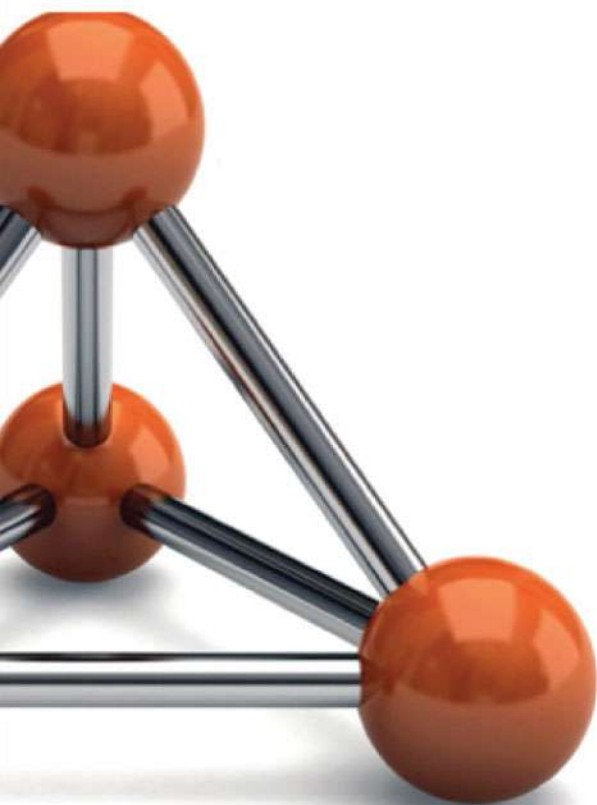


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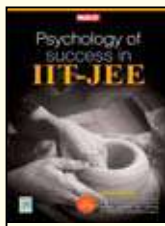
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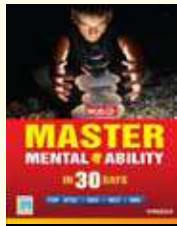
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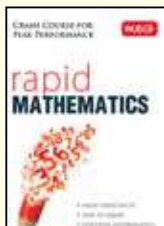
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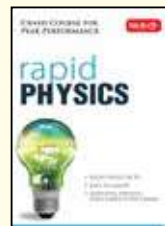
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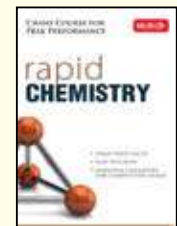
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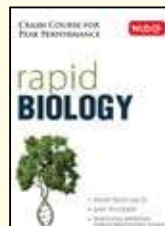
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P R E F A C E

“Good things come in small packages.”

Rapid Chemistry (High Yield Facts Book) is designed for people who have only enough time to glance at a book-literally. Our goal is to create an effective memory aid for those who wish to review chemistry.

The book covers complete syllabus in points form. The quality of the writing leaves the reader with the potential to achieve a good understanding of a given topic within a short period of learning. It gives a concise overview of the main principles and reactions of chemistry, for students studying chemistry and related courses at undergraduate level. Based on the highly successful and student friendly “at a glance” approach, the material developed in this book has been chosen to help the students grasp the essence of chemistry, ensuring that they can confidently use that knowledge when required.

The books has been crafted extremely well for a very specific purpose: review. A person who has been away from chemistry (but who understood it very well at the time) can use this book effectively for a rapid review of any basic topic. The book is so highly compressed that every page is like a food with a rich sauce that needs to be slowly savored and slowly digested for maximum benefit. You may only glance into the book, but you can think about the chemistry for much longer.

All the best!

Catalysed by : **Zarrin Khan**
M.Sc. Chemistry
Karabi Ghosh
M.Tech.

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atoms, molecules & chemical arithmetic

Significant figures

The total number of digits in the number is called the number of significant figures (S.F.). It equals the number of digits written including the last one, even though its value is uncertain. The following rules should be followed in counting of (S.F.) in a given measured quantity.

- (i) All digits are significant except zero at the beginning of the number.
- (ii) The zeros to the right of the decimal point are significant.
- (iii) The above rules purpose that the numbers are expressed in scientific notation. In this term, every number is written as $N \times 10^n$, where N = a number with a single non-zero digit to the left of the decimal point, n = an integer

We can write 20,000 in scientific notation as

$$\begin{array}{ccc} 2 \times 10^4 & 2.0 \times 10^4 & 2.00 \times 10^4 \\ \text{having} & 1 \text{ S.F.} & 2 \text{ S.F.} & 3 \text{ S.F.} \end{array}$$

- (iv) Zero at the end of a number and before the decimal point may or may not be significant.

Any number can be conveniently transformed to scientific notation by moving the decimal point in the number to obtain a new number, A greater than or equal to 1 and less than 10. If the decimal point is moved to the left, you multiply A by 10^n , when n equals the number of places moved. If the decimal point is moved to the right, multiply A by 10^{-n} .

Digit	S.F.	Rule
101	3	i
0.101	3	i
0.0101	3	i
101.0	4	ii
101.00	5	ii

S.F. in numerical calculations

To express the result of an experiment, we have to often add, subtract, multiply or divide the numbers obtained in different measurements.

Rule I : S.F. rule in multiplication/division

The result of multiplication and/or division may carry no more S.F. than the least precisely known quantity in the calculation. In the following multiplication, the result should be in three S.F. : $14.79 \times 12.11 \times 5.05 = 904.48985 = 904 = 9.04 \times 10^2$
 (4 S.F.) (4 S.F.) (3 S.F.) (3 S.F.)

In the following division, the result should be reported in two S.F.

$$\frac{0.18 \text{ (2 S.F.)}}{2.487 \text{ (4 S.F.)}} = 0.0723766 = 0.072 = 7.2 \times 10^{-2}$$

(2 S.F.) (2 S.F.)

and the following in three S.F.

$$\frac{5.28 \times 0.156 \times 3.00}{0.0428} = 57.73438 = 57.7$$

Rule II : S.F. rule in addition/subtraction

The result of addition and/or subtraction must be expressed with the same number of decimal places as the term carrying the smallest number of decimal places.

$$\left\{ \begin{array}{l} \begin{array}{cccccc} 22.2 & + & 2.22 & + & 0.222 & = & 24.642 & = & 24.6 \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{One least} & & \text{Two} & & \text{Three} & & \text{Three} & & \text{One} \end{array} \\ \\ \begin{array}{cccccc} 5.2748 & - & 5.2722 & = & 0.0026 \\ \downarrow & & \downarrow & & \downarrow \\ \text{Four} & & \text{Four} & & \text{Three} \end{array} \end{array} \right.$$

Rule III : S.F. rule for each exact number

Exact numbers can be considered to have an unlimited number of S.F.

“Rounding off” the numerical results

To three S.F., we should express 15.453 as 15.5 and 14755 as 1.48×10^4 . It is called “Rounding off” the result.

- If the first digit removed is less than 5, round down by dropping it and all following digits. Thus, 5.663507 becomes 5.66 when rounded off to three S.F. because first of the dropped digits (3) is less than 5.
- If the first digit removed is 6 or greater than 6 round off by adding 1 to the digit on the left.
- Thus 5.663507 becomes 5.7 when rounded off to two S.F.
- If the first digit removed is 5 and there are more non-zero digits following round up. Thus, 5.663507 becomes 5.664 when rounded off to four S.F.
- If the digit removed is 5 and there is no digit after, then add one to the preceding digit if it is odd, otherwise write as such if it is even.

Thus, 4.7475 becomes 4.748 when rounded off to four S.F.



(odd digit before 5)

and 4.7465 becomes 4.746 when rounded off to four S.F.



(even digit before 5)

S.I. Units (Inter-national System of Units)

The S.I. has seven base units (table 1) from whom all other units are derived. The standard prefixes, which allow us to reduce or enlarge the base units are given in table 2.

Table 1 : The seven basic units

Physical quantity	Unit	Unit symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd
Plane angle*	radian	rad
Solid angle*	steradian	sr

* These are two other fundamental quantities with dimensionless units.

Table 2 : SI Prefixes

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}	zepto	z
10^1	deca	da	10^{-24}	yocto	y

Problem solving**The conversion factor method (dimensional analysis)**

A number of quantities must be derived from measured value of the SI base quantities. Two sets of derived units are given, those whose names follow directly [table 3 (a)] from the base units and those that are given special names [table 3(b)].

Table 3(a) : Derived units

Physical quantity	Unit	Symbol
Area	square metre	m^2
Volume	cubic metre	m^3
Velocity	metre per second	m s^{-1}
Acceleration	metre per second square	m s^{-2}
Density	kilogram per cubic metre	kg m^{-3}
Molar mass	kilogram per mole	kg mol^{-1}
Molar volume	cubic metre per mole	$\text{m}^3 \text{mol}^{-1}$
Molar concentration	mole per cubic metre	mol m^{-3}

Table 3(b) : Derived units

Physical quantity	Unit	Symbol	In terms of SI unit
Frequency	hertz	Hz	s^{-1}
Force	newton	N	kg ms^{-2}
Pressure	pascal	Pa	Nm^{-2}
Energy	joule	J	$\text{kg m}^2 \text{s}^{-2}$
Power	watt	W	Js^{-1} , $\text{kg m}^2 \text{s}^{-3}$
Electric charge	coulomb	C	A s^{-1}
Electric potential difference	volt	V	$\text{J A}^{-1} \text{s}^{-1}$
Electric resistance	ohm	Ω	VA^{-1}

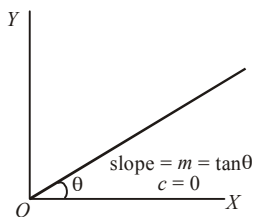
Many of the calculations of general chemistry simply require that we convert quantities from one set of units to another. We can do this by using **Conversion Factor (C.F.)**. A C.F. must always have the numerator and denominator representing equivalent quantities.
Information sought = *information given* \times C.F.

Table 4 : Conversion factors

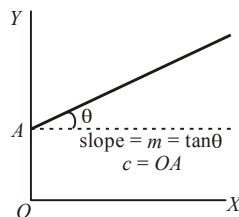
1 m	= 39.37 inch	1 year	= 365 days
1 inch	= 2.54 cm		= 3.1536×10^7 s
1 litre	= 1000 mL = 1000 cm ³	1 curie (Ci)	= 3.7×10^{10} dps or Bq
	= 10^{-3} m ³ = 1 dm ³	1 rutherford	= 1×10^6 dps or Bq
1 gallon	= 3.785412 L	(Ru)	
1 lb	= 453.59237 g	1 debye (D)	= 1×10^{-18} esu cm
1 newton	= 1 kg m s ⁻²	1 mol of	= 22.4 L at STP
1 J	= 1 Nm = 1 kg m ² s ⁻²	a gas	
1 cal	= 4.184 J	1 mol of a	= N_0 molecules
	= 2.613×10^{19} eV	substance	
1 eV	= 1.602189×10^{-19} J	1 g atm	= N_0 atoms
	= 3.827×10^{-20} cal	t (°F)	= $\frac{9}{5}t$ (°C) + 32
1 eV/atom	= 96.485 kJ mol ⁻¹	1 g cm ⁻³	= 1000 kg m ⁻³
1 amu	= $1.6605653 \times 10^{-27}$ kg		
	= 931.5016 MeV	equivalent wt. of an acid	= $\frac{\text{molecular weight}}{\text{basicity of the acid}}$
1 kilo watt hour (kWh)	= 3600 kJ		
1 horse power (hp)	= 746 watt	equivalent wt. of a base	= $\frac{\text{molecular weight}}{\text{acidity of a base}}$
1 joule	= 10^7 erg		
1 e.s.u	= 3.3356×10^{-10} C	equivalent wt. in a redox reaction	= $\frac{\text{mol. wt. (stoichiometric)}}{\text{change in O.N. per atom}}$
1 dyne	= 10^{-5} N		
1 atm	= 101325 Nm ⁻²		
	= 101325 Pa		
1 bar	= 1×10^5 N m ⁻²		
1 litre atm	= 101.3 J = 24.21 cal		

Graphical analysis

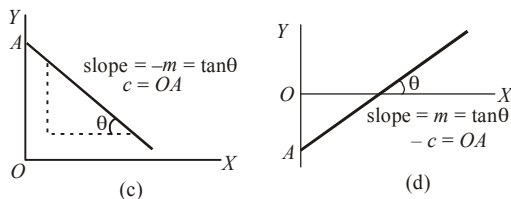
It requires less time to give more information than lengthy and tedious calculations. For this one has to compare the results with a standard graph. Generally we make a graph between y (along y -axis) and x (along x -axis) to have a straight line; its nature varies equation to equation.



(a)



(b)



Graph	Equation	Slope	Intercept
(a)	$y = mx$	m	0
(b)	$y = mx + c$	m	$+c = OA$
(c)	$y = -mx + c$	$-m$	$+c = OA$
(d)	$y = mx - c$	m	$-c = OA$

Unit analysis

Unit of the final result is also the important part like its numerical value. If proper units are not used for the given parameters, unit of the final result can be absurd.

General data and fundamental constants

Quantity	Symbol	Commonly used value
Speed of light (in vacuum)	c	$3.0 \times 10^8 \text{ m s}^{-1}$
Elementary charge	e	$1.6 \times 10^{-19} \text{ C}$
Avogadro number	N_0	$6.02 \times 10^{23} \text{ mol}^{-1}$
Faraday	$F = eN_0$	96500 C mol^{-1}
Gas constant	$R = kN_0$	$8.314 \text{ mol}^{-1} \text{ K}^{-1}$ $8.21 \times 10^{-2} \text{ dm}^3$ $\text{atm mol}^{-1} \text{ K}^{-1}$ $62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$
Boltzmann constant	k	$1.381 \times 10^{-23} \text{ JK}^{-1}$
Planck constant	h	$6.63 \times 10^{-34} \text{ Js}$
	$\hbar = \frac{h}{2\pi}$	$1.05 \times 10^{-34} \text{ Js}$
Atomic mass unit	u	$1.66 \times 10^{-27} \text{ kg atom}^{-1}$
Mass of electron	m_e	$9.1 \times 10^{-31} \text{ kg}$
Mass of proton	m_p	$1.67 \times 10^{-27} \text{ kg}$
Mass of neutron	m_n	$1.67 \times 10^{-27} \text{ kg}$
Bohr radius	a_0	$5.29 \times 10^{-11} \text{ m}$
Rydberg constant (in hydrogen)	R_H	$1.09677 \times 10^7 \text{ m}^{-1}$
Standard acceleration of free fall	g	9.8 m s^{-2}
Atmospheric pressure	P	$1.01 \times 10^5 \text{ N m}^{-2}$
Molar volume of a gas at S.T.P.	V_m	0.0224 m^3

Laws of chemical combination

- (i) *Law of Conservation of Mass.*
Total mass of reactants = Total mass of products
- (ii) *Law of Constant Composition/Definite Proportions.*

For the same compound, obtained by different methods, calculate the percentage of each element. This should be same in each case.

- (iii) *Law of Multiple Proportions* - For two elements combining to form two or more compounds, calculate the weights of one element which combine with the fixed weight (1 g or 100 g) of the other. They should be in a simple whole number ratio.
- (iv) *Law of Reciprocal Proportions* - Calculate the ratio of the weights of two elements *A* and *B* which combine with a fixed weight of the third element *C*. Also calculate the ratio of the weights of *A* and *B* which combine directly with each other. The two ratios should be same or simple multiple of each other.
- (v) *Gay Lussac's law of gaseous volumes* - When gases react together, they always do so in volumes which bear a simple ratio to one-another and to the volumes of products, if gaseous at same temperature and pressure conditions.

Mole concept

- (i) 1 Mole of atoms = Gram atomic mass (or 1 g atom)
= 6.022×10^{23} atoms
- (ii) 1 Mole of molecules = Gram molecular mass (or 1 g molecule)
= 6.022×10^{23} molecules
= 22.4 L at STP.
- (iii) 1 Mole of ionic compound = Gram formula mass
= 6.022×10^{23} formula units.

Calculation of molecular weight

- (i) Molecular mass = $2 \times$ Vapour density
- (ii) Molecular mass = Mass of 22.4 L of vapour at STP
- (iii) Rates of diffusion, $\frac{r_1}{r_2}$ = $\sqrt{\frac{M_2}{M_1}}$

Calculation of equivalent weight

- (i) Eq. wt. of metal = $\frac{\text{wt. of metal}}{\text{wt. of H}_2 \text{ displaced}} \times 1.008$
or = $\frac{\text{wt. of metal}}{\text{Vol. of H}_2 \text{ in ml displaced at STP}} \times 11200$
- (ii) Eq. wt. of metal = $\frac{\text{wt. of metal}}{\text{wt. of oxygen combined}} \times 8$
or = $\frac{\text{wt. of metal}}{\text{wt. of O}_2 \text{ displaced/combined in ml at STP}} \times 5600$
- (iii) Eq. wt. of metal = $\frac{\text{wt. of metal}}{\text{wt. of chlorine combined}} \times 35.5$
or = $\frac{\text{wt. of metal}}{\text{Vol. of Cl}_2 \text{ combined in ml at STP}} \times 11200$
- (iv) $\frac{\text{wt. of metal added to a salt solution}}{\text{wt. of metal displaced}} = \frac{\text{Eq. wt. of metal added}}{\text{Eq. wt. of metal displaced}}$

- (v)
$$\frac{\text{wt. of salt } AB \text{ added to salt } CD \text{ (in solution)}}{\text{wt. of ppt. } AD \text{ formed}} = \frac{\text{Eq. wt. of radical } A + \text{Eq. wt. of radical } B}{\text{Eq. wt. of radical } A + \text{Eq. wt. of radical } D}$$
- (vi) Eq. wt. = wt. deposited by 1 Faraday (96500 coulombs)
- (vii) On passing the same quantity of electricity through two different electrolytic solutions,

$$\frac{\text{wt. of } X \text{ deposited}}{\text{wt. of } Y \text{ deposited}} = \frac{\text{Eq. wt. of } X}{\text{Eq. wt. of } Y}$$
- (viii) Eq. wt. of an acid = wt. of the acid neutralized by 1000 cc of 1N base solution
 Eq. wt. of a base = wt. of the base neutralized by 1000 cc of 1N acid solution
- (ix) For an organic acid (RCOOH)

$$\frac{\text{Eq. wt. of silver salt (RCOOAg)}}{\text{Eq. wt. of silver (108)}} = \frac{\text{wt. of silver salt}}{\text{wt. of silver}}$$

 Eq. wt. of acid (RCOOH) = Eq. wt. of RCOOAg – 107.
- (x) For a compound (I) being converted into another compound (II) of the same metal

$$\frac{\text{wt. of compound I}}{\text{wt. of compound II}} = \frac{\text{Eq. wt. of metal} + \text{Eq. wt. of anion of compound I}}{\text{Eq. wt. of metal} + \text{Eq. wt. of anion of compound II}}$$

- (xi) Eq. wt. of an acid = $\frac{\text{Mol. wt. of the acid}}{\text{Basicity}}$
 Eq. wt. of a base = $\frac{\text{Mol. wt. of the base}}{\text{Acidity}}$
 Eq. wt. of a salt = $\frac{\text{Mol. wt. of the salt}}{\text{Total positive valency of the metal atoms}}$
- (xii) Eq. wt. of oxidizing/reducing agent = $\frac{\text{Mol. wt. of the substance}}{\text{No. of electrons gained/lost by one molecule}}$

Calculation of atomic weight

- (i) Atomic wt. \times specific heat = 6.4 approx

(Dulong and Petit's law for solids)

$$\therefore \text{Approx. atomic weight} = \frac{6.4}{\text{Sp. heat}}, \text{Valency} = \frac{\text{Approx. At. wt.}}{\text{Eq. wt.}}$$

$$\text{Exact atomic weight} = \text{Eq. wt.} \times \text{valency}$$

- (ii) Valency of the metal whose chloride is volatile = $\frac{2 \times \text{V.D. of metal chloride}}{\text{Eq. wt. of metal} + 35.5}$

$$\text{Atomic weight} = \text{Eq. wt.} \times \text{valency.}$$

states of matter

GASEOUS STATE

- Gases are easily compressed by application of pressure to a movable piston fitted in the container.
- The volume of the container is the volume of the gas sample and it is usually given in litre (L) or millilitre (mL).
- Pressure of a gas is measured with a manometer and is equal to the difference in levels of Hg in the two limbs with a closed limb manometer and is equal to atm pressure minus difference in levels in case of an open limb manometer.
- The pressure of a gas is defined as the force exerted by the impacts of its molecules per unit surface area in contact.
- The unit of pressure, millilitre of mercury is also called torr.
- For gases S.T.P. conditions are 273 K (0°C) and 1 atm-pressure.
- **Boyle's law** states that at a constant temperature (T), the pressure (P) of a given mass (or moles, n) of any gas varies inversely with the volume (V).

$$i.e. P \propto \frac{1}{V} \text{ (for given } n \text{ and } T)$$

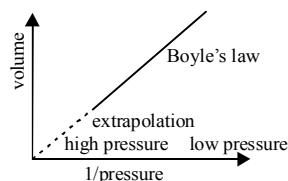
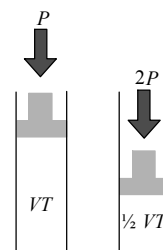
$$PV = K = \text{constant} \text{ or } P_1V_1 = P_2V_2$$

In a container with a movable piston the product volume times pressure is constant. If the pressure is doubled the volume decreases to half of its original value.

- Boyle's law suggests that the graph $V=f(1/P)$ is a straight line. The extrapolation to $1/P = 0$ (infinite pressure) yields $V = 0$ which obviously is impossible. At elevated pressure Boyle's law is not valid.
- **Charles' law** : n and P are constant.

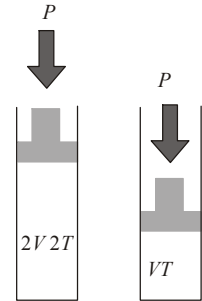
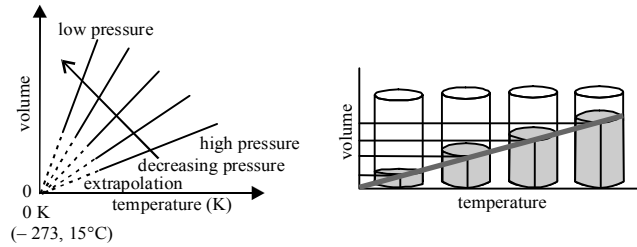
$$T_1/V_1 = T_2/V_2$$

Example : If 1 litre of gas at 300 K (27°C) and at a pressure of 1 bar is heated at constant pressure to 600 K (327°C) its volume raises to two litres.



Charles' law suggests that the volume of a gas depends linearly on its temperature. For every sample the plot $V = f(T)$ should be a straight line with the origin $V = 0 \text{ m}^3$ at $T = 0 \text{ K}$.

Obviously the extrapolation of Charles' law to very low temperatures does not make sense.



If a gas is heated at constant pressure it expands. Doubling the temperature (K) causes the volume to double.

- Combined gas law can be stated as for a fixed mass of gas, the volume is directly proportional to Kelvin temperature and inversely proportional to the pressure. If k be the proportionality constant,

$$V = \frac{kT}{P} \quad (n \text{ constant}) \quad \text{or,} \quad \frac{PV}{T} = k \quad (n \text{ constant}).$$

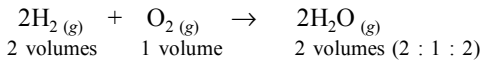
- At one condition, for a given mass of a gas P_1 , V_1 and T_1 are pressure, volume and temperature and at some other condition P_2 , V_2 and T_2 are new pressure, volume and temperature, then

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Gay Lussac's law states that the pressure of a given mass of any gas is directly proportional to the absolute temperature at constant volume. $P \propto T$ (for constant n and V)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- Gay Lussac's law of combined volume states that when measured at same temperature and pressure, the ratios of volumes of the gases that combined, and of gases that were products (in a chemical reaction), were always some whole numbers.



- The temperature at which solid ice, liquid water and water vapour i.e. all the three states of the substance exist together is called **triple point**.
- **Avogadro's law** : P and T are constants.

$$n_1 V_1 = n_2 V_2$$

At constant temperature and pressure the number of moles of a gas in a container is proportional to the container's volume. Or, at a given temperature and pressure equal volumes contain an equal number of moles, independent of the kind of gas.

Example : At a given temperature and pressure 9 atoms and 9 tri-atomic molecules occupy the same volume.

At a pressure of 1 bar and 0°C, all gases (to the point where they are “ideal gases” under these conditions) have the same volume of 22.4 litre. 22.4 litre is the molar volume of gases under the so called “STP” (standard temperature pressure) conditions.

- **Rule of thumb** : At 25°C and 1 bar one mol of gas has a volume of 25 litre.
- 1 mole contains 6.023×10^{23} molecules (a number called as Avogadro's number).
- Universal gas law or ideal gas law may be stated as the volume of a given amount of gas is directly proportional to the number of moles of gas, directly proportional to the temperature and inversely proportional to the pressure.

$$V = R \frac{nT}{P}$$

This is called **ideal gas equation** and constant R is called **gas constant**.

- In the international system (SI) the unit of pressure is the Pascal (1 Pa = 1 N.m⁻²) and the unit of volume is the cubic meter, m³. In the SI system the value of the gas constant R is 8.3145 J mol⁻¹ K⁻¹. Sometimes it is more convenient to use units of everyday life: bar for pressure (1 bar ~ 1 atmosphere) and litre for volume (dm³).

$$R = 0.083145 \text{ bar lit. mol}^{-1} \text{ K}^{-1}$$

Explanation : 1 J = 1 Nm

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ J m}^{-3}$$

$$1 \text{ bar} = 10^5 \text{ J m}^{-3} = 10^2 \text{ J dm}^{-3}$$

$$\text{Therefore, } 1 \text{ J} = 10^{-2} \text{ bar dm}^3.$$

- Gases which obey the ideal gas equation are called as **ideal gases**. Ideal gases obey the gas equation at all temperatures and pressures.
- Ideal gases do not show any cooling or heating effect on adiabatic expansion because there are no intermolecular forces of attraction present in them.
- The gases which deviate from gas equation are called as real gases. These gases obey gas laws only at low pressure and high temperature.
- **Partial pressure** : Actually the pressure of a gas is due to the elastic shocks of the molecules with the walls of the container.
- In a gas mixture, the partial pressure exerted by one component is proportional to its concentration.

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots = \left(\frac{n_1}{V_{\text{tot}}} + \frac{n_2}{V_{\text{tot}}} + \frac{n_3}{V_{\text{tot}}} + \dots \right) R \cdot T$$

The total pressure is the sum of the partial pressures.

This is called **Dalton's law**.

- Dalton's law of partial pressure is applicable only to non-reacting gases.
- The **partial pressure** is defined as the pressure of a gas would exert if it was alone in the container at the same temperature and pressure conditions.

Example: Air consists of 78 % N₂, 21 % O₂, 1 % Ar and 0.03 % CO₂ (percent of volume = percent of moles). When the pressure of the air is 1 bar, the partial pressures are: $p(\text{N}_2) = 0.78 \text{ bar}$, $p(\text{O}_2) = 0.21 \text{ bar}$, $p(\text{Ar}) = 0.01 \text{ bar}$ and $p(\text{CO}_2) = 0.0003 \text{ bar}$.

- Process of mixing of gases by random motion of the molecules is called **diffusion**.

- **Graham's law of diffusion** states that under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses. Mathematically the law can be expressed as $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ where r_1 and r_2 are the rates of diffusion of gases 1 and 2, while M_1 and M_2 are their molecular masses.

- A gas confined to a container at high pressure than the surrounding atmosphere will escape from a small hole which is opened in the container until the pressure outside and inside have been equalised. This process is called **effusion**.
- The rate of diffusion of a gas is also proportional to the pressure of gas (or number of molecules) at a given temperature. In that case, the rate of diffusion is given as

$$r \propto \frac{P}{\sqrt{d}}$$

- If two gases 1 and 2 at different pressures P_1 and P_2 are allowed to effuse through a small hole in a container then the ratio of rates of diffusion of two gases is given by

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

- When a real gas is allowed to expand adiabatically through a porous plug or a fine hole into a region of low pressure, it is accompanied by cooling (except for hydrogen and helium which get warmed up). This effect is known as **Joule-Thomson effect**.
- **Kinetic theory of gases** : The macroscopic behaviour of gases can be explained by a model containing three hypotheses.
 - (i) A gas is an ensemble of particles in continuous, fast random motion, moving in straight lines until they collide.
 - (ii) The particles are infinitely small and (on the average) far from each other. (volume of the particles \ll volume of the gas).
 - (iii) The particles do not influence one another except during collisions. The collisions of the particles with each other and with the wall of the container are elastic, *i.e.* the kinetic energy of the particles is maintained (there is no transformation of kinetic energy into heat of friction).

The pressure of a gas exerted on the walls of the container is caused by the collision of the gas particles with the wall.

- $PV = (1/3) mNu^2$ is the fundamental equation of the kinetic molecular theory of gases. It is called **kinetic gas equation**.
- The average translational kinetic energy of one molecule of an ideal gas will be given by

$$E_t = \frac{K.E.}{N_A} = \frac{(3/2)RT}{N_A} = \frac{3}{2}kT \quad \text{where } (R/N_A) \text{ is } \mathbf{Boltzmann\ constant}.$$

- At absolute zero (*i.e.* $T = 0$), kinetic energy is zero. In other words, thermal motion ceases completely at absolute zero.
- In 1860, James Clark Maxwell derived the following equation for the distribution of molecular velocities.

$$\frac{dN_C}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\frac{MC^2}{2RT}} C^2 dC$$

dN_C = number of molecules having velocities between C and $(C + dC)$, N = total number of molecules, M = molecular mass, T = temperature on absolute scale (K).

The above relation is called **Maxwell's law of distribution of molecular velocities**.

- The **average velocity** of a gas is given by the arithmetic mean of the different velocities possessed by the molecules of the gas at a given temperature.

$$\text{Average velocity or } C_{av} = \frac{C_1 + C_2 + C_3 + \dots + C_N}{N}$$

$$\text{Also } C_{av} = \sqrt{\frac{8RT}{\pi M}} \quad (M \text{ is in kg})$$

- The **root mean square velocity** is defined as the square root of the mean of the squares of different velocities possessed by molecules of a gas at a given temperature.

$$C_{rms} = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots}{N}}, \quad C_{rms} = \sqrt{\frac{3RT}{M}}$$

- The **most probable velocity** is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature.

$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

- Relation between average velocity, RMS velocity and most probable velocity is given as
Average velocity = $0.9213 \times$ RMS velocity
Most probable velocity = $0.8165 \times$ RMS velocity

- The variation of volume V with temperature T , keeping pressure P constant is called the **coefficient of thermal expansion** or the **coefficient of isobaric expansion** or simply **expansivity**, α of the fluid. Thus, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$.

- The variation of V with P , keeping T constant is called **coefficient of isothermal compressibility** or simply **compressibility**, β of the fluid. Thus, $\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

- The distance between the centres of two molecules at the point of their closest approach is known as **collision diameter** and it is represented by σ .

- **Collision number** gives the number of collisions suffered by a single molecule per unit time per unit volume of the gas. Thus $N_C = \sqrt{2} \pi \sigma^2 \langle C \rangle n$.

- The mean distance travelled by a molecule between two successive collisions is called the **mean free path**. It is denoted by λ .

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where P = pressure of the gas

d = density of the gas and

η = coefficient of viscosity of the gas.

- The mean free path is directly proportional to the absolute temperature and inversely proportional to the pressure of a gas at constant temperature.
- **Collision frequency** is the number of molecular collisions occurring per unit time per unit volume of the gas.
- The collision frequency of a gas increases with increase in temperature, molecular size and the number of molecules per c.c.
- Collision frequency is given by $Z = \frac{\pi C \sigma^2 n^2}{\sqrt{2}}$
- Collision frequency is directly proportional to the square root of absolute temperature and also directly proportional to the square of the pressure of the gas.
- The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities is called **atmolyis**. It has been applied with success for the separation of isotopes and other gaseous mixtures.
- **Specific heat** of a substance is defined as the amount of heat required to raise the temperature of 1 g of the substance through 1°C. It is represented in calories.
- **Molar heat** of a substance is defined as the quantity of heat required to raise the temperature of one mole of the substance through 1°C. Evidently, Molar heat = specific heat × molar mass of the substance.
- One **calorie** is defined as the amount of heat required to raise the temperature of 1 g of water through 1°C.
- **Specific heat at constant volume** is the amount of heat required to raise the temperature of one gas through 1°C while the volume is kept constant and the pressure is allowed to increase. It is denoted by the symbol C_V .
- **Specific heat at constant pressure** is defined as the amount of heat required to raise the temperature of one gram of gas through 1°C, the pressure remaining constant while the volume is allowed to increase. It is written as C_p .
- The pressure exerted by the water vapour at a particular temperature is called **aqueous tension** at that temperature. It depends only on temperature.
- **Values of molar heat capacities (in S.I. units).**

Gas (mol^{-1})	C_V (JK^{-1})	C_p	$C_p - C_V = R$	$C_p/C_V = \gamma$	Atomicity
Helium	12.6	20.9	8.3	1.659	1
Argon	12.5	20.8	8.3	1.664	1
Mercury vapour	12.5	20.8	8.3	1.664	1
Hydrogen	20.4	28.8	8.4	1.412	2
Oxygen	20.9	29.3	8.4	1.402	2
CO	21.0	29.3	8.3	1.395	2
CO ₂	28.7	37.2	8.5	1.294	3
Ethylene	34.3	42.8	8.5	1.247	n

- The **degrees of freedom** of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely.

- The **centre of gravity** of any molecule has three translational degrees of freedom.
- All linear molecules such as CO_2 and C_2H_2 have two rotational degrees of freedom because their rotational motion is similar to that of a diatomic molecule.
- Non-linear molecules such as H_2O , H_2S , CH_4 , C_6H_6 can undergo rotation about the three Cartesian axes so that they have three rotational degrees of freedom.
- There are $3n - 6$ vibrational degrees of freedom for a non-linear molecule and $3n - 5$ vibrational degrees of freedom for a linear molecule.
- A normal mode of vibration is defined as a molecular motion in which all the atoms in the molecule vibrate with the same frequency and all the atoms pass through their equilibrium positions simultaneously.
- CO_2 molecule (linear) has 4 vibrational degrees of freedom.
- In the solid state, the solids possess only vibrational degrees of freedom. The translational and rotational motion in solids are converted into vibrational motion where the atoms in the lattice vibrate about their equilibrium positions.
- According to the Born-Oppenheimer approximation, the total energy of a molecule is given by

$$E_{\text{total}} = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

where E_{tr} is the translational energy, E_{rot} is the rotational energy, E_{vib} is the vibrational energy and E_{el} is the electronic energy.

- The variation of pressure with altitude is given by the barometric formula

$$P = P_0 e^{(-Mgx/RT)}$$

- van der Waal's equation for n moles of a gas is given by

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

where n = number of moles, a and b are new empirical constants varying for different gases.

- The **critical temperature**, T_C of a gas may be defined as that temperature above which it cannot be liquefied no matter how great the pressure applied.
- The **critical pressure**, P_C is the minimum pressure required to liquefy the gas at its critical temperature.
- The **critical volume**, V_C is the volume occupied by one mole of the gas at the critical temperature and critical volume.
- The numerical values of critical constant derived from van der Waal's equation are

$$T_C = \frac{8a}{27Rb}; \quad P_C = \frac{a}{27b^2}; \quad V_C = 3b$$

- The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is known as **Boyle's temperature** (T_B). Boyle's temperature of a gas is always higher than its critical temperature (T_C).

$$T_B = \frac{a}{Rb}.$$

- The P - V curves of a gas at constant temperature are called **isotherms** or isothermals.
- When a gas under high pressure is permitted to expand into a region of low pressure, it suffers a fall in temperature. This phenomenon is known as Joule Thomson effect.
- The constant a in van der Waal's equation is a measure of intermolecular forces of attraction. Greater the value of a , more easily the gas can be liquefied.
- The constant b in van der Waal's equation is related to the volume of the molecules and takes into account the fact that the space actually occupied by the molecules themselves is unavailable for the molecules to move in and hence must be subtracted from the total volume of the gas (V). b is also called co-volume or excluded volume.
- At low pressures, van der Waal's equation is written as

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT \quad \text{or,} \quad Z = \frac{PV_m}{RT} = 1 - \frac{a}{V_m RT},$$

where Z is known as the **compressibility factor**.

- At higher pressures, the gas equation is written as

$$P(V_m - b) = RT \quad \text{or,} \quad Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$$



IMPORTANT FACTS ABOUT GAS CONSTANT R

1. In ideal gas equation, $PV = nRT$, R is known as **universal gas constant**.
2. The value of R depends on the units of measurement of P , V and T .
3. R has the dimensions of energy.
4. For one mole of an ideal gas $PV = RT$ (since $n = 1$).
5. Only very few gases such as H_2 , He and N_2 show some ideal behaviour.
6. Real gases show ideal behaviour at low pressure and high temperatures.
7. Gas constant for single molecule is known as Boltzmann constant k . ($R/N = k$).

$$\begin{aligned} k &= 1.38 \times 10^{-16} \text{ erg/degree-molecule} \\ &= 1.38 \times 10^{-23} \text{ Joule/degree-molecule.} \end{aligned}$$

8. $R = 0.0821 \text{ lit-atm/deg.mole} = 8.314 \text{ Joule/degree-mole}$
 $= 1.987 \text{ cal/degree-mole} = 82.1 \text{ mL-atm/degree-mole}$
 $= 8.314 \times 10^7 \text{ erg/degree-mole} = 62.4 \text{ lit-mm/degree-mole}$
 $= 6.24 \times 10^4 \text{ mL-mm/degree-mole} = 0.002 \text{ k.cal/degree-mole}$
 $= 5.28 \times 10^{19} \text{ eV/degree-mole.}$

LIQUID STATE

- Liquid state is intermediate between gaseous and solid states. They possess fluidity like gases but incompressibility like solids.
- In terms of kinetic molecular model, the nature of the liquid state is described as follows:

- (i) Liquids are composed of molecules.
- (ii) The molecules of liquids are held together by appreciable intermolecular forces.
- (iii) Due to weak intermolecular forces, the molecules are in constant random motion.
- (iv) The average kinetic energy of molecules in a given sample is proportional to the absolute temperature.

Properties of Liquids

- **Shape** : Liquids have no shape of their own but assume the shape of the container in which they are kept.
- **Volume** : In liquids the intermolecular forces are strong and therefore, they do not expand to occupy all the space available (as gases do).
- **Density** : The higher densities of liquids than gases are due to the fact that molecules of liquids are more closely packed than gases. In general, the density of the liquids decreases with increase in temperature.
- **Compressibility** : The molecules in a liquid are held in such close contact by their mutual attractive forces that the volume of any liquid decreases very little with increased pressure. Thus, liquids are relatively incompressible compared to gases.
- **Diffusion** : The diffusion of liquids is defined as the process of intermixing of the molecules of two or more liquids to form a homogenous mixture solution. However, the rate of diffusion of a liquid can be increased by raising the temperature the temperature which increases the kinetic energy of the molecules.
- **Evaporation** : The process of change of liquid into vapour state below its boiling point is termed evaporation.

The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces.

Rate of evaporation \propto surface area

Rate of evaporation \propto temperature

- **Heat of vaporisation** : The amount of heat required to evaporate 1 mole of a given liquid at a constant temperature is known as the heat of evaporation or heat of vaporisation.
The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature.
- **Vapour Pressure** : “The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the vapour pressure.”
- **Boiling point** is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
- **Freezing point** : The temperature at which the vapour pressures of solid and liquid forms of a substance become equal is termed as freezing point.
- **Surface tension** may be defined as force per unit length acting perpendicular to the tangential line on the surface.

The units of surface tension are force per unit length i.e., dynes cm^{-1} . In S.I. the unit is Nm^{-1} . For example, the surface tension of water is $72.75 \times 10^{-3} \text{ Nm}^{-1}$ and that of mercury is $47.5 \times 10^{-2} \text{ Nm}^{-1}$.

- Surface tension decreases with rise in temperature.

I. Let γ_1 and d_1 be the surface tension and density of water and γ_2 and d_2 be surface tension and density of the liquid whose surface tension is to be determined.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

- **Viscosity** : The internal resistance to flow in liquids which one layer offers to another layer trying to pass over it is called viscosity.

Force of friction ' f ' between two cylindrical layers each having area ' A ' sq. cm separated by a distance ' x ' cm and having a velocity difference ' v ' cm/sec is given by

$$f \propto A \frac{v}{x}; \quad f = \eta A \frac{v}{x}$$

- Viscosity is generally determined by Ostwald's method.

$$\frac{\eta}{\eta_w} = \frac{d \times t}{d_w \times t_w}$$

where η_w and η = coefficient of viscosity of water and liquid respectively, d = density of liquid d_w = density of water ; t = time of flow of liquid ; t_w = time of flow of water.

SOLID STATE

- Solids are characterized by their high density, low compressibility, definite shape, considerable mechanical strength and rigidity. These properties are due to the existence of very strong forces of attraction amongst the molecules, atoms or ions of the solids.
- The solid state represents the physical state of matter in which the constituent molecules, atoms or ions have no translatory motion although they vibrate about the fixed position, that they occupy in a crystal lattice.

Crystalline solids have definite shape and volume. They are rigid, incompressible, *anisotropic*, i.e. their mechanical, electrical properties depend on the direction along which these are measured. Amorphous solids (like plastic, glass) however, are *isotropic*.

- **Crystalline solids**

- have definite geometrical shape, sharp melting point.
- are anisotropic
- have definite order close-packed structure.
- can be ionic, covalent, molecular and metallic.

- **Amorphous solids**

- do not have definite shape (glass, plastic, rubber, wood) and melting point
- are isotropic
- have short-range order packing.

- **Intermolecular forces**

Solids have been classified based on type of intermolecular forces existing in them.

– **Dispersion forces or London forces**

When distribution of electrons around the nucleus is not symmetrical then there is formation of instantaneous electric dipole. Field produced due to this distorts the electron distribution in the neighbouring atom or molecule so that it acquires a dipole moment itself. The two dipole will attract and this makes the basis of London forces or dispersion forces. These forces are attractive in nature and the interaction energy due to this is proportional to $(1/r^6)$. Thus, these forces are important at short distances. This force also depends on the polarisability of the molecule.

– **Dipole-dipole forces**

These type of forces occur between molecules having permanent electric dipole. In HCl, bond between H and Cl is formed by sharing of electrons, but shared electron pair is near to chlorine because of higher electronegativity compared to H-atom. Thus bond formed is said to be polar and a partial charge is developed on both atoms.

– **Dipole-induced dipole forces**

Attractive forces are operative not only between the two molecules with permanent dipoles but also between a molecule having a dipole moment and a molecule without any dipole moment like CH_4 . As the size of the atom increases the influence of the electric dipole on it also increases. The electron cloud of the molecule is deformed in the electric field of the permanent dipole. This causes a shift in the centre of gravity of the negative charge relative to the nuclear charge and leads to the formation of an induced dipole moment.

● **Crystal**

Crystal is made of a number of unit cells, each possessing a definite geometry and bound by plane faces. *Face* is a planar surface arranged on a definite plane which binds the crystals. Faces in a crystal may be like or unlike, all faces together constitute a *form*.

Edges are the intersection of two adjacent faces and the angle between the normals to the two intersecting faces is called *interfacial angle*.

● **Law of crystallography**

– *Law of constancy of interfacial angles* - A crystal may have different shapes according to the number and size of the faces, but the angle of intersection of two adjacent faces is always constant.

– *Hauy's law of rationality of indices* - The intercepts of any face of a crystal on a suitable axes can be expressed by small multiples of three unit distances a , b , c or their integral multiples (m, n, p) .

– *Law of symmetry* - All crystals of the same substance possess same elements of symmetry. A crystal can have three types of symmetry.

– *Plane of symmetry* is present in a crystal when an imaginary plane passing through its centre gives two parts which are mirror images.

- *Axes of symmetry* is an imaginary line passing through the crystal such that when the crystal is rotated about it, it gives the same appearance more than once in a complete revolution.
- If similar appearance occurs twice, thrice and so on the axis is respectively called a diad, triad, tetrad, hexad, etc.
- *Centre of symmetry* is an imaginary point within a crystal such that any line passing through it intersects the surface of the crystal at equal distances on each side of the point.

Nature of solids

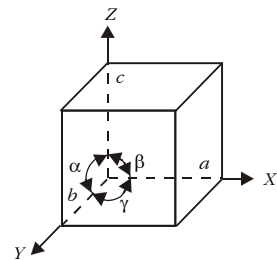
Types of solid	Constituents	Bonding	Examples	Physical nature	Melting point	Electrical conductivity
Ionic	Ions	Coulombic	NaCl, KCl, CaO, MgO	Hard but brittle	High ≈ 1000 K	Conductor (in molten state and in aq. solution)
Covalent	Atoms	Electron sharing	SiO ₂ (quartz), SiC (diamond), C (graphite)	Hard	Very high ≈ 4000 K	Insulator
Molecular	Simple covalent molecules	Molecular interactions (intermolecular forces),	I ₂ , S ₈ , P ₄ , CO ₂ , CCl ₄	Soft	Low (≈ 300 K to 600 K)	Insulator
		Hydrogen bonding	starch, sucrose, water, ice	Soft	Low (≈ 273 K to 400 K)	
Metallic	Positive ions and electrons	Metallic	sodium, magnesium, metals and alloys	Ductile malleable	High (≈ 800 K to 1000 K)	Conductor

- **Unit cell**

Unit Cell is the smallest repeating unit in a three dimensional space or crystal lattice.

- **Characteristics of a unit cell**

- Primitives or the three sides, a , b , c of a unit cell are also known as characteristic intercepts.
- Crystallographic axes are lines drawn parallel to lines of intersection of any three faces of the unit cell which are not in the same plane.
- Interfacial angles α , β , γ are made between the three crystallographic axes.



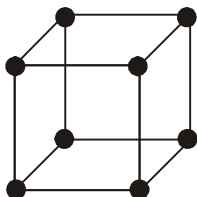
Crystallographic axes : OX, OY, OZ
 Interfacial angles : α , β , γ
 Primitives : a , b , c

- **Space lattice or Crystal lattice** is a three dimensional arrangement of points showing the particles (atoms,

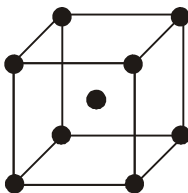
molecules, or ions) in a definite orderly distribution.

Bravais also showed that there are basically four types of unit cells depending on the manner in which they are arranged in a given shape.

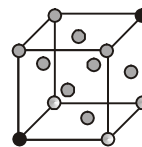
These are: Primitive, Body Centred, Face Centred and End Centred.



Primitive cubic
unit cell



Body centred
cubic unit cell



Face centred
cubic unit cell

- **Atoms per unit cell**

There are three kinds of lattice points in a unit cell, points at the corners and face centres are shared by other cells, whereas point within the cell is not shared.

Based on the location of points and their contribution to each cell we can calculate the number of atoms per unit cell.

A point that is at the corners of a unit cell is shared by eight unit cells and contributes $1/8$ to each cell.

A point on an edge is shared by four unit cells and contributes $1/4$ to each cell.

A face centred point is shared between two unit cells only and contributes $1/2$ to each.

A point in the centre of the body is not shared and contributes wholly to the unit cell.

- **Co-ordination number**

It is number of nearest neighbours or spheres in contact with the sphere under consideration.

Co-ordination number of a crystal depends upon its structure.

- simple cubic structure has $CN = 6$

- face centred cubic structure (fcc) has $CN = 12$

- body centred cubic structure (bcc) has $CN = 8$

Density of lattice matter is the ratio of mass per unit cell to the total volume of unit cell:

$$D = \frac{\text{mass per unit cell}}{\text{volume of unit cell}} = \frac{n \times \text{at. wt.}}{\text{Av. no.} \times \text{Volume of unit cell}}$$

n = no. of atoms per unit cell, a^3 = volume for cubic crystal systems

Packing-fraction or density of packing is the ratio of volumes occupied by atoms in a unit cell (v) to the total volume of the unit cell (V).

Packing fraction = v/V .

The density of packing can show how closely the atoms are packed in a unit cell. Calculations reveal that close packing in cubic crystal system follows the order: $fcc > bcc > sc$.

- **Dimensions of unit cells** are actually the inter atomic distances in a unit cell and can be calculated for different crystal structures if its density, molecular weight and Avagadro's number are known.

$$\text{Simple cubic structure, } a = \sqrt[3]{\frac{1 \times A}{\text{Av. No} \times \rho}}$$

$$\text{Face centred cubic structure, } a = \sqrt[3]{\frac{4 \times A}{\text{Av. No} \times \rho}}$$

$$\text{Body centred cubic structure, } a = \sqrt[3]{\frac{2 \times A}{\text{Av. No} \times \rho}}$$

A = at. weight, ρ = density

- Density of a unit cell = $\frac{z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3}$ (for a cube)

where z is the number of atoms in a unit cell and V is the volume of unit cell.

For a cube $V = a^3$ where a is the edge length of the cubic unit cell.

- Packing fraction or density of packing

$$= \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

For simple cubic structure

V = volume of the unit cell is a^3 and since one atom is present in a unit cell,

$$\therefore \text{Volume } V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\therefore \text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3 / 6}{a^3} = \frac{\pi a^3}{6} \cdot \frac{1}{a^3} = \frac{\pi}{6} = 0.52$$

\therefore Percentage efficiency = 52%

For fcc structure, there are four atoms present in a unit cell, therefore total volume is

$$V = 4 \times \left(\frac{4}{3} \pi r^3\right)$$

$$\text{for } fcc \quad r = \frac{a}{2\sqrt{2}}$$

$$\therefore V = \frac{16}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3 \Rightarrow V = \frac{\pi}{3\sqrt{2}} a^3$$

$$\begin{aligned} \text{Packing fraction} &= \frac{\pi a^3}{3\sqrt{2}a^3} \quad [\because V = a^3] \\ &= \frac{\pi}{3\sqrt{2}} = 0.74 \end{aligned}$$

\therefore Percentage efficiency is 74% i.e. 74% of the unit cell is occupied by atoms and 26% is empty.

In bcc structure, there are two atoms present in unit cell, therefore, their volume is

$$V = 2 \times \frac{4}{3} \pi r^3$$

$$\text{for bcc } r = \frac{\sqrt{3}}{4} a$$

$$\therefore V = 2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a \right)^3 = \frac{\sqrt{3}}{8} \pi a^3$$

Since the volume of unit cell, $V = a^3$

$$\therefore \text{packing fraction} = \frac{\sqrt{3}}{8} \frac{\pi a^3}{a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

i.e. 68% of the unit cell is occupied by atoms and 32% is empty.

- **Bragg's equation**

Bragg's Equation interprets the diffraction pattern resulting from scattering of X-rays by regular arrangement of atoms or ions:

$$n\lambda = 2d \sin \theta$$

$$n = 1, 2, 3 \dots \text{ (diffraction order)}$$

$$\lambda = \text{wavelength of X-rays incident on crystal}$$

$$d = \text{distance between atomic planes}$$

$$\theta = \text{angle at which interference occurs}$$

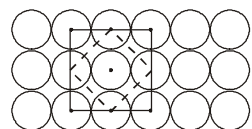
Radius Ratio is the ratio of the radii of positive and negative ions in a crystal:

$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}} = \frac{r^+}{r^-}$$

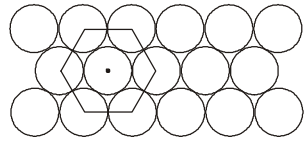
- **Packing of constituents in crystals**

Constituents of a crystal have a tendency to pack as closely as possible to have maximum density and stability.

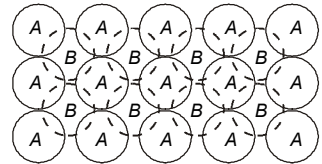
- **Square Close Packing** system has spheres of adjacent rows one over the other, showing a vertical as well as horizontal alignment to form a square.



- **Hexagonal Close Packing** system has spheres of energy second row placed in the depression between spheres of the first row. Subsequently, spheres of third row are vertically aligned with those of the first row.



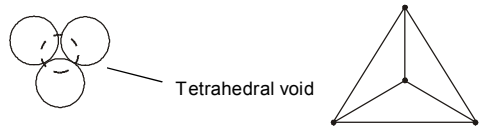
- **Body Centred Cubic** arrangement (bcc) is not the closest system, it is obtained when the spheres of the first row (layer) are slightly open and not in contact with each other.



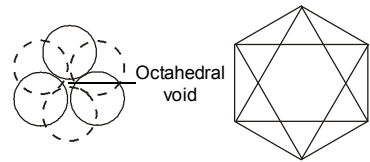
- **Void space or holes**

In a unit cell some empty space exists between spheres, this is called void space or hole, also called interstitial void, or interstices.

- **Tetrahedral Voids** are holes or interstices surrounded by four spheres present at the corners of a tetrahedron. CN of tetrahedral void is 4



- **Octahedral Voids** are holes surrounded by six spheres located on a regular tetrahedron. CN of octahedral void is 6.



Structures of Simple Ionic Compounds

- **AB Type Structures**

The three common types of structure sodium chloride, caesium chloride and zinc sulphide are described below

1. **Sodium chloride or rock salt structure** : NaCl has *fcc* structure with each sodium atom surrounded by 6 Cl^- ions and vice versa. Therefore, there will be one Na^+ ion for every Cl^- ion. Thus, the ratio of Na^+ and Cl^- ions in this structure is 1 : 1.

In this octahedral arrangement, coordination number of both Na^+ and Cl^- is 6.

2. **Caesium chloride structure** : It is a body centred cubic structure. Cs^+ ion is surrounded by 8 Cl^- ions which are disposed towards the corners of a cube. Cl^- ion is also surrounded by 8 Cs^+ ions. Thus the coordination number of Cs^+ and Cl^- is 8 : 8.

3. **Zinc sulphide or sphalerite structure** : In this face centered cubic lattice each zinc ion is surrounded by four sulphide ions. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions. Therefore, there is one zinc ion for every sulphide ion. Thus, the compound has the formula ZnS.

- **A_2B and AB_2 Type Structures**

The common example of AB_2 type structure is calcium fluoride (CaF_2) called fluorite structure and of A_2B type structure is sodium oxide (Na_2O) called antifluorite structure.

In CaF_2 the Ca^{2+} ions are located at face centred cubic lattice points and therefore

have cubic closed packed arrangement. The F^- ions occupy all the eight tetrahedral voids. In this structure, each F^- ion is surrounded by four Ca^{2+} ions, while Ca^{2+} ion is surrounded by eight F^- ions. Thus, the coordination number of Ca^{2+} and F^- ions are 8 : 4.

In the antifluorite structure *i.e.* in A_2B structure the position of cations and anions are reversed. In this structure, the small cation (Na^+) occupy the positions of fluoride ions and the larger anions (O^{2-}) occupy the positions of the calcium ions in the fluorite structure.

The coordination number of Na^+ ions is 4 and that of O^{2-} ions is 8. Thus Na_2O has 4 : 8 coordination. There are several oxides and sulphides which have antifluorite structure such as Li_2O , K_2O , Rb_2O and Rb_2S .

- **Crystal defects**

- In a crystalline solid the atoms, ions or molecules are arranged in a definite repeating pattern, but some defects may occur in the pattern. Deviations from perfect arrangement may occur due to temperature changes or presence of additional particles.
- Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, that are located between the regular positions for atoms.

Nature of defects in crystals

Defect	Nature of defect
1. Schottky	Atom or ion missing from the lattice point and thus giving a vacancy. Density of the crystal is lowered.
2. Interstitial	Atom or ion in a vacant void, also called hole, (or interstitial site).
3. Frenkel	This is a hybrid type of defect produced from the combination of (1) and (2). Atom or ion at the lattice point displaced to an interstitial site creating a vacancy.
4. F-centre	Electron trapped in an anionic vacancy is called F-centre. If the concentration of F-centres is high, colourless crystals (like KCl, LiCl, NaCl) develop some colour.
5. Dislocation	Line defects are called dislocations.
6. Non-stoichiometric	It is in cases where the compounds contain the combining elements in a ratio different from that required by their stoichiometric formulae. VO_x ($x = 0.6$ to 1.3), $Fe_{0.95}O$.

End

atomic structure

- Until the 19th century and the development of the Bohr model, it was believed that atoms were tiny, indivisible particles. An atom is a microscopic structure found in all ordinary matter around us.
- **John Dalton** (1809) regarded the atom as a hard dense and smallest indivisible particle of matter.
- When an electric discharge from a high potential source is passed through a gas contained in a Geissler discharge tube at a very low pressure of the order of a few millimeters, invisible rays are emitted from the cathode of the discharge tube and are known as **cathode rays**.
- The mass of an electron equals to 5.5×10^{-4} amu or 9.1019×10^{-28} g or 9.1019×10^{-31} kg. This is called the rest mass of the electron, *i.e.* the mass which it possesses when it is moving with velocity much smaller than that of light. At high speeds, the mass of the electron in accordance with the theory of relativity, is given by

$$m' = \frac{m}{(1 - (v^2/c^2))^{1/2}}$$

(where m' is the mass of the electron moving with velocity v , c is the velocity of light and m is the rest mass of the electron).

- In 1932, **James Chadwick** discovered the neutron.
- The mass of neutron 1.675×10^{-24} g is slightly greater than that of a proton ($= 1.673 \times 10^{-24}$ g).
- **Mosley** postulated the frequency of the X-rays was related to the charge present on the nucleus of the atom of the element used as anticathode and found that $\sqrt{\nu} = a(z - b)$, where ν is the frequency, z is the nuclear charge and a and b are constants.
- The number of unit positive charges carried by the nucleus of an atom is called the **atomic number** of the element.
- An atom consists of minute positively charged body located at its centre, called the **nucleus** and contains protons and neutrons.
- The nucleus has a diameter of the order of 10^{-15} m while atom has the diameter of the order of 10^{-10} m.
- The sum of the number of protons and neutrons is called the **mass number**.