

المحاضرة الاولى

Analytical Chemistry (1) - (1st stage - 1st course)

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 - Part per million (ppm) and part per billion (ppb)
 - > The relationship between molarity, normality and part per million
 - Titer expression of concentration

□ Stoichiometric relationship

الكتاب المعتمد

• "Fundamental of Analytical Chemistry" by Doglas A. Skooge, Donald M. West and James Holler, Eighth Edition, 1988.

كتب مساعدة

- "Analytical Chemistry" by Gary D. Christian, Purnendu K. (Sandy) Dasgupta, Kevin A. Schug, 7th Edition, 2014.
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Safety and Hazard Compounds

Chemical safety is a very important subject in chemistry, academic laboratories, and even in our daily lives. It contains many aspects of scientific knowledge and technical components such as the property of chemical information, toxicity and environmental data, exposure and risk assessment, and a more detailed knowledge of the environment and human health.

The purpose of the Chemical Safety Section is to provide information useful in the recognition, evaluation, and control of workplace hazards and environmental factors existing within and/or associated with the laboratories of the University.

Chemical Safety - being secure from undergoing or causing hurt, injury, or loss when working with elements, chemical compounds, or mixtures of elements and/or compounds.

Chemical Hazards - elements, chemical compounds, or mixtures of elements and/or compounds which spoes potential risk to safety or health.

Hazardous Materials Definition

A hazardous material is defined as any material or substance which by its inherent properties or if improperly handled can be damaging to health or the environment.

Such materials cover a broad range of types which may be classified as follows:

1. Poisons or toxic agents including drugs, chemicals, and natural or synthetic products.

2. Biological materials including all laboratory specimens or materials consisting of, containing, or contaminated with blood, plasma, serum, urine, feces, or other human or animal tissues or fluids.

3. Corrosive chemicals, such as sodium hydroxide or sulfuric acid.

4. Flammable materials including (a) organic solvents, (b) finely divided metals or powders and (c) chemicals that either evolve or absorb oxygen during storage.

5. Explosives and strong oxidizing agents such as peroxides and nitrates.

6. Materials in which dangerous heat buildup occurs on storage.

Know the Hazards

- 1) Understand the hazardous properties of the chemicals involved
- 2) Understand the reaction and the products during chemicals in use

- 3) May the process generate heat and/or gases?
- 4) Is there any side reaction involved? What are the side products?
- 5) Are the products dangerous substances? What are the hazardous properties?
- 6) Understand the effect of the environment to the reaction, the reactants and the products

7) May light, heat and shape of the container affect the reaction so that it will be out of control?

8) May light, heat, air and water affect the reactants and the products so that other reactions will occur?

Chemical Safety Guidelines

Always follow these guidelines when working with chemicals:

- 1. Assume that any unfamiliar chemical is hazardous and treat it as such.
- 2. Know all the hazards of the chemicals with which you work.
- 3. Never underestimate the potential hazard of any chemical or combination of chemicals.
- 4. Date all chemicals when they are received and again when they are opened.
- 5. Follow all chemical safety instructions.
- 6. Minimize your exposure to any chemical, regardless of its hazard rating, and avoid repeated exposure.
- 7. Use Personal Protective Equipment (PPE), as appropriate for that chemical.
- 8. Use the buddy system when working with hazardous chemicals.
- 9. Don't work in the laboratory alone.

The scope of analytical chemistry

The science seeks ever-improved means of measuring the chemical composition of natural and artificial materials by using techniques to identify the substances that may be present in a material and to determine the exact amounts of the identified substance.

Analytical chemistry involves the analysis of matter to determine its composition and the quantity of each kind of matter that is present. Analytical chemists detect traces of toxic chemicals in water and air. A detection of the component in qualitative analysis can be the basis of the method or the procedure of its quantitative analysis.

The reaction may be incomplete in qualitative analysis, while in quantitative analysis the

reaction should be complete and give clear and known products

Analytical chemistry consists of:

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

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

(1) Volumetric analysis (Titrimetric analysis): is measured the volume of a solution containing sufficient reagent to react completely with the analyte.

(2) Gravimetric analysis: Gravimetric methods, determine the mass of the analyte or some compound chemically related to it.

(3) Instrumental analysis: These methods are based on the measurement of physical or chemical properties using special instruments. These properties are related to the concentrations or amounts of the components in the sample. These methods are compared directly or indirectly with typical standard methods.

These methods consists of:

- a) **Spectroscopic methods**: are based on measurement of the interaction between electromagnetic radiation and analyte atoms or molecules or on the production of such radiation by analytes (ultraviolet, visible, or infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy (absorption, fluorescence).
- b) **Electroanalytical methods**: involve the measurement of such electrical properties that wanted to be determined, such as pH measurements, electrodeposition, voltametry, thermal analysis, potential, current, resistance, and quantity of electrical charge.
- c) **Separation methods:** They mean the isolation of one component or more from a mixture of components in solid, liquid and gas cases. These methods are included with instrumental methods since the instruments and equipments are used in separation processes. These methods involve precipitation, volatilization, ion exchange, extraction with solvent and various chromatographic methods.

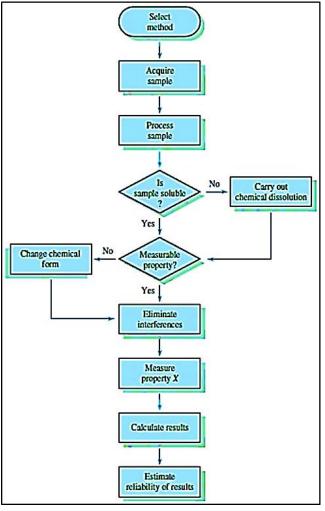


Atypical quantitative analysis in volves the sequence of steps show in the flowing:

- 1) Choosing a method
- 2) Acquiring the sample
- 3) Processing the sample
- 4) Eliminating interferences
- 5) Calibrating and measuring concentration
- 6) Calculating results
- 7) Evaluating results by estimating their reliability.

Example: Find the cause of deers death. They suggested of the death by arsine in the grass.

- **1.** *Selecting a method:* Distillation of arsenic as arsine, which is then determined by colorimetric measurement.
- Acquiring the sample: obtains representative. The kidneys were removed for analysis. Preparing laboratory sample. Each kidney was cut into pieces and homogenized in a high speed blender.
- **3.** *Processing the sample:* Defining replicate sample. Three (10 g) samples of the homogenized tissue from each deer were placed in porcelain crucibles.
- **4.** *Doing chemistry:* Dissolving samples to obtain an aqueous solution of the analyte for analysis. Burning the samples to convert organic matrix to CO_2 and H_2O , until the sample stopped smoking (555 °C) for two hours, the (As) convert to As_2O_5 which dissolved in dilute HCl to form H_3AsO_4 .
- 5. *Eliminating interferences:* separate arsenic earn from other substances that might interfere in the analysis by converting it to arsine. AsH_3 a toxic, colorless gas that is evolved when a solution of H_3AsO_4 is treated with zinc.



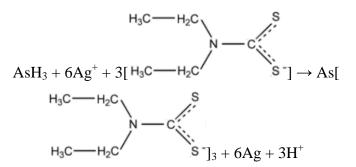
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The solutions resulting from the deer and grass samples were combined with Sn^{+2} and a small amount of iodide ion. Was added to catalyze the reduction of H_3AsO_4 to H_3AsO_3

$$H_3AsO_4 + SnCl_2 + 2HCl \rightarrow H_3AsO_3 + SnCl_4 + H_2O$$

$$H_3AsO_3 + 3Zn + 6HCl \rightarrow AsH_{3(g)} + 3ZnCl_2 + 3H_2O$$

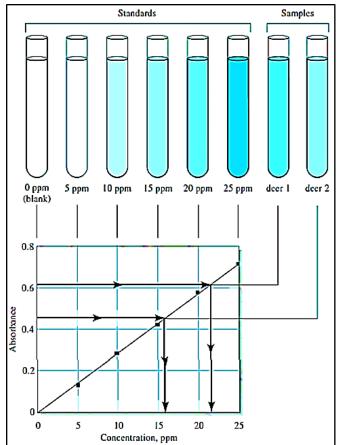
 $A_{s}H_{3(g)}$ can be collected in the absorber solution then silver diethyldithiocarbamate was added to form a colored complex compound according to the following equation:



6. *Measuring the amount of the Analyte:* The amount of arsenic in each sample was determined by using an instrument called a spectrophotometer to measure the intensity of color formed in the cell.

Calibration curve to determine the concentration of Arsenic

7. Calculating the concentration: 16 ppm,
22 ppm from calibration curve. Arsenic in the kidney of an animal is toxic at levels above about 10 ppm.



المحاضرة الثانية

Some Basic Concepts Solutions

A solution is a mixture of one solute or more with a solvent or mixture of solvents. The solute particle (ions, atoms, molecules) is always the little amount and the solvent should be in large amount. When water is the solvent, the solutions are called aqueous solutions like the solutions of sodium chloride, sugar, hydrochloric acid and solution is called-non-aqueous solution like the solution of Sulphur in carbon disulphide (CS_2).

The solute may be a solid, liquid and gas materials. Solids in liquids and liquids in liquids solutions are the most solution considered in this study.

Solute (lesser amount) + Solvent (larger amount) \rightarrow Solution

 $NaCl_{(s)} + H_2O_{(l)} \rightarrow Salt Solution$

Concentrated Solution has a large amount of solute, **Dilute Solution** has a small amount of solute.

Solute	Solvent			
Solute	Gas	Liquid	Solid	
Gas	$O_2(g)$ in $N_2(g)$, Air	CO ₂ (g) in H ₂ O(l), Soda	H ₂ (g) in Pd(s), H ₂ catalyst	
Liquid	Perfume	Alcohol(l) in H ₂ O(l)	Hg(l) in Ag(s), Dental filling	
Solid	Dust air, Smoke industry	NaCl(s) in H ₂ O(l), salt water, saline sol	Zn(s) in Cu(s), Brass alloy	

Classification of solution

A- 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. examples are solutions of dust in water or powdered chalk in water.

(3) Colloidal solution: homogeneous mixture, which does not settle nor are their components filterable, solute particle visible with electron microscope. Examples are milk gelatin and Arabic gum.

B- based on the amount of solute in solvent:

(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. This means that the solvent can

get extra amount of solute. Such as the solubility of 5 grams of NaCl in 100 mL of water at definite temperature.

(2) Saturated solutions: is one in which no more solute can dissolve in a given amount of solvent at a given temperature, or if the amount of solute equal to capacity of solvent. Any extra addition of the solute will settle in the bottom of the container at certain temperature. Such as sufficient amount of Na_2CO_3 in 100 mL of water.

(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. If the temperature is lowered, some amount of the solute will be separated and settled in the bottom of container.

The three types of these solutions can be distinguished by adding a crystals of the solute to these solutions:

- 1. If it dissolves, the solution is unsaturated.
- 2. If it settles, the solution is saturated.
- 3. If it grows and its size becomes larger, the solution is supersaturated.

Electrolytes and non-electrolytes

Electrolytes are solutes which ionize in a solvent to produce an electrically conducting medium. Most of the solutes are electrolytes, which form ions when dissolved in water or certain other solvents and thus produce solutions that conduct electricity.

Strong electrolytes: are completely ionized in the solvent like HNO₃, HCl, NaOH, KOH, and most salts.

Weak electrolytes: are partially ionized in the solvents like H_2CO_3 , H_3BO_3 , NHO, halides, cyanides and thiocyanates of Hg, Zn and Cd. this means that a solution at a weak electrolyte will not conduct electricity as well as a solution containing an equal concentration of a strong electrolyte.

Non-electrolytes: are solutes which do not ionize in their solvent, and therefore, tile solution does not conduct electricity. Examples are solutions of sugar, urea and ethanol in water.

Table shows various solutes that act as strong and weak electrolytes in water. H_2SO_4 is completely dissociated into HSO_4^- and H_3O^+ ions and for this reason is classified as a strong electrolyte. HSO_4^- ion is a weak electrolyte, being partially dissociated into SO_4^{-2} and H_3O^+ .



Strong electrolytes	Weak electrolytes
1. Inorganic acid such as HNO ₃ , HClO ₄ , H ₂ SO ₄ ,	1. Many inorganic acids, including H ₂ CO ₃ , H ₃ BO ₃ , H ₂ S,
HCl, HI, HBr, HClO ₃ , HBrO ₃	H_2SO_3 .
2. Alkali and Alkali-earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases.
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd.

المحاضرة الثالثة

Acid-base theories

1) Arrhenius Theory $(H^+ and OH^-)$

Acid: any substance that ionizes (partially or completely) in water to give hydrogen ion (which associate with the solvent to give hydronium ion H_3O^+):

$$\mathrm{HA} + \mathrm{H_2O} \leftrightarrow \mathrm{H_3O^+} + \mathrm{A^-}$$

Base: any substance that ionizes in water to give hydroxyl ions. Weak (partially ionized) to generally ionize as follows:-

$$B + H_2 O \leftrightarrow BH^+ + OH^-$$

While strong bases such as metal hydroxides (Example NaOH) dissociate as

$$M(OH)_n \leftrightarrow M^{n+} + nOH^{-}$$

This theory is obviously restricted to water as the solvent.

2) 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:

 $Acid = H^+ + Base$

The acid and base of half reaction are called conjugate pairs. Free protons do not exist in solution and there must be a proton acceptor (base) before a proton donor (acid) will release its proton.

3) Lewis Theory (taking and giving electrons)

Acid: is an electron-pair accepter.

Base: is an electron-pair donor. The latter frequently contains oxygen or nitrogen as the electron donor. Thus, non-hydrogen containing substances are included as acids.

AlCl₃+:0
$$\langle {}^{R}_{R} \longrightarrow Cl_{3}Al:0 \langle {}^{R}_{R}$$

H₂O + H⁺ \leftrightarrow H₂O: H⁺ (H₃O⁺)
HO:⁻+ H⁺ \leftrightarrow H: OH

Lewis concepts of acids and bases go further toward freeing acid-base behavior from involvement of protons and largely increase the number of processes that can be considered as acid-base reactions as well.

Salts

Any compound that produce from reaction of acid with base, some of the salts are anhydrous materials like NaCl, KCl, KMnO₄ and K₂CO₇. Other salts are hydrous such as CaCl₂.2H₂O, CuSO₄.5H₂O, Na₂B₄O₇.10H₂O. X-rays show that the salts are ionized in its solid state. Therefore, sodium chloride is ionized in its crystalline case into Na⁺, which is surrounded by six ions of Cl⁻, and Cl⁻ which is surrounded by six ions of Na⁺ these ions are attached to each other by electrostatic strengths. Thus, these salts are completely ionized in solvent of high dielectric constant like water.

Dissociation of 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)

 $HOAc + H_2O \leftrightarrow H_3O^+ + OAc^-$ (weak acid, partially ionized, a few percent)

Pure water ionizes slightly, or undergoes autoprotolysis (self-ionization of solvent to give a cation and anion):

Aqueous solution contain small concentrations of hydronium and hydroxide ions as a consequence of the dissociation reaction

$$2H_20 \leftrightarrow H_30^+ + 0H^-$$

The equilibrium constant for this is:



$$\mathrm{Kw} = \frac{\mathrm{aH}_3\mathrm{O}^+ \times \mathrm{aOH}^-}{\mathrm{aH}_2\mathrm{O}^2}$$

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

$$Kw = aH_3O^+ \times aOH^-$$

Kw, thermodynamic outoprotolysis or self – ionization, constant)

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).

$$K(H_2O)^2 = Kw = [H_3O^+][OH^-]$$

Where the new constant Kw is given a special name , the ion-product constant for water . - $\log Kw = -\log [H_3O^+] - \log[OH^-]$

- pKw = pH + pOH
- 14 = pH + pOH at 25 °C

$$H_20 \leftrightarrow H^+ + 0H^-$$

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

 $1 \times 10^{-14} = [H^+][OH^-]$ at 25 °C

Because OH⁻ and H₃O⁺ are formed only from the dissociation of water, their concentrations must be equal $[H_3O^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$

The concentration of water in dilute solutions is enormous, however when compared with the concentration of H_3O^+ , OH^- ions , so can be taken as constant.

p – Function

p – Function or p – Value is the negative logarithm of the molar concentration of that species, thus for the species X.

 $-\log [X] = pX$

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

Example: Calculate the p – Value for each ion in a solution that is 2×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

Solution: $pH = -log[H^+] = -log(5.4 \times 10^{-4}) = 3.27$ To obtain pNa , We write

$$pNa = -log (2 \times 10^{-3}) = -log 2 \times 10^{-3} = 2.699$$



The total Cl⁻ concentration is given by the sum of the concentration of the tow Solutes.

$$\begin{bmatrix} Cl^{-} \end{bmatrix} = 2 \times 10^{-3} \text{ M} + 5.4 \times 10^{-4} \text{ M}$$
$$= 2.54 \times 10^{-3} \text{ M}$$
$$= -\log 2.54 \times 10^{-3} = 2.595$$

Example: Calculate the molar concentration of Ag^+ in a Solution that has a pAg of 6.372?

Solution:

$$pAg = -log \left[Ag^{+} \right] = 6.372$$
$$log \left[Ag^{+} \right] = -6.372$$

Example:

 $[Ag^+] = 4.246 \times 10^{-7} M$ the hydronium and hydroxide Calculate ion concentration and the pH and pOH of 0.20 M aqueous NaOH at 25 °C.

Solution: Sodium hydroxide is a strong electrolyte, the OH⁻ and H_3O^+ ions are formed in equal amounts form dissociation of water . Therefore we write $[OH^-] = 0.2$

> $pOH = -\log 0.2 = 0.699$ $[H_3O^+] = Kw/[OH^-] = 1 \times 10^{-14}/0.2 = 5 \times 10^{-14} M$ $pH = -log[5 \times 10^{-14}] = 13.301$

Example: A 1×10^{-3} M solution of HCl prepared. What is the hydroxyl ion concentration?

<u>Solution:</u> $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ $1 \times 10^{-3} \times [OH^{-}] = 1 \times 10^{-14}$ $[OH^{-}] = 1 \times 10^{-11} M$

The pH scale: the concentration of OH^- or H^+ in aqueous solution can vary over extremely wide ranges, form 1M or greater to 10⁻¹⁴ M

 $pH = -\log[H^+]$ & pH = 1 - 14

Example: Calculate the pH of a 2×10^{-3} M HCl?

Solution:
$$[H^+] = 2 \times 10^{-3}$$

 $pH = -\log[H^+] = -\log(2 \times 10^{-3}) = 3 - \log 2 = 2.70$
Example: Calculate the pOH of a 5×10^{-2} M NaOH?
Solution: $[OH^-] = 5 \times 10^{-2}$ 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

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?

Solution:
$$[H^+] = 1 \times 10^{-3} M$$

mmol H⁺ = M × V = 1 × 10⁻³ × 2 = 2 × 10⁻³ mmol pOH = 14 - pH = 14 - 10 = 4 $[OH^{-}] = 1 \times 10^{-4} M$

mmol $OH^- = M \times V = 1 \times 10^{-4} \times 3 \text{ mL} = 3 \times 10^{-4} \text{ mmol}$

There is an excess of acid:-

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

Example: The pH of a solution is 9.67. Calculate the hydrogen ion conc. in the solution? **Solution:** $pH = -\log[H^+] & [H^+] = 10^{-pH}$ $[H^+] = 10^{-9.67}$ $[H^+] = 10^{-10} \times 10^{0.33} = 2.1 \times 10^{-10} M$

المحاضرة الرابعة

Stoichiometric Calculations

• Gram atomic weight (g. Aw sometime <u>A. w</u>): 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 12 g of carbon 12 (this is Avogadro's number = 6.022×10^{23} atoms).

• Gram molecular weight (g. Mw sometime <u>M. w</u>): Defined as the sum of the atomic weight of the atoms that make up a molecular compound.

The gram molecular weight is employed in stead of gram formula weight when the real chemical species is concerned. Therefore the gram molecular weight of H_2 is its gram formula

weight (2.016 g), while NaCl in water, it should be assigned as gram ionic weight of Na⁺ (23 g) and gram ionic weight of Cl⁻ (35.45 g).

One molecular weight of a species contains 6.023×10^{23} particles of that species. This quantity refers to the mole of the species.

• Gram formula weight (g. Fw sometime $\underline{F. w}$): The summation of the atomic weight in grams 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. Example strong electrolytes-acids, bases, salts). Sometimes use the term molar mass (Molecular weight, M. w) in place of gram formula weight, g. Fw).

The formula weight may equal the empirical formula such as chemical formula of H_2 . On other hand, the chemical formula may or may not actually exist.

For example NaCl is not found as NaCl in its solid state or in aqueous solution and it is existed as sodium ions (Na⁺) and chloride ions (Cl⁻). However, the formula as NaCl is convenient for stoiciometric accounting.

Empirical formula: is the simplest combination of atoms in a substance.

Molecular formula: is actual expression of the structure of the substance or compound.

<u>Example</u>: Calculate the number of grams in one mole of $CaSO_4.7H_2O$ (calculate gram molecular or formula weight).

<u>Solution</u>: One mole is the formula weight expressed in grams. The formula weight is (Ca=40.08; S=32.06; O=16; H=1.01)

 $CaSO_4.7H_2O = 40.08 + 32.06 + (16 \times 4) + 7[(2 \times 1.01) + 16] = 262.25 \text{ g/mol}$ For glucose $C_6H_{12}O_6 = 6 \text{ mol } C + 12 \text{ mol } H + 6 \text{ mol } O = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180 \text{ g/mol}$ **Chemical Formulas:** The Simplest or empirical formula of a compound gives the simplest whole number ratio between the numbers of atoms of the different elements.

Example: is the simplest formula of water H_2O , which 2:1 tells us that. There are twice an many hydrogen atoms as oxygen atoms.

Example: The simplest formula for potassium chlorate is $KClO_3$ and the atoms ratio are 1:1:3. **Simplest Formulas from analysis:** In order to determine the simplest formula of a Compound. We must establish by chemical analysis the proportions by mass of the elements making up the compound as shown:

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Example: are determined by burning a sample weighting 2 mg , the masses of CO_2 and H_2O formed are 3 mg and 0.816 mg respectively. What are the percentages of C , H and O?

Solution:

The mass of Carbon in 3.0 mg of CO_2 is

milligrams C = 3.0 mg CO₂ × $\frac{12.0 \text{ g C}}{44 \text{ g CO}_2}$ = 0.818 mg C milligrams H= 0.816 mg H₂O × $\frac{2.02 \text{ g H}}{18 \text{ g H}_2\text{O}}$ = 0.0916 mg H The Sample weight 2.0 mg , We have

$$%C = \frac{0.818}{2.0} \times 100 = 40.9\%$$

%H = $\frac{0.0916}{2.0} \times 100 = 4.58\%$

We obtain the percentage of Oxygen by difference = % O = 100 - (40.9 + 4.6) = 54.5%From these date,

determine the empirical formula . We need know the relative numbers of atoms of C, H and O. In 100 g we have 40.9 g of C, 4.58 g of H and 54.5 g of O.

Converting to numbers of gram atomic masses (GAM) we obtain for C, H and O.

$$40.9 \text{ g C} \times \frac{1 \text{ GAM C}}{12. \text{ g C}} = 3.41 \text{ GAM}$$

$$4.58 \text{ g H} \times \frac{1 \text{ GAM C}}{1.01 \text{ g H}} = 4.53 \text{ GAM}$$

$$54.5 \text{ g O} \times \frac{1 \text{ GAM C}}{16.0 \text{ g O}} = 3.41 \text{ GAM}$$

The number of atoms of C, H and O in Vitamin C are in the ratio 3.41 : 4.53 : 3.41.

To deduce the Simplest formula, we need to know the simplest whole numbers, to obtain this, we divide each number by the smallest, 3.41.

$$C = \frac{3.41}{3.41} = 1.0$$
, $H = \frac{4.53}{3.41} = 1.33$, $O = \frac{3.41}{3.41} = 1.0$

We have for every C atom 3, 4 H atoms and 3 oxygen atom, we have 3C: 4H: 3O so the simplest formula is $C_3H_4O_3$

Example: A sample of calcium Chloride weighting 1.641 g is dissolved in water and treated with Ag^+ . A Precipitae of AgCl 4.238 g forms. Determine the Percentage Composition and the simplest formula of calcium Chloride .



 Solution:
 The mass of Chlorine in the AgCl is

 grams Cl = 4.238 g AgCl × $\frac{35.45}{143.32 \text{ g AgCl}}$ = 1.048 g Cl

 % Cl = $\frac{1 \text{ GAM}}{143.32 \text{ g AgCl}}$ × 100 = $\frac{1.048}{1.641}$ × 100 = 63.86

 % Ca = 100 - 63.86 = 36.14

 36.14 Ca × $\frac{1 \text{ GAM Ca}}{40.08 \text{ Ca}}$ = 0.902 GAM Ca

 63.86 g Cl × $\frac{1 \text{ GAM}}{35.45 \text{ g Cl}}$ = 1.80 GAM Cl

1.80 / 0.902 = 2, so the simplest formala is CaCl₂

Mole Concept

A mole of a chemical species 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

1. Avogadro's number of items

One mole of Fe atoms = 6.02×10^{23} Fe atoms One mole of CO₂ molecules = 6.02×10^{23} CO₂ molecules One mole of Cl⁻ ions = 6.02×10^{23} Cl⁻ ions

One mole of C - C bonds = 6.02×10^{23} C - C bonds

2. One Gram Formula Mass of a Substance (GFM)

One GFM Fe = 6.02×10^{23} atoms Fe = 55.85 g Fe = 1 mole Fe One GFM CO₂ = 6.02×10^{23} moleculer CO₂ = 44.01 g CO₂ = 1 mole CO₂ One mol SnO₂ = 1 GFM SnO₂ = 118.69 g + 2 (16.0 g) = 150.69 g SnO₂ One mole Fe = 1 GFM Fe = 55.85 g Fe One mole CO₂ = 1 GFM CO₂ =12.01 g + (2×16) = 44.01 g CO₂ One mole NaCl = 1 GFM NaCl = 22.99 g + 35.45 = 58.44 g NaCl A mole is the amounts of molecular compounds, free elements and ions.

One mole of	H_2O	Contains	18.01 g
One mole of	Na_2SO_4	Contains	142.04 g
One mole of	Na^+	Contains	23 g
One mole of	Cl_2	Contains	70.90 g
One mole of	Cl^{-}	Contains	35.45 g

The number of moles are calculated of grams divided by formula weight of the species.

$Mole = \frac{weight (g)}{(g)}$			
$Mole = \frac{0}{\text{formula weig}}$	ht $\left(\frac{g}{mol}\right)$ '		
mmole = weight	z (mg)		
$mmole = \frac{weight}{formula weight}$	ght (<u>mg</u>)		
Moles of urea =	grams		
	60.06		
Moles of $SO_4^{2-}=$	grams		
	96.06		
Moles of $Ag^+ =$	grams		
C	107.87		

Where formula weight represents the atomic or molecular weight of the substance. The molar mass (M) of substance is the mass in grams of 1 Mole of that substance.

The millimole (mmol) is 1/1000 of a moler 1/1000 of the molar mass.

 $1 \text{ mmol} = 10^{-3} \text{ mol}$

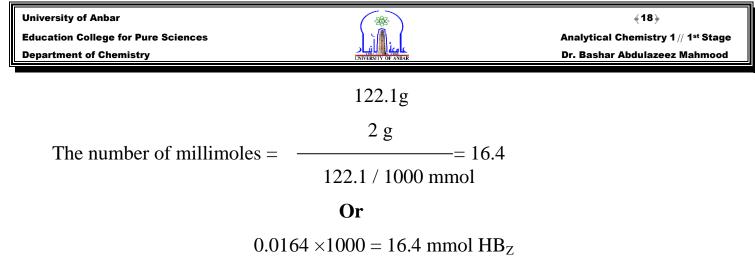
Example: How many moles and millimoles of benzoic acid (M w.=122.1 g/mol) are contained in 2 g of the pure acid?

Solution:

1 mole of HB_Z has a mass of 122.1 g

$$Mole = \frac{\text{weight (g)}}{\text{formula weight (}\frac{g}{\text{mol}}\text{)}}$$

 $= 0.0164 \text{ mol HB}_Z$



<u>Example</u>: One mole of the over of Copper is malachite a bright green mineral which has the Simplest formula $Cu_2CO_5H_2$.

a – What is the percentage of Copper in malachite?

b – How much Copper can be obtained from 340 g of malachite ?

5	olution:	a - In One mole of malachite	there are
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2 GAM Cu = 2 (63.55 g) = 127.1 g 1 GAM C = 12.0 g 5 GAM O = 5 (16.0 g) = 80.0 g 2 GAM H = 2 (1.008 g) = 2.016 g 221.13 g % Cu = $\frac{127.1 \text{ g}}{221.13 \text{ g}} \times 100 = 57.48 \%$ **b** - Mass Cu = 340 g × $\frac{57.48}{100} = 195 \text{ g}$

Example: Calculate the number of moles in 500 mg Na₂WO₄.

<u>Solution</u>: mmole = $\frac{w (mg)}{M.w \left(\frac{mg}{mmol}\right)}$ = $\frac{500 (mg)}{293.8 \left(\frac{mg}{mmol}\right)}$ = 1.706 mmol Mole = $\frac{mmol}{1000}$ = $\frac{1.706}{1000}$ = 0.00170 mol

Example: How many molecules are contained in 25 g H_2 ?

<u>Solution:</u> moles $H2 = \frac{W(g)}{FW}$



$$=\frac{25 \text{ g}}{2.016 \frac{\text{g}}{\text{mol}}} = 12.40 \text{ mol}$$

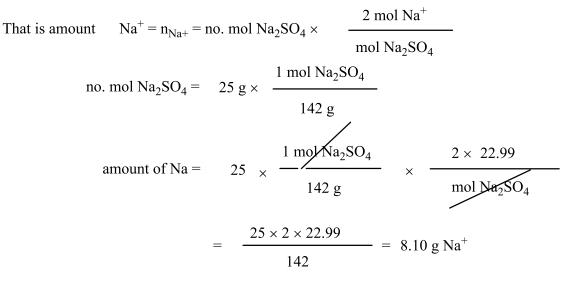
№ molecules = № moles × Avogadro number = $12.40 \times 6.022 \times 10^{23} = 7.74 \times 10^{24}$ molecule **Example:** How many milligrams are in 0.250 mmole Fe₂O₃ (ferric oxide).

Solution: w (mg) = mmole × M. w
$$\left(\frac{\text{mg}}{\text{mmol}}\right)$$

= 0.250 mmole × 159.7 $\frac{\text{mg}}{\text{mmol}}$ = 39.9 mg

Example: How many of Na^+ (22.99) g/mol are contained in 25 g of Na_2SO_4 (142 g/mol)?

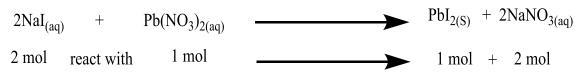
Solution:



The Chemical formula tells us that 1mol of Na₂SO₄ Contains 2 mol of Na⁺.

المحاضرة الخامسة

Stoichiometric relationship



Example: (a) What mass of AgNO₃ (169.9 g/mol) in needed to convert of 2.33 g Na₂CO₃ (106 g/mol) to Ag₂CO₃?

(b) What mass of Ag_2CO_3 (275.7 g/mol) will be formed?

Solution:

(a) $1Na_2CO_{3(aq)} + 2AgNO_{3(aq)} \longrightarrow Ag_2CO_{3(S)} + 2NaNO_3(aq)$

Step - 1: no. mol $Na_2CO_3 = 2.33 / 106 = 0.02198$ mol

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Step -2 : the balanced equation reveals that: no. mol AgNO₃ = $0.02198 \times 2 = 0.04396$ mol Here the stoichoiometric factor is (2 mol) (AgNO₃) / (1 mol Na₂CO₃) Step - 3 : mass (weight) = 0.04396×169.9 AgNO₃ = 7.47 g AgNO₃

(**b**) no. mol $Ag_2CO_3 =$ no. mol Na_2CO_3 = 0.02198 mol

mass
$$Ag_2CO_3 = 0.02198 \times 275.7 = 6.06 \text{ g}$$

Example: what mass of Ag_2CO_3 (275.7 g/mol) is formed when 25 mL of 0.2 M AgNO₃ are mixed with 50 mL of 0.08 M Na₂CO₃?

Solution: amount AgNO₃ = $\frac{25}{100} \times 0.2 = 5 \times 10^{-3} \text{ mol}$ no. mol Na₂CO₃ = $\frac{50}{1000} \times 0.08 = 4 \times 10^{-3} \text{ mol}$ $2 \times 4 \times 10^{-3} = 8 \times 10^{-3} \text{ mol AgNO}_3$ mass Ag₂CO₃ = $5 \times 10^{-3} \times \frac{1}{2} \times 275.7 = 0.689 \text{ g Ag}_2\text{CO}_3$

<u>H.W:</u> 1: Find the number of Na^+ ions in 2.92 g of Na_3PO_4 ?

2: Find the number of K^+ ions in 3.41 mol of K_2HPO_4 ?

- 3: Find the amount of the indicated element (in moles) in:
 - (a) 8.75 g of <u>B</u>₂O₃.
 - (b) 167.2 mg of $Na_2B_4O_7$. 10H₂O.
 - (c) 4.96 g of Mn_3O_4 .
 - (d) 333 mg of $Ca\underline{C_2}O_{4}$.

4: Find the amount in millimoles of the indicated species in:

- (a) 850 mg of P_2O_5 .
- (b) 40 g of <u>C</u>O₂.
- (c) 12.92 g of NaHCO₃.
- (d) 57 mg of $\underline{Mg}NH_4PO_4$

5: a – Determine the mass in grams of 2.6 mol of backing Soda, NaHCO₃ b – How many moles of penicillin $C_{16}H_{18}O_4N_2S$ are there in 218 g?

المحاضرة السادسة

Methods of expressing concentration of solutions

(1) Molarity concentration (M)

A: - Solutions prepared from dissolving solid solute in liquid solvent:-

Defined is the number of moles of that species in 1L of solution. The unit of molar concentration is molarity M, which has dimensions of mol/L.

$$\begin{aligned} \text{Molarity } (\text{M}) &= \frac{N \text{e} \text{ mole of solute}}{\text{volume of solution } (\text{L})} = \frac{\text{mol}}{\text{L}} \\ \text{Molarity } (\text{M}) &= \frac{N \text{e} \text{ mmole of solute}}{\text{volume of solution } (\text{mL})} = \frac{\text{mmol}}{\text{mL}} \\ \text{M} &= \frac{N \text{e} \text{ mole of solute}}{\text{Volume of solute}} = \frac{\frac{\text{W}(\text{g})}{\text{M}.\text{ w}(\frac{\text{g}}{\text{mol}})}}{\frac{\text{V}(\text{mL})}{1000(\frac{\text{mL}}{\text{L}})}} = \frac{\text{w}(\text{g})}{\text{M}.\text{ w}(\frac{\text{g}}{\text{mol}})} \times \frac{1000(\frac{\text{mL}}{\text{L}})}{\text{V}(\text{mL})} \end{aligned}$$

Example: A solution is prepared by dissolving 1.26 g 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:
$$M = \frac{w(g)}{M.w(\frac{g}{(mol)})} \times \frac{1000(\frac{mL}{L})}{V(mL)} = \frac{1.26(g)}{169.9(\frac{g}{(mol)})} \times \frac{1000(\frac{mL}{L})}{250(mL)} = 0.0297 \text{ mol/L}$$

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

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

Solution:
$$M = \frac{w(g)}{M.w(\frac{g}{mol})} \times \frac{1000}{V(mL)}$$

 $0.250 M = \frac{w(g)}{58.4(\frac{g}{mol})} \times \frac{1000}{1(mL)}$
 $w(g) = 0.0146 \frac{g}{mL}$

Example: How many grams Na₂SO₄ should be weight out to prepare 500 mL of a 0.100 M

Solution:
$$M = \frac{w(g)}{M.w(\frac{g}{mol})} \times \frac{1000(\frac{mL}{L})}{V(mL)}$$

$$0.10 \text{ mol/L} = \frac{w(g)}{142 (\frac{g}{\text{mol}})} \times \frac{1000 (\frac{\text{mL}}{\text{L}})}{500 (\text{mL})}$$
$$w(g) = \frac{0.10 (\frac{\text{mol}}{\text{L}}) \times 142 (\frac{g}{\text{mol}})}{2 (\frac{\text{mL}}{\text{L}})} = 7.1 \text{ g}$$

Example: Calculate the concentration of potassium ion in grams per litter after mixing 100 mL of 0.250 M KCl and 200 mL of 0.100 M K₂SO₄.

 $\underbrace{Solution:} \mod (K^+) = \mod (KCl) + 2 \times \mod (K_2SO_4) \\ = V (mL) \times M \left(\frac{mmol}{mL}\right) + 2 \left[V (mL) \times M \left(\frac{mmol}{mL}\right)\right] \\ = 100 (mL) \times 0.250 \left(\frac{mmol}{mL}\right) + 2 \left[200 (mL) \times 0.1 \left(\frac{mmol}{mL}\right)\right] \\ = 25 \mod + 2 \left[20 \mod \right] = 25 \mod + 40 \mod = 65 \mod in 300 \ mL \\ \min e = \frac{w (mg)}{M.w \left(\frac{mg}{mmol}\right)} \& w = 65 \pmod{x} \times 39.1 \left(\frac{mg}{mmol}\right) \\ = \frac{2541.5 (mg)}{1000 \left(\frac{mg}{\sigma}\right)} = 2.541 \ g \ in \ 300 \ mL = \frac{2.541 \ (g) \times 1000 \ (\frac{mL}{L})}{300 \ (mL)} = 8.47 \ (\frac{g}{L})$

Example: Describe the preparation of 500 mL of 0.0740 M Cl⁻ solution from solid BaCl₂.2H₂O (244.3 g/mol).

Solution:
$$M = \frac{W(g)}{M.w} \times \frac{1000}{V ml}$$

 $0.074 = \frac{g}{244.3} \times \frac{1000}{500} = 4.52 g$

4.52 g of BaCl₂.2H₂O dissolve in water and dilute to 500 mL.

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

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^2$$
$$\frac{0.01}{2} \qquad 0.01$$



 $M_{Na_{2}CO_{3}} = \frac{w}{M.w} \times \frac{1000}{V(mL)}$ $0.005 = \frac{w}{106} \times \frac{1000}{500}$ $2 \times w = 0.005 \times 106$ $w = \frac{0.005 \times 106}{2} = 0.265 \text{ g } \text{Na}_{2}\text{CO}_{3}$

<u>H.W:</u>-

(1) How many grams of K_2SO_4 are contained in 50 mL of 0.200 M?

(2) How many millimoles of K_2SO_4 are present?

(3) Calculate the molar concentration (Molarity M) of ethanol in solution that contains 2.3 g of C_2H_5OH (46.07 g/mol) in 3.5 L of solution?

B: - Solution prepared from dissolved liquid solute in liquid solvent:-

Density: is the weight per unit volume at the specified temperature, usually (g/mL) or (g/cm^3) in 20 °C (is the ratio of the mass in (g) and volume (mL).

Specific gravity (sp. gr.): defined as 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).

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

Example: Calculate the molarity of 28% NH₃, specific gravity 0.898.

Solution:
$$M. \le NH_3 = 14 + (3 \times 1) = 17$$

$$M = \frac{\% \times \text{sp.gr. (density)} \times 1000}{M.w}$$
$$M = \frac{\frac{28}{100} \times 0.898 \times 1000}{17} = 16.470 \frac{\text{mol}}{\text{L}} = 16.470 \frac{\text{mmol}}{\text{mL}} = 16.470 \text{ M}$$

Example: How many millilitres of concentrated sulphuric acid, 94% (g/100 g solution), density 1.831 g/cm^3 , are required to prepare 1 litter of a 0.100 M solution.

Solution:
$$M = \frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} = 17.5 \left(\frac{\text{mmol}}{\text{mL}}\right)$$

No of mmol (conc.) = 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 H_2SO_4 must be diluted to 1L (1000 mL) to prepare (become) 0.1 M.

<u>Another solution</u>: $\mathbb{N}_{\mathbb{P}}$ of mmol (conc.) = $\mathbb{N}_{\mathbb{P}}$ mmol (dilu.)

$$(M_{1} \times V_{1})_{conc.} = (M_{2} \times V_{2})_{dilu.}$$

$$\frac{\% \times \text{sp. gr. (density)} \times 1000}{M. w} \times V_{1} = (M_{2} \times V_{2})_{dilu.}$$

$$\frac{94}{100} \times 1.831 \times 1000}{98.1} \times V_{1} = 0.1 \times 1000$$

$$V_{1} = 5.71 \text{ mL}$$

Diluting Solutions

Example: You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of KMnO₄ 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, 2, 5, and 10×10^{-3} M KMnO₄ solutions?

<u>Solution:</u>

1) 1×10⁻³ M

$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$
$$0.1 \left(\frac{\text{mmol}}{\text{mL}}\right) \times V_1 = 1 \times 10^{-3} \left(\frac{\text{mmol}}{\text{mL}}\right) \times 100 \text{ (mL)}$$

 $V_1 = 1$ mL stock solution (conc.), Also to prepare 2, 5, 10×10^{-3} M

Example: You are analyzing for the manganese content in an ore sample by dissolving it and oxidizing the manganese to permanganate for spectrophotometric measurement. The ore contains about 5% Mn. A 5 g sample is dissolved and diluted to 100 mL, following the oxidation step. By how much the solution be diluted to be in the range of the calibration curve prepared in example, about 3×10^{-3} M permanganate.

The solution contains 0.05 (5%) \times 5 g sample = 0.25 g Mn

$$M = \frac{w(g)}{M.w(\frac{g}{mol})} \times \frac{1000}{V(mL)} = \frac{0.25(g)}{55(\frac{g}{mol})} \times \frac{1000}{100}$$
$$= 4.5 \times 10^{-3} \text{ mol } MnO_4^- \text{ in } 100 \text{ mL} = 4.5 \times 10^{-2} \text{ M}$$
$$(M_1 \times V_1)_{\text{conc.}} = (M_2 \times V_2)_{\text{dilu.}}$$
$$(M_1 \times V_1)_{\text{orignal}} = (M_2 \times V_2)_{\text{final}}$$

 $4.5 \times 10^{-2} \times V_1 (mL) = 3 \times 10^{-3} M \times 100 mL$

 $V_1 = 6.7 \text{ mL}$ needed for dilution to 100 mL

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.

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

 $0.250 \left(\frac{mmol}{mL}\right) \times V_1(mL) = 0.1 \left(\frac{mmol}{mL}\right) \times 500 \text{ mL}$
 $V_1 = 200 \text{ mL}$

Example: Describe the Preparation of 100 mL of 6 M HCl from a concentrated Solution that has a Specific gravity 1.18 and is 37% HCl (36.5 g/mol).

Solution:

$$M = \frac{d \times \% \times 1000}{M. w} = \frac{1.18 \times \frac{37}{100} \times 1000}{36.5} = 12 M$$

 $6 \text{ M} \times 100 = 12 \text{ M} \times \text{V} \text{ ml}$

Vml = 50, Thus dilute 50 mL of the concentrated acid to 100 mL

<u>H.W:-</u> Calculate the molar concentration (M) of HNO_3 (63 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5 % HNO_3 .

المحاضرة السابعة

(2) Normal concentration (Normality) N

It is the number of equivalents of solute per litter of solution, or the number of milliequivalents per millilitre of solution.

$$N = \frac{N_{\underline{0}} \text{ of equivalent}}{\text{Volume of solution (L)}} = \frac{(\frac{\text{Weight}}{\text{Equivalent Weight}})(\frac{g}{\text{Eq}})}{\frac{V (\text{mL})}{1000 (\frac{\text{mL}}{\text{L}})}}$$

$$N = \frac{w}{Eq. w} \times \frac{1000}{V (mL)} = (\frac{Eq}{L}) = (\frac{meq}{mL})$$

Equivalent weight (Eq. w)

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



 $(Eq. w) \text{ for acid } - \text{ base reaction} = \frac{\text{formula weight (F. w)}}{N_{\Omega} \text{ of } H^{+} \text{ or } OH^{-}}$ $Number \text{ of equivalent (Eq)} = \frac{w (g)}{Eq. w (\frac{g}{Eq})}$ $Number \text{ of equivalent (Eq)} = N \left(\frac{Eq}{L}\right) \times \text{Volume (L)}$ $Number \text{ of milliequivalent (meq)} = \frac{w (mg)}{Eq. w (\frac{mg}{mL})}$ $Number \text{ of milliequivalent (meq)} = N \left(\frac{meq}{mL}\right) \times \text{Volume (mL)}$ Equivalent weight of salts: its weight which equivalent to one ionic weight of cation or anion. $Eq. w \text{ of } NaCl = -\frac{23+35.5}{1} = 58.5$

Eq. w of CaCl2 =
$$\frac{40+35.5\times2}{2} = 55.5$$

Eq. w of FeCl₃ =
$$\frac{55.85 + 3 \times 35.5}{3} = 54.12$$

If there is hydrated water combined with the salt, it should be involved in the calculations.

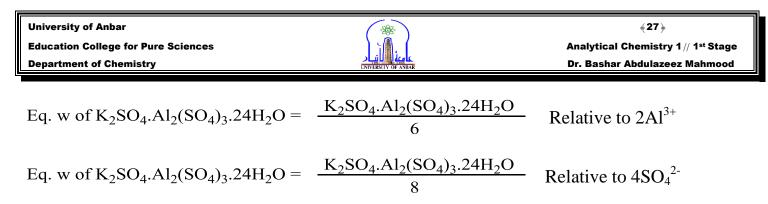
Eq. w of CaCl_{2.2}H₂O =
$$\frac{40+2\times35.5+2\times18}{2}$$
=73.5

For acidic salt, the Eq. w is calculated relative to the required ion:

Eq. w NaH2PO4 =
$$\frac{\text{NaH2PO4}}{1}$$
, relative to Na⁺
Eq. w NaH2PO4 = $\frac{\text{NaH2PO4}}{2}$, relative to H⁺
Eq. w NaH2PO4 = $\frac{\text{NaH2PO4}}{3}$, relative to PO₄³⁻

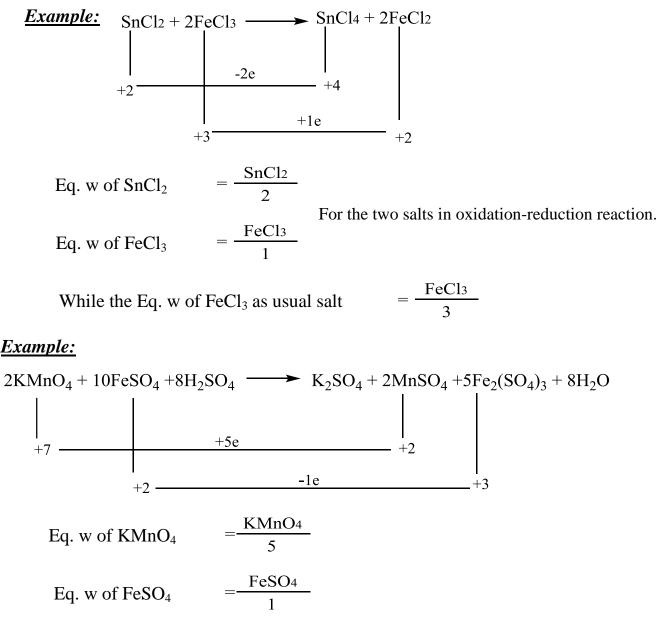
For double salt, equivalent weight is calculated relative to the required ion, for example the double salt K_2SO_4 . $Al_2(SO_4)_3.24H_2O$:

Eq. w of
$$K_2SO_4.Al_2(SO_4)_3.24H_2O = \frac{K_2SO_4.Al_2(SO_4)_3.24H_2O}{2}$$
 Relative to K^+

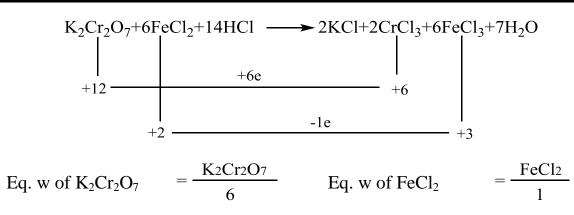


Equivalent weight of oxidants and reductants: its weight which accepts or donates one mole of electrons in oxidation-reduction reaction.

(Eq. w) for oxidation – reduction reaction = $\frac{\text{formula weight (F. w)}}{N_{\text{O}} \text{ of electron}}$



Example:



Some compounds may have more than one equivalent weight. For example, when silver ion is titrated with a solution of potassium cyanide, an end point can be detected for either the two following reactions :

$$2CN^{-} + 2Ag^{+} \longrightarrow Ag[Ag(CN)_{2}]$$
$$2CN^{-} + Ag^{+} \longrightarrow Ag(CN)_{2}^{-}$$

In the first reaction, the equivalent weight of potassium cyanide would be identical to its formula weight. In the second reaction, it would be twice the formula weight. The second reaction is an example of an equivalent weight greater than formula weight.

Example: Calculate the equivalent weight of the following substances: (a) NH_3 , (b) $H_2C_2O_4$ (in reaction with NaOH), and (c) $KMnO_4$ [Mn(VII) is reduced to Mn^{2+}].

(a) Eq. w =
$$\frac{M.w}{N_{\odot} \text{ of } H^+ \text{ or } OH^-} = \frac{17.03}{1} = 17.03 \text{ g/Eq}$$

(b) Eq. w =
$$\frac{90.04}{2}$$
 = 45.02 g/Eq

(c)
$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$$

Eq. w = $\frac{M.w}{N_2 \text{ of electron}} = \frac{158.04}{5} = 31.608 \text{ g/Eq}$

Example: Calculate the normality of the solutions containing the following: (a) 5.300 g/L Na_2CO_3 (when the CO_3^{-2} reacts with two protons), (b) 5.267 g/L K₂Cr₂O₇ (the Cr is reduced to Cr³⁺).

Solution: (a)
$$N = \frac{w}{Eq.w} \times \frac{1000}{V(mL)} = \frac{5.3}{\frac{105.99}{2}} \times \frac{1000}{1000} = 0.10 Eq/L$$

(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
 $= \frac{5.267}{\frac{294.19}{6}} \times \frac{1000}{1000} = 0.1074 Eq/L$

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

<u>Solution:</u> N = nM ($n = N_2$ of equivalent (H^+ , OH^- , or electron) $N_{H_2SO_4} = 2 \times 0.25$

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

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

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

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

$$V_{\text{H}_2\text{SO}_4} = 5 \text{ mL}$$

Example: A solution of sodium carbonate is prepared by dissolving 0.212 g Na₂CO₃ and diluting to 100 mL. Calculate the normality of the solution:

(a) if it is used as a monoacidic base

(**b**) if it is used as a diacidic base.

Solution: (a)
$$N = \frac{W}{Eq.w} \times \frac{1000}{V(mL)} = \frac{0.212}{\frac{106}{1}} \times \frac{1000}{100} = 0.020 \text{ meq/mL}$$

(b) $N = \frac{0.212}{\frac{106}{2}} \times \frac{1000}{100} = 0.040 \text{ meq/mL}$

Example: Iddine (I₂) is an oxidizing agent that in reactions with reducing agent is reduced to iddide (I⁻). How many grams I₂ would you weigh out to prepare 100 mL of a 0.10 N I₂ solution?

Solution:

$$I_2 + 2e \rightarrow 2I^-$$

$$N = \frac{w}{Eq. w} \times \frac{1000}{V (mL)} \to 0.1 = \frac{w}{\frac{254}{2}} \times \frac{1000}{100} \to w = 1.27 \text{ g}$$

Example: Calculate the normality of a solution of 0.25 g/L $H_2C_2O_4$, both as an acid and as a reducing agent.

Solution:

$$H_2C_2O_4 \rightarrow 2CO_2 + H_2$$
$$N = \frac{W}{Eq. W} \times \frac{1000}{V(mL)} = \frac{0.259}{\frac{90.04}{2}} \times \frac{1000}{1000} = 0.00555 \text{ meq/mL}$$

Example: How many milliequivalents are involved in 43.50 mL of 0.1379 N K₂Cr₂O₇. *Solution:* $N_{\rm P}$ of milliequivalents = N × V

0.00



$$= 0.1379 \frac{\text{meq}}{\text{mL}} \times 43.50 \text{ mL} = 5.9987 \text{ meq}$$

Normal concentration (Normality) N for liquid

$$N = \frac{\% \times \text{sp. gr. (density)} \times 1000}{\text{Eq. w}}$$

Example: Calculate the Molarity and Normality H_2SO_4 (d = 1.98), % = 98, M. w = 98 *Solution:*

$$M = \frac{1.98 \times 98 / 100 \times 1000}{98} = 19 M$$
$$N = \frac{1.98 \times 98 / 100 \times 1000}{49} = 38 N$$

or $N = nM = 2 \times 19 = 38$

n = number of hydrogen atoms in acid

The relation between molarity (M) and normality (N)

Normality is either equal or larger than it is. Therefore $N \ge M$ and N = nM n is a factor which obtained by divided the molecular weight of the material on its equivalent weight. It is an integral number.

When equivalent weight = molecular weight such as HCl, NH₃ and NaCl: n=l and N=M.

When equivalent weight is less than molecular weight, such as H_2SO_4 , $Ca(OH)_2$. Then N > M or N=nM, Where n= 1, 2, 3etc.

المحاضرة الثامنة

(3) Formal concentration (Formality) F

The term use for solutions of ionic salts that do not exist as molecules in the solid or in solution. Operationally, is identical to molarity.

Analytical concentration: The concentration for molecules do not dissociation in solution (don't ionization) or total concentration for all species in solution (Cs) or original concentration prepared by dissolving solute (g) in solvent (L).

 $CH_3COOH + H_2O = CH_3COO^- + H_3O^+$

Analytical conc. (Cs) = $[CH_3COOH] + [CH_3COO^-] = [CH_3COOH] + H_3O^+$

Equilibrium concentration [X]: The concentration for ions and molecules after ionization (equilibrium). Equilibrium conc. for $CH_3COOH = [CH_3COOH]$

Equilibrium conc. for $[H_3O^+] = [CH_3COO^-]$

Example: Exactly 4.57 g of BaCl₂.2H₂O are dissolved in sufficient water to give 250 mL of solution. Calculate the formal concentration of $BaCl_2$ and Cl^- in this solution.

Solution:

$$F_{BaCl_2} = \frac{w}{F_{W}} \times \frac{1000}{V \,\text{mL}} = \frac{4.57}{244} \times \frac{1000}{250} = 0.0749 \,\text{F} \,\text{BaCl}_2.2\text{H}_2\text{O}$$

$$BaCl_2 \rightarrow Ba^{2+} + 2\text{Cl}^-$$

$$0.0749 \,\text{F} \quad 0.0749 \,\text{F} \times 2 = 0.149 \,\text{F} \,\text{Cl}^-$$

Example: Calculate the formal concentration of: (a) an aqueous solution that contains 1.80 g of ethanol in 750 mL. (b) an aqueous solution that contains 365 mg of iodic acid HIO₃ in 20 mL (the acid is 71% ionized in this solution).

(a) $F_{C_2H_5OH} = \frac{W}{F_W} \times \frac{1000}{VMI} = \frac{1.80}{46.1} \times \frac{1000}{750} = 0.0521 \text{ F} C_2H_5OH$ <u>Solution:</u>

The only solute species present in significant amount in an aqueous solution of ethanol is $C_{2}H_{5}OH$, therefore; M = F = 0.0521

(b) F =
$$\frac{W}{F.W} \times \frac{1000}{V \,\text{mL}} = \frac{\frac{365}{1000}}{176} \times \frac{1000}{20} = 0.104 \,\text{F}$$

Here, only 29% (100%-71%) of the solute exists as undissociated HIO₃. Thus, the molar concentration of this species will be:

$$\frac{29}{100} \times 0.104 \text{ F} = 0.0302 \text{ F HIO}_3$$

Example: Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (F. w =163.4) in 10 mL (the acid is 73% ionized in water). Employing HA as the symbol for Cl₃CCOOH, we substitute into equation (law) to obtain the analytical or total concentration of the acid.

Solution:
$$C_{HA} = \frac{w}{M.w} \times \frac{1000}{V \,\text{mL}} = \frac{\frac{285}{1000}}{163.4} \times \frac{1000}{10} = 0.174 \,\text{mmol HA/mL} = 0.174 \,\text{M HA}$$

Because all but 27% of the acid is dissociated into H_3O^+ and A^- , the species concentration of HA is:



$$[\text{HA}] = \text{C}_{\text{HA}} \times \frac{27}{100} = 0.047 \,\frac{\text{mmol}}{\text{mL}} = 0.047 \,\text{M}$$

The molarity of H_3O^+ as well as that of A^- equal to the analytical concentration of the acid minus the species concentration of undissociated acid

$$[H_3O^+] = [A^-] = 0.174 - 0.047$$

= 0.127 mmol/mL = 0.127 M

Note: the analytical concentration of HA is the sum of the species concentration of HA and A

$$C_{HA} = [HA] + [A^-] = [HA] + [H_3O^+]$$

Formal concentration (Formality) F for liquid

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

<u>H.W:-</u>

Calculate the Formal and Molar concentrations of the constituents in 2.30 g of ethanol (g. fw = 46.1) in 3.50 litres of aqueous solution.

(4) 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.

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

<u>Solution</u>: Molality (m) = $\frac{W}{M.W} \times \frac{1000}{W(g)} = \frac{4 \text{ g}}{40 \text{ g/mol}} \times \frac{1000}{500} = 0.2 \text{ m}$

المحاضرة التاسعة

(5) Concentration by percent

Chemists frequently express concentrations in term of percentage Common methods include:

a. Weight percent (w/w):

It is the number of grams of solute per 100 g of solvent or solution (w/w)

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

b. Weight-Volume percent (w/v):

It is the number of grams of solute per 100 mL of solvent or solution (w/v)

$$\left(\frac{W}{V}\%\right) = \frac{W \text{ of solute (g)}}{V \text{ of solution or sample (mL)}} \times 100 = \frac{W \text{ of solute (mg)}}{V \text{ of solution or sample (}\mu\text{L})} \times 100$$

c. Volume percent (v /v):

It is the number of millilitre of solute per 100 mL of solvent or solution (v /v)

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

Example: Calculate the weight percentage of solution prepare by mixing 5 g AgNO₃ with 100 mL water (density 1 g/cm³).

Solution:

$$\left(\frac{w}{w}\%\right) = \frac{w \text{ of solute } (g)}{w \text{ of solution } (g)} \times 100 = \frac{w \text{ of solute } (\text{AgNO}_3)(g)}{w \text{ of solute+w of solvent } (\text{H}_2\text{O})(g)} \times 100$$
$$= \frac{5 \text{ g}}{5 \text{ g} + (100 \text{ mL} \times 1\frac{\text{g}}{\text{mL}})} \times 100 = \frac{5 \text{ g}}{105 \text{ g}} \times 100 = 4.76\%$$

Example: Calculate number of grams in 500 mL saline solution (w/v % = 0.859%).

Solution:
$$\left(\frac{w}{v}\%\right) = \frac{w \text{ of solute (g)}}{V \text{ of solution (mL)}} \times 100$$

 $0.859\% = \frac{w \text{ NaCl (g)}}{500} \times 100$
 $w \text{ NaCl} = \frac{0.859 \times 500}{100} = 4.25 \text{ g NaCl}$

Example: Calculate the weight of glucose in litter solution (w/v % = 5 %).

Solution:
$$\left(\frac{w}{v}\%\right) = \frac{w \text{ of solute (g)}}{V \text{ of solution (mL)}} \times 100$$

 $\left(\frac{w}{V}\%\right) = \frac{w \text{ glucose (g)}}{V \text{ of solution (mL)}} \times 100$
 $5\% = \frac{w \text{ glucose (g)}}{1000 \text{ (mL)}} \times 100$
 $w \text{ glucose} = \frac{5 \times 1000}{100} = 50 \text{ g}$

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

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

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

The relationship between molarity and normality with percentage concentration

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

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

(6) Mole fraction concentration (X)

The ratio between number of moles of solute divided by the total moles of solute and solvent, or the number of moles of solvent divided by the total number of moles of solute and solvent.

Example: One litter of acetic acid solution contain 80.8 g of acetic acid, the solution density 1.00978 g/cm3. Calculate the mole fraction?

Solution: Mole fraction for solute $(X_1) = \frac{N_2 \text{ mole of solute } (n_1)}{N_2 \text{ mole of solute } (n_1) + N_2 \text{ mole of solvent } (n_2)}$

$$= \frac{\left(\frac{W}{M.w}\right)_{CH_{3}COOH}}{\left(\frac{W}{M.w}\right)_{CH_{3}COOH} + \text{density} = \frac{W}{V} \& w = d \times \text{volume}}$$

$$= \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{W \text{ solvent} = w \text{ solution} - w \text{ solute} = 1.009791 \text{ cm}^{3} \times 1000 \text{ cm}^{3} - 80.8}{18}\right)}{18}$$

$$= 0.025$$
Mole fraction for solvent (X₂) = $\frac{N_{\text{e}} \text{ mole of solvent}}{N_{\text{e}} \text{ mole of solvent}}$

$$= \frac{\frac{1.0097 \times 1000 - 80.8}{18}}{\left(\frac{1.0097 \times 1000 - 80.8}{19}\right) + \frac{80.8}{60.1}} = 0.975$$

$$X_1 + X_2 = 1$$
 unit = 0.025 + 0.975 = 1 unit

(7) Concentration in parts per thousand, million and billion (common units for expressing trace concentrations)

These types of concentration are used in trace analysis. 1 ppm solution contain 1 mg of solute per 10^6 mg of a solvent. Since 1 litre of water is about one million milligrams. A 1 ppm solution also contain about 1 mg of 1 solute litre of solution, ppm is always defined as mg/L, even though a litre of the solution may weigh somewhat more or less than 1 kg. When dealing with solids, the ppm unit must be used in terms of mg of constituent per kg of solid.

If a solution contain 50.3 ppm of substance, it mean that one litre of solution contains 50.3 mg.

part per thousand (ppt)
$$\left(\frac{w}{w}\right) = \frac{w \text{ of solute } (g)}{w \text{ of solution } (\text{sample})(g)} \times 10^3 = \frac{w (\text{mg})}{w (g)} = \frac{w (g)}{w (kg)}$$

part per million (ppm) $\left(\frac{w}{w}\right) = \frac{w \text{ of solute } (g)}{w \text{ of solution } (\text{sample})(g)} \times 10^6 = \frac{w (\mu g)}{w (g)} = \frac{w (\text{mg})}{w (kg)}$
part per billion (ppb) $\left(\frac{w}{w}\right) = \frac{w \text{ of solute } (g)}{w \text{ of solution } (\text{sample})(g)} \times 10^9 = \frac{w (\text{ng})}{w (g)} = \frac{w (\mu g)}{w (kg)}$
Example: How can you prepare 500 mL of solution containing 1000 ppm Ca from CaCl₂,

Ca=40, Cl =35.5

1 ppm = 1 mg/L = 10^{-3} g/L 1000 ppm = 1000 mg/ L = 1 g/ L

Thus, the solution should contain 1 g of calcium in litre of solution. But the weighted material is $CaCl_2$ rather than Ca. Therefore, the weight of $CaCl_2$ should be calculated in 500 mL of solution to give 1000 ppm Ca.

M. w of $CaCl_2 = 111 \text{ g/mol}$

	С	Ca					
		CI	Unit	Abbreviation	wt/wt	wt/vol	vol/vol
	a	Cl_2	Parts per million	ppm	mg/kg	mg/L	$\mu L/L$
wei			$(1 \text{ ppm} = 10^{-4}\%)$		μg/g	µg/mL	nL/mL
	1	Х	Parts per billion	ppb	μg/kg	$\mu g/L$	nL/L
ght			$(1 \text{ ppb} = 10^{-7}\% = 10^{-3} \text{ ppm})$	01	ng/g	ng/mL	pL/mL ^a
F.	4		Milligram percent	mg%	mg/100 g	mg/100 mL	
1.	т	111					
W	0		$^{a}pL = picoliter = 10^{-12} L.$				
vv	U						

w of
$$CaCl_2 = 1 \times \frac{111}{40} = 2.77 \text{ g}$$

w of CaCl₂ =
$$2.77 \times \frac{500}{1000} = 1.3875 \text{ g}$$

Therefore, when 1.3875 g of $CaCl_2$ is dissolved in 500 mL of solution, it gives 1000 ppm of Ca.

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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?

$$\underbrace{Solution:} \quad \text{ppm} = \frac{w \, (\mu g)}{w \, (g)} = \frac{3.6 \, \mu g}{2.6 \, g} = 1.4 \frac{\mu g}{g} = 1.4 \, \text{ppm}$$

$$ppb = \frac{w \, (ng)}{w \, (g)} = \frac{3.6 \, \times 10^3 \, \text{ng}}{2.6 \, \text{g}} = 1.4 \times 10^3 \frac{\text{ng}}{\text{g}} = 1400 \, \text{ppb}$$

$$ppt \, (\frac{w}{V}) = \frac{w \, \text{of solute} \, (g)}{V \, \text{of solution} \, (\text{sample})(\text{mL})} \times 10^3 = \frac{w \, (\text{mg})}{V \, (\text{mL})} = \frac{w \, (g)}{V \, (\text{L})}$$

$$ppm \, (\frac{w}{V}) = \frac{w \, \text{of solute} \, (g)}{V \, \text{of solution} \, (\text{sample})(\text{mL})} \times 10^6 = \frac{w \, (\mu g)}{V \, (\text{mL})} = \frac{w \, (\text{mg})}{V \, (\text{L})}$$

$$ppb \, \left(\frac{w}{V}\right) = \frac{w \, \text{of solute} \, (g)}{V \, \text{of solution} \, (\text{sample})(\text{mL})} \times 10^9 = \frac{w \, (\text{ng})}{V \, (\text{mL})} = \frac{w \, (\mu g)}{V \, (\text{L})}$$

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

Solution: Note: 1dL = 100 mL

$$ppm = \frac{w (\mu g)}{V (mL)} = \frac{26.7 (\mu g)}{\frac{25 (\mu L)}{1000 (\frac{\mu L}{mL})}} = \frac{26.7 (\mu g)}{0.025 (mL)} = 1.07 \times 10^3 (\frac{\mu g}{mL}) = 1.07 \times 10^3 \text{ ppm}$$
$$\frac{w (mg)}{V (dL)} = \frac{26.7 \ \mu g \ \times 10^{-3} \frac{mg}{\mu g}}{0.025 \ mL \times 10^{-2} \frac{dL}{mL}} = 107 \ mg/dL$$

Example: What is the molarity of K^+ in a Solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (M. w = 329.3 g/mol) ?

Solution:

$$M = \frac{w (g)}{M.w} \times \frac{1000}{V mL} \Longrightarrow w (g) = \frac{63.3}{1000} \Longrightarrow M = \frac{0.0633}{329.3} \times \frac{1000}{1000}$$
$$= \frac{63.3 / 1000}{\frac{329.3}{L}}$$
$$1.922 \text{ mol/L} = 1.922 \times 10^{-4}$$

$$\begin{bmatrix} K^+ \end{bmatrix} = 1.922 \times 10^{-4} \times 3 \text{ mol } \text{K}^+$$
$$= 5.77 \times 10^{-4} \text{ mol/L} = 5.77 \times 10^{-4} \text{ M}$$

<u>H.W:</u> 1- A solution of KCl (its volume =500 mL) contains 7.45 ppm KCl. Calculate its Molarity and Normality.

2- Calculate the weight of solute in grams for each of the followings solutions:

- (a) 43.5 mL of O.175 N Hg(NO₃)₂
- (b) 10 mL of 0.03 N KI if the reaction product is Agl
- (c) 5 litres of 0.25 N K₂CO₇ in acidic medium.

المحاضرة العاشرة

The relationship between molarity, normality and part per million

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

<u>Example</u>: (a) Calculate the molar conc. of 1 ppm solutions each of Li^+ and Pb^{+2} . (b) What weight of $Pb(NO_3)_2$ will have to be dissolved in 1L of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

$$\begin{array}{ll} \underline{fon:} & M = \frac{ppm}{M.w \times 1000} \\ (a) & M_{Li} + = \frac{1}{6.94 \times 1000} = 1.44 \times 10^{-4} \ \text{mol/L} \\ & M_{Pb} + 2 = \frac{1}{207 \times 1000} = 4.83 \times 10^{-6} \ \text{mol/L} \\ (b) & M = \frac{100}{207 \times 1000} = 4.83 \times 10^{-4} \ \text{mol/L} \\ & M = \frac{W}{M.w} \times \frac{1000}{V \ (\text{mL})} = 4.83 \times 10^{-4} = \frac{W}{283.2} \times \frac{1000}{1000} \\ & w = 0.137 \ \text{g Pb}(\text{NO}_3)_2 \end{array}$$

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

Solution:
$$N = \frac{ppm}{Eq. w \times 1000}$$

= $\frac{ppm}{\frac{A.w}{2} \times 1000} = \frac{1}{\frac{65.4}{2} \times 1000} = 3.06 \times 10^{-5} \frac{Eq}{L}$
= $3.06 \times 10^{-5} \times 1000 = 3.06 \times 10^{-2} meq/L$

Therefore, when 1.3875 g of CaCl₂ is dissolved in 500 mL of solution, it gives 1000 ppm of Ca. *Example:* A solution of KCl volume = 500 mL contains 7.45 ppm KCl. Calculate its Molarity and Normality.

Solution: 7.45 ppm KCl = $7.45 \text{ mg/L} = 7.45 \times 10^{-3} \text{ g/L}$



$$M = N = \frac{\text{w of solute per L}}{M. \text{ w} = \text{Eq. w}}$$
$$M = N = \frac{7.45 \times 10^{-3}}{74.5} = \frac{10^{-4} \text{ Eq/ L or meq/mL}}{\text{or mol/ L or mmol/mL}}$$

Example: A solution of NaCl has concentration of 0.01N. Express the concentration in ppm as NaCl, Na⁺ and Cl⁻.

Solution: w of NaCl in litre of solution = N × Eq. w \rightarrow = 0.01×58.5 \rightarrow = 0.585 g/L \rightarrow = 585 mg/L \rightarrow = 585 ppm as NaCl.

$$585 \times \frac{23}{58.5} = 230 \text{ mg/L} = 230 \text{ ppm as} \text{ Na}^+$$

$$585 \times \frac{35.5}{58.5} = 355 \text{ mg/L} = 355 \text{ ppm as} \text{ Cl}^{-1}$$

Example: A solution contains 55 ppb of Ca, calculate its molar and normal concentrations.

Solution: 55 ppb = 55 mg/mL \longrightarrow = 55×10⁻³ g/mL \longrightarrow = 55 µg/L 55 µg/L = 55×10⁻⁶ g/L

$$M = \frac{W \text{ per litre}}{M. W} = \frac{55 \times 10^{-6}}{40} = 1.4 \times 10^{-6} \text{ mol/L}$$

N=
$$\frac{\text{w per litre}}{\text{Eq. w}} = \frac{55 \times 10^{-6}}{20} = 2.8 \times 10^{-6} \text{ eq/L}$$

Titer expression of concentration

It is weight of substance which is chemically equivalent to one millilitre of solution. Therefore a silver nitrate solution having a titer of 1 mg of chloride will contain enough concentration of silver nitrate in each millilitre to react completely with that weight of Cl^{-} ion.

The titer may be expressed in g or mg of KCl, $BaCl_2$ and NaI or any other compound which reacts with AgNO₃. This type of concentration is usually used in titration methods when the titration is frequently repeated with special reagent as a titrant. If the titer is known, the weight can be calculated from: *Titer* × *the volume of titrant*.

The titer can be altered into normality (N) from the following relations:



$$T = mg/mL$$
, $N = T mg/mL \times \frac{1}{Eq. w}$, $T = N \times Eq. w$

If the titer of HCl solution = 4 mg/mL of NaOH, therefore the normality of the solution (N) can be obtained by dividing the titer on the Eq. w of NaOH:

N=T mg/mL $\times \frac{1}{\text{Eq. w}}$ = 4.00 mg/mL $\times \frac{1}{40 \text{ mg/meq}}$ = 0.1 meq/mL

Example: Calculate a) NH₃ titer from 0.12 N HCl. b) BaO titer from 0.12 N HCl.

Solution:

Eq. w of NH₃ = $\frac{14+3\times 1}{1} = \frac{17}{1} = 17$ mg/meq.

Eq.w of BaO = $\frac{153.4}{2}$ = 76.7 mg/meq.

 $T_{NH3} = N \times Eq. \text{ w } NH_3 = 0.12 \times 17 = 2.04 \text{ mg/mL } NH_3$

-NH3

 $T_{BaO} = N \times Eq. \text{ w BaO} = 0.12 \times 76.7 = 9.204 \text{ mg/mL BaO}$

Example: A solution of NaOH has a titer of oxalic acid (M. w =126) = 9.45 mg/mL. Calculate the normality of NaOH solution.

Solution:

N=T mg/mL
$$\times \frac{1}{\text{Eq. w}}$$
 = 9.45 mg/mL $\times \frac{1}{63 \text{ mg/meq}}$ = 0.15 meq/mL or Eq/L

Example: What is the normality of $AgNO_3$ which has a titer of 5.63 mg $BaCl_2.2H_2O/mL$. *Solution:*

Eq. w of BaCl₂.2H₂O =
$$\frac{137.43 + 2 \times 35.5 + 2 \times 18}{2} = 122.171$$

N = T mg/mL× $\frac{1}{\text{Eq. w}}$ = 5.63 mg/mL× $\frac{1}{122.171}$ = 0.046 meq/mL

Example: What is the normality of solution of KMnO₄ has a titer = 11 mg Fe₂O₃/mL for the reaction.

Solution: $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$



$$N = T mg/mL \times \frac{1}{Eq. w}$$

Eq. w of
$$Fe_2O_3 = \frac{2 \times 55.58 + 3 \times 16}{6} = 26.62$$

$$N = 11 \times \frac{1}{26.62} = 0.4132 \text{ meq/mL}$$

= 0.4132 Eq/L

Example: 25 mL of Na₂CO₃ solution of titer 0.0053 g/mL was titrated with H_2SO_4 solution. The volume of the latter was 25.50 mL, calculate the titer of H_2SO_4 .

Solution: w of Na₂CO₃ in 25 mL = $25 \times 0.0053 = 0.1325$ g/25 mL

 $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

Every 53 mg/meq $Na_2CO_3 \equiv 49$ mg/meq H_2SO_4

0.1325 Na₂CO₃ \equiv 0.1225 g H₂SO₄ in 25.5 mL

 $T_{H2SO4} = \frac{0.1225}{25.50} = 0.005 \text{ g/mL}.$

Example: 38.2 g of borax (Na₂B₄O₇.10H₂O) is dissolved in 1080 g of water. Calculate the molarity, normality, (w/w)%, (w/v)%, molality and mole fraction of this solution. the density of the solution = 1.01 g/mL.

Solution: M. w of borax $(Na_2B_4O_7.10H_2O) = 2 \times 23 + 4 \times 11 + 7 \times 16 + 10 \times 18 = 382 \text{ g/mol.}$

Eq. w of Na₂B₄O₇.10H₂O =
$$\frac{382}{2} = 191g/Eq$$

Volume of solution =
$$\frac{1080}{1.01}$$
 = 1069.3 mL

$$M = \frac{W}{M. W} \times \frac{1000}{V} = \frac{38.2}{382} \times \frac{1000}{1069.3} = 0.0935 \text{ mol/L}$$

$$N = \frac{W}{Eq. W} \times \frac{1000}{V} = \frac{38.2}{191} \times \frac{1000}{1069.3} = 0.1870 \text{ eq/L}$$

$$m = \frac{W}{M. W} \times \frac{1000}{W \text{ of solution}} = \frac{38.2}{382} \times \frac{1000}{1080} = 0.0.0926 \text{ mol/kg}$$



w percent = $\frac{38.2 \times 100}{1080}$ = 3.54 % (w/w)

w/v percent =
$$\frac{38.2 \times 100}{1069.3}$$
 = 3.6 % (w/v)

Number of moles of borax = $\frac{38.2}{382}$ = 0.1 mole

Number of moles of water = $\frac{1080}{18}$ = 60 mole

Mole fraction of borax =
$$\frac{0.1}{0.1+60} = 0.0017$$

Mole fraction of water =
$$\frac{60}{0.1+60} = 0.9983$$

<u>H.W:-</u> 1-Show by calculations how could you prepare the following solutions:

- a) 750 mL of 0.172 F $K_2Cr_2O_7$ from the solid salt.
- b) 50 litres of a solution that is 0.1 F in Na₂SO₄ from solid Na₂SO₄.
- c) 2 litres of a solution that is 0.015 M in Na^+ from solid NaCl.
- d) 20 litres of a solution that is 0.202 M in Na^+ from a 2.42 F solution of Na_2SO_4 .
- 2- A solution of concentrated HCl has specific gravity of 1.185 and percentage is 36.5 % (w/w) HCl. Explain how 1.50 litres of approximately 0.3 F HCl should be prepared from the concentrated solution.
- 3- Describe the preparation of 400 mL of 6 F H_3PO_4 from the commercial solution which is 85% (w/w) H_3PO_4 and has density of 1.69 g/mL.
- 4- Describe the preparation of 200 mL of 3 F H_2SO_4 from the concentrated solution which is 95% (w/w) H_2SO_4 and has density of 1.84 g/mL.
- 5- Calculate the formal concentration of 12% (w/w) CuSO₄ solution which has density of 1.13 g/mL.
- 6- A solution was prepared by dissolving 1.68 g of $K_4Fe(CN)_6$ in water and diluting exactly to 500 mL. Calculate:
 - a) the formal concentration of $K_4 Fe(CN)_6$.
 - b) The molar concentration of K⁺ assuming complete dissociation.
 - c) the weight-volume percent of K_4 Fe(CN)₆.

- d) the weight-weight percent of K_4 Fe(CN)₆ if the density of solution = 1.008 g/mL.
- e) The number of moles $Fe(CN)_6^{4-}$ in 16 mL of the solution.
- 7- Calcium concentration in sea water is 4×10^2 ppm, calculate its formal concentration if the average density of sea water =1.024 g/mL.
- 8- An impure 1 g sample of arsenious acid (H_3AsO_3) is oxidised to H_3AsO_4 by titration with 45 mL of 0.08 N iodine. Calculate the percentage of H_3AsO_3 (F.w=125.9) and percentage of As.