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Term 2nd Sem. 2nd

ANALYTICAL CHEMISTRY

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Syallbus : 2019 Pattern

Chapter No. 2

Chapter Name : Calculations Used In Analytical Chemistry

Calculations used in Analytical Chemistry Some important units of measurements

Distinction between mass and weight:

The terms "mass" and "weight" are used interchangeably in ordinary conversation, but the two words don't mean the same thing. The difference between mass and weight is that mass is the amount of matter in a material, while weight is a measure of how the force of gravity acts upon that mass.

- Mass is the measure of the amount of matter in a body. Mass is denoted using m or M.
- Weight is the measure of the amount of force acting on a mass due to the acceleration due to gravity. Weight usually is denoted by W. Weight is mass multiplied by the acceleration of gravity (g).

W = m * g$W = m * g$

Comparing Mass and Weight

Mass	Weight
The quantity of matter in a body is known as the mass	Weight is the gravitational force with which the Earths attracts objects towards its centre.
Mass is a scalar quantity	Weight is vector quantity
The mass of the body is constant everywhere in the universe.	The weight of the body is variable. The weight of a body depends on the location.
The mass of a moving body is m = f/a.	The weight of the body is given by W = mg
The unit of mass is kg	The unit of weight is N.

Difference Between Mass and Weight

Sl. No.	Differentiating Property	Mass	Weight
1	Definition	Mass is simply the measure of the amount of matter in a body.	Weight is the measure of the amount of force acting on a mass due to

			acceleration due to gravity.
2	Denotation	Mass is denoted by "M".	Weight is denoted by "W".
3	Formula	Mass is always constant for a body and there are several formulas to calculate mass. One way to calculate mass is: Mass = volume × density	Weight is the measure of the gravitational force acting on a body. Weight can be calculated from the following formula: Weight = mass × acceleration due to gravity
4	Quantity Type	Mass is a base quantity. Mass only has magnitude and so, it is a scalar quantity.	Weight is a derived quantity. Weight has both magnitude and direction (towards the centre of gravity) and so, it is a vector quantity.
5	Unit of Measurement	The SI unit of mass is Kilogram (Kg).	The SI unit of weight is Newton (N).
6	Gravitational Effect	Mass does not depend upon gravity and is constant everywhere. Mass can never be zero.	Weight is dependent on gravity and so, it varies from place to place. Weight can be zero where there is no gravity (like space).
7	Measuring Instrument	Mass can be easily measured using any ordinary balance like beam balance, lever balance, pan balance, etc.	Weight can be measured by a spring balance or by using its formula.

The mole (symbol: mol) is the unit of measurement for amount of substance in the International System of Units (SI). It is defined as exactly 6.02214076×1023 particles, which may be atoms, molecules, ions, or electrons.

The definition was adopted in November 2018 as one of the seven SI base units, revising the previous definition that specified one mole as the amount of substance in 12 grams of carbon-12 (^{12}C), an isotope of carbon.

The number $6.02214076 \times 10^{23}$ (the Avogadro number) was chosen so that the mass of one mole of a chemical compound in grams is numerically equal, for most practical purposes, to the average mass of one molecule of the compound in daltons. Thus, for example, one mole of water contains $6.02214076 \times 10^{23}$ molecules, whose total mass is about 18.015 grams and the mean mass of one molecule of water is about 18.015 daltons.

The mole is widely used in chemistry as a convenient way to express amounts of reactants and products of chemical reactions.

For example, the chemical equation $2H_2 + O_2 \rightarrow 2H_2O$ can be interpreted to mean that for each 2 mol dihydrogen (H_2) and 1 mol dioxygen (O_2) that react, 2 mol of water (H_2O) form. The mole may also be used to measure the amount of atoms, ions, electrons, or other entities.

The concentration of a solution is commonly expressed by its molarity, defined as the amount of dissolved substance in mole(s) per unit volume of solution, for which the unit typically used is moles per litre (mol/l), commonly abbreviated M.

The term gram-molecule (g mol) was formerly used for "mole of molecules", and gram-atom (g atom) for "mole of atoms". For example, 1 mole of $MgBr_2$ is 1 gram-molecule of $MgBr_2$ but 3 gram-atoms of $MgBr_2$.

Millimole : The amount of a substance equal to a thousandth of a mole (a measure of the amount of a substance)

Significant Figures

The Significant Figures of a number refer to those digits that have meaning in reference to a measured or specified value. Correctly accounting for Significant Figures is important while performing arithmetic so that the resulting answers accurately represent numbers that have computational significance or value.

Significant Figures Rules:

The rules for deciding the number of significant figures are:

1. Non-zero digits are significant unless indicated otherwise.
2. Zeros between two non-zero digits are significant.
3. Zeros before the first non-zero digit (i.e. “leading zeros”) are not significant (for instance 0.003 has only one significant figure).
4. Zeros after the decimal point and after the first non-zero digit (i.e. “final zeros”) are significant (for instance 3.200cm has four significant figures).
5. Zeros required before the decimal point are significant if the decimal point is shown (for instance 100.cm).
6. Zeros after the last non-zero digit when there is no decimal point may or may not be significant (for instance 1,200km). In such cases, you can make your own assumption of which figures you think are significant. You should indicate what

assumption you have made. For instance, you might write: “1,200km (2 sig fig)” or “1,200km (4 sig fig)”.

7. Include the unit of the measurement when expressing how well a value is known. (For example, the distance 32.56m is known to 0.01m).

8. To avoid round-off error, we encourage you to keep two insignificant figures in intermediate calculations and to show the significant figures with the designation “_|”. For instance, a calculation that results in a mass that is only significant to a hundredth of a gram, could be written 103.00|52g.

Solution:

A solution is a homogeneous mixture of two or more substances. A solution may exist in any phase.

A solution consists of a solute and a solvent. The solute is the substance that is dissolved in the solvent. The amount of solute that can be dissolved in solvent is called its solubility. For example, in a saline solution, salt is the solute dissolved in water as the solvent.

For solutions with components in the same phase, the substances present in lower concentration are solutes, while the substance present in highest abundance is the solvent. Using air as an example, oxygen and carbon dioxide gases are solutes, while nitrogen gas is the solvent.

The term "aqueous solution" is used when one of the solvents is water.

The Concentration of a Solution

The amount of solute in a given solution is called the concentration of a solution. The proportion of solute and solvent in solutions are not even. Depending upon the proportion of solute, a solution can be:

- Diluted
- Concentrated
- Saturated

$$\text{The concentration of solution} = \frac{\text{Amount of solute}}{\text{Amount of solution}}$$

$$\text{The concentration of solution} = \frac{\text{Amount of solute}}{\text{Amount of solvent}}$$

Molar concentration :

To calculate the Molar Concentration, we will find the molar concentration by dividing the moles by liters of water used in the solution.

The molar concentration formula is given by,

$$\text{Molar concentration} = \frac{\boxed{\text{Amount in Moles}}}{\boxed{\text{Volume of solution in mL}}}$$

Molar analytical concentration :

Molar analytical concentration is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution. The molar analytical concentration describes how a solution of a given concentration can be prepared.

Molar equilibrium concentrations :

In a chemical reaction, when both the reactants and the products are in a concentration which does not change with time any more, it is said to be in a state of chemical equilibrium. For a reaction, if you know the initial concentrations of the substances, you can calculate the equilibrium concentration.

Percent Concentration

There are two types of percent concentration: percent by mass and percent by volume.

Percent By Mass

Percent by mass (m/m) is the mass of solute divided by the total mass of the solution, multiplied by 100 %.

Percent by mass = mass of solute/total mass of solution × 100 %

Percent By Volume

Percent by volume (v/v) is the volume of solute divided by the total volume of the solution, multiplied by 100 %.

Percent by volume = volume of solute/total volume of solution × 100 %

Weight to volume percent :

It is often used to indicate the composition of dilute aqueous solutions of solid reagents. For example, 8% (w/v) aqueous sodium chloride usually refers to a solution prepared by dissolving 8 g of sodium chloride in sufficient water to give 100 mL of solution.

Parts per Million, Parts per Billion and Parts per Thousand

Parts per million (ppm), Parts per billion (ppb) and parts per thousand (ppt) is a convenient way to express concentrations of very dilute solutions. In IUPAC terminology, parts per billion, parts per million and parts per thousand are mass cocentrations.

Parts per million (ppm) : It is the number parts of solute per million (10^6) parts of solution. A common rule for calculating parts per million is to remember that for dilute aqueous solutions whose densities are approximately 1.00 g mL^{-1}

1 ppm = 1.00 mg L^{-1}.

$$\text{Concentration in ppm } (C_{ppm}) = \frac{\boxed{\text{Mass of solute (g)}}}{\boxed{\text{Mass of solution (g)}}} \times 10^6 \text{ ppm}$$

It is also expressed as;

$$\text{Concentration in ppm } (C_{ppm}) = \frac{\boxed{\text{Mass of solute (g)}}}{\boxed{\text{Mass of solution (L)}}} \text{ ppm}$$

More conveniently it is also defined as 1 ppm is the 1 mg of solute in 1 liter of solution. In other words, the mass concentration expressed in g/g is a factor of 10^6 larger than the mass concentration expressed in mg L^{-1}. Therefore, if we wish to express the mass concentration in ppm and the units are mg L^{-1}, we merely use ppm. If it is expressed in g/g, we must multiply the ratio by 10^6 ppm.

Parts per billion (ppb) : It is the number parts of solute per billion (10^9) parts of solution. It is expressed as

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

It is also expressed as;

$$\boxed{\text{Mass of solute } (\mu\text{g})}$$

Concentration in ppb (C_{ppb}) = $\dfrac{}{\boxed{\text{Mass of solution (L)}}}$ ppb

More conveniently it is also defined as 1 ppb is the 1 μg of solute in 1 liter of solution. In other words, the mass concentration expressed in g/g is a factor of 10^6 larger than the mass concentration expressed in μg L^{-1}. Therefore, if we wish to express the mass concentration in ppb and the units are μg L^{-1}, we merely use ppm. If it is expressed in g/g, we must multiply the ratio by 10^9 ppb.

Parts per thousand (ppt) : It is the number parts of solute per thousand (10^3) parts of solution. It is expressed as

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

It is also expressed as;

$$\text{Concentration in ppt } (C_{ppt}) = \frac{\boxed{\text{Mass of solute (g)}}}{\boxed{\text{Mass of solution (L)}}} \text{ ppt}$$

Common units to express the concentration of solution

Name	Unit or formula	Symbol
Molarity	$\dfrac{\text{No.of moles of solute}}{\text{Liters of solution}}$	M
Molality	$\dfrac{\text{No.of moles of solute}}{\text{Kilograms of solution}}$	m
Normality	$\dfrac{\text{No.of equivalent weight of solute}}{\text{Liters of solution}}$	N
Weight percent	$\dfrac{\text{g of solute}}{\text{100 g of solution}}$	% (w/w)
Volume percent	$\dfrac{\text{g of solute}}{\text{100 mL of solution}}$	% v/v)
Weight to volume percent	g of solute	% (w/v)

	100 mL of solution	
Parts per million	$\frac{\text{g of solute}}{10^6 \text{ g of solution}}$	ppm
Parts per billion	$\frac{\text{g of solute}}{10^9 \text{ g of solution}}$	ppb
Parts per thousand	$\frac{\text{g of solute}}{10^3 \text{ g of solution}}$	ppt

Solution –dilatant volume ration, functions

The composition of a dilute solution sometimes specified in terms of the volume of a more concentrated solution and the volume of the solvent used in diluting it. The volume of the former is separated from that of the letter by a colon. For example, 1:4 HCl solution contains four volumes of water for each volume of concentrated hydrochloric acid. This method of notation is not commonly used to express the concentration of the original solution. Moreover, under some circumstances 1:4 means dilute one volume with three volumes. Because of of such uncertainties, we should avoid using solution -diluent ratios.

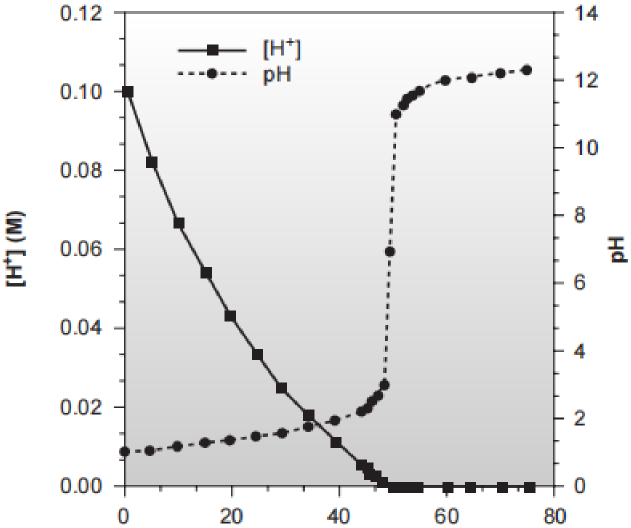
p- function

scientist frequently express the concentration of a solute species is in terms of its p function, or p value.

For exaqmple during a reaction a reactant's concentration may change by many orders of magnitude. If we are interested in viewing the progress of the reaction graphically, we might wish to plot the reactant's concentration as a function of the volume of a reagent being added to the reaction. The plot of molar concentration of H^+ is plotted as a function of the volume of NaoH added to a solution of HCl. The initial $[H^+]$ is 0.10 M and its concentration after adding 75 mL of NaOH is 5 X 10^{-13} M. We can easily follow changes in the $[H^+]$ over the first 14 additions of NaOH. For the last ten additions of NaOH however, changes in the $[H^+]$ are too small to be seen. When working with concentrations that span many orders of magnitude, it is often more convenient to express concentration as a p-function

The p value is the negative logarithm to the base 10 of the molar concentration of that solute species. Thus, for the solute species X,

pX = - log [X].



Graph of [H^+] versus volume of NaOH and pH versus volume of NaOH for the reaction of 0.10 M HCl with 0.10 M NaOH.

Density and Specific Gravity of solutions

In Analytical chemistry two physical quantities that is density and specific gravity are commonly used and they are inter-related each other. The density of a substance is its mass per unit volume and its specific gravity is ratio of its mass to the mass of an equal volume water at 4℃. Density has units of kilograms per litre or grams per ml (cubic centimetre) in the metric system. Specific gravity is dimensionless quantity and so is not commonly used to any particular system of units. The specific gravity is widely used in describing analytical reagent grade or laboratory grade Chemicals purchased commercially. Since the density of water is approximately 1 g mL^{-1} and we use the metric system throughout this chapter we use density and specific gravity interchangeably.

Specific Gravities of commerical concentrated Acids and Bases

Reagent	Concentration % (w/w)	Specific Gravity
Acetic acid	99.7	1.05
Ammonia	29.0	0.90
Hydrochloric acid	37.2	1.19
Hydrofluoric acid	49.5	1.15
Nitric acid	70.5	1.42
Perchloric acid	71.0	1.67
Phosphoric acid	86.0	1.71

Sulphuric acid	96.5	1.84

Chemical Stoichometry

The word " stoichiometry" is derived from the Greek word "stoikhein" meaning element and "metron" meaning measure.

The stoichiometry of a reaction is the relationship among the number of moles of reactants and products as represented by a balanced chemical equation.The quantitative aspects dealing with mass and volume relationship between the reactants and products is called stoichiometry. When the substances taking part in a chemical reaction are represented by their symbols and molecular formulae, the chemical reaction can be expressed in the form of chemical equation. These chemical equations give us a powerful symbolic notation to express the particularly quantitative aspects of chemical reactions.

Empirical Formulas and Molecular Formulas

1. Empirical Formula :

An empirical formula gives the simplest whole number ratio of atoms of atoms of each element present in a molecule or chemical compounds. Example CH is the empirical formula of benzene. It indicates that benzene is composed of carbon and hydrogen in the ratio of 12:1 by weight. Two or more compounds may have same empirical formula, example the empirical formula of compound $C_6H_{12}O_6$ and CH_3CO_2H is the same as CH_2O.

2. Molecular Formula

Molecular formula of a compound is one which indicates the actual number of atoms of each element present in one molecule. The molecular formula specifies the number of atoms in a molecule. Two or more substances may have the same empirical formula but different molecular formulas. For example CH_2O is both the empirical formula and the molecular formula for formaldehyde; it is it is also the empirical formula for such diverse substances as acetic acid $C_2H_4O_2$; glyceraldehyde $C_3H_6O_3$; and glucose, $C_6H_{12}O_6$ as well as more than 50 other substances containing 6 or more carbon atoms. We may calculate the empirical formula of a compound from its percent composition. To determine the molecular formula, we must know the molar mass of the compound.

molecular formula = n× empirical formula

Where n = molecular formula weight / empirical formula weight

Molecular formula indicates the various elements present in the number of atoms of each element. Molecular formula weight or molar mass of the compound can be calculated by adding atomic weights of elements in the molecular formula. For example molecular weight molecular weight or molar mass of carbon dioxide = $1\times 12 + 2 \times 16 = 44$ g mol^{-1}

A structural formula provides additional information for example the chemically different ethanol and dimethyl ether share the same molecular formula C_2H_6O. Their structural formulas are C_2H_5O and CH_3OCH_3 respectively indicates the structural difference between these compounds that are not shown in their common molecular formula.

Determination of Empirical and Molecular formula

The following steps are followed to determine the empirical formula of the compound

1. The percentage composition of the compound is determined by quantitative analysis.
2. The percentage of each element is divided by its atomic weight giving atomic ratio of the elements present in the compound.
3. Atomic ratio of each element is divided by the minimum value of atomic ratio as to get simplest ratio of atoms of elements.
4. If the simplest ratio is fractional then values of simplest ratio of each element are multiplied by a smallest integer to get a simplest whole number for each element.
5. To get empirica formula, symbols of various elements are written side by side with their respective whole number ratio as a subscript to the lower right hand corner of the symbol.
6. The molecular formula may be determined from the empirical formula if the molar mass of the substance is known.
7. The molecular formula is always a simple multiple of empirical formula and the value of simple multiple is obtained by dividing molar mass with empirical formula mass.

Stoichiometric Calculations

A balanced chemical reaction indicates the quantitative relationship between the moles of reactants and products. These stoichiometric relationships provide the basis for many analytical calculations.

The folowing general steps are involved for making stoichiometric calculations:

1. When the mass of a reactant or product is given, the mass is first converted to the number of moles, using the molar mass.

2. The stoichiometric ratio given by the chemical equation for the reaction is then used to find the number of moles of another reactant that combines with the original substances or the number of moles of product that forms.

3. Finally the mass of the other reactant or the product is composed from its molar mass.

A balanced chemical equation gives the combining ratios or stoichiometry in units of moles of reacting substances and their products. For example

$$2NaI_{(aq)} + Pb(NO_3)_{2\ (aq)} \longrightarrow PbI_2(_s) + 2NaNO_3(_{aq)}$$

Therefore balanced chemical equation indicates that 2 moles of aqueous sodium iodide combine with 1 mole of aqueous lead nitrate to produce 1 mole of solid lead iodide and 2 moles of aqueous sodium nitrate.