## Knowledge... Everywhere

## Chemistry

## Atoms, Molecules \& Chemical Arithmetic

## Table of Content

1. Significant figures.
2. Units for measurement.
3. Separation of mixtures or Purification of an impure substance.
4. Laws of chemical combination.
5. Important hypothesis.
6. Atomic, Molecular and Equivalent masses.
7. The mole concept.
8. Percentage composition \& Molecular formula.
9. Chemical equations and its balancing.
10. Chemical stoichiometry.
11. Limiting reagent or reactant.

Chemistry is basically an experimental science. In it we study physical and chemical properties of substance and measure it up to 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.

## 1. 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 zeroes 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 zeroes 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 zeroes 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 zeroes before 8 are not significant again 1.00 has three significant figures.

Rule 5. All zeroes 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 zeroes on the right of the last non zero digit become significant, when they come from a measurement.

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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 ${ }^{3.050 \times 10^{5} \mathrm{~cm}}$. 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 zeroes, 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 zeroes, 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.

## 2. 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 (centimeter), Mass (gram), Time (second)
(2) M.K.S. System : Length (meter), 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 $\mathrm{m} / \mathrm{s}$ or $\mathrm{ms}^{-1}$. The unit of force (mass $\times$ acceleration) is $\mathrm{kg} \mathrm{ms}^{-2}$ and the unit for acceleration is $m s^{-2}$.

Seven basic SI units

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



Derived Units

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

Standard prefixes use to reduce the basic units

| Multiple | Prefix | Symbol | Submultiple | Prefix | Symbol |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 1024 | yotta | Y | $10-1$ | deci | d |
| 1021 | zetta | Z | $10-2$ | centi | c |
| 1018 | exa | E | $10-3$ | milli | m |
| 1015 | peta | P | $10-6$ | micro | M |
| 1012 | tera | T | $10-9$ | nano | n |
| 109 | giga | G | $10-12$ | pico | p |
| 106 | mega | M | $10-15$ | femto | f |
| 103 | kilo | k | $10-18$ | atto | a |
| 102 | hecto | h | $10-21$ | zeto | z |
| 101 | deca | da | $10-24$ | yocto | y |



Conversion factors

| $1 \mathrm{~m}=39.37 \mathrm{inch}$ | $1 \mathrm{cal}=4.184 \mathrm{~J}$ | 1 e.s.u. $=3.3356 \times 10-10$ <br> C | 1 mole of a gas $=22.4 \mathrm{~L}$ at STP |
| :--- | :--- | :--- | :--- |
| $1 \mathrm{inch}=2.54 \mathrm{~cm}$ | $1 \mathrm{eV}=1.602 \times 10-19 \mathrm{~J}$ | 1 dyne $=10-5 \mathrm{~N}$ | 1 mole a substance $=\mathrm{N} 0$ <br> molecules |
| 1 litre $=1000 \mathrm{~mL}$ | $1 \mathrm{eV} /$ atom $=96.5 \mathrm{~kJ}$ <br> $\mathrm{~mol}-1$ | $1 \mathrm{~atm}=101325 \mathrm{~Pa}$ | 1 g atom $=\mathrm{N} 0$ atoms |

## 3. Separation of mixtures or purification of an impure substance.

Each component of a mixture retains its own properties and thus a mixture can be separated into its components by taking advantages of the difference in their physical and chemical properties. The different methods which are employed to separate the constituents from a mixture to purify an impure sample of a substance are,
(1) Sedimentation : It is also called gravity separation. It is used for a mixture in which one component is a liquid and the other is insoluble solid heavier than the liquid. Example: Sand dispersed in water.
(2) Filtration: It is used for a mixture containing two components one of which is soluble in a particular solvent and the other is not. Example: (i) A mixture of salt and paper using water as solvent (ii) A mixture of sand and sulphur using carbon disulphide as solvent. (iii) A mixture of glass powder and sugar, using water as a solvent in which sugar dissolves but glass does not. (iv) A mixture of sand and sulphur, using carbon disulphide as the solvent in which sulphur dissolves but sand does not.

(3) Sublimation: It is used for a mixture containing a solid component, which sublimes on heating from non-volatile solids. Example: A mixture of sand + naphthalene or powdered glass + $\mathrm{NH}_{4} \mathrm{Cl}$ / camphor / iodine etc. can be separated by the method of sublimation because substances like naphthalene, $\mathrm{NH}_{4} \mathrm{Cl}$ , iodine, camphor etc. form sublimates whereas sand, glass etc. do not.
(4) Evaporation: It is used for a mixture in which one component is a non-volatile soluble salt and other is a liquid. Example: Sodium chloride dissolved in sea-water.
(5) Crystallization: It is a most common method for a mixture containing solid components and based upon the differences in the solubilities of the components of the mixture into a solvent. For separation, a suitable solvent is first selected. It is of two types:
(i) Simple crystallization: It is applicable when there is a large difference in the solubilities of different components of a mixture.
(ii) Fractional crystallization: It is applicable when there is a small difference in the solubilities of different components of a mixture in the same solvent. Example: $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ and KCl . Here $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ is less soluble in water and hence crystallizes first. A series of repeated crystallization separates the two components in pure form.
(6) Distillation: It is the most important method for purifying the liquids. It involves the conversion of a liquid to its vapors on heating (vaporization) and then cooling the vapors back into the liquid (condensation). It can be used to separate, (i) A solution of a solid in a liquid. e.g., aqueous copper sulphate solution. (ii) A solution of two liquids whose boiling points are different. Several methods of distillation are employed.
(i) Simple distillation: It is used only for such liquids which boil without decomposition at atmospheric pressure and contain non-volatile impurities. Example: (a) Pure water from saline water. (b) Benzene from toluene.
(ii) Fractional distillation: It is used for the separation and purification of a mixture of two or more miscible liquids having different boiling points. The liquid having low boiling point vaporizes first, gets condensed and is collected in the receiver. The temperature is then raised to the boiling point of second so that the second liquid vaporizes and is collected in other receiver. If two liquids present in a mixture have their boiling points closer to each other, a fractionating column is used. Example: (a) Crude petroleum is separated into many useful products such as lubricating oil, diesel oil, kerosene and petrol by fractional distillation. (b) A mixture of acetone and methyl alcohol.

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(iii) Vacuum distillation or distillation under reduced pressure: It is used for such liquids which decompose on heating to their boiling points. At reduced pressure, the boiling point of liquid is also reduced.

Example: Glycerol is distilled under pressure as it decomposes on heating to its boiling point.
(iv) Steam distillation: It is used for liquids which are partially miscible with water, volatile in steam. e.g., aniline, oils etc. are purified by steam distillation. The principle involved is of reduced pressure distillation. If Pw and PI are vapor pressures of water and liquid at distillation temperature, then $P_{w}+P_{l}=P=76 \mathrm{~cm}$ i.e., atmospheric pressure. Thus, a liquid boils at relatively low temperature than its boiling point in presence of steam.

Example: Some solids like naphthalene, o-nitrophenol which are steam volatile can be purified. Nitrobenzene, chlorobenzene, essential oils are also extracted or separated by this process
(7) Solvent extraction: It is used for the separation of a compound from its solution by shaking with a suitable solvent. The extraction follows Nernst distribution law. The solvent used must be insoluble with other phase in which compound is present as well as the compound should be more soluble in solvent. The extraction becomes more efficient if the given extracting liquid is used for more number of extractions with smaller amounts than using it once with all extracting liquid. Example: (i) Aqueous solution of benzoic acid by using benzene. (ii) Aqueous solution of Iodine by using chloroform or carbon tetrachloride. (iii) Flavor of tea from the tea leaves by boiling with water.
(8) Magnetic separation: It is used for a mixture in which one component is magnetic while the other is non-magnetic. Example: iron ore from the non-magnetic impurities.
(9) Chromatography: It is based on the differences in the rates at which different components of a mixture are absorbed on a suitable solvent. It is used in separation, isolation, purification and identification of a substance. It was proposed by a Russian botanist Tswett.
(10) Atmolysis: It is used for separation of the mixture of gases or vapors. It is based on the difference in their rates of diffusion through a porous substance. Example: $\mathrm{H}_{2}, \mathrm{SO}_{2}, \mathrm{CH}_{4}$ and $\mathrm{O}_{2}, U^{235} \& U^{238}$ in the form of their hexa-fluorides.
(11) Electrophoresis: It is based upon the differences in the electrical mobility of the different components of the mixture.

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(12) Ultracentrifugation: It is based upon the difference in sedimentation velocity of the components in a centrifugal field.

## 4. Laws of chemical combination.

Various chemical reactions take place according to the certain laws, known as the Laws of chemical combination. These are as follows,
(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.

Example: A reaction between $\mathrm{AgNO}_{3}$ solution and KI solution.

$$
\begin{aligned}
& \mathrm{AgNO}_{3(a q)}+\mathrm{KI}_{(a q)} \longrightarrow \mathrm{AgI}+\mathrm{NaNO}_{3_{(a q)}} \text { (Yellow ppt.) } \\
& \text { Mass of } \mathrm{AgNO}_{3_{(a q)}}+\text { Mass of } K I_{(a q)}=\text { Mass of the ppt.of } \mathrm{AgI}+\text { Mass of } \mathrm{NaNO}_{3(a q)}
\end{aligned}
$$

According to the modified statement of the law, the total sum of mass and energy of the system remains constant.
(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.

Example: $\mathrm{CO}_{2}$ can be formed by either of the following processes:
(i) By heating $\mathrm{CaCO}_{3}: \mathrm{CaCO}_{3} \xrightarrow{\Delta} \mathrm{CaO}+\mathrm{CO}_{2}$
(ii) By heating $\mathrm{NaHCO}_{3}: 2 \mathrm{NaHCO}_{3} \xrightarrow{\Delta} \mathrm{Na}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
$\mathrm{CO}_{2}$ Is collected separately as a product of each reaction and the analysis of $\mathrm{CO}_{2}$ of each collection reveals that it has the combination ratio of carbon and oxygen as $12: 32$ by weight.

(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.

Example: Nitrogen forms as many as five stable oxides. The analysis of these oxides $\left(\mathrm{N}_{2} \mathrm{O}, \mathrm{NO}, \mathrm{N}_{2} \mathrm{O}_{3}, \mathrm{~N}_{2} \mathrm{O}_{4}\right.$ and $\left.\mathrm{N}_{2} \mathrm{O}_{5}\right)$ reveals that for 28 gm . nitrogen, the weight of oxygen that combines is in the ratio 16:32:48:64:80 i.e., $1: 2: 3: 4: 5$ in $N_{2} \mathrm{O}, \mathrm{NO}, \mathrm{N}_{2} \mathrm{O}_{3}, \mathrm{~N}_{2} \mathrm{O}_{4}$ and $\mathrm{N}_{2} \mathrm{O}_{5}$ respectively.
(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.

Example: Formation of $\mathrm{H}_{2} \mathrm{~S}, \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{SO}_{2}$ can be done as follows,
(i) Hydrogen combines with sulphur forming hydrogen sulphide; 2 gm . of hydrogen reacts with 32 gm of sulphur. (ii) Hydrogen combines oxygen forming water; 2 gm . of hydrogen reacts with 16 gm . of oxygen. (iii) Sulphur combines with oxygen forming sulphur dioxide; 32 gm . of sulphur reacts with 32 gm . of oxygen i.e., in the ratio $32: 32$. This ratio is double of the ratio weights of these elements which combine with 2 gm . of hydrogen. i.e., $32 / 16: 32 / 32=2: 1$


Law of Reciprocal proportion can be used to obtain equivalent weights of elements. As elements always combine in terms of their equivalent weights.
(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.

Example: (i) Reaction between hydrogen and oxygen.

$$
H_{2(g)}+\frac{1}{2} O_{2(g)} \longrightarrow H_{2} O_{(v)}
$$

One volume of $\mathrm{H}_{2}$ reacts with half volume of $\mathrm{O}_{2}$ to give one volume of $\mathrm{H}_{2} \mathrm{O}$.
(ii) Reaction between nitrogen and hydrogen. ${ }_{2(g)}+3 H_{2(g)} \rightarrow 2 \mathrm{NH}_{3(g)}$

One volume of ${ }^{N_{2}}$ reacts with three volumes of $H_{2}$ to give two volumes of $\mathrm{NH}_{3}$.

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## 5. 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 follows,
(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 $C a^{40}$ and $A r^{40}$.
(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 $\left(C_{12} H_{22} O_{11}\right)$, 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 vapor density (V.D.) and molecular masses of substances.

Vapor density $=\frac{\text { Volume of definite amount of a gas }}{\text { Volume of same amount of hydrogen }}$
or $\quad$ Vapor density $=\frac{\text { Mass of 'n' molecule of a gas }}{\text { Mass of 'n' molecule of hydrogen }}$
Mass of 1 molecule of a gas
Vapor density $=$ Mass of 1 molecule of hydrogen
Vapour density $=\frac{\text { Molecular mass }}{2}$
Molecular mass $=2 \times$ vapour density
(iii) It helps in the determination of mass of fixed volume of a particular gas.

Vapor density $=\frac{\text { Mass of } 1 \text { molecule of gas }}{\text { Mass of } 1 \text { molecule of } \mathrm{H}_{2}}=\frac{\text { Mass of } 1 \mathrm{ml} \text { of gas }}{\text { Mass of } 1 \mathrm{ml} \text { of } \mathrm{H}_{2}}=\frac{\text { Mass of } 1 \mathrm{ml} \text { of gas }}{0.0000897}$

$$
\left(\because 1 m l \quad H_{2}=0.0000897 \mathrm{gm} .\right) \text { At NTP }
$$

$\therefore$ Mass of ${ }^{1 \mathrm{ml}}$ gas $=$ V.D. $\times 0.0000897 \mathrm{gm}$.

(iv) It also helps in the determination of molar volume at N.T.P.
$\because$ V.D. $\times 0.0000897 \mathrm{gm}$. gas has volume $=1 \mathrm{ml}$
$\therefore 2 \times$ V.D. (i.e., molecular mass) gm. has volume $=\frac{1 \times 2 \times V . D .}{V . D . \times 0.0000897} \mathrm{ml}=22400 \mathrm{ml}$
$\therefore$ Molar mass of a gas or its 1 mole occupies 22.4 L volume at S.T.P.

Note: 22.4 liters of any gas at S.T.P. weigh equal to the molecular weight of the gas expressed in grams. This is called Gram-molecular volume (G.M.V.) law.
(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.

## 6. 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 $\mathrm{m}: \mathrm{n}$, then average atomic mass $=\frac{(m \times a)+(n \times b)}{m+n}$. since the atomic mass is a ratio, it has no units and is expressed in amu, $1 \mathrm{amu}=1.66 \times 10^{-24} \mathrm{~g}$. One atomic mass unit (amu) is equal to $\frac{1}{12}$ 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 or mole atoms $=\frac{\text { Mass of an element }}{\text { GAM }}$
(ii) Mass of an element in gm. $=$ Number of gm. atom $\times$ GAM
(iii) Number of atoms in 1 GAM $=6.02 \times 10^{23}$
$\therefore \quad$ Number of atoms in a given substance $=$ No. of GAM $\times 6.02 \times 10^{23}=\frac{\text { Mass }}{\text { GAM }} \times 6.02 \times 10^{23}$
$\frac{6.02 \times 10^{23}}{4)^{23}}$
(iv) Number of atoms in 1 gm of element $=\overline{\text { Atomic mass }}$
(v) Mass of one atom of the element (in gm.) $=\frac{\mathrm{GAM}}{6.02 \times 10^{23}}$

Methods of determination of atomic mass
(i) Dulong and Pettit's method: According to Dulong and Pettit's law

Atomic mass $\times$ Specific heat $=6.4$ (approx. )

$$
6.4
$$

Atomic mass (approx.) $=$ Specific heat (in cals.)
This law is applicable to solid elements only except $\mathrm{Be}, \mathrm{B}, \mathrm{C}$ and Si .
Atomic mass $=$ Equivalent mass $\times$ Valency

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

(ii) Vapor density method: It is suitable for elements whose chlorides are volatile.
Valency of the element $=\frac{\text { Molecular mass of chloride }}{\text { Equivalent mass of chloride }}=\frac{2 \times \text { Vapour density of chloride }}{\text { Equivalent mass of metal }+35.5}$
Atomic mass $=$ Equivalent mass of metal $\times$ Valency
(iii) Specific heat method: It is suitable only for gases. The two types of specific heats of gases are CP (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).

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

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(iv) Volatile chloride method: Different steps are given below

Step I. The element (M) whose atomic mass is to be determined is converted into its volatile chloride whose vapor density is determined by Victor Meyer method.

Thus, Molecular mass of the chloride $=2 \times \mathrm{V}$. D .
Step II. Equivalent mass of the element $(M)$ of Valency $X$ is determined as usual.
Atomic mass of the element $=$ Equivalent mass of the element $\times X=Z \times X$
Step III. The formula of the volatile chloride is derived as below,


Step IV. Molecular mass of the chloride $=(Z \times X)+(35.5 \times X)=X^{(Z+35.5)}$

$$
\text { From (I) and (IV) } \quad X(Z+35.5)=2 \times \text { Vapor density or } \quad X=\frac{2 \times V . D .}{Z+35.5}
$$

Thus, Atomic mass of the element $=\mathrm{Z} \times \mathrm{X}$
(v) Isomorphism method: It is based on law of isomorphism which states that compounds having identical crystal structure have similar constitution and chemical formulae.

Example: $\mathrm{K}_{2} \mathrm{SO}_{4}, \mathrm{~K}_{2} \mathrm{CrO}_{4}$ and $\mathrm{K}_{2} \mathrm{SeO}_{4}$ (Valency of $\mathrm{S}, \mathrm{Cr}, \mathrm{Se}=6$ ),

$$
\mathrm{ZnSO}_{4} .7 \mathrm{H}_{2} \mathrm{O}, \mathrm{MgSO}_{4} .7 \mathrm{H}_{2} \mathrm{O}, \mathrm{FeSO}_{4} .7 \mathrm{H}_{2} \mathrm{O} \text { (Valency of } \mathrm{Zn}, \mathrm{Mg}, \mathrm{Fe}=2 \text { ). }
$$

Applications of isomorphism

- The valencies of two elements forming isomorphism salts are essentially same. Thus if Valency of one of the elements is known that of other will be the same.
- Masses of two elements, that combine with the same mass of other elements in their respective isomorphous compounds, are in the ratio of their atomic masses i.e.
$\frac{\text { Mass of element } A \text { that combines with a certain mass of other elements }}{\text { Mass of element } B \text { that combines with the same mass of other elements }}=\frac{\text { Atomic mass of } A}{\text { Atomic mass of } B}$
- By knowing the percentage of two elements of their isomorphous compound and atomic mass of one element, atomic mass of other element can be calculated.
(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 $\frac{1}{12}$ 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 $=$ Molecular mass $\times 1.66 \times 10^{-24} \mathrm{gm}$.
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 or mole molecules $=\frac{\text { Mass of substances }}{\text { GMM }}$
Mass of substances in gm $=$ Number of gm. molecules $\times \mathrm{GMM}$
Volume occupied by one mole of any gas at STP is called Gram molar volume. The value of gram molar volume is 22.4 liters. Volume of 1 mole of any gas at STP $=22.4$ liters

Expression for mass and density
Mass of $11.2 L$ of any gas at STP = V.D. of that gas in gm.
Density of a gas at NTP $=\frac{\text { Mol.mass in } \mathrm{gm} .}{22400 \mathrm{ml}}$
Important generalizations
Number of atoms in a substance $=$ Number of GMM $\times 6.02 \times 1023 \times$ Atomaticity
Number of electrons in given substance $=$ Number of GMM $\times 6.02 \times 1023 \times$ 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) Vapor density method (For gases only): Mass of a fixed volume of the vapor is compared with the mass of the same volume of hydrogen under same conditions. The ratio of these masses is called Vapor density or Relative density.

Molecular mass $=2 \times$ Vapour desity

Note: Vapor density of a substance increases due to molecular association (e.g., $\mathrm{CH}_{3} \mathrm{COOH}, \mathrm{HF}$ ) and decreases due to dissociation (e.g., $\mathrm{NH}_{4} \mathrm{Cl}, \mathrm{PCl}_{5}$, etc.)
(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 vapors 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
$\bar{A}_{\text {(Average atomic mass) }}=\frac{\sum A_{i} X_{i}}{\sum X_{\text {total }}} ; \bar{M}$ (Average molecular mass) $=\frac{\sum M_{i} X_{i}}{\sum X_{\text {total }}}$
Where $\quad A_{1}, A_{2}, A_{3}, \ldots$ are atomic mass of species $1,2,3, \ldots$ etc. with $\%$ ratio as $\mathrm{X}_{1}, X_{2}, X_{3} \ldots \ldots \ldots$ 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.

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 $=\frac{\text { Atomic mass }}{\text { Valency }}$
(ii) EM of an acid $=\frac{\text { Molecular mass }}{\text { Basicity }}$
(Basicity of acid is the number of replaceable hydrogen atoms in one molecule of the acid).
(iii) EM of a base $=\frac{\text { Molecular mass }}{\text { Acidity }}$
(Acidity of a base is the number of replaceable- OH groups in one molecule of the base).
Formula mass
(iv) EM of a salt = Total positive or negative charge

Formula mass
(v) EM of a reducing agent $=\overline{\text { Number of electrons lost per molecule or Totalchange in oxidation number }}$ Example: Eq. mass of oxalic acid $\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4}\right)$

$$
\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-} \longrightarrow 2 \mathrm{CO}_{2}+2 e^{-}
$$

(O.N. of $C=+3) \quad($ O.N. of $C=+4)$
$\therefore$ Number of electrons lost $=2$
or Change in O.N. per C atom (from +3 to +4 ) $=1$
$\therefore$ Total change in O.N. $=1 \times 2=2$
$\therefore$ Equivalent mass of $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4}=\frac{90}{2}=45$


## Formula mass

(vi) EM of an oxidizing agent $=\overline{\text { Number of electrons gained per molecule or Totalchange in O.N. }}$

Equivalent mass of common oxidizing agent changes with the medium of the reaction.
Example: (a) Equivalent mass of $\mathrm{KMnO}_{4}$ in acidic medium

$$
\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{e}^{-}
$$

Change in O.N. of $M n$ from +7 to $+2=+5$
$\therefore$ Equivalent mass of $\mathrm{KMnO}_{4}=\frac{158}{5}=31.60$
(b) Equivalent mass of $\mathrm{KMnO}_{4}$ in neutral medium

$$
\mathrm{MnO}_{4}^{-}+4 \mathrm{H}^{+}+3 e^{-} \longrightarrow \mathrm{MnO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \text { or } \mathrm{KMnO}_{4} \longrightarrow \mathrm{MnO}_{2}
$$

$$
\therefore \text { Equivalent mass of } \mathrm{KMnO}_{4}=\frac{158}{3}=52.67
$$

(c) Equivalent mass of $\mathrm{KMnO}_{4}$ in basic medium
$\mathrm{MnO}_{4}^{-}+e^{-} \longrightarrow \mathrm{MnO}_{4}^{2-}$ or $\mathrm{KMnO}_{4} \longrightarrow \mathrm{~K}_{2} \mathrm{MnO}_{4}$
Equivalent mass of $\mathrm{KMnO}_{4}=\frac{158}{1}=158$
(vii) EM of radicals $=\frac{\text { Formula mass of radical }}{\text { Number of units of charge }}$

Example: Equivalent mass of $\mathrm{SO}_{4}^{2-}=\frac{96}{2}=48$


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 $=\frac{\text { Mass of metal }}{\text { Mass of } \mathrm{H}_{2} \text { displaced }} \times 1.008=\frac{\mathrm{W}}{\mathrm{M}} \times 1.008 \mathrm{~g}$
(b) Equivalent mass of metal $=\frac{\text { Mass of metal }}{\text { Vol. (ml)of } \mathrm{H}_{2} \text { displaced at STP }} \times 11200=\frac{W}{V} \times 11200$

This method is useful for metals which can displace hydrogen from acids or can combine with hydrogen ( $\mathrm{Mg}, \mathrm{Zn}, \mathrm{Na}, \mathrm{Ca}$ 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 $=\frac{\text { Mass of metal }}{\text { Mass of oxygen }} \times 8$
(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 $=\frac{\text { Mass of metal }}{\text { Mass of chlorine }} \times 35.5$
(b) Equivalent mass of metal $=\frac{\text { Mass of metal }}{\text { Vol. of } C l_{2}(\text { in ml. }) \text { at STP }} \times 11200$

(iv) Neutralization method: (For acids and bases).

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

Where $\mathrm{W}=$ Mass of acid or base in gm., $\mathrm{V}=\mathrm{Vol}$. of base or acid in litre required for neutralization and 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.

$$
\frac{\text { Mass of metal added }}{\text { Mass of metal displaced }}=\frac{\text { Eq. mass of metal added }}{\text { Eq. mass of metal displaced }} \quad \frac{W_{1}}{W_{2}}=\frac{E_{1}}{E_{2}}
$$

(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.

$$
\text { Gram equivalent mass }=\text { Electrochemical equivalent } \times 96500
$$

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: $A B+C D \longrightarrow A D \downarrow+C B$

$$
\begin{aligned}
& \frac{\text { Mass of compound } A B}{\text { Mass of compound } A D}=\frac{\text { Eq. mass of } A+\text { Eq. mass of } B}{\text { Eq. mass of } A+\text { Eq. mass of } D} \\
& \quad \frac{\text { Mass of salt taken }\left(W_{1}\right)}{\text { Mass of ppt.obtained }\left(\mathrm{W}_{2}\right)}=\frac{\text { Eq. mass of salt }\left(E_{1}\right)}{\text { Eq. mass of salt in ppt. }\left(E_{2}\right)}
\end{aligned}
$$

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

$$
\frac{\text { Mass of compound I }\left(W_{1}\right)}{\text { Mass of compound } \mathrm{II}\left(W_{2}\right)}=\frac{E+\text { Eq. mass of radical I }}{E+\text { Eq. mass of radical II }}
$$

( $\mathrm{E}=\mathrm{Eq}$. mass of the metal)

(ix) Volatile chloride method

Valency of metal $=\frac{2 \times \text { V.D. of Chloride }}{\text { Eq. mass of metal chloride }}=\frac{2 \times \text { V.D. }}{\mathrm{E}+35.5} \quad \therefore \mathrm{E}=\frac{2 \times \mathrm{V} . \mathrm{D} . \text { of Chloride }}{\text { Valency }}-35.5$
(x) Silver salt method (For organic acids)

Equivalent Mass of acid $=\frac{108 \times \text { Mass of silver salt }}{\text { Mass of } \mathrm{Ag} \text { metal }}-107$
Molecular mass of acid $=$ Equivalent mass of acid $\times$ Basicity

## 7. The mole concept.

The mole (abbreviated as mol) is the SI base unit for an amount of a chemical species. It is always associated with a chemical formula and refers to Avogadro's number ( $6.022 \times 10^{23}$ ) of particles represented by the formula. It is designated as $N_{0}$. Thus, 12 molecules of HCl is a dozen, 144 molecules of HCl is a gross and $6.022 \times 10^{23}$ molecules of HCl is a mole.


1 mole of a substance $=6.022 \times 10^{23}$ species
The molar mass of a substance is the mass in grams of 1 mole of that substance.
Mole of a substance $=\frac{\text { mass in grams }}{\text { molar mass }}$
Under STP conditions when temperature is 273 K and pressure is 1 atm, volume of one mole of an ideal gas is 22.4 L

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## 8. 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) Empirical formula: The chemical formula that gives the simplest whole number ratio between the atoms of various elements present in one molecule of the compound is known as empirical formula (simplest formula).

For example, the empirical formula of glucose is $\mathrm{CH}_{2} \mathrm{O}$ which shows that $\mathrm{C}, \mathrm{H}$ and O are present in the ratio 1: 2: 1 in a molecule of glucose.

Empirical formula mass of a compound is equal to the sum of atomic masses of all atoms present in the empirical formula of the compound.

Calculation of the empirical formula: The empirical formula of a chemical compound can be deduced by knowledge of the, (i) Percentage composition of different elements. (ii) Atomic masses of the elements.

The following steps are involved in the calculation of the empirical formula,
Step I. Calculate the relative number of atoms or atomic ratio.

$$
\text { Atomic ratio }=\frac{\text { Percentage of an element }}{\text { Atomic mass of the same element }}
$$

Step II. Calculate the simplest atomic ratio.
Step III.Calculate the simple whole number ratio.
Step IV. Write the empirical formula.
(3) Molecular formula: The chemical formula that gives the actual number of atoms of various elements present in one molecule of the compound. For example, the molecular formula of glucose is $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$.

Relation between empirical and molecular formula: The molecular formula of a compound is a simple whole number multiple of its empirical formula.

Molecular formula $=n \times$ Empirical formula ; Where n is any integer such as $1,2,3 \ldots$.etc.


The value of ' n ' can be obtained from the following relation: $n=\frac{\text { Molecular mass }}{\text { Empirical formula mass }}$
The molecular mass of a volatile compound can be determined by Victor Meyer's method or by employing the relation, Molecular mass $=2 \times$ Vapour density.

Calculation of the molecular formula: The molecular formula of a compound can be deduced from its:
(i) Empirical formula,
(ii) Molecular mass

The determination of molecular formula involves the following steps:
Setp I. Calculation of empirical formula from the percentage composition.
Setp II. Calculation of empirical formula mass.
Setp III. Calculation of the value of ' $n$ '.
Setp IV. Calculation of molecular formula by multiplying the empirical formula of the compound by ' n '.

## 9. Chemical equations and its balancing.

(1) Chemical equations: Chemical reactions are represented in a concise way by chemical equations. A chemical equation represents an actual chemical change taking place in terms of the symbols and the formulae of the reactants and products. e.g., Methane burns in oxygen to produce carbon dioxide and

$$
\mathrm{CH}_{4}+2 \mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

water. The chemical reaction can be represented as: Reactants Products

## Essentials of a chemical equation

(i) It must represent an actual chemical reaction.
(ii) It must be balanced i.e., the total number of atoms of various substances involved on both sides of the equation must be equal.
(iii) It should be molecular. The elementary gases like hydrogen, oxygen etc. must be written in the molecular form as $\mathrm{H} 2, \mathrm{O} 2$ etc.


Information conveyed by a chemical equation: A Chemical equation conveys both qualitative and quantitative information.
(i) Qualitative information: Qualitatively a chemical equation conveys the names of the reactants and products taking part in the reaction.
(ii) Quantitative information: Quantitatively a chemical equation conveys the following information:
(a) It conveys the actual number of reactants and product species (atoms or molecules) taking part in the reaction.
(b) It tells the relative masses of the reactants and products participating in the reaction.
(c) It conveys the relative number of reactant and product moles.
(d) It also conveys the volumes of the gaseous reactants and products if present.

Example: Reaction between CaCO 3 and aqueous HCl .

$$
\underset{\substack{100 \mathrm{gm.} \\ 1 \text { mole }}}{\mathrm{CaCO}_{3}}+\underset{\substack{73 \mathrm{gm.} \\ 2 \text { molele }}}{2 \mathrm{HCl}} \longrightarrow \underset{\substack{111 \mathrm{gm.} \\ 1 \text { molele }}}{\mathrm{CaCl}_{2}}+\underset{\substack{18 \mathrm{gm} . \\ 1 \text { mole }}}{\mathrm{H}_{2} \mathrm{O}}+\underset{\substack{44 \mathrm{gm.} \\ \text { 1 mole } \\ 22.4 \text { lites } \\ \text { at STP }}}{\mathrm{CO}_{2}}
$$

Note: All chemical equations are written under STP conditions provided no other conditions are mentioned.

Limitations of a chemical equation and their removal: Although a chemical equation conveys a number of information, it suffers from certain limitations or drawbacks. The major limitations and the steps taken for their removal are given below:
(i) Physical states of the reactants and products: The chemical equation fails to convey the physical states of the reactants and products. These are specified by the use of letters 's' (for solids), 'l' (for liquids), 'g' (for gases) and 'aq' (for aqueous solutions).

Example:

$$
\mathrm{CaCO}_{3(s)}+2 \mathrm{HCl}_{(a q)} \longrightarrow \mathrm{CaCl}_{2(s)}+\mathrm{H}_{2} \mathrm{O}_{(l)}+\mathrm{CO}_{2(g)}
$$

(ii) Conditions of temperature, pressure and catalyst: These conditions are normally not mentioned in the equation. These can be expressed on the arrow head which separates the reactants from the products.

Example:

$$
\mathrm{N}_{2(g)}+3 \mathrm{H}_{2(g)} \xrightarrow[600 \mathrm{~atm}]{\mathrm{Fe}, 723 \mathrm{~K}} 2 \mathrm{NH}_{3(g)}
$$


(iii) Speed of reaction: The speed of a particular reaction whether slow or fast can be mentioned by writing the word slow or fast on the arrow head.

Example:

$$
\begin{gathered}
N O_{2(g)}+F_{2(g)} \xrightarrow{\text { slow }} N O_{2} F_{(g)}+F_{(g)} \\
N O_{2(g)}+F_{(g)} \xrightarrow{\text { fast }}{N O_{2}} F_{(g)}
\end{gathered}
$$

(iv) Heat change accompanying the reaction: The heat evolved or absorbed in a chemical reaction can be written on the product sides. The S.I. unit of heat is kJ.

Example:

$$
\mathrm{CH}_{4(g)}+2 \mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{2(g)}+2 \mathrm{H}_{2} \mathrm{O}_{(l)}+\underset{\text { (Heat isevolved) }}{393.5 \mathrm{KJ}}
$$

$$
\mathrm{H}_{2(g)}+\mathrm{I}_{2(g)} \longrightarrow 2 \mathrm{HI}_{(g)}-53.9 \mathrm{KJ}
$$

(v) Reversible nature of a reaction: Certain chemical reactions proceed both in the forward and backward directions. The reversible nature of the reaction can be indicated by two arrows pointing in the opposite direction $(\rightleftharpoons)$.

Example:

$$
H_{2(g)}+C l_{2(g)} \quad \text { Forward } \underset{\text { Backward }}{2 H E l_{(g)}}
$$

(vi) Formation of precipitate and evolution of a gas: Formation of a precipitate in the chemical reaction can be indicated by writing the word ppt. or by an arrow pointing downwards.

$$
\mathrm{Ag} \mathrm{NO}_{3(a q)}+\mathrm{NaCl}_{(a q)} \longrightarrow \underset{(\mathrm{ppt})}{\mathrm{AgCl} \downarrow}+\mathrm{NaNO}_{3(a q)}
$$

The evolution of a gas is expressed by an arrow which points upwards.

$$
\mathrm{Mg}_{(s)}+2 \mathrm{HCl}_{(a q)} \longrightarrow \mathrm{MgCl}_{2(a q)}+\mathrm{H}_{2(g)} \uparrow
$$

(2) Balancing of chemical equations: A correct chemical equation must be in accordance with the law of conservation of mass i.e., the number of atoms of each kind in the reactants must be equal to the number of atoms of same kind in the products. Balancing of a chemical equation means to equalize the atoms of different elements or compounds which are involved in it.

Let us consider a chemical reaction which occurs due to passing of steam over red hot iron forming iron oxide and hydrogen gas. It can be represented as:


Skeleton equation:

$$
\mathrm{Fe}_{(s)}+\mathrm{H}_{2} \mathrm{O}_{(v)} \longrightarrow \mathrm{Fe}_{3} \mathrm{O}_{4(s)}+\mathrm{H}_{2(g)}
$$

Balanced equation: $3 \mathrm{Fe}_{(s)}+4 \mathrm{H}_{2} \mathrm{O}_{(v)} \longrightarrow \mathrm{Fe}_{3} \mathrm{O}_{4(s)}+4 \mathrm{H}_{2(g)}$
The balancing of equations is done by the following methods:
(i) Hit and Trial method,
(ii) Partial Equation method
(iii) Oxidation-Number method,
(iv) Ion-Electron method

The first two methods are discussed here, while the remaining two methods will be taken up for discussion in redox reactions.
(i) Hit and Trial method: This method involves the following steps:
(a) Write the symbols and formulae of the reactants and products in the form of skeleton equation.
(b) If an elementary gas like $\mathrm{H} 2, \mathrm{O} 2$ or N 2 etc. appears on either side of the equation, write the same in the atomic form.
(c) Select the formula containing maximum number of atoms and start the process of balancing.
(d) In case the above method is not convenient, then start balancing the atoms which appear minimum number of times.
(e) Balance the atoms of elementary gases in the last.
(f) When the balancing is complete, convert the equation into molecular form.

Let us balance the skeleton equation $\mathrm{Mg}_{3} \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{Mg}(\mathrm{OH})_{2}+\mathrm{NH}_{3}$
The balancing is done in the following steps
Step I. Balance the Mg atoms $\mathrm{Mg}_{3} \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 3 \mathrm{Mg}(\mathrm{OH})_{2}+\mathrm{NH}_{3}$
Step II. Balance the N atoms $\mathrm{Mg}_{3} \mathrm{~N}_{2}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 3 \mathrm{Mg}(\mathrm{OH})_{2}+2 \mathrm{NH}_{3}$
Step III. Balance the O atoms $\mathrm{Mg}_{3} \mathrm{~N}_{2}+6 \mathrm{H}_{2} \mathrm{O} \longrightarrow 3 \mathrm{Mg}(\mathrm{OH})_{2}+2 \mathrm{NH}_{3}$


The hydrogen atoms are already balanced. Hence, final balanced equation is

$$
\mathrm{Mg}_{3} \mathrm{~N}_{2}+6 \mathrm{H}_{2} \mathrm{O} \longrightarrow 3 \mathrm{Mg}(\mathrm{OH})_{2}+2 \mathrm{NH}_{3}
$$

(ii) Partial equation method: Chemical equations which involve a large number of reactants and products cannot be balanced easily by the hit and trial method. In partial equation method, the overall reaction is assumed to take place into two or more simpler reactions known as partial equations. The balancing of the equation involves the following steps:
(a) Split the chemical equation into two or more simpler equations or partial equations.
(b) Balance each partial equation separately by hit and trial method.
(c) Multiply the partial equations with suitable coefficient if necessary so as to cancel out the final substances which do not appear in the final equation.
(d) Finally, add up the partial equations to get the final equation.

Let us balance the skeleton equation $\mathrm{NaOH}+\mathrm{Cl}_{2} \longrightarrow \mathrm{NaCl}+\mathrm{NaClO}_{3}+\mathrm{H}_{2} \mathrm{O}$
This reaction is supposed to take place in the following steps:

The probable partial equations for the above reaction are:
$\mathrm{NaOH}+\mathrm{Cl}_{2} \longrightarrow \mathrm{NaCl}+\mathrm{NaClO}+\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{NaClO} \longrightarrow \mathrm{NaClO} \mathrm{O}_{3}+\mathrm{NaCl}$
Balance the partial chemical equations separately by hit and trial method as
$2 \mathrm{NaOH}+\mathrm{Cl}_{2} \longrightarrow \mathrm{NaCl}+\mathrm{NaClO}+\mathrm{H}_{2} \mathrm{O}$ and ${ }^{3} \mathrm{NaClO}_{3} \longrightarrow \mathrm{NaClO}_{3}+2 \mathrm{NaCl}$
Multiply the first partial equation by 3 in order to cancel out NaClO which does not appear in the final equation. Finally add the two partial equations to get the final equation.

$$
\begin{gathered}
\left.2 \mathrm{NaOH}+\mathrm{Cl}_{2} \longrightarrow \mathrm{NaCl}+\mathrm{NaClO}+\mathrm{H}_{2} \mathrm{O}\right] \times 3 \\
\frac{3 \mathrm{NaClO} \longrightarrow \mathrm{NaClO}_{3}+2 \mathrm{NaCl}}{6 \mathrm{NaOH}+3 \mathrm{Cl}_{2} \longrightarrow \mathrm{NaClO}_{3}+5 \mathrm{NaCl}+3 \mathrm{H}_{2} \mathrm{O}}
\end{gathered}
$$



## 10. Chemical Stoichiometry.

Calculation based on chemical equations is known as chemical stoichiometry. Stoichiometry can be broadly classified into two groups: (1) Gravimetric analysis (Stoichiometry-I), (2) Volumetric analysis (Stoichiometry-II)
(1) Gravimetric analysis (Stoichiometry-I): With the help of chemical equation, we can calculate the weights of various substances reacting and weight of substances formed. For example,

$$
\mathrm{MgCO}_{3} \longrightarrow \mathrm{MgO}+\mathrm{CO}_{2} \uparrow
$$

This equation implies:
(i) 1 mol of $\mathrm{MgCO}_{3}$ gives 1 mol of MgO and 1 mol of $\mathrm{CO}_{2}$.
(ii) 84 g of $\mathrm{MgCO}_{3}$ (Mol. wt. of $\mathrm{MgCO}_{3}$ ) gives 40 g of MgO and 44 g of $\mathrm{CO}_{2}$.

Hence, chemical equation provide us information regarding:
(i) Molar ratio of reactants and products.
(ii) Mass ratio between reactants and products.
(iii) Volume ratio between gaseous reactant and products.

The calculation based upon chemical equation (Stoichiometry-I) are based upon three types namely:
(a) Mass-mass relationship
(b) Mass-volume relationship
(c) Volume-volume relationship
(2) Volumetric analysis (Stoichiometry-II): 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 summarized as follows:
(i) Redox titrations: To determine the strength of oxidizing agents or reducing agents by titration with the help of standard solution of reducing agents or oxidizing agents.

Examples:

$$
\begin{gathered}
\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}+4 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{~K}_{2} \mathrm{SO}_{4}+\mathrm{Cr}_{2}\left(\mathrm{SO}_{4}\right)_{3}+4 \mathrm{H}_{2} \mathrm{O}+3[\mathrm{O}] \\
{\left[2 \mathrm{FeSO}_{4}+\mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{O} \rightarrow \mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}+\mathrm{H}_{2} \mathrm{O}\right] \times 3} \\
\hline 6 \mathrm{FeSO}_{4}+\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}+7 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow 3 \mathrm{Fe}\left(\mathrm{SO}_{4}\right)_{3}+\mathrm{K}_{2} \mathrm{SO}_{4}+\mathrm{Cr}_{2}\left(\mathrm{SO}_{4}\right)_{3} 7 \mathrm{H}_{2} \mathrm{O} \\
2 \mathrm{KMnO}_{4}+3 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{~K}_{2} \mathrm{SO}_{4}+2 \mathrm{MnSO}_{4}+3 \mathrm{H}_{2} \mathrm{O}+5[\mathrm{O}] \\
{\left[2 \mathrm{FeSO}_{4}+\mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{O} \rightarrow \mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}+\mathrm{H}_{2} \mathrm{O}\right] \times 5} \\
\hline 10 \mathrm{FeSO}_{4}+2 \mathrm{KMnO}_{4}+8 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow 5 \mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3}+\mathrm{K}_{2} \mathrm{SO}_{4}+2 \mathrm{MnSO}_{4}+8 \mathrm{H}_{2} \mathrm{O}
\end{gathered}
$$

Similarly with $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$

$$
2 \mathrm{KMnO}_{4}+3 \mathrm{H}_{2} \mathrm{SO}_{4}+5 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \rightarrow \mathrm{~K}_{2} \mathrm{SO}_{4}+2 \mathrm{MnSO}_{4}+8 \mathrm{H}_{2} \mathrm{O}+10 \mathrm{CO}_{2} \text { Etc. }
$$

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

Example: $\mathrm{NaOH}+\mathrm{HCl} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{NaOH}+\mathrm{CH}_{3} \mathrm{COOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ etc.
(iii) Iodiometric titrations: To determine the reducing agents with the help of standard iodine solution is known as iodiometry.

$$
\mathrm{As}_{2} \mathrm{O}_{3}+2 \mathrm{I}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{As}_{2} \mathrm{O}_{3}+4 \mathrm{HI}
$$

For example: Reducing agent

$$
\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}+\mathrm{I}_{2} \rightarrow \mathrm{Na}_{2} \mathrm{~S}_{4} \mathrm{O}_{6}+2 \mathrm{NaI}
$$

(iv) Iodiometric titrations: To determine the oxidizing agent indirectly by titration of liberated $I_{2}$ with the help of standard hypo solution is known as iodometric titrations.

Examples: Oxidizing agents such as $\mathrm{KMnO}_{4}, \mathrm{~K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}, \mathrm{CuSO}_{4}$, ferric salts, etc. are reduced quantitatively when treated with large excess of KI in acidic or neutral medium and liberate equivalent amount of $I_{2}$.

$$
\begin{gathered}
2 \mathrm{CuSO}_{4}+4 \mathrm{KI} \rightarrow \mathrm{Cu}_{2} \mathrm{I}_{2}+2 \mathrm{~K}_{2} \mathrm{SO}_{4}+\mathrm{I}_{2} \\
\mathrm{Kr}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}+7 \mathrm{H}_{2} \mathrm{SO}_{4}+6 \mathrm{KI} \rightarrow \mathrm{Cr}_{2}\left(\mathrm{SO}_{4}\right)_{3}+4 \mathrm{~K}_{2} \mathrm{SO}_{4}+7 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{I}_{2}
\end{gathered}
$$



This $I_{2}$ is estimated with hypo

$$
\mathrm{I}_{2}+2 \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} \rightarrow \mathrm{Na}_{2} \mathrm{~S}_{4} \mathrm{O}_{6}+2 \mathrm{NaI}
$$

(v) Precipitation titrations: To determine the anions like $\mathrm{CN}^{-}, \mathrm{AsO}_{3}^{3-}, \mathrm{PO}_{4}^{3-}, \mathrm{X}^{-}$etc., by precipitating with $\mathrm{AgNO}_{3}$ provides examples of precipitation titrations.

$$
\mathrm{NaCl}+\mathrm{AgNO}_{3} \rightarrow \mathrm{AgCl} \downarrow+\mathrm{NaNO}_{3} ; \quad \mathrm{KSCN}+\mathrm{AgNO}_{3} \rightarrow \mathrm{AsSCN} \downarrow+\mathrm{KNO}_{3}
$$

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 oxidizing 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 $\mathrm{N} / 2$ or 0.5 N solution.

Formula used in solving numerical problems on volumetric analysis
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 $\times$ Eq. wt. of the solute
(4) Molarity $=\frac{\text { Moles of solute }}{\text { Volume in litre }}$
(5) Number of moles $=\frac{\text { Wt.in } g m}{\text { Mol.wt. }}=M \times V_{(i n l)}=\frac{\text { Volume in litres }}{22.4}$ At NTP (only for gases)
(6) Number of millimoles $=\frac{\text { Wt.in } g m \times 1000}{\text { mol. wt. }}=$ Molarity $\times$ Volume in ml .
(7) Number of equivalents $=\frac{\text { Wt.in } g m}{\text { Eq. wt. }}=x \times$ No. of moles $\times$ Normality $\times$ Volume in litre

(8) Number of milliequivalents (meq.) $=\frac{\text { Wt.in } g m \times 1000}{\text { Eq. wt. }}=$ normality $\times$ Volume in $m l$.
(9) Normality $=x \times$ No. of millimoles $=x \times$ Molarity $=\frac{\text { Strength in } g m \text { litre }^{-1}}{\text { Eq. wt. }}$

Where $\quad x=\frac{\text { Mol.wt. }}{\text { Eq. wt. }, x^{*}=\text { Valency or change in oxi. Number. }}$
(10) Normality formula, $N_{1} V_{1}=N_{2} V_{2}$
(11) \% by weight $=\frac{\text { Wt.of solvent }}{\text { Wt.of solution }} \times 100$
(12) \% by volume $=\frac{\text { Wt.of solvent }}{\text { Vol. of solution }} \times 100$
(13) \% by strength $=\frac{\text { Vol. of solvent }}{\text { Vol. of solution }} \times 100$
(14) Specific gravity $=\frac{\text { Wt.of solution }}{\text { Vol. of solution }}=$ Wt.of 1 ml . of solution
(15) Formality
$=\frac{\text { Wt.of ionic solute }}{\text { Formula Wt.of solute } \times V_{\text {inl }}}$
(16) Mol. Wt. = V.D $\times 2$ (For gases only)


## 11. 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 .

$$
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{v})
$$

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


