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First year



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***** Definition of analytical chemistry:

Is often described as the area of chemistry responsible for characterizing the composition of matter, both qualitatively (what is present) and quantitatively (how much is present).

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.

***** There are several different areas of analytical chemistry :

- 1- Clinical analysis: blood, urine, etc. For use in diagnosis.
- 2- **Pharmaceutical analysis**: establish the physical properties, toxicity, metabolites, quality control, etc.
- 3- Environmental analysis: poll tans, soil and water analysis, pesticides.
- 4- **Forensic analysis:** analysis related to criminology, DNA finger printing, finger print detection, blood analysis.
- 5- Industrial quality control- required by most companies to control product quality
- 6- **Bioanalytical chemistry and analysis:** detection and/or analysis of biological components (proteins, DNA, RNA, carbohydrates, metabolites, etc.)



* Classification of Analytical Chemistry

• According to the purpose of analysis:

• (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).

There are several methods for the chemical identity of the analysts on:

- a) Using A sense
 - 1) A taste used to identify between sugar and salt
 - 2) Different on color and crystal shape (Coal and sulfur)
- b) Using chemical reagent

Therefore, qualitative information is required before a quantitative analysis

AgNO ₃	+ HCl	HNO3 + AgCl 🖡
NaNO ₃		HNO ₃ + NaCl

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



Classification of Analytical Chemistry According to the method of analysis:

- 1) **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), fluorimeter, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy (absorption, fluorescence).
- 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).

For example, to determine the chloride ion content in drinking water, Silver Nitrate (AgNO₃) will be added to the sample solution, resulting in the precipitation of silver chloride (AgCl), as below equation:

$$Ag(aq) + Cl^{-}(aq) \implies AgCl(s)$$

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



3) Volumetric analysis (Titrimetric analysis): the most important Method in quantitative analysis. The analyte reacts with a measured volume of reagent of known concentration, in a process called titration.

Selecting a method of analysis

Selecting the method to solve an analytical problem is a vital first step in any quantitative analysis. The selecting will based on such consideration as:

- 1. Accuracy
- 2. Reliability
- 3. Time
- 4. Cost / number of analysis
- 5. Complexity of sample

The success or failure of an analysis is often critically depend upon the proper selection of method

Electrolytes: Electrolytes are salts or molecules that ionize completely in solution. As a result, electrolyte solutions readily conduct electricity.

An electrolyte is any salt or ionizable molecule that, when dissolved in solution, will give that solution the ability to conduct electricity. This is because when a salt dissolves, its dissociated ions can move freely in solution, allowing a charge to flow.

- Electrolyte solutions are normal formed when a salt it placed into a solvent such as water. For example, when table salt, NaCl, is placed in water, the salt (a solid) dissolves into its component ions, according to the dissociation reaction: $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
- Nonelectrolytes: do not dissociate into ions in solution; nonelectrolyte solutions do not, therefore conduct electricity.
- Nonelectrolyte Solutions are compounds that do not ionize at all in solution. As a result, solutions containing nonelectrolytes will not conduct electricity. Typically, nonelectrolytes are primarily held together by covalent rather than ionic bonds. A common example of a nonelectrolyte is glucose, or C₆H₁₀O₆. Glucose (sugar) readily dissolves in water, but because it does not dissociate into ions in solution, it is considered a nonelectrolyte; solutions containing glucose do not, therefore, conduct electricity.

Strong electrolyte: ionize almost completely in a solvent.

Weak solvent: ionize only partially

• Having explained the volumetric analysis (titration), few expressions needs to explain to fully understand the process:

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

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

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

NaCl (s) + H2O (l) Salt solution

Classification of solution

A) 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 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 at high temperature.

B) 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 (Amoxcycilline Antibiotics), particle of solute visible to naked eye.
- (3) Colloidal solution: homogeneous mixture, which does not settle nor are their components filterable, solute particle visible with electron microscope (milk).



Stoichiometric Calculations

- Gram atomic weight (gAw sometimes 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 10g of carbon 10 (this number is Avogadro's number = $(6.022 \times 10^{23} \text{ atoms})$.
- Gram molecular weight (gMw sometimes M.wt): Defined as the sum of the atomic weight of the atoms that make up a molecular compound.
- Gram formula weight (gFw sometimes 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.q 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 CaSO₄.4H₂O (calculate gram molecular or formula weight).

Sol: One mole is the formula weight expressed in grams. The formula weight is (Ca=40.04; S=32.06; O=16.00; H=1.01)

 $CaSO_{4}. \ 7H_{2}O = 40. \ 08 + 32. \ 06 + (16. \ 0 \times 4) + 7[(2 \times 1. \ 01) + 16. \ 00] = 262. \ 25 \ g/mol$

EX:

- (a) What is the mass of one atom of Cl?
- (b) What is the atomic mass of Cl?
- (c) What is the gram atomic mass of Cl?

Sol. (a) Mass of one atom of Cl = 35.5 amu.

(b) Atomic mass of Cl = $\frac{\text{Mass of an atom in amu}}{\text{lamu}} = \frac{35.5 \text{amu}}{\text{lamu}} = 35.5$ (c) Gram atomic mass of Cl = [Mass of 1 Cl atom × NA] = 35.5 amu × N_A = $\frac{35.5}{N_A}$ × N_A gram = 35.5 gram Equivalent weight: The mass of a compound containing one equivalent (EW).



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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.

$$Mole = \frac{Weight (g)}{formula weight (\frac{g}{mole})}$$

$$mMole = \frac{Weight (mg)}{formula weight (\frac{mg}{mmole})}$$
2- N = n N_A
acc الجزئيات = عدد المولات × عدد أفوجادرو

3- $n = M V_{(L)}$ عدد المولات = التركيز المولاري (M) × حجم المحلول بوحدة اللتر

EX: What will be the mass of 5 mole of SO₂?

Ans. Molecular mass of $SO_0 = 64$ gm



Ex: Sample Calculations of Molar Mass Na₂HPO₄

- Na_2 2 x 22.99 = 45.98
- H $1 \ge 1.008 = 1.008$
- P 1 x 30.97 = 30.97
- $O_4 4 x 16.00 = 64$

141.96 g/mol

Concentration of Solutions

The concentration: of a solution is a measure of the amount of solute that is dissolved in a given quantity of solvent.

A dilute solution is one that contains a small amount of solute.

A concentrated solution contains a large amount of solute.



Molarity (M)

Molarity (**M**): is the number of moles of solute dissolved in one liter of solution.

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

Where **M**= Molarity for solid compound,

wt = weight in gm,

M.wt or sometimes 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 AgNO3 in a 250 ml volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles AgNO3 were dissolved?

Solution:

$$M = \frac{\text{wt}(g)}{\text{M.wt}(\frac{g}{\text{mol}})} \times \frac{1000}{\text{V}(\text{mL})}$$
$$= \frac{1.26 \text{ (g)}}{169.9 (\frac{g}{\text{mol}})} \times \frac{1000}{250 \text{ (mL)}} = 0.0297 \text{ mol/L}$$
$$Millimoles = M \left(\frac{\text{mmol}}{\text{mL}}\right) \times \text{V}(\text{mL})$$
$$= 0.0297 \left(\frac{\text{mmol}}{\text{mL}}\right) \times 250 \text{ mL} = 7.42 \text{ mmole}$$

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

$$M = \frac{\text{wt } (g)}{\text{M. wt } (\frac{g}{\text{mol}})} \times \frac{1000}{\text{V } (\text{mL})}$$
$$0.250 \text{ M} = \frac{\text{wt } (g)}{58.4 \left(\frac{g}{\text{mol}}\right)} \times \frac{1000}{1 (\text{mL})}$$
$$\text{wt } (g) = 0.0146 \frac{g}{\text{mL}}$$

H.W: What mass of sodium iodide (Nal) is contained in 251 mL of a 0.5 M solution?





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 $(gm.cm^3)$ in 20^oC (is the ratio of the mass in (gm) and volume (mL).

Percentage (%) = percentage of chemical species.

Example: Calculate the molarity of 28% NH₃ specific gravity 0.898? Solution: M. wt NH₃ = $14 + (3 \times 1) = 14$

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

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

Example: How many grams Na₂SO₄ should be weight out to prepare 500 mL of a 0.1 M solution.

$$M = \frac{\text{wt}(g)}{\text{M.wt}(\frac{g}{\text{mol}})} \times \frac{1000 \left(\frac{\text{mL}}{\text{L}}\right)}{\text{V}(\text{mL})}$$
$$0.10 \text{ mol/L} = \frac{\text{wt}(g)}{142 \left(\frac{g}{\text{mol}}\right)} \times \frac{1000 \left(\frac{\text{mL}}{\text{L}}\right)}{500 (\text{mL})}$$
$$\text{wt}(g) = \frac{0.10 \left(\frac{\text{mol}}{\text{L}}\right) \times 142 \left(\frac{g}{\text{mol}}\right)}{2 \left(\frac{1}{\text{L}}\right)} = 7.1 \text{ g}$$

DILUTION

- Solutions are often prepared from more concentrated ones by adding water, this process is called dilution.
- When more water is added to a solution, the *volume increases*, causing a *decrease in concentration*. However, the *amount of solute does not change*.
- The amount of solute depends on the concentration and the volume of the solution. Therefore,

$\mathbf{M1} \mathbf{x} \mathbf{V1} = \mathbf{M2} \mathbf{x} \mathbf{V2}$

Examples:

1. What is the molarity of the final solution when 75 mL of 6 M KCl solution is diluted to 150 mL? '

$$M_1 = 6.0 \text{ M} \qquad V_1 = 75 \text{ mL} \qquad M_2 = \frac{M_1 V_1}{V_2} = \frac{(6.0 \text{ M})(75 \text{ mL})}{150 \text{ mL}} = 3.0 \text{ M}$$
$$M_2 = ??? \qquad V_2 = 150 \text{ mL}$$

H.W

2. What volume (mL) of 0.2 M HCl solution can be prepared by diluting 50.0 mL of 1.0 M HCl?

Example: You wish to prepare 500 mL of $0.1 \text{ M K}_2\text{Cr}_2\text{O}_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL.

$$(M_1 \times V_1)_{conc.} = (M_2 \times V_2)_{dilu.}$$
$$0.250 \left(\frac{mmol}{mL}\right) \times V_1(mL) = 0.1 \left(\frac{mmol}{mL}\right) \times 500 \text{ mL}$$
$$V_1 = 200 \text{ mL}$$

Molality (m): is the number of moles of solute dissolved in one gram of solution.

 $\mathbf{m} = \frac{\mathbf{n}}{\mathbf{wt}}$ $\mathbf{m} = \frac{\mathbf{Wt}_{\text{solute}}}{\mathbf{M}.\mathbf{wt}} \times \frac{\mathbf{1000}}{\mathbf{Wt}_{\text{solvent}}}$

Normality

Normality (N): Normal concentration: Number of equivalent solute in solution volume in litre.

Normality must be specified with respect to a definite reaction.

- **a.** For acid-base reactions, 1 equivalent = 1 mole of hydrogen ions (or 1 mole of hydroxide ion) donated.
- **b.** For oxidation-reduction reactions, 1 equivalent = 1 mole of electrons.
- **c.** For determining electrolyte concentration, 1 equivalent = 1 mole of charge.

Normality = (Molarity) (electrons transferred), or

= (Molarity) (hydrogen ions neutralized)

= (Molarity) (hydroxide ions neutralized)

$$N = \frac{\text{No. of equivalent}}{\text{Solution Volumn (L)}} = \frac{\text{Equivalent Weight } (\frac{\text{gm}}{\text{eq}})}{\frac{V(\text{mL})}{1000 (\frac{\text{mL}}{\text{L}})}}$$
$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V(\text{mL})}$$
$$N = (\frac{\text{Eq}}{\text{L}}) = (\frac{\text{meq}}{\text{mL}})$$

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).

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

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

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

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

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

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

Example: Calculate the equivalent weight of the following substances:

- (a) HCl
- (b) $H_2C_2O_4$ (in reaction with NaOH),
- (c) KMnO₄ [Mn^{+3} is reduced to Mn^{+2}].



(b)
Eq wt =
$$\frac{90.04}{2}$$
 = 45.02 gm/Eq

(c)

$$MnO_{4}^{-} + 8H^{+} + 5e = Mn^{+2} + 4H_{2}O$$

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

Example:-What is the molarity and normality of a 13% solution of H_2SO_4 ? To what volume should 100 ml of acid be diluted in order to prepare a 1.50 N solution?

from specific gravity table in the appendix, the specific gravity of the acid is **1.09**.

Solution:

N=a M = 2×1.45=2.9 N.

 $N_1 V_1 = N_2 V_2$ 2.9×100 = 1.50×V2

V2 = 193 ml.

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

Solution:

N = nM (n = No. of equivalent (H⁺, OH⁻, or electron)

$$N_{H_2SO_4} = 2 \times 0.25$$

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

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

$$(N \times V)_{H_2SO_4} = (N \times V)_{NaOH}$$

$$(0.5 \times V) H_2SO_4 = (0.25 \times 10) \text{NaOH}$$

$$V_{H_2SO_4} = 5.0 \text{ mL}$$

Example:-A solution of sodium carbonate is prepared by dissolving 0.212 gm Na₂CO₃ and diluting to 100 mL. 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)

$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{\text{V}(\text{mL})} = \frac{0.212}{\frac{106.0}{1}} \times \frac{1000}{100} = 0.020 \text{ meq/mL}$$
(b)
$$N = \frac{0.212}{\frac{106.0}{2}} \times \frac{1000}{100} = 0.040 \text{ meq/mL}$$

Other concentration units

• Percentage

$$\%$$
(w/w) = $\frac{\text{wt sloute (g)}}{\text{wt sample (g)}}X100 = \frac{\text{wt solute (g)}}{\text{wt solution (g)}}X100$

• Parts per thousands, ppt

$$ppt (w/w) = \frac{wt \text{ sloute (g)}}{wt \text{ sample (g)}} X10^3 = \frac{wt \text{ solute (g)}}{wt \text{ solution (g)}} X10^3$$

• Parts per million, ppm

ppm (w/w) =
$$\frac{\text{wt sloute (g)}}{\text{wt sample (g)}}X10^6 = \frac{\text{wt solute (g)}}{\text{wt solution (g)}}X10^6$$

• Parts per billion

ppb (w/w) =
$$\frac{\text{wt sloute (g)}}{\text{wt sample (g)}}X10^9 = \frac{\text{wt solute (g)}}{\text{wt solution (g)}}X10^9$$

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	m L/L
$(1 \text{ ppm} = 10^{-4}\%)$	Victoria Ge	m g/g	m g/mL	nL/mL
Parts per billion	ppb	m g/kg	m g/L	nL/L
$(1 \text{ ppb} = 10^{-7}\% = 10^{-3} \text{ ppm})$		ng/g	ng/mL	pL/mL ^c
Milligram percent	mg%	mg/100 g	mg/100 mL	: The second sec

Example: A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μ g zinc. What is the concentration of zinc in the plant in ppm? In ppb?

Concentration of Zn in ppm = $\frac{3.6X10^{-6}g}{2.6g}X10^{6} = 1.380 \ ppm$ Concentration of Zn in ppb = $\frac{3.6X10^{-6}g}{2.6g}X10^{9} = 1380 \ ppb$

Concentration by percent

$$\begin{pmatrix} wt \\ wt \end{pmatrix} = \frac{wt \text{ solute } (g)}{wt \text{ solution or sample } (g)} \times 100$$
$$= \frac{wt \text{ solute } (mg)}{wt \text{ solution or sample } (mg)} \times 100$$
$$\begin{pmatrix} wt \\ V \end{pmatrix} = \frac{wt \text{ solute } (g)}{V \text{ solution or sample } (mL)} \times 100$$
$$= \frac{wt \text{ solute } (mg)}{V \text{ solution or sample } (\muL)} \times 100$$
$$\begin{pmatrix} V \\ V \end{pmatrix} = \frac{V \text{ solute } (mL)}{V \text{ solution or sample } (mL)} \times 100$$
$$= \frac{V \text{ solute } (mL)}{V \text{ solution or sample } (mL)} \times 100$$

Example:-Calculate the weight percentage of solution prepare by mixing 5.0 g AgNO₃ with 100mL water (density $1g/cm^3$).

Solution

$$\left(\frac{\text{wt}}{\text{wt}}\%\right) = \frac{\text{wt solute (g)}}{\text{wt solution (g)}} \times 100$$
$$= \frac{\text{wt solute (AgNO_3)(g)}}{\text{wt solute + wt solvent (H_2O) (g)}} \times 100$$
$$= \frac{5 \text{ g}}{5 \text{ g} + (100 \text{ mL} \times 1 \frac{\text{g}}{\text{mL}})} \times 100$$
$$= \frac{5 \text{ g}}{105 \text{ g}} \times 100 = 4.76\%$$

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

$$\left(\frac{\text{wt}}{\text{V}}\%\right) = \frac{\text{wt solute (g)}}{\text{V solution (mL)}} \times 100$$
$$0.859 \% = \frac{\text{wt NaCl (g)}}{500} \times 100$$
$$\text{wt NaCl} = \frac{0.859 \times 500}{100} = 4.25 \text{ g NaCl}$$

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

Solution:

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

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

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

The relationship between molarity, normality and part per million:

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

 $ppm = M \times M.wt \times 1000$ $ppm = N \times Eq.wt \times 1000$

Example :-

(a) Calculate the molar conc. of 1.0 ppm solutions each of Li^+ and Pb^{+2} .

(b) What weight of $Pb(NO_3)^2$ will have to be dissolved in 1 liter of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

(a)

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

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

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

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

$$M = \frac{\text{wt}}{\text{M.wt}} \times \frac{1000}{\text{V (mL)}}$$
$$4.83 \times 10^{-4} = \frac{\text{wt}}{283.2} \times \frac{1000}{1000}$$
$$\text{wt} = 0.137\text{g Pb}(\text{NO}_3)_2$$

Volumetric analysis

Volumetric analysis: is when the analysis is completed by measuring the volume of a solution of known concentration needed to react completely with the substance being determined.

Titration: it is by measuring a process for determining the amount of substance the quantity of a reagent (titrant) required to react completely with that substance.

4 The requirements of a titration are as follows:-

(1) The reaction must be stoichiometric: That is, there must be a well defined and known reaction between the analyte and the titrant.

$CH_{3}COOH + NaOH \rightarrow CH_{3}COONa + H_{2}O$

- (2) The reaction should be rapid. Most ionic reactions.
- (3) There should be no side reaction, and the reaction should be specific
- (4) There should be a marked change in some property of the solution when the reaction is complete. This may be a change in color of the solution or in some electrical or other physical property of the solution (by used indicator or pH meter)
- (5) The point at which an equivalent or stoichiometric amount of titrant is added is called the equivalence point. The point at which the reaction is observed to be complete is called the end point, that is, when a change in some property of the solution.
- (6) The reaction should be quantitative. That is, the equilibrium of the reaction should be far to the right so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy. The equivalence point is the theoretical end of the titration where the number of moles of titrant = number of moles of analyte. The end point is the observed end of the titration.

Standard solution: A solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a primary standard and diluting to an accurately known volume in a volumetric flask.

Primary standard: is a highly purified chemical compound used for standardization of the standard solution.

- A primary standard should fulfil these requirements:-
- (1) It should be 99.8% pure, although 0.1 to 0.2% impurity is tolerable if it accurately known.
- (2) It should be stable to drying temperature, and it should be stable indefinitely at room temperature. The primary standard always dried before weighing.
- (3) It should be readily available and inexpensive.
- (4) Althogh not necessary, it should have a high formula weight.
- (5) If it is to use in titration, it should possess the properties required for a titration listed above. In particular, the equilibrium of the reaction should be far to the right so that a very sharp end point will be obtained.

A solution standardized by titrating a primary standard is itself a secondary standard. It will be less accurate than a primary standard solution due to the errors of titrations. A high formula weight means a larger weight must be taken for a given number of moles. This reduces the error in weighing.

Classification of volumetric or titration methods:

- (1) Neutralization (acid-base) titrations: Either many compounds both inorganic and organic are acids or bases can be titrated with a standard solution of a strong base or a strong acid. The end point of these titrations are easy to detect, either by means of indicator or by following the change in pH with a pH meter. HA + B ↔ HB+ + A-
- (2) **Precipitation titrations:** In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate.

$$M(aq) + nL(aq) \leftrightarrow MLn(s)$$

3) **Complexometric titrations** : In complexometric titrations ,the titrant is a reagent that forms a water-soluble complex with the analyte , a metal ion .The titrant is often a chelating.

$$M(aq) + nL \leftrightarrow MLn(aq)$$

4) **Reduction-Oxidation titrations :**These (redox) titrations involve the titration of an oxidizing agent with a reducing agent ,or vice versa .An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

$$A_{Ox} + B_{Red} \leftrightarrow A_{Red} + B_{OX}$$

- Equivalence point: is where the titration should really end. At this point we have added stoichiometric amount of titrant (reagent) to the titrated substance (analyte).
- So we can say that the **End point** is where the titration ends in practice. The closer the end point to the equivalence point the better.

Example: - A 0.471g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 M hydrochloric acid solution, requiring 40.72 mL. The reaction is: $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ calculate the percent sodium bicarbonate in the sample.

Solution:

$$\begin{array}{l} \mbox{millimoles NaHCO}_3 = \mbox{millimoles HCl} \\ (\frac{\mbox{wt}(\mbox{g})}{\mbox{M.wt}(\mbox{g})})_{\mbox{NaHCO}_3}\mbox{X1000} = (\mbox{M}\times\mbox{V})_{\mbox{HCl}} \\ (\frac{\mbox{wt}(\mbox{g})}{\mbox{84.01}(\mbox{g})})\mbox{X1000} = 0.\mbox{1067}\times\mbox{40.72} \\ \mbox{wt} = 0.\mbox{365 g} \end{array}$$

 $\% NaHCO_{3} = \frac{wt \, NaHCO_{3}}{wt \, sample} \times 100 = \frac{0.365 \, g}{0.4671 \, g} \times 100 = 78.14 \, \%$

Aqueous Solutions and Chemical Equilibria:

Classifying Solutions of Electrolytes

Strong electrolytes ionize essentially completely in a solvent.

Weak electrolytes ionize only partially.

Type of Solute	Dissociation	Particles in Solution	Conducts Electricity?	Examples
Strong electrolyte	Complete	Ions only	Yes	Ionic compounds such as NaCl, KBr, MgCl ₂ , NaNO ₃ ; NaOH, KOH; HCl, HBr, HI, HNO ₃ , HClO ₄ , H ₂ SO ₄
Weak electrolyte	Partial	Mostly molecules and a few ions	Yes, but poorly	HF, H ₂ O, NH ₃ , HC ₂ H ₃ O ₂ (acetic acid)
Nonelectrolyte	None	Molecules only	No	$\begin{array}{l} Carbon \ compounds \ such \ as \\ CH_3OH \ (methanol), \\ C_2H_5OH \ (ethanol), \\ C_{12}H_{22}O_{11} \ (sucrose), \\ CH_4N_2O \ (urea) \end{array}$

Acid-Base Equilibria

Acid-Base Equilibria in water: when an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or base. A strong electrolyte is completely dissociated, while a weak electrolyte is partially dissociated.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$ (strong acid, completely ionized)

HOAc +H₂O H₃O⁺ +OAc⁻

Thermodynamic acidity constant K

$$\mathbf{K}^{\circ} = \frac{\mathbf{a}\mathbf{H}_{3}\mathbf{O}^{+} \times \mathbf{a}\mathbf{O}\mathbf{A}\mathbf{c}^{-}}{\mathbf{a}\mathbf{H}_{2}\mathbf{O} \times \mathbf{a}\mathbf{H}\mathbf{O}\mathbf{A}\mathbf{c}}$$

In dilute solutions, the activity of water remains essentially constant, and is takenas unity at standard state:

$$K_{a}^{\circ} = \frac{aH_{3}O^{+} \times aOAc^{-}}{aHOAc}$$
$$2H_{2}O \leftrightarrow H_{3}O^{+} + OH^{-}$$

The equilibrium constant for this is:

$$\mathbf{K}_{\mathbf{w}}^{\circ} = \frac{\mathbf{a}\mathbf{H}_{3}\mathbf{O}^{+} \times \mathbf{a}\mathbf{O}\mathbf{H}^{-}}{\mathbf{a}\mathbf{H}_{2}\mathbf{O}^{2}}$$

Again, the activity of water is constant in dilute solution (its concentration is essentially constant at ~ 55.3 M), so:-

$$K_w^\circ = aH_3O^+ \times aOH^-$$

We will use H_+ in place of H_3O_+ for simplification, also, molar concentration will generally be used instead of activities and represented by square brackets [] around the species)

HCl ↔ H⁺ + Cl⁻
HOAc ↔ H⁺ + OAc⁻, K_a =
$$\frac{[H^+][OAc^-]}{HOAc}$$

H₂O ↔ H⁺ + OH⁻, K_w = [H⁺][OH⁻]
1. 0 × 10⁻¹⁴ = [H⁺][OH⁻] at 25°C
Therefore [H⁺] = [OH⁻] = 1. 0 × 10⁻⁷ M

The equilibrium constant

 $K = \frac{\text{concentrations of Products}}{\text{concentration of Reactants}}$

aA + bB ≒ cC + dD
⇒ K =
$$\frac{[C]^{\circ}[D]^{d}}{[A]^{\circ}[B]^{\circ}}$$

• Water autoionization and Kw

 $\mathrm{H}_{2}\mathrm{O}(l) + \mathrm{H}_{2}\mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{OH}^{-}(aq)$

 $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $K_W = \frac{[OH^-][H_3O^+]}{[1][1]}$

$[H_3O^+] = [OH^-]$ in pure water

In pure water at 25°C, $K_w = 1.0 \times 10^{-14}$

Therefore, $[OH^{-}] = [H_3O^{+}] = 1.0 \times 10^{-7}$

Kw is given a special name, the ion-product constant for water

Why [H₂O] Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions

In a dilute aqueous solution, the molar concentration of water is

$$[H_2O] = \frac{1000 \text{ g-H}_2\Theta}{\text{L} \text{ H}_2O} \times \frac{1 \text{ mol } \text{H}_2O}{18.0 \text{ g-H}_2\Theta} = 55.6 \text{ M}$$

Suppose we have 0.1 mol of HCl in 1 L of water. The presence of this acid will shift the equilibrium shown in Equation 9-9 to the left. Originally, however, there was only 10^{-7} mol/L OH⁻ to consume the added protons. Therefore, even if all the OH⁻ ions are converted to H₂O, the water concentration will increase to only

$$[H_2O] = 55.6 \frac{\text{mol } H_2O}{\text{L } H_2O} + 1 \times 10^{-7} \frac{\text{mol } OH^{-}}{\text{L } H_2O} \times \frac{1 \text{ mol } H_2O}{\text{mol } OH^{-}} \approx 55.6 \text{ M}$$

The percent change in water concentration is

$$\frac{10^{-7} \,\mathrm{M}}{55.6 \,\mathrm{M}} \times 100\% = 2 \times 10^{-7}\%$$

which is insignificant. Thus, $K[H_2O]^2$ in Equation 9-10 is for all practical purposes a constant, that is,

 $K(55.6)^2 = K_w = 1.00 \times 10^{-14} \text{ at } 25^{\circ}\text{C}$

Kw is given a special name, **the ion-product constant** for water

Example: A 1×10^{-3} M solution of HCl prepared what is the hydroxyl ion concentration [OH⁻].

$$\begin{split} \mathbf{K}_{\mathbf{w}} &= [\mathbf{H}^+] [\mathbf{O}\mathbf{H}^-] = \mathbf{1}.\,\mathbf{0}\times\mathbf{10^{-14}} \\ \mathbf{1}.\,\mathbf{0}\times\mathbf{10^{-3}}\times[\mathbf{O}\mathbf{H}^-] = \mathbf{1}.\,\mathbf{0}\times\mathbf{10^{-14}} \\ & [\mathbf{O}\mathbf{H}^-] = \mathbf{1}.\,\mathbf{0}\times\mathbf{10^{-11}}\ \mathbf{M} \\ & \mathbf{p}\mathbf{H} = -\log[\mathbf{H}^+]\ , \quad \mathbf{p}\mathbf{H} = \mathbf{1}-\mathbf{14} \end{split}$$

Example: Calculate the pH of a 2×10⁻³ M HCl?

$$[H^+] = 2 \times 10^{-3} \qquad pH = -\log[H^+]$$
$$= -\log(2.0 \times 10^{-3}) = 3 - \log 2.0 = 2.70$$
$$pOH = -\log[OH^-] \qquad pK_w = pH + pOH = 14$$

Example: Calculate the pOH and pH of a 5×10⁻² M NaOH?

$$\begin{array}{ll} [0H^{-}] = 5 \times 10^{-2} M & pOH = -\log[OH^{-}] \\ = -\log(5 \times 10^{-2}) = 2 - \log 5 = 2 - 0.70 = 1.30 \\ pH + pOH = 14 & pH = 14 - pOH & = 14 - 1.30 = 12.70 \end{array}$$

Example: Calculate the pH of a solution prepared by mixing 2 mL of a strong acid solution (keep track of millimoles) of pH = 3 and 3 mL of a strong base of pH = 10?

$$\begin{split} [H^+] &= 1.0 \times 10^{-3} M \quad , \quad mmol \ H^+ = M \times V \\ &= 1.0 \times 10^{-3} \times 2.0 = 2 \times 10^{-3} \ mmol \\ pOH &= 14 - pH = 14 - 10 = 4.0 [OH^-] = 1.0 \times 10^{-4} M \\ mmol \ OH^- &= M \times V = 1.0 \times 10^{-4} \times 3.0 \ mL = 3.0 \times 10^{-4} mmol \end{split}$$

There is an excess of acid:-

mmol H⁺ = 2.0 × 10⁻³ - 3.0 × 10⁻⁴ = 1.7 × 10⁻³ mmol
[H⁺] =
$$\frac{1.7 \times 10^{-3} \text{mmol}}{5\text{mL}(2+3)}$$
 = 3.4 × 10⁻⁴M
pH = -log 3.4 × 10⁻⁴ = 4 - 0.53 = 3.47

P - Functions

Scientists frequently express the concentration of a species in terms of its **p-function**, or **p-value**.

The p-value is the negative logarithm (to the base 12) of the molar concentration of that species. Thus, for the species X,

$\mathbf{p}\mathbf{X} = -\log [\mathbf{X}]$

P-values offer the advantage of allowing concentrations that vary over ten or more orders of magnitude to be expressed in terms of small positive numbers.

Properties of Logarithms

The Product Rule for Logarithms	$\log_{b}\left(MN ight) = \log_{b}\left(M ight) + \log_{b}\left(N ight)$
The Quotient Rule for Logarithms	$\log_b\left(rac{M}{N} ight) = \log_b M - \log_b N$
The Power Rule for Logarithms	$\log_b{(M^n)} = n \log_b{M}$

$$log_b 1 = 0.$$

$$log_b b = 1.$$

$$log_b b^2 = 2.$$

$$log_b b^x = x.$$

Calculate the p-value for each ion in a solution that is 2.00 \times 10 $^{-3}$ M in NaCl and 5.4 \times 10 $^{-4}$ M in HCl.

Solution

$$pH = -\log [H^+] = -\log (5.4 \times 10^{-4}) = 3.27$$

To obtain pNa, we write

$$pNa = -log[Na^+] = -log(2.00 \times 10^{-3}) = -log(2.00 \times 10^{-3}) = 2.699$$

The total Cl⁻ concentration is given by the sum of the concentrations of the two solutes:

$$[Cl^{-}] = 2.00 \times 10^{-3} \text{ M} + 5.4 \times 10^{-4} \text{ M}$$

= 2.00 × 10⁻³ M + 0.54 × 10⁻³ M = 2.54 × 10⁻³ M
pCl = -log[Cl⁻] = -log 2.54 × 10⁻³ = 2.595





The PH of a sample of human blood was measured to be 7.41 at 25°C. Calculate POH, $[H^+]$, and $[OH^-]$ for the sample.

1)
$$14 = PH + POH$$

 $14 = 7.41 + POH \implies POH = 6.59$
2) $[H+] = anti \log - PH$
 $= anti \log - 7.41 = 3.89 \times 10^{-8} M$
3) $[OH-] = anti \log - POH$
 $= anti \log - 6.59 = 2.57 \times 10^{-7} M$

• In the laboratory, we can detect acids and bases in solution in several ways. Perhaps the simplest test uses a substance called litmus. It turns red in acidic conditions and blue in basic conditions



Acid dissociation constant



$$egin{aligned} &K_a = rac{[H^+][A^-]}{[HA]} \ &-\log K_a = -\log rac{[H^+][A^-]}{[HA]} \ &-\log K_a = -\log [H^+] - \log rac{[A^-]}{[HA]} \ &pK_a = pH - \log rac{[A^-]}{[HA]} \ &pH = pK_a + \log rac{[A^-]}{[HA]} \end{aligned}$$

Base dissociation constant

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

$$egin{aligned} &K_b = rac{[OH^-][HB^+]}{[B]} \ &-\log K_b = -\log rac{[OH^-][HB^+]}{[B]} \ &-\log K_b = -\log [OH^-] - \log rac{[HB^+]}{[B]} \ &pK_b = pOH - \log rac{[HB^+]}{[B]} \ &pOH = pK_b + \log rac{[HB^+]}{[B]} \end{aligned}$$

What is
$$K_b$$
 for the equilibrium
 $CN^- + H_2O \Longrightarrow HCN + OH^-$
Solution
 K_a value of 6.2×10^{-10} for HCN. Thus,
 $K_b = \frac{K_w}{K_a} = \frac{[HCN][OH^-]}{[CN^-]}$
 $K_b = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$

Example: Calculate the p-value for each ion in a solution that is 2.0×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl

Solution
$$pH = -log [H^+] = -log (5.4 \times 10^{-4}) = 3.27$$

 $pNa = -log (2.00 \times 10^{-3}) = -log 2.00 \times 10^{-3} = 2.699$
 $[CI^-] = 2.00 \times 10^{-3} M + 5.4 \times 10^{-4} M$
 $= 2.00 \times 10^{-3} M + 0.54 \times 10^{-3} M = 2.54 \times 10^{-3} M$
 $pCl = -log 2.54 \times 10^{-3} M = 2.595$

Q36: Calculate the PH values , assuming complete ionization , of (a) 4.9×10^{-4} M monoprotic acid (b) 0.0016 M monoprotic base ?

Solve:

(a)
$$[H^+] = 4.9 \times 10^{-4}$$
 PH = $-\log [H^+] = -\log(4.9 \times 10^{-4}) = -\log 4.9 + 4 = 3.31$
(b) $K_w = [H^+] [OH^-] = 1.0 \times 10^{-14}$ [H^+] = $10^{-14} / [OH^-]$
 $[H^+] = 10^{-14} / 1.6 \times 10^{-3}$
PH = $-\log 10^{-14} / 1.6 \times 10^{-3} = -(-14 - \log 1.6 + 3) = 14 + 0.20 - 3 = 11.20$

What is a buffer solution?

A *buffer solution* is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. It has the property that the pH of the solution changes very little when a small amount of acid or base is added to it. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. **Buffers can be divided in two main groups:**

1.) *An acidic buffer solution* is simply one which has a pH less than 3. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.

2.) An alkaline buffer solution has a pH greater than 3. Alkaline buffer solutions are commonly made from a weak base and one of its salts. A frequently used example is a mixture of ammonia solution and ammonium chloride solution (NH₄OH/NH₄Cl).

Calculating the pH of Buffered Solutions

Buffers must be chosen for the appropriate pH range that they are called on to control. The pH range of a buffered solution is given by the Henderson-Hasselbalch equation. For the purpose of the derivation, we will imagine a buffer composed of an acid, HA, and its conjugate base, A⁻. We know that the acid dissociation constant pK_a of the acid is given by this expression

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

$$K_a = \frac{[H_3O^+[A^-]]}{[HA]}$$

The equation can be rearranged as follows:

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking the -lg of this expression and rearranging the terms to make each one positive gives *the Henderson-Hasselbalch equation*:

$$pH = pKa + lg \frac{[A^-]}{[HA]}$$

where A⁻denotes the salt of the corresponding acid HA In analogy to the above equations, the following equation is valid:

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

$$pH = 14 - pKB - \log \frac{[HB^+]}{[B]}$$

where HB denotes the salt of the corresponding base B^- .

A buffer problem can be simple to solve, provided not all the other chemistry you know confuses you.

For example, let's calculate the pH of a solution that is 0.1 M acetic acid and 0.1 M sodium acetate, both before and after enough 0.01 mol of HCl is dissolved $(Ka(CH_3COOH)=1.75\times10^{-5})$. Before the acid is added, we can use the Henderson-Hasselbalch equation to calculate the pH.

$$pH = pK_a + lg \frac{[A-]}{[HA]}$$

And

$$pK_a = -\lg(1.75x10^{-5}) = 5 - \lg 1.75 = 5 - 0.24 = 4.76$$

Then

$$pH = 4.76 + \lg \frac{0.1}{0.1} = 4.76$$

To calculate the pH after the acid is added, we assume that the acid reacts with the base in solution and that the reaction has a 100% yield. Then

$$pH = 4.76 + \lg \frac{0.1 - 0.01}{0.1 - 0.01} = 4.76 - \lg \frac{0.09}{0.11} = 4.76 + \lg 0.82 = 4.76 - 0.09 = 4.67$$

As it can be seen from the above calculation, if the reaction takes place without usage of buffer solution, the pH of the solution as a whole will be changed from 3 to 0 when an acid is added. If we present a buffer solution in the chemical reaction, then the change in the pH of the solution when an acid added will be only 2225 units (4236-4263)

Couple of important conclusion can made based upon the Henderson-Hasselbalch equation:

- 1. It is necessary to know the pKa and pKb of the acid or base if we want to prepare a buffer solution with certain pH. Also a suitable ration between the salt concentration and acid concentration or base concentration
- 2. Dilution of solution is equal to changes in the concentration of [HA] or [B] as well as changes in the concentration of its salt [HB] or [A⁻]. pH does not undergo any changes.

Buffer capacity:

Buffer capacity is a quantitative measure of the resistance of a buffer solution to pH change on addition of hydroxide ions. It can defined as follows.

$$\beta = \frac{\Delta C_{base}}{\Delta pH} = -\frac{\Delta C_{acid}}{\Delta pH}$$

where ΔC_{base} and ΔC_{acid} are the concentration of the strong base or strong acid and ΔpH is the resulting change in pH.

The mathematical sign minus in front of the second part of the equatation is due to the fact that adding an acid will lead to decrease in the pH-value.

Applications

Their resistance to changes in pH makes buffer solutions very useful for chemical manufacturing and essential for many biochemical processes. The ideal buffer for a particular pH has a pK_a equal (or close) to that pH, since such a solution has maximum buffer capacity.

Example :-Calculate the pH of a solution prepared by adding 25 mL of 0.1 M sodium hydroxide to 30 mL of 0.2 M acetic acid (this would actually be a step in a typical titration ?

mmol HOAc = $0.2M \times 30mL = 6.0mmol$

 $mmol NaOH = 0.1M \times 25mL = 2.5mmol$

these react as follows:-

$$HOAc + NaOH \leftrightarrow NaOAc + H_2O$$

 $\begin{array}{l}mmol \ NaOAc = 2. \ 5mmol \\mmol \ HOAc = 6. \ 0 - 2. \ 5 = 3. \ 5mmol \\\end{array} \right] \ after \ reaction$

$$pH = pK_a + log \frac{[salt]}{[acid]} = 4.76 + log \frac{2.5}{3.5} = 4.61$$

What is spectroscopy?

Originally, the study of the dispersion of visible light into its component colors (visible spectrum). Now it means the study of electromagnetic (EM) and other spectra including mass, electron and acoustic spectroscopy's.

Spectroscopy generally involves measuring the absorption of light by a sample or the emission of light by sample

Electromagnetic Spectrum		
•γray	$< 1 \text{ nm} (10^4 - 10^6 \text{ eV})$	
• X ray	$1 - 50 \text{ nm} (10^2 - 10^4 \text{ eV})$	
• far UV	10 – 200 nm	
• near UV	200 – 350 nm	
• Visible	350 – 800 nm	
• near IR	0.8 μm –	
• IR	– 2.5 µm	
• Microwave	400 μm – 30 cm	
• radio wave	100 cm and above	

UV-Visible (and IR) Spectrophotometry



UV-Visible Spectrophotometry

- Technique based on absorption of light
- Sample (analyte) is exposed to a beam of light
- Sample absorbs light...
- Instrument measures transmitted light
- Concentration of analyte is proportional to the amount of light absorbed



Beer Lambert Law

- States that absorbance of electromagnetic radiation by a given species is directly proportional to the concentration of the analyte.
- It is expressed as: $A = \varepsilon bC$
- Where A is the absorbance, ε is the molar absorptivity, b is the path length and C is the concentration of analyte.
- Because ε and b are fixed under experimental conditions, the result is a linear relationship between absorbance and concentration.





For the spectrum above, a (1.42 • 10^{-5} M) solution the aldehyde in 95% ethanol was placed in a 1 cm cuvette for measurement. Using the Beer Lambert Law formula, $\varepsilon = 36,600$ for the 395 nm peak, and 14,000 for the 255 nm peak.

Measurement of Absorbance

- Absorbance is not directly measurable
- Instead measure "transmittance", the fraction of incident radiation transmitted by the solution

$$\mathbf{T} = \mathbf{I}/\mathbf{Io}$$

Where T = transmittance, Io = Incident radiation,

- I = exiting (transmitted) radiation
- · Absorbance is:

$$\mathbf{A} = -\log \mathbf{T} = \log \left(\mathbf{Io} / \mathbf{I} \right)$$

Processes affecting T

- Reflection loss at air/cuvette interface
- Scattering losses in solution
- Absorption by analyte
- · Absorption by cuvette material
- · Absorption by interfering species

Analytical Applications

- pH determination (use of indicator dye)
- Nutrient analysis
- Organic compound analysis
- Metals analysis (complexes)
- Gas analysis (IR, e.g., CO₂)
- Pharmaceutical Industry

Applications of UV-VIS Spectrometry to Nutrient Analysis

- Applicable to natural waters or wastewater
- · High regulatory and research importance
- Analysis of N species (NO₂⁻, NO₃⁻, NH₄⁺)
- Analysis of PO₄⁻³
- Analysis of Si(OH)₄
- · Determination of Organic N and P
- Various operationally defined forms (TKN, or total N by persulfate oxidation)

Infrared spectroscopy

- measurement of IR radiation absorbed by or reflected from a sample
- absorption of IR radiation is related to the changes of vibrational or rotational energy states of molecules
- applications:
 - analysis of gaseous, liquid or solid samples
 - identification of compounds
 - quantitative analysis
- information deduced from IR spectrum:
 - functional groups of molecules, constitution of molecules
 - interaction among molecules

Instrumentation for IR spectroscopy

Main components of an instrument

- radiation source
- measuring (and reference) cell
- wavelength selector
- detector (transducer)

Types of instruments

- simple instruments with a filter
- classical instruments with a monochromator
- instruments based on an interferometer (FTIR)

Sources of IR radiation

- for NIR: tungsten lamp
- for MIR:
 - Globar = electrically heated (1100 °C) silicon carbide rod - it gives maximum intensity at $\lambda = 2 \mu m$; at lower temp. - shift of maximum to a longer wavelength (600 °C $\rightarrow \lambda_{max} = 3,5 \mu m$)
 - lasers CO₂, PbS $\lambda_{max} = 9-11 \ \mu m$