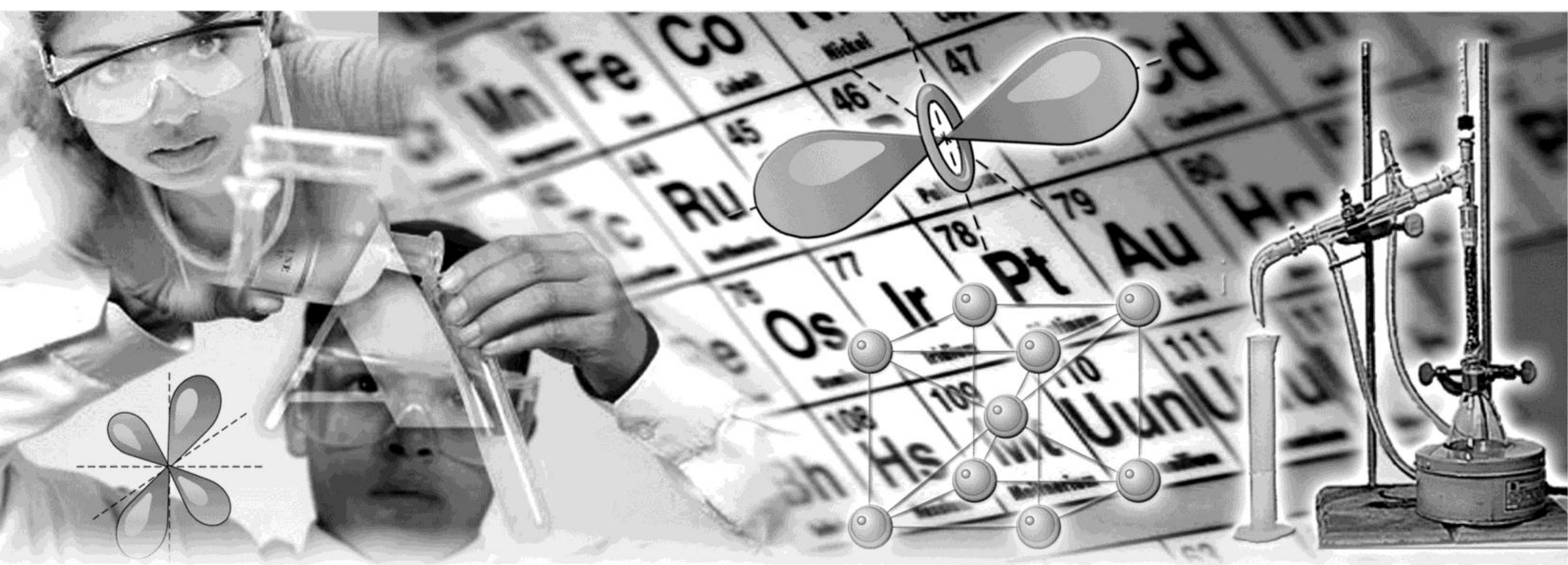

## Chapter
## 1
# Chemical Arithmetic

Chemistry is basically an experimental science. In it we study physical and chemical properties of substance and measure it upto possibility. The results of measurement can we reported in two steps,

(a) Arithmetic number, (b) Unit of measurement.

Every experimental measurement vary slightly from one another and involves some error or uncertainty depending upon the skill of person making the measurements and measuring instrument. The closeness of the set of values obtained from identical measurement called ***precision*** and a related term, refers to the closeness of a single measurement to its true value called ***accuracy***.

## Significant figures

In the measured value of a physical quantity, the digits about the correctness of which we are surplus the last digit which is doubtful, are called the significant figures. Number of significant figures in a physical quantity depends upon the least count of the instrument used for its measurement.

(1) **Common rules for counting significant figures** Following are some of the common rules for counting significant figures in a given expression

**Rule 1.** All non zero digits are significant.

Example : $x = 1234$ has four significant figures. Again $x = 189$ has only three significant figures.

**Rule 2.** All zeros occurring between two non zero digits are significant.

Example : $x = 1007$ has four significant figures. Again $x = 1.0809$ has five significant figures.

**Rule 3.** In a number less than one, all zeros to the right of decimal point and to the left of a non zero digit are not significant.

Example : $x = 0.0084$ has only two significant digits. Again, $x = 1.0084$ has five significant figures. This is on account of rule 2.

**Rule 4.** All zeros on the right of the last non zero digit in the decimal part are significant.

Example : $x = 0.00800$ has three significant figures 8, 0, 0. The zeros before 8 are not significant again 1.00 has three significant figures.

**Rule 5.** All zeros on the right of the non zero digit are not significant.

Example : $x = 1000$ has only one significant figure. Again $x = 378000$ has three significant figures.

**Rule 6.** All zeros on the right of the last non zero digit become significant, when they come from a measurement.

Example : Suppose distance between two stations is measured to be 3050 *m*. It has four significant figures. The same distance can be expressed as 3.050 *km* or $3.050 \times 10^5\ cm$. In all these expressions, number of significant figures continues to be four. Thus we conclude that change in the units of measurement of a quantity does not change the number of significant figures. By changing the position of the decimal point, the number of significant digits in the results does not change. Larger the number of significant figures obtained in a measurement, greater is the accuracy of the measurement. The reverse is also true.

(2) **Rounding off :** While rounding off measurements, we use the following rules by convention

**Rule 1.** If the digit to be dropped is less than 5, then the preceding digit is left unchanged.

Example : $x = 7.82$ is rounded off to 7.8, again $x = 3.94$ is rounded off to 3.9.

**Rule 2.** If the digit to be dropped is more than 5, then the preceding digit is raised by one.

Example : $x = 6.87$ is rounded off to 6.9, again $x = 12.78$ is rounded off to 12.8.

**Rule 3.** If the digit to be dropped is 5 followed by digits other than zero, then the preceding digit is raised by one.

Example : $x = 16.351$ is rounded off to 16.4, again $x = 6.758$ is rounded off to 6.8.

**Rule 4.** If digit to be dropped is 5 or 5 followed by zeros, then preceding digit is left unchanged, if it is even.

Example : $x = 3.250$ becomes 3.2 on rounding off, again $x = 12.650$ becomes 12.6 on rounding off.

**Rule 5.** If digit to be dropped is 5 or 5 followed by zeros, then the preceding digit is raised by one, if it is odd.

Example : x = 3.750 is rounded off to 3.8, again $x = 16.150$ is rounded off to 16.2.

(3) **Significant figure in calculation**

(i) Addition and subtraction : In addition and subtraction the following points should be remembered

(a) Every quantity should be changed into same unit.

(b) If a quantity is expressed in the power of 10, then all the quantities should be changed into power of 10.

(c) The result obtained after addition or subtraction, the number of figure should be equal to that of least, after decimal point.

(ii) **Multiplication and division**

(a) The number of significant figures will be same if any number is multiplied by a constant.

(b) The product or division of two significant figures, will contain the significant figures equal to that of least.

## Units for measurement

The chosen standard of measurement of a quantity which has essentially the same nature as that of the quantity is called the ***unit*** of the quantity. Following are the important types of system for unit,

(1) **C.G.S. System :** Length (*centimetre*), Mass (*gram*), Time (*second*)

(2) **M.K.S. System** : Length (*metre*), Mass (*kilogram*), Time (*second*)

(3) **F.P.S. System** : Length (*foot*), Mass (*pound*), Time (*second*)

(4) **S.I. System :** The 11th general conference of weights and measures (October 1960) adopted *International system of units*, popularly known as the *SI units*. The SI has *seven basic units* from which all other units are derived called *derived units*. The standard prefixes which helps to reduce the basic units are now widely used.

***Dimensional analysis*** **:** The seven basic quantities lead to a number of derived quantities such as pressure, volume, force, density, speed etc. The units for such quantities can be obtained by defining the derived quantity in terms of the base quantities using the base units. For example, speed (velocity) is expressed in distance/time. So the unit is $m/s$ or $ms^{-1}$. The unit of force $(\text{mass} \times \text{acceleration})$ is $kg\ ms^{-2}$ and the unit for acceleration is $ms^{-2}$.

**Table 1.1 Seven basic S.I. units**

| Length | Mass | Time | Temperature | Electric Current | Luminous Intensity | Amount of substance |
|---|---|---|---|---|---|---|
| metre (*m*) | Kilogram (*kg*) | Second (*s*) | Kelvin (*K*) | Ampere (*A*) | Candela (*Cd*) | Mole (*mol*) |

**Table 1.2 Derived Units**

| Physical quantity | Unit | Symbol |
|---|---|---|
| Area | square metre | $m^2$ |
| Volume | cubic metre | $m^3$ |
| Velocity | metre per second | $ms^{-1}$ |
| Acceleration | metre per second square | $ms^{-2}$ |
| Density | kilogram per cubic metre | $kg\ m^{-3}$ |
| Molar mass | kilogram per mole | $kg\ mol^{-1}$ |
| Molar volume | cubic metre per mole | $m^3\ mol^{-1}$ |
| Molar concentration | mole per cubic metre | $mol\ m^{-3}$ |
| Force | newton (*N*) | $kg\ m\ s^{-2}$ |
| Pressure | pascal (*Pa*) | $N\ m^{-2}$ |
| Energy work | joule (*J*) | $kg\ m^2\ s^{-2}$, $Nm$ |

**Table 1.3 Standard prefixes use to reduce the basic units**

| Multiple | Prefix | Symbol | Submultiple | Prefix | Symbol |
|---|---|---|---|---|---|
| $10^{24}$ | yotta | Y | $10^{-1}$ | deci | d |
| $10^{21}$ | zetta | Z | $10^{-2}$ | centi | c |
| $10^{18}$ | exa | E | $10^{-3}$ | milli | m |
| $10^{15}$ | peta | P | $10^{-6}$ | micro | μ |
| $10^{12}$ | tera | T | $10^{-9}$ | nano | n |

| | | | | | |
|---|---|---|---|---|---|
| $10^9$ | giga | G | $10^{-12}$ | pico | p |
| $10^6$ | mega | M | $10^{-15}$ | femto | f |
| $10^3$ | kilo | k | $10^{-18}$ | atto | a |
| $10^2$ | hecto | h | $10^{-21}$ | zeto | z |
| $10^1$ | deca | da | $10^{-24}$ | yocto | y |

**Table 1.4 Conversion factors**

| | | | |
|---|---|---|---|
| 1 m = 39.37 inch | 1 cal = 4.184 J | 1 e.s.u. = $3.3356 \times 10^{-10}$ C | 1 mole of a gas = 22.4 L at STP |
| 1 inch = 2.54 cm | 1 eV = $1.602 \times 10^{-19}$ J | 1 dyne = $10^{-5}$ N | 1 mole a substance = $N_0$ molecules |
| 1 litre = 1000 mL | 1 eV/atom =96.5 kJ $mol^{-1}$ | 1 atm = 101325 Pa | 1 g atom = $N_0$ atoms |
| 1 gallon (US) = 3.79 L | 1 amu = 931.5016 MeV | 1 bar = $1 \times 10^5$ N $m^{-2}$ | t (°F) = 9/5 t (°C) + 32 |
| 1 lb = 453.59237 g | 1 kilo watt hour = 3600 kJ | 1 litre atm = 101.3 J | 1 g $cm^{-3}$ = 1000 kg $m^{-3}$ |
| 1 newton =1 kg m $s^{-2}$ | 1 horse power = 746 watt | 1 year = $3.1536 \times 10^7$ s | 1Å = $10^{-10}$m |
| 1 J = 1 Nm =1 kg $m^2$ $s^{-2}$ | 1 joule = $10^7$ erg | 1 debye (D) = $1 \times 10^{-18}$ esu cm | 1nm = $10^{-9}$ m |

## Laws of chemical combination

Various chemical reactions take place according to the certain laws, known as the *Laws of chemical combination.*

(1) **Law of conservation of mass :** *It was proposed by Lavoisier and verified by Landolt.* According to this law, *Matter is neither created nor destroyed in the course of chemical reaction though it may change from one form to other.* The total mass of materials after a chemical reaction is same as the total mass before reaction.

(2) **Law of constant or definite proportion :** *It was proposed by Proust.* According to this law, *A pure chemical compound always contains the same elements combined together in the fixed ratio of their weights whatever its methods of preparation may be.*

(3) **Law of multiple proportion :** *It was proposed by Dalton and verified by Berzelius.* According to this law, *When two elements A and B combine to form more than one chemical compounds then different weights of A, which combine with a fixed weight of B, are in proportion of simple whole numbers.*

(4) **Law of equivalent proportion or law of reciprocal proportion :** *It was proposed by Ritcher.* According to this law, The weights of the two or more elements which separately react with same weight of a third element are also the weights of these elements which react with each other or in simple multiple of them.

(5) **Gay-Lussac's law :** It was proposed by Gay–Lussac and is applicable only for gases. According to this law, When gases combine, they do so in volumes, which bear a simple ratio to each other and also to the product formed provided all gases are measured under similar conditions. The Gay-Lussac's law, was based on experimental observation.

## Important hypothesis

(1) **Atomic hypothesis** : Keeping in view various law of chemical combinations, a theoretical proof for the validity of different laws was given by John Dalton in the form of hypothesis called **Dalton's atomic hypothesis**. Postulates of Dalton's hypothesis is as followes,

(i) Each element is composed of extremely small particles called **atoms** which can take part in chemical combination.

(ii) All atoms of a given element are identical *i.e.,* atoms of a particular element are all alike but differ from atoms of other element.

(iii) Atoms of different elements possess different properties (including different masses).

(iv) Atoms are indestructible *i.e.,* atoms are neither created nor destroyed in chemical reactions.

(v) Atoms of elements take part to form molecules *i.e.,* compounds are formed when atoms of more than one element combine.

(vi) In a given compound, the relative number and kinds of atoms are constant.

(2) **Modern atomic hypothesis** : The main modifications made in Dalton's hypothesis as a result of new discoveries about atoms are,

(i) Atom is no longer considered to be indivisible.

(ii) Atoms of the same element may have different atomic weights. *e.g.,* isotopes of oxygen $O^{16}$, $O^{17}$, and $O^{18}$.

(iii) Atoms of different element may have same atomic weights. *e.g.,* isobars $Ca^{40}$ and $Ar^{40}$.

(iv) *Atom is no longer indestructible. In many nuclear reactions, a certain mass of the nucleus is converted into energy in the form of $\alpha$, $\beta$ and $\gamma$ rays.*

(v) Atoms may not always combine in simple whole number ratios. *e.g.,* in sucrose $(C_{12}H_{22}O_{11})$, the elements carbon, hydrogen and oxygen are present in the ratio of 12 : 22 : 11 and the ratio is not a simple whole number ratio.

(3) **Berzelius hypothesis :** "Equal volumes of all gases contain equal number of atoms under same conditions of temperature and pressure". When applied to law of combining volumes, this hypothesis predicts that atoms are divisible and hence it is contrary to Dalton's hypothesis.

(4) **Avogadro's hypothesis :** "Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules." Avogadro hypothesis has been found to explain as follows,

(i) Provides a method to determine the atomic weight of gaseous elements.

(ii) *Provides a relationship between vapour density (V.D.) and molecular masses of substances.*

$$\text{Molecular mass} = 2 \times \text{vapour density}$$

(iii) *It helps in the determination of mass of fixed volume of a particular gas.*

Mass of $1\,ml$ gas = V.D. × 0.0000897 *gm.*

(iv) *It also helps in the determination of molar volume at N.T.P.*

$\because$ V.D. × 0.0000897 *gm.* gas has volume = $1\,ml$

$\therefore$ 2 × V.D.(i.e., molecular mass) *gm.* has volume $= \dfrac{1 \times 2 \times V.D.}{V.D. \times 0.0000897}\,ml = 22400\,ml$

$\therefore$ Molar mass of a gas or its 1 mole occupies 22.4 *L* volume at S.T.P.

(v) It helps in determination of molecular formulae of gases and is very useful in gas analysis. By knowing the molecular volumes of reactants and products of reaction, molecular composition can be determined easily.

## Atomic, Molecular and Equivalent masses

(1) **Atomic mass :** It is the average relative mass of atom of element as compared with an atom of carbon –12 isotope taken as 12.

$$\text{Atomic mass} = \frac{\text{Average mass of an atom}}{1/12 \times \text{Mass of an atom of } C^{12}}$$

**Average atomic mass :** If an elements exists in two isotopes having atomic masses '*a*' and '*b*' in the ratio *m* : *n*, then average atomic mass $= \dfrac{(m \times a) + (n \times b)}{m + n}$. Since the atomic mass is a ratio, it has no units and is expressed in *amu*, 1 *amu* = $1.66 \times 10^{-24}\,g$. One atomic mass unit (amu) is equal to $\dfrac{1}{12}th$ of the mass of an atom of carbon-12 isotope.

**Gram atomic mass (GAM) :** Atomic mass of an element expressed in grams is called *Gram atomic mass or gram atom or mole atom.*

(i) Number of gram atoms = $\dfrac{\text{Mass of an element}}{\text{GAM}}$

(ii) Mass of an element in *gm.* = No. of *gm.* atom × GAM

(iii) Number of atoms in 1 GAM = 6.02 × $10^{23}$

$\therefore$ Number of atoms in a given substance

= No. of GAM × 6.02 × $10^{23}$ = $\dfrac{\text{Mass}}{\text{GAM}}$ × 6.02 × $10^{23}$

(iv) Number of atoms in 1*gm* of element = $\dfrac{6.02 \times 10^{23}}{\text{Atomic mass}}$

(v) Mass of one atom of the element (in *gm.*) $= \dfrac{\text{GAM}}{6.02 \times 10^{23}}$

**Methods of determination of atomic mass**

(i) **Dulong and Pettit's method :** According to Dulong and Pettit's law

Atomic mass × Specific heat = 6.4 (*approx.*)

Atomic mass (*approx.*) = $\dfrac{6.4}{\text{Specific heat (in cals.)}}$

*This law is applicable to solid elements only except Be, B, C and Si because their specific heat is variable with temperature.*

Atomic mass = Equivalent mass × Valency

$$\text{Valency} = \frac{\text{Approximate atomic mass}}{\text{Equivalent mass}}$$

(ii) **Vapour density method :** It is suitable for elements whose chlorides are volatile.

Valency of the element = $\dfrac{\text{Molecular mass of chloride}}{\text{Equivalent mass of chloride}}$

$= \dfrac{2 \times \text{Vapour density of chloride}}{\text{Equivalent mass of metal} + 35.5}$

Atomic mass = Equivalent mass of metal × Valency

(iii) **Specific heat method :** It is suitable only for gases. The two types of specific heats of gases are $C_p$ (at constant pressure) and $C_v$ (at constant volume). *Their ratio is known as $\gamma$ whose value is constant (1.66 for monoatomic, 1.40 for diatomic and 1.33 for triatomic gases).*

$$\text{Atomic mass of a gaseous element} = \frac{\text{Molecular mass}}{\text{Atomicity}}$$

(iv) **Isomorphism method :** It is based on law of isomorphism which states that compounds having identical crystal structure have similar constitution and chemical formulae.

Example : $K_2SO_4$, $K_2CrO_4$ and $K_2SeO_4$

(valency of *S, Cr, Se* = 6),

$ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$

(valency of *Zn, Mg, Fe* = 2).

(2) **Molecular mass :** Molecular mass of a molecule, of an element or a compound may be defined as a *number which indicates how many times heavier is a molecule of that element or compound as compared with $\dfrac{1}{12}$ of the mass of an atom of carbon*–12. Molecular mass is a ratio and hence has no units. It is expressed in *a.m.u.*

$$\text{Molecular mass} = \frac{\text{Mass of one molecule of the substance}}{1/12 \times \text{Mass of one atom of C - 12}}$$

Actual mass of one molecule = Mol. mass $\times 1.66 \times 10^{-24}$ *gm.*

Molecular mass of a substances is the additive property and can be calculated by adding the atomic masses present in one molecule.

**Gram molecular mass (GMM) and Gram molar volume :** Molecular mass of an element or compound when expressed in *gm.* is called its gram molecular mass, gram molecule or mole molecule.

Number of *gm* molecules = $\dfrac{\text{Mass of substances}}{\text{GMM}}$

Mass of substances in *gm* = No. of *gm.* molecules × GMM

Volume occupied by one mole of any gas at STP is called **Gram molar volume**. The value of gram molar volume is 22.4 *litres. Volume of 1 mole of any gas at STP = 22.4 litres*

**Expression for mass and density**

Mass of $11.2L$ of any gas at STP = V.D. of that gas in *gm.*

Density of a gas at NTP = $\dfrac{\text{Mol. mass in } gm.}{22400\,ml}$

**Important generalisations**

Number of atoms in a substance

$= \text{Number of GMM} \times 6.02 \times 10^{23} \times \text{Atomicity}$

Number of electrons in given substance

$= \text{Number of GMM} \times 6.02 \times 10^{23} \times \text{Number of electrons}$

### Methods of determination of molecular mass

Following methods are used to determine molecular mass,

(i) **Diffusion method** (For gases) **:** The ratio of rates of diffusion of two gases is inversely proportional to the square root of their molecular masses.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

(ii) **Vapour density method** (For gases only) : Mass of a fixed volume of the vapour is compared with the mass of the same volume of hydrogen under same conditions. The ratio of these masses is called **Vapour density** or **Relative density**.

$$\text{Molecular mass} = 2 \times \text{Vapour desity}$$

(iii) **Victor Meyer method** (For volatile liquids or solids)

*It is based on Dalton's law of partial pressure and Avogadro's hypothesis (gram molar volume).*

22400 *ml* of vapours of a substance = Molecular mass of that substance

(iv) **Colligative property method** (For non-volatile solids)

Discussed in colligative properties of solutions.

### Average atomic mass and molecular mass

$\overline{A}$ (Average atomic mass) $= \dfrac{\Sigma A_i X_i}{\Sigma X_{\text{total}}}$

$\overline{M}$ (Average molecular mass) $= \dfrac{\Sigma M_i X_i}{\Sigma X_{\text{total}}}$

Where $A_1, A_2, A_3.....$ are atomic mass of species 1, 2, 3,.... etc. with % ratio as $X_1, X_2, X_3.....$ etc. Similar terms are for molecular masses.

(3) **Equivalent mass :** The number of parts by mass of a substance that combines with or displaces 1.008 parts by mass of hydrogen or 8.0 parts of oxygen or 35.5 parts of chlorine is called its *equivalent mass* (EM). On the other hand *quantity of a substance in grams numerically equal to its equivalent mass is called its gram equivalent mass (GEM) or gram equivalent.*

$$\text{Number of GEM} = \frac{\text{Mass of the substance in grams}}{\text{GEM of the substance}}$$

### Expressions for equivalent mass (EM)

(i) EM of an element $= \dfrac{\text{Atomic mass}}{\text{Valency}}$

(ii) EM of an acid $= \dfrac{\text{Molecular mass}}{\text{Basicity}}$

(*Basicity of acid is the number of replaceable hydrogen atoms in one molecule of the acid*).

(iii) EM of a base $= \dfrac{\text{Molecular mass}}{\text{Acidity}}$

*(Acidity of a base is the number of replaceable* $-OH$ *groups in one molecule of the base).*

(iv) EM of a salt $= \dfrac{\text{Formula mass}}{\text{Total positive or negative charge}}$

(v) EM of an oxidising agent

$$= \frac{\text{Formula mass}}{\text{Number of electrons gained per molecule or Total change in O.N.}}$$

Equivalent mass of common oxidising agent changes with the medium of the reaction.

### Methods of determination of equivalent mass

(i) **Hydrogen displacement method :** The mass of metal which displaces 11200 *ml* of hydrogen at NTP from an acid, alkali or alcohol is the equivalent mass of the metal.

(a) Equivalent mass of metal

$$= \frac{\text{Mass of metal}}{\text{Mass of H}_2\text{ displaced}} \times 1.008 = \frac{W}{M} \times 1.008 g$$

(b) Equivalent mass of metal

$$= \frac{\text{Mass of metal}}{\text{Vol.(ml) of H}_2\text{ displaced at STP}} \times 11200 = \frac{W}{V} \times 11200$$

*This method is useful for metals which can displace hydrogen from acids or can combine with hydrogen* $(Mg, Zn, Na, Ca\ \text{etc.})$

(ii) **Oxide formation method :** The mass of the element which combines with 8 grams of oxygen is the equivalent mass of the element.

(a) Equivalent mass of metal $= \dfrac{\text{Mass of metal}}{\text{Mass of oxygen}} \times 8$

(b) Equivalent mass of metal

$$= \frac{\text{Mass of metal}}{\text{Vol. of } O_2 \text{ at S.T.P. in ml}} \times 5600$$

(iii) **Chloride formation method :** The mass of an element which reacts with 35.5 *gm.* of chlorine is the equivalent mass of that element.

(a) Equivalent mass of metal $= \dfrac{\text{Mass of metal}}{\text{Mass of chlorine}} \times 35.5$

(b) Equivalent mass of metal

$$= \frac{\text{Mass of metal}}{\text{Vol. of } Cl_2 \text{ (in ml.) at STP}} \times 11200$$

(iv) **Neutralisation method :** (For acids and bases).

$$\text{Equivalent mass of acid (or base)} = \frac{W}{V \times N}$$

Where ,

*W* = Mass of acid or base in *gm.,*

*V* = Vol. of base or acid in litre required for neutralisation

*N* is Normality of base or acid

(v) **Metal displacement method :** *It is based on the fact that one gm. equivalent of a more electropositive metal displaces one gm equivalent of a less electropositive metal from its salt solution.*

$$\frac{\text{Mass of metal added}}{\text{Mass of metal displaced}} = \frac{\text{Eq. mass of metal added}}{\text{Eq. mass of metal displaced}}$$

$$\frac{W_1}{W_2}=\frac{E_1}{E_2}$$

(vi) **Electrolytic method :** The quantity of substance that reacts at electrode when 1 faraday of electricity is passed is equal to its gram equivalent mass.

Gram equivalent mass = Electrochemical equivalent × 96500

The ratio of masses of two metals deposited by the same quantity of electricity will be in the ratio of their equivalent masses.

$$\frac{W_1}{W_2}=\frac{E_1}{E_2}$$

(vii) **Double decomposition method**

$$AB + CD \longrightarrow AD \downarrow + CB$$

$$\frac{\text{Mass of compound } AB}{\text{Mass of compound } AD}=\frac{\text{Eq. mass of } A+\text{Eq. mass of } B}{\text{Eq. mass of } A+\text{Eq. mass of } D}$$

or $$\frac{\text{Mass of salt taken } (W_1)}{\text{Mass of ppt. obtained } (\text{W}_2)}=\frac{\text{Eq. mass of salt} (E_1)}{\text{Eq. mass of salt in ppt.} (E_2)}$$

(viii) **Conversion method :** When one compound of a metal is converted to another compound of the same metal, then

$$\frac{\text{Mass of compound I} (W_1)}{\text{Mass of compound II} (W_2)}=\frac{E+\text{Eq. mass of radical I}}{E+\text{Eq. mass of radical II}}$$

($E$ = Eq. mass of the metal)

(ix) **Volatile chloride method**

Valency of metal $=\dfrac{2\times \text{V.D. of Chloride}}{\text{Eq. mass of metal chloride}}=\dfrac{2\times \text{V.D.}}{\text{E}+35.5}$

$$\therefore\ E=\frac{2\times \text{V.D. of Chloride}}{\text{Valency}}-35.5$$

(x) **Silver salt method** (For organic acids)

Equivalent Mass of acid $=\dfrac{108\times \text{Mass of silver salt}}{\text{Mass of } Ag \text{ metal}}-107$

Molecular mass of acid = Equivalent mass of acid × Basicity

## The mole concept

One mole of any substance contains a fixed number $(6.022\times 10^{23})$ of any type of particles (atoms or molecules or ions) and has a mass equal to the atomic or molecular weight, in grams. Thus it is correct to refer to a mole of helium, a mole of electrons, or a mole of $Na^+$, meaning respectively *Avogadro's number* of atoms, electrons or ions.

$$\therefore\ \text{Number of moles } =\frac{\text{Weight(grams)}}{\text{Weight of one mole (g/mole)}}$$

$$=\frac{\text{Weight}}{\text{Atomic or molecular weight}}$$

## Percentage composition & Molecular formula

(1) **Percentage composition of a compound**

Percentage composition of the compound is the relative mass of each of the constituent element in 100 parts of it. If the molecular mass of a compound is $M$ and $B$ is the mass of an element in the molecule, then

$$\text{Percentage of element }=\frac{\text{Mass of element}}{\text{Molecular mass}}\times 100=\frac{X}{M}\times 100$$

(2) **Determination of empirical formula :** The empirical formula of a molecule is determined using the % of elements present in it. Following method is adopted.

| Element | % | Relative no. of atoms = %/at. wt. | Simplest Ratio | Empirical Formula |
|---|---|---|---|---|

**Relative no. of atoms :** Divide the percentage of each element present in compound by its at. weight. This gives the relative no. of atoms of element in molecule.

**Simplest ratio :** Find out lowest value of relative no. of atoms and divide each value of relative no. of atoms by this value to estimate simplest ratio of elements.

It the simplest ratio obtained are not complete integers, multiply them by a common factor to get integer values of simplest ratio.

**Empirical formula :** Write all constituent atoms with their respective no. of atoms derived in simplest ratio. This gives empirical formula of compound.

**Molecular formula :** Molecular formula $=n\times$ empirical formula where '$n$' is the whole no. obtained by

$$n=\frac{\text{molecular weight of compound}}{\text{empirical formula weight of compound}}$$

## Chemical stoichiometry

Stoichiometry (pronounced "stoy-key om-e-tree") is the calculation of the quantities of reactants and products involved in a chemical reaction. That means quantitative calculations of chemical composition and reaction are referred to as stoichiometry.

Basically, this topic involves two types of calculations.

(a) Simple calculations (gravimetric analysis) and

(b) More complex calculations involving concentration and volume of solutions (volumetric analysis).

There is no borderline, which can distinguish the set of laws applicable to gravimetric and volumetric analysis. All the laws used in one are equally applicable to the other i.e., mole as well as equivalent concept. But in actual practise, the problems on gravimetric involves simpler reactions, thus mole concept is convenient to apply while volumetric reactions being complex and unknown (unknown simple means that it is not known to you, as it's not possible for you to remember all possible reactions), equivalent concept is easier to apply as it does not require the knowledge of balanced equation.

(1) **Gravimetric analysis :** In gravimetric analysis we relate the weights of two substances or a weight of a substance with a volume of a gas or volumes of two or more gases.

**Problems Involving Mass-Mass Relationship**

Proceed for solving such problems according to the following instructions,

(i) Write down the balanced equation to represent the chemical change.

(ii) Write the number of moles below the formula of the reactants and products. Also write the relative weights of the reactants and products (calculated from the respective molecular formula), below the respective formula.

(iii) Apply the unitary method to calculate the unknown factor (s).

**Problems Involving Mass-Volume Relationship**

For solving problems involving mass-volume relationship, proceed according to the following instructions,

(i) Write down the relevant balanced chemical equations (s).

(ii) Write the weights of various solid reactants and products.

(iii) Gases are usually expressed in terms of volumes. In case the volume of the gas is measured at room temperature and pressure (or under conditions other than N.T.P.), convert it into N.T.P. by applying gas equation.

(iv) Volume of a gas at any temperature and pressure can be converted into its weight and vice-versa with the help of the relation, by $PV = \frac{g}{M} \times RT$ where $g$ is weight of gas, $M$ is mole. wt. of gas, $R$ is gas constant.

Calculate the unknown factor by unitary method.

**Problems Based on Volume-Volume Relationship**

Such problems can be solved according to chemical equation as,

(i) Write down the relevant balanced chemical equation.

(ii) Write down the volume of reactants and products below the formula to each reactant and product with the help of the fact that $1 gm$ molecule of every gaseous substance occupies 22.4 litres at N.T.P.

(iii) In case volume of the gas is measured under particular (or room) temperature, convert it to volume at NTP by using ideal gas equation.

Take the help of Avogadro's hypothesis "*Equal volume of different gases under the similar conditions of temperature and pressure contain the same number of molecules".*

(2) **Volumetric analysis :** It is a method which involves quantitative determination of the amount of any substance present in a solution through volume measurements. For the analysis a standard solution is required. (A solution which contains a known weight of the solute present in known volume of the solution is known as standard solution.)

To determine the strength of unknown solution with the help of known (standard) solution is known as titration. Different types of titrations are possible which are summerised as follows,

(i) *Redox titrations* : To determine the strength of oxidising agents or reducing agents by titration with the help of standard solution of reducing agents or oxidising agents.

Examples:

$$\begin{array}{c}
K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O] \\
[2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3 \\
\hline
6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 7H_2O
\end{array}$$

$$\begin{array}{c}
2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\
[2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 5 \\
\hline
10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O
\end{array}$$

Similarly with $H_2C_2O_4$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow$$

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \text{ etc.}$$

(ii) *Acid-base titrations* : To determine the strength of acid or base with the help of standard solution of base or acid.

Example: $NaOH + HCl \rightarrow NaCl + H_2O$

and $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$ etc.

(iii) *Iodimetric titrations* : This is a simple titration involving free iodine. This involves the titration of iodine solution with known sodium thiosulphate solution whose normality is $N$. Let the volume of sodium thiosulphate is $V ml$.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$n = 2$, $n = 1$

Equivalents of $I_2$ = Equivalent of $Na_2S_2O_3$

$\therefore$ Equivalents of $I_2 = N \times V \times 10^{-3}$

Moles of $I_2 = \frac{N \times V \times 10^{-3}}{2}$

Mass of free $I_2$ in the solution $= \left[\frac{N \times V \times 10^{-3}}{2} \times 254\right] g$.

(iv) *Iodometric titrations* : This is an indirect method of estimation of iodine. An oxidising agent is made to react with excess of solid $KI$. The oxidising agent oxidises $I^-$ to $I_2$. This iodine is then made to react with $Na_2S_2O_3$ solution.

Oxidising Agent

$$(A) + KI \rightarrow I_2 \xrightarrow{2Na_2S_2O_3} 2NaI + Na_2S_4O_6$$

Let the normality of $Na_2S_2O_3$ solution is $N$ and the volume of thiosulphate consumed to $V ml$.

Equivalent of $A$ = Equivalent of $I_2$ = Equivalents of $Na_2S_2O_3$

Equivalents of $I_2$ liberated from $KI = N \times V \times 10^{-3}$

Moles of $I_2$ liberated from $KI = \frac{N \times V \times 10^{-3}}{2}$

Mass of $I_2$ liberated from $KI = \left[\frac{N \times V \times 10^{-3}}{2} \times 254\right] g$.

(v) *Precipitation titrations* : To determine the anions like $CN^-, AsO_3^{3-}, PO_4^{3-}, X^-$ etc, by precipitating with $AgNO_3$ provides examples of precipitation titrations.

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$

$$KSCN + AgNO_3 \rightarrow AgSCN \downarrow + KNO_3$$

**End point and equivalence point :** *The point at which titration is stopped is known as end point, while the point at which the acid and base* (*or oxidising and reducing agents*) *have been added in equivalent quantities is known as equivalence point.* Since the purpose of the indicator is to stop the titration close to the point at which the reacting substances were added in equivalent quantities, it is important that the equivalent point and the end point be as close as possible.

**Normal solution :** *A solution containing one gram equivalent weight of the solute dissolved per litre is called a normal solution*; *e.g.* when 40 *g* of *NaOH* are present in one litre of *NaOH* solution, the solution is known as normal (*N*) solution of *NaOH*. Similarly, a solution containing a fraction of gram equivalent weight of the solute dissolved per litre is known as subnormal solution. For example, a solution of *NaOH* containing 20 *g* (1/2 of *g* eq. wt.) of *NaOH* dissolved per litre is a sub-normal solution. It is written as *N*/2 or 0.5 *N* solution.

**Formula used in solving numerical problems on volumetric analysis**

(1) Strength of solution = Amount of substance in $g\ litre^{-1}$

(2) Strength of solution = Amount of substance in *g moles* $litre^{-1}$

(3) Strength of solution = Normality × Eq. wt. of the solute

= molarity × Mol. wt. of solute

(4) $\text{Molarity} = \dfrac{\text{Moles of solute}}{\text{Volume in litre}}$

(5) $\text{Number of moles} = \dfrac{\text{Wt. in } gm}{\text{Mol. wt.}} = M \times V_{(inl)}$

$= \dfrac{\text{Volume in litres}}{22.4}$ at NTP (only for gases)

(6) Number of millimoles $= \dfrac{\text{Wt. in } gm \times 1000}{\text{mol. wt.}}$

$= \text{Molarity} \times \text{Volume in } ml.$

(7) Number of equivalents

$= \dfrac{\text{Wt. in } gm}{\text{Eq. wt.}} = x \times \text{No. of moles} \times \text{Normality} \times \text{Volume in litre}$

(8) Number of milliequivalents (meq.)

$= \dfrac{\text{Wt. in } gm \times 1000}{\text{Eq. wt.}} = \text{normality} \times \text{Volume in } ml.$

(9) Normality $= x \times \text{No. of millimoles}$

$= x \times \text{Molarity} = \dfrac{\text{Strength in } gm\ litre^{-1}}{\text{Eq. wt.}}$

where $x = \dfrac{\text{Mol. wt.}}{\text{Eq. wt.}}$, *x* = valency or change in oxi. Number.

(10) Normality formula, $N_1V_1 = N_2V_2$

(11) % by weight $= \dfrac{\text{Wt. of solvent}}{\text{Wt. of solution}} \times 100$

(12) % by volume $= \dfrac{\text{Wt. of solvent}}{\text{Vol. of solution}} \times 100$

(13) % by strength $= \dfrac{\text{Vol. of solvent}}{\text{Vol. of solution}} \times 100$

(14) Specific gravity

$= \dfrac{\text{Wt. of solution}}{\text{Vol. of solution}} = \text{Wt. of } 1\ ml. \text{ of solution}$

(15) Formality $= \dfrac{\text{Wt. of ionic solute}}{\text{Formula Wt. of solute} \times V_{inl}}$

(16) Mol. Wt. = V.D × 2 (For gases only)

## Limiting reagent or reactant

In many situations, an excess of one or more substance is available for chemical reaction. Some of these excess substances will therefore be left over when the reaction is complete; the reaction stops immediately as soon as one of the reactant is totally consumed.

*The substance that is totally consumed in a reaction is called limiting reagent because it determines or limits the amount of product. The other reactant present in excess are called as excess reagents.*

Let us consider a chemical reaction which is initiated by passing a spark through a reaction vessel containing 10 mole of $H_2$ and 7 mole of $O_2$.

$$2\ H_2\,(g) + O_2\,(g) \longrightarrow 2\ H_2O\,(v)$$

| | | | |
|---|---|---|---|
| Moles before reaction | 10 | 7 | 0 |
| Moles after reaction | 0 | 2 | 10 |

The reaction stops only after consumption of 5 moles of $O_2$ as no further amount of $H_2$ is left to react with unreacted $O_2$. Thus $H_2$ is a *limiting reagent* in this reaction.

## Tips & Tricks

- Law of conservation of mass does not hold good for nuclear reactions.
- Law of definite proportions do not hold good for non-stoichiometric compounds e.g., Wusitite $Fe_{0.95}O$.
- Law of definite proportions, law of multiple proportions and law of reciprocal proportions do not hold good when same compounds is obtained by using different isotopes of te same element e.g. $H_2O$ and $D_2O$.
- The term atom was introduced by Ostwald and the term molecule was introduced by Avogadro.
- The concept of element was introduced by Robert Boyle.
- The number of atoms present in a molecule of a gaseous element is called Atomicity.
- Both atomic mass and molecular mass are just rations and hence have no units.
- 1 mol of $H_2O$ # 22400 *cc* of $H_2O$ (because it is a liquid). Instead,

  1 mol of $H_2O$ = 18*cc* of $H_2O$

  (because density of $H_2O$ = 1 *g/cc*)
- 1 *M* $H_2SO_4$ = 2*N* $H_2SO_4$.
- Minimum molecular mass of a macromolecular substance can be calculated by analysing it for one of the minar components. Minimum molecular mass is obtained when it is supposed that one molecule of the macromolecule contains only one atom or molecule of the minor component.

  Minimum molecular mass

$$= \frac{\text{Atomic/molecular mass of minor component}}{\text{Mass of minor component per gram of macromolecule}}$$