1:1, 1:2, 1:4, 1:8, etc.) until the last dilution does not give a positive test for the presence of the virus. This value is known as the titer.

Having explained the volumetric analysis (titration), a few expression needs to be explained to fully understand the process:

1. Solution: is a homogenous mixture of two or more substances.
2. Solute: the substance which is dissolved.
3. Solvent: The substance in which the solute is dissolved.

A common example of a solution in everyday life is salt or sugar (solute) dissolved in water (solvent):

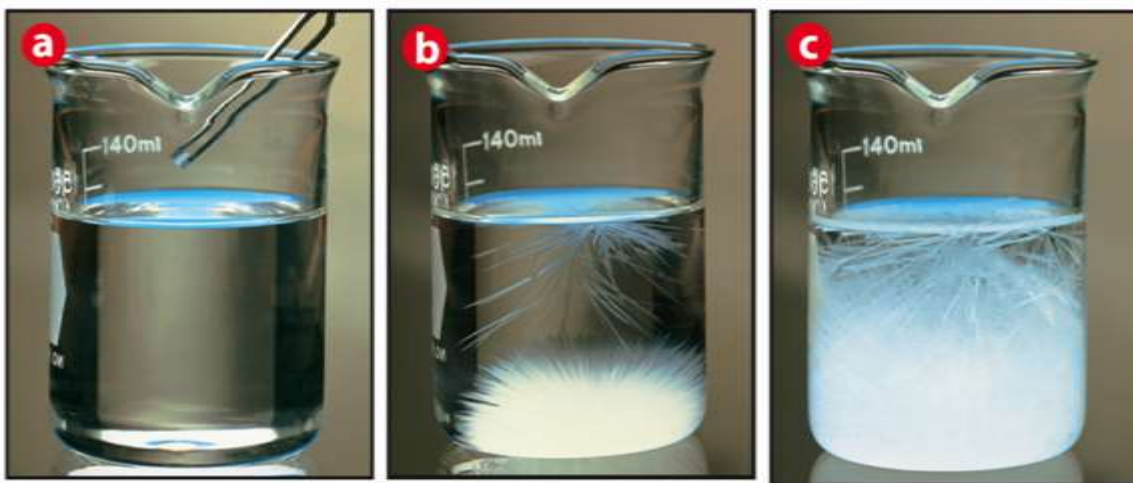


➤ **Classification of solutions**

The solution can be classified according to the amount of solute, solute particle size and concentration of solvent as follow:

A. Classification according to the amount of solute:

- Unsaturated solution: A solution (*with less solute than the saturated solution*) that completely dissolves, leaving no remaining substances (a).
- Saturated solution: A saturated solution is a chemical solution containing the maximum amount of a solute dissolved in the solvent. The additional solute will not dissolve in a saturated solution (b).
- Supersaturated solution: the definition of a supersaturated solution is one which contains more dissolved solute than could ordinarily dissolve into the solvent. A minor disturbance of the solution or introduction of the tiny crystal of solute will force crystallization of excess solute (c).



B. According to solute particle size:

	True Solution	Suspension	Colloid
Definition	A mixture of two or more chemical substances.	A mixture between two substances, one of which is finely divided and dispersed in the other.	Intermediate between a solution and a suspension.
Appearance	Clear, transparent and homogeneous	Cloudy, heterogeneous, at least two substances visible	Cloudy but uniform and homogeneous
Separation	A solution cannot be filtered but can be separated using the process of distillation	Many particles of a suspension can be separated through a filter	a colloid will not separate
Visibility	Particles non visible even under the microscope	Particles visible even with naked eye	Particles visible under microscope
Example	Sugar in water	include sand in water, dust in the air, and droplets of oil in the air	milk

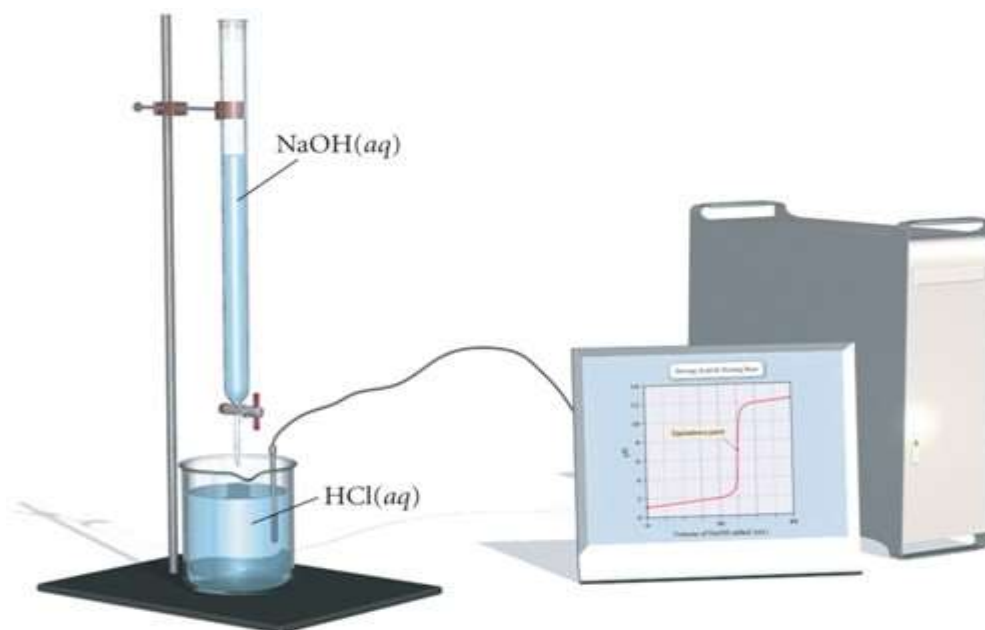


➤ Types of titrations:

There are various types of titrations including acid-base titrations, redox titrations, complexation titrations and precipitation titrations.

1. Neutralization (acid-base) titration:

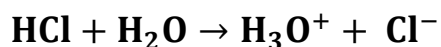
These titrations are based on the neutralization reaction that occurs between an acid and base when mixed in solution. The endpoint of these titrations is easy to detect, either using an indicator or by following the change in pH with a pH meter.



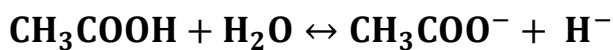
Acid-base theories include:

A) Arrhenius Theory (H^+ and OH^-):

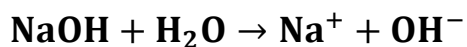
Acid: any substance that ionizes in water to give hydrogen ion (which associate with the solvent to give hydronium ion (H_3O^+)): The acids which are completely ionized in aqueous solutions, is termed as strong acids :



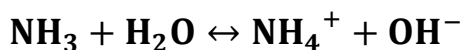
Whereas the acids which are weakly ionized in aqueous solution, is termed as weak acids:



Base: any substance that ionizes in water to give hydroxyl ions. Strong bases such as metal hydroxides (e.g. NaOH) dissociate as follow:



While the weak (partially ionized) base is generally ionized as follows:

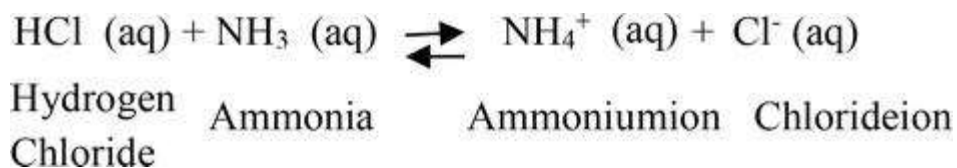


This theory is restricted to water as the solvent.

B) Bronsted-Lowry Theory (taking and giving protons, H^+):

Acid: any substance that can donate a proton.

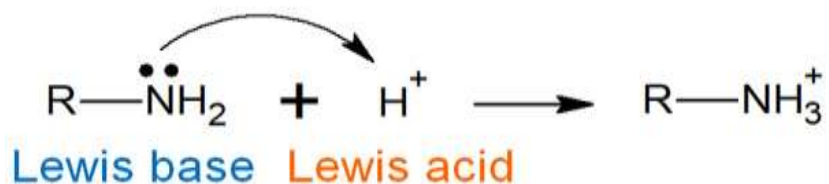
Base: any substance that can accept a proton. Thus, we can write a half-reaction:



C) Lewis Theory (taking and giving electrons):

Acid: a substance that can accept an electron pair (i.e., an electrophile).

Base: a substance that can donate an electron pair (i.e., a nucleophile).



Strong acids: H_2SO_4 , HClO_4 , HNO_3 , HI and HCl .

Strong bases: LiOH , KOH , NaOH and Ca(OH)_2 .

➤ Buffer

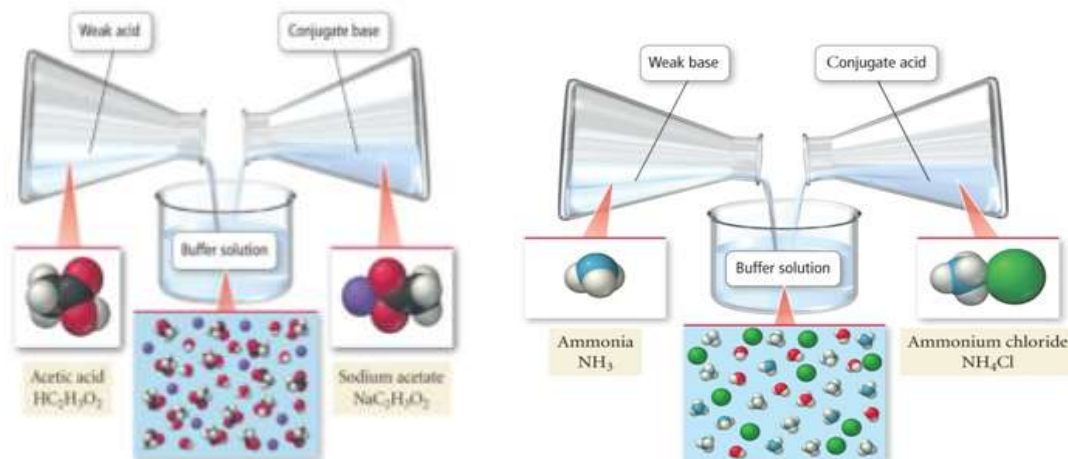
A buffer is defined as a solution that resists the change in pH when a small amount of an acid or base is added or the solution is diluted. A buffer solutions consist of a weak base and their salt (conjugate acid) or a weak acid and its salt (conjugate base). A conjugated acid is a substance formed when a base accepts a proton, while a conjugated base is a substance formed when an acid loses a proton.

A) Acidic buffers:

As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong acid. An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.

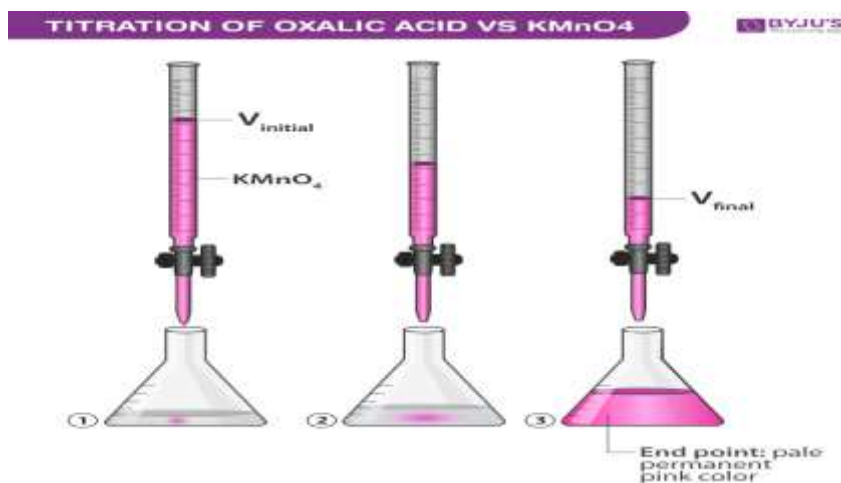
B) Alkaline (basic) buffer:

These buffers solutions are used to maintain basic conditions. Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with a strong base. The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.



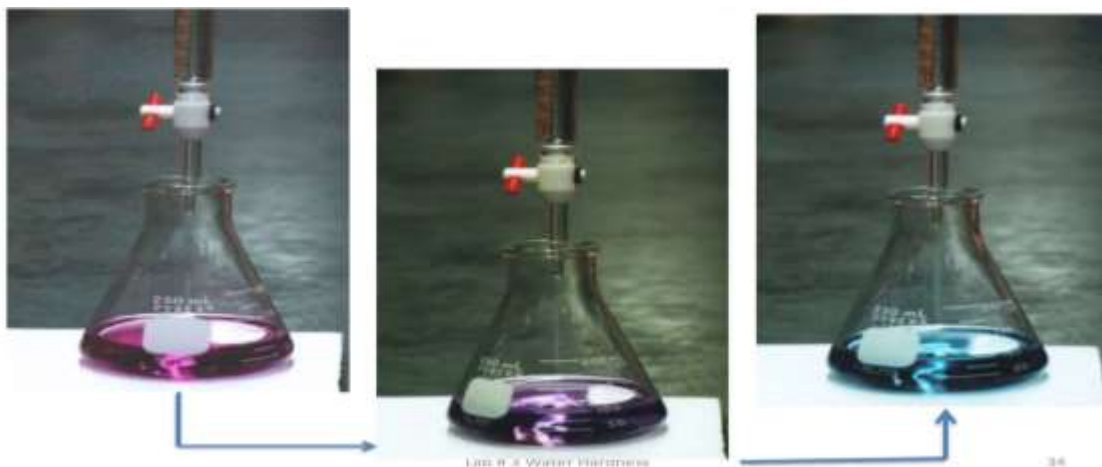
2. Reduction-Oxidation (Redox) titration

These titrations are based on a redox reaction between an oxidizing agent and a reducing agent or vice versa, for example, the titration of potassium permanganate (KMnO_4) against oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$). An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.



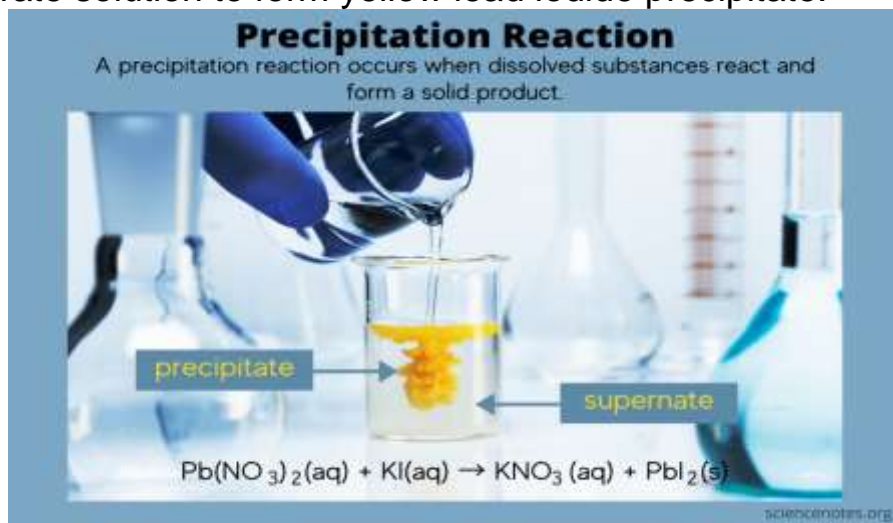
3. Complexation titration

These titrations are based on the formation of a complex between the analyte and the titrant. The chelating agent ethylene diamine tetra acetic acid (EDTA) is very commonly used to titrate metal ions in solution.



4. Precipitation titration

This titration depends on the titrant formation of insoluble products with the analyte. An example is a titration of potassium iodide ion with lead nitrate solution to form yellow lead iodide precipitate.



C. Instrumental analysis

Scientific instruments are used in this field of analytical chemistry to investigate the analyte. Instrumental methods can be divided into three main categories: Chromatography including liquid chromatography (LG), gas chromatography (GC), High-performance liquid chromatography (HPLC), and paper chromatography (PG), second category is spectrometry such as UV/Visible and infrared. The third category contains electrochemical instruments including potentiometry, coulometry, and voltammetry. The qualitative and quantitative analysis can be performed, often with the same instrument and may use light interaction, heat interaction, electric fields or magnetic fields. Often the same instrument can separate, identify and quantify an analyte.

➤ **Application**

Having gone through an overview of the background of the quantitative analysis, the subsequent section will focus on the application, exploring how it is carried out in the real world:

1. Quantitative analysis is crucial to the formulation and testing of food and drugs, as it is used to measure nutrient levels and provide an accurate accounting of dosage.
2. It is also critical in determining the level of contaminants or the impurity of a sample. While qualitative analysis might be able to determine the presence of lead in the paint on a toy, for example, it is a quantitative analysis that detects how much concentration exists.
3. If you're performing a chemical reaction, quantitative analysis helps you predict how much product to expect and determine your actual yield.
4. Some reactions occur when one component's concentration reaches a critical level. For example, an analysis of a radioactive material might indicate there is enough of a key component for the specimen to undergo spontaneous fission.
5. Medical tests rely on quantitative analysis for a patient's health information. For example, the quantitative analysis could determine blood cholesterol levels or the ratio of lipoproteins in plasma or the amount of protein excreted in the urine. Here again, quantitative analysis complements qualitative analysis, since the latter identifies the nature of a chemical while the former tells you how much there is.

➤ **Recent development in analytical chemistry**

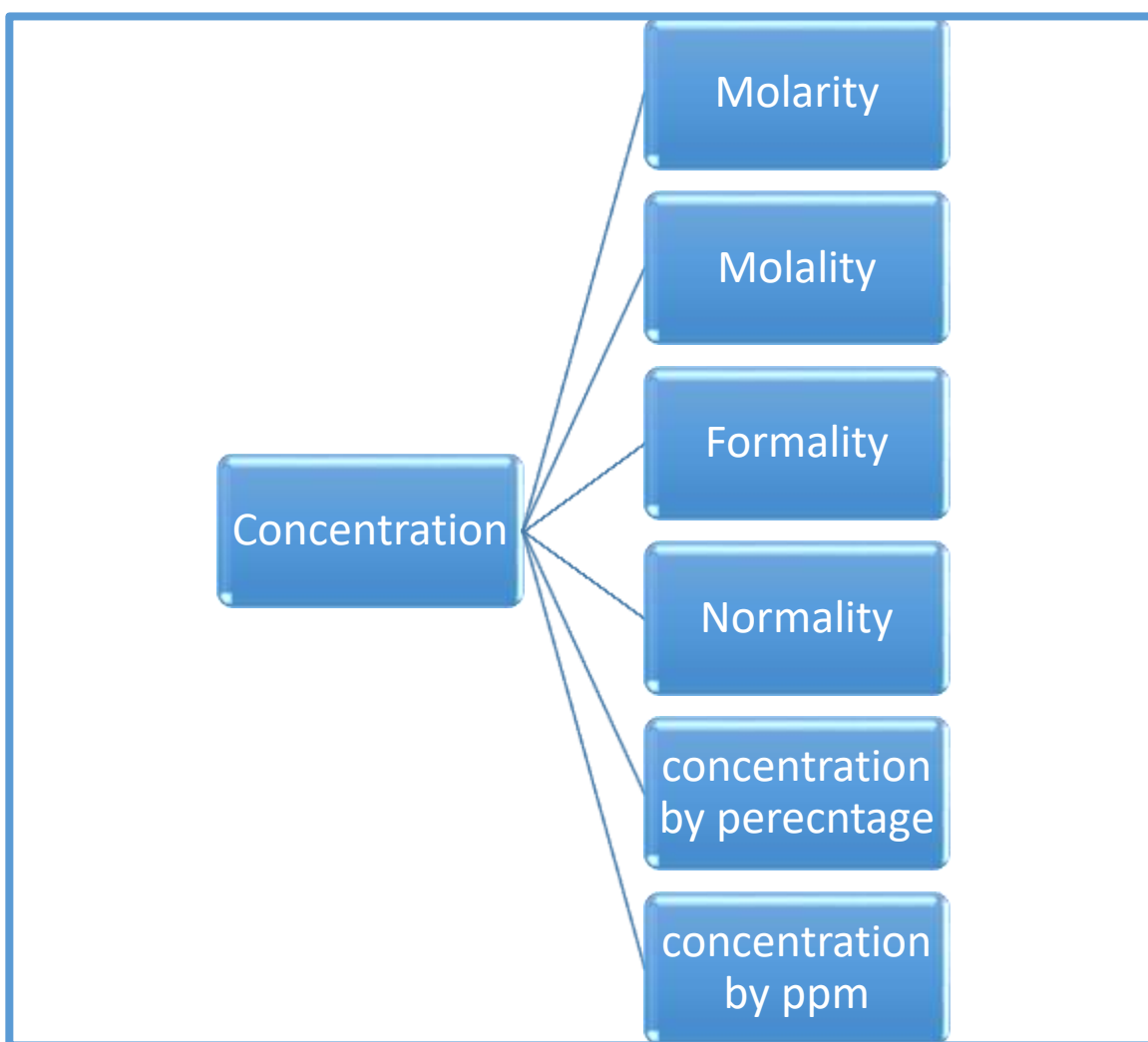
A new development in analytical chemistry consists of the use of a technology that takes analysis outside of the laboratory setting and away from the use of more costly conventional methods, it is time-saving, more efficient and integrated several processes into one device. As a result, there is a need for the construction of portable, disposable, automated and miniaturized systems, such as lab-on-a-chip (LOC) devices, point-of-care (POC) systems, micro total analysis system (μ TAS), and drug delivery system (DDS), etc., which can provide valuable information. Due to the minimization of the device the in/out fluid must be minimized to microfluidic size. The design and approach for these components can vary greatly within research groups but with each sharing an end goal, to produce a device that can function easier and just as well as the conventional methods are currently available. This encouraged researchers to apply it in the diverse area including chemistry, medicine, engineering, forensics and bio analytical researches, for example for DNA separation and analysis, cell separation and manipulation, enzyme kinetic studies, drug discovery, and immunoassay, etc.



➤ **Stoichiometric calculation**

This section will cover a range of stoichiometric calculations of which are fundamental to analytical chemistry and provides how these calculations are applied in the determination of the concentration of an analyte in a sample.

As shown from the below scheme; concentration can be defined by six main expressions, which will be detailed:



1. Molarity (M)

Molar concentration (also called molarity) is well defined as the amount of substance (solute) per unit volume of solution. The unit used to express the molarity is the number of moles per litre, having the unit symbol mol/L. Molarity can measure the concentration of a chemical species in two different types (solid and Liquid):

Solid material

$$\text{Molarity (M)} = \frac{\text{No. of mole solute}}{\text{solution volume (L)}} = \frac{\text{mole}}{\text{L}}$$

$$\text{Molarity (M)} = \frac{\text{No. of mmole solute}}{\text{solution volume (mL)}} = \frac{\text{mmole}}{\text{mL}}$$

$$M = \frac{\text{No of mole solute}}{\text{Volume solution (L)}} = \frac{\frac{\text{wt (g)}}{\text{M. wt } (\frac{\text{g}}{\text{mole}})}}{\frac{V \text{ (mL)}}{1000 (\frac{\text{mL}}{\text{L}})}} = \frac{\text{wt (g)}}{\text{M. wt } (\frac{\text{g}}{\text{mole}})} \times \frac{1000}{V \text{ (mL)}}$$

Where M= Molarity for solid compound,

wt = weight in gm,

M.wt or some times gMw (molecular weight) = the sum of the atomic weight of the atoms that make up a molecular compound,

v = volume in litter.

Example:-A solution is prepared by dissolving 1.26 gm AgNO_3 in a 250 mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles AgNO_3 were dissolved?

Solution:

$$M = \frac{\text{wt (g)}}{\text{M. wt } \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000}{V \text{ (mL)}}$$
$$= \frac{1.26 \text{ (g)}}{169.9 \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000}{250 \text{ (mL)}} = 0.0297 \text{ mol/L}$$

$$\text{Millimoles} = M \left(\frac{\text{mmol}}{\text{mL}}\right) \times V \text{ (mL)}$$
$$= 0.0297 \left(\frac{\text{mmol}}{\text{mL}}\right) \times 250 \text{ mL}$$
$$= 7.42 \text{ mmole}$$

Example:-How many grams per millilitre of NaCl are contained in a 0.250 M solution.

$$M = \frac{\text{wt (g)}}{\text{M. wt } \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000}{V \text{ (mL)}}$$
$$0.250 \text{ M} = \frac{\text{wt (g)}}{58.4 \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000}{1 \text{ (mL)}}$$

$$\text{wt (g)} = 0.0146 \frac{\text{g}}{\text{mL}}$$

Example:-How many grams Na_2SO_4 should be weight out to prepare 500 mL of a 0.100 M solution.

$$M = \frac{\text{wt (g)}}{\text{M. wt } \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000 \left(\frac{\text{mL}}{\text{L}}\right)}{V \text{ (mL)}}$$

$$0.10 \text{ mol/L} = \frac{\text{wt (g)}}{142 \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000 \left(\frac{\text{mL}}{\text{L}}\right)}{500 \text{ (mL)}}$$

$$\text{wt (g)} = \frac{0.10 \left(\frac{\text{mol}}{\text{L}}\right) \times 142 \left(\frac{\text{g}}{\text{mol}}\right)}{2 \left(\frac{\text{mL}}{\text{L}}\right)} = 7.1 \text{ g}$$

Liquid material

$$M = \frac{\% \times \text{sp. gr.} \times 1000}{\text{M. wt}} = \frac{\% \times \text{density} \times 1000}{\text{M. wt}}$$

Where sp.gr (specific gravity) = is the ratio of the mass of a body (e.g. a solution) usually at 20°C to the mass of an equal volume of water at 4°C (or sometimes 20°C) or (is the ratio of the densities of the two substances).

Density = is the weight per unit volume at the specified temperature, usually (gm/mL) or (gm.cm³) in 20°C (is the ratio of the mass in (gm) and volume (mL).

% = percentage of chemical species.

Example:-Calculate the molarity of 28.0% NH₃, specific gravity 0.898.

Solution:

$$\text{M. wt NH}_3 = 14 + (3 \times 1) = 17$$

$$M = \frac{\% \times \text{sp. gr. (density)} \times 1000}{\text{M. wt}}$$

$$M = \frac{\frac{28}{100} \times 0.898 \times 1000}{17} = 16.470 \frac{\text{mol}}{\text{L}} = 16.470 \frac{\text{mmol}}{\text{mL}} = 16.470 \text{ M}$$

Example:-How many millilitres of concentrated sulphuric acid, 94.0% (g/100g solution), density 1.831 g/cm³, are required to prepare 1 liter of a 0.100 M solution.

Solution:

$$\begin{aligned} M &= \frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} \\ &= 17.5 \left(\frac{\text{mmol}}{\text{mL}} \right) \end{aligned}$$

$$\text{no. of mmol (conc.)} = \text{no. mmol (dilu.)}$$

$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$

$$17.5 \times V_1 = 0.1 \times 1000$$

$$V_1 = 5.71 \text{ mL}$$

Of concentrated H₂SO₄ must be diluted to 1L (1000mL) to prepare (become) 0.1M.

Another solution: no. of mmol (conc.) = no. mmol (dilu.)

$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$

$$\frac{\% \times \text{sp. gr. (density)} \times 1000}{\text{M. wt}} \times V_1 = (M_2 \times V_2)_{\text{dilu.}}$$

$$\frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} \times V_1 = 0.1 \times 1000$$

$$V_1 = 5.71 \text{ mL}$$

Diluted solution

Dilution: Dilution is the procedure of reducing the concentration of a solute in a solution, usually simply by mixing with more solvent like adding more water to a solution containing the solute. To dilute a solution means to add more solvent without the addition of more solute. The concentrated solution are usually called standard or stock solution and less concentrated solutions are called diluted solutions. For an example normal saline are used for dilution of a bacteria.

$$M_{\text{stock}} \times V_{\text{stock}} = M_{\text{diluted}} \times V_{\text{diluted}}$$

Example:-You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of KMnO_4 and a series of 100 mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and 10.0×10^{-3} M KMnO_4 solutions?

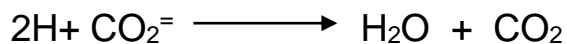
Solution 1.0×10^{-3} M

$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$

$$0.1 \left(\frac{\text{mmol}}{\text{mL}} \right) \times V_1 = 1.0 \times 10^{-3} \left(\frac{\text{mmol}}{\text{mL}} \right) \times 100 \text{ (mL)}$$

$V_1 = 1.0 \text{ mL}$ stock solution (conc.), Also to prepare 2.0, 5.0, 10.0×10^{-3} M

Example:-A solution contains 3.30 gm of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in each 15 ml. What is its molarity? What is its normality? With how many millilitres of 3.1N acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, will 25 ml of the carbonate react according to the equation



With how many millilitres of 3.1 N H_2SO_4 will 25 ml of the carbonate react?

Solution:

$$M = \frac{\text{wt (g)}}{\text{M. wt } (\frac{\text{g}}{\text{mol}})} \times \frac{1000}{V \text{ (mL)}}$$

$$M = \frac{3.30}{286 (\frac{\text{g}}{\text{mol}})} \times \frac{1000}{15 \text{ (mL)}}$$

$$M = 0.77\text{M}$$

$$N = a M = 2 \times 0.77 = 1.53\text{N}$$

$$N_1 V_1 = N_2 V_2 \quad ,$$

$$3.1 \times V_1 = 1.53 \times 25$$

$$V_1 = 12.4 \text{ ml acetic acid.}$$

$$V_1 = 12.4 \text{ ml } \text{H}_2\text{SO}_4$$

Example:-You wish to prepare 500 mL of 0.1 M $K_2Cr_2O_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL.

$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$

$$0.250 \left(\frac{\text{mmol}}{\text{mL}} \right) \times V_1(\text{mL}) = 0.1 \left(\frac{\text{mmol}}{\text{mL}} \right) \times 500 \text{ mL}$$

$$V_1 = 200 \text{ mL}$$

Example:-What is the molarity and normality of a 13.0% solution of H_2SO_4 ? To what volume should 100 ml of acid be diluted in order to prepare a 1.50 N solution?

Solution: from specific gravity table in the appendix, the specific gravity of the acid is 1.090.

$$M = \% \times \text{SP.gr} \times 1000 / \text{M.wt} = 0.13 \times 1.090 \times 1000 / 98 = 1.45 \text{ M.}$$

$$N = a \text{ M} = 2 \times 1.45 = 2.9 \text{ N.}$$

$$N_1 V_1 = N_2 V_2 \quad 2.9 \times 100 = 1.50 \times V_2$$

$$V_2 = 193 \text{ ml.}$$

Example:-Prepare 500mL of 0.010M solution of Na^+ from Na_2CO_3 .

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

$$\frac{0.01}{2} \quad 0.01$$

$$M_{Na_2CO_3} = \frac{\text{wt}}{\text{M. wt}} \times \frac{1000}{V(\text{mL})}$$

$$0.005 = \frac{\text{wt}}{106} \times \frac{1000}{500}$$
$$2 \times \text{wt} = 0.005 \times 106$$
$$\text{wt} = \frac{0.005 \times 106}{2} = 0.265 \text{ g Na}_2\text{CO}_3$$

Problems

Q1: Calculate the formula weights of the following substance :(a) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, (b) $\text{Ag}_2\text{Cr}_2\text{O}_7$, (c) $\text{Ca}(\text{PO}_4)_2$.

Q2: A solution containing 10 mmol CaCl_2 is diluted to 1 L. Calculate the number of grams of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ per milliliter of the final solution?

Q3: Calculate the molarity of each of the following solutions:

(a) 10 gm H_2SO_4 in 250 ml of solution, (b) 6 gm NaOH in 500 ml of solution, (c) 25 gm AgNO_3 in 1L of solution.

Q4: Calculate the number of grams in 500 ml of each of the following solutions: (a) 0.1 M Na_2SO_4 , (b) 0.250 M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, (c) 0.667 M $\text{Ca}(\text{C}_9\text{H}_6\text{ON})_2$.

Q5: Calculate the grams of each substance required to prepare the following solutions :(a) 250 ml of 0.1 M KOH ,

(b) 1L of 0.0275 M $\text{K}_2\text{Cr}_2\text{O}_7$, (c) 500 ml of 0.05 M CuSO_4 .

Q6: How many milliliters of concentration hydrochloric acid, 38 % (wt/wt), specific gravity 1.19, are required to prepare 1L of a 0.1 M solution?

Q7: Calculate the molarity of each of the following commercial acid or base solutions :(a) 70% HClO_4 , sp. grv. 1.668, (b) 69% HNO_3 , sp. grv.

1.409 , (c) 85% H_3PO_4 , sp. grv. 1.689 ,(d)99.5% $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid) , sp. grv. 1.051 , (e)28% NH_3 , sp. grv. 0.898 .

Q8/A 12.5-mL portion of a solution is diluted to 500 mL, and its molarity is determined to be 0.125. What is the molarity of the original solution?

Q9/ What volume of 0.50 M H_2SO_4 must be added to 65mL of 0.20 M H_2SO_4 to give a final solution of 0.35 M? Assume volumes are additive.

Q10/You are required to prepare working standard solutions of 1.00×10^{-5} , 2.00×10^{-5} , 5.00×10^{-5} , and 1.00×10^{-4} M glucose from a 0.100 M stock solution. You have available 100-mL volumetric flasks and pipets of 1.00-, 2.00-, 5.00-, and 10.00-mL volume. Outline a procedure for preparing the working standards.

2. Molality (Molal concentration)

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

$$\text{Molality (m)} = \frac{\text{wt}}{\text{M. wt}} \times \frac{1000}{\text{wt (g)}}$$

Example:-Calculate the molal concentration for solution preparing from mixing 4 g NaOH with 500 g water.

$$\text{Molality (m)} = \frac{\text{wt}}{\text{M. wt}} \times \frac{1000}{\text{wt (g)}}$$

$$= \frac{4 \text{ g}}{40 \text{ g/mol}} \times \frac{1000}{500} = 0.2 \text{ m}$$

3. Formality (F):

Formal concentration (also called Formality):- Chemists sometime use the term formality for solutions of ionic salts that do not exist as molecules in the solid or in solution. The concentration is given as formal (F). Formality is numerically the same as molarity.

The formal concentration of a solution of glucose, for example, is the same as its molarity. (A solution that is 0.0259 M in glucose is 0.0259 F in glucose as well.). For a compound that ionizes in solution, such as NaCl, molarity and formality are different. Dissolving 0.1 moles of CaCl_2 in 1 L of water gives a solution containing 0.1 moles of Ca^{2+} and 0.2 moles of Cl^- .

$$F = \frac{\text{wt (g)}}{F.\text{wt} \left(\frac{\text{g}}{\text{mol}} \right)} \times \frac{1000}{V \text{ (mL)}}$$

Where F = Formality for solid compound,

wt = weight in gm,

F.wt or some times gFw (gram formula weight) = 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).

V = volume in liter.

4. Normality (N):

Where normal concentration (Normality) N: the conc. of solution produce from dissolving number of equivalent solute in solution volume in liter. The conc. of solution produce from dissolving number of equivalent solute in solution volume in liter.

$$N = \frac{\text{No. of equivalent}}{\text{Solution Volume (L)}} = \frac{\text{Equivalent Weight } (\frac{\text{gm}}{\text{eq}})}{\frac{V \text{ (mL)}}{1000 (\frac{\text{mL}}{\text{L}})}}$$

$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V \text{ (mL)}}$$

$$N = \left(\frac{\text{Eq}}{\text{L}} \right) = \left(\frac{\text{meq}}{\text{mL}} \right)$$

Where equivalent weight (Eq.wt):- is the formula weight divided by the number of reacting units (H^+ for acid-base and electron for oxidation-reduction reaction).

$$(\text{Eq. wt}) \text{ for acid - base reaction} = \frac{\text{formula weight (F. wt)}}{\text{No. of } \text{H}^+ \text{ or } \text{OH}^-}$$

$$(\text{Eq. wt}) \text{ for oxidation - reduction reaction} = \frac{\text{formula weight (F. wt)}}{\text{No. of electron}}$$

$$\text{Number of equivalent (Eq)} = \frac{\text{wt (gm)}}{\text{Eq. wt } \left(\frac{\text{gm}}{\text{Eq}}\right)}$$

$$\text{Number of equivalent (Eq)} = N \left(\frac{\text{Eq}}{\text{L}}\right) \times \text{Volume (L)}$$

$$\text{Number of milliequivalent (meq)} = \frac{\text{wt (mg)}}{\text{Eq. wt } \left(\frac{\text{mg}}{\text{mL}}\right)}$$

$$\text{Number of milliequivalent (Eq)} = N \left(\frac{\text{meq}}{\text{mL}}\right) \times \text{Volume (mL)}$$

Example: Calculate the equivalent weight of the following substances:

(a) NH_3 , (b) $\text{H}_2\text{C}_2\text{O}_4$ (in reaction with NaOH), and (c) KMnO_4 [Mn(VII) is reduced to Mn^{2+}].

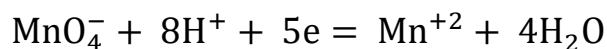
(a)

$$\text{Eq wt} = \frac{\text{Mwt}}{\text{No. of H}^+ \text{ or OH}^-} = \frac{17.03}{1} = 17.03 \text{ gm/Eq}$$

(b)

$$\text{Eq wt} = \frac{90.04}{2} = 45.02 \text{ gm/Eq}$$

(c)



$$\text{Eq wt} = \frac{\text{M. wt}}{\text{No. of electron}} = \frac{158.04}{5} = 31.608 \text{ gm/Eq}$$

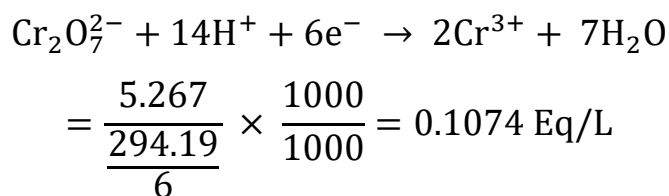
Example:-Calculate the normality of the solutions containing the following: (a) 5.300gm/L Na_2CO_3 (when the CO_3^{2-} reacts with two protons), (b) 5.267 gm/L $\text{K}_2\text{Cr}_2\text{O}_7$ (the Cr is reduced to Cr^{3+}).

Solution

(a)

$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V \text{ (mL)}} = \frac{5.3}{\frac{105.99}{2}} \times \frac{1000}{1000} = 0.10 \text{ Eq/L}$$

(b)



Example:-How many millilitres of a 0.25M solution of H_2SO_4 will react with 10mL of a 0.25M solution of NaOH .

Solution:

$$N = nM \quad (n = \text{No. of equivalent } (\text{H}^+, \text{OH}^-, \text{ or electron}))$$

$$N_{\text{H}_2\text{SO}_4} = 2 \times 0.25$$

$$= 0.5 \left(\frac{\text{Eq}}{\text{L}} \right) \text{ or } \left(\frac{\text{meq}}{\text{mL}} \right) \text{ or } N$$

$$N_{\text{NaOH}} = 1 \times 0.25 = 0.25 \text{ N}$$

$$(N \times V)_{\text{H}_2\text{SO}_4} = (N \times V)_{\text{NaOH}}$$

$$(0.5 \times V)_{\text{H}_2\text{SO}_4} = (0.25 \times 10)_{\text{NaOH}}$$

$$V_{\text{H}_2\text{SO}_4} = 5.0 \text{ mL}$$

Example:-A solution of sodium carbonate is prepared by dissolving 0.212 gm Na_2CO_3 and diluting to 100mL. Calculate the normality of the solution (a) if it is used as a monoacidic base, and (b) if it is used as a diacidic base.

Solution:(a)

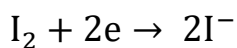
$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V (\text{mL})} = \frac{0.212}{\frac{106.0}{1}} \times \frac{1000}{100} = 0.020 \text{ meq/mL}$$

(b)

$$N = \frac{0.212}{\frac{106.0}{2}} \times \frac{1000}{100} = 0.040 \text{ meq/mL}$$

Example:-Iodine (I_2) is an oxidizing agent that in reactions with reducing agent is reduced to iodide (I^-). How many grams I_2 would you weigh out to prepare 100mL of a 0.10N I_2 solution?

Solution:



$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V (\text{mL})}$$

$$0.1 = \frac{\text{wt}}{\frac{254}{2}} \times \frac{1000}{100}$$

$$\text{wt} = 1.27\text{g}$$

Example:-Calculate the normality of a solution of 0.25 g/L $\text{H}_2\text{C}_2\text{O}_4$, both as an acid and as a reducing agent.

Solution:

Solution:



$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V (\text{mL})} = \frac{0.259}{\frac{90.04}{2}} \times \frac{1000}{1000}$$

$$= 0.00555 \text{ meq/mL}$$

Example:-How many milliequivalents are involved in 43.50mL of 0.1379 N K₂Cr₂O₇?

Solution: no.of milliequivalents=N×V

$$=0.1379 \text{ meq/mL} \times 43.50 \text{ mL}$$

$$=5.9987 \text{ meq}$$

Problems

Q1:To what volume must 750 ml of 2.4 N solution be diluted in order to make it 1.7N?

Q2:How much 0.6 N base must be added to 750 ml of a 0.2 N base in order the solution to be 0.3 N ?

Q3: How many volume of 0.1421 N KOH solution are required to neutralize 13.72 ml of 0.0686 M H₂SO₄ ?

5. Concentration by percent

$$\left(\frac{\text{wt}}{\text{wt}}\%\right) = \frac{\text{wt solute (g)}}{\text{wt solution or sample (g)}} \times 100$$

$$= \frac{\text{wt solute (mg)}}{\text{wt solution or sample (mg)}} \times 100$$

$$\left(\frac{\text{wt}}{V}\%\right) = \frac{\text{wt solute (g)}}{V \text{ solution or sample (mL)}} \times 100$$

$$= \frac{\text{wt solute (mg)}}{V \text{ solution or sample (}\mu\text{L)}} \times 100$$

$$\left(\frac{V}{V}\right) \% = \frac{V \text{ solute (mL)}}{V \text{ solution or sample (mL)}} \times 100$$

$$= \frac{V \text{ solute } (\mu\text{L})}{V \text{ solution or sample } (\mu\text{L})} \times 100$$

Example:-Calculate the weight percentage of solution prepare by mixing 5.0g AgNO₃ with 100mL water (density 1g/cm³).

Solution:

$$\left(\frac{\text{wt}}{\text{wt}}\right) \% = \frac{\text{wt solute (g)}}{\text{wt solution (g)}} \times 100$$

$$= \frac{\text{wt solute (AgNO}_3\text{)(g)}}{\text{wt solute} + \text{wt solvent (H}_2\text{O) (g)}} \times 100$$

$$= \frac{5 \text{ g}}{5 \text{ g} + (100 \text{ mL} \times 1 \frac{\text{g}}{\text{mL}})} \times 100$$

$$= \frac{5 \text{ g}}{105 \text{ g}} \times 100 = 4.76\%$$

Example:-Calculate number of grams in 500mL silane solution (wt/v % = 0.859%).

Solution:

$$\left(\frac{\text{wt}}{V}\right) \% = \frac{\text{wt solute (g)}}{V \text{ solution (mL)}} \times 100$$

$$0.859 \% = \frac{\text{wt NaCl (g)}}{500} \times 100$$

$$\text{wt NaCl} = \frac{0.859 \times 500}{100} = 4.25 \text{ g NaCl}$$

Example:-Calculate the weight of glucose in liter solution (wt/v % = 5 %).

Solution:

$$\left(\frac{\text{wt}}{V}\right) \% = \frac{\text{wt solute (g)}}{V \text{ solution (mL)}} \times 100$$

$$\left(\frac{\text{wt}}{V}\right) \% = \frac{\text{wt glucose (g)}}{V \text{ solution (mL)}} \times 100$$

$$5\% = \frac{\text{wt glucose (g)}}{1000 \text{ (mL)}} \times 100$$

$$\text{wt glucose} = \frac{5 \times 1000}{100} = 50 \text{ g}$$

Example:-Calculate the volume percentage of solution preparing by mixing 50mL methyl alcohol with 200mL water.

Solution:

$$\left(\frac{V}{V}\right) \% = \frac{V \text{ solute (mL)}}{V \text{ solution or sample (mL)}} \times 100$$

$$= \frac{V \text{ methyl alcohol (mL)}}{V \text{ methyl alcohol} + V \text{ water (mL)}} \times 100$$

$$= \frac{50 \text{ mL}}{(50 + 200)\text{mL}} \times 100 = 20\%$$

Example:-Calculate the molar concentration for 0.85% (w/v%) sodium chloride solution.

$$M = \frac{\text{wt (g)}}{\text{M. wt}} \times \frac{1000}{V \text{ mL}} = \frac{\text{wt (g)}}{\text{M. wt}} \times \frac{1000}{100} = \frac{\text{wt}}{V} \% \times \frac{1000}{\text{M. wt}} = \frac{0.85}{100} \times \frac{1000}{58.5} = 0.145\text{M}$$

6. Concentration in parts per thousand or million or billion:-

$$\text{part per thousand (ppt)} \left(\frac{\text{wt}}{\text{wt}} \right) = \text{get} \times 10^3$$

$$= \frac{\text{wt (mg)}}{\text{wt (g)}} = \frac{\text{wt (g)}}{\text{wt (kg)}}$$

$$\text{part per million (ppm)} \left(\frac{\text{wt}}{\text{wt}} \right) = \frac{\text{wt solute (g)}}{\text{wt solution (sample)(g)}} \times 10^6$$

$$= \frac{\text{wt (}\mu\text{g)}}{\text{wt (g)}} = \frac{\text{wt (mg)}}{\text{wt (kg)}}$$

$$\text{part per billion (ppb)} \left(\frac{\text{wt}}{\text{wt}} \right) = \frac{\text{wt solute (g)}}{\text{wt solution (sample)(g)}} \times 10^9$$

$$= \frac{\text{wt (ng)}}{\text{wt (g)}} = \frac{\text{wt (}\mu\text{g)}}{\text{wt (kg)}}$$

Example:-A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μg zinc, what is the concentration of zinc in the plant in ppm? in ppb?

$$\text{ppm} = \frac{\text{wt (}\mu\text{g)}}{\text{wt (g)}}$$

$$= \frac{3.6 \mu\text{g}}{2.6 \text{ g}} = 1.4 \frac{\mu\text{g}}{\text{g}} = 1.4 \text{ ppm}$$

$$\text{ppb} = \frac{\text{wt (ng)}}{\text{wt (g)}} = \frac{3.6 \times 10^3 \text{ ng}}{2.6 \text{ g}}$$

$$= 1.4 \times 10^3 \frac{\text{ng}}{\text{g}} = 1400 \text{ ppb}$$

$$\begin{aligned} \text{pt} \left(\frac{\text{wt}}{\text{V}} \right) &= \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^3 \\ &= \frac{\text{wt (mg)}}{\text{V (mL)}} = \frac{\text{wt (g)}}{\text{V (L)}} \end{aligned}$$

$$\begin{aligned} \text{ppm} \left(\frac{\text{wt}}{\text{V}} \right) &= \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^6 \\ &= \frac{\text{wt (}\mu\text{g)}}{\text{V (mL)}} = \frac{\text{wt (mg)}}{\text{V (L)}} \end{aligned}$$

$$\begin{aligned} \text{ppb} \left(\frac{\text{wt}}{\text{V}} \right) &= \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^9 \\ &= \frac{\text{wt (ng)}}{\text{V (mL)}} = \frac{\text{wt (}\mu\text{g)}}{\text{V (L)}} \end{aligned}$$

$$\begin{aligned} \text{ppt} \left(\frac{\text{wt}}{\text{V}} \right) &= \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{12} \\ &= \frac{\text{wt (pg)}}{\text{V (mL)}} = \frac{\text{wt (ng)}}{\text{V (L)}} \end{aligned}$$

The relationship between molarity, normality and part per million:-

$$M = \frac{\text{ppm}}{\text{M. wt} \times 1000} \qquad N = \frac{\text{ppm}}{\text{Eq. wt} \times 1000}$$

Example :-(a) Calculate the molar conc. of 1.0 ppm solutions each of Li^+ and Pb^{+2} . (b) What weight of $\text{Pb}(\text{NO}_3)_2$ will have to be dissolved in 1 litre of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

$$M = \frac{\text{ppm}}{\text{M. wt} \times 1000}$$

(a)

$$M_{\text{Li}^+} = \frac{1.0}{6.94 \times 1000} = 1.44 \times 10^{-4} \text{ mole/L}$$

$$M_{\text{Pb}^{+2}} = \frac{1.0}{207 \times 1000} = 4.83 \times 10^{-6} \text{ mole/L}$$

(b)

$$M = \frac{100}{207 \times 1000} = 4.83 \times 10^{-4} \text{ mole/L}$$

$$M = \frac{\text{wt}}{\text{M. wt}} \times \frac{1000}{V (\text{mL})}$$

$$4.83 \times 10^{-4} = \frac{\text{wt}}{283.2} \times \frac{1000}{1000}$$

$$\text{wt} = 0.137 \text{g Pb(NO}_3)_2$$

Example:-The concentration of Zinc ion in blood serum is about (1ppm). Express this as meq/L.

$$\begin{aligned} N &= \frac{\text{ppm}}{\text{Eq. wt} \times 1000} = \frac{\text{ppm}}{\frac{\text{A. wt}}{2} \times 1000} = \frac{1}{\frac{65.4}{2} \times 1000} = 3.06 \times 10^{-5} \text{Eq/L} \\ &= 3.06 \times 10^{-5} \times 1000 = 3.06 \times 10^{-2} \text{ meq/L} \end{aligned}$$

Problems

Q1:A solution contains 6 μ mole Na_2SO_4 in 250 ml. How much ppm sodiums does it contain? of sulfate?

Q2: Calculate the molar concentration of 1 ppm solutions of each of the following?

a) AgNO_3 b) $\text{Al}(\text{SO}_4)_3$ c) CO_2 d) HClO_4

Q3: Calculate the ppm conc. Of 2.5×10^{-4} M solutions of each of the following?

a) Ca^{+2} b) CaCl_2 c) HNO_3 d) KCN

Q4: You want to prepare 1L of a solution containing 1ppm Fe^{+2} . How many grams ferrous ammonium sulfate, $\text{Fe SO}_4 \cdot (\text{NH}_4) \text{SO}_4 \cdot 6\text{H}_2\text{O}$, must be dissolved and diluted in 1L? What would be the molarity of this solution?

Q5: How many grams NaCl should be weighed out to prepare 1L of a 100 ppm solution of a) Na^+ and b) Cl^-

➤ **Unites used in analytical chemistry**A. Units of concentration

Name	Abbreviation	Concentration unitss
molar	M	Mol/L
millimolar	mM	10^{-3} mol/L
micromolar	μ M	10^{-6} mol/L
nanomolar	nM	10^{-9} mol/L
picomolar	pM	10^{-12} mol/L
femtomolar	fM	10^{-15} mol/L
attomolar	aM	10^{-18} mol/L
zeptomolar	zM	micromolar
yoctomolar	yM ^[3]	10^{-24} mol/L (1 particle per 1.6 L)

B. Units of volume

Name	Abbreviation	Volume unites
decilitre	DI	10^{-1} L
centilitre	CI	10^{-2} L
millilitre	MI	10^{-3} L
microlitre	MI	10^{-6} L
nanolitre	NI	10^{-9} L
picolitre	PI	10^{-12} L
femtolitre	FI	10^{-15} L
attolitre	AI	10^{-18} L
zeptolitre	ZI	10^{-21} L
yoctolitre	YI	10^{-24} L