

CHEMISTRY

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CHAPTER 1

PERIODIC TABLE

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IMPORTANT NOTES

CHAPTER 1

PERIODIC TABLE

PART-A (PERIODIC TABLE)

INTRODUCTION :

The arrangement of all the known elements according to their properties in such a way that the elements of similar properties are grouped together in a tabular form is called periodic table.

Development of periodic table :

(A) LAVOISIER CLASSIFICATION OF ELEMENTS

At first Lavoisier classified the elements into two categories.

- (i) Metal
- (ii) Non-metal

Note : This classification cannot categorise the metalloid variety.

(B) DOBEREINER'S TRIAD RULE [1817]

- (i) He made groups of three elements having similar chemical properties called TRIAD.
- (ii) In Dobereiner triad, atomic weight of middle element is nearly equal to the average atomic weight of first and third element.

e.g.

	Cl	Br	I	
	35.5	[80.0]	127	$\frac{35.5 + 127}{2} = 81.25$

	Ca	Sr	Ba	
	40	[87.5]	137	$\frac{40 + 137}{2} = 88.5$

	Li	Na	K	
	7	[23]	39	At. wt of Na = $\frac{7 + 39}{2} = 23$

(iii) Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

(C) NEWLAND'S OCTAVE RULE [1865]

- (i) He arranged the elements in the increasing order of their atomic mass and observed that properties of every 8th element was similar to the 1st one, like in the case of musical vowels notation.

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
1	2	3	4	5	6	7	8

- (ii) At that time inert gases were not known.

Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca					Cl

- (iii) The properties of Li are similar to 8th element i.e. Na, Be are similar to Mg and so on.

Drawbacks or Limitations :

- (a) This rule is valid only upto Ca. because after Ca due to filling of d-orbitals there is difference of 18 elements instead of 8 element.
- (b) After the discovery of inert gas this law had to be dropped out.
- (c) He failed in the case of heavier metals as Fe has been placed along with O and S.

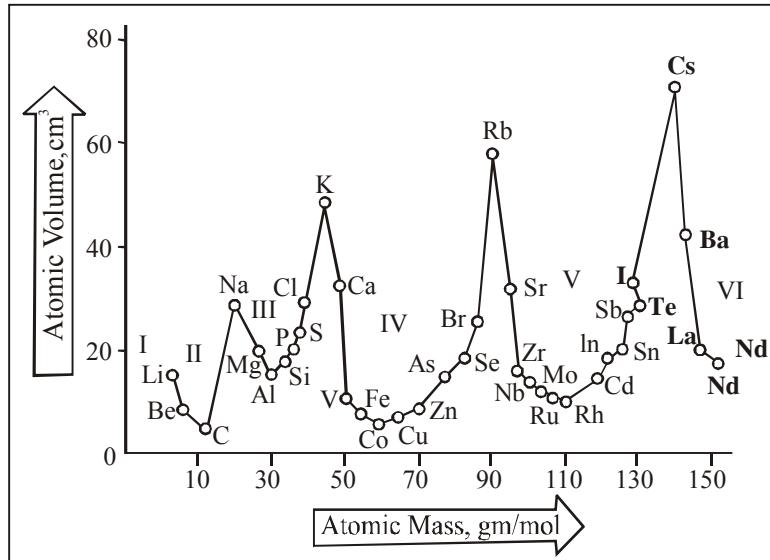
(D) LOTHER MEYER'S CURVE [1869]

- (i) He plotted a curve between atomic weight and atomic volume of different elements.
- (ii) The following observations can be made from the curve –
 - (a) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak portions of the curve.
 - (b) Less electropositive i.e. alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupy the descending portions of the curve.
 - (c) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
 - (d) Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending portion of the curve.

Note : Elements having similar properties occupy similar portions of the curve.

Conclusion :

On the basis of this curve, Lother Meyer proposed that the physical properties of the elements are periodic function of their atomic weight and this became the basis of Mendeleev's periodic table.

**(E) MENDELEEV'S PERIODIC TABLE [1869]**

- (i) **Mendeleev's periodic law** – The physical and chemical properties of elements are the periodic function of their atomic weight
- (ii) **Characteristic of Mendeleev's periodic table** –
 - (a) It is based on atomic weight
 - (b) 63 elements were known, noble gases were not discovered.
 - (c) He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.

- (d) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.
- (e) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
- (f) Each group upto VIIth is divided into A & B subgroups.'A' sub group elements are called normal elements and 'B' sub group elements are called transition elements.
- (g) The VIIIth group consists of 9 elements in three rows.
- (h) The elements belonging to same group exhibit similar properties.

(iii) Merits or advantages of Mendeleev's periodic table –

- (a) ***Study of elements*** – For the first time, all known elements were classified in groups according to their similar properties. So study of the properties of elements became easier.
- (b) ***Prediction of new elements*** – It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium), Ga (Gallium), Ge (Germanium), Tc (Technetium)

were the elements whose position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

e.g. - Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element (*discovered later*) was named Germanium .

Similarly other elements discovered after mendeleev periodic table were :

Eka aluminium – Gallium(Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

- (c) ***Correction of doubtful atomic weights***– Corrections were done in atomic weight of some elements.

$$\text{Atomic Weight} = \text{Valency} \times \text{Equivalent weight.}$$

Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent ($V = 3$), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent ($V = 2$). So, the weight of Be became $2 \times 4.5 = 9$ and there was a space between Li and B for this element in Mendeleev's table.

Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

(iv) Demerits of Mendeleev's periodic table –

(a) Position of hydrogen – Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties so Mendeleev could not decide where to place it.

(b) Position of isotopes – As atomic weight of isotopes differs, they should have been placed in different position in Mendeleev's periodic table. But there was no such place for isotopes in Mendeleev's table.

(c) Anomalous pairs of elements – There were some pair of elements which did not follow the increasing order of atomic wts.

eg : Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

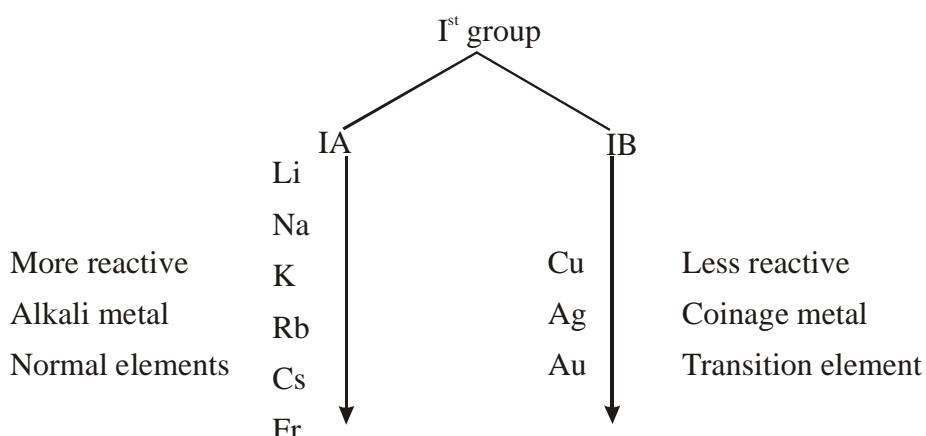


(d) Like elements were placed in different groups.

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev's table.



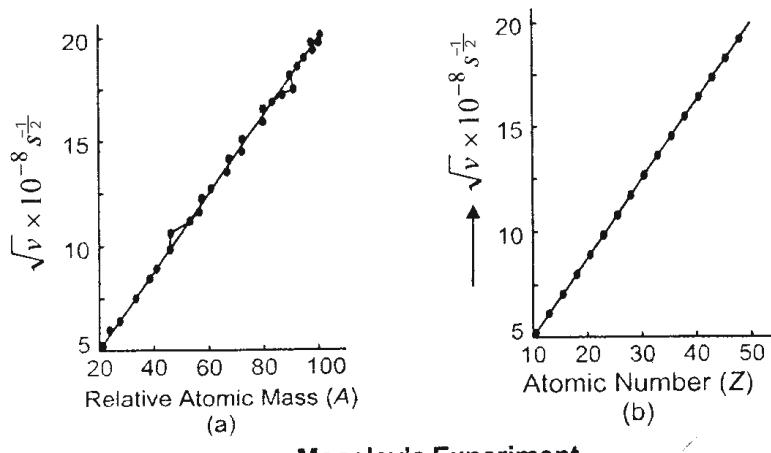
(e) Unlike elements were placed in same group.



Cu, Ag and Au placed in Ist group along with Na, K etc. While they differ in their properties (Only similar in having ns¹ electronic configuration)

(F) MODERN PERIODIC TABLE (MODIFIED MENDELEEV PERIODIC TABLE)

- (i) It was proposed by Moseley (1913).
- (ii) Modern periodic table is based on atomic number.
- (iii) Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays.



Moseley's Experiment

He found out that $\sqrt{\nu} \propto Z$ (where ν = frequency) of X-rays from this experiment, Moseley concluded that the physical and chemical properties of the elements are periodic function of their atomic number. It means that when the elements are arranged in the increasing order of their atomic number, elements having similar properties gets repeated after a regular interval. This is also known as '**Modern Periodic Law**'.

- (iv) **Modern periodic law** – The physical & chemical properties of elements are a periodic function of their atomic number.
- (v) **Characteristics of modern periodic table** –
 - (a) 9 vertical columns called groups.
 - (b) IA to VIIA, IB to VIIB, VIII and 0
 - (c) Inert gases were introduced in periodic table by Ramsay.
 - (d) 7 horizontal series called periods.

(G) LONG FORM / PRESENT FORM OF MODERN PERIODIC TABLE

(It is also called as 'Bohr-Burry & Rang, Werner Periodic Table.)

- (i) It is based on the Bohr-Burry electronic configuration concept and atomic number.
- (ii) This model was proposed by Rang & Werner

- (iii) It consists of 7 horizontal periods and 18 vertical columns (groups)
- (iv) According to I. U. P. A. C. 18 vertical columns are named as 1st to 18th group.
- (v) The co-relation between the groups in long form of periodic table and in modern form of periodic table are given below.
- IA, IIA, IIIB, IVB, VB, VIB, VIIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, 0

1	2	3	4	5	6	7	<u>8, 9, 10</u>	11	12	13	14	15	16	17	18
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- (vi) Elements belonging to same group have same no. of electrons in the outermost shell so their properties are similar.

Description of periods :

Period	n	Sub shell	No. of elements	Element	Name of Period
1.	1	1s	2	₁ H – ₂ He	Shortest
2.	2	2s, 2p	8	₃ Li – ₁₀ Ne	Short
3.	3	3s, 3p	8	₁₁ Na – ₁₈ Ar	Short
4.	4	4s, 3d, 4p	18	₁₉ K – ₃₆ Kr	Long
5.	5	5s, 4d, 5p	18	₃₇ Rb – ₅₈ Xe	Long
6.	6	6s, 4f, 5d, 6p	32	₅₅ Cs – ₈₆ Rn	Longest
7.	7	7s, 5f, 6d, 7p	32	₈₇ Fr – ₁₁₈ Og	Longest

Extended or Long Form of the Periodic Table

		Periodic Table of Elements																							
		Main Group Elements							Transition Metals							Post-Transition Elements									
		s-Block Elements		p-Block Elements					d-Block Elements						f-Block Elements										
Group	Period	Elements by Block										Elements by Type													
1	1	IA (1)		IIA (2)					d-Block Elements						f-Block Elements		p-Block Elements		s-Block Elements						
1	1	H 1.0079 Hydrogen		Li 6.940 Lithium		B 9.0122 Beryllium		Mg 24.305 Magnesium		Ca 40.078 Calcium		Sc 44.956 Scandium		Ti 50.941 Titanium		V 51.996 Vanadium		Cr 54.938 Chromium		Mn 55.847 Manganese					
2	2																								
3	3	Na 22.990 Sodium		K 39.098 Potassium		Ca 40.078 Calcium		Mg 24.305 Magnesium		Sc 44.956 Scandium		Ti 50.941 Titanium		V 51.996 Vanadium		Cr 54.938 Chromium		Mn 55.847 Manganese		Fe 58.933 Iron					
4	4																								
5	5	Rb 85.468 Rubidium		Sr 87.62 Strontium		Y 88.906 Yttrium		Zr 91.224 Zirconium		Nb 92.906 Niobium		Mo 95.94 Molybdenum		Tc 98 Technetium		Ru 101.07 Ruthenium		Rh 102.91 Rhodium		Pd 106.42 Palladium					
6	6																								
7	7	Fr 223 Francium		Ra 226 Radium		Ac** 227 Actinium		Ac*** 227 Actinium		Db 270 Dubnium		104 267 Rutherfordium		105 270 Rutherfordium		106 271 Seaborgium		107 270 Bh Berkelium		108 277 Hs Hassium					
6	6	* Lanthanide Series										58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 145 Pm Promethium	62 150.36 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.07 Yb Ytterbium	71 174.97 Lu Lutetium
7	7	** Actinide Series										90 231.04 Th Thorium	91 232.04 Pa Protactinium	92 238.03 U Uranium	93 237 Np Neptunium	94 244 Pu Plutonium	95 243 Am Americium	96 247 Cm Curium	97 251 Bk Berkelium	98 252 Cf Californium	99 257 Md Mendelevium	100 258 Fm Fermium	101 262 No Nobelium	102 262 Lr Lawrencium	

IUPAC designations of groups of elements are given in brackets

CLASSIFICATION OF ELEMENTS INTO s , p , d & f BLOCK ELEMENTS:

s – block :

- (i) configuration $n\ s^{1-2}$
- (ii) last e^- enters in s orbital
- (iii) two groups IA or 1 ; IIA or 2

p – block :

- (i) configuration $n\ s^2\ n\ p^{1-6}$
- (ii) last e^- enters in p orbital
- (iii) six groups IIIA, IVA, VA, VIA, VIIA, zero or 13, 14, 15, 16, 17, 18

d – block : [Transition Elements]

- (i) configuration $(n-1)\ d^{1-10}\ n\ s^{0-2}$
- (ii) last e^- enters in d orbital
- (iii) their two outermost shell are incomplete
- (iv) 10 groups IIIB, IVB, VB, VIB, VIIIB, VIII (Triad), IB, IIB or 3, 4, 5, 6, 7, (8, 9, 10), 11, 12 .
- (v) four series 3d, 4d, 5d, 6d belong to 4th, 5th, 6th & 7th period respectively in long form of Periodic table.

f – block : [Inner Transition]

- (i) configuration $(n-2)\ f^{0-14}\ (n-1)\ d^{0-2}\ ns^2$
- (ii) last e^- enters in f orbital
- (iii) two series 4f Lanthanides & 5f Actinides belong to 6th & 7th period respectively in long form of Periodic table.

Neil Bohr's classification of elements :

Using electronic configuration as the criteria, elements are of four types. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

Inert Gases :

- (a) s – and p-orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is ns^2np^6 .
- (b) Helium is also inert gas but its electronic configuration is $1s^2$

Representative or Normal Elements :

- (a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.
- (b) s-and p-block elements except inert gases are called normal or representative elements.

Transition Elements :

- (a) These metals were placed between s-block metals and p-block elements so, are named transition metals.
- (b) Their outermost electronic configuration is similar to d-block elements i.e. $(n-1)d^{1-10}ns^{1-2}$.
- (c) Last two shells of these elements namely outermost and penultimate shells are incomplete.
- (d) The last shell contains one or two electrons and the penultimate shell may contain more than eight and up to eighteen electrons.
- (e) According to definition of transition elements, those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state.

Inner Transition Elements :

- (a) In these elements last three shells i.e. last, penultimate and prepenultimate shells are incomplete.
- (b) These are related to IIIB i.e. group 3.
- (c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18, up to 32 electrons.
- (d) Their outermost electronic configuration is similar to f-block element
i.e. $(n-2)f^{0-14}(n-1)d^{0-2}ns^2$

METALS, NON-METALS & METALLOIDS

Apart from classifying elements into s, p, d and *f*-blocks, there is yet another broad classification of elements based on their properties. The elements can be broadly classified into

(a) Metals:

Majority of the elements in periodic table are metals and appears on the left side of the periodic table.

Properties:

- (i) These are usually solid at room temperature [exception - mercury]
- (ii) They have high melting and boiling point [exception Gallium & Cesium have very low melting point (303 K and 302 K respectively)]
- (iii) They are good conductor of heat and electricity.
- (iv) They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires)

(b) Non-Metals:

These are placed at the top right hand side of periodic table. As we move horizontally along a period, the property of elements changes from metallic (on left) to non-metallic (on the right).

Properties :

- (i) These are usually solids or gases at room temperature.
- (ii) They have low melting point and boiling point (exception : Boron, Carbon).
- (iii) Most Non-metallic solids are brittle and are neither malleable nor ductile.

(c) Metalloids (Semi-metals):

Properties of these elements show the characteristics of both metals and non-metals.

Silicon (Si), Germanium(Ge), Arsenic(As), Antimony(Sb) and Tellurium(Te) are metalloids.

ESTIMATING POSITION OF AN ELEMENT FROM ITS ELECTRONIC CONFIGURATION

The last electron enters in which subshell gives idea of its block.

[ **Think** : $1s^1$ and $1s^2$ belongs to which block]

Period number = Principal quantum number of valence shell electron in ground state electronic configuration.

Group number for s block = number of valence shell electrons

Group number for p block = $10 + \text{number of valence shell electrons}$

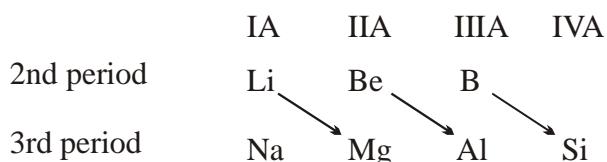
Group number for d block = number of $[\text{ns} + (\text{n}-1) \text{d}]$ electrons

Group number for f-block = 3

[ **Use these carefully while locating the position.]**

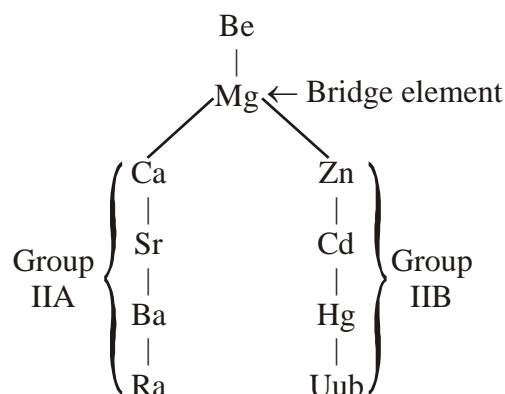
SOME COMMONLY USED TERMS

1. **Noble Gases** : Element of group 18 are called noble gases. These are also called as inert gases because their outermost ns and np orbitals are completely filled (except He and $1s^2$) and these gases are non-reactive in nature under ordinary conditions.
2. **Typical elements** : Elements of second and third period are known as typical elements.
3. **Diagonal relationship** : Properties of elements of second period resemble with the element of third period. This resemblance between properties of 2nd & 3rd period is called diagonal relationship.



4. Bridge elements :

The typical elements of third period are also called bridge elements as the division between two subgroups A and B starts from these elements. In second group Mg acts as a bridge element. The properties of bridge element are somewhat mixed of the elements of two subgroups as magnesium shows similarities with alkaline earth metals (IIA) on one hand and with zinc metals (IIB) on the other.



IUPAC NOMENCLATURE OF THE ELEMENT :

The names are derived by using roots for the three digits in the atomic number of the element and adding the ending –ium. The roots for the number are

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Thus element with atomic number 109 will be named as **une** (**u** for 1, **n** for 0 and **e** for 9). Table summarises the names of the elements with atomic number above 100.

PART-B (PERIODIC PROPERTIES)

PERIODICITY :

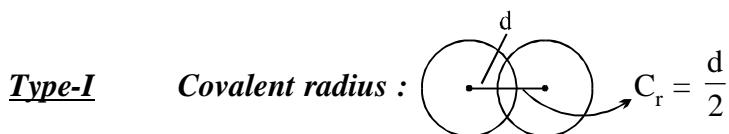
- (a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.
- (b) In a period, the ultimate shell remain same, but the number of electrons gradually increases.
- (c) In a group, the number of electrons in the ultimate shell remains same, but the values of n increases.

Cause of periodicity

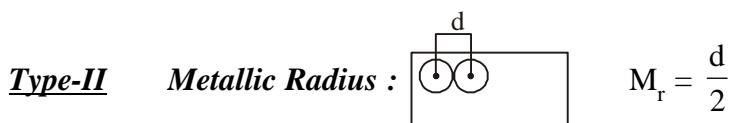
- (a) The cause of periodicity in properties is due to the same outermost shell electronic configuration repeating over regular intervals.
- (b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called magic numbers.

ATOMIC RADIUS :

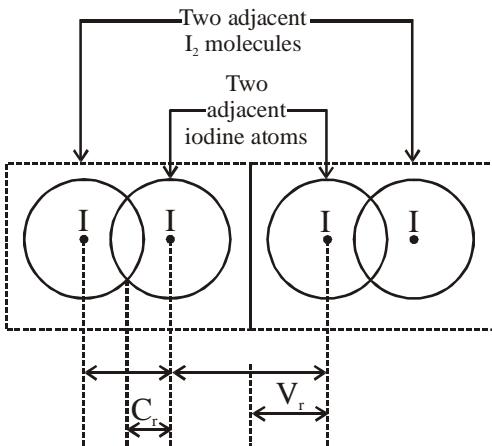
Since there is a problem in calculating actual size of atom, three types of radii can be defined:



[Used for H_2 , Cl_2 and such molecules]



[Used for metals]



VanderWaals radius = $\frac{1}{2} \times$ Internuclear distance between nuclei of two neighbouring atoms belonging to nearest molecules.

VanderWaals radius > Metallic radius > Covalent radius

The VanderWaals radius and covalent radius of chlorine atom are 1.80 Å and 0.99 Å respectively.

Ionic Radius

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions.

(a) **Radius of Cation**

Radius of cation is smaller than that of corresponding atom. Since due to removal of electron(s), Z_{eff} increases.

(b) **Radius of an Anion**

Radius of an anion is invariably larger than that of the corresponding atom, since due to addition of electron(s) Z_{eff} decreases.

Factors affecting atomic radius:

- | | |
|--|--|
| (a) Z_{eff} increases, atomic radius decreases | $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$ |
| (b) Number of shell(n) increases, atomic radius increases | $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ |
| (c) Screening effect increases, atomic radius increases. | |
| (d) Magnitude of -ve charge increases, atomic radius increases | $\text{O} < \text{O}^- < \text{O}^{2-}$ |
| (e) Magnitude of +ve charge increases, atomic radius decreases | $\text{Mn} > \text{Mn}^{+2} > \text{Mn}^{+3} > \text{Mn}^{+4}$ |
| (f) Bond order increases, atomic radius decreases | $>\text{N}—\text{N}< >-\text{N}=\text{N}->\text{N}\equiv\text{N}$ |

Periodic Trend :

(a) **For normal elements:**

- (i) **Across a period :** It decreases from left to right in a period as Z_{eff} increases.

Ex. $\text{Ne} > \text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$

- (ii) **In a group :** It increases from top to bottom in a group as number of shells increases.

Ex. $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

 **Note :** In III A group size of Al and Ga is nearly same (transition contraction)

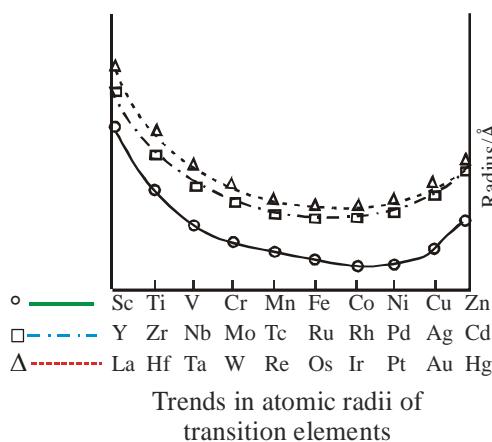
(b) For inert gases:

In respective period generally, the atomic radius of inert gas is largest, because for inert gas VanderWaal's radius is defined. The VanderWaal's radius of inert gases also increases on moving from top to bottom in the group.

(c) For transition elements:

From left to right in a period:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Covalent radius (\AA)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25



In a group :

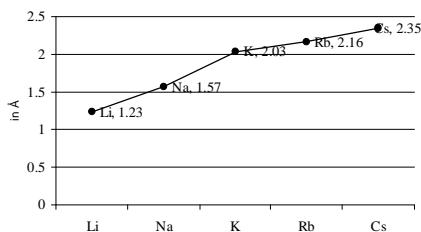
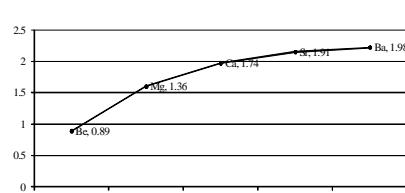
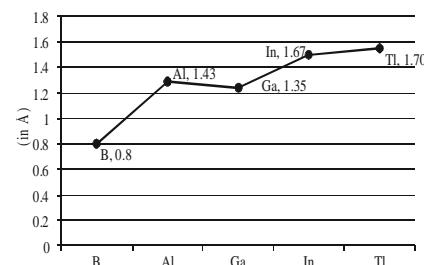
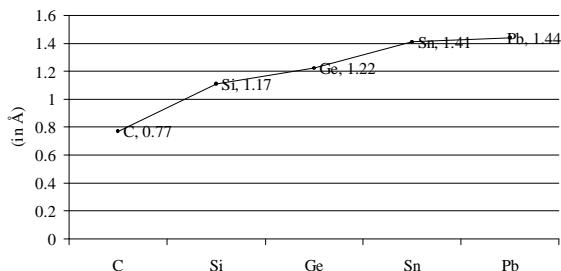
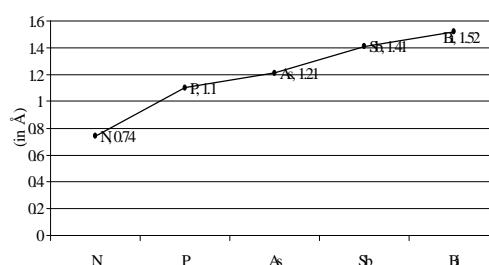
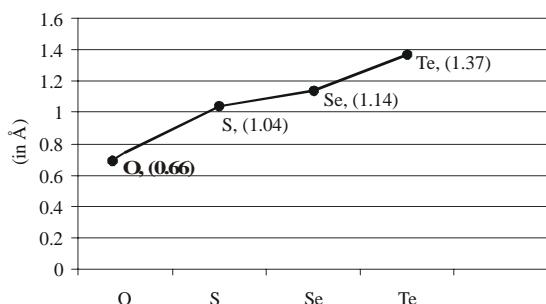
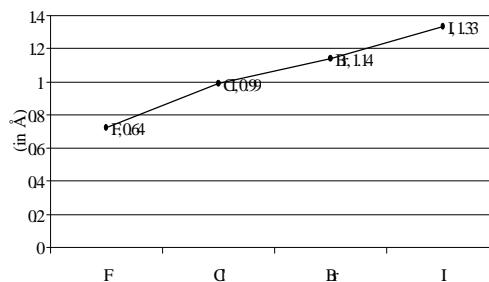
- (i) The atomic radius of elements increases on moving down the first transition series (3d) to second transition series (4d). This is due to the increases in number of shells with the increase in atomic number.
- (ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La(57)

(d) For inner transition elements:

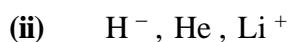
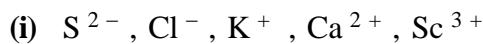
As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction*.

Exceptions :

- (1) Noble gases have largest atomic sizes [Vander waal radii]. However, their covalent radii are smaller e.g. Xe.
- (2) Size of Al > Ga, [Z_{eff} increasing]
- (3) Size of Hf & Zr are same (lanthanide contraction)

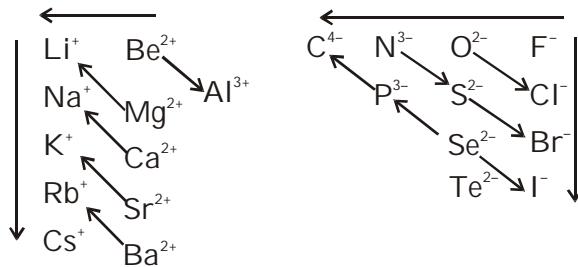
Graphical representation of atomic radius :
ALKALI METALS

ALKALINE EARTH METALS

BORON FAMILY

CARBON FAMILY

NITROGEN FAMILY (PNICOGENS)

CHALCOGENS

HALOGENS


Q. what can you predict or say about the increment in size along a group and decrement along a period?

ISOELECTRONIC MONOATOMIC SPECIES [Size $\propto 1/Z$] :


(iv)
$$\frac{\text{radius of cation}}{\text{radius of anion}} = \frac{Z_{\text{eff}} \text{ of Anion}}{Z_{\text{eff}} \text{ of Cation}}$$

Note:- In the direction of arrow (\rightarrow) ionic size increases.

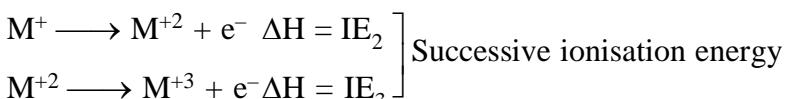
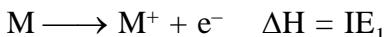


IONISATION ENERGY :

Amount of energy required to remove the most loosely bonded electron from an isolated gaseous atom from its ground state electronic configuration.

Units : kJ mol^{-1} , k cal mol^{-1} , eV per atom.

Ionisation is endothermic (endoergic) i.e. requires energy. Hence $\Delta H_{\text{ionsation}}$ is +ve.



$$\text{IE}_3 > \text{IE}_2 > \text{IE}_1 \text{ (always)}$$

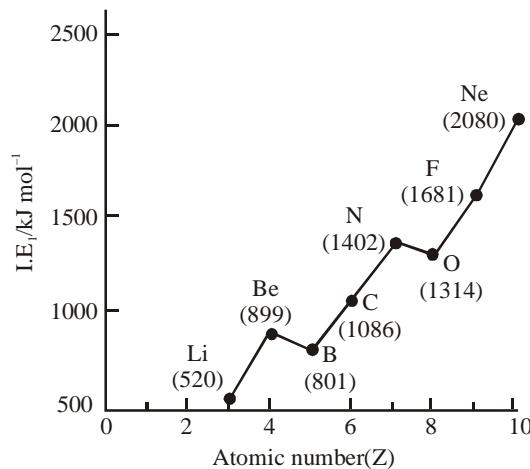
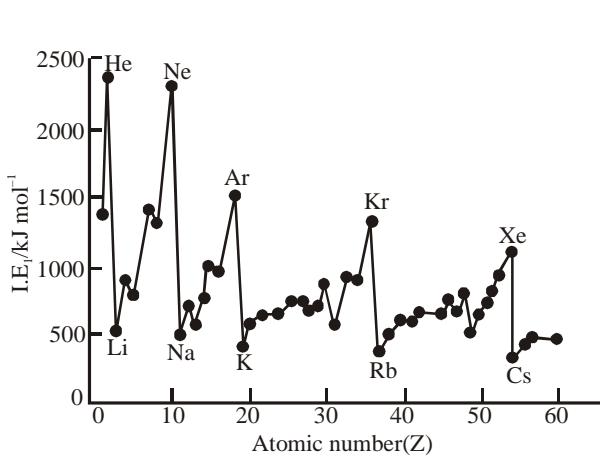
FACTORS AFFECTING IONISATION ENERGY :

- (1) Atomic size : Varies inversely
- (2) Screening effect : Varies inversely
- (3) Nuclear charge (Z) : Varies directly
- (4) Special electronic configuration of outermost electron (half filled / fully filled)
- (5) Type of orbitals involved in Ionisation : $s > p > d > f$.

Note : Half filled and full filled inner orbitals, affects d-block and f-block trends.

General Trend: Along period I.E. increases [with some exception] [$Z_{\text{eff}} \uparrow$]

Along a group I.E. decrease [Z_{eff} constant, $n \uparrow$]



Exception :

- (1) Along a period, half filled and fully filled configurations have higher I.E.
e.g. $\text{Be} > \text{B}$ and $\text{N} > \text{O}$.
- (2) along a group, $\text{Ga} \approx \text{Al}$

PROPERTIES AFFECTED BY IONISATION ENERGY :

- (1) Metallic character (Varies inversely)
- (2) Reducing power (Varies inversely)
- (3) Tendency to stay in which state A^{+1} , A^{+2} or A^{+3}

 **Note :**

- (a) Helium (He) has the highest ionisation energy (IE_1) among all the elements and Caesium (Cs) has the least (IE_1) value.
- (b) Ionisation potential of inert gases is very high due to most stable $s^2 p^6$ electronic configuration.

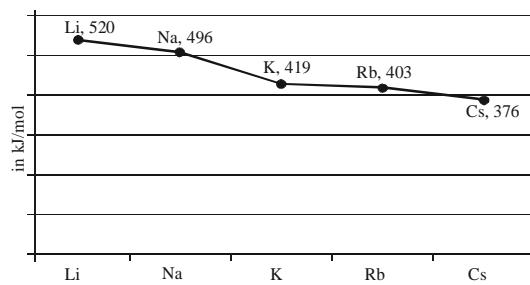
Element	He	Ne	Ar	Kr	Xe	Rn
IE_1 (eV)	24.5	21.6	15.8	14.0	12.1	10.7

- (c) For isoelectronic species I.E. increases with positive charge and decreases with negative charge.

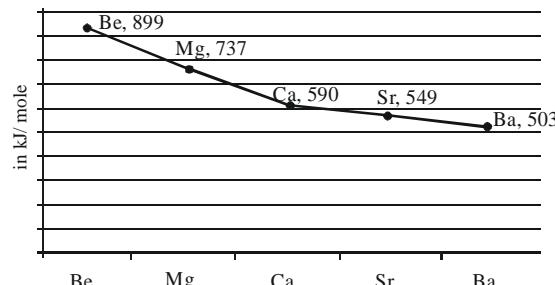
e.g. $Al^{+3} > Mg^{+2} > Na^+ > F^- > O^{-2} > N^{-3}$

Graphical representation of ionisation energy :

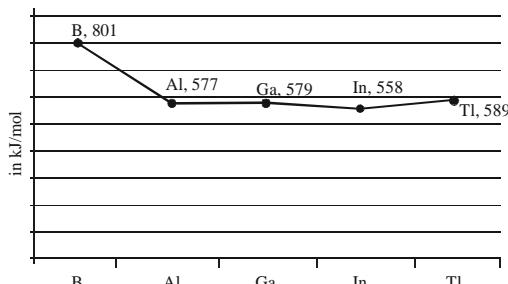
ALKALI METALS



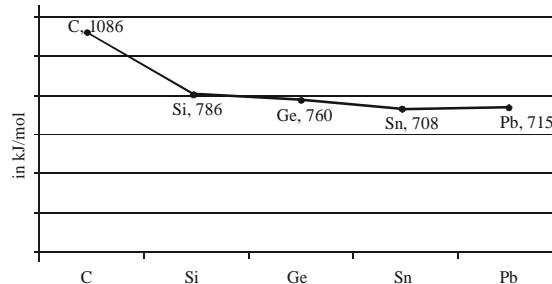
ALKALINE EARTH METALS



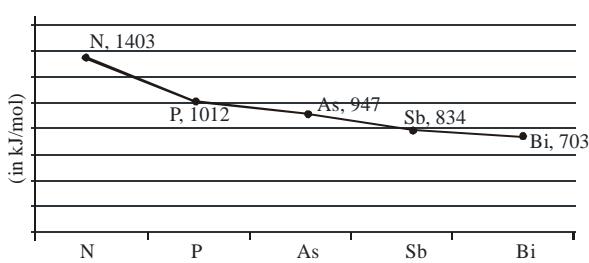
BORON FAMILY



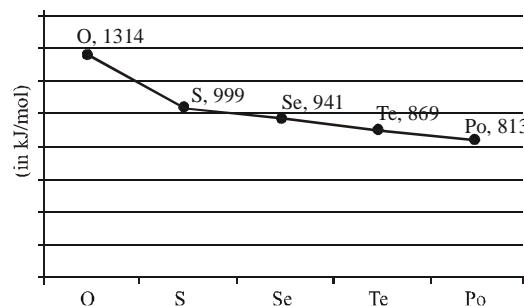
CARBON FAMILY



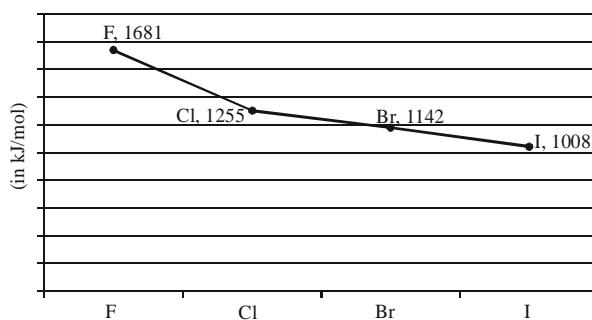
NITROGEN FAMILY (PNICOGENS)



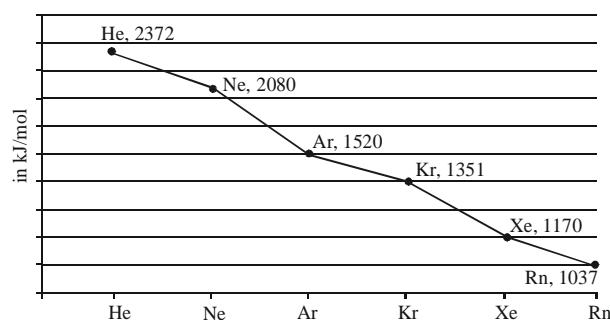
CHALCOGENS



HALOGENS



NOBLE GASES



Ionisation energy of d-block elements :

1st, 2nd, 3rd IE's are increasing from left to right for 1st Transition series, but not regularly.

For 2nd IE Cr > Fe > Mn and Cu > Zn

For 3rd IE Mn > Cr > Fe and Zn has highest.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration										
M	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁴ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ¹⁰ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²
M ²⁺	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹	3d ¹⁰
M ³⁺	[Ar]	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	—	—
Enthalpy of atomisation, $\Delta_a H^\circ / \text{kJ mol}^{-1}$	326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, $\Delta_i H^\circ / \text{kJ mol}^{-1}$	I	631	656	650	653	717	762	758	736	745
$\Delta_i H^\circ$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556
										3829

ELECTRON AFFINITY & ELECTRON GAIN ENTHALPY (EGE) :

Electron Affinity : Amount of energy released when an electron is added to an isolated gaseous atom.

Units : k J mol⁻¹, k Cal mol⁻¹ and eV per atom.

Addition of electron results in release of energy in most of the cases but for addition of second electron energy is always required. The sum of EA₁ & EA₂ is +ve (energy required)

$$\text{EA} \propto \frac{1}{\text{atomic size}} \propto Z_{\text{eff}}$$

(Cl has the highest E.A.)

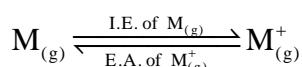
Electron gain Enthalpy (EGE) : When expressed in terms of enthalpy change (ΔH_{eg}) then it is termed as EGE Remember that $\Delta H = -$ ve for exothermic change.

For EA_1 , energy is released $\therefore \Delta H_{eg1} = -$ ve (Not always)

For $EA_2, EA_3 \dots$energy is required $\therefore \Delta H_{eg2} = +$ ve (always)

In general $EA_1 + EA_2$, energy is required. $\therefore (\Delta H_{eg1} + \Delta H_{eg2}) > 0$

Note : $\Delta H_{e.g.} \approx -EA$



Ionisation energy of element is equal to electron affinity of its cation.

FACTORS AFFECTING ELECTRON AFFINITY :

- (1) **Atomic size :** Varies inversely
- (2) **Nuclear charge :** Varies directly
- (3) For stable electronic configuration i.e. half filled and fully filled shells EA decreases.

General Trend : Along a period, electron affinity increases [with a few exceptions] as $Z_{eff} \uparrow$. Along a group, electron affinity decreases after 3rd period. Between 2nd and 3rd period in p block electron affinity of 2nd period is lesser.

Exception :

- (1) A fully filled and half filled configuration have low values of EA or even sometimes energy is required rather than getting released.
- (2) 2nd period has lower value than 3rd owing to repulsion between electrons in small sized 2nd period elements.

Electron affinity of the main-group elements (in electron volts)

1 H								18 He
+0.754	2	13	14	15	16	17	-0.5	
Li	Be	B	C	N	O	F	Ne	
+0.618	≤ 0	$\leq +0.277$	+1.263	-0.07	+1.461	+3.399	-1.2	
Na	Mg	Al	Si	P	S	Cl	Ar	
+0.548	≤ 0	+0.441	+1.385	+0.747	+2.077	+3.617	-1.0	
K	Ca	Ga	Ge	As	Se	Br	Kr	
+0.502	-	+0.03	+1.2	+0.81	+2.021	+3.365	-1.0	
Rb	Sr	In	Sn	Sb	Te	I	Xe	
+0.486	-	+0.3	+1.2	+1.07	+1.971	+3.059	-0.8	

ELECTRO NEGATIVITY :

Property of an atom in a molecule

F has highest electronegativity in the periodic table.

Decreasing order → F > O > Cl ≈ N > Br > S ≈ C > I > H.

Pauling Scale : $|X_A - X_B| = 0.208\sqrt{\Delta_{A-B}}$ Δ in kcal/mol

$$|X_A - X_B| = 0.102 \sqrt{\Delta_{A-B}} \quad \Delta \text{ in kJ/mol}$$

$$\Delta_{A-B} = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}$$

Where, E_{A-B} = Bond energy of A–B; E_{A-A} = Bond energy of A–A; E_{B-B} = Bond energy of B–B

Mulliken's Scale : $X_M = \frac{IP + EA}{2}$ (IP & EA are expressed in eV)

Mulliken's values of EN are about 2.8 times higher than values on Pauling's scale.

$$\text{i.e. } X_P = \frac{X_M}{2.8}$$

Allred-Rochow's Scale : $X_{AR} = \frac{0.359Z_{eff}}{r^2} ; X_P = X_{AR} + 0.744$

r = covalent radius of atom (in Å)

Z_{eff} = Effective nuclear charge on periphery

FACTORS AFFECTING ELECTRO NEGATIVITY :

- (1) **Nuclear attraction** : Varies directly
- (2) **Atomic radius** : Varies inversely
- (3) **Charge on ions** : More positive charge, more electronegativity and more –ve charge, less electronegativity.
- (4) **Hybridisation** : To be discussed later in chemical bonding chapter.

General Trends : Along a period, electronegativity increases

Along a group, electronegativity decreases

Exceptions : Not Noteworthy.

 **Note:** Electronegativity of F > Cl but Electron affinity of Cl > F
Electronegativity of Some Elements (on Paulling's Scale)

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

In Pauling's Scale, elements having almost same electronegativity are-

C ≈ S ≈ I ≈ 2.5

N = Cl = 3.0

P = H = 2.1

Cs = Fr = 0.7

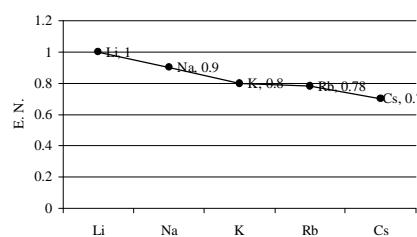
Be = Al = 1.5

PROPERTIES DEPENDENT ON ELECTRO NEGATIVITY :

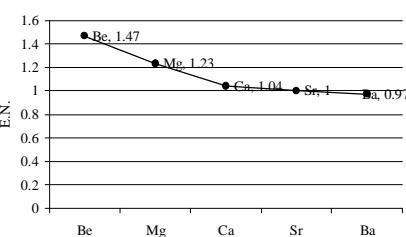
- (1) % ionic character
- (2) Strength of bond
- (3) Bond Length
- (4) Nature of hydrides
- (5) Nature of hydroxide.

Graphical representation of Electronegativity :

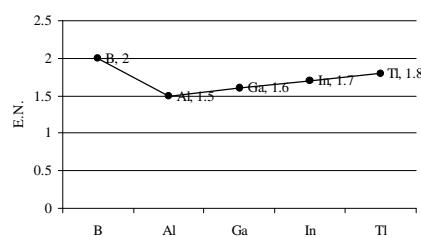
ALKALI METALS



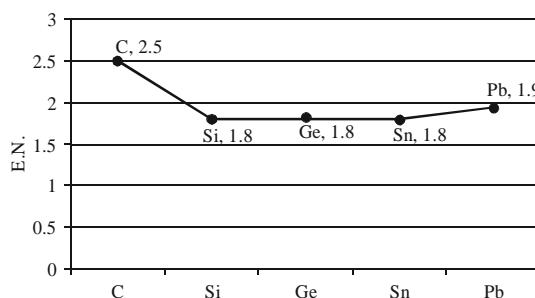
ALKALINE EARTH METALS



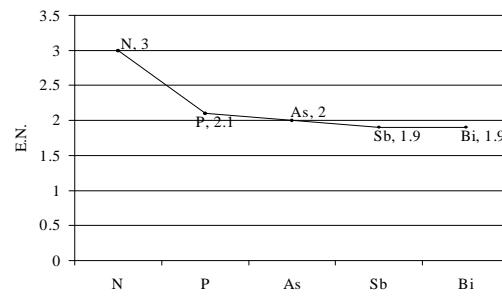
BORON FAMILY



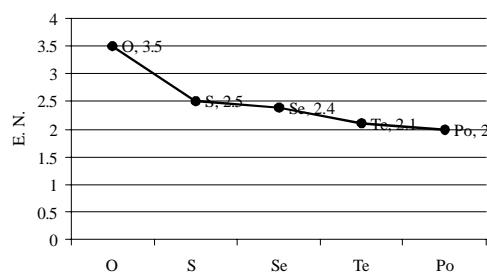
CARBON FAMILY



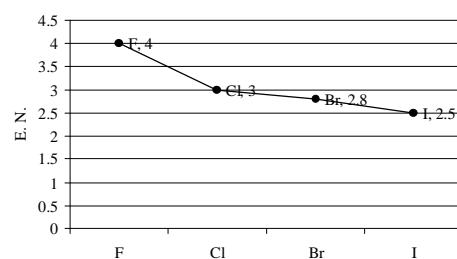
NITROGEN FAMILY (PNICOGENS)



CHALCOGENS



HALOGENS



LATTICE ENERGY :

The amount of energy released during the formation of 1 mole crystal lattice from constituent gaseous ions.



OR

The lattice energy of an ionic compound is the energy required to separate 1 mole of solid ionic substance completely into gaseous ions.



Lattice energies are large and positive because of attraction between positive and negative ions.

The potential energy of two interacting charged particles is given by:

$$E = K \frac{Q_1 Q_2}{r} \quad \text{where, } r = r^+ + r^- ; r^+ \rightarrow \text{radius of cation, } r^- \rightarrow \text{radius of anion}$$

Where Q_1 and Q_2 are the charge on the particles in coulombs, and r is the distance between their centres in meters. The constant K has the value $9.0 \times 10^9 \text{ J} - \text{m/C}^2$.

Factors affecting lattice energy :

- (a) The lattice energy increases as the charge on the ions increases and as their radii decreases.
- (b) The magnitude of lattice energies however depends primarily on the ionic charges because ionic radii do not vary over a wide range.

For Example :

The lattice energy order for some compounds is given below.

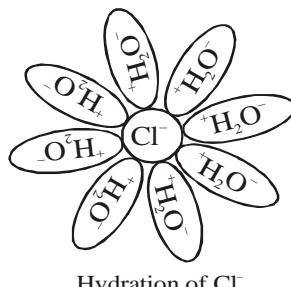
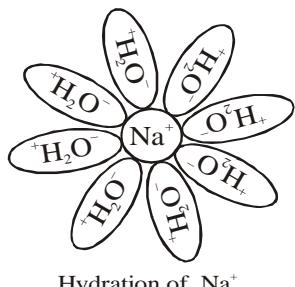


HYDRATION ENERGY :

It is the energy released when 1 mol of gaseous ions are hydrated in water. It is directly proportional to nuclear charge and inversely proportional to size. It always decreases down the group.

- (a) As the charge density of ion increases hydrated size (or aqueous radius) increases.

Size : $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) > \text{Cs}^+(\text{aq})$



- (b) As the hydrated size of ion increases ionic mobility decreases, which thus, decreases conductivity of ions.

Mobility : $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$

Conductivity : $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$

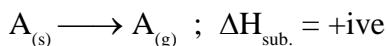
- (c) Hydration energy also affects the solubility of ionic compounds. If hydration energy is greater than lattice energy then ionic compound will be soluble in water. More is the hydration energy, greater is the solubility, whereas, if lattice energy decreases, solubility of ionic compound increases.

BORN-HABER CYCLE :

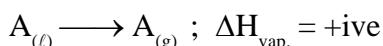
The Born-Haber cycle is an approach to analyze reaction energies.

Various energy terms

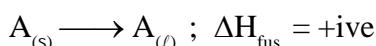
- ⇒ **Heat of sublimation ($\Delta H_{\text{sub.}}$) :** It is heat required to change one mole of a substance from solid state to gaseous state.



- ⇒ **Heat of vaporisation ($\Delta H_{\text{vap.}}$) :** It is heat required to change one mole of liquid substance into gas.

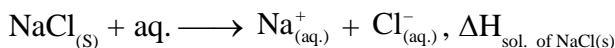


- ⇒ **Heat of fusion ($\Delta H_{\text{fus.}}$) :** It is heat required to change one mole of solid substance into liquid.



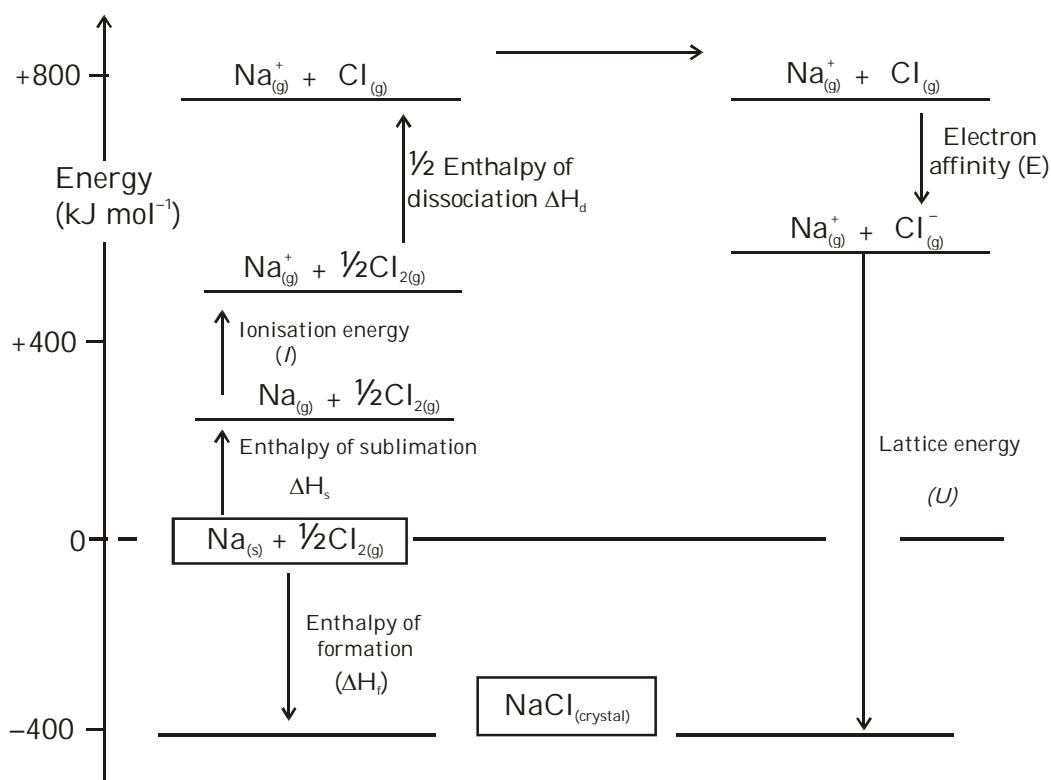
- ⇒ **Heat of atomization (ΔH_{atm}) :** It is change in enthalpy when one mole of a substance is converted into its constituent gaseous atoms.

- ⇒ **Heat of solution ($\Delta H_{\text{sol.}}$) :** It is the change in enthalpy when one mole of a solute is dissolved in excess amount of solvent.



- ⇒ **Bond dissociation energy (B.D.E.) and Bond Energy (B.E.) :** It is the amount of heat required to break one mole of bond between two atoms of a gaseous molecule into gaseous atoms.

- ⇒ **Heat of formation (ΔH_f) :** It is the change in enthalpy when one mole of substance is formed from its element in standard state.

Born -Haber cycle for $\text{NaCl}_{(\text{s})}$.


$$\Delta H_f = \Delta H_s + I + \frac{1}{2}\Delta H_d + E + U$$

 Examples : MgO , AlF_3

MISCELLANEOUS CHEMICAL PROPERTIES :

1. Periodicity of hydra acids :

- (a) Acidic character of hydra acid increases from left to right in a period.
- (b) Acidic character of hydra acid increases from top to bottom in a group.

2. Periodicity of oxy acids :

- (a) Acidic character of oxy acid increases from left to right in a period.
- (b) Acidic character of oxy acid decreases from top to bottom in a group.

3. Periodicity of nature of oxide :

- (a) On moving from left to right in a period acidic nature of oxide generally increases.
e.g. $\text{CO}_2 < \text{P}_2\text{O}_5 < \text{SO}_3 < \text{Cl}_2\text{O}_7$
- (b) On moving from top to bottom in a group acidic nature of oxide generally decreases.

4. General trends

- (a) **Hydration energy** decreases along a group.
- (b) **Lattice energy** decreases along a group.

:: Some points to Remember ::

(without considering radioactive elements)

1. Second most electronegative element is Oxygen
2. Hydrogen is the lightest element and Lithium is lightest metal.
3. Helium has the highest value of I.P.
4. In periodic table metalloids are only in p-block.
5. Total gaseous elements are 11 (He, Ne, Ar, Kr, Xe, Rn, H₂, N₂, O₂, Cl₂, F₂)
6. Liquid metal at room temperature is – Hg.
7. Diamond is hardest natural substance.
8. Halogens have highest electron affinity and amongst them, Cl has the highest amongst them.
9. The largest cation of the periodic table = Cs⁺.
10. The smallest cation of the periodic table = H⁺.
11. The smallest anion of the periodic table = F⁻.
12. The biggest element of periodic table = Fr.
13. The smallest element of periodic table = H.
14. Br is liquid non-metal element at room temperature.
15. Osmium is the heaviest element known.
16. Fluorine is the most electronegative element.

EXERCISE (S-1)

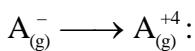
1. Find out the atomic number of element whose IUPAC name is Unnilpentium.

Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.

2. Select total number of acidic compounds out of given below.

CsOH, OC(OH)₂, SO₂(OH)₂, Sr(OH)₂, Ca(OH)₂, Ba(OH)₂, BrOH, NaOH, O₂NOH

3. Total number of enthalpy(s) (out of given eight) of A(g) which is/are **not** associated with conversion of



IE₁, IE₂, IE₃, IE₄, IE₅, IE₆, EGE₁, EGE₂

(IE = ionization energy, EGE = electron gain enthalpy)

4. Write the number of pairs in which size of first element or ion is higher as compared to IInd out of following eight pairs.

(O,S) , (He, Ne) , (Kr, Ne), (Na, Na⁺), (Cl, Cl⁻), (I⁻, Cl⁻), (Li, Na), (Li⁺, Na⁺)

5. Total number of elements which have less IE₁ than that of 'N'.

Be, B, C, F, P, He

6. Size of H⁻ is smaller than how many elements among these ?

H, Li, Be, B, C, N, O, F, F⁻

7. How many orders are **CORRECT**

(a) Acidic strength \Rightarrow ClOH < BrOH < IOH

(b) Basic strength \Rightarrow MgO < CaO < SrO < BeO

(c) Electronegativity \Rightarrow I < Br < N < O < F

(d) Electron affinity \Rightarrow Mg < Na < Si < S < Cl

(e) % Ionic character \Rightarrow NaF < KF < RbF

8. _____ is higher for fluorine as compared to chlorine.

Find the number of properties given below to fill the blank space to make a correct statement.

Atomic mass, Covalent radius, Ionic radius (X⁻), Ionization energy, Electron affinity, Electronegativity, Hydration energy of uninegative ion (X⁻),

9. Upto argon find the number of elements which have lower IE_1 as compared to He.
10. The number of pairs, in which EA of the second element is more than that of the first element is :
[O, S], [C, N], [O, N], [N, P], [Cl^+ , F^-], [K^+ , Na^+]
11. For an element the successive ionisation energy values (in eV/atom), are given below.
14.534, 29.601, 47.448, 77.472, 97.888, 552.057, 667.029
Find the number of valence shell electrons in that element.

Subjective :

12. Calculate E.N. of chlorine atom on Pauling scale if I.E. of Cl^- is 4eV & of E.A. of Cl^+ is + 13.0 eV.
13. Increasing order of ionic size :
 N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+}

EXERCISE (O-1)

Periodic Table

1. Which is not anomalous pair of elements in the Mendeleev's periodic table:-
 (A) Ar and K (B) Co and Ni (C) Te and I (D) Al and Si
2. Representative elements belong to :
 (A) s-and p-block (B) d-block (C) d- and f-block (D) f-block
3. True statement is :-
 (A) All the transuranic elements are synthetic elements
 (B) Elements of third period are called transition elements
 (C) Element of [Ar] $3d^{10}4s^2$ configuration is placed in IIA group
 (D) Electronic configuration of elements of a group is same
4. Which of the following match is correct :-
 (A) Last natural element – Uub
 (B) General electronic configuration of IA group – ns^2
 (C) Inert gas elements lies between 2nd – 6th period
 (D) Typical elements – 3rd period elements
5. The electronic configuration of elements X and Z are $1s^2 2s^2 2p^6 3s^2 3p^5$ and $1s^2 2s^2 2p^5$ respectively.
 What is the position of element X with respect to position of Z in the periodic table -
 (A) Just below element Z (B) Just above Z
 (C) Left to the Z (D) right to the Z
6. Which of the following is not a Dobereiner triad :
 (A) H, F, Cl (B) N, O, F (C) P, As, Sb (D) S, Se, Te
7. Select the incorrect statement for Lother Meyer's curve :
 (A) Curve is plotted between atomic weight and atomic volume
 (B) Alkali metals occupy maxima of curve
 (C) Halogens occupy descending portions of the curve
 (D) Transition metals occupy bottom portions of the curve

Atomic & Ionic Radii

8. The size of the following species increases in the order:
 (A) $Mg^{2+} < Na^+ < F^-$ (B) $F^- < Na^+ < Mg^{2+}$
 (C) $Mg^{2+} < F^- < Na^+$ (D) $Na^+ < F^- < Mg^{2+}$

9. Highest size will be of
(A) Br^- (B) I (C) I^- (D) I^+

10. Element Cu has two oxidation states Cu^{+1} & Cu^{+2} . the right order of radii of these ions.
(A) $\text{Cu}^{+1} > \text{Cu}^{+2}$ (B) $\text{Cu}^{+2} > \text{Cu}^{+1}$ (C) $\text{Cu}^{+1} = \text{Cu}^{+2}$ (D) $\text{Cu}^{+2} \geq \text{Cu}^{+1}$

11. The correct order of increasing atomic size of element N,F, Si & P.
(A) N < F < Si < P (B) F > N < P < Si (C) F < N < P < Si (D) F < N < Si < P

12. The correct order of atomic or ionic size
(A) N < Li < B (B) Cl < Mg < Ca (C) $\text{Ca}^{+2} < \text{S}^{-2} < \text{Cl}^-$ (D) $\text{Na}^+ < \text{Mg}^{+2} < \text{Cl}^-$

13. In isoelectronic series largest difference between size is observed in N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} :
(A) N^{3-} , Mg^{2+} (B) N^{3-} , O^{2-} (C) Mg^{2+} , Na^+ (D) F^- , Na^+

14. Mg, Mg^{2+} , Al and Al^{3+} are arranged in decreasing order of size 1 > 2 > 3 > 4. Species which are present at 1 and 4 position respectively are :
(A) Al, Mg^{2+} (B) Mg, Al^{3+} (C) Mg^{2+} , Al (D) Al^{3+} , Mg

Ionization Energy or Potential

15. In which of the following electronic configuration, ionisation energy will be maximum in
(A) [Ne] 3s² 3p¹ (B) [Ne] 3s² 3p² (C) [Ne] 3s² 3p³ (D) [Ar] 3d¹⁰ 4s² 4p³

16. The correct order of second ionisation potential of C, N, O and F is:
(A) C > N > O > F (B) O > N > F > C (C) O > F > N > C (D) F > O > N > C

17. The ionization energy will be maximum for which process?
(A) Ba → Ba⁺ (B) Be → Be⁺ (C) Cs → Cs⁺ (D) Li → Li⁺

18. Amongst the following, the incorrect statement is
(A) IE₁ (Al) < IE₁ (Mg) (B) IE₁ (Na) < IE₁ (Mg)
(C) IE₂ (Mg) > IE₂ (Na) (D) IE₃ (Mg) > IE₃ (Al)

19. Decreasing ionization potential for K, Ca & Ba is
(A) Ba > K > Ca (B) Ca > Ba > K (C) K > Ba > Ca (D) K > Ca > Ba

20. Alkaline earth metals always form dipositive ions due to
(A) IE₂ – IE₁ > 10 eV (B) IE₂ – IE₁ = 17 eV
(C) IE₂ – IE₁ < 10 eV (D) None of these

21. The correct order of second I.P.
(A) Na < Mg > Al < Si (B) Na > Mg < Al > Si
(C) Na > Mg > Al < Si (D) Na > Mg > Al > Si

Electron affinity or Electron Gain Enthalpy

22. The process requires absorption of energy is
- (A) $F \rightarrow F^-$ (B) $Cl \rightarrow Cl^-$ (C) $O^- \rightarrow O^{2-}$ (D) $H \rightarrow H^-$
23. Of the following elements, which possesses the highest electron affinity?
- (A) As (B) O (C) S (D) Se
24. Electron affinities of O,F,S and Cl are in the order.
- (A) $O < S < Cl < F$ (B) $O < S < F < Cl$
 (C) $S < O < Cl < F$ (D) $S < O < F < Cl$
25. Increasing order of Electron affinity for following configuration.
- (a) $1s^2, 2s^2 2p^2$ (b) $1s^2, 2s^2 2p^4$
 (c) $1s^2, 2s^2 2p^6 3s^2 3p^4$ (d) $1s^2, 2s^2 2p^6, 3s^2 3p^3$
 (A) $d < a < b < c$ (B) $d < a < c < b$ (C) $a < b < c < d$ (D) $a < b < d < c$
26. Highest electron affinity is shown by
- (A) F^- (B) Cl^- (C) Li^+ (D) Na^+
27. Which of the following statements is not true?
- (A) F atom can hold additional electron more tightly than Cl atom
 (B) Cl atom can hold additional electron more tightly than F atom
 (C) The incoming electron encounters greater repulsion for F atom than for Cl atom
 (D) It is easier to remove an electron from F^- than Cl^- .

Electronegativity

28. The outermost electronic configuration of most electronegative element amongst the following is:
- (A) $ns^2 np^3$ (B) $ns^2 np^4$ (C) $ns^2 np^5$ (D) $ns^2 np^6$
29. In the following, which is the correct representation ?
- (A) $C - F$ (B) $C - \overset{\delta+}{Cl}$ (C) $\overset{\delta+}{F} - \overset{\delta-}{Cl}$ (D) $\overset{\delta-}{O} - \overset{\delta+}{F}$
30. On the Pauling's electronegativity scale, which element is next to F .
- (A) Cl (B) O (C) Br (D) Ne
31. Which one is not correct order of electronegativity.
- (A) $F > Cl > Br > I$ (B) $Si > Al > Mg > Na$
 (C) $Cl > S > P > Si$ (D) None of these

32. The increasing order of acidic nature of Li_2O , BeO , B_2O_3
- (A) $\text{Li}_2\text{O} > \text{BeO} < \text{B}_2\text{O}_3$ (B) $\text{Li}_2\text{O} < \text{BeO} < \text{B}_2\text{O}_3$
(C) $\text{Li}_2\text{O} < \text{BeO} > \text{B}_2\text{O}_3$ (D) $\text{Li}_2\text{O} > \text{BeO} > \text{B}_2\text{O}_3$
33. The lowest electronegativity of the element from the following atomic number is.
- (A) 37 (B) 55 (C) 9 (D) 35

Miscellaneous

34. Which of the following does not reflect the periodicity of element
- (A) Bonding behaviour (B) Electronegativity
(C) Ionisation potential (D) Neutron/ Proton ratio
35. Among the following, which species is/are paramagnetic ?
- (i) Sr^{2+} (ii) Fe^{3+} (iii) Co^{2+} (iv) S^{2-} (v) Pb^{2+}
(A) i, iv, v (B) i, ii, iii (C) ii, iii (D) iv, v
36. Choose the s-block element from the following:
- (A) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$ (B) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
(C) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ (D) all of the above
37. False statement for periodic classification of elements is
- (A) The properties of the elements are periodic function of their atomic numbers.
(B) No. of non-metallic elements is less than the no. of metallic elements.
(C) First ionization energy of elements does not increase regularly with the increase in atomic number in a period.
(D) d-subshell is filled by final electron with increasing atomic number of inner transition elements.
38. Which of the following order is incorrect against the property indicated :
- (A) $\text{Mg} < \text{Ar} < \text{Na}$ (2nd I.E.) (B) $\text{Be} < \text{F} < \text{Cl}$ ($|\Delta H_{eg}|$)
(C) $\text{Rb} < \text{Na} < \text{K} > \text{Ca}$ (atomic radius) (D) $\text{P} < \text{S} < \text{N}$ (electronegativity)
39. If each orbital can hold a maximum of three electrons, the number of elements in 9th period of periodic table (long form) will be
- (A) 48 (B) 162 (C) 50 (D) 75
40. Which of the following element has highest metallic character .
- | Element | IP |
|---------|-------|
| (A) P | 17 eV |
| (B) Q | 2 eV |
| (C) R | 10 eV |
| (D) S | 13 eV |

EXERCISE (O-2)

Atomic & Ionic Radius

1. Select correct order of size :

- (A) $Ti^{2+} < Ti < Zr$ (B) $Ti^{2+} < Ti < Hf$ (C) $Zr^{2+} < Zr \approx Hf$ (D) $Hf^{2+} < Hf \approx Zr$

2. Which of the following orders of atomic / Ionic radius is correct ?

- (A) $B < Al \approx Ga$ (B) $Sc > Cu < Zn$ (C) $C < O < N$ (D) $Al^{+3} < Al^{+2} < Al^+$

Electron Affinity

3. Which of the following is correct order of EA.

- (A) $N < C < O < F$ (B) $F > Cl > Br > I$ (C) $Cl > F > Br > I$ (D) $C < N < O < F$

4. The electron affinity of the members of oxygen family of the periodic table, follows the sequence

- (A) $O > S > Se$ (B) $S > O < Se$ (C) $O < S > Se$ (D) $Se > O > S$

Ionisation Energy

5. Considering the following ionisation steps :



Select the correct statements :

- | | |
|--------------------------------|----------------------------------|
| (A) IE_1 of $A(g)$ is 100 eV | (B) IE_1 of $A^+(g)$ is 150 eV |
| (C) IE_2 of $A(g)$ is 150 eV | (D) IE_2 of $A(g)$ is 250 eV |

6. Which of the following are correct ?

- | | |
|--|--------------------------|
| (A) $IE_2(Mg) < IE_2(Na)$ | (B) $EA(N) < EA(P)$ |
| (C) Atomic size $Mg^{+2} >$ Atomic size (Li^+) | (D) IP of $Na < Mg < Al$ |

Electronegativity

7. Amongst the following statements, which is / are correct?

- (A) Electronegativity of sulphur is greater than that of oxygen.
- (B) Electron affinity of oxygen is smaller than that of sulphur.
- (C) Electron gain enthalpy of fluorine is most negative
- (D) Electron gain enthalpy of chlorine is most negative

8. An element 'E' have $IE = x$ eV/atom and $EA = y$ eV / atom and EN on Pauling scale is 1.2.
 Find EN of 'E' on Mullikan scale :

(A) $\frac{x+y}{2}$

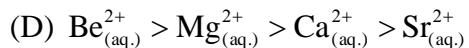
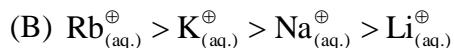
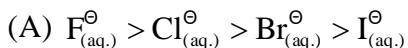
(B) 1.2×2.8

(C) $\frac{x+y}{2.8} - 1.2$

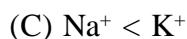
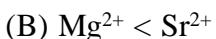
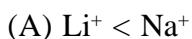
(D) $1.2 - \frac{x+y}{2}$

Hydration Energy

9. Choose the INCORRECT order of hydrated size of the ions -



10. Find the correct ionic mobility order in aqueous solution from the following options-



Miscellaneous

11. Select the correct statement(s).

(A) The value of electron gain enthalpy of an element can be -ve or +ve.

(B) In the periodic table, metallic character of the elements increases down the group and decreases across the period

(C) The Cl^- & S^{2-} are isoelectronic species but first one is not smaller in size than the second

(D) Ionization enthalpy of an atom is equal to electron gain enthalpy of cation

12. In halogens, which of the following properties increase from iodine to fluroine

(A) Ionisation energy

(B) Electronegativity

(C) Bond length

(D) Electron affinity

13. In which of the following set of elements 1st element is more metallic than second.

(A) Ba, Ca

(B) Sb, Sn

(C) Ge, S

(D) Na, F

14. Which of the following order(s) is / are **CORRECT** :

(A) $Li < Be < B < C$ (IE_1)

(B) $HF < HCl < HBr < HI$ (Bond length)

(C) $Na_2O < MgO < Al_2O_3 < SiO_2 < P_2O_5$ (Acidic)

(D) $Li^+(g) < Na^+(g) < K^+(g) < Cs^+(g)$ (Ionic radius)

15. Which of the following order is correct :

- (A) P < Si < Be < Mg < Na (Metallic character)

(B) Mg²⁺ < Na⁺ < F⁻ < O²⁻ (Ionic radius)

(C) Li < B < Be < C < N < O (2nd ionization energy)

(D) Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺ (Ionic mobility)

16. The ionic compound $A^+ B^-$ is formed easily when the

17. Which of the following is/are correct?

- (A) For $A(g) + e^- \rightarrow A^-(g)$ ΔH may be negative
 - (B) For $A^-(g) + e^- \rightarrow A^{2-}(g)$ ΔH may be negative
 - (C) For $A^-(g) + e^- \rightarrow A^{2-}(g)$ ΔH must be positive
 - (D) For $Ne(g) + e^- \rightarrow Ne^-(g)$ ΔH may be zero

EXERCISE (JM)

Based on data provided, the value of electron gain enthalpy of fluorine would be :

- (1) -300 kJ mol^{-1} (2) -328 kJ mol^{-1} (3) -350 kJ mol^{-1} (4) -228 kJ mol^{-1}

- 7.** The order of increasing sizes of atomic radii among the elements O, S, Se and As is :

[JEE-MAIN 2013 (On-Line)]

- | | |
|---------------------|---------------------|
| (1) As < S < O < Se | (2) O < S < As < Se |
| (3) Se < S < As < O | (4) O < S < Se < As |

- 8.** Which is the correct order of second ionization potential of C, N, O and F in the following ?

[JEE-MAIN 2013 (On-Line)]

- | | |
|-------------------|-------------------|
| (1) O > F > N > C | (2) O > N > F > C |
| (3) C > N > O > F | (4) F > O > N > C |

- 9.** Which of the following series correctly represents relations between the elements from X to Y ?

[JEE-MAIN 2014 (On-Line)]



- | | |
|---------------------------------------|---|
| (1) ${}_{18}Ar \rightarrow {}_{54}Xe$ | Noble character increases |
| (2) ${}_{3}Li \rightarrow {}_{19}K$ | Ionization enthalpy increases |
| (3) ${}_{6}C \rightarrow {}_{32}Ge$ | Atomic radii increases |
| (4) ${}_{9}F \rightarrow {}_{35}Br$ | Electron gain enthalpy with negative sign increases |

- 10.** The ionic radii (in Å) of N^{3-} , O^{2-} and F^- are respectively :-

[JEE-MAIN 2015 (Off-Line)]

- | | |
|-------------------------|-------------------------|
| (1) 1.71, 1.40 and 1.36 | (2) 1.71, 1.36 and 1.40 |
| (3) 1.36, 1.40 and 1.71 | (4) 1.36, 1.71 and 1.40 |

- 11.** In the long form of the periodic table, the valence shell electronic configuration of $5s^2\ 5p^4$ corresponds to the element present in:

[JEE-MAIN 2015 (On-Line)]

- | | |
|---------------------------|---------------------------|
| (1) Group 16 and period 5 | (2) Group 17 and period 6 |
| (3) Group 17 and period 5 | (4) Group 16 and period 6 |

- 12.** Which of the following atoms has the highest first ionization energy ?

[JEE-MAIN 2016 (Off-Line)]

- | | | | |
|--------|--------|--------|-------|
| (1) Sc | (2) Rb | (3) Na | (4) K |
|--------|--------|--------|-------|

- 13.** The non-metal that does not exhibit positive oxidation state is :

[JEE-MAIN 2016 (On-Line)]

- | | | | |
|------------|--------------|------------|--------------|
| (1) Oxygen | (2) Fluorine | (3) Iodine | (4) Chlorine |
|------------|--------------|------------|--------------|

- 14.** The electronic configuration with the highest ionization enthalpy is:-

[JEE-MAIN 2017]

- | | | | |
|------------------------------|-----------------------|-----------------------|-----------------------|
| (1) [Ar] $3d^{10}4s^2\ 4p^3$ | (2) [Ne] $3s^2\ 3p^1$ | (3) [Ne] $3s^2\ 3p^2$ | (4) [Ne] $3s^2\ 3p^3$ |
|------------------------------|-----------------------|-----------------------|-----------------------|

15. Consider the following ionization enthalpies of two elements 'A' and 'B' : [JEE-MAIN 2017]

Element	Ionization enthalpy (kJ/mol)		
	1 st	2 nd	3 rd
A	899	1757	14847
B	737	1450	7731

Which of the following statements is correct ?

- (1) Both A and B belong to group-2 where A comes below B
- (2) Both A and B belong to group-1 where A comes below B
- (3) Both A and B belong to group-1 where B comes below A
- (4) Both A and B belong to group-2 where B comes below A

16. In the following reactions, ZnO is respectively acting as a/an : [JEE-MAIN 2017]

- (a) $\text{ZnO} + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{ZnO}_2$
- (b) $\text{ZnO} + \text{CO}_2 \rightarrow \text{ZnCO}_3$
- (1) base and acid (2) base and base (3) acid and acid (4) acid and base

17. The group having isoelectronic species is :- [JEE-MAIN 2017]

- (1) O^{2-} , F^- , Na^+ , Mg^{2+}
- (2) O^- , F^- , Na , Mg^+
- (3) O^{2-} , F^- , Na , Mg^{2+}
- (4) O^- , F^- , Na^+ , Mg^{2+}

18. The correct order of electron affinity is :- [JEE-MAIN 2018]

- (1) $\text{Cl} > \text{F} > \text{O}$
- (2) $\text{F} > \text{O} > \text{Cl}$
- (3) $\text{F} > \text{Cl} > \text{O}$
- (4) $\text{O} > \text{F} > \text{Cl}$

19. For Na^+ , Mg^{2+} , F^- and O^{2-} ; the correct order of increasing ionic radii is : [JEE-MAIN 2018]

- (1) $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-}$
- (2) $\text{O}^{2-} < \text{F}^- < \text{Na}^+ < \text{Mg}^{2+}$
- (3) $\text{Na}^+ < \text{Mg}^{2+} < \text{F}^- < \text{O}^{2-}$
- (4) $\text{Mg}^{2+} < \text{O}^{2-} < \text{Na}^+ < \text{F}^-$

20. The amphoteric hydroxide is : [JEE-MAIN ONLINE 2019]

- (1) $\text{Ca}(\text{OH})_2$
- (2) $\text{Be}(\text{OH})_2$
- (3) $\text{Sr}(\text{OH})_2$
- (4) $\text{Mg}(\text{OH})_2$

21. The correct option with respect to the Pauling electronegativity values of the elements is :-

[JEE-MAIN ONLINE 2019]

- (1) $\text{Ga} < \text{Ge}$
- (2) $\text{Si} < \text{Al}$
- (3) $\text{P} > \text{S}$
- (4) $\text{Te} > \text{Se}$

22. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means :
(1) decrease in both atomic and ionic radii [JEE-MAIN ONLINE 2019]
(2) increase in atomic radii and decrease in ionic radii
(3) increase in both atomic and ionic radii
(4) decrease in atomic radii and increase in ionic radii
23. When the first electron gain enthalpy ($\Delta_{eg}H$) of oxygen is -141 kJ/mol , its second electron gain enthalpy is : [JEE-MAIN ONLINE 2019]
(1) almost the same as that of the first
(2) negative , but less negative than the first
(3) a positive value
(4) a more negative value than the first
24. The correct order of hydration enthalpies of alkali metal ions is - [JEE-MAIN ONLINE 2019]
(1) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (2) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Rb}^+$
(3) $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (4) $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Cs}^+ > \text{Rb}^+$
25. The IUPAC symbol for the element with atomic number 119 would be : [JEE-MAIN ONLINE 2019]
(1) unh (2) uun (3) une (4) uue
26. The element having greatest difference between its first and second ionization energies, is : [JEE-MAIN ONLINE 2019]
(1) Ca (2) K (3) Ba (4) Sc
27. The correct statements among I to III regarding group 13 element oxides are,
(I) Boron trioxide is acidic. [JEE-MAIN ONLINE 2019]
(II) Oxides of aluminium and gallium are amphoteric.
(III) Oxides of indium and thallium are basic.
(1) (I), (II) and (III) (2) (II) and (III) only (3) (I) and (III) only (4) (I) and (II) only
28. Consider the hydrates ions of Ti^{2+} , V^{2+} , Ti^{3+} and Sc^{3+} . The correct order of their spin-only magnetic moments is : [JEE-MAIN ONLINE 2019]
(1) $\text{Sc}^{3+} < \text{Ti}^{3+} < \text{Ti}^{2+} < \text{V}^{2+}$ (2) $\text{Ti}^{3+} < \text{Ti}^{2+} < \text{Sc}^{3+} < \text{V}^{2+}$
(3) $\text{Sc}^{3+} < \text{Ti}^{3+} < \text{V}^{2+} < \text{Ti}^{2+}$ (4) $\text{V}^{2+} < \text{Ti}^{2+} < \text{Ti}^{3+} < \text{Sc}^{3+}$
29. The pair that has similar atomic radii is : [JEE-MAIN ONLINE 2019]
(1) Sc and Ni (2) Ti and Hf (3) Mo and W (4) Mn and Re

30. Within each pair of elements of F & Cl , S & Se, and Li & Na, respectively, the elements that release more energy upon an electron gain are- [JEE-MAIN ONLINE 2020]
- (1) F, Se and Na (2) F, S and Li (3) Cl, S and Li (4) Cl, Se and Na
31. The atomic radius of Ag is closest to : [JEE-MAIN ONLINE 2020]
- (1) Cu (2) Hg (3) Au (4) Ni
32. The third ionization enthalpy is minimum for : [JEE-MAIN ONLINE 2020]
- (1) Fe (2) Ni (3) Co (4) Mn
33. B has a smaller first ionization enthalpy than Be. Consider the following statements :
- (I) It is easier to remove 2p electron than 2s electron
- (II) 2p electron of B is more shielded from the nucleus by the inner core of electrons than the 2s electrons of Be.
- (III) 2s electron has more penetration power than 2p electron.
- (IV) atomic radius of B is more than Be
- (Atomic number B = 5, Be = 4)

The correct statements are :

[JEE-MAIN ONLINE 2020]

- (1) (I), (II) and (III) (2) (II), (III) and (IV)
- (3) (I), (III) and (IV) (4) (I), (II) and (IV)

EXERCISE (JA)

1. **Statement-1 :** F atom has a less negative electron gain enthalpy than Cl atom. **[JEE 2000]**
Statement-2 : Additional electron is repelled more efficiently by 3p electron in Cl atom than by 2p electron in F atom.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

2. The correct order of radii is: **[JEE 2000]**
(A) N < Be < B (B) F⁻ < O²⁻ < N³⁻ (C) Na < Li < K (D) Fe³⁺ < Fe²⁺ < Fe⁴⁺

3. The IE₁ of Be is greater than that of B. **[T/F]** **[JEE 2001]**

4. The set representing correct order of IP₁ is **[JEE 2001]**
(A) K > Na > Li (B) Be > Mg > Ca (C) B > C > N (D) Fe > Si > C

5. Identify the least stable ion amongst the following: **[JEE 2002]**
(A) Li⁻ (B) Be⁻ (C) B⁻ (D) C⁻

6. The increasing order of atomic radii of the following group 13 elements is **[JEE 2016]**
(A) Al < Ga < In < Tl (B) Ga < Al < In < Tl
(C) Al < In < Ga < Tl (D) Al < Ga < Tl < In

7. The option(s) with only amphoteric oxides is (are): **[JEE 2017]**
(A) Cr₂O₃, CrO, SnO, PbO (B) NO, B₂O₃, PbO, SnO₂
(C) Cr₂O₃, BeO, SnO, SnO₂ (D) ZnO, Al₂O₃, PbO, PbO₂

ANSWER KEY**EXERCISE (S-1)**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	6	4	3	3	4	0	3	3	17	4
Que.	11	12	13							
Ans.	5	3.03 (Pauling)	$Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$							

EXERCISE (O-1)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	A	A	D	A	B	C	A	C	A
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	B	A	B	C	C	B	C	B	C
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	C	B	A	C	A	C	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	B	B	D	C	C	D	C	D	B
Que.	41	42	43	44	45	46	47	48		
Ans.	C	B	D	A	A	C	A	D		

EXERCISE (O-2)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B,C,D	A, B, D	A, C	B, C	A, B, C	A, B	B, D	A, B	B, C	A,B,C,D
Que.	11	12	13	14	15	16	17			
Ans.	A, B, D	A, B	A, C, D	B, C, D	A, B, D	A, B, C	A, C			

EXERCISE (JM)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	4	3	2	4	2	4	1	3	1
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	1	1	2	4	4	4	1	1	1	2
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	1	1	3	1	4	2	1	1	3	3
Que.	31	32	33							
Ans.	3	1	1							

EXERCISE (JA)

Que.	1	2	3	4	5	6	7	
Ans.	C	B	T	B	B	B	C, D	

CHAPTER 2

CHEMICAL BONDING

**Chapter
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IMPORTANT NOTES

CHAPTER 2

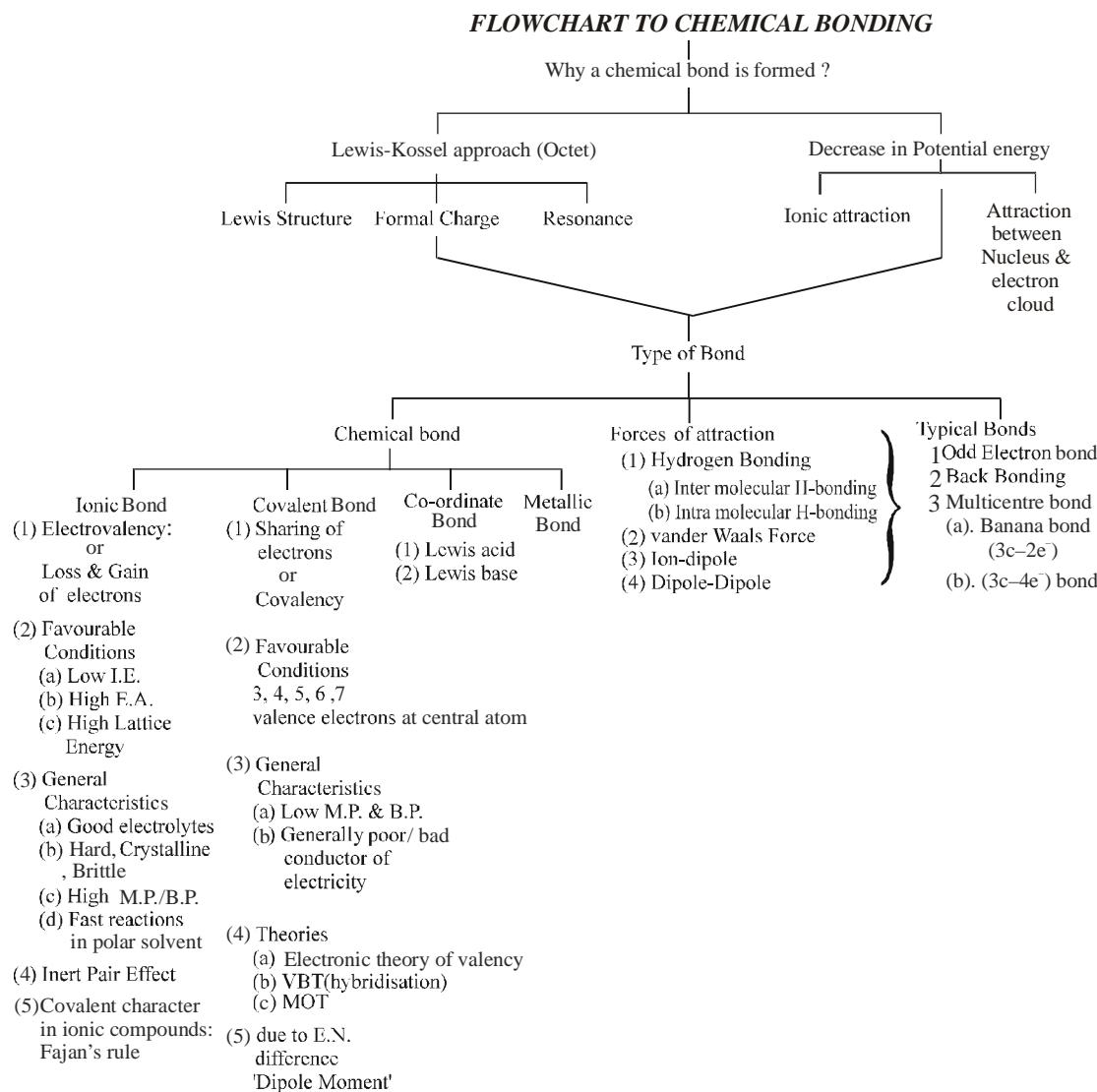
CHEMICAL BONDING

1.0 INTRODUCTION

It is well known fact that except for inert gases, no other element exists as independent atoms under ordinary condition. Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.

1.1 Chemical Bond

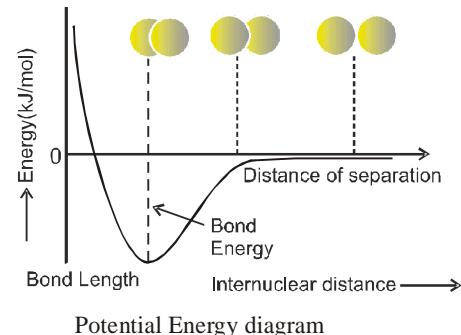
- (a) A force that acts between two or more atoms to hold them together as a stable molecule.
 - (b) It is union of two or more atoms involving redistribution of e^- among them.
 - (c) This process is accompanied by decrease in energy.
 - (d) Decrease in energy \propto Strength of the bond.
 - (e) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms. Therefore molecules are more stable than atoms.



1.2 Cause of chemical combination

Tendency to acquire minimum energy

- When two atoms approaches to each other- Nucleus of one atom attracts the electron of another atom.
- Two nuclei and electron of both the atoms repels each other.
- If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- So Attraction \propto 1/energy \propto Stability.
- Bond formation is an exothermic process.



- Octet rule**

Octet rule was given by Lewis & Kossel.

Atoms combine to complete an octet of electrons in their outer most orbit. Complete orbital represents to get most stable state. Hence all atoms have a tendency to acquire octet ($s^2 p^6$) configuration in their outermost orbit.

The octet may be complete in following manner:

Complete transfer of electrons from one atom to another.

Ex. NaCl, CaCl₂ & MgO etc. (Ionic Bond)

Sharing of electrons between atoms.

- Sharing of equal number of electron between two atoms.

Ex. Cl₂, N₂, O₂ etc., (Covalent bond)

- Sharing of electron pair given by only one atom

Ex. [NH₃ → H⁺] & NH₃ → BF₃ (Co-ordinate Bond)

Exceptions of octet rule

(i) Transition metal ions

Cr ³⁺	Mn ²⁺	Fe ²⁺
[Ar]3d ³	[Ar]3d ⁵	[Ar]3d ⁶
[2, 8, 11]	[2, 8, 13]	[2, 8, 14]

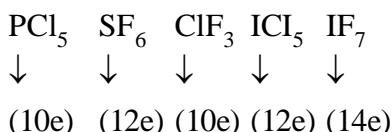
(ii) Pseudo inert gas configuration [$s^2 p^6 d^{10}$]

Zn ²⁺	Cd ²⁺
[Ar]3d ¹⁰	[Kr]4d ¹⁰

(iii) Contraction of octet (incomplete octet)

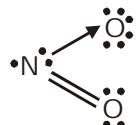
BeF ₂	BF ₃	AlCl ₃	BCl ₃
(4e)	(6e)	(6e)	(6e)

(iv) **Expansion of Octet (due to empty d-orbitals)**



(v) **Odd electron species**

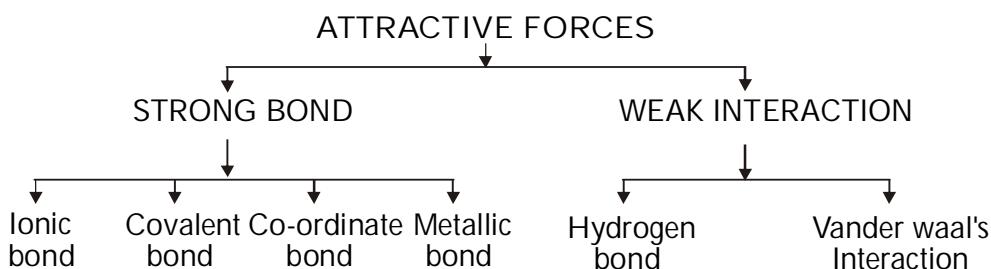
Ex. NO, NO₂, ClO₂ etc.



(vi) **Compounds of Noble gases**

Noble gases which have already completed their octets (or doublet in case of He.) should not form compounds. However, their compounds like XeF₂, XeF₆ & KrF₂ etc., have been actually prepared.

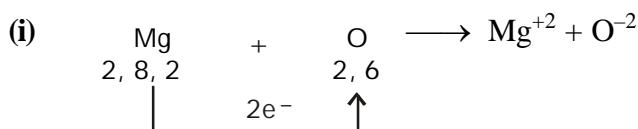
2.0 CLASSIFICATION OF BONDS



3.0 ELECTROVALENT OR IONIC BOND

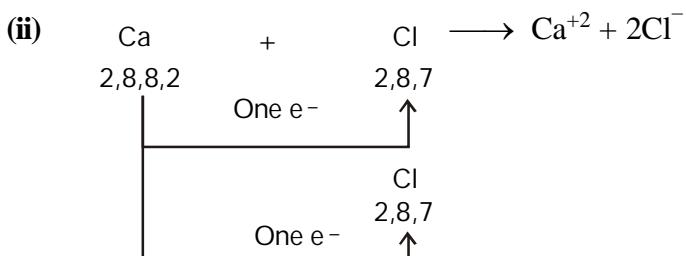
- (a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.
- (b) Electro positive atom loses electron (group IA to IIIA)
- (c) Electro negative atom gains electron (group VA to VIIA)
- (d) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.
- (e) Total number of electron lose or gained is called electrovalency.

Ex. :



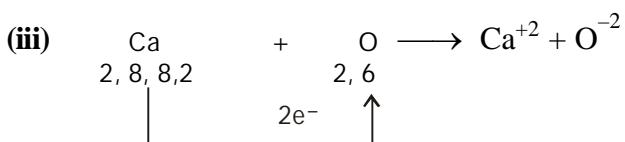
electrovalency of Mg = 2

electrovalency of O = 2



electrovalency of Ca = 2

electrovalency of Cl = 1



electrovalency of Ca = 2

electrovalency of O = 2

(f) The force of attraction is equal in all direction so ionic bond is non-directional.

(g) A definite three dimensional structure is formed called crystal lattice.

(h) Ionic compound do not have molecular formula. It has only empirical formula.

Ex. : NaCl is empirical formula of sodium chloride

3.1 Variable Electrovalency

While some metal show a single electrovalency some show variable electrovalency. 's' block metals show single valency where as 'd' and 'p' block metals show variable valencies because of following factor.

Inert Pair Effect : In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than it's +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

Group 13	Group 14
B III	C IV
Al III	Si IV
Ga III, I	Ge IV, II
In III, I	Sn IV, II
Tl III, I	Pb IV, II

Order of stability : $\text{Tl}^{+1} > \text{In}^{+1} > \text{Ga}^{+1}$ (due to inert pair effect)

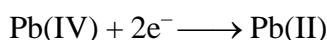
Order of stability : $\text{Pb}^{+2} > \text{Sn}^{+2} > \text{Ge}^{+2}$ (due to inert pair effect)

Instability of the Core : Various ions in 'd' block do not attain inert gas configuration & hence they have unstable core. Also since there is comparatively moderate difference in successive ionization energy therefore they can exist in multiple valancies.

Illustrations

Illustration 1. PbCl_4 is stable at room temperature, PbBr_4 does exist but unstable at room temperature whereas PbI_4 doesn't exist.

Solution. Due to inert pair effect Pb(IV) is less stable than Pb(II) . Hence it is very good oxidant.



Reducing abilities of halides follows the sequence



So we can say, simultaneous co-existence of Pb(IV) and I^- is not possible, hence PbI_4 does not exist.

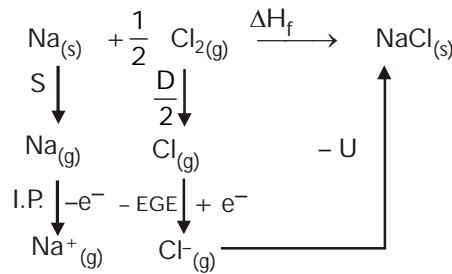
3.2 Formation of ionic compound - Born Haber Cycle

- (a) When elements react to form compounds, ΔG (the free energy of formation) is negative. For a reaction to proceed spontaneously, the free energy of the products must be lower than that of the reactants. [To be dealt in thermodynamics]
- (b) Usually the energy changes are measured as enthalpy values ΔH , and ΔG is related to ΔH by the equation

$$\Delta G = \Delta H - T\Delta S$$

- (c) A whole series of energy changes is involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.

Formation of NaCl (s) involves



$$\text{thus } S + \text{I.P.} + \frac{D}{2} - \text{EGE} - U = \Delta H_f$$

here S = heat of sublimation of Na(s)
 I.P. = ionisation potential of Na(g)
 D = bond dissociation energy of Cl_2
 EGE = electron gain enthalpy of Cl(g)
 U = lattice energy
 ΔH_f = enthalpy heat of formation of NaCl(s)

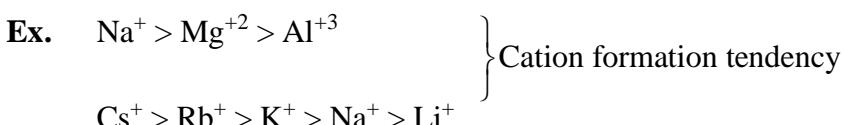
If lattice is $\text{MgX}_2(\text{s})$ then

$$S + (IP_1 + IP_2) + D - 2EGE - U = \Delta H_f \quad (\text{X} = \text{F, Cl})$$

where $(IP_1 + IP_2)$ = total ionisation energy to form $\text{Mg}^{2+}_{(\text{g})}$ from $\text{Mg}_{(\text{g})}$.

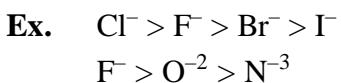
3.3 Factors favouring Ionic Bonding

- (a) Ionisation energy :** Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)
 Lesser Ionization energy → Greater tendency to form cation.



- (b) Electron affinity :** Amount of energy released when an electron is added to an isolated gaseous atom to form –ve ion (anion) energy released.

Higher electron affinity → Greater tendency to form anion



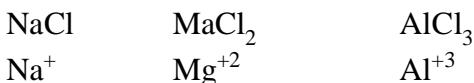
- (c) Lattice energy -** (Energy released) : The energy released in the formation of 1g mole electrovalent compound from isolated gaseous ions is called lattice energy (U) of that compound.

Higher lattice energy → Greater will be the stability or strength of ionic compound.

- **Factors affecting lattice energy**

- (i)** Magnitude of charge → $U \propto z^+ z^-$ (Ionic charge)

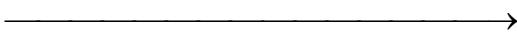
Lattice energy \propto Magnitude of charge



- Charge on cation increases.
- Size of cation decreases.
- Lattice energy increases

- (ii) Size of Cation :- Lattice energy $\propto \frac{1}{r^+ + r^-}$

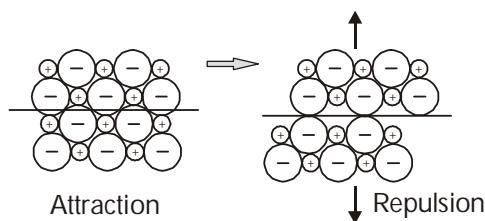
LiCl NaCl KCl RbCl CsCl



- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases.

3.4 Properties of Ionic Compound

- (a) **Physical state** – Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.
 Brittleness \rightarrow { Same charged ions comes nearer. So they repel each other }



- (b) **Isomorphism** – Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism
 Ex. NaF, MgO, ZnSO₄ · 7H₂O, FeSO₄ · 7H₂O. All alums M₂'SO₄ · M₂''(SO₄)₃ · 24H₂O.
- (c) **Boiling point and melting point** – Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.
- (d) **Conductivity** – It depends on ionic mobility.
 - (i) In solid state - No free ions - Bad conductor of electricity.
 - (ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.**Conductivity order :** Solid state < fused state < Aqueous solution
- (e) **Solubility of salts** : Solubility of compound is defined as the molar concentration of saturated solution at given temperature. Saturated solution is that solution in which no more solute can be dissolved at the given temperature.

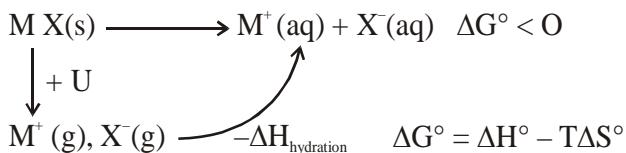
3.5 Factor affecting solubility

- (a) **Dielectric constant of solvent** – The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by ϵ .
 - (i) Water has maximum dielectric constant ($\epsilon = 80$)
 - (CH₃OH $\epsilon = 35$), (Acetone $\epsilon = 21$)
 - (C₂H₅OH $\epsilon = 27$), (Ether $\epsilon = 4.1$)
 - (Benzene $\epsilon = 2.3$)
 - H₂O > CH₃OH > CH₃CH₂OH > CH₃COCH₃ > CH₃OCH₃ > C₆H₆
 - (ii) Ionic compounds are more soluble in the solvents, having high dielectric constant.

☞ **Note :**

H₂SO₄ and H₂O₂ have high dielectric constant but these are not a good solvent due to oxidising nature.

(b) Lattice energy and Hydration energy –



For the solubility of ionic compounds in water, it is necessary that ΔG° must be negative. Favourable conditions for solubility of ionic compound in water is

$$\Delta H_{\text{hydration}} > \Delta H_{\text{Lattice-energy}}$$

$$\text{LE} \propto \frac{1}{r^+ + r^-}, \quad \text{HE} \propto \frac{1}{r^+} + \frac{1}{r^-}$$

If lattice energy decreases, solubility increases

If hydration energy decreases, solubility decreases

In s-block moving down the group, solubility of most of the salts decreases because hydration energy decreases more rapidly as compared to lattice energy.

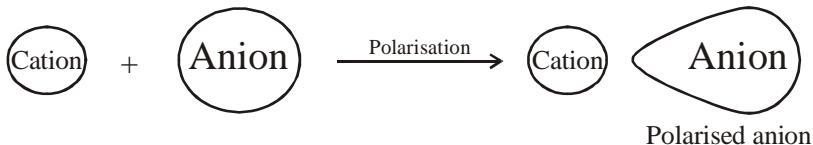
4.0 TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character.

Terms used in polarisation in ionic compounds.

Polarisation Power :

The ability of cation to polarise a nearby anion is called Polarisation power of cation.



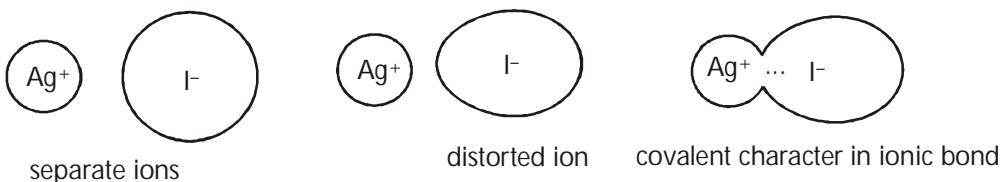
Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

Polarizability :

- (i) It is the ability of anion to get polarised by the cation.
- (ii) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
- (iii) Increase in polarisation increases covalent character.
- (iv) Magnitude of polarisation depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



4.1 Factors influencing ion – Deformation or increasing covalent character

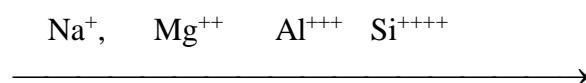
- (i) **Large charge on the ions** – The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl , AlF_3 , AgF are ionic.
- (ii) **Small cation and large anion** – For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalent character with a small cation and a large anion, as in AgI .
- (iii) **Cation with a pseudo-inert gas type of electronic configuration** – A cation with a 18 electron in outermost shell such as Ag^+ ($[\text{Kr}] 4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+ . The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+ . Thus AgI is more covalent than KI , although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

4.2 Application of the concept of polarisation

- (a) **To determine covalent and ionic character of molecule**

$$\phi \propto \frac{\text{Covalent character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period ϕ increases so covalent character increases.



- charge increases
- size decreases ϕ increases
- Covalent character increases with particular anion

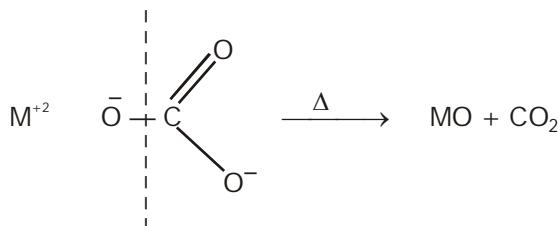
From top to bottom in a group ϕ decreases so covalent character decreases.



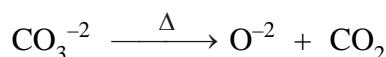
- | | | |
|---------------|---|--|
| Na^+ | - | Size increases (charge is fix) |
| K^+ | - | ϕ decreases |
| Rb^+ | - | Hence covalent character decreases with particular anion |
| Cs^+ | | |

(b) To determine thermal stability of metal carbonates

Stability $\propto \frac{1}{\phi}$ (Covalent nature)



More smaller the size of metal cation, its polarisation capacity increases - strength of M—O bond increases and C—O bond decreases. So thermal stability of carbonates decreases.



From top to bottom thermal stability of carbonates increases (as size of cation increases)
(Ionic character increases or covalent character decreases)

BeCO ₃	\downarrow	– size of cation increases – ϕ decreases (covalent character decreases) – Thermal stability increases
MgCO ₃		
CaCO ₃		
SrCO ₃		
BaCO ₃		

(c) Colour density $\propto \phi$ (Covalent character)

To explain colour of compounds

More the covalent character, more will be the colour intensity.

Ex.	AgCl	AgBr	AgI
	(White)	(Light yellow)	(Dark yellow)
	SnO ₂	SnS ₂	
	(White)	(Yellow)	

Illustrations

Illustration 1. Which of the following is most covalent ?



Solution. $\text{Mn}^{2+} < \text{Mn}^{4+} < \text{Mn}^{7+} \rightarrow$ Polarising power

So, $\text{MnO} < \text{MnO}_2 < \text{Mn}_2\text{O}_7 \rightarrow$ Covalent Character

Illustration 2. Compare the thermal stability of following carbonates.



Solution. $\text{Pb}^{2+} \rightarrow (18+2)\text{e}^-$ configuration

$\text{Ca}^{2+} \rightarrow 8\text{V.es}^-$

$\text{Cd}^{2+} \rightarrow 18\text{V.es}^-$ (Pseudo inert e^- configuration)

Polarisation power of $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Ca}^{2+}$

So stability order $\rightarrow \text{CaCO}_3 > \text{PbCO}_3 > \text{CdCO}_3$

BEGINNER'S BOX-1

Chemical bond formation and Ionic bond

- 1.** An electrovalent bond or ionic bond is formed between :-
(A) Two electronegative atoms
(B) Two metals
(C) Electropositive and electronegative atoms
(D) Two electropositive atoms

2. Most favourable conditions for electrovalent bonding are :-
(A) Low ionisation potential of one atom and high electron affinity of the other atom
(B) High electron affinity and high ionisation potential of both the atoms
(C) Low electron affinity and low ionisation potential of both the atoms
(D) High ionisation potential of one atom and low electron affinity of the other atom

3. The electronegativity of cesium is 0.7 and that of fluorine is 4.0. The bond formed between the two is
(A) Covalent (B) Electrovalent/ionic (C) Coordinate (D) Metallic

4. Electrovalent bond or ionic bond is formed by :-
(A) Sharing of electrons (B) Donation of electrons
(C) Transfer of electrons (D) None of these

5. Element X is strongly electropositive and Y is strongly electronegative. Both are univalent. The compound formed would be :
(A) $X^+ Y^-$ (B) $X - Y$ (C) $X^- Y^+$ (D) $X \rightarrow Y$

6. Element A has 3 electrons in the outermost orbit and element B has 6 electrons in the outermost orbit. The formula of the compound formed between A and B would be :-
(A) A_2B_3 (B) A_2B_6 (C) A_2B (D) A_3B_2

7. Compound of a metal 'M' is M_2O_3 , The formula of its nitride will be:-
(A) M_3N (B) MN (C) M_3N_2 (D) M_2N_3

8. Correct order of covalent character of alkaline earth metal chloride in
(A) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$ (B) $BeCl_2 < CaCl_2 < SrCl_2 < MgCl_2$
(C) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2$ (D) $SrCl_2 > BeCl_2 > CaCl_2 > MgCl_2$

9. When two atoms combine to form a molecule:-

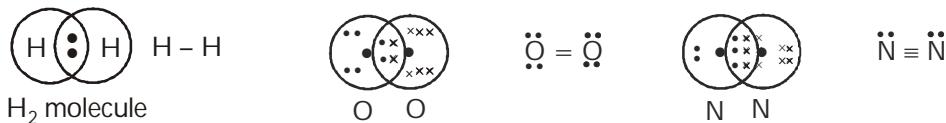
- (A) Energy is released
- (B) Energy is absorbed
- (C) Energy is neither released nor absorbed
- (D) Energy may either released or absorbed

10. Which condition favours the bond formation:

- (A) Maximum attraction and maximum potential energy
- (B) Minimum attraction and minimum potential energy
- (C) Minimum potential energy and maximum attraction
- (D) None of the above

5.0 COVALENT BOND

- (a) A covalent bond is formed by the mutual sharing of electrons between two atoms of same electronegativity to complete their octet.(Except H which completes its duplet)

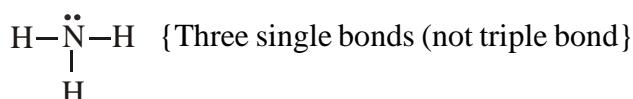


- (b) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.
- (c) Sharing of electrons may occurs in three ways –

No. of electrons shared Bonded Electron pair Bond.
between two atoms

2	1	Single bond (-)
4	2	Double bond (=)
6	3	Triple bond (≡)

Ex.



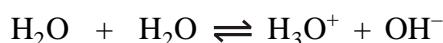
$\text{N} \equiv \text{N}$ Triple bond. (not three single bond) $\text{O} = \text{O}$ (Double bond) $\text{H} - \text{O} - \text{H}$ (Two single bonds)

5.1 Characteristic of Covalent Compound

- (i) **Physical state:-** Covalent compounds are found in all the three states - Gas, Solid & Liquid.
 Separate molecules – In gaseous state
 Associate molecules – In liquid & solid state
 (Due to strong vander waal's force and hydrogen bonding among the molecules.)
 As the size of molecule increases physical state changes -

eg. $\begin{array}{ccc} \text{F}_2, \text{Cl}_2 & \text{Br}_2 & \text{I}_2 \\ \text{gas} & \text{liquid} & \text{solid} \end{array} \rightarrow$

- (ii) **Covalent solid :** Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure.
 e.g. Diamond, Graphite, AlN, SiC, SiO₂ etc.
 Molecular solid : Discrete (separate) molecules are formed by covalent bonds and then the molecules associated due to intermolecular force of attraction. (Vander waal force)
 eg. Solid I₂, dry ice (Solid CO₂) etc.
- (iii) **Conductivity :** Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity.e.g. H₂O, liq. NH₃ etc.



Free ions are formed which can conduct electricity.

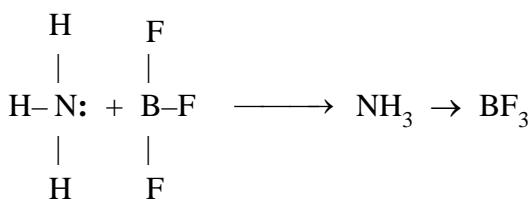
Exceptions:- Graphite, HCl in water.

- (iv) **Solubility:-** Non polar compound are soluble in non polar solvents. Non polar compounds forms Vander waal bond with non polar solvent molecules.
- (v) **Isomerism :** Covalent bond is rigid and directional, so it shows isomerism.
 eg. Organic compounds.
- (vi) **Reaction:-** Reaction between covalent compounds are slow. Because it involves breaking of existing bonds and formation of new bonds.

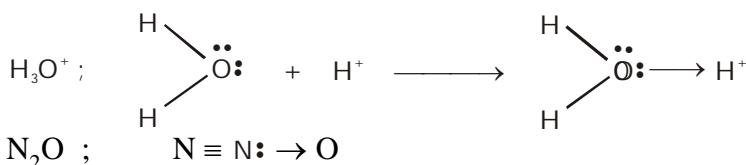
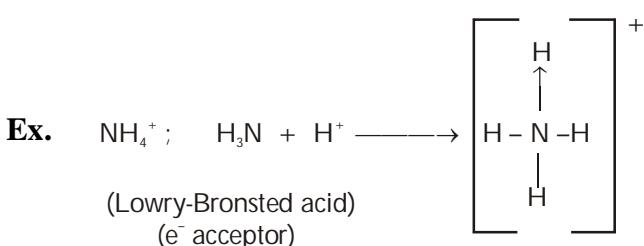
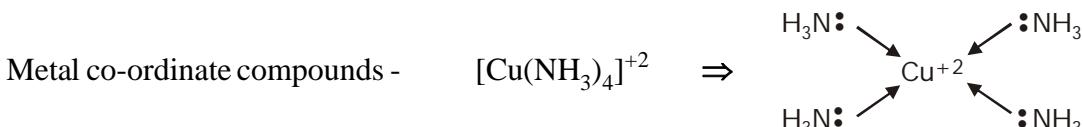
5.2 Co-ordinate bond

- (a) It is a covalent bond in which the shared electron pair come from one atom is called coordinate bond.
- (b) Necessary conditions for the formation of co-ordinate bond are -
- (i) Octet of donor atom should be complete and should have atleast one lone pair of electron.
 - (ii) Acceptor atom should have a deficiency of at least one pair of electron.
- (c) Atom which provide electron pair for shairing is called donor.

- (d) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.



BF_3 is electron deficient compound.



 Note :

Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -

NH₄Cl, CuSO₄.5H₂O, K₄[Fe(CN)₆], KNC, KNO₃, etc.

5.3 Variable valency in covalent bonds

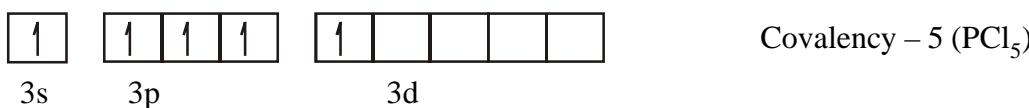
- (i) Variable valencies are shown by those elements which have empty orbitals in outermost shell.
 - (ii) Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
 - (iii) The energy required for excitation of electrons is called promotion energy.
 - (iv) Promotion rule – Excitation of electrons in the same orbit.

Ex.

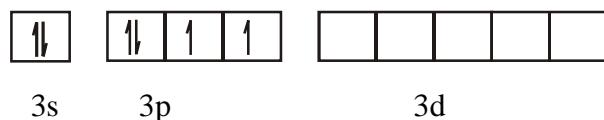
(a) Phosphorus \rightarrow Ground state



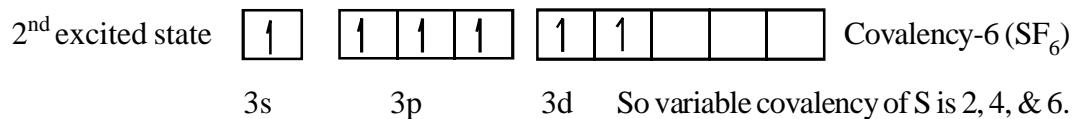
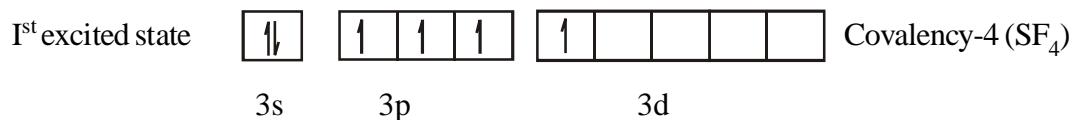
Phosphorus → Excited state



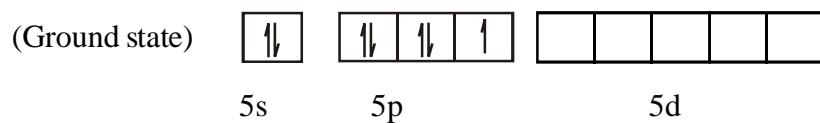
(b) Sulphur \rightarrow Ground state.



Sulphur \rightarrow Excited state



(c) Iodine has three lone pair of electrons



So it shows three excited states – Maximum number of unpaired electrons = 7
Variable Valencies are 1, 3, 5, 7

6.0 LEWIS DOT STRUCTURES OR LEWIS SYMBOLS

According to lewis in the formation of a molecule, only the outer most shell electrons take part in chemical combination & they are called valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols or Lewis dot structure.

Lewis symbols for atoms and monoatomic ions :

Lewis symbol for second period elements are :

$\cdot Li \cdot Be \cdot \cdot B \cdot \cdot C \cdot \cdot N \cdot \cdot O \cdot \cdot F \cdot \cdot Ne \cdot$

Number of dots around the symbol represents the number of valence electrons.

Lewis symbol for some anions are

$\ddot{\cdot} F \cdot^- \quad \ddot{\cdot} O \cdot^{2-}$

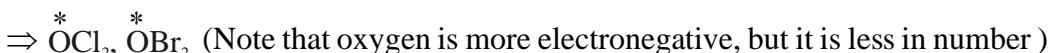
How to draw the Lewis electron dot/Bond line structure of inorganic covalent compounds :

1. (i) First of all, identify the central atom in the given species. Central atom in a given molecule/ion is usually that atom which is least electronegative.
- (ii) Hydrogen can't be central atom as its covalency is one.
- (iii) Sometimes the central atom is that atom which is less in number.
- (iv) Sometimes the central atom in the given molecule/ion can't be decided on the basis of electronegativity or number of atoms (less). In such cases, that atom is central atom which appears in central position of given formula of molecule/ion.

To make it more clear, central atoms in the following species are starred (*).

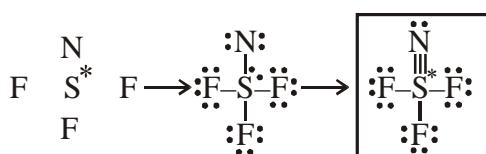


(Note—that electronegativity of H is less than that of central atom).



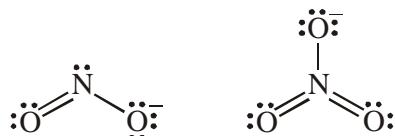
2. Surrounding atoms are the atoms which are directly bonded to central atom.
3. Arrange the surrounding atoms around the central atom and first form single bond between all surrounding atom with central atom.
4. Always make sure that octet of all the surrounding atoms is complete. It is not achieved by forming single bond, then try to make the double bond or triple bond between central atom and surrounding atom, as required to complete the octet of surrounding atoms.

E.g.,

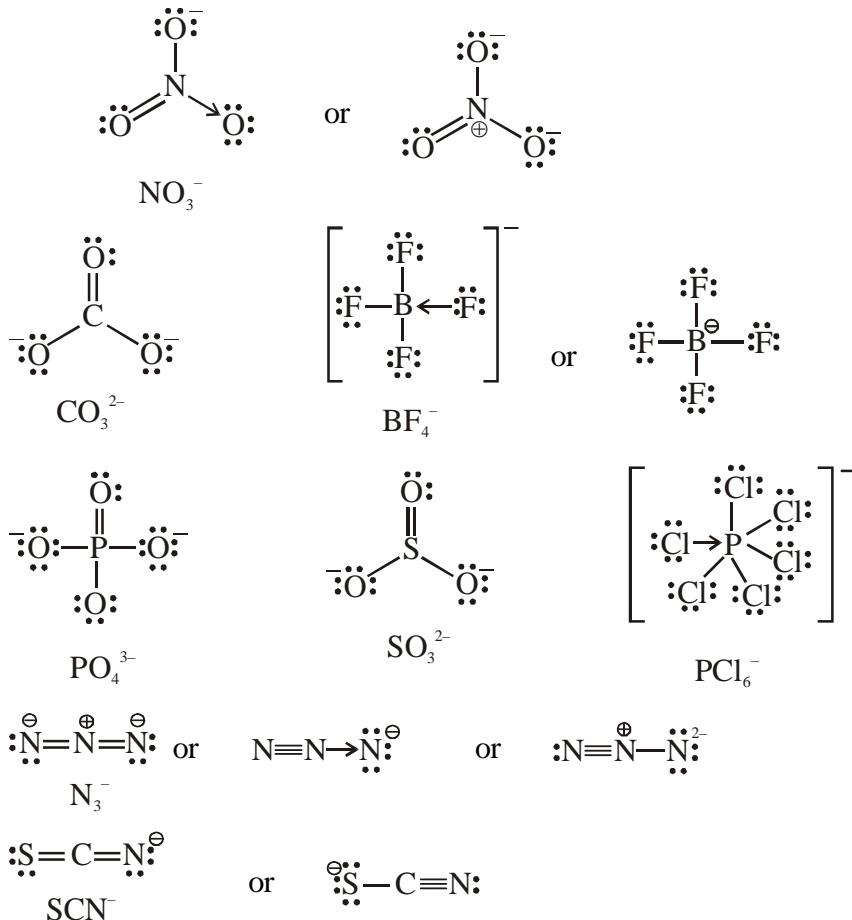


5. After the bond formation, represent the lone pair of electrons on central atom as well as on surrounding atoms.
6. Make sure that, in the structure you have made, the octet of the all surrounding atoms must be completed.
7. If the central atom belongs to second period, it can have ≤ 8 (max.) electrons i.e. ≤ 4 bonds, but never greater than 8 electrons (i.e. > 4 bonds).
8. However, if the central atom belongs to third or lower period it can have ≥ 8 electrons.
9. At last verify the covalency of central atom.

10. Lewis Structure of ions : Distribute the negative charge on surrounding atom in such a way that octet of none of the surrounding atom is complete before the bond formation with central atom. If however, the octet of surrounding atom is complete by making it uninegatively charged (particularly in case of halogen which contain seven valence electron), then such surrounding atom will attach itself with central atom through a co-ordinate covalent bond.



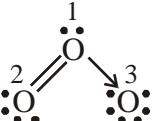
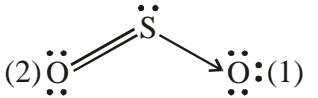
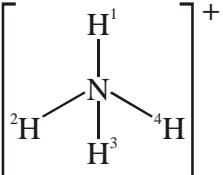
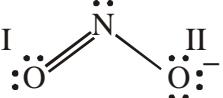
But the above structures of NO_3^- is incorrect as the central nitrogen belongs to second period, it can never form five covalent bond i.e., it can't have more than 8 electrons, so its actual structure is:



6.1 Formal Charge

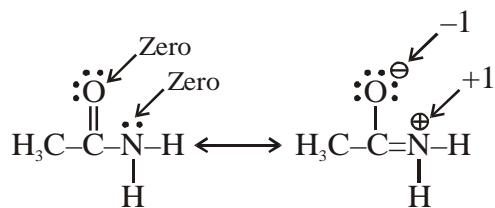
Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

$$\boxed{\text{Formal charge (F.C.)} \text{ on an atom in a Lewis structure} = \left[\text{Total number of valence electron in the free atom} \right] - \left[\text{Total number of non bonding (lone pair) electrons} \right] - \frac{1}{2} \left[\text{Total number of bonding(shared) electrons} \right]}$$

Molecule	Structure	Formal Charge
O ₃		O(1) = $6 - 2 - \frac{1}{2}(6) = +1$ O(2) = $6 - 4 - \frac{1}{2}(4) = 0$ O(3) = $6 - 6 - \frac{1}{2}(2) = -1$
SO ₂		S = $6 - 2 - \frac{1}{2} \times 6 = +1$ O(1) = $6 - 6 - \frac{1}{2} \times 2 = -1$ O(2) = $6 - 4 - \frac{1}{2} \times 4 = 0$
CO		C = $4 - 2 - \frac{1}{2} \times 6 = -1$ O = $6 - 2 - \frac{1}{2} \times 6 = +1$
CN [−]		C = $4 - 2 - \frac{1}{2} \times 6 = -1$ N = $5 - 2 - \frac{1}{2} \times 6 = 0$
NH ₄ ⁺		N = $5 - 0 - \frac{1}{2}(8) = +1$ On each H = $1 - 0 - \frac{1}{2}(2) = 0$
NO ₂ [−]		N = $5 - 2 - \frac{1}{2}(6) = 0$ O(I) = $6 - 4 - \frac{1}{2}(4) = 0$ O(II) = $6 - 6 - \frac{1}{2}(2) = -1$

It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule/ion. **Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

For example :



This structure is
lower in energy

This structure is
higher in energy

Formal charges are useful for helping decide which of the several possible Lewis structures is best.

1. A Lewis structure with small formal charges are preferable to large formal charges.
2. Lewis structure with negative formal charges on the more electronegative atom are preferable than Lewis structures with negative formal charges on the less electronegative atom.
3. Lewis structures with unlike charges close together are more likely than Lewis structure with opposite charges widely separated.
4. Lewis structures with like charges on adjacent atoms are very unlikely.

7.0 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. **Sidwick and Powel in 1940**, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows :

1. The shape of the molecule is determined by repulsion between all of the electron pairs present in the valence shell. (This is the same as the Sidgwick-Powell theory)
2. A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. Thus the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape. If the angle between a lone pair, the central atom and a bond pair is increased, it follows that the actual bond angles between the atom must be decreased. lone pair (lp) - lone pair (lp) > lone pair (lp) - bond pair (bp) > bond pair (bp) - bond pair (bp)

3. The magnitude of repulsion between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
4. Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.
5. The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small.

8.0 WAVE MECHANICAL CONCEPT OF CO-VALENT BONDING

8.1 Modern Concept of Covalent Bond (VBT)

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 ($434.2 \text{ kJ mol}^{-1}$, 74 pm) and F_2 ($150.6 \text{ kJ mol}^{-1}$, 42 pm); although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two Important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

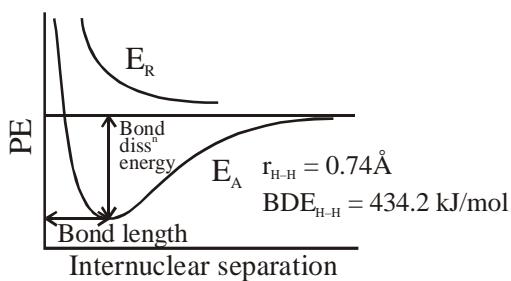
9.0 VALENCE BOND THEORY

It was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals and the hybridization of atomic orbitals.

Formation of H_2 molecule :

When two 'H'-atoms approaches towards each other for the formation of H_2 molecule. The following interactions takes place.

- (i) e-e repulsion
- (ii) e-p attraction
- (iii) p-p repulsion



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .

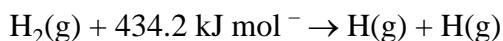
Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.

At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms.

Bond Length : Internuclear distance at minimum potential energy is called bond length.

Bond Dissociation Energy : The amount of energy released when one mole of same type of bonds are formed is called B.D.E.

434.2 kJ/mol of energy is required to dissociate one mole of H₂ molecule.



10.0 ORBITAL OVERLAP CONCEPT

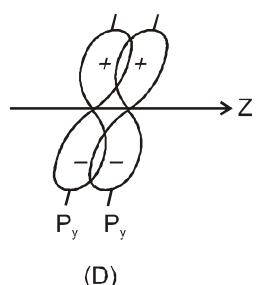
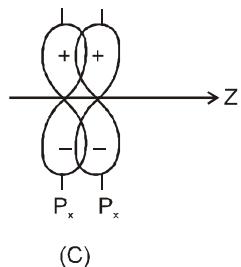
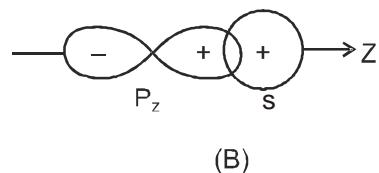
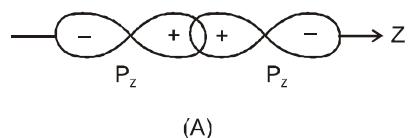
In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing or merging of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons, present in the valence shell having opposite spins.

Directional Properties of Bonds : The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH₄, NH₃ and H₂O, etc. in terms of overlap and hybridisation of atomic orbitals.

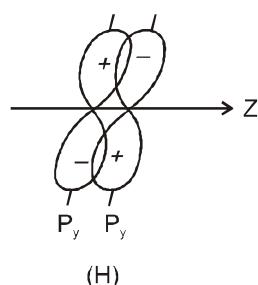
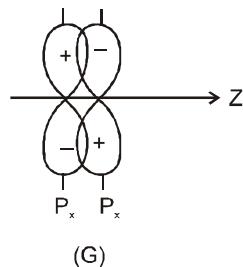
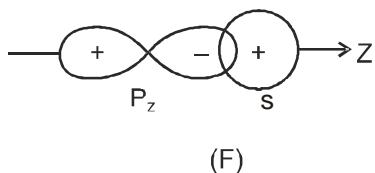
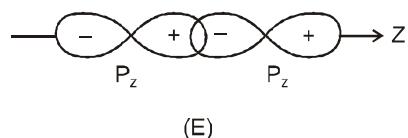
Overlapping of Atomic Orbitals : When two atoms come closer to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figures.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4 , NH_3 and H_2O , the VB theory has to account for their characteristic shapes as well.

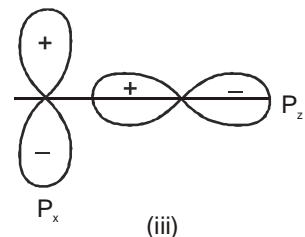
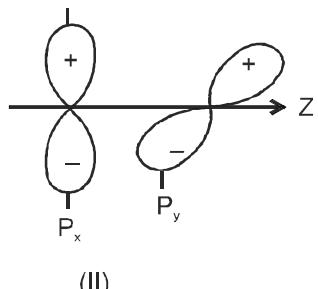
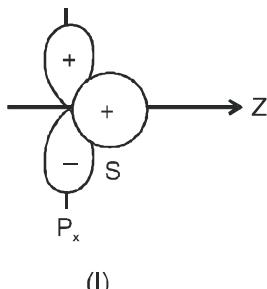
Positive overlap



Negative overlap



Zero overlap



Positive, negative and zero overlaps of s and p atomic orbitals

10.1 Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into following types depending upon the types of overlapping :-

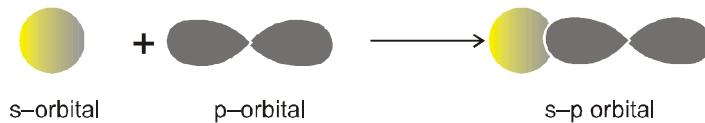
- (i) sigma(σ) bond (ii) pi (π) bond (iii) delta(δ) bond

(i) Sigma (σ) bond : This type of covalent bond is formed by the end to end (head on or axial) overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combinations of atomic orbitals.

- s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



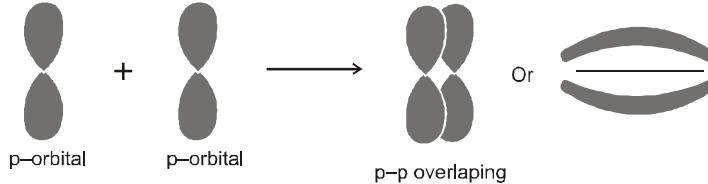
- s-p overlapping: This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom.



- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.



(ii) pi(π) bond : In the formation of π bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



Strength of sigma and pi Bonds : Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Difference between sigma and pi-bond

Sigma-bond	Pi-bond
1. A σ -bond is formed by the axial overlapping of atomic orbitals.	A π -bond is formed by the side ways overlapping of orbitals.
2. σ -bond formation involves overlapping of s-s, s-p and p-p orbitals.	It involves overlapping of p-p orbitals.
3. σ -bond is stronger because of larger extent of overlapping.	π -bond is relatively weaker because of smaller extent of overlapping.
4. The molecular orbital is symmetrical about internuclear axis and electron cloud is present on this axis.	The molecular orbital is discontinuous and consists of two electron clouds below and above the internuclear axis.
5. Free rotation exists around a σ -bond.	Free rotation does not exist around π -bonds.
6. A sigma bond may exist either alone or or along with π -bonds.	A π -bond is always present along with a sigma-bond .
7. Hybridised orbitals or unhybridised orbitals are involved in σ -bond.	Hybridised orbitals are generally not involved in π -bond.

Advantages of VBT

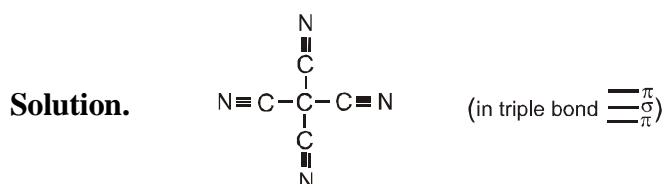
- It explain various bond characteristics e.g., bond length, bond strength.
- It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- This theory redefined the stability of molecules e.g. BF_3 , AlCl_3 , PCl_5 , SF_6 etc which are exception to octet rule.

Disadvantages of VBT

- According to this theory three bond angle in CH_4 should be 90° , as these are formed by p-p overlapping, but actually it has four $109^\circ 28$ angles. In NH_3 & H_2O , angle should be 90° . This is in disagreement with the actual bond angles of 107° & 104.5° in NH_3 & H_2O molecules respectively.
- In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4 , NH_3 , H_2O etc. Pauling introduced the concept of hybridisation.

Illustrations

Illustration 3. What are the total number of σ & π bonds in tetracyanomethane.



From the structure it is clear that it has 8σ and 8π bonds.

Illustration 4. Which of the following combination of orbitals does not form covalent bond (x-axis is internuclear axis) ?

- Ans.** (A) $s + p_y$ (B) $p_y + p_y$ (C) $p_z + p_z$ (D) $d_{xy} + d_{xy}$

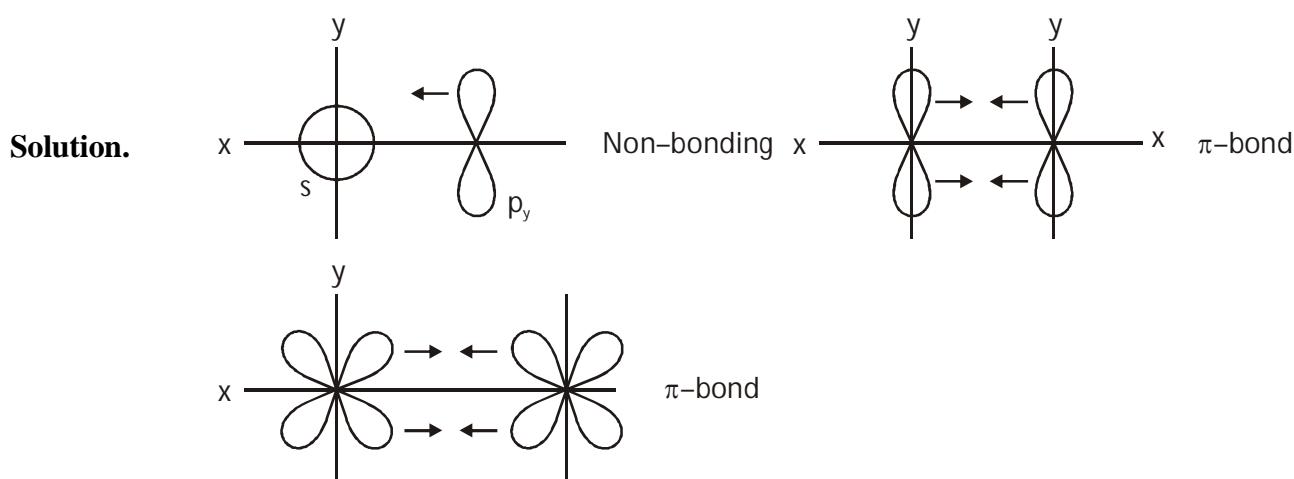
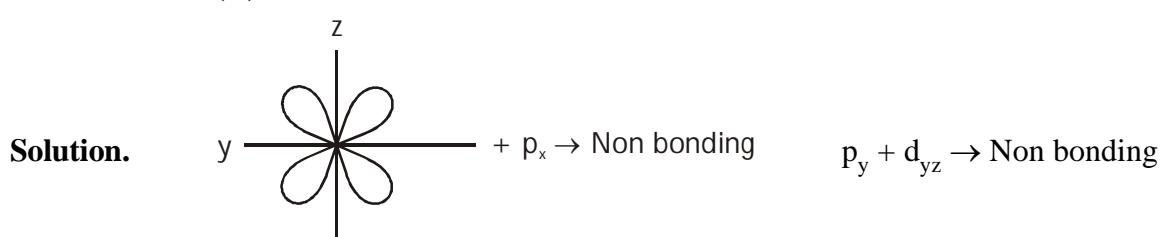


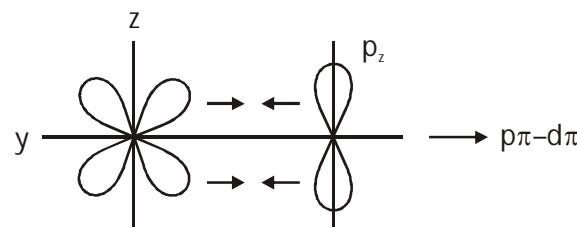
Illustration 5. Which of the following p-d overlapping form π -bond.

- (A) $p_x + d_{yz}$; x – internuclear axis (B) $p_y + d_{yz}$; y – internuclear axis
 (C) $d_{x^2-y^2} + d_{x^2-y^2}$; z – internuclear axis (D) $p_z + d_{yz}$; y – internuclear axis

- Ans.** (D)



$$d_{x^2-y^2} + d_{x^2-y^2} \rightarrow \text{Non bonding}$$



BEGINNER'S BOX-2

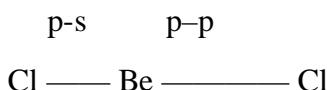
Covalent bond, Co-ordinate bond and Lewis dot structure

11.0 HYBRIDISATION THEORY

- (a) It is introduced by pauling and slater, to explain equivalent nature of covalent bonds in a molecule.

Consider an example of Be compound :- BeCl_2

If it is formed without hybridisation then -



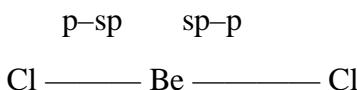
both the Be–Cl bonds should have different parameters and p–p bond strength $>$ s–p bond strength.

Practically bond strength and distance of both the Be–Cl bonds are same.

This problem may overcome if hybridisation of s and p-orbital occurs.

- (b) **Definition :** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals. and the phenomenon is called hybridisation.

Now after considering s–p hybridisation in BeCl_2



bond strength of both the bonds will be equal.

11.1 Characteristic of Hybridisation

- (a) Hybridisation is a mixing of orbitals not electrons. Therefore in hybridisation fully filled, half filled and empty orbitals may take part.
- (b) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
- (c) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (d) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.
- (e) One element can represent many hybridisation state depending on experimental conditions
Ex. C showing sp, sp^2 and sp^3 hybridisation in its compounds.
- (f) Hybrid orbitals are differentiated as sp, sp^2 , sp^3 etc.
- (g) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond.

11.2 Determination of hybridisation state

Method (I)

Count the following pair of e^- around the central atom :

- (a) Number of σ -bond
- (b) Number of lone pairs

$$\text{Number of hybrid orbitals} = \text{Number of } \sigma\text{-bond} + \text{Number of lone pair}$$

Method (II)

To predict hybridisation following formulae may be used :

$$\text{No. of hybrid orbital} = \frac{1}{2} [\text{Total number of valence } e^- \text{ in the central atom} + \text{total number of}$$

monovalent atoms - charge on cation + charge on anion]

Ex. NH_4^+ $\frac{1}{2} [5 + 4 - 1] = 4$ sp^3 hybridisation.

SF_4 $\frac{1}{2} [6 + 4] = 5$ sp^3d hybridisation.

SO_4^{2-} $\frac{1}{2} [6 + 2] = 4$ sp^3 hybridisation.

('O' is divalent so add only charge on anion)

NO_3^- $\frac{1}{2} [5 + 1] = 3$ sp^2 hybridisation.

If such type of e^- pairs are –

two	–	sp	hybridisation	three	–	sp^2	hybridisation
four	–	sp^3	hybridisation	five	–	sp^3d	hybridisation
six	–	sp^3d^2	hybridisation	seven	–	sp^3d^3	hybridisation

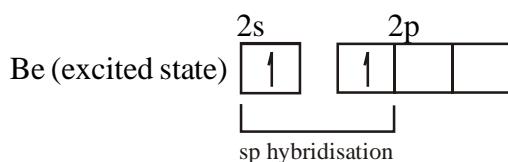
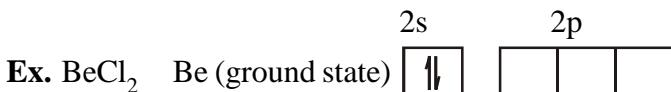
11.3 Types of Hybridisation

(i) sp hybridisation

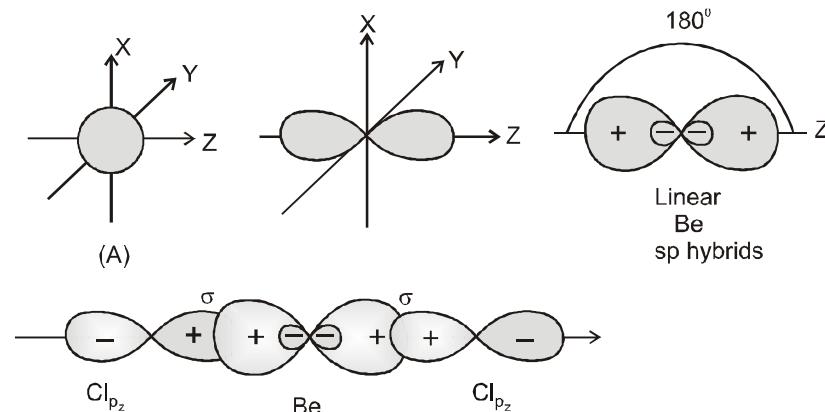
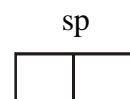
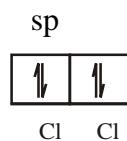
(a) In this hybridisation one s & one p orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.

(b) These two sp hybrid orbitals are arranged in straight line & at bond angle 180° .

(c) s-character 50%



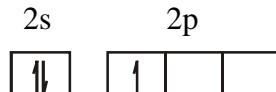
Be atom share two electrons
with Cl in BeCl_2 ,



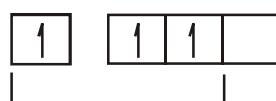
(ii) sp^2 Hybridisation

- (a) In this hybridisation one s & two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are in same shape & equivalent energies.
- (b) These three sp^2 hybrid orbitals are at angle of 120° & give trigonal planar shape.
- (c) s-character 33.33% in each orbital.

Ex. BCl_3 B (ground state)

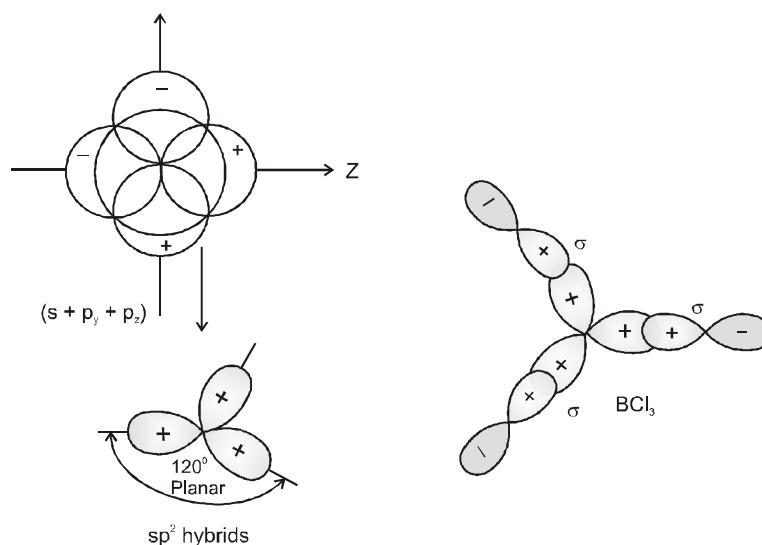
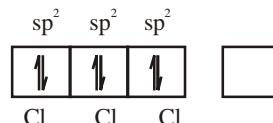


B (excited state)



sp^2 hybrid orbitals

B atom share 3 electrons
with 3 Cl atoms in BCl_3



(iii) sp^3 Hybridisation

(a) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

(b) The angle between these four hybrid orbitals will be $109^\circ 28'$

Ex. CH_4 C (ground state)

2s	2p
1	1 1

C (excited state)

1	1	1	1
sp ³ hybridisation			

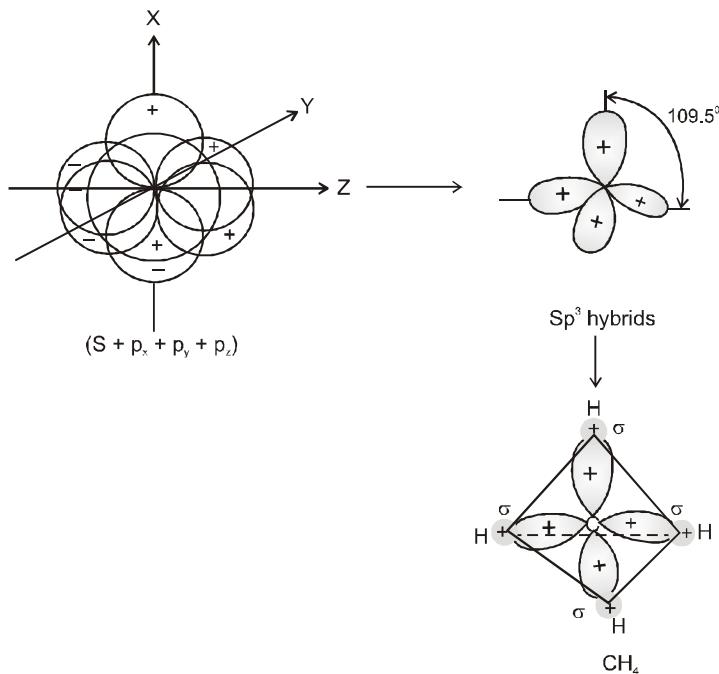
C atom share

sp ³	sp ³	sp ³	sp ³
1	1	1	1
H	H	H	H

four electrons with

4 hydrogen atoms

(c) The shape obtained from these hybrid orbitals would be tetrahedral.



(iv) sp^3d Hybridisation

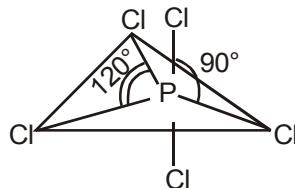
(a) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

(b) Out of these five hybrid orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyramidal.

For example, PCl_5 showing sp^3d hybridisation

	3s	3p	3d	
P (ground state)	1	1 1 1		
P* (excited state)	1	1 1 1	1	
				↓
				sp^3d hybridisation
P atom share five e ⁻ with Cl	1 1 1 1 1			
	Cl Cl Cl Cl Cl			

- (c) In this hybridisation dz^2 orbital is hybridised with s and p orbitals. In this way five sp^3d hybrid orbitals form five sigma bond with five Cl atoms and give a molecule of PCl_5 , shape of this molecule is trigonal bipyramidal.



- (d) Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial b.p. of e^- and 2 axial b.p. of e^-

(v) sp^3d^2 Hybridisation

- (a) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.

- (b) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.

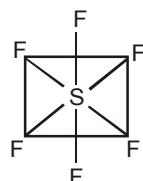
- (c) The angle between all hybrid orbitals will be 90° .

Ex. SF_6 , AlF_6^{-3} , PF_6^- , ICl_5 , XeF_4 , XeOF_4 , ICl_4^- ,

- (d) Two 'd' orbital participates in the hybridisation are dx^2-y^2 and dz^2 .

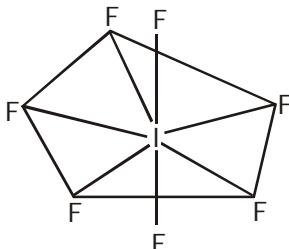
	3s	3p	3d	
SF_6 S (ground state)	1	1 1 1		
S (II nd excited state)	1	1 1 1	1 1	
				↓
				sp^3d^2 hybridisation

S (after hybridisation) share $6e^-$ with 6 F atoms



(vi) sp^3d^3 Hybridisation

- (a) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.
- (b) In this hybridisation d-orbitals used are d_{xy} , $d_{x^2-y^2}$ & d_{z^2} orbitals.
- (c) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.
- (d) Five bond angles are of 72° & two bond angles of 90° .
- (e) The following examples showing sp^3d^3 hybridisation – IF_7 & XeF_6 .



Illustrations

Illustration 6. Which of the following are sp^2 hybridised species ?

- (A) CO_3^{2-} (B) NO_3^- (C) BF_3 (D) All are correct

Ans. (D)

Solution. $CO_3^{2-} \Rightarrow sp^2$

$NO_3^- \Rightarrow sp^2$

$BF_3 \Rightarrow sp^2$

Illustration 7. Descending order of electronegativity of sp^3 , sp^2 & sp hybridised orbitals

- (A) sp^2 , sp , sp^3 (B) sp^3 , sp^2 , sp (C) sp , sp^2 , sp^3 (D) sp , sp^3 , sp^2

Ans. (C)

Solution. Electron negativity \propto % s-character.

BEGINNER'S BOX-3
Modern theory for covalent bond formation

1. A sp^3 hybrid orbital contains:-

- (A) $\frac{3}{4}$ s-character (B) $\frac{1}{4}$ p - character (C) $\frac{3}{4}$ p - character (D) $\frac{1}{2}$ s - character

2. In the compound

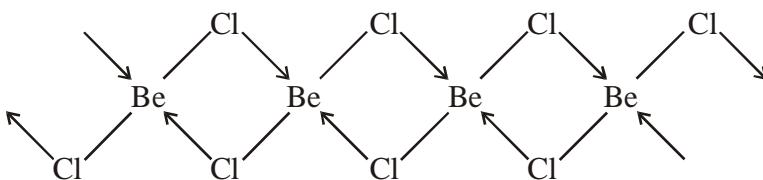
$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{C}\equiv\overset{6}{CH}$, the C_2-C_3 bond is formed by the overlapping of :-
 (A) $sp-sp^2$ (B) sp^3-sp^3 (C) $sp-sp^3$ (D) sp^2-sp^3

- 3.** The shape of sulphate ion is :-
 (A) Hexagonal (B) Square planar (C) Trigonal bipyramidal (D) Tetrahedral
- 4.** In which following set of compound/ion has linear geometry:-
 (A) CH_4 , NH_4^+ , BH_4^- (B) CO_3^{2-} , NO_3^- , BF_3 (C) NO_2^+ , CO_2 , N_3^- (D) BeCl_2 , BCl_3 , CH_4
- 5.** Which of the molecule is trigonal bipyramidal
 (A) BF_3 (B) CH_4 (C) PCl_5 (D) SF_6
- 6.** The type of hybrid orbitals used by chlorine atom in ClO^- , ClO_2^- , ClO_3^- and ClO_4^- is/are :-
 (A) sp, sp^2 , sp^3 and sp^3d (B) sp and sp^3
 (C) Only sp^3 (D) Only sp
- 7.** Which of the following having a square planar structure is
 (A) NH_4^+ (B) BF_4^- (C) XeF_4 (D) CCl_4
- 8.** Which of the following will be octahedral ?
 (A) SF_6 (B) BF_4^- (C) PCl_5 (D) XeF_6
- 9.** In which of the following compounds there is more than one kind of hybridization for carbon
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 (c) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (d) $\text{H}-\text{C}\equiv\text{C}-\text{H}$
 (A) b only (B) a and b (C) b, c and d (D) b and d
- 10.** Carbon atoms in $\text{C}_2(\text{CN})_4$ are :
 (A) sp-hybridized (B) sp^2 -hybridized
 (C) sp- and sp^2 hybridized (D) sp, sp^2 and sp^3 - hybridized

12.0 HYBRIDISATION IN SOLID STATE

Hybridisation in Ionic solid species :

Species	Cationic part	Anionic part
PCl ₅	PCl ₄ ⁺ (sp ³)	PCl ₆ ⁻ (sp ³ d ²)
PBr ₅	PBr ₄ ⁺ (sp ³)	Br ⁻
XeF ₆	XeF ₅ ⁺ (sp ³ d ²)	F ⁻
N ₂ O ₅	NO ₂ ⁺ (sp)	NO ₃ ⁻ (sp ²)
I ₂ Cl ₆ (liquid)	ICl ₂ ⁺ (sp ³)	ICl ₄ ⁻ (sp ³ d ²)
Cl ₂ O ₆	ClO ₂ ⁺ (sp ²)	ClO ₄ ⁻ (sp ³)
(BeCl ₂) _n	(BeCl ₂) _n (sp ³)	



13.0 BENT'S RULE

- (i) A lone pair of electron prefers to occupy that hybrid orbital which has greater percentage of s-character.
- (ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

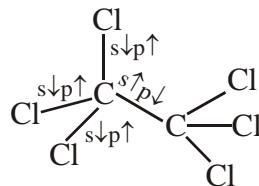
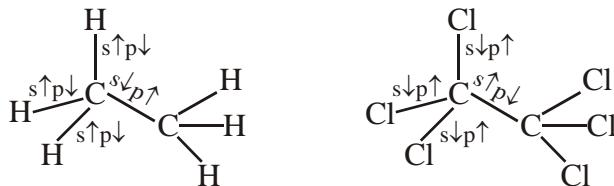
As s-orbital is more close to nucleus, the electron pair present in s-orbital will experience more attraction of the nucleus, i.e. stability of the system increases, therefore, a lone pair prefers to occupy that hybrid orbital which has greater percentage of s-character.

A more electronegative atom has tendency to attract the shared pair of electron towards itself, thus it will prefer to overlap with that hybrid orbital which has less percentage of s-character (i.e. relatively more distant from nucleus of central atom) because by doing so, it increases the stability of the system.

Illustrations

Illustration 7. Compare C–C bond length in C₂H₆ and C₂Cl₆

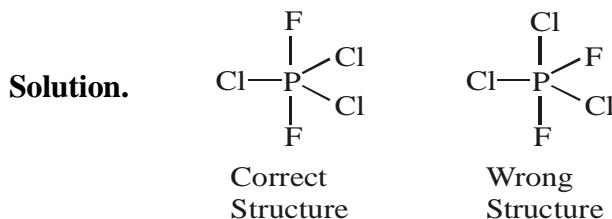
Solution. In C₂H₆ and C₂Cl₆ both carbon atom are sp³ hybrid and there is no lone pair of electron on central atom, but all the four sp³ hybrid orbital around any of the carbon are non-equivalent. In C₂H₆ molecule, to one of the C-atom three hydrogen atom (less electronegative) and one carbon atom (more electronegative than H) is attached. According to Bent rule, more electronegative carbon will overlap with that hybrid orbital has less character of s-character.



whereas in C₂Cl₆ molecule three Cl-atom (attached to any one of the carbon) will overlap with that hybrid orbital which has less s-character and the other (fourth atom attached with one carbon) being less electronegative will overlap with hybrid orbital which has more s-character. Due to more p-character in C–C bond, bond length in C₂H₆ is more than that in C₂Cl₆. Hence.

$$\text{C}-\text{C}_{(\text{C}_2\text{H}_6)} > \text{C}-\text{C}_{(\text{C}_2\text{Cl}_6)}$$

Illustration 8. Draw the geometry of PCl_3F_2



Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

14.0 DRAGO GENERALISATION

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

- (i) Belongs to third or lower period in periodic table
- (ii) Contain atleast one lone pair of electron, and
- (iii) Electronegativity of surrounding atom is ≤ 2.5

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactorily if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals.

In such molecules bond angle is approximately 90° .

Group 15	Bond angle	Group 16	Bond angle
NH_3	$107^\circ 48'$	H_2O	$104^\circ 28'$
PH_3	$93^\circ 36'$	H_2S	92°
AsH_3	$91^\circ 48'$	H_2Se	91°
SbH_3	$91^\circ 18'$	H_2Te	90.5°

- Right order of bond angle.
 - (a) $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
 - (b) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$

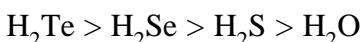
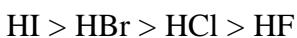
15.0 BOND PARAMETERS

15.1 Bond length

- (i) The internuclear distance between the two single covalently bonded atoms is called bond length or bond distance.
- (ii) If the electronegativities of both the atoms are equal, then the bond length is equal to the sum of the covalent radii of two bonded atoms. $d_{A-A} = r_A + r_B$
- (iii) If the electronegativities of two bonded atoms differ, then the bond length is smaller than the sum of their covalent radii. $d_{A-B} < r_A + r_B$

- **Factors affecting bond length**

(i) **Size of atoms :**

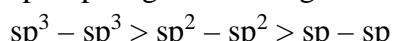


(ii) **Hybridization state of the bonded atoms:** If the s-character in hybridization state of the bonded atoms increases, the C–H bond distance decreases.

Ex. In C – C single bond.



Bond length decreases in the order



(iii) **Resonance or delocalisation of electrons of the bond:** Bond length between atoms are changed if a molecule shows resonance.

15.2 Bond angle

The angle between two bonds is known as bond angle.

- **Factors affecting bond angle**

(i) **Hybridisation state of central atom:** Compounds having different hybridisation have different bond angle.

Ex.	BeH_2	BH_3	CH_4
Hybridisation	sp	sp^2	sp^3
Bond angle	180°	120°	$109^\circ 28'$

(ii) **Lone pair of electron:** If compounds have same hybridisation states then bond angle depends on lone pair of electron.

Ex.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
Lone pair e^-	zero	one	two
Bond angle	$109^\circ 28'$	107°	105°

The difference in bond angle is explained on the basis of following repulsion sequence

The repulsion between

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

(iii) **Electronegativity:** When compounds having same hybridisation state of central atom and same number of lone pair of electrons, then bond angle depends on electronegativity.

Bond angle \propto electronegativity

Ex.	$\text{H}_2\text{O} > \text{H}_2\text{S}$
	$\text{NH}_3 > \text{PH}_3$

E.N. of oxygen is more than sulphur therefore the bond angle in H_2O will be more than H_2S .

(iv) **Size of terminal atoms:** When size of terminal atoms increases, bond angle increases.

Ex.	$\text{OF}_2 < \text{Cl}_2\text{O} < \text{Br}_2\text{O}$
	$\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3$

15.3 Bond Energy

- (i) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as the bond energy of that particular bond.
- (ii) B.E. is expressed in KJ mol⁻¹ (in SI units) or in Kcal mol⁻¹.
- **Factors affecting bond energy**
 - (a) **Electronegativity difference of the bonded atoms :** As the EN difference of the bonded atoms increases the bond energy increases because the ionic nature of the bond increases.
Ex. Bond strength of hydrogen halides decreases in the order
 $\text{H} - \text{F} > \text{H} - \text{Cl} > \text{H} - \text{Br} > \text{H} - \text{I}$
 - (b) **Bond Order** Bond energy \propto Bond order, therefore the increasing order of bond energy is
 $\text{C} - \text{C} < \text{C} = \text{C} < \text{C} \equiv \text{C}$
 - (c) **Hybridisation state of the bonded atoms :** Bond energy \propto s-character
Ex. $-\text{C} - \text{H} < -\text{C} = \text{H} < -\text{C} \equiv \text{H}$
 $\text{sp}^3 \quad \text{sp}^2 \quad \text{sp}$
 - (d) **Atomic size of bonded atoms :** Atoms with small atomic radii form stronger bonds because the extent of overlapping of atomic orbitals is more
Ex. B.E. of halogens is of the order
 $\text{Cl} - \text{Cl} > \text{Br} - \text{Br} > \text{I} - \text{I}$
 because their atomic sizes are in the order $\text{Cl} < \text{Br} < \text{I}$.
 - (e) **Extent of overlapping of atomic orbitals:** A larger extent of overlapping of component atomic orbitals imparts great strength to the bond.
 - (f) **Repulsion between the lone pairs of electrons of bonded atoms:**

$$\text{Bond energy} \propto \frac{1}{\text{No. of lone pair of electron on the bonded atoms}}$$

Ex. the bond energies of the following single bonds having zero, one, two and three lone pair of electrons are in the order.

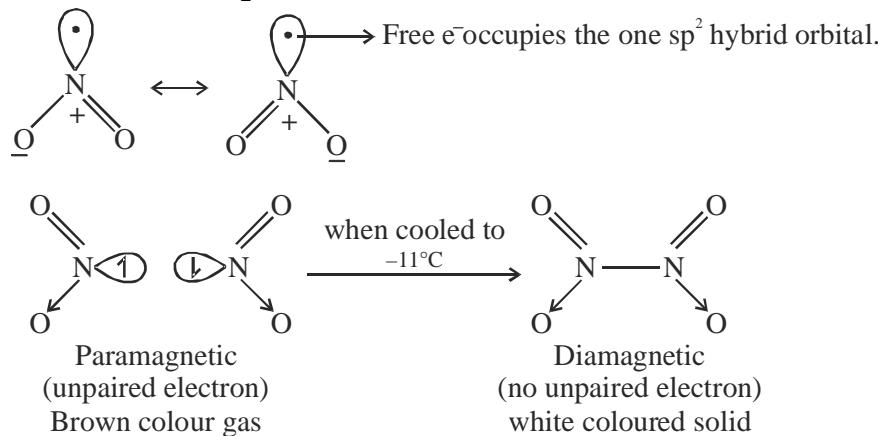


16.0 TYPICAL CONCEPTS IN BONDING

16.1 Odd Electronic Species

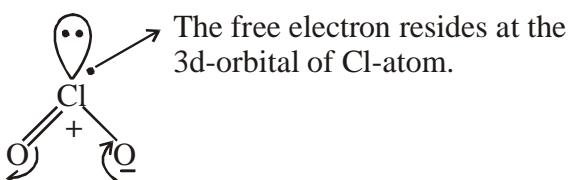
- (1) **NO₂ :** It is observed that the N–O bond length is in between single bond length and double bond length.

Structure of NO₂ :



(2) ClO_2 : The Cl–O bond length is in between single bond & double bond length,

Structure :



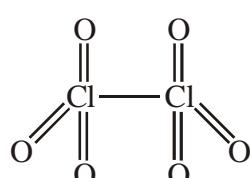
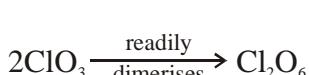
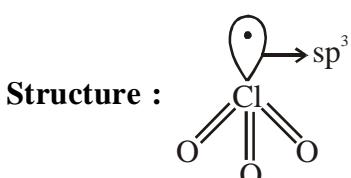
Since the free electron is delocalised in d-orbital, it's dimer formation tendency is very less as compared to NO_2 .

(3) ClO_3 :

Bond angle = 119°

Hybridisation = sp^3

Shape = pyramidal

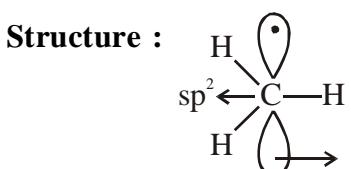


(4) $\dot{\text{C}}\text{H}_3$:

Bond angle = 120°

Hybridisation = sp^2

Shape = planer



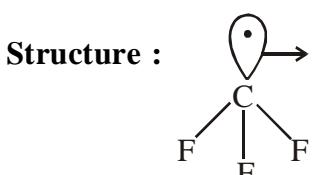
P_z (containing free electron)

(5) $\dot{\text{C}}\text{F}_3$:

Bond angle = $109^\circ 28'$

Hybridisation = sp^3

Shape = pyramidal



free electron present in one sp^3 hybrid orbital

Since the fluorine is more electronegative element which increases the p character in its attached orbital and finally accesses the sp^3 hybridisation hence it is pyramidal in shape.

16.2 Molecules that do not exist

- (i) SF₄, SF₆, PF₅ exists while. OF₄, OF₆, NF₅ do not exists

Reason :- Due to the non availability of vacant 2d-orbital, N and O atom can't expand their octet.

- (ii) (a) PI₅(vap) & SCl₆ do not exist

Reason :- Due to the steric crowding of the surrounding atoms.

- (b) SCl₆ does not exists while TeCl₆ exists

Reason :- Size of Te > Size of S.

- (iii) SF₆, PF₅, XeF₆, XeF₄, XeF₂ exists while SH₆, PH₅, XeH₆, XeH₄, XeH₂ do not exist

Reason :- F is more electronegative and causes **d-orbital contraction** by which the required hybridisation is possible and H is less electronegative, can't do so and the required hybridisation is not possible, hence above compounds do not exist.

Illustrations

Illustration 9. Higher is the bond order, greater is -

- | | |
|------------------------------|------------------------|
| (A) Bond dissociation energy | (B) Covalent character |
| (C) Bond length | (D) Paramagnetism |

Ans. (A)

Solution. Bond order \propto Bond dissociation energy \propto 1/Bond length.

Illustration 10. Which of the following is non existing due to steric reasons :

- | | | | |
|---------------------------------|----------------------------------|----------------------------------|---------------------------------|
| (A) F ₃ ⁻ | (B) Cl ₃ ⁻ | (C) Br ₃ ⁻ | (D) I ₃ ⁻ |
|---------------------------------|----------------------------------|----------------------------------|---------------------------------|

Ans. (B)

Solution. F₃⁻ \Rightarrow Non existing due to absence of vacant d-orbital.

Cl₃⁻ \Rightarrow Non existing due to steric hinderance.

Br₃⁻ & I₃⁻ \Rightarrow existing species.

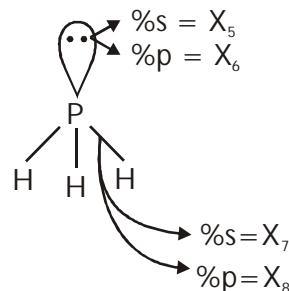
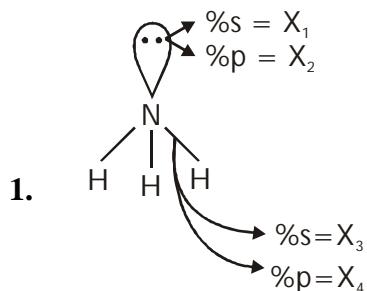
Illustration 11. Which of the following pair is of non existing species ?

- | | |
|---|--|
| (A) XeH ₂ , XeF ₄ | (B) PH ₅ , PCl ₅ |
| (C) PF ₅ , XeF ₂ | (D) XeH ₄ , SH ₆ |

Ans. (D)

Solution. Due to surrounding more electronegative element d-orbital contraction take place.

So XeH₄ & SH₆ will non existing.

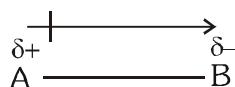
BEGINNER'S BOX-4**Application of hybridisation and Bond parameters**

Correct relation is :

- (A) $X_1 > X_2$ (B) $X_1 > X_5$ (C) $X_8 > X_2$ (D) $X_3 > X_4$
2. d_{z^2} orbital is not involved in which of the following hybridisation ?
 (A) dsp^2 (B) sp^3d (C) sp^3d^3 (D) sp^3d^2
3. The bond having the highest bond energy is :
 (A) C = C (B) C = S (C) C = O (D) P = N
4. The incorrect order of bond dissociation energy will be :
 (A) H – H > Cl – Cl > Br – Br (B) Si – Si > P – P > Cl – Cl
 (C) C – C > N – N > O – O (D) H – Cl > H – Br > H – I
5. In which of the following change, adjacent bond angle increases ?
 (A) $\text{BeF}_2 + 2\text{F}^- \rightarrow \text{BeF}_4^{2-}$ (B) $\text{SiF}_4 + 2\text{F}^- \rightarrow \text{SiF}_6^{2-}$
 (C) $\text{BF}_3 + \text{F}^- \rightarrow \text{BF}_4^-$ (D) $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$
6. The highest H–C–H bond angle present in :
 (A) CH_2F_2 (B) CH_4 (C) CH_3Cl (D) CH_3F
7. Which of the following bond angle order is not correct ?
 (A) $\text{BCl}_3 > \text{PCl}_3 > \text{AsCl}_3$ (B) $\text{H}_2\text{S} < \text{SF}_2 < \text{NH}_3 < \text{BF}_3$
 (C) $\text{OF}_2 < \text{H}_2\text{O} < \text{CH}_3\text{O}-\text{CH}_3$ (D) $\text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{ClO}_4^-$
8. In which of the following species all A–X bond length are identical.
 (A–central atom, X–terminal atoms) ?
 (A) NO_3^- (B) HCO_3^- (C) ClF_3 (D) CH_2Cl_2

17.0 DIPOLE MOMENTS & MOLECULAR POLARITY

- (a) The degree of polarity of covalent bond is given by the dipole moment (μ), which is the product of charge (e) and the distance (d) between them. $\mu = e \times d$. 'e' is the order of magnitude of the electronic charge, i.e., about 10^{-10} esu and d is the distance between the atomic centres, i.e., about 10^{-8} cm.
- (b) Hence dipole moments may be expected to have value around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm. It is however, general particle to express dipole moments in **Debye units (D)**, $1 D = 10^{-18}$ esu-cm.



Electronegativity of A < Electronegativity of B

If the charge is in SI units (Coulombs) and d in metre, μ will be coulomb-metre (cm) unit.

$$1 D = 3.336 \times 10^{-30} \text{ C.m}$$

- (c) Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compound containing such bonds will have dipole moment, for the polarity of the molecule as a whole is the vector sum of the individual bond moment.

$$\mu_{\text{resultant}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

- (i) For example, CO_2 is a linear molecule, $\text{O} = \text{C} = \text{O}$, so that the dipole moments of the two $\text{C}=\text{O}$ bonds cancel out.
- (ii) The $\text{C} \rightarrow \text{Cl}$ bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the $4\text{C} - \text{Cl}$ bond moments is zero.
- (iii) On the contrary CH_3Cl , CH_2Cl_2 and CHCl_3 have definite dipole moments.

 **Note :**

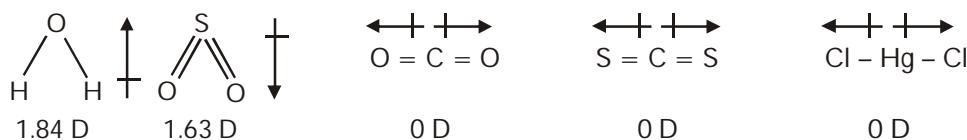
(Order of dipole moment $\text{CH}_3\text{Cl} > \text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4 = \text{CH}_4$)

17.1 Application of Dipole Moment Measurements

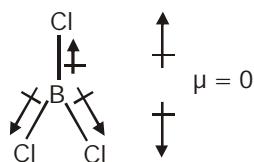
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shape of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated.

(i) Inorganic substances:

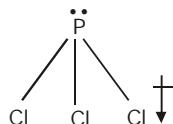
- (a) Monoatomic molecules such as He, Ne, etc., have zero dipole moment because they are symmetrical.
- (b) Homodiatomc molecules such as H₂, Cl₂ and N₂ have no dipole moment; so these molecules are symmetrical.
- (c) Triatomic molecules some of these molecules possess zero dipole moment so they have a symmetrical linear structure, **Ex.** CO₂, CS₂, HgCl₂. Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)



- (d) Tetratomic molecules some molecules like BCl₃ have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other example are BF₃, BBr₃, CO₃²⁻, and NO₃⁻

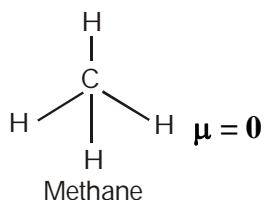


- (e) PCl₃, AsCl₃, NH₃, PH₃, AsH₃, H₃O⁺ have appreciable dipole moment. They possess trigonal pyramidal structure.

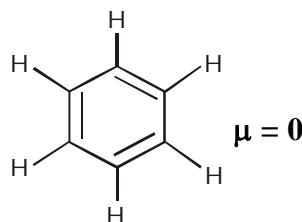


(ii) Organic substances

- (a) Methane and CCl₄ have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.

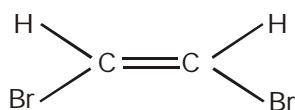


- (b)** Benzene has zero dipole moment. All the 6C and 6H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

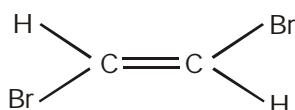


- (c)** Measurement of dipole moments will enable us to detect cis-and trans isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.

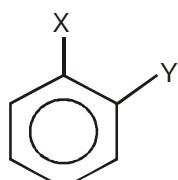


cis-dibromoethylene ($\mu = 1.4\text{D}$)

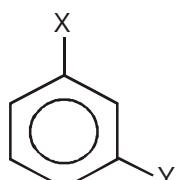


trans-dibromoethylene ($\mu = 0$)

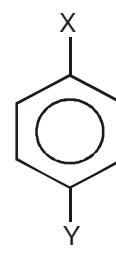
- (d)** The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers. o-nitrophenol, m-nitrophenol and p-nitrophenol. We also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



Ortho

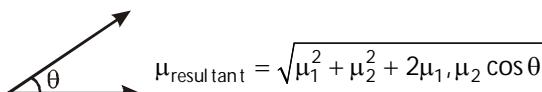


Meta



Para

In those cases where $X = Y$, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other (NO_2) is electron withdrawing while in aminophenols, both the groups (OH and NH_2) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment.



$$\mu_{\text{resultant}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

17.2 Dipole moment and percentage ionic character

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge = 4.8×10^{-10} e.s.u.

1 D = 1×10^{-18} e.s.u \times cm.

$$\therefore \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Theoretical dipole moment is confined when we assume that the bond is 100% ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

Illustrations

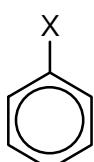
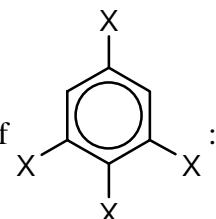
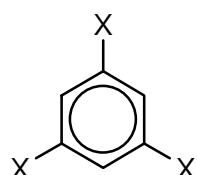


Illustration 12. Dipole moment of is 1.5 D. The dipole moment of



Ans.

(A)



Solution.

$\mu_{\text{net}} = 0$; due to symmetry

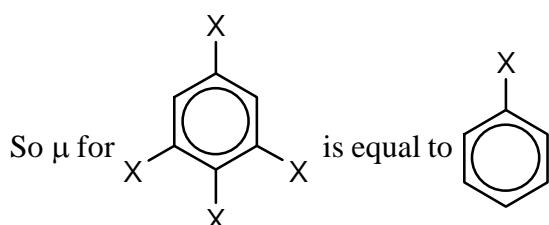
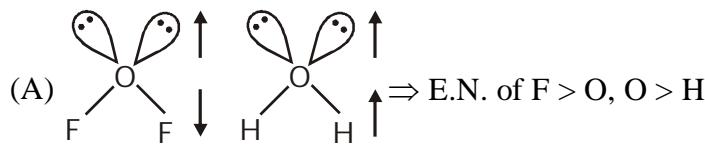


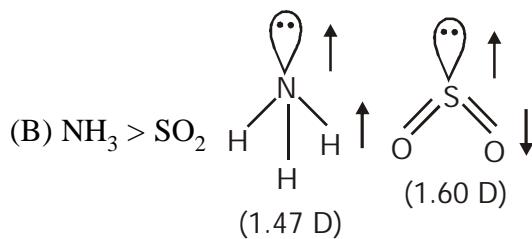
Illustration 13. Correct order of dipole moment is :

- (A) $\text{OF}_2 > \text{OH}_2$ (B) $\text{NH}_3 > \text{SO}_2$
 (C) $\text{PCl}_3\text{F}_2 > \text{PCl}_2\text{F}_3$ (D) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl}$

Ans. (D)



Solution.



- (C) $\text{PCl}_3\text{F}_2 < \text{PCl}_2\text{F}_3$
(D) $\text{CH}_3\text{--F} < \text{CH}_3\text{--Cl}$

As size of F is very small so for $\text{CH}_3\text{-F}$, $q \times \ell$ is less than that for $\text{CH}_3\text{-Cl}$.

BEGINNER'S BOX-5

Dipole moment

18.0 MOLECULAR ORBITAL THEORY

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

- (i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals. We know the names of atomic orbitals like s, p, d and f orbitals but the molecular orbitals will be having different names as well as different electronic distributions.
- (ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule.
Thus an atomic orbital is monocentric while a molecular orbital is polycentric.
- (iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- (vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital , the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- (vii) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like $(n + l)$ rule in case of atomic orbitals.

 **Note :**

(In Valence Bond Theory we modify the pure orbitals of a single atom first - in hybridisation and then use these modified or hybridised orbitals to form the bonds while in Molecular orbital Theory orbitals of different atom are used to form new kind of orbitals called molecular orbitals).

18.1 Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals(LCAO)

In principle, Schrodinger equation can be written for any molecule. However, since it can not be solved exactly for any system containing more than one electron, molecular orbitals which are one electron wave functions for the molecules are difficult to obtain directly from the solution of the Schrodinger equation. This difficulty is overcome by resorting to an approximation method called the **Linear Combination of Atomic Orbitals(LCAO) method to form molecular orbitals.**

Let us consider the application of the LCAO method to the homonuclear diatomic hydrogen molecule. The two hydrogen atoms in the H_2 molecule, for the sake of convenience may be labelled as A and B. Each hydrogen atom in ground state has one electron in the 1s orbital. These atomic orbitals may be represented by the wave functions Ψ_A and Ψ_B . Mathematically the formation of molecular orbitals is described by the linear combination (addition or subtraction of the wave functions of the individual atomic orbitals) of Ψ_A and Ψ_B as shown below.

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

Therefore, two molecular orbitals σ and σ^* are formed

$$\sigma = \Psi_A + \Psi_B$$

$$\sigma^* = \Psi_A - \Psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** and the molecular orbital σ^* formed by the subtraction of atomic orbitals is called **antibonding molecular orbital (Fig.)**

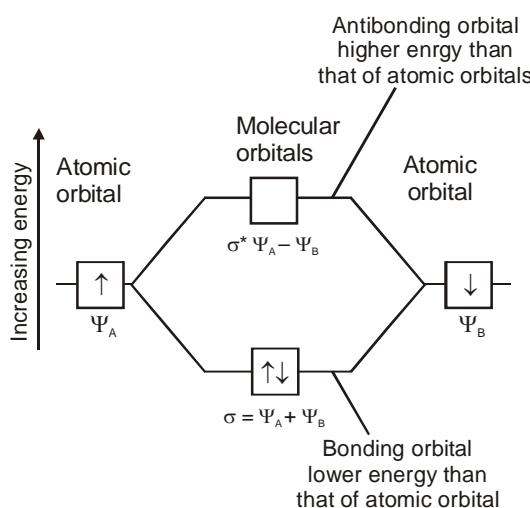


Fig. Formation of bonding (σ) and antibonding (σ^) molecular orbitals by the linear combination of atomic orbitals Ψ_A and Ψ_B centered on two atoms A and B respectively.*

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other (constructive interference) while in the formation of antibonding molecular orbital, these electron waves cancel each other (destructive interference).

The result is that in a bonding molecular orbital most of the electron density is located between the nuclei of the bonded atoms and hence the repulsion between the nuclei is very low while in an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei, as a matter of fact there is a *nodal plane* (i.e., plane in which the electron density is zero) between the nuclei. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. A bonding molecular orbital is, therefore, always of lower energy than either of the atomic orbitals that have combined to form it. In contrast, electrons placed in the antibonding molecular orbital destabilize the molecule. The attraction between the electrons and the nuclei is less than the mutual repulsion of electrons in this orbital and this produces a net increase in energy. Consequently, the electrons placed in this molecular orbital tend to destabilise the molecule and that is why this orbital is said to be antibonding.

It needs to be pointed out that the energy of the antibonding orbital is raised above the energy of the atomic orbitals that have combined by an amount more than that by which the energy of the bonding orbital has been lowered. The total energy for two molecular orbitals however remains the same as that of the two original atomic orbitals.

18.2 Conditions for the combination of atomic orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied :

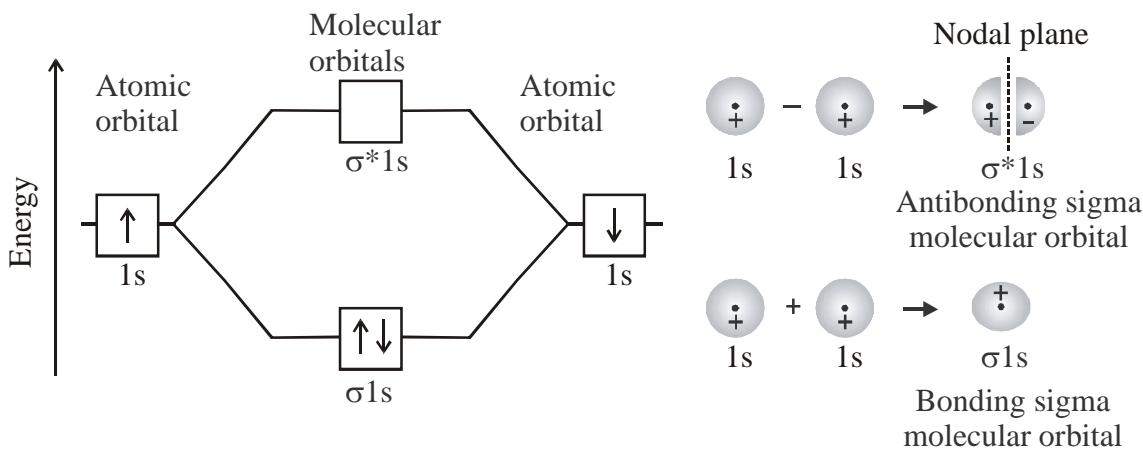
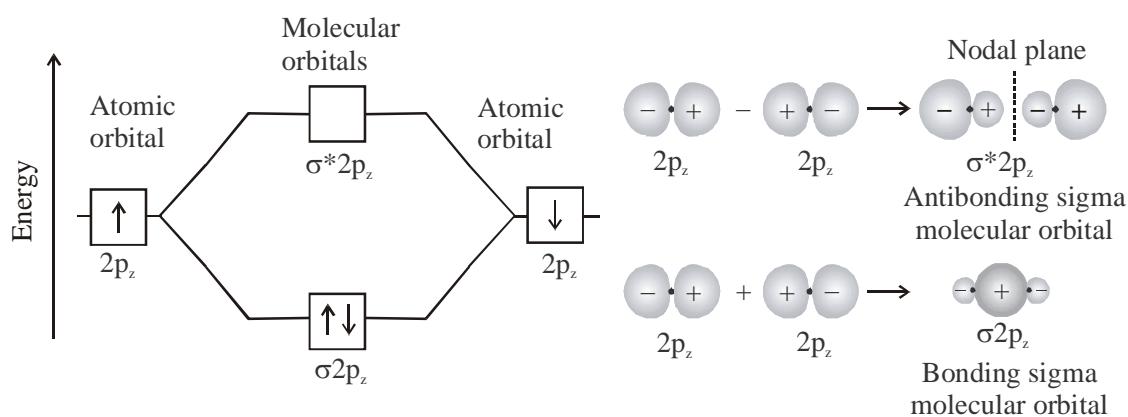
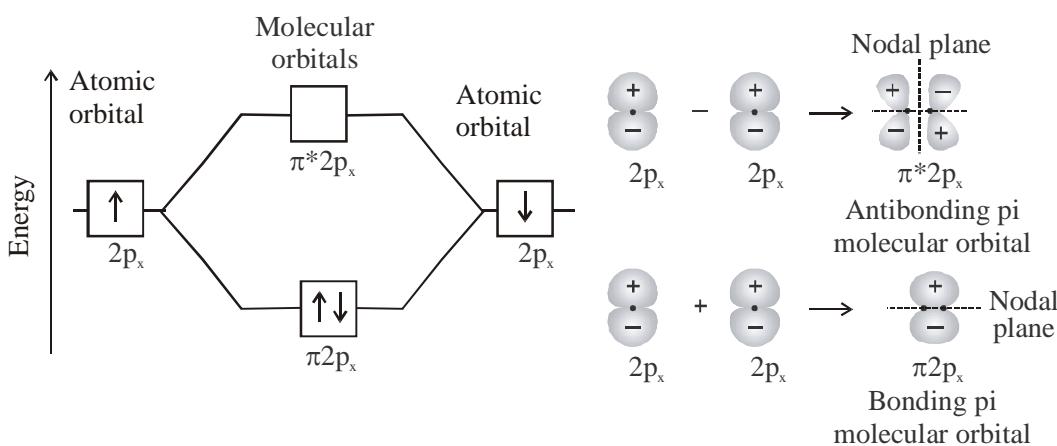
- (i) **The combining atomic orbitals must have the same or nearly the same energy.**
This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.
- (ii) **The combining atomic orbitals must have the same symmetry about the molecular axis.**
By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.
- (iii) **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

18.3 Types of molecular orbitals

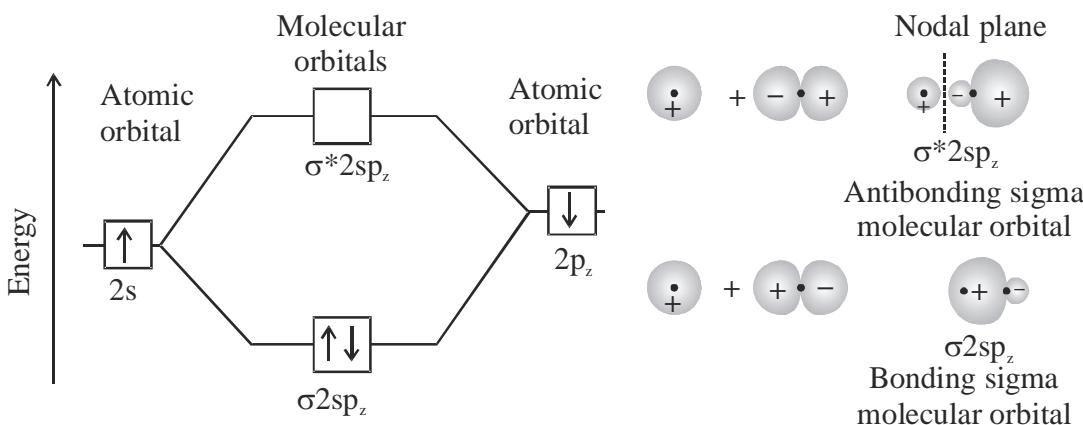
Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical**. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbital's are of the σ type and are designated as σ 1s and σ^* 1s [Fig.(a)]. If internuclear axis is taken to be in the direction, it can be seen that a linear combination of $2p_z$ - orbitals of two atoms also produces two sigma molecular orbitals designated as σ $2p_z$ and σ^* $2p_z$. [Fig. (b)] Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes plane. Such molecular orbitals, are labelled as π and π^* [Fig. (c)]. A π bonding MO has large electron density above and below the inter nuclear axis. The π^* antibonding MO has a node between the nuclei.

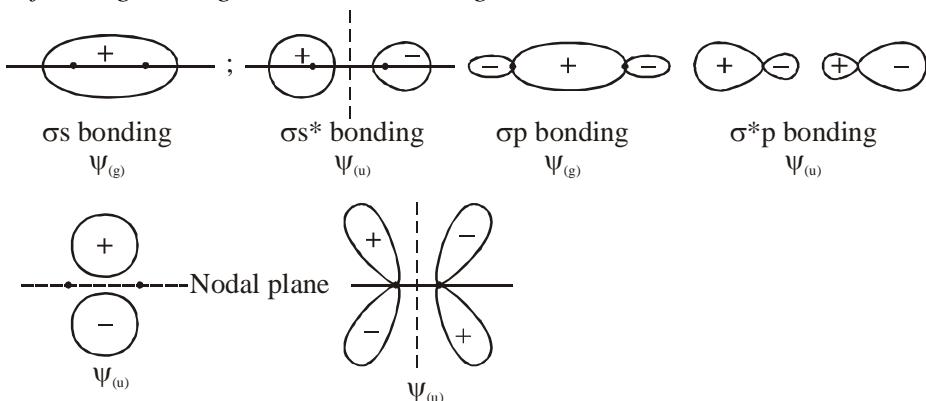
δ -type of molecular orbitals are obtained by involving of d-orbitals into bonding which is not required for us to study.

(a) s-s combination of orbitals

(b) p-p combination of orbitals(end to end overlap)

(c) p-p combination of orbitals (side by side overlap)


(d) s-p combination of orbitals

**Note :**

The molecular orbital wave functions are designated as $\psi_{(g)}$ & $\psi_{(u)}$; 'g' stands for gerade (even) and 'u' for ungerade (odd). 'g' & 'u' refers to symmetry of the orbital about its centre. For determining symmetry of the MO is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is gerade & if the sign changes, the orbital is ungerade.

**18.4 Energy level diagram for molecular orbitals**

We have seen that 1s atomic orbitals on two atoms from two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals :

Antibonding	MO's $\sigma^* 2s$	$\sigma^* 2p_z$	$\pi^* 2p_x$	$\pi^* 2p_y$
Bonding	MO's $\sigma 2s$	$\sigma 2p_z$	$\pi 2p_x$	$\pi 2p_y$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O₂ and F₂ is given below

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li₂, Be₂, B₂, C₂, N₂. For instance, it has been observed experimentally that for molecules such as B₂, C₂, N₂ etc. the increasing order of energies of various molecular orbitals is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

18.5 Electronic configuration and molecular behaviour

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

- (i) The molecule is stable if N_b is greater than N_a , and
- (ii) The molecule is unstable if N_b is less than N_a . In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

N_b – number of e^- in bonding molecular orbitals and N_a – number of e^- in antibonding Molecular orbitals.

- **Bond order**

Bond order (B.O.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding molecular orbitals i.e.,

$$\text{Bond order (b.o.)} = \frac{1}{2} (N_b - N_a)$$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows : A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

- **Nature of the bond**

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

- **Bond-length**

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

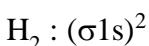
- **Magnetic nature**

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

18.6 Bonding in some Homonuclear diatomic molecules

In this section we shall discuss bonding in some homonuclear diatomic molecules.

- (i) **Hydrogen molecule (H_2) :** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ 1s molecular orbital. So electronic configuration of hydrogen molecule is

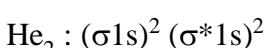


The bond order of H₂ molecule can be calculated as given below :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol⁻¹ and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

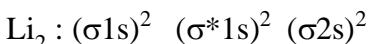
- (ii) **Helium molecule (He₂)** : The electronic configuration of helium atoms is 1s². Each helium atom contains 2 electrons, therefore, in He₂ molecule there would be 4 electrons. These electrons will be accommodated in σ 1s and σ*1s molecular orbitals leading to electronic configuration:



Bond order of He₂ is $\frac{1}{2}(2 - 2) = 0$

He₂ molecule is therefore unstable and does not exist. Similarly, it can be shown that Be₂ molecule ($\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ does not exist.

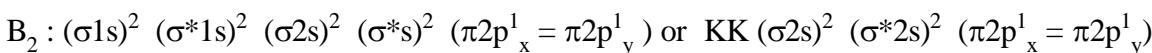
- (iii) **Lithium molecule (Li₂)** : The electronic configuration of lithium is 1s², 2s¹. There are six electrons in Li₂. The electrons in Li₂. The electronic configuration of Li₂ molecule, therefore, is



The above configuration is also written as KK(σ2s)² where KK represents the closed K shell structure ($\sigma 1s)^2 (\sigma^* 1s)^2$.

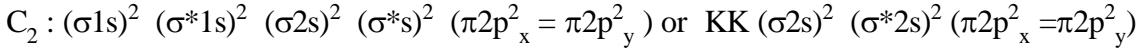
From the electronic configuration of Li₂ molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is $\frac{1}{2}(4 - 2) = 1$. It means that Li₂ molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li₂ molecules are known to exist in the vapour phase.

- (iv) **Boron molecule (B₂)** : The electronic configuration of boron is 1s² 2s² 2p¹. There are ten electrons in B₂. The electronic configuration of B₂ molecule, therefore, is



The bond order of B₂ is $\frac{1}{2}(6 - 4) = 1$ and B₂ should be paramagnetic.

- (v) **Carbon molecule (C₂)** : The electronic configuration of carbons is 1s² 2s² 2p². There are twelve electrons in C₂. The electronic configuration of C₂ molecule, therefore, is



The bond order of C₂ is $\frac{1}{2}(8 - 4) = 2 = 2$ and C₂ should be diamagnetic. Diamagnetic C₂ molecules have indeed been detected in vapour phase. It is important to note that double bond in C₂ consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

(vi) Nitrogen molecule (N_2) :

Electronic configuration : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$
or KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$

$$\text{B.O. of } N_2 = \frac{1}{2}(10 - 4) = 3. \text{ one sigma and two } \pi \text{ bonds.}$$

(vii) N_2^- : Though $15e^-$ but derived from N_2 , hence EC will be according to N_2

Electronic configuration : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2, (\pi^* 2px)^1$
or KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2, (\pi^* 2px)^1$

$$\text{B.O. of } N_2^- = \frac{1}{2}(10 - 5) = 2.5$$

(viii) N_2^+ : B.O. = 2.5, out of N_2^+ and N_2^- , N_2^- is less stable though both have equal bond order but N_2^- has greater number of antibonding electrons.

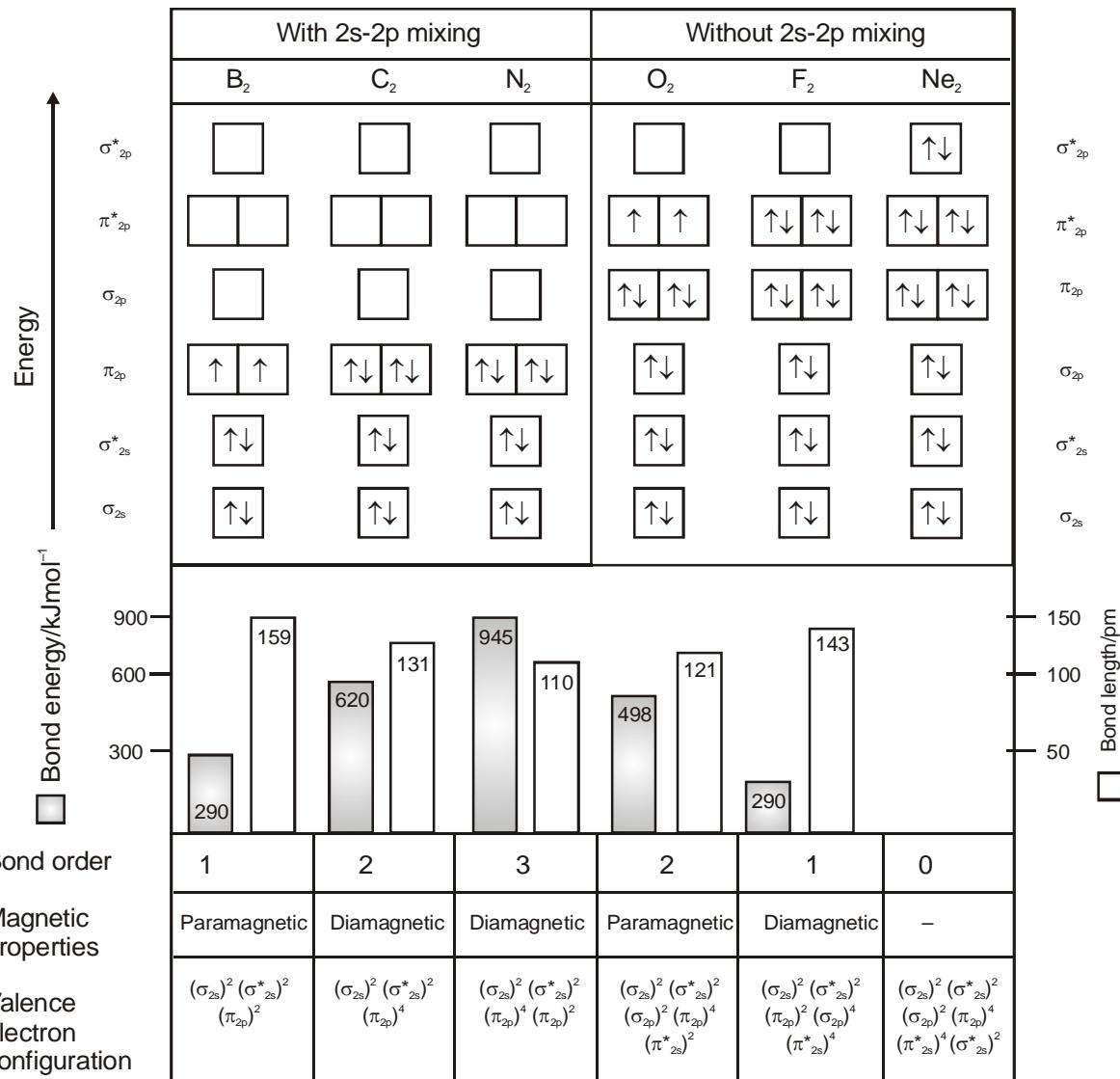
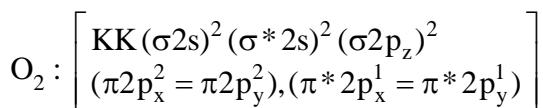
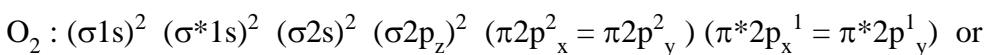


Fig. MO occupancy and molecular properties for B₂ through Ne₂.

(ix) **Oxygen molecule (O_2)** : The electronic configuration of oxygen atoms is $1s^2 \ 2s^2 \ 2p^4$.

Each oxygen atom has 8 electrons, hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is



From the electronic configuration of O_2 molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$$

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals, therefore, **O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation.** In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig. are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2 . The sequence of MOs and their electron population are shown. The bond energy bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagrams.

(x) O_2^+ : B.O. = 2.5 paramagnetic.

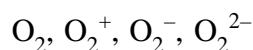
(xi) O_2^- : B.O. = 1.5 paramagnetic.

(xii) O_2^{2-} : B.O. = 1 diamagnetic.

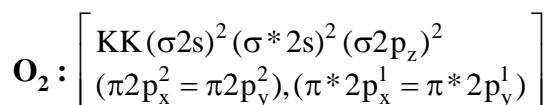
	O_2^{2-}	O_2^-	O_2	O_2^+	O_2^{2+}
No. of unpaired e⁻s	0	1	2	1	0
B.O.	1.0	1.5	2.0	2.5	3.0

Illustrations

Illustration 14. Give the correct order of Bond length for



Solution. Bond length \propto 1/ Bond order



$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$$

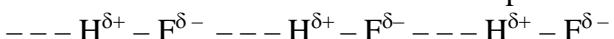


BEGINNER'S BOX-6

Molecular orbital theory

19.0 HYDROGEN BOND

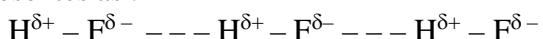
Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form covalent bond, the electrons of the covalent bond are tends towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other electronegative atom. This bond is known as hydrogen bond and is weaker than covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :



Here, hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

• Cause of Formation of Hydrogen Bond

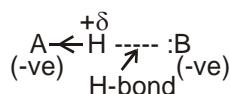
When hydrogen is bonded to strongly electronegative element 'X'. the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (+) while X' attain fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :



The magnitude of H – bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong Influence on the structure and properties of the compounds.

Note :

- Energy of H-bond is usually low but there are examples in which H-bond energy is found to be nearly 220 kJ/mol (comparable to covalent bond) Therefore H-bond can be classified into 3 categories.
 - (a) Weak BE < 25 kJ/mol.
 - (b) Medium 25 – 35
 - (c) Strong > 35 kJ/mol ex : $K^+HF_2^-$ or $[HF_2^-]$ ion energy = 220 kJ/mol.
- H-bond is due to electrostatics attraction between the pole of H and l.p. of e^- s on another -ve atom

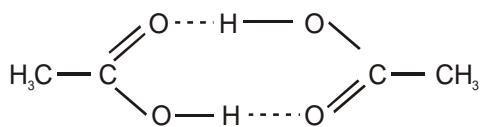
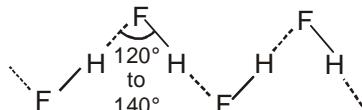
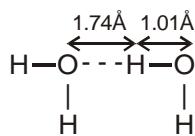


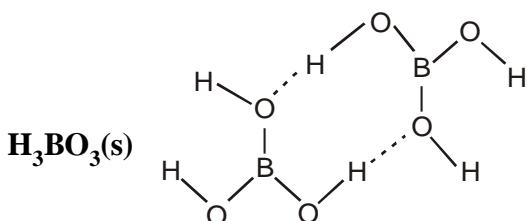
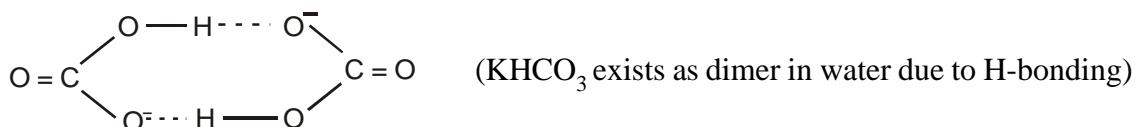
- H-bonds are found to be much stronger with F-atoms but in case of other atoms the relative strength of H-bond will depend upon + δ charge of H (\uparrow possibility when atom A is more -ve) and availability of l.p. on B-atom. (B must be relatively less -ve)
- $\begin{array}{c} \text{A} \leftarrow \text{H} \cdots \text{:B} \\ x \qquad \qquad \qquad y \end{array}$ (generally distance $x < y$)
But in case of very strong H-bonding
 $x = y$,

19.1 Types of H-Bonding

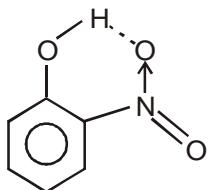
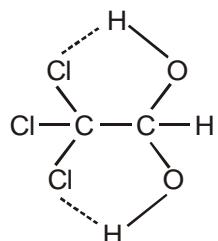
(A) Intermolecular

Ex. : H_2O , HF, R – OH, CH_3COOH / HCOOH , $\text{NH}_3(\text{R})$, R – NH_2 ,



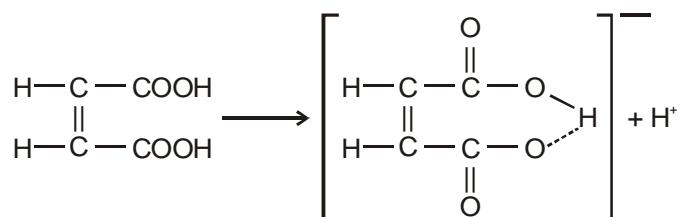
HCO₃⁻ in KHCO₃**(B) Intramolecular :**

(i) O-nitrophenol

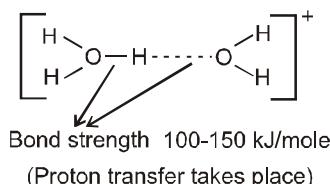
(ii) Chloral-hydrate \longrightarrow CCl₃CH(OH)₂

2 – OH groups are stabilised on the same C-atom.

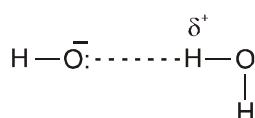
(iii) Maleic Acid :



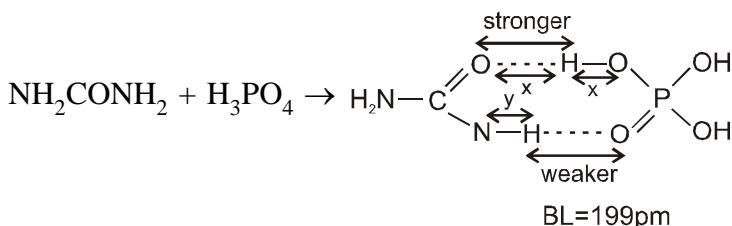
- (v) An interesting hydrate of Hydronium ion with the formula $H_3O^+(H_2O)_{20}$ in which H_2O molecules are hydrogen bonded. Some lower species like $H_5O_2^+$ have also been observed where the 2 water molecules are linked three H bonds.



Similarly $H_3O_2^-$ ions are also observed which is actually hydrate OH^- ion.



It is found urea and phosphoric Acid form H bond with each other



2 types of H–bond

$$B.L.OH \Rightarrow x = 122 \text{ pm} ; \quad B.L. N-H \Rightarrow y = 100 \text{ pm}$$

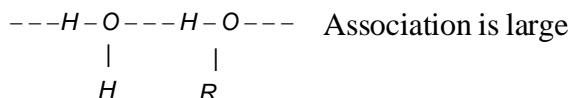
19.2 Application of Hydrogen Bonding

- (i) H_2O is liquid but H_2S is gas
 (ii) HF is liquid but HCl is gas.

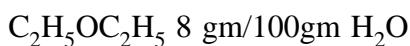
Due to intermolecular H bonding molecules undergo association (molecular assoication) due to which that substance become liquid or solid at room temperature.

\therefore its B.pt \uparrow

- (iii) C_2H_5OH is soluble in water but ether is much less soluble

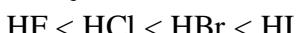


\therefore solubility of ether is much less.



Hydrocarbon chain $\uparrow \therefore$ solubility \downarrow

(iv) $\text{HF}_{(\text{aq.})}$ is a weak acid



(v) Ice floats on water

No. of water molecule attached to 1 H_2O molecule = 4

No. of H bonds in a molecule = 2

One H_2O is tetrahedrally bonded with 4 H_2O molecules.

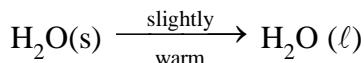
Intermolecular spacing $\uparrow \therefore \rho^-$ of ice \downarrow



density of $\text{D}_2\text{O}(\text{s}) >$ density of $\text{H}_2\text{O}(l)$

\therefore it sinks in $\text{H}_2\text{O}(l)$ but floats on $\text{D}_2\text{O}(l)$

(vi) Density of water max at 4°C



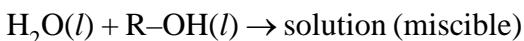
density increases with increase in temperature upto 4°C .

In this temperature region some of the ice melts and hence some H_2O molecule go into the cages of remaining ice structure.

$\therefore V \downarrow d \uparrow$ becoming max at 4°C but beyond this temp thermal effects become dominating $V \uparrow$

$\therefore d \downarrow$

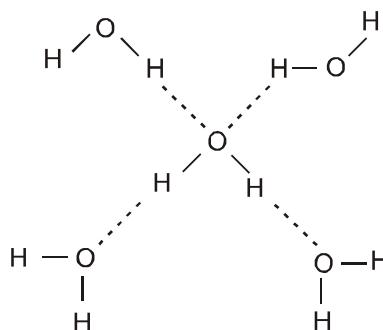
(vii) Water can extinguish the burning alcohol but not the burning petrol or a Hydrocarbon (in general).



(No H bonding)

density of open chain HC $< \text{H}_2\text{O}$ i.e. lighter than water.

\therefore continue burning even in presence of H_2O



Illustrations

Illustration 15. Boiling point of o-nitrophenol is less than m-nitrophenol or p-nitrophenol and this compound is much less soluble in water than the remaining two. Explain.

Solution. Due to intramolecular H-bonding in o-nitrophenol

Due to intermolecular H-bonding in m-p-nitrophenol.

Illustration 16. Which of the following H-bond strength order is not correct ?

- (A) $\text{D}_2\text{O} > \text{H}_2\text{O}$ (B) $\text{H}_2\text{O} > \text{H}_2\text{O}_2$ (C) $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$ (D) $\text{HF} > \bar{\text{F}} \dots \text{H}-\text{F}$

Ans. (D)

Solution. $\text{H}-\text{F} = \bar{\text{F}} \dots \text{H}-\text{F}$

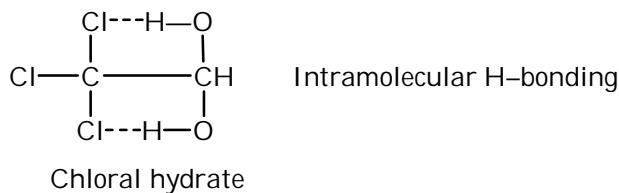
Illustration 17. Correct match is

Column - I	Column - II
(A) Chloral hydrate	(p) Form Zig-zag chain
(B) HF	(q) Form 2-D-sheet structure
(C) H_3BO_3	(r) Intermolecular H-bond
(D) H_2SO_4	(s) Intramolecular H-bond
(A) (a) - (s), (b) - (p), (c) - (q), (d) - (r)	
(B) (a) - (s), (b) - (p), (c) - (r), (d) - (q)	
(C) (a) - (p), (b) - (s), (c) - (q), (d) - (r)	
(D) (a) - (p), (b) - (q), (c) - (r), (d) - (p)	

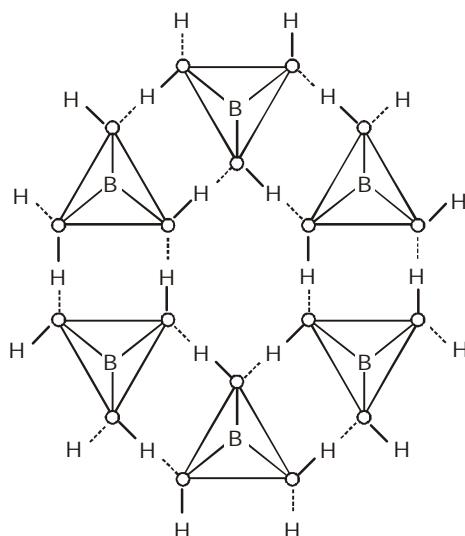
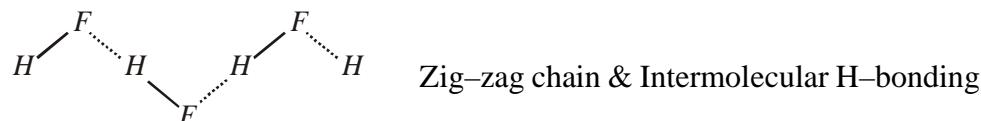
Ans.

(A)

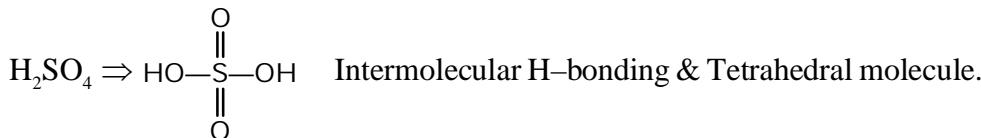
Solution.



Chloral hydrate

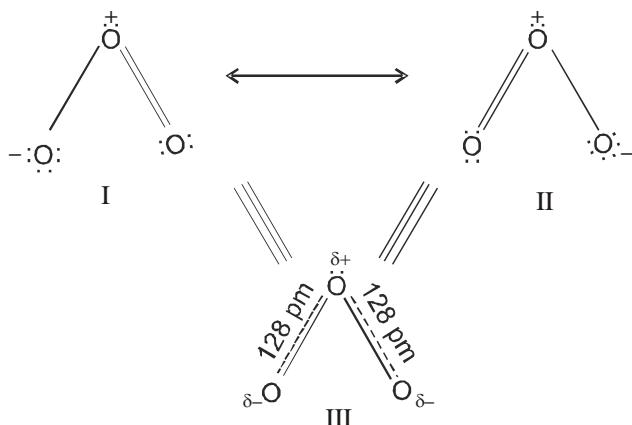


Planar Structure, Intermolecular H–bonding (Boron sp²).



20.0 RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below :



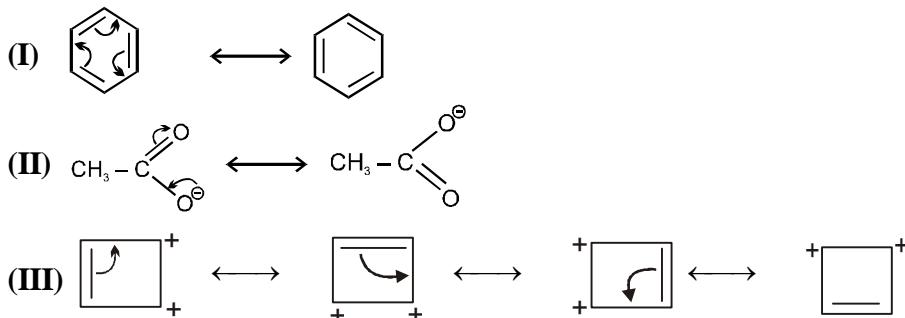
Resonance in the O_3 molecule

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)
 In both structures we have a $O - O$ single bond and a $O = O$ double bond. The normal $O - O$ and $O = O$ bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the Type of difficulty experienced in the depiction of accurate structures of molecules like O_3 . According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 , more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow. Some of the other examples of resonance structures are provided by the carbonate Ion and the carbon dioxide molecule.

20.1 Definition

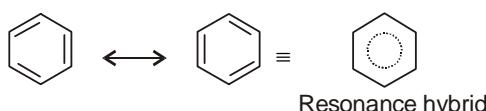
Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound





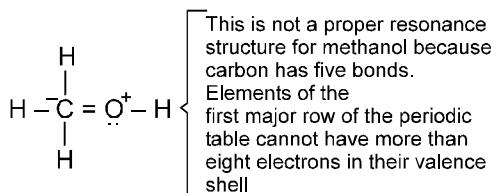
20.2 Resonance Hybrid

It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.

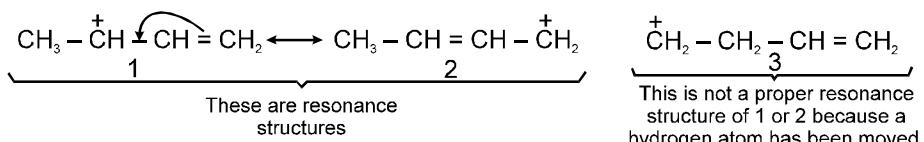


20.3 Rules for Resonance

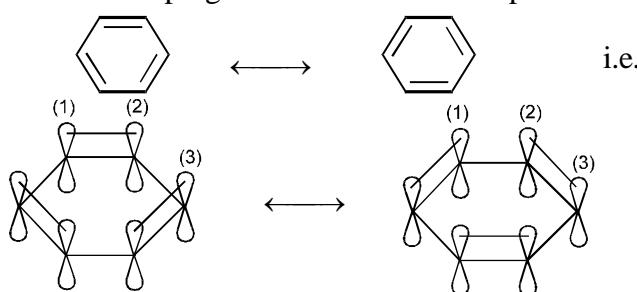
- (a) All the canonical forms (resonating structure) must have proper lewis structure. For instance none of them may have a carbon atom with five bonds.



- (b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structure 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atoms and this is not permitted :



- (c) All atoms taking part in the resonance (π -electron resonance) must lie in a plane so that orbitals overlapping for resonance become parallel to each other.



- (d) The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.
(e) All canonical forms do not contribute equally to the true molecule. The more stable a structure is the greater contributor to its resonance hybrid.

[To be dealt in detail in General organic chemistry]

☛ **Note :**

Many misconceptions are associated with resonance and the same need to be dispelled.

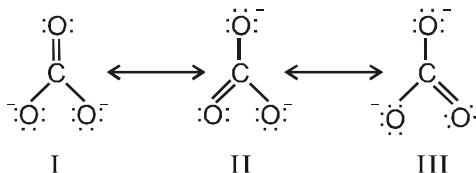
You should remember that :

- (i) The canonical forms have no real existence.
- (ii) The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.
- (iii) There is no such equilibrium between the canonical forms as we have between tautomeric forms (keto and enol) in tautomerism.
- (iv) The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be depicted by a single Lewis structure.

Illustrations

Illustration 18. Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution. The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.



Resonance in CO_3^{2-} , I, II and III represent the three canonical forms.

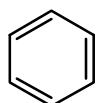
Illustration 19. Give correct order of bond strength of C–C bond in following species :

- | | | | |
|----------------------------|-----------------------------|------------------------------|-----------------------------|
| (i) C_2H_4 | (ii) C_6H_6 | (iii) C_2H_2 | (iv) C_2H_6 |
|----------------------------|-----------------------------|------------------------------|-----------------------------|

Solution.

Bond order

$\text{H}_3\text{C}-\text{CH}_3$	1
$\text{H}_2\text{C}=\text{CH}_2$	2
$\text{HC}\equiv\text{CH}_2$	3



Between 1–2(1.5) (Due to resonance)

Bond strength \propto Bond order

So order of Bond strength : $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{C}_6\text{H}_6 > \text{C}_2\text{H}_6$

21.0 BACK BONDING

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period)

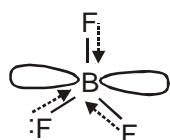
Back bonding increases the bond strength and decreases the bond length

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example **Back bonding in boron trihalides**

Boron trihalides :

BF_3	BCl_3	BBr_3	BI_3
↓	↓	↓	↓
sp^2	sp^2	sp^2	unstable (stearic hindrance)

- Observed bond length in BF_3 molecule is found to be less than the expected.



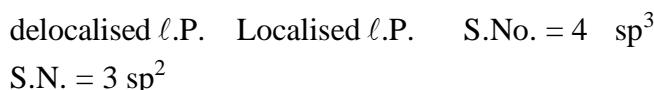
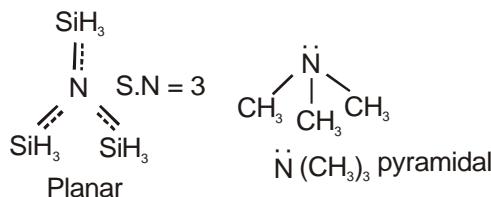
There will be $p\pi - p\pi$ back bonding between 2p of B atom & 2p of F atom. Bond length of B - F will decrease

- The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order



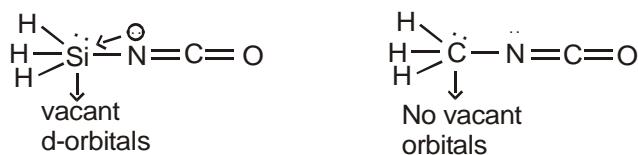
for example,

Trisilylamine is a planar molecular and does not act as a lewis base while trimethyl is a pyramidal and act as lewis base



But in a similar compound $N(PH_3)_3$ the shape is found to be pyramidal, so N atom must be sp^3 hybridised due to much less extent of back bonding into the vacant orbitals of P.

Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain !



$\ell.P.$ of N can be delocalised

(Back bonding)

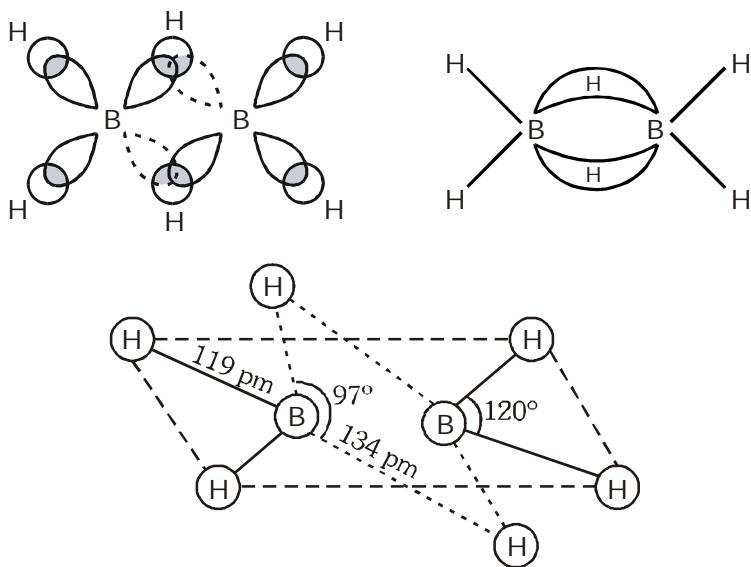
S.N of N = 2 (sp) S.N = 3 (sp^2)

$p\pi - d\pi$ back bonding.

21.1 Diborane (3c-2e TYPE BONDING)

The structure of diborane is shown in fig. The four terminal hydrogen atoms and the two boron atoms lie in one plane. There are two bridging hydrogen atoms are out of plane i.e. one on either side of plane.

The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre - two e⁻ bonds.



The structure of diborane B_2H_6

Bonding in diborane : Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as **banana bonds**.

Illustrations

Illustration 20. Compare B-F bond length in BF_3 and $[\text{BF}_4]^-$.

Solution. $\text{BF}_3 + \text{KF} \longrightarrow \text{K}^+ [\text{BF}_4]^-$

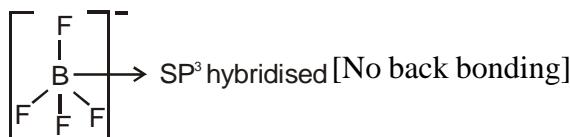
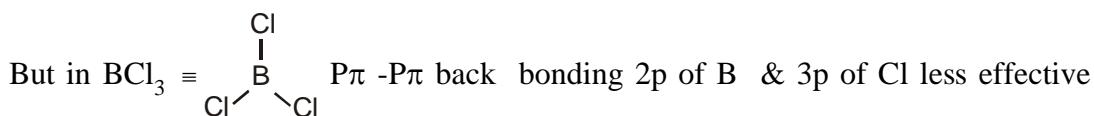


Illustration 21. All boron trihalides are lewis acids also explain their order.

Solution. Boron trihalides are electron deficient molecules therefore act as a Lewis acids

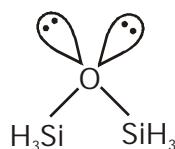


tendency to accept L.P in $\text{BCl}_3 > \text{BF}_3$. Lewis acid strength $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.

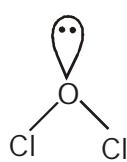
Illustration 22. Which of the following molecule has maximum extent of back bonding ?

- (A) $\text{O}(\text{SiH}_3)_2$ (B) OCl_2 (C) NF_3 (D) PF_3

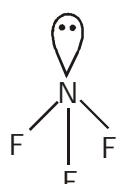
Ans. (A)



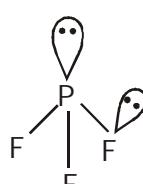
Solution. as Si has no lone pair, so maximum extent of back bonding.



'Cl' has lone pair, so tendency of back bonding decreases



No back bonding



'p' has lone pair, so tendency of back bonding decreases

BEGINNER'S BOX-7**Hydrogen Bond & Back Bonding**

1. The hydrogen bond is strongest in:-
 (A) O – H - - - S (B) S – H - - - O (C) F – H - - - F (D) O – H - - - O

2. H_2O boils at higher temperature than H_2S , because it is capable of forming:-
 (A) Ionic bonds (B) Covalent bonds (C) Hydrogen bonds (D) Metallic bonds

3. The correct order of volatility is:-
 (A) $\text{NH}_3 < \text{H}_2\text{O}$ (B) p-nitro phenol < o-nitro phenol
 (C) $\text{CH}_3\text{OH} > \text{CH}_3 - \text{O} - \text{CH}_3$ (D) $\text{HF} > \text{HCl}$

4. Intramolecular H-bond :-
 (A) Decreases Volatility (B) Increases melting point
 (C) Increases viscosity (D) Increases vapour pressure

5. The high boiling point of water is due to the presence of
 (A) Dative bond (B) Covalant bond (C) Hydrogen bond (D) Vander waals bond

6. Hydrogen bonding absent in :-
 (A) CH_3COOH (B) H_2O (C) CH_4 (D) $\text{C}_2\text{H}_5\text{OH}$

7. Correct order of volatility is :-
 (A) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ (B) $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$
 (C) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (D) $\text{HBr} < \text{HCl} < \text{HI} < \text{HF}$

8. In which of the following species hybridisation of central atom does not change due to back bonding ?
 (A) H_3BO_3 (B) BF_3 (C) PF_3 (D) All

9. Maximum extent of H-bond is in–
 (A) H_2O (B) CH_3OH (C) $\text{C}_2\text{H}_5\text{OH}$ (D) H_2S

22.0 INTERMOLECULAR FORCES (VAN DER WAAL'S FORCES)

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

- (a) Ion-dipole attraction :
- (b) Dipole-dipole attraction :
- (c) Ion-induced dipole attraction :
- (d) Dipole-induced dipole attraction :
- (e) Induced dipole-Induced dipole : (Dispersion force or London forces)

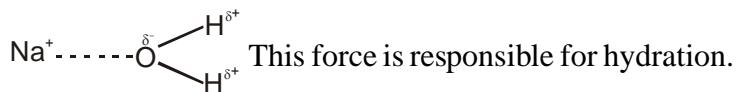
☞ **Note :**

strength of van der Waal's forces a > b > c > d > e

22.1 Ion-dipole attraction

Exists between an ion and a polar molecule. Its strength depends on

- (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule.

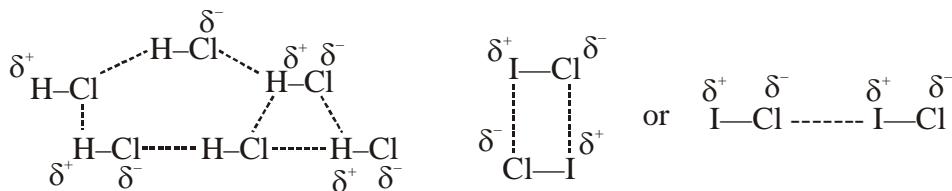


☞ **Note :**

*These are short range forces which are more sensitive to distance as compared to ion-ion attraction
(The interaction energy is inversely proportional to square of the distance between species.)*

22.2 Dipole-dipole interaction

In the case of polar molecules which have permanent dipoles, the van der Waals forces are mainly due to electrical interaction between the dipoles. Ends of the dipoles possess partial charges & these charges are shown by (δ). Partial charges are always less than unit electronic charges ($1.6 \times 10^{-19} C$). Polar molecules interact with neighbouring molecules. These interactions are known as dipole-dipole interactions. For instances, gases such as ammonia, sulphur dioxide, hydrogen fluoride, hydrogen chloride, etc., have permanent dipoles as a result of which there is appreciable dipole interaction directly depends upon the dipole moment of the molecule concerned. This interaction is stronger than the London forces but is weaker than ion-ion interactions because only partial charges are involved.



☞ **Note :**

The attractive forces decreases with the increase of distance between the dipoles. The interaction energy is inversely proportional to distance between polar molecules. Dipole-Dipole interaction energy between stationary polar molecules (as in solid) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$, where r is the distance between polar molecules. Besides dipole-dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecule increases.

22.3 Ion-induced dipole attraction

Exists between ion and non-polar molecules. When a charged ion is introduced into the neighbourhood of an uncharged molecule it polarises the molecule generating dipole-induced dipole interaction.



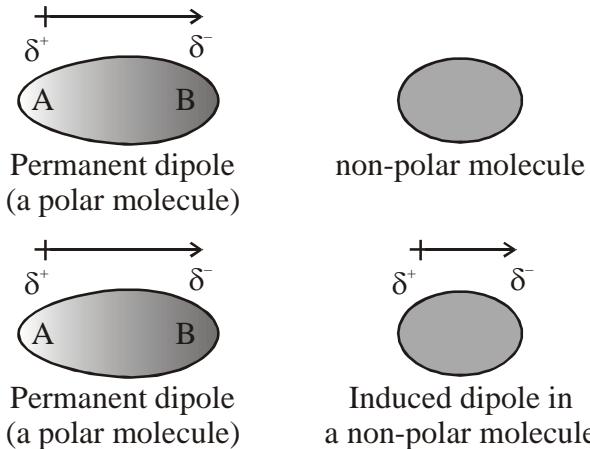
☞ **Note :**

These are short range forces which are more sensitive to distance as compared to ion–ion attraction (The interaction energy is inversely proportional to fourth power of the distance between species).

22.4 Dipole-induced Dipole Interaction

A polar molecule may sometimes polarise a neutral molecule which lies in its vicinity and thus induce polarity in that molecule just as a magnet induces magnetic polarity in a neutral piece of iron lying close by. The induced dipole then interacts with the dipole moment of the first molecule and thereby the two molecules are attracted together. The magnitude of this interaction would, evidently, depend upon the magnitude of the dipole moment of the polar molecule and the polarizability of the neutral molecule.

Induced dipole moment depend upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. Molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.



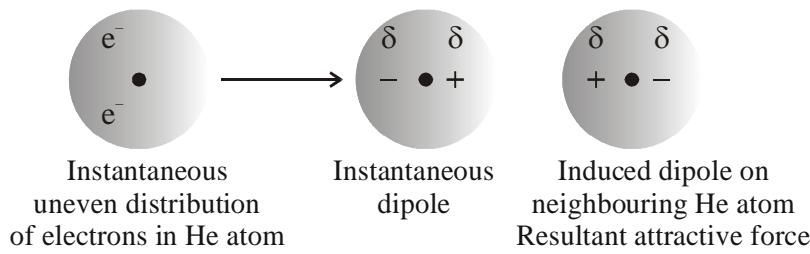
☞ **Note :**

In this case also interaction energy is proportional to $1/r^6$ where r is the distance between two molecules.

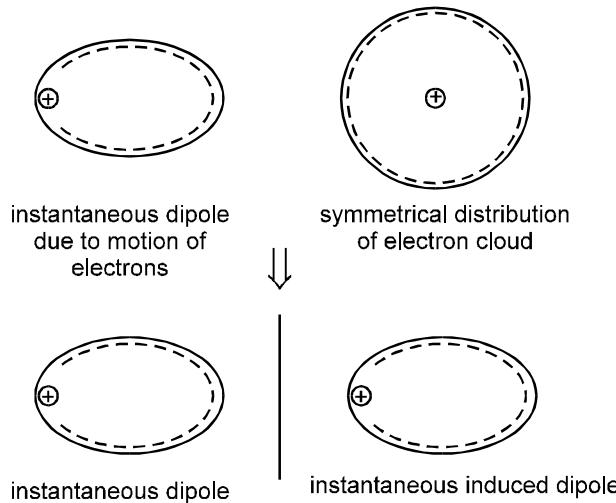
22.5 Instantaneous dipole- Instantaneous induced dipole attraction

Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other. It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical i.e., the charge cloud is more on one side than the other. This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipole of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London and for this reason force of attraction between two temporary dipoles is known as London force. Another name for this force is dispersion force. These forces are always attractive.



Exists among the non-polar molecules like H_2 , O_2 , Cl_2 etc. in solid or liquid states



Note :

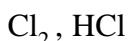
(i) Strength of vander waal force \propto molecular mass.

van der Waal's force \propto Boiling point.

(ii) In this case also interaction energy is proportional to $1/r^6$ where r is the distance between two molecules.

Illustrations

Illustration 23. Give the order of boiling point of following



Solution. Dispersion force in $\text{Cl}_2 - \text{Cl}_2$ and dipole-dipole attraction in $\text{HCl} - \text{HCl}$
 \therefore Boiling point will be high in HCl.

Illustration 24. Arrange the inert gases, according to their increasing order of boiling points

Solution. $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ Boiling point

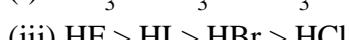
Because strength of van der Waal's force increases down the group with increase in molecular mass.

Illustration 25. Give correct order of Boiling point in follows :



Solution. $\downarrow^{\text{U}}_{\text{D}} \rightarrow \text{M.mass} \uparrow, \text{V.W.F.} \uparrow \rightarrow \text{B.P.} \uparrow$

But $\text{NH}_3, \text{H}_2\text{O}$ & HF show intermolecular H–bonding.



23.0 METALLIC BOND

Metallic bond is defined as the force that binds a metal atom to a number of electrons within its sphere of influence.

23.1 Factors affecting metallic bonding

Since it is electrical attraction between delocalised electrons (i.e. mobile electrons) and the positive part of the atom (i.e. kernel) therefore strength of metallic bond depends upon following factors :

- **No. of metallic bonds per atom**

Larger the number of metallic bonds (number of valence electrons) per atom, stronger is the metallic bonding.

- (i) Alkali metals-only one valence electron and therefore, one metallic bond per atom and thus gives weakest metallic bonding. Hence their melting points are low.
- (ii) Alkaline earth metals-two valence electrons and form two metallic bonds per atom and, therefore, gives a comparatively bit stronger metallic bonding.
- (iii) Transition metals may use inner -d-electrons along with the outer electrons for bonding as $(n-1)$ d and ns have nearly same energy. So in them number of metallic bonds per atoms is quite large (more than two always). Hence their melting points are higher.

- Type of hybrid orbitals participating in metallic bonding

More directional and diffused hybrid orbitals form more stronger metallic bonds. ds hybrid orbitals (in transition metals) are more directional and diffused than sp hybrid orbitals (in alkali & alkaline earth metals)

Therefore, much stronger metallic bonding takes place in transition metals.

- #### • Radius of metallic atom

Smaller the radius of atom, shorter is the bond length, hence greater is the bond strength.

23.2 Boiling points and melting points

- (a) It is a property of aggregate of atoms and not of a single atom.

i.e. why it is a molecular property.

- (b) Melting point of a solid depend on —

(c) Structure of solid made up of (i) atomic solid (ii) molecular solid (iii) metallic solid

Order of decreasing melting point is : **Atomic solid > Metallic solid > Molecular solid**

- (d) Chemical bond among particles in solid. Order of bond strength is –

Covalent bond > Metallic bond > Vander waal bond

- (e) Bond energy – Covalent solids like diamond, SiO_2 etc have only covalent bonds between atoms so their bond energy is higher than molecular or metallic solids.

Periodic variation :

In period from left to right boiling point and melting point first increases then decreases.

Alkali metals – Crystal structure BCC (low boiling point & melting point)

Transition metals – " FCC (High boiling point & melting point)

- Inert gases Lowest boiling point & melting point (Vander waal force)
- Transition elements Highest melting point

Metals W(Tungsten) maximum melting point (3410°C)
 Hg(Mercury) lowest melting point (-38°C)

Non metals Carbon (In the form of diamond) Highest melting point (3727°C)
Helium Lowest melting point (-270°C)

In Group

(a) In **s-block** elements boiling point & melting point decreases down the group.

Li, Na (solid) → Cs, Fr (liquid)

It is due to weak cohesive energy of metallic bond in IA.

(b) In **d-block** elements boiling point & melting point increases down the group (due to lanthanide contraction, z_{eff} increases and hence bond energy increases)

(c) In **p-block** elements

(i) From IIIA – IVA group boiling point & melting point decreases down the group and from VA to '0' group, boiling point & melting point increases down the group.

(Atomic or molecular weight \propto van der waal force)

(ii) boiling point and melting point of monoatomic molecules are lesser than diatomic molecules.

'0' group < Halogens

(iii) Atomic solid non metals like B, C and Si has higher boiling point and melting point due to strong covalent bond.

(iv) Boiling point & melting point of molecular solids are less because of weaker van der waal force among molecules **Ex.** I_2 .

Order of melting point

Li > Na > K > Cs

C > Si > Ge

He < Ne < Ar < Rn

Be > Ca > Sr > Ba > Mg

C > B > Si

Zn > Cd > Hg

F_2 < Cl_2 < Br_2 < I_2

B > Al > Ga

Cu > Au > Ag

Illustrations

Illustration 26. Give correct order of Melting point of following metals :

Sc, Ti, V, Cr

Solution. Melting point \propto Metallic strength \propto Number of unpaired electrons in metal atom.

Sc < Ti < V < Cr

BEGINNER'S BOX-8

Resonance, Metallic Bonds, Intermolecular forces & Miscellaneous

1. Boron forms BX_3 type of halides. The correct increasing order of Lewis-acid strength of these halides is

(A) BF_3 > BCl_3 > BBr_3 > BI_3	(B) BI_3 > BBr_3 > BCl_3 > BF_3
(C) BF_3 > BI_3 > BCl_3 > BBr_3	(D) BF_3 > BCl_3 > BI_3 > BBr_3
2. Which of the following is false ?
 - Vander Waals forces are responsible for the formation of molecular crystals
 - Branching lowers the boiling points of isomeric organic compounds due to decrease in vander Waals forces of attraction
 - In graphite, vander Waals forces act between the carbon layers
 - In diamond, vander Waals forces act between the carbon layers

3. The structure of diborane, (B_2H_6) contains
- (A) Four (2c–2e) bonds and two (2c–3e) bonds
 - (B) Two (2c–2e) bonds and two (3c–2e) bonds
 - (C) Four (2c–2e) bonds and four (3c–2e) bonds
 - (D) None
4. Which of the following models best describes the bonding between layer of the graphite structure ?
- (A) metallic bonding
 - (B) ionic bonding
 - (C) non-metallic covalent bonding
 - (D) van der Waals forces
5. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :
- (A) van der Waal's forces
 - (B) Covalent attraction
 - (C) Hydrogen bond formation
 - (D) Dipole-dipole attraction
6. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is
- (A) H_2O because of hydrogen bonding
 - (B) H_2Te because of higher molecular weight
 - (C) H_2S because of hydrogen bonding
 - (D) H_2Se because of lower molecular weight
7. London force works in
- (A) Polar molecule
 - (B) Non-polar molecule
 - (C) All polar and non-polar molecule
 - (D) Only in polar molecule
8. London forces depends upon
- (A) Molecular weight
 - (B) Number of polarisable electron
 - (C) Molecular size
 - (D) None of these

GOLDEN KEY POINTS

- Ionic compounds are soluble if hydration energy is greater than lattice energy.
- Covalent character in Ionic compound can be explained with the help of Fajan's rule smaller cation, big anion & pseudo inert gas configuration of cation favours covalent character in ionic compound.
- If an ionic compound is having two or more than two crystalline structures then it is said to be polymorphous.
- Incomplete octet: BeF_2 , BF_3 , Al_3Cl_3 , BCl_3 .
- Expansion of octet: PCl_5 , SF_6 , ClF_3 , IF_7 .
- A σ – bond is formed by axial overlap of atomic orbitals and π – bond is formed by sideways overlap of orbitals.

S.NO.	TYPE OF HYDRIDISATION	MOLECULAR SHAPE	EXAMPLES
1.	sp	linear	BeCl_2 , CO_2 , C_2H_2
2.	sp^2 (3 B.P.)	Δ Planar	BF_3 , C_2H_4
3.	sp^2 (2 B.P. + 1 $\ell.p$)	V/Bent/Angular	SnCl_2
4.	sp^3 (4 B.P.)	Tetrahedral	CH_4 , CCl_4 , SiCl_4
5.	sp^3 (3 B.P. + 1 $\ell.p$)	Trigonal pyramidel	$\ddot{\text{N}}\text{H}_3$, $\ddot{\text{P}}\text{F}_3$
6.	sp^3 (2 B.P. + 2 $\ell.p$)	V/Bent/Angular	H_2O , OF_2
7.	sp^3d (5 B.P.)	Trigonal bipyramidel	PCl_5 , PF_5
8.	sp^3d (4 B.P. + 1 $\ell.p$)	See-saw	SF_4 , $[\text{PF}_4]^-$
9.	sp^3d (3 B.P. + 2 $\ell.p$)	T-Shaped	ClF_3 , IF_3
10.	sp^3d (2 B.P. + 3 $\ell.p$)	Linear	XeF_2 , IF_2^-
11.	sp^3d^2 (6 B.P.)	Octahedral	SF_6 , PCl_6^-
12.	sp^3d^2 (5 B.P. + 1 $\ell.p$)	Dist. Square Pyramidel	IF_5 , BrF_5
13.	sp^3d^2 (4 B.P. + 2 $\ell.p$)	Square Planar	XeF_4 , IF_4^-
14.	sp^3d^3 (7 B.P.)	Pentagonal bipyramidel	IF_7
15.	sp^3d^3 (6 B.P. + 1 $\ell.p$)	Capped Octahedral	XeF_6
16.	sp^3d^3 (5 B.P. + 2 $\ell.p$)	Pentagonal planar	$[\text{XeF}_5]^-$

- A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B - F bonds are polar in BF_3 but BF_3 has $\mu = 0$ due to its symmetrical geometry.

- If molecule have $\mu = 0$.

then it should be linear or having symmetrical geometry.

e.g. linear – CO_2 , CS_2 , BeCl_2 (g).

symmetrical geometry – BF_3 , CH_4 , PCl_5 , SF_6 , IF_7 , XeF_4

- If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.

e.g. angular – SnCl_2 , PbCl_2 , SO_2 ,

Unsymmetrical geometry – NH_3 , H_2O , NF_3 , SF_4 , H_2S ,

- % Ionic character = $\frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100 = \frac{\mu_{(\text{Observed})}}{\mu_{(100\% \text{ Ionic compound})}} \times 100$

- Bond order = $\frac{1}{2}(\text{N}_b - \text{N}_a)$

A positive bond order ($\text{N}_b > \text{N}_a$) means a stable molecule while a negative or zero bond order means an unstable molecule.

Bond order \propto Bond strength

$$\propto \frac{1}{\text{Bond length}}$$

\propto Stability

- Energy of Molecular orbital is given by experimental order not by $(n + l)$ rule.
- $\text{A}^{\delta-} \dots \text{H}^{\delta+} \dots \text{B}^{\delta-} \Rightarrow$ Hydrogen bond can be intermolecular or intramolecular hydrogen bonding.

Intermolecular H - bond $\Rightarrow \text{ROH}, \text{H}_2\text{O}, \text{ROH} \& \text{H}_2\text{O}$

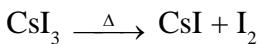
Intramolecular H - bond \Rightarrow Salicylic acid, Maleic acid.

- Vander wall's force are weakest type of intermolecular force. These are non-directional, non-valence cohesive forces. V.W. force \propto Molecular weight \propto Boiling point.

SOME WORKED OUT ILLUSTRATION

Illustration 1.

If it is known that on heating a ionic compound of a polyhalide with a cation it decomposes into more stable halide of that cation due to high lattice energy, for example



The complex compound Rb[IBrCl] after strong heating will

- (A) RbI + BrCl (B) RbCl + IBr (C) RbBr + ICl (D) None

Solution.

(B)

$(\text{L.E.})_{\text{RbCl}} > (\text{L.E.})_{\text{RbBr}} > (\text{L.E.})_{\text{RbI}}$ and more stable compound is formed first.

Illustration 2.

Which of the following overlaps is **incorrect** [assuming z-axis to be the internuclear axis]

- | | |
|---|---|
| (a) $2 p_y + 2 p_y \rightarrow \pi 2 p_y$ | (b) $2 p_z + 2 p_z \rightarrow \sigma 2 p_z$ |
| (c) $2 p_x + 2 p_x \rightarrow \pi 2 p_x$ | (d) $1 s + 2 p_y \rightarrow \pi (1 s-2 p_y)$ |
| (A) 'a' & 'b' | (B) 'b' & 'd' |
| | (C) only 'd' |
| | (D) None of these |

Solution.

(C)

Orbitals should have same orientation & energy.

Illustration 3.

Which of the following combination of ion will have highest polarisation

- (A) $\text{Fe}^{2+}, \text{Br}^-$ (B) $\text{Ni}^{4+}, \text{Br}^-$ (C) $\text{Ni}^{2+}, \text{Br}^-$ (D) Fe, Br^-

Solution.

(B)

Polarization \propto Charge.

Illustration 4.

In which of the following molecule bonding is taking place in excited state

- (A) CH_4 (B) BF_3 (C) ICl (D) PCl_3

Solution.

(AB)

sp^3 hybridisation in Carbon

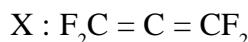
1	1	1	1
---	---	---	---

sp^2 in boron

1	1	1	
---	---	---	--

Illustration 5.

Consider the structures of the following two molecules



In which of these two it is impossible for all the four F atoms to lie in the same plane

Solution.

(A)

In cumulated dienes, planes will be perpendicular.

Illustration 6.

Match the isostructure pairs

Hint : Having same hybridization and same Number of lone pair

- | | | | |
|------------|-------------------------------|--------------|--------------------------------|
| (a) | SF ₄ | (i) | IF ₆ ⁺ |
| (b) | PCl ₅ | (ii) | ClF ₄ ⁺ |
| (c) | ICl ₃ | (iii) | SnCl ₅ ⁻ |
| (d) | I ₃ ⁻ | (iv) | ClF ₃ |
| (e) | ICl ₄ ⁻ | (v) | ClF ₂ ⁻ |
| (f) | PCl ₆ ⁻ | (vi) | XeF ₄ |

Solution.

(a-ii),(b-iii),(c- iv), (d-v),(e-vi),(f-i).

Illustration 7.

VESPR theory does not state

- (A) the order of repulsion between different pair of electrons is $\ell p - \ell p > \ell p - bp > bp - bp$
(ℓp = lone pair electrons, bp = bond pair electrons.)
 - (B) as the number of lone pair of electrons on central atom increase, the deviation in BA from normal BA (Bond-Angle) also increase.
 - (C) the number of lone pair on O in H_2O is 1 while on N in NH_3 is 2.
 - (D) the structures of Xenon-fluorides and Xenon-oxyfluorides could be explained on the basis of VESPR theory.

Solution.

(C)

H_2O has 2 lone pair.

Illustration 8.

The correct expected order of decreasing lattice energy is

- | | |
|-----------------------------------|-----------------------------------|
| (A) CaO > MgBr ₂ > CsI | (B) MgBr ₂ > CaO > CsI |
| (C) CsI > MgBr ₂ > CaO | (D) CsI > CaO > MgBr ₂ |

Solution.

(A)

Lattice energy depends on charge & inversely depends on size.

Illustration 9.

Which of the following is ionic solid :

- | | | | |
|--------------------------|--------------------------|--------------------------|---------|
| (A) XeF ₆ (s) | (B) PBr ₅ (s) | (C) CaC ₂ (s) | (D) All |
|--------------------------|--------------------------|--------------------------|---------|

Solution.

All are ionic solids

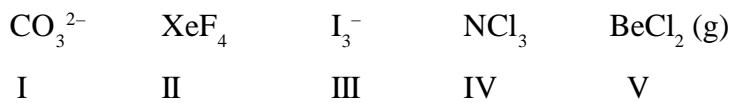
XeF₆ (S) consists XeF₅⁺ & F⁻

PBr₅ (s)..... PBr₄⁺ & Br⁻

CaC₂ (s) Ca⁺⁺ & C₂^{- -}

Illustration 10.

The correct order of increasing s character (in percentage) in the hybrid orbitals in below molecules / ions is (assume all hybrid orbitals are exactly equivalent) :



- | | |
|---------------------------|---------------------------|
| (A) II < III < IV < I < V | (B) II < IV < III < V < I |
| (C) III < II < I < V < IV | (D) II < IV < III < I < V |

Solution.

(A)

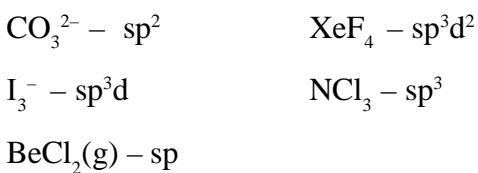


Illustration 11.

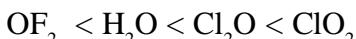
Which of the following is correct about the bond angle.

- | | |
|---|---|
| (A) $\text{OF}_2 < \text{H}_2\text{O} < \text{Cl}_2\text{O} < \text{ClO}_2$ | (B) $\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3 < \text{PI}_3$ |
| (C) $\text{NH}_3 > \text{NF}_3$ | (D) $\text{KrF}_4 < \text{SF}_2 < \text{N}_2\text{H}_2$ |

Solution.

(ABCD)

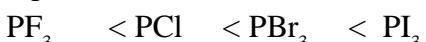
All given order are correct



$\text{sp}^3 \quad \text{sp}^3 \quad \text{sp}^3 \quad \text{sp}^3$

low bp-bp larger

repulsion size of Cl



$97.7^\circ \quad 100.3^\circ \quad 101.0^\circ \quad 102^\circ$



$107^\circ \quad 104^\circ$



$\text{sp}^3\text{d}^2 \quad \text{Sp}^3 \quad \text{sp}^2 (< 120^\circ)$

$(90^\circ\text{C}) \quad (< 109^\circ 28') \quad \text{sp}^2 (< 120^\circ)$

All gives order are order are correct

Illustration 12.

On the basis of MOT which is correct -

- (A) The bond order for C_2 molecule is two and both bonds are π -bonds
- (B) The LUMO in this molecule is $\sigma 2p$ molecular orbital
- (C) The HOMO in this molecule are π type of antibonding m.o. containing total 4 electrons
- (D) None of the above is correct

Solution.

(AB)

LUMO is lowest unoccupied molecular orbital.

HOMO is highest occupied molecular orbital.

Illustration 13.

Which of the following statements is not correct from the point of view of molecular orbital?

- (A) Be_2 is not a stable molecule
- (B) He_2 is not stable but He_2^+ is expected to exist
- (C) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules
- (D) The order of energies of molecular orbitals in F_2 molecule is $\pi^b 2p_x < \sigma^b 2p_z$

Solution.

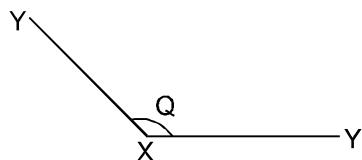
(D)

Correct order of energy in F_2 $\pi^b 2p_x > \sigma^b 2p_z$.

Illustration 14.

Which bond angle Q would result in the maximum dipole moment for the triatomic molecule XY_2 shown below

- (A) $Q = 90^\circ$
- (B) $Q = 120^\circ$
- (C) $Q = 150^\circ$
- (D) 180°

**Solution.**

- (A)

$$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta} ; \text{ as } \theta \uparrow, R \downarrow$$

Illustration 15.

Which of the following molecule is/are non polar

- (A) XeF_2
- (B) PCl_3F_2
- (C) XeF_4
- (D) All

Solution.

- (D)

Illustration 16.

The dipole moment of HBr is 2.60×10^{-30} C.m, and the interatomic spacing is 1.41\AA . What is the percent ionic character of HBr?

Solution.

The dipole moment of a 100% ionic “molecule” at the given internuclear distance would be $(1.60 \times 10^{-19}\text{C})(1.41 \times 10^{-10}\text{m}) = 2.26 \times 10^{-29}\text{ C.m}$

The actual dipole is less; the percent ionic character is given by

$$\frac{2.60 \times 10^{-30}\text{C.m}}{2.26 \times 10^{-29}\text{C.m}} \times 100\% = 11.5\%$$

Illustration 17.**Column-I**

- (A) $HCl < HF$
- (B) $PH_3 < NH_3$
- (C) $H_2O < D_2O$
- (D) $H_2S < H_2O$

Column-II

- (p) Intermolecular forces
- (q) Dipole moment
- (r) Boiling point
- (s) Molar mass

Solution.

(A – p, q, r) ; (B – p, q, r) ; (C – p, q, r, s) ; (D – p, q, r)

(A) In HF hydrogen bonding takes place and dipole moment is more than HCl.

(B) In NH_3 hydrogen bonding takes place which is absent in PH_3 .

(C) In D_2O dipole moment is more than H_2O as D is less electronegative than hydrogen

(D) In H_2O hydrogen bonding is present

Illustration 18.

- I.** When ice is melted hydrogen bond starts breaking molecule of water come closer by moving into vacant space. As a result density of water decreases upto 4°C.
 - II.** Due to open cage like structure, ice has a relatively large volume for a given mass of liquid water.
 - III.** In ice there are four water molecules attached tetrahedrally.
- Which of the above statement is true.
- (A) I, II and III (B) I and III (C) II and III (D) II only

Solution.

(C)

- I.** density of water increases up to 4°C
- II.** in case of ice each water molecule is attached with other molecules tetrahedrally forming a cage like structure.

Illustration 19.

Which of the following conditions is required for the formation of the hydrogen bond

- (A) Hydrogen atom should be bonded to a highly electronegative atom
(B) The size of electronegative atom should be small
(C) There should be a lone pair of electron on the electronegative atom.
(D) All of the above

Solution.

(D)

Illustration 20.

Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.

S_1 : HF boils at a higher temperature than HCl

S_2 : HBr boils at lower temperature than HI

S_3 : Bond length of N_2 is less than N_2^+

- (A) T F T (B) T T F (C) T T T (D) F T T

Solution.

(C)

S_1 : Due to intermolecular H-bonding in HF it boils at higher temperature than HCl

S_2 : Mol. wt. of HBr < Mol. wt. of HI

S_3 : Bond order of N_2 is more than N_2^+ .

ANSWER KEY

BEGINNER'S BOX-1

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (C) | 2. (A) | 3. (B) | 4. (C) | 5. (A) |
| 6. (A) | 7. (B) | 8. (C) | 9. (A) | 10. (C) |

BEGINNER'S BOX-2

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (C) | 2. (C) | 3. (D) | 4. (A) | 5. (B) |
| 6. (B) | 7. (B) | 8. (D) | 9. (A) | 10. (D) |

BEGINNER'S BOX-3

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (C) | 2. (D) | 3. (D) | 4. (C) | 5. (C) |
| 6. (C) | 7. (C) | 8. (A) | 9. (A) | 10. (C) |

BEGINNER'S BOX-4

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (C) | 2. (A) | 3. (C) | 4. (B) | 5. (D) |
| 6. (A) | 7. (D) | 8. (A) | | |

BEGINNER'S BOX-5

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (B) | 2. (A) | 3. (D) | 4. (C) | 5. (D) |
| 6. (A) | | | | |

BEGINNER'S BOX-6

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (C) | 2. (D) | 3. (A) | 4. (A) | 5. (C) |
| 6. (A) | 7. (D) | 8. (C) | 9. (B) | 10. (D) |

BEGINNER'S BOX-7

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (C) | 2. (C) | 3. (B) | 4. (D) | 5. (C) |
| 6. (C) | 7. (B) | 8. (D) | 9. (A) | |

BEGINNER'S BOX-8

- | | | | | |
|--------|--------|----------|--------|--------|
| 1. (B) | 2. (D) | 3. (D) | 4. (D) | 5. (C) |
| 6. (A) | 7. (B) | 8. (ABC) | | |

EXERCISE (S-1)

NUMERICAL ANSWER BASED QUESTIONS

1. Consider the following species & find out how many are polar & can act as Lewis acid
 CO_2 , SO_2 , CCl_4 , AlCl_3 , HCHO , SO_3 , SiCl_4 , BCl_3 , CF_4
2. In the compound $\text{PCl}_k \text{F}_{5-k}$, possible values of k are 0 to 5 then sum of all possible value of k for the compounds having zero dipole moment, is :
3. Find the total number of non-linear species out of given species:
 I_3^- , $\text{BeCl}_{2(\text{g})}$, NH_2^- , OH_2 , XeF_2 , N_2O , SO_2 , SF_2
4. In cation of $\text{XeF}_{6(\text{s})}$ total number of orbitals of Xe involved in hybridisation is:
5. Total number of covalent bonds in C_3O_2 is
6. In how many of the following cases ratio of σ -bond and π -bond is 1 : 1 ?
 - (i) $\text{C}_2(\text{CN})_4$
 - (ii) $(\text{CN})_2$
 - (iii) SO_3
 - (iv) C_3O_2
 - (v) CO_2
 - (vi) S_3O_9
 - (vii) P_4O_6
 - (viii) P_4O_{10}

MATRIX - MATCH QUESTIONS

- | | |
|---|--|
| <p>7. Column-I</p> <p>(A) O_3
 (B) $\text{H}_2\text{O}_{(\ell)}$
 (C) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (D) $(\text{NH}_4)_2\text{SO}_4$</p> <p>8. Column-I</p> <p>(A) N_2^+ is stable than N_2^- / In N_2^+ & N_2^-
 (B) NO can easily loss its electron than N_2 / In NO & N_2
 (C) NO have large bond length than NO^+ / In NO & NO^+
 (D) He_2^+ exist but less stable than H_2^+ / In He_2^+ & H_2^+</p> <p>9. Matching :</p> <p>List-I</p> <p>(A) $(\text{CH}_3)_3\text{B}$
 (B) ICl_4^-
 (C) NH_4Cl
 (D) PCl_5</p> | <p>Column-II</p> <p>(p) covalent bond
 (q) Co-ordinate bond
 (r) Hydrogen bond
 (s) Ionic bond</p> <p>Column-II</p> <p>(p) due to one have higher electrons in antibonding than other
 (q) one have B.O. 3 and other have 2.5
 (r) both are paramagnetic with same bond order
 (s) one paramagnetic and other diamagnetic</p> <p>List-II</p> <p>(p) Square planar
 (q) Tetrahedral
 (r) Trigonal bipyramidal
 (s) Trigonal planar</p> |
|---|--|

EXERCISE (O-1)

SINGLE CHOICE CORRECT QUESTIONS

1. An ionic bond A^+B^- is most likely to be formed when :
 - (A) the ionization energy of A is high and the electron gain enthalpy of B is low
 - (B) the ionization energy of A is low and the electron gain enthalpy of B is high
 - (C) the ionization energy of A and the electron gain enthalpy of B both are high
 - (D) the ionization energy of A and the electron gain enthalpy of B both are low
2. The compound which contains ionic as well as covalent bonds is
 - (A) $C_2H_4Cl_2$
 - (B) CH_3I
 - (C) KCN
 - (D) H_2O_2
3. The electronic configuration of element A is $1s^2, 2s^2 2p^6, 3s^2$ while of the element B is $1s^2, 2s^2 2p^5$. The formula of the compound containing A and B will be :
 - (A) AB
 - (B) AB_2
 - (C) A_2B
 - (D) A_3B_2
4. Which of the following contains electrovalent and polar covalent bonds ?
 - (A) CH_4
 - (B) H_2O_2
 - (C) NH_4Cl
 - (D) HCN
5. According to the Lewis structure for $H-N=N-H$, the number of σ bonds, π bonds and lone pairs of electrons respectively are :
 - (A) 2, 2, 2
 - (B) 3, 2, 2
 - (C) 3, 1, 2
 - (D) 3, 2, 1
6. Which of the following has/have a strong covalent bond?
 - (A) Cl-F
 - (B) F-F
 - (C) C-Cl
 - (D) C-F
7. Which of the following species are hypervalent?

1. PCl_5 ,	2. BF_3 ,	3. XeF_2 ,	4. CO_3^{2-}
(A) 1, 2, 3	(B) 1, 3	(C) 3, 4	(D) 1, 2
8. The types of bond present in $N_2O_5(g)$ are

(A) only covalent	(B) only ionic
(C) ionic and covalent	(D) covalent & coordinate
9. NH_3 and BF_3 combine readily because of the formation of :

(A) a covalent bond	(B) a hydrogen bond
(C) a coordinate bond	(D) an ionic bond
10. Which of the following molecule does not have coordinate bonds?

(A) CH_3-NC	(B) CO
(C) O_3	(D) CO_3^{2-}
11. In the following compound $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-C\equiv CH$, the C_2-C_3 bond is of the type :

(A) $sp-sp^2$	(B) sp^3-sp^3
(C) $sp-sp^3$	(D) sp^2-sp^3

- 12.** Which of the following has a geometry different from the other three species (having the same geometry)?
- (A) BF_4^- (B) SO_4^{2-} (C) XeF_4 (D) PH_4^+
- 13.** Maximum bond energy is in :
- (A) F_2 (B) N_2 (C) O_2 (D) equal
- 14.** The hybridisation and shape of BrF_3 molecule are :
- (A) sp^3d and bent T shape (B) sp^2d^2 and tetragonal
 (C) sp^3d and bent (D) none of these
- 15.** The percentage d-character in the hybrid orbitals of ICl_5 is
- (A) 20% (B) 33% (C) 43% (D) 50%
- 16.** The structure of XeF_2 involves hybridization of the type :
- (A) sp^3 (B) dsp^2 (C) sp^3d (D) sp^3d^2
- 17.** In the context of carbon, which of the following is arranged in the correct order of electronegativity :
- (A) $sp > sp^2 > sp^3$ (B) $sp^3 > sp^2 > sp$ (C) $sp^2 > sp > sp^3$ (D) $sp^3 > sp > sp^2$
- 18.** The electronegativities of the P, Q, R, S and T are given below
- | | | | | |
|-----|-----|-----|-----|-----|
| P | Q | R | S | T |
| 0.7 | 1.1 | 1.6 | 2.5 | 1.7 |
- Which of the following bonds has the most ionic character ?
- (A) P-S (B) P-Q (C) R-S (D) T-S
- 19.** Which of the following has been arranged in order of decreasing dipole moment ?
- (A) $CH_3Cl > CH_3F > CH_3Br > CH_3I$ (B) $CH_3F > CH_3Cl > CH_3Br > CH_3I$
 (C) $CH_3Cl > CH_3Br > CH_3I > CH_3F$ (D) $CH_3F > CH_3Cl > CH_3I > CH_3Br$
- 20.** The experimental value of the dipole moment of HCl is 1.03 D. The length of the $H - Cl$ bond is 1.275\AA . The percentage of ionic character in HCl is :
- (A) 43 (B) 21 (C) 17 (D) 7
- 21.** Which of the following compounds is polar and also has the central atom as sp^2 hybridised ?
- (A) H_2CO_3 (B) SiF_4 (C) BF_3 (D) SO_4^{2-}
- 22.** Which of the following compounds would have significant intermolecular hydrogen bonding ?
- HF, CH_3OH, N_2O_4, CH_4
- (A) HF, N_2O_4 (B) HF, CH_4, CH_3OH (C) HF, CH_3OH (D) CH_3OH, CH_4

EXERCISE (O-2)

MULTIPLE CHOICE CORRECT QUESTIONS

1. Which combination (s) given below is / are correct ?

(A) Cl_2O – angular	(B) ClF_3 – T shaped
(C) ICl_4^- – square planar	(D) XeF_6 – pentagonal bipyramidal
2. Pick out among the following species isoelectronic with CO_2 :

(A) N_3^-	(B) $(\text{CNO})^-$	(C) $(\text{NCN})^{2-}$	(D) NO_2^-
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3. Which of the following statement(s) is / are not correct?

(A) Hybridization is the mixing of atomic orbitals of large energy difference.
(B) sp^2 – hybrid orbitals are formed from two p - atomic orbitals and one s - atomic orbital
(C) sp^3d^2 – hybrid orbitals are all at 90° to one another
(D) sp^3 – hybrid orbitals are directed towards the corners of a regular tetrahedron
4. Which of the following species is (are) isostructural with XeF_4 ?

(A) ICl_4^-	(B) I_3^-	(C) BrF_4^-	(D) XeO_4
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5. There is change in the hybridisation when:

(A) NH_3 combines with H^+	(B) AlH_3 combines with H^-
(C) NH_3 forms NH_2^-	(D) SiF_4 forms SiF_6^{2-}
6. State the wrong statement :

(A) Free rotation around the single bond is not possible.
(B) p -orbitals always overlap sideways
(C) s -orbitals never form π - bonds
(D) There can be more than one sigma bond between two atoms
7. Which of the following has (have) regular octahedral geometry :

(A) SbCl_6^-	(B) SnCl_6^{2-}	(C) XeF_6	(D) IO_6^{5-}
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8. Which of the following have same shape as NH_2^+ ?

(A) CO_2	(B) SnCl_2	(C) SO_2	(D) BeCl_2
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9. For propadiene $\text{H}_2\underset{1}{\text{C}}=\underset{2}{\text{C}}=\underset{3}{\text{CH}}_2$, correct statement(s) is / are :

(A) Molecule is non planar
(B) Molecule is nonpolar
(C) Nodal plane of π -bond formed by C_1 & C_2 is perpendicular to that of formed by C_2 & C_3 .
(D) Nodal plane of π -bond formed by C_1 & C_2 is coplanar with that of formed by C_2 & C_3 .
10. Which of the following bonds/forces is/are relatively weaker ?

(A) covalent bond	(B) vander Waals force
(C) ionic bond	(D) london force

COMPREHENSION BASED QUESTIONS (SINGLE CHOICE CORRECT QUESTION)

Comprehension-1

In order to explain the shape and geometry of molecules. The valence bond theory was supplemented by the concept of Hybridization. This is a Hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produced a set of entirely new orbitals of equivalent energy is known as Hybridization.

11. The hybridization of carbon atoms in C – C single bond of H – C ≡ C – CH = CH₂ is :
 (A) sp³ – sp³ (B) sp² – sp³ (C) sp – sp² (D) sp³ – sp
12. In XeF₂, XeF₄ and XeF₆ the number of lone pairs on Xe is respectively :
 (A) 2, 3, 1 (B) 1, 2, 3 (C) 4, 1, 2 (D) 3, 2, 1
13. Which of the following is the correct set :
 (A) H₂O ; sp³, angular (B) H₂O ; sp², linear
 (C) NH₃ ; sp², pyramidal (D) BF₃ ; sp³, trigonal planar
14. In NO₃⁻ ion, number of bond pair and lone pairs of electrons on nitrogen atom are :
 (A) 2, 2 (B) 3, 1 (C) 1, 3 (D) 4, 0
15. T-shape is exhibited by molecule :
 (A) ClF₃ (B) CHCl₃ (C) CCl₄ (D) PCl₅

Comprehension-2

The phenomenon of polarization is used to compare the covalent characters associated with ionic compounds. Fajan's rule give an idea about the polarizing powers of different cations and polarisability of the anions.

16. In which of the halides, there is maximum polarization
 (A) AlF₃ (B) AlCl₃ (C) AlBr₃ (D) AlI₃
17. Which is most covalent in nature?
 (A) NaCl (B) MgCl₂ (C) AlCl₃ (D) CaCl₂
18. Non- aqueous solvent like ether is added to a mixture of LiCl, NaCl and KCl; which will be extracted in ether?
 (A) NaCl (B) LiCl (C) KCl (D) none
19. Which is the highest melting point halide among the following?
 (A) NaCl (B) NaBr (C) NaI (D) NaF
20. The correct decreasing order of polarisability is
 (A) Cl⁻, Br⁻, I⁻, F⁻ (B) F⁻, I⁻, Br⁻, Cl⁻ (C) I⁻, Br⁻, Cl⁻, F⁻ (D) F⁻, Cl⁻, Br⁻, F⁻

EXERCISE (JM)

1. Among the following the maximum covalent character is shown by the compound :-

[AIEEE-2011]

- (1) AlCl_3 (2) MgCl_2 (3) FeCl_2 (4) SnCl_2

2. The structure of IF_7 is :-

- (1) octahedral (2) pentagonal bipyramidal
 (3) square pyramid (4) trigonal bipyramidal

3. The hybridisation of orbitals of N atom in NO_3^- , NO_2^+ and NH_4^+ are respectively :-

[AIEEE-2011]

- (1) sp , sp^3 , sp^2 (2) sp^2 , sp^3 , sp (3) sp , sp^2 , sp^3 (4) sp^2 , sp , sp^3

4. Which of the following has maximum number of lone pairs associated with Xe ?

[AIEEE-2011]

- (1) XeO_3 (2) XeF_4 (3) XeF_6 (4) XeF_2

5. The number of types of bonds between two carbon atoms in calcium carbide is :-

- (1) One sigma, two pi (2) One sigma, one pi [AIEEE-2011]
 (3) Two sigma, one pi (4) Two sigma, two pi

6. Ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because :-

- (1) Melting point of o-Nitrophenol is lower than those of m- and p- isomers [AIEEE-2012]
 (2) o-Nitrophenol is more volatile in steam than those of m- and p- isomers
 (3) o-Nitrophenol shows Intramolecular H-bonding
 (4) o-Nitrophenol shows Intermolecular H-bonding

7. Among the following species which two have trigonal bipyramidal shape ?

[AIEEE ONLINE - 2012]

- (I) NI_3 (II) I_3^- (III) SO_3^{2-} (IV) NO_3^-
 (1) II and III (2) III and IV (3) I and IV (4) I and III

8. Among the following, the species having the smallest bond is :- [AIEEE ONLINE - 2012]

- (1) NO (2) NO^+ (3) O_2 (4) NO^-

9. Which of the following has the square planar structure :-

[AIEEE ONLINE - 2012]

- (1) NH_4^+ (2) CCl_4 (3) XeF_4 (4) BF_4^-

10. The compound of Xenon with zero dipole moment is :-

[AIEEE-ONLINE - 2012]

- (1) XeO_3 (2) XeO_2 (3) XeF_4 (4) XeOF_4

11. Among the following the molecule with the lowest dipole moment is :-

[AIEEE-ONLINE - 2012]

- (1) CHCl_3 (2) CH_2Cl_2 (3) CCl_4 (4) CH_3Cl

12. Although CN^- ion and N_2 molecule are isoelectronic, yet N_2 molecule is chemically inert because of :-

[AIEEE-ONLINE - 2012]

- (1) Uneven electron distribution
 (2) Absence of bond polarity
 (3) Presence of more number of electrons in bonding orbitals
 (4) Long bond energy

13. Bond order normally gives idea of stability of a molecular species. All the molecules viz. H_2 , Li_2 and B_2 have the same bond order yet they are not equally stable. Their stability order is :

[JEE MAINS - ONLINE - 2013]

- (1) $\text{Li}_2 > \text{H}_2 > \text{B}_2$ (2) $\text{H}_2 > \text{B}_2 > \text{Li}_2$ (3) $\text{B}_2 > \text{H}_2 > \text{Li}_2$ (4) $\text{Li}_2 > \text{B}_2 > \text{H}_2$

14. Which has trigonal bipyramidal shape ?

[JEE MAINS - ONLINE - 2013]

- (1) XeOF_4 (2) XeO_3 (3) XeO_3F_2 (4) XeOF_2

15. Which one of the following does **not** have a pyramidal shape ?

[JEE MAINS - ONLINE - 2014]

- (1) $\text{P}(\text{CH}_3)_3$ (2) $(\text{SiH}_3)_3\text{N}$ (3) $(\text{CH}_3)_3\text{N}$ (4) $\text{P}(\text{SiH}_3)_3$

16. The geometry of XeOF_4 by VSEPR theory is:-

[JEE MAINS - ONLINE - 2015]

- (1) Trigonal bipyramidal (2) Octahedral
 (3) Pentagonal planar (4) Square pyramidal

17. The correct order of thermal stability of hydroxides is :

[JEE MAINS - ONLINE - 2015]

- (1) $\text{Ba}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Mg}(\text{OH})_2$
 (2) $\text{Mg}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
 (3) $\text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
 (4) $\text{Ba}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Mg}(\text{OH})_2$

18. Which among the following is the most reactive ?

[JEE (MAIN) 2015]

- (1) Cl_2 (2) Br_2 (3) I_2 (4) ICl

19. Which intermolecular force is most responsible in allowing xenon gas to liquefy ?

[JEE MAINS - ONLINE - 2016]

- (1) Ionic (2) Instantaneous dipole- induced dipole
 (3) Dipole - dipole (4) Ion - dipole

20. The bond angle H-X-H is the greatest in the compound : [JEE MAINS - ONLINE - 2016]

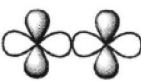
- (1) NH_3 (2) H_2O (3) PH_3 (4) CH_4

- 31.** The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF_4 , respectively, are : [JEE MAINS - ONLINE - 2019]
- (1) sp^3d and 1 (2) sp^3d and 2 (3) sp^3d^2 and 1 (4) sp^3d^2 and 2
- 32.** The amphoteric hydroxide is : [JEE MAINS - ONLINE - 2019]
- (1) Ca(OH)_2 (2) Be(OH)_2 (3) Sr(OH)_2 (4) Mg(OH)_2
- 33.** The ion that has sp^3d^2 hybridization for the central atom, is : [JEE MAINS - ONLINE - 2019]
- (1) $[\text{ICl}_2]^-$ (2) $[\text{IF}_6]^-$ (3) $[\text{ICl}_4]^-$ (4) $[\text{BrF}_2]^-$
- 34.** The covalent alkaline earth metal halide ($\text{X} = \text{Cl, Br, I}$) is : [JEE MAINS - ONLINE - 2019]
- (1) CaX_2 (2) SrX_2 (3) BeX_2 (4) MgX_2
- 35.** Among the following molecules / ions, $\text{C}_2^{2-}, \text{N}_2^{2-}, \text{O}_2^{2-}, \text{O}_2$ [JEE MAINS - ONLINE - 2019]
which one is diamagnetic and has the shortest bond length?
- (1) C_2^{2-} (2) N_2^{2-} (3) O_2 (4) O_2^{2-}
- 36.** Among the following, the molecule expected to be stabilized by anion formation is : [JEE MAINS - ONLINE - 2019]
- $\text{C}_2, \text{O}_2, \text{NO}, \text{F}_2$ (1) NO (2) C_2 (3) F_2 (4) O_2
- 37.** Among the following species, the diamagnetic molecule is [JEE MAINS - ONLINE - 2019]
- (1) O_2 (2) NO (3) B_2 (4) CO
- 38.** The group number, number of valence electrons, and valency of an element with atomic number 15, respectively, are [JEE MAINS - ONLINE - 2019]
- (1) 16, 5 and 2 (2) 16, 6 and 3 (3) 15, 5 and 3 (4) 15, 6 and 2
- 39.** The relative strength of interionic/intermolecular forces in decreasing order is : [JEE MAINS - ONLINE - 2020]
- (1) ion-dipole > ion-ion > dipole-dipole (2) dipole-dipole > ion-dipole > ion-ion
(3) ion-dipole > dipole-dipole > ion-ion (4) ion-ion > ion-dipole > dipole-dipole
- 40.** If the magnetic moment of a dioxygen species is 1.73 B.M, it may be : [JEE MAINS - ONLINE - 2020]
- (1) O_2^- or O_2^+ (2) O_2 or O_2^+ (3) O_2 or O_2^- (4) $\text{O}_2, \text{O}_2^-, \text{O}_2^+$

EXERCISE (JA)

1. The nitrogen oxide(s) that contain(s) N–N bond(s) is/are [JEE 2009]
 (A) N_2O (B) N_2O_3 (C) N_2O_4 (D) N_2O_5
2. The species having pyramidal shape is/are : [JEE 2010]
 (A) SO_3 (B) BrF_3 (C) SiO_3^{3-} (D) OSF_2
3. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) [JEE 2012]
 (A) sp and sp^3 (B) sp and sp^2 (C) only sp^2 (D) sp^2 and sp^3
4. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen- [JEE 2012]
 (A) HNO_3 , NO , NH_4Cl , N_2 (B) HNO_3 , NO , N_2 , NH_4Cl [JEE 2012]
 (C) HNO_3 , NH_4Cl , NO , N_2 (D) NO , HNO_3 , NH_4Cl , N_2
5. The shape of XeO_2F_2 molecule is : [JEE 2012]
 (A) Trigonal bipyramidal (B) Square planar
 (C) tetrahedral (D) see-saw
6. The total number of lone-pairs of electrons in melamine is. [JEE 2013]
7. Hydrogen bonding plays a central role in the following phenomena: [JEE 2014]
 (A) Ice floats in water
 (B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solution
 (C) Formic acid is more acidic than acetic acid.
 (D) Dimerisation of acetic acid in benzene.
8. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is [JEE 2014]
 (A) Be_2 (B) B_2 (C) C_2 (D) N_2
9. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. [JEE 2014]

List-I

- P. 
- Q. 
- R. 
- S. 

List-II

1. $\text{p} - \text{d} \pi$ antibonding
2. $\text{d} - \text{d} \sigma$ bonding
3. $\text{p} - \text{d} \pi$ bonding
4. $\text{d} - \text{d} \sigma$ antibonding

Code:

P	Q	R	S
(A) 2	1	3	4
(B) 4	3	1	2
(C) 2	3	1	4
(D) 4	1	3	2

ANSWER KEY**EXERCISE (S-1)****NUMERICAL ANSWER BASED QUESTIONS**

1. (2) 2. (8) 3. (4) 4. (6) 5. (8) 6. (4)

MATRIX MATCH QUESTIONS

7. (A) - (pq), (B) - (pr), (C) - (pqrs), (D) - (pqrs)
 8. (A) - (pr), (B) - (pqrs), (C) - (pqrs), (D) - (pr)
 9. (A) - (s), (B) - (p), (C) - (q), (D) - (r)

EXERCISE (O-1)

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	C	B	C	C	D	B	D	C	D	D	C	B	A	B
Que.	16	17	18	19	20	21	22								
Ans.	C	A	A	A	C	A	C								

EXERCISE (O-2)**MULTIPLE CHOICE CORRECT QUESTIONS**

1. (ABC) 2. (ABC) 3. (AC) 4. (AC) 5. (BD)
 6. (ABD) 7. (ABD) 8. (BC) 9. (ABC) 10. (BD)

COMPREHENSION BASED QUESTIONS

11. (C) 12. (D) 13. (A) 14. (D) 15. (A)
 16. (D) 17. (C) 18. (B) 19. (D) 20. (C)

EXERCISE (JM)

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	4	4	1	3	Bonus	2	3	3	3	2	2	3	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	3	4	2	4	4	2	1	4	1	3	3	2	4	1
Que.	31	32	33	34	35	36	37	38	39	40					
Ans.	3	2	4	3	1	2	4	3	4	1					

EXERCISE (JA)

1. (ABC) 2. (D) 3. (B) 4. (B) 5. (D)
 6. (6) 7. (ABD) 8. (C) 9. (C) 10. (BC)
 11. (4) 12. (8) 13. (AC) 14. (BC) 15. (5)
 16. (6) 17. (ACD) 18. (BD) 19. (4)

CHAPTER 3

IDEAL GAS

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IMPORTANT NOTES

CHAPTER 3

IDEAL GAS

1. INTRODUCTION

Matter, as we know, broadly exist in three states - solid, liquid and gas.

There are always two opposite tendencies between particles of matter which determine the state of matter :

- Intermolecular forces.
- The molecular motion / random motion (energy of particles)

Intermolecular forces are the forces of attraction and repulsion between atoms or molecules.

Attractive intermolecular forces are known as *vander Waals forces*. These are dispersion forces, dipole-dipole forces & dipole induced forces. When two molecules are brought very close, they will exert repulsive forces. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquid & solids are hard to compress. In these states, molecules are already in close contact, therefore they resist further compression (in that case repulsive interaction will increase)

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called *thermal motion*. Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

2. GENERAL CHARACTERISTICS OF SOLID, LIQUID & GAS

Each physical state of matter possesses characteristics properties of its own. For example,

❖ **Solids :**

All solids show the following characteristics :

- Solids are rigid and incompressible.
- Solids have fixed shape and definite volume.
- Solids have their melting and boiling points above room temperature.
- Density of solid is high.

❖ **Liquids :**

All liquids show the following characteristics :

- (i) Liquids are almost incompressible but less incompressible than solids.
- (ii) Liquids have fixed volume but no fixed shape.
- (iii) Liquids have their melting points below room temperature and boiling points above room temperature, under normal conditions.
- (iv) Density of liquids is lower than that of solids but much higher than that of gases.

❖ **Gases :**

All gases show the following characteristics :

- (i) Gases are highly compressible, i.e. gases can be compressed easily by applying pressure.
- (ii) Gases have no fixed volume and shape. Gases fill the container of any size and shape completely.
- (iii) Gases can diffuse into each other rapidly.
- (iv) Gases have their melting and boiling points both below room temperature.
- (v) Gases generally have low density.

3. MEASURABLE PROPERTIES OF GASES

The characteristics of gases are described fully in terms of four parameters or measurable properties:

- (I) Amount of the gas (i.e., mass or number of moles).
- (II) Volume (V) of the gas.
- (III) Temperature (T)
- (IV) Pressure (P)

I. Amount of the gas :

- (i) The mass of a gas can be determined by weighing the container in which the gas is enclosed and again weighing the container after removing the gas. The difference between the two masses gives the mass of the gas.

$$\text{Mass of gas (m)} = \text{Mass of filled container} - \text{mass of empty container}$$

- (ii) The mass of the gas is related to the number of moles of the gas as

$$\text{Moles of gas (n)} = \text{Mass in grams} / \text{Molar mass} = m/M$$

- (iii) Mass is expressed in gram or kg.

II. Gas volume :

- (i) Since gases occupy the entire space available to them, the measurement of volume of a gas only requires a measurement of the container confining the gas.
- (ii) Volume is expressed in litres (L), millilitres (mL) or cubic centimeters (cm^3) or cubic meters (m^3).
- (iii) $1 \text{ L} = 1000 \text{ mL}$; $1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$
 $1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^6 \text{ mL} = 10^3 \text{ L}$
 $1 \text{ mL or } 1 \text{ cc} = 1 \text{ cm}^3$

III. Temperature :

- (i) Gases expand on increasing the temperature.
- (ii) Temperature is measured in degree centigrade ($^\circ\text{C}$) or Celsius degree with the help of thermometers. Temperature is also measured in degree Fahrenheit ($^\circ\text{F}$).
- (iii) S.I. unit of temperature is kelvin (K) or absolute degree
 $K = ^\circ\text{C} + 273$
- (iv) Relation between $^\circ\text{F}$ and $^\circ\text{C}$ is
 $^\circ\text{C}/5 = (^{\circ}\text{F} - 32)/9$

IV. Pressure :

Force exerted by the gas per unit area of the walls of the container in all directions. Thus,

$$\text{Pressure (P)} = \text{Force(F) / Area(A)}$$

❖ Atmospheric pressure :

The pressure exerted by atmosphere on earth's surface at sea level is called atmospheric pressure. Generally its unit is atm.

$$\begin{aligned} \text{Pressure(P)} &= \text{Force(F) / Area(A)} \\ &= \text{Mass(m)} \times \text{Acceleration(g) / Area(a)} \\ &= \text{Volume} \times \text{density} \times \text{Acceleration(g) / Area(a)} \\ &= \text{Area (a)} \times \text{height (h)} \times \text{density (\rho)} \times \text{Acceleration(g) / Area(a)} \end{aligned}$$

$$\text{Pressure(P)} = h\rho g$$

where h = Height of mercury column in the barometer.

ρ = Density of mercury.

g = Acceleration due to gravity.

Pressure does not depend on the cross section of tube, but only on the vertical height of the Hg. If area is doubled, volume also gets doubled and mass will also get doubled. Now it will rest on twice area but pressure exerted remains same.

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^5 \text{ Pa}$$

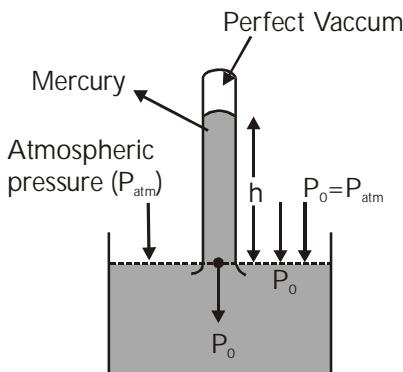
$$1 \text{ atm} = 76 \text{ cm of Hg} = 760 \text{ mm of Hg} = 760 \text{ torr}$$

□ PRESSURE MEASURING DEVICES

Generally, the instruments used for the calculation of pressure of a gas are **barometer** and **manometer**.

(i) **Barometer** : A barometer is an instrument that is used for the measurement of atmospheric pressure.

The construction of the barometer is as follows -



A thin narrow calibrated capillary tube is filled up to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid. Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced.

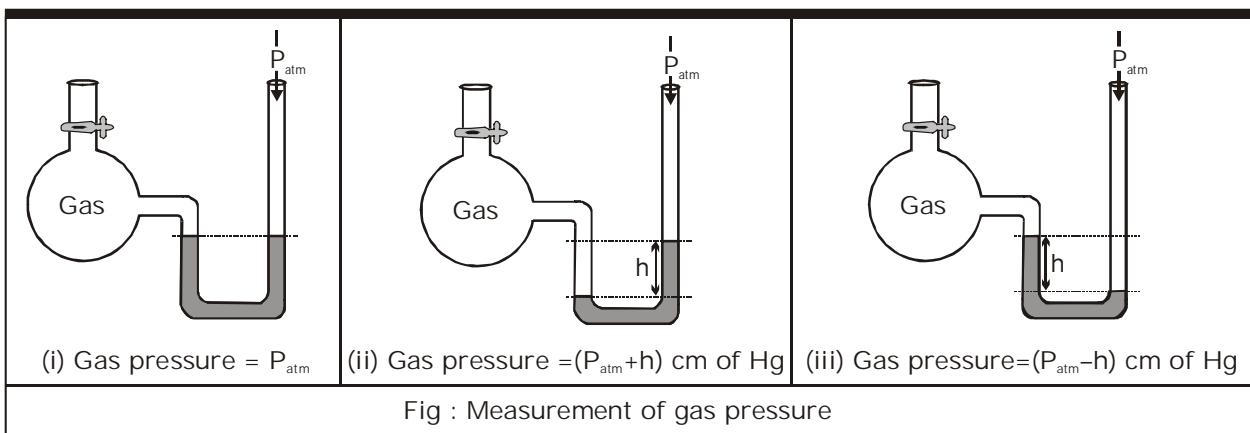
$$\Rightarrow P_0 \times A = \rho A \times gh$$

$$\Rightarrow P_0 = \rho gh ; \text{ where } \rho \text{ is the density of the fluid.}$$

(ii) **Manometer** :

(a) **Open end manometer** :

It consists of a U-shaped tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas whereas the longer limb is open as shown in fig. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.



Where $P_{atm} = 76$ cm of Hg and h = Height in cm of Hg

There are three possibilities as described below :

- (i) If the level of Hg in the two limbs is same, then gas pressure = atmospheric pressure (P_{atm}).
- (ii) If the level of Hg in the longer limbs is higher, gas pressure

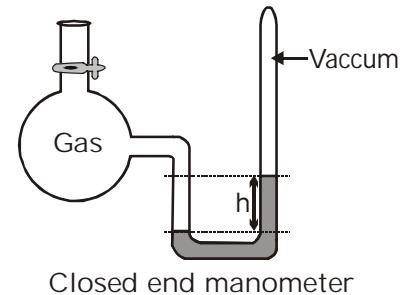
$$= P_{atm} + (\text{difference between the two levels}) \\ = P_{atm} + h.$$

- (iii) If the level of Hg in the shorter limb is higher, then gas pressure

$$= P_{atm} - (\text{difference between the two levels}) \\ = P_{atm} - h.$$

(b) Closed end manometer :

This is generally used to measure low gas pressure. It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in fig. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.



Gas pressure = [Difference in the Hg level in two limbs]

Ex.1 Why mercury is used in the barometer tube?

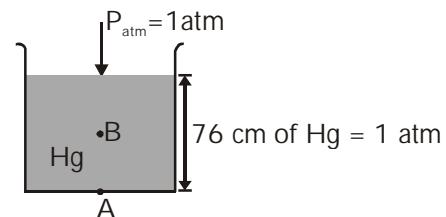
Sol. Mercury, a liquid with very high density, is normally used in the barometer because it does not stick to the surface of the glass tube. Mercury is also non-volatile at room temperature. Therefore, there are hardly any vapours of mercury above the liquid column and their pressure, if any, can be neglected. Due to high density of mercury, height of mercury column will be small and can be easily measured.

Ex.2 An open tank is filled with Hg upto a height of 76cm.

Find the pressure at the

- (a) Bottom (A) of the tank
- (b) Middle (B) of the tank.

(If atmospheric pressure is 1 atm)



Sol. (a) At bottom,

$$P_A = P_{atm} + P_{Hg} \\ = 1 + 1 = 2 \text{ atm}$$

(b) At middle,

$$P_B = P_{atm} + P_{Hg} \\ = 1 + \frac{1}{2} = 1.5 \text{ atm}$$

Ex.3 Find the height of water upto which water must be filled to create the same pressure at the bottom, as in above problem.

Given that $d_w = 1 \text{ gm/cm}^3$, $d_{Hg} = 13.6 \text{ gm/cm}^3$, $h_{Hg} = 76 \text{ cm}$

Sol. $P_{\text{water}} = P_{Hg}$

$$h_w d_w g = h_{Hg} d_{Hg} g$$

$$h_w d_w = h_{Hg} d_{Hg}$$

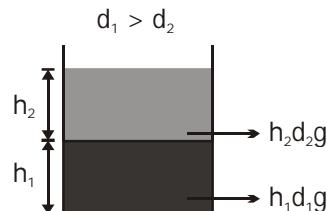
$$h_w \times 1 \text{ g/cm}^3 = 76 \text{ cm} \times 13.6 \text{ g/cm}^3$$

$$h_w = 1033.6 \text{ cm}$$

Ex.4 What will be the pressure if two immiscible fluid is filled according to given diagram.

- (a) Find the pressure at the bottom of tank.
- (b) Find the pressure at the middle point of bottom layer.

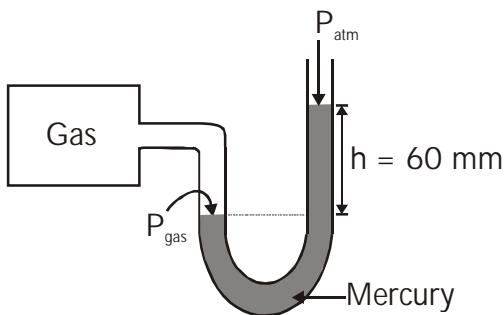
Sol. (a) $P_{\text{atm}} + h_2 d_2 g + h_1 d_1 g$;



(b) $P_{\text{atm}} + h_2 d_2 g + \frac{h_1}{2} d_1 g$

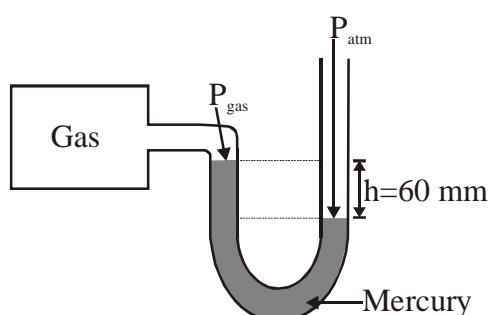
Ex.5 Find the pressure of the gas inside a container if the open manometer attached to the container shows a difference of 60 mm.

Sol. **Case-I :** $P_{\text{atm}} < P_{\text{gas}}$



$$\begin{aligned} P_{\text{gas}} &= P_{\text{atm}} + 60 \text{ mm} \\ &= 760 \text{ mm} + 60 \text{ mm} \\ &= 820 \text{ mm of Hg} \end{aligned}$$

Case-II : $P_{\text{atm}} > P_{\text{gas}}$



$$\begin{aligned} P_{\text{atm}} &= P_{\text{gas}} + 60 \text{ mm} \\ &= 760 \text{ mm} = P_{\text{gas}} + 60 \\ &= P_{\text{gas}} = 700 \text{ mm} \end{aligned}$$

4. GAS LAWS

The behaviour of the gases is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas.

The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as **Boyle's Law**. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from *Avogadro* and others provided lot of information about gaseous state.

4.1 Boyle's Law :

For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

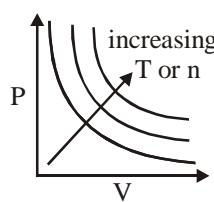
$$\Rightarrow V \propto \frac{1}{P}$$

$$\Rightarrow \text{Hence , } PV = \text{const. (K)}$$

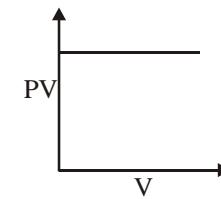
$$\Rightarrow \boxed{P_1 V_1 = P_2 V_2}$$

❖ Graphical representation of Boyle's law :

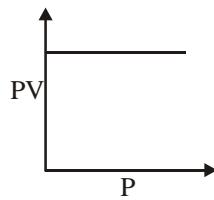
(i) **P v/s V :**



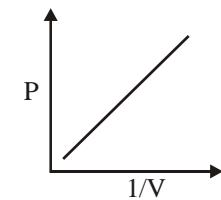
(ii) **PV v/s V :**



(iii) **PV v/s P :**



(iv) **P v/s 1/V :**



4.2. Charle's Law :

For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$\Rightarrow V \propto T$$

$$\Rightarrow V = KT$$

$$\boxed{\frac{V}{T} = \text{constant (K)}}$$

T = Temperature on absolute scale, kelvin scale or ideal gas scale.

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

$$\boxed{V = V_0 + bt}$$

$$\boxed{V = b'T}$$

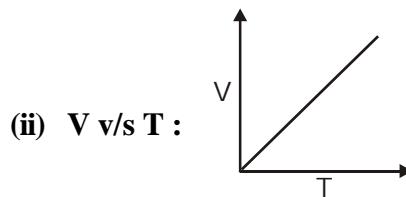
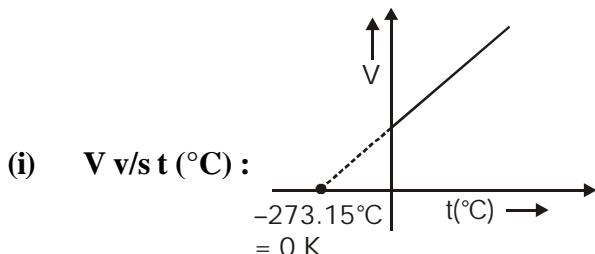
t = temperature on centigrade scale.

T = absolute temperature (K)

V_0 = volume of gas at 0°C .

b, b' = constants

❖ Graphical representation of Charle's Law :



❖ Important Points :

- Since volume is proportional to absolute temperature, the volume of a gas should be theoretically zero at absolute zero temperature.
- In fact, no substance exists as gas at a temperature near absolute zero, though the straight line plots can be interpolated to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering -273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

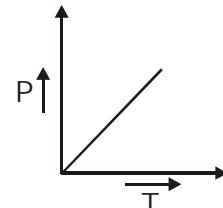
4.3. Gay-lussac's law :

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$\Rightarrow P \propto T$$

$$\frac{P}{T} = \text{constant (K)}$$

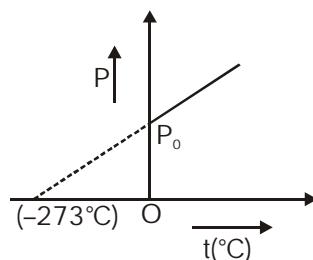
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{Temperature on absolute scale, kelvin scale or ideal gas scale.}$$



Note: Originally, the law was developed on the centigrade scale, where it was found that pressure

is a linear function of temperature $\Rightarrow [P = P_0 + bt]$,

where 'b' is a constant and ' P_0 ' is pressure at zero degree centigrade.



But for kelvin scale : $[P = b''T]$ where T is in K.

4.4. Avogadro's law :

Equal volumes of all the gases under similar conditions of temperature and pressure contains equal number of molecules or moles of molecules (not atoms).

$$V \propto N \quad (\text{Temperature and pressure constant})$$

$$V \propto n \quad (\text{Temperature and pressure constant})$$

Where, N = number of molecules, n = number of moles of molecules

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2} \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume.

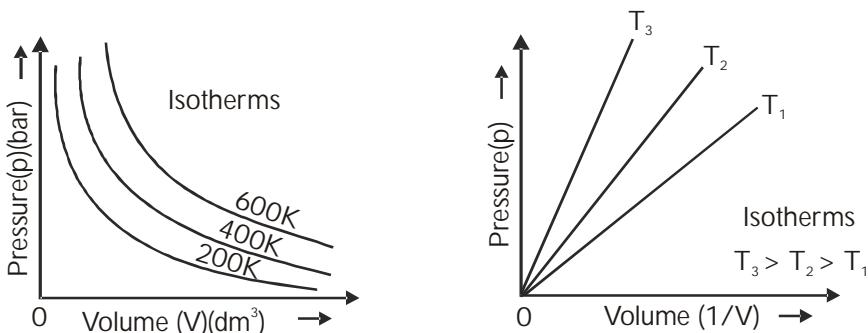
Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. At STP, molar volume of an ideal gas or a combination of ideal gases is $22.71098 \text{ L mol}^{-1}$.

Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

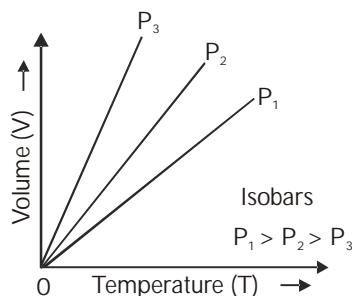
Ex.6 What is a pressure-volume isotherm ?

Sol. Graph between P & V at constant temperature is called **PV-isotherm**.



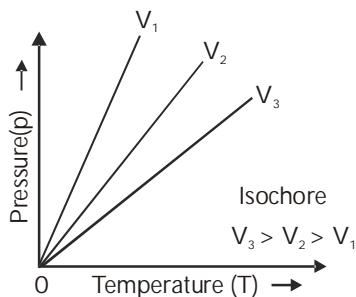
Ex.7 What is Isobar ?

Sol. Graph plotted at constant pressure is called isobar. Graph between V & T at constant pressure is called VT-isobar.



Ex.8 What is Isochore ?

Sol. Graph plotted at constant volume is called isochore. Graph between P & T at constant volume is called PT-isochore.



5. IDEAL GAS EQUATION

A single equation which is combination of Boyle's, Charle's & Avogadro's Law is known as ***Ideal gas equation***. Or we can say a single equation which describe the simultaneous effects of the change in temperature & pressure on volume of the given amount of the gas is called the ***Ideal gas equation***.

$$PV = nRT$$

According to Boyle's law, $V \propto \frac{1}{P}$ (at constant T and n)

According to Charle's law, $V \propto T$ (at constant P and n)

According to Avogadro's law, $V \propto n$ (at constant T and P)

According to the three laws, $V \propto \frac{nT}{P}$ or $PV \propto nT$

or $PV = nRT$ [Equation of state or combined gas law]

Where R is a constant called ***Universal gas constant***, which does not depend on variables (P, V, n, T) and nature of gas.

- Molar volume is the volume of 1 mole of gas.

$$\text{Molar volume } (V_m) = \frac{\text{Volume}}{\text{mole}}$$

$$PV_m = RT$$

Volume of 1 mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.7 L mol⁻¹.

- Dimension of R :**

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Mole} \times \text{Temperature}} = \frac{(\text{Force} / \text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Temperature(K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Temperature(K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Temperature(K)}}$$

- Physical significance of R :**

The dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1 K isobarically.

- **Units of R :**

(i) In lit-atm $R = \frac{1 \text{ atm} \times 22.4 \text{ lit.}}{1 \text{ mol} \times 273 \text{ K}} = 0.0821 \text{ lit-atm mol}^{-1} \text{K}^{-1}$

(ii) In C.G.S system $R = \frac{1 \times 76 \times 13.6 \times 980 \text{ dyne cm}^{-2} \times 22400 \text{ cm}^3}{1 \text{ mol} \times 273 \text{ K}}$
 $= 8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}$.

(iii) In M.K.S.system $R = 8.314 \text{ Joule mole}^{-1} \text{K}^{-1}$. [10⁷ erg = 1 joule]
 (SI units)

(iv) In calories, $R = \frac{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}{4.184 \times 10^7 \text{ erg}}$
 $= 1.987 \approx 2 \text{ calorie mol}^{-1} \text{K}^{-1}$.

Ex.9 A sample of gas occupies 100 dm³ at 1 bar pressure and at T °C. If the volume of the gas is reduced to 5 dm³ at the same temperature, what additional pressure must be applied ?

Sol. From the given data :

$$\begin{aligned} P_1 &= 1 \text{ bar } P_2 = ? \\ V_1 &= 100 \text{ dm}^3 \quad V_2 = 5 \text{ dm}^3 \end{aligned}$$

Since the temperature is constant, Boyle's law can be applied

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

$$P_2 = \frac{(1 \text{ bar}) \times (100 \text{ dm}^3)}{(5 \text{ dm}^3)} = 20 \text{ bar}$$

∴ Additional pressure applied = 20 – 1 = **19 bar**

Ex.10 A certain amount of a gas at 27°C and 1 bar pressure occupies a volume of 25 m³. If the pressure is kept constant and the temperature is raised to 77°C, what will be the volume of the gas ?

Sol. From the available data :

$$V_1 = 25 \text{ m}^3 \quad T_1 = 27 + 273 = 300 \text{ K}$$

$$V_2 = ? \quad T_2 = 77 + 273 = 350 \text{ K}$$

Since the pressure of the gas is constant, Charles law is applicable

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

$$\text{or } V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{(25 \text{ m}^3) \times (350 \text{ K})}{(300 \text{ K})} = 29.17 \text{ m}^3$$

Ex.11 The density of a gas is found to be 1.56 g dm^{-3} at 0.98 bar pressure and 65°C . Calculate the molar mass of the gas.

Use $R = 0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$

Sol. We know that :

$$M = \frac{dRT}{P} = \frac{(1.56 \text{ g dm}^{-3}) \times (0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times 338\text{K}}{(0.98 \text{ bar})} = 44.66 \text{ g mol}^{-1}$$

Ex.12 A glass bulb of 2 L capacity is filled by helium gas at 10 atm pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is 1 atm.

$$P_1 \times V_1 = P_2 \times V_2$$

$$\Rightarrow 10 \times 2 = 1 \times V$$

$$\Rightarrow 20 = V$$

$$V = V' + 2 \text{ L}$$

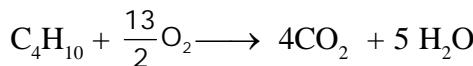
$$20 = V' + 2 \text{ L}$$

$$V' = 18 \text{ L}$$

\Rightarrow total volume of gas leaked

Ex.13 LPG is a mixture of n-butane & iso-butane. What is the volume of oxygen needed to burn 1 kg of LPG at 1 atm, 273 K ?

Sol. During the burning of LPG following reaction takes place -



Now, for complete combustion of 1 mole of LPG $\longrightarrow \frac{13}{2}$ moles of O_2 are required.

\therefore for $\frac{1000}{58}$ moles of LPG $\longrightarrow \frac{13}{2} \times \frac{1000}{58}$ moles of O_2 are required.

Thus, the volume of oxygen needed to burn 1 kg of LPG at 1 atm & 273K would be

$$\text{Vol. of O}_2 = \text{Moles of O}_2 \times 22.4 \text{ L} = \frac{13}{2} \times \frac{1000}{58} \times 22.4 = 2510 \text{ L}$$

Ex.14 The best vacuum so far attained in laboratory is 10^{-10} mm of Hg. What is the number of molecules of gas remain per cm^3 at 20°C in this vacuum ?

Sol. Given conditions -

$$P = 10^{-10} \text{ mmHg} = \frac{10^{-10}}{760} \text{ atm} ; V = 1 \text{ cm}^3 = \frac{1}{1000} \text{ L} ; T = 20^\circ\text{C} = 293 \text{ K}$$

No. of molecules, $N = ?$

Now, applying

$$PV = nRT$$

$$\therefore \text{number of molecules per } \text{cm}^3, N = \frac{N_A \times P \times V}{RT}$$

$$\Rightarrow N = \frac{6.023 \times 10^{23} \times (10^{-10}/760) \times (1/1000)}{(0.0821)(293)}$$

$$N = 3.29 \times 10^6 \text{ molecules}$$

6. DALTON'S LAW OF PARTIAL PRESSURES

6.1 Partial pressure :

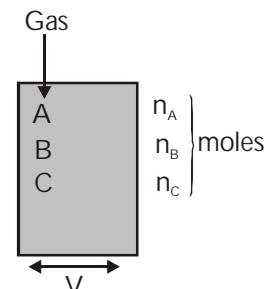
In a mixture of non-reacting gases, partial pressure of any component gas is defined as the pressure exerted by the individual gas if whole of the volume of mixture had been occupied by this component only.

Partial pressure of component gases are -

$$P_A = \frac{n_A RT}{V} = \text{partial pressure of A}$$

$$P_B = \frac{n_B RT}{V} = \text{partial pressure of B}$$

$$P_C = \frac{n_C RT}{V} = \text{partial pressure of C}$$



6.2 Dalton's Law :

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$$P_{\text{Total}} = p_1 + p_2 + p_3 + \dots \quad (\text{At constant } V \text{ and } T)$$

$$= \left(\frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots \right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$$

Where $n = n_1 + n_2 + n_3 + \dots$ = Total moles, V = Total volume

$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$

- Dalton's law of partial pressure is applicable only to non-reacting gases.**

If the two non-reacting gases A and B having n_A and n_B number of moles respectively are filled in a vessel of volume V at temperature T, then

$$\frac{P_A}{P} = \frac{n_A RT / V}{(n_A + n_B)RT / V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

$$P_A = x_A \times P, \quad \text{Similarly } P_B = x_B \times P$$

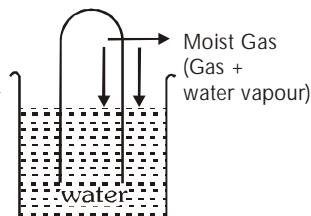
$$\text{Partial pressure of a component} = \text{Mole fraction} \times \text{total pressure}.$$

- 6.3 It has been observed that gases are generally collected over water and therefore are moist.**

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

$$\text{or Pressure of dry gas} = \text{Pressure of moist gas} - \text{aqueous tension}$$

The pressure exerted by water vapour is constant when it is in equilibrium with liquid water at a particular temperature. It is called vapour pressure of water or **aqueous tension**, which varies with the temperature and becomes 760 mm at 100°C.



- 6.4 Relative Humidity (RH) =** $\frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water (aq.tension)}}$

7. AMAGAT'S LAW OF PARTIAL VOLUME

7.1 Partial Volume :

Partial volume of any component is defined as the volume occupied by that particular component when it is kept at same total pressure and temperature as of the mixture.

7.2 Amagat's law :

According to this law at constant temperature and pressure, the total volume of mixture of non-reacting gases is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + \dots$$

Let us consider three non-reacting gases A, B and C are present in a container which have no. of moles n_A , n_B and n_C respectively. For each gas partial volume is

$$V_A = n_A \left(\frac{RT}{P} \right) = \text{partial volume of A}$$

$$V_B = n_B \left(\frac{RT}{P} \right) = \text{partial volume of B}$$

$$V_C = n_C \left(\frac{RT}{P} \right) = \text{partial volume of C}$$

- **Total volume :**

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C) \left(\frac{RT}{P} \right) = n_T \left(\frac{RT}{P} \right)$$

$$\frac{V_A}{V_T} = \frac{n_A}{n_T} = x_A \quad (\text{Mole fraction of gas A})$$

$$\frac{V_B}{V_T} = \frac{n_B}{n_T} = x_B \quad (\text{Mole fraction of gas B})$$

$$\frac{V_C}{V_T} = \frac{n_C}{n_T} = x_C \quad (\text{Mole fraction of gas C})$$

∴ **Partial volume of a gas = Mole fraction × Total volume**

- Ex.15** (a) Find the total pressure and partial pressure of each component if a container of volume 8.21 lit. contains 2 moles of A and 3 mole of B at 300K.
- (b) What will be the final pressure and partial pressure of each component if 5 moles of C is also added to the container at same temperature.

Sol. (a) $P_A = \frac{n_A RT}{V} = \frac{2 \times 0.821 \times 300}{8.21} = 6 \text{ atm}$

$$P_B = \frac{n_B RT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$

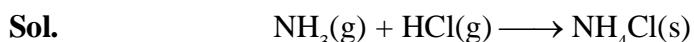
$$\text{Total pressure } P_T = P_A + P_B = 6 + 9 = 15 \text{ atm}$$

(b) $P_C = \frac{n_C RT}{V} = \frac{5 \times 0.821 \times 300}{8.21} = 15 \text{ atm}$

Note: If we add or remove a non reacting gas partial pressure of other gases remains unchanged.

$$P_T = P_A + P_B + P_C = 6 + 9 + 15 = 30 \text{ atm}$$

- Ex.16** 2 moles of $\text{NH}_3(\text{g})$ and 1 mole of $\text{HCl}(\text{g})$ are taken in a container of capacity 8.21 lit at 300K to produce $\text{NH}_4\text{Cl}(\text{s})$. Find the total pressure after the reaction.



initial	2	1
after rxn	1	0

In this reaction HCl is L.R. so it will be completely consumed. We don't consider pressure due to solid.

$$\therefore P_T = \frac{n R T}{V} = \frac{1 \times 0.821 \times 300}{8.21} = 3 \text{ atm}$$

Ex.17 A closed container containing O_2 and some liquid water was found to exert 740 mm pressure at $27^\circ C$.

- (a) Then calculate the pressure exerted by O_2 if aqueous tension at $27^\circ C$ is 20 mm.
- (b) What will be the final pressure if volume is reduced to half.
(consider volume of liquid water negligible)
- (c) What will be the final pressure if volume is doubled.

Sol. (a) $P_T = P_{\text{dry gas}} + P_{\text{aq. tension}}$

$$740 = P_{O_2} + 20$$

$$P_{O_2} = 740 - 20 = 720 \text{ mm}$$

(b) $(P_{O_2} V_{O_2})_{\text{initial}} = (P_{O_2} V_{O_2})_{\text{final}}$ (Boyle's law)

$$720 \times V = P_{O_2} \times \frac{V}{2}$$

$$P_{O_2} = 1440 \text{ mm}$$

$$P_T = P_T = P_{O_2} + P_{\text{aq.}}$$

$$= 1440 + 20 = 1460 \text{ mm}$$

(c) $(P_{O_2} V_{O_2})_{\text{initial}} = (P_{O_2} V_{O_2})_{\text{final}}$

$$720 \times V = P_{O_2} \times 2V$$

$$P_{O_2} = 360 \text{ mm}$$

$$P_T = P_{O_2} + P_{\text{aq.}}$$

$$= 360 + 20 = 380 \text{ mm}$$

8. PROBLEM RELATED WITH DIFFERENT TYPE OF CONTAINERS

I. Closed Container :

In this case gas can neither go outside nor it can come inside. So number of moles of gas is always constant.

Closed container can be of following types -

- (a) **Closed rigid container** : In this case number of moles constant, volume constant.

At this condition :

Initial Final

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

Example : Gas cylinder

(b) Closed non rigid container : (fitted with freely movable piston)

In this kind of container inside pressure is always equal to outside pressure, i.e., atmospheric pressure so that $n = \text{constant}$, $p = \text{constant}$

Ex: Balloon, Water bubble

Initial Final

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

Ex.18 A balloon is inflated to $\frac{7}{8}$ of its maximum volume at 27°C then calculate the minimum temperature above which it will burst.

Sol. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{7V}{8 \times 300} = \frac{V}{T}$$

$$T = 342.8 \text{ K}$$

Ex.19 A gas cylinder containing cooking gas can with stand a pressure of 18 atm. The pressure gauge of cylinder indicates 12 atm at 27°C . Due to sudden fire in building the temperature start rising at what temperature will the cylinder explode.

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

$$\frac{12}{300} = \frac{18}{T}$$

$$T = 450 \text{ K}$$

II. Tyre tube type container :

In this case temperature is always constant. Initially on adding gas volume of tube will increase and pressure of tube will remain constant until it will gain maximum volume.

$$\therefore V \propto n$$

Initial Final

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

After attaining maximum volume on adding gas pressure reach to a maximum possible pressure. Hence at this condition volume constant or temperature constant.

$$V = \text{constant} \quad T = \text{constant}$$

$$P \propto n$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

Ex.20 A tyre tube of maximum volume 8.21 lit. can withstand a pressure of 10 atm. Initially the tube is empty.

- Calculate the number of moles required to inflate completely the tube upto a pressure of 1 atm & 300 K temperature.
- Calculate the minimum number of moles required to burst the tyre tube at 300 K.

Sol. (i) $PV = nRT$

$$1 \times 8.21 = n_1 \times 0.0821 \times 300$$

$$n_1 = \frac{1}{3}$$

(ii) $PV = nRT$

$$10 \times 8.21 = n_2 \times 0.0821 \times 300$$

$$n_2 = \frac{10}{3}$$

III. Open rigid container : When air is heated in an open vessel , pressure is always atmospheric pressure i.e., constant and volume is also constant.

At this condition

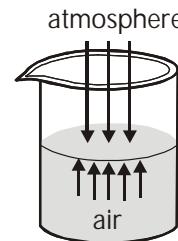
Initial Final

$$n_1 T_1 = n_2 T_2$$

n_1 = initial number of moles

n_2 = final number of moles

$$n_{\text{initial}} = n_{\text{final}} + n_{\text{removed}}$$



Ex.21 An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that

- 1/3rd of air measured in the container at 27°C escape out.
- 1/3rd of air measured in the container at final temperature escape out.

Sol. (a) $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times 300} = \frac{1}{300} - \frac{1}{T} = \frac{1}{900}$$

$$\frac{1}{T} = \frac{1}{300} - \frac{1}{900} = \frac{3-1}{900} = \frac{2}{900} \Rightarrow T = 450 \text{ K} = 177^\circ\text{C}$$

(b) $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times T}$$

$$\frac{1}{300} - \frac{1}{T} = \frac{1}{3 \times T}$$

$$\Rightarrow T = 400 \text{ K} = 127^\circ\text{C}$$

- Ex.22** A bulb of unknown volume containing air is heated from 27°C to 227°C at constant pressure. The expelled air is measured at different temperature of determine volume of container. What will be volume of container if -
- 200 ml of air measured at 227°C was expelled.
 - 200 ml of air measured at 27°C was expelled.
 - 200 ml of air measured at 127°C was expelled.

Sol. (a) $\mathbf{n_{initial} - n_{final} = n_{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 500}$$

$$\frac{V}{3} - \frac{V}{5} = \frac{200}{5}$$

$$\frac{5V - 3V}{15} = \frac{200}{5}$$

$$\Rightarrow 2V = \frac{200 \times 15}{5} \Rightarrow V = 300 \text{ ml}$$

(b) $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 300} = \frac{2V}{15} = \frac{200}{3} \Rightarrow V = \frac{100 \times 15}{2 \times 3} = 500 \text{ ml}$

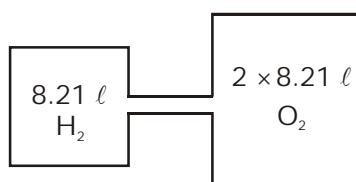
(c) $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 400}$

$$\frac{2V}{15} = \frac{200}{4} \Rightarrow V = \frac{200 \times 15}{2 \times 4} = 375 \text{ ml}$$

IV. Connected Container :

If containers are connected for substantial time then gases move from one container to another container till partial pressure of each component of mixtures becomes equal in all connected containers (irrespective whether containers have same or different temperature and volumes)

- Ex.23** A container of 8.21 lit. capacity is filled with 1 mole of H_2 at 300 K and it is connected to another container of capacity 2×8.21 lit. containing 4 moles of O_2 at 300 K, then find the final pressure & partial pressure of each gas.



Sol. $P_f V_f = n_f RT$

$$P_f (3 \times 8.21) = 5 \times 0.0821 \times 300$$

$$P_f = 5 \text{ atm}$$

$$P_{H_2} = x_{H_2} P_f = \frac{1}{1+4} \times 5 = 1 \text{ atm}$$

$$P_{O_2} = x_{O_2} P_f = \frac{4}{1+4} \times 5 = 4 \text{ atm}$$

Ex.24 A 10 litre container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

- (a) Moles and pressure of gas in both the containers before heating.
- (b) Moles and pressure in two containers after heating.

(Assume that initially the larger container is completely evacuated.)

Sol. (a) Before heating :

$$P_I = P_{II}$$

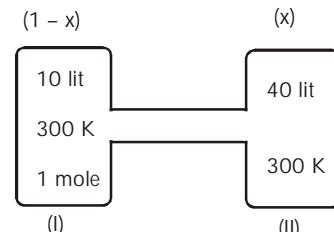
$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$x = 0.8 \text{ moles}$$

$$n_I = 1 - x = 0.2 \text{ mole}$$

$$n_{II} = x = 0.8 \text{ mole}$$

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$



- (b) After heating :

$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$x_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

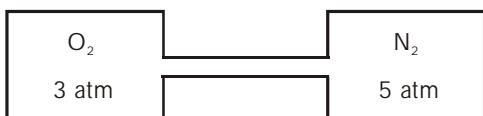
$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.0821 \times 600}{40} = 0.821 \text{ atm}$$

9. GRAHAM'S LAW OF DIFFUSION & EFFUSION

9.1 Diffusion :

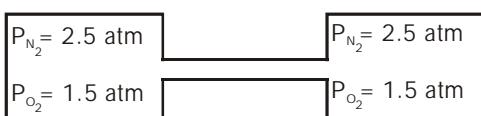
The **diffusion** is the process of gradual mixing of molecules of one gas with molecules of another gas due to their molecular motion (kinetic energy). The diffusion always proceeds from a region of high concentration to a region of lower concentration (or high partial pressure to low partial pressure). For example, when a bottle of perfume is opened at one end of the room, the person sitting at the other end of the room can smell the perfume because of the diffusion process of perfume molecules.

Note : Initially



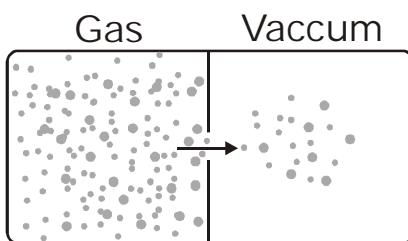
When stop cock is removed flow will be from both sides, N₂ will try to equalise its partial pressure in both the vessels, and so will O₂.

Finally



9.2 Effusion :

The effusion is the process of forcing a gas through a pin hole or small orifice from one compartment to another empty (vacuum) compartment.



9.3 Graham's Law :

Under similar condition of pressure (partial pressure) and temperature, the rate of diffusion of different gases is inversely proportional to square root of their density.

$$\Rightarrow \text{rate of diffusion, } r \propto \frac{1}{\sqrt{d}}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{V.D_2}}{\sqrt{V.D_1}}$$

where, d = density of gas

V.D = vapour density

M = molar mass of gas

- Under conditions of same temperature but different pressure, we have -

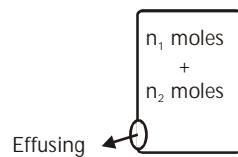
$$r \propto \frac{P}{\sqrt{M}}$$

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

If both gases are present in the same container at same temperature.

$$P \propto n$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$



Rate of diffusion/effusion can be expressed as -

$$r = \frac{\text{volume diffused}}{\text{time taken}} \quad \text{or} \quad \frac{\text{moles diffused}}{\text{time taken}} \quad \text{or} \quad \frac{\text{pressure dropped}}{\text{time taken}}$$

$$\text{or} \quad \frac{\text{distance travelled in horizontal tube of uniform cross-section}}{\text{time taken}}$$

Ex.25 32 ml of He effuses through a fine orifice in 1 minute. Then what volume of CH₄ will diffuse in 1 minute under the similar condition.

Sol. ∵ $r \propto \frac{1}{\sqrt{M}}$

$$r = \frac{\text{volume diffused}}{\text{time}}$$

∴ time is same so

$$\frac{V_{CH_4}}{V_{He}} = \sqrt{\frac{M_{He}}{M_{CH_4}}}$$

$$\frac{V_{CH_4}}{32} = \sqrt{\frac{4}{16}}$$

$$V_{CH_4} = \frac{1}{2} \times 32 = 16 \text{ mL}$$

Ex.26 20 dm³ of Ne diffuse through a porous partition in 60 seconds. What volume of SO₃ will diffuse under similar conditions in 30 sec. (**Atomic wt. of Ne = 20, S = 32**)

Sol. $\frac{r_{Ne}}{r_{SO_3}} = \sqrt{\frac{M_{SO_3}}{M_{Ne}}} \Rightarrow \frac{V_{Ne}/t_{Ne}}{V_{SO_3}/t_{SO_3}} = \sqrt{\frac{M_{SO_3}}{M_{Ne}}}$

$$\Rightarrow V_{SO_3} = \frac{V_{Ne} \times t_{SO_3}}{t_{Ne}} \times \sqrt{\frac{M_{Ne}}{M_{SO_3}}} = \frac{20 \times 30}{60} \times \sqrt{\frac{20}{80}} = \frac{10}{2} = 5 \text{ dm}^3$$

Ex.27 A gaseous mixture of O₂ and X containing 20% (mole %) of X, diffused through a small hole in 234 seconds while pure O₂ takes 224 seconds to diffuse through the same hole. Molecular weight of X is :

Sol. $\frac{t_{\text{mix}}}{t_{\text{O}_2}} = \sqrt{\frac{M_{\text{mix}}}{M_{\text{O}_2}}}$

$$\frac{234}{224} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

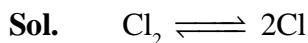
$$\therefore M_{\text{mix}} = 34.921.$$

As the mixture contains 20% (mole %) of X, the molar ratio of O₂ and X may be represented as 0.8n : 0.2n, n being the total no. of moles.

$$\therefore M_{\text{mix}} = \frac{32 \times 0.8n + M_x \times 0.2n}{n} = 34.921$$

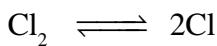
$$\therefore M_x (\text{mol. wt. of X}) = 46.6$$

Ex.28 At 1200°C, mixture of Cl₂ and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms. M(Kr) = 83.8 g mol⁻¹.



$$\frac{r(\text{Cl}_2 \text{ and Cl mix})}{r(\text{Kr})} = 1.16 \sqrt{\frac{M(\text{Kr})}{M_{\text{av}}(\text{Cl}_2 + \text{Cl})}} = \sqrt{\frac{83.8}{M_{\text{av}}}}$$

$$\therefore M_{\text{av}} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$



Initial mole	1	0
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After dissociation	(1 - x)	2x
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(x = degree of dissociation)

Total moles after dissociation = 1 - x + 2x = (1 + x)

$$\therefore \frac{(1 - x)M(\text{Cl}_2) + 2xM(\text{Cl})}{(1 + x)} = 62.28 \Rightarrow \frac{(1 - x) \times 71 + 2x \times 35.5}{1 + x} = 62.28$$

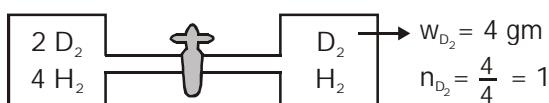
$$x = 0.14$$

$$\therefore \% \text{ dissociation} = 14\%$$

Ex.29 A mixture containing 2 moles of D_2 and 4 moles of H_2 is taken inside a container which is connected to another empty container through a nozzle. The nozzle is opened for certain time and then closed. The second bulb was found to contain 4 gm D_2 . Then find % by moles of the lighter gases in second container.

Sol.

I



$$w_{D_2} = 4 \text{ gm}$$

$$n_{D_2} = \frac{4}{4} = 1$$

lighter gas = H_2

$$\frac{r_{H_2}}{r_{D_2}} = \frac{n_{H_2}}{n_{D_2}} \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n_{H_2}^i / t}{n_{D_2}^i / t}$$

$$(\% \text{ mole of } H_2)_{II} = \left(\frac{n_{H_2}^i}{n_{H_2}^i + n_{D_2}^i} \right) \times 100$$

$$\therefore \frac{n_{H_2}^i}{n_{D_2}^i} \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \frac{n_{H_2}^i}{n_{D_2}^i} \Rightarrow \frac{4}{2} \sqrt{\frac{4}{2}} = \frac{n_{H_2}^i}{1}$$

$$\Rightarrow n_{H_2}^i = 2\sqrt{2} \quad \Rightarrow \quad n_{D_2}^i = 1$$

$$(\% \text{ mole of } H_2)_{II} = \frac{(2\sqrt{2})}{(2\sqrt{2}+1)} \times 100 = \frac{2 \times 1.44}{[(2 \times 1.44) + 1]} \times 100 = \frac{(2.8)}{(2.8+1)} \times 100 = \frac{(2.8)}{(2.8+1)} \times 100$$

$$= 73.87\%$$

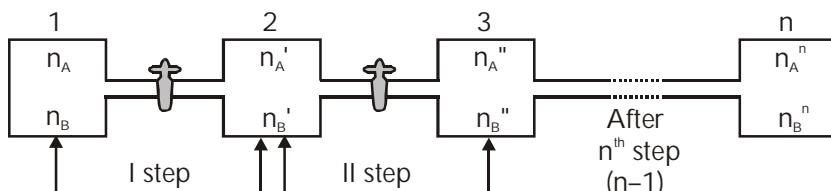
Ex.30 Why a heavier gas from a gas mixture effuses at slower rates ?

Sol. In a gas mixture, the average kinetic energy of each gas $\left(\frac{1}{2}mv^2\right)$ is the same $\left(\frac{3}{2}RT\right)$. Hence, heavier gas has smaller speed.

9.4 APPLICATION OF GRAHAM'S LAW OF DIFFUSION IN ENRICHMENT OF ISOTOPES

❖ Enrichment factor or Isotopic separation factor :

When two gases present in a container are allowed to diffuse in another container then gas having lower molecular mass will diffuse more and if this process is continued for large number of steps then we can obtain a mixture which is rich in a gas having lower molecular mass. Hence ultimately in the ultimate (last) container amount of lighter gas is larger as compared to heavier gas.



where, $M_A > M_B$ [similar condition of T and V] & $n_B^n \ggg n_A^n$

Enrichment factor (f) is defined as the ratio of final ratio of moles in the mixture [after n^{th} step] with initial mole ratio of the mixture.

$$f = \frac{\left(\frac{n_A^n}{n_B^n}\right)}{\left(\frac{n_A}{n_B}\right)} = \left(\sqrt{\frac{M_B}{M_A}}\right)^n = \frac{\text{final molar ratio}}{\text{initial molar ratio}}$$

10. KINETIC THEORY OF GASES

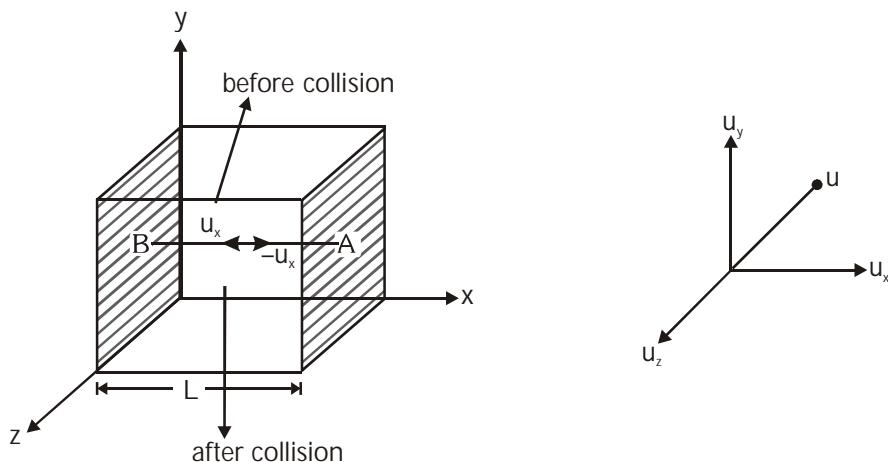
This is a theoretical model for ideal gas which can correlate the experimental facts (like Boyle's law, Charle's law & Avogadro's law etc.). It was presented by **Bernoulli in 1738** and developed in 1860 by **Clausius, Maxwell, Kroning and Boltzmann**. Postulates of kinetic theory of gases are:

- (i) All the gases consist of very small molecules or atoms whose volume is negligible compared to volume of container.
- (ii) There are no attractive or repulsive forces between the molecules.
- (iii) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)
- (iv) Due to the continuous motion, collision between gaseous molecules and with the wall of container occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.
- (v) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.
- (vi) Collision among gas particles molecules is perfectly elastic, i.e., there is no loss in kinetic energy and moment during such collision.
- (vii) The average kinetic energy of gas particles will depends on absolute temperature only.

10.1 Kinetic gas equation :

Let us consider a cube of side L, that has N molecules each of mass m moving with velocity u in all direction and thus colliding with one each other and against sides of the container. Velocity u can be resolved into three components u_x , u_y and u_z along there axis such that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$



For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity u_x . After collision against face B it moves towards face A with velocity $(- u_x)$ collision being elastic (which results in change in direction but not speed)

$$\therefore \text{Momentum before collision on face B} = mu_x$$

$$\text{Momentum after collision on face B} = -mu_x$$

$$\text{Change in momentum due to one collision on face B} = mu_x - (-mu_x) = 2mu_x$$

To strike face B again distance travelled = $2L$

$$\text{Time taken to strike face B again} = \frac{2L}{u_x} \text{ seconds}$$

$$\therefore \text{Number of collisions per second on face B along x-axis} = \frac{u_x}{2L}$$

$$\therefore \text{Rate of change in momentum due to } \frac{u_x}{2L} \text{ collisions per second on face B along x-axis.}$$

$$= 2mu_x \cdot \frac{u_x}{2L} = \frac{mu_x^2}{L}$$

$$\text{Similarly for y-axis change in momentum per second} = \frac{mu_y^2}{L} \text{ and for z-axis} = \frac{mu_z^2}{L}$$

$$\text{Net force by N molecules on a wall, } F_x = \frac{mu_{x_1}^2}{L} + \frac{mu_{x_2}^2}{L} + \dots + \frac{mu_{x_N}^2}{L} = \frac{m}{L} \cdot \Sigma u_x^2$$

$$\text{Now pressure} = \frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{m}{L} \cdot \Sigma u_x^2}{L^2} = \frac{m \cdot \Sigma u_x^2}{L^3} = \frac{m \cdot \Sigma u_x^2}{V} \quad [L^3 = \text{volume V}]$$

$$\therefore PV = m \cdot \Sigma u_x^2$$

$$\text{As } \Sigma u_x^2 = \Sigma u_y^2 = \Sigma u_z^2 \text{ and } \Sigma u_x^2 + \Sigma u_y^2 + \Sigma u_z^2 = \Sigma u^2$$

$$\therefore PV = m \cdot \Sigma u_x^2 = \frac{1}{3} m \cdot \Sigma u^2$$

$$PV = \frac{1}{3} m \left(\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N} \right) \cdot N$$

$$\therefore PV = \frac{1}{3} m N u_{\text{rms}}^2$$

This equation is called kinetic gas equation.

10.2 Kinetic energy of gas molecules :

Total translational K.E. of molecules

$$= \frac{1}{2}m u_1^2 + \frac{1}{2}m u_2^2 + \dots + \frac{1}{2}m u_N^2 = \frac{1}{2}m \sum u_i^2 = \frac{1}{2}m N u_{\text{rms}}^2 = \frac{3}{2}PV = \frac{3}{2}nRT$$

$$\therefore \text{Average translational K.E. per mole} = \frac{3}{2}RT$$

$$\text{and (K.E.)}_{\text{per molecule}} = \frac{3}{2} \left(\frac{R}{N_A} \right) T = \frac{3}{2} kT$$

$$\text{Where } k = \text{Boltzmann constant} = \frac{R}{N_A} = \frac{8.314 \text{ J/mol K}}{6.02 \times 10^{23}} = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

- $(\text{K.E.})_{\text{per molecule}}$ and $(\text{K.E.})_{\text{per mol}}$ only depend on absolute temperature. It does not depend on the nature of gas. This conclusion is known as "**Maxwell's Generalisation**".

Ex.31 Calculate the kinetic energy of 8 gram methane (CH_4) at 27°C temperature.

$$\text{Sol. } n = \frac{8}{16} = \frac{1}{2}, T = (27 + 273) = 300 \text{ K}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$(\text{K.E.})_{\text{n mol}} = n \times \frac{3}{2}RT = \frac{1}{2} \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ J}$$

Ex.32 Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-25} kg, in a container of volume $1 \times 10^{-3} \text{ m}^3$ and having root mean square velocity of 10^3 ms^{-1} . Also calculate total kinetic energy and Temperature of the gas.

Sol. By kinetic theory

$$P = \frac{1}{3} \frac{mNu^2}{V} = \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}} = 3.33 \times 10^6 \text{ N m}^{-2}$$

$$\text{Total KE} = \left(\frac{1}{2} m u_{\text{rms}}^2 \right) \times N = \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4 \text{ J}$$

$$\text{Also total KE} = \frac{3}{2} nRT, \text{ where } n (\text{mole}) = \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023 \times 10^{23}}$$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$\therefore T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$

10.3 Root Mean Square Velocity (u_{rms}) by kinetic gas equation :

$$PV = \frac{1}{3}mN u_{\text{rms}}^2$$

$$\therefore u_{\text{rms}} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3RT}{M}}$$

10.4 Different kind of speed of molecules :

$$(i) \text{ Average or mean speed, } u_{\text{avg}} = \frac{u_1 + u_2 + \dots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$

$$(ii) \text{ Root mean square speed, } u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}} = \sqrt{\frac{3RT}{M}}$$

$$(iii) \text{ Most probable speed, } u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

It is the speed at which maximum fraction of molecules are travelling

❖ Ratio of speeds :

$$\begin{aligned} U_{\text{rms}} : U_{\text{avg}} : U_{\text{mps}} &= \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} \\ &= \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.22 : 1.13 : 1 : 00 = 1.00 : 0.92 : 0.816 \end{aligned}$$

11. MAXWELL'S DISTRIBUTION OF SPEEDS

It has already been pointed out that a gas is a collection of tiny particles separated from one another by large empty spaces and moving rapidly at random in all directions. In the course of their motion, they collide with one another and also with the walls of the container. Due to frequent collisions, the speeds and directions of motion of the molecules keep on changing. Thus, all the molecules in a sample of gas do not have same speed. Although it is not possible to find out the speeds of individual molecule, yet from probability considerations it has become possible to work out the distribution of molecules in different speed intervals. This distribution is referred to as the Maxwell-Boltzmann distribution in honour of the scientists who developed it. It may be noted that the distribution of speeds remains constant at a particular temperature although individual speeds of molecules may change.

$$dN = 4\pi N \left[\frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2 du = 4\pi N \left[\frac{m}{2\pi kT} \right]^{3/2} e^{-\frac{mu^2}{2kT}} \cdot u^2 \cdot du$$

Here, dN = Number of molecules having speeds between u and $u + du$.

N = Total number of molecules.

M = Molar mass of gas (kg/mol)

u = Root mean square velocity

du = Velocity interval

$$\frac{dN}{N} = 4\pi \left[\frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2 du$$

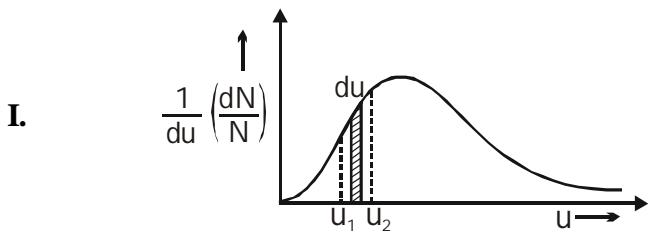
Here, $dN/N = \text{fraction of molecules having speeds between } u \text{ and } u + du$.

and $\frac{1}{N} \left(\frac{dN}{du} \right) = \text{fraction of molecules having speed between } u \text{ to } u + du \text{ per unit interval of speed.}$

= Maxwell distribution function.

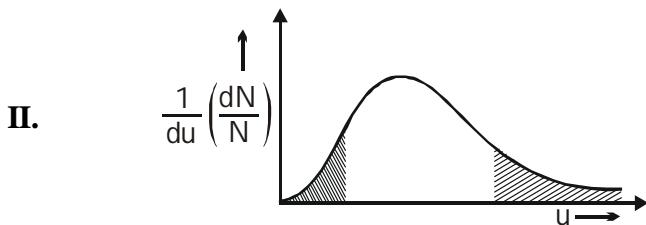
According to this expression, the fraction $\frac{dN}{N}$ of molecules depends only on temperature having speeds between u and $u + du$ for a gas of molar mass M . Thus for a given temperature, this fraction has a constant value.

11.1 Properties of Maxwell's graph :

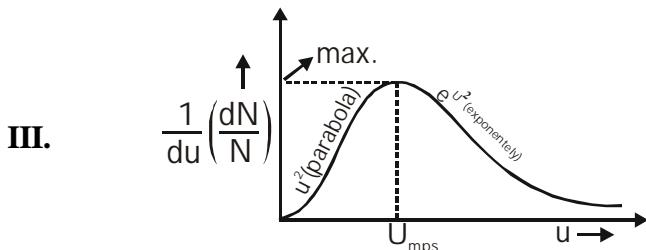


$$\text{Area between } u_1 \text{ and } u_2 = \int_{u_1}^{u_2} \frac{1}{du} \left(\frac{dN}{N} \right) du = \int_{u_1}^{u_2} \left(\frac{dN}{N} \right) du$$

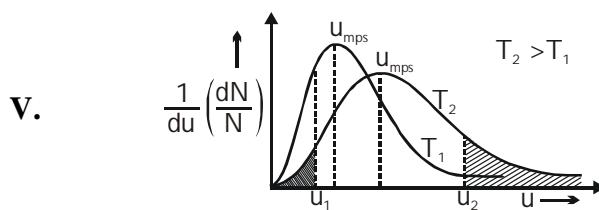
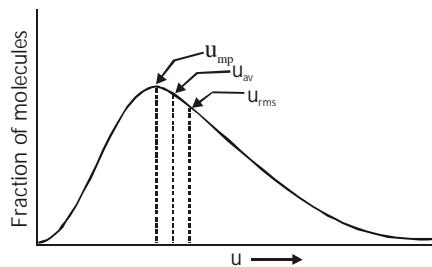
Hence, total fraction of particles with speed between u_1 and u_2
 = Area under the curve represents fraction of molecules.



It can be seen from the above figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers.

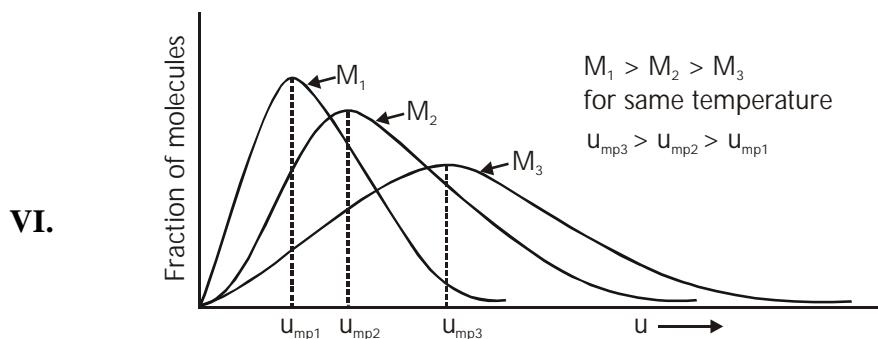


The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u , however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed (U_{mps}). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

IV Graph between fraction of molecules vs molecular speeds :


Total area under the curve will be constant and will be unity at all temperatures. The above figure illustrates the distribution of speeds at two temperatures T_1 and T_2 . Since the total no. of molecules is same at both temperatures, increase in the K.E. of the molecules results decrease in fraction of molecules having lower speed range and increase in fraction of molecules having higher speed range on increasing the temperature.

On increasing temperature the value of u_{mps} (most probable speed) will increase. Also the curve at the higher temperature T_2 has its u_{mps} shifted to a higher value compared with that for T_1 , whereas corresponding fraction of molecules has decreased. But at the same time, the curve near u_{mps} has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

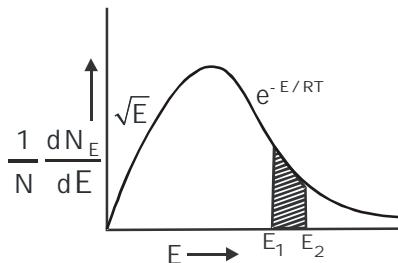


At a given temperature u_{mps} will be more for lighter gas (M_3) but fraction of molecules moving with u_{mps} will be more for heavier gas (M_1).

Note : Effect of M and T are opposite.

11.2 Maxwell Distribution of kinetic energy :

By Maxwell equation : $dN = 4\pi N \left(\frac{M}{2\pi RT} \right)^{3/2} \cdot e^{-\frac{Mu^2}{2RT}} u^2 du = 2\pi \left(\frac{1}{\pi RT} \right)^{3/2} \sqrt{E} \cdot e^{-E/RT} dE$



The shaded area of this graph indicate the fraction of particles having energy between E_1 and E_2

Ex.33 Four particles have speed 2, 3, 4 and 5 cm/s respectively. Find their avg. & rms speed :

Sol. $U_{avg.} = \frac{U_1 + U_2 + U_3 + \dots + U_N}{N}$

$$U_{avg.} = \frac{2+3+4+5}{4} = 3.5 \text{ cm/s}$$

$$U_{r.m.s.} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2 + \dots}{N}}$$

$$u_{rms} = \sqrt{\frac{2^2 + 3^2 + 4^2 + 5^2}{4}} = \frac{\sqrt{54}}{2} \text{ cm/s}$$

Ex.34 At what temperature do the average speed of $\text{CH}_{4(g)}$ molecule equal the average speed of O_2 molecule at 300 K ?

Sol. $(U_{avg})_{\text{CH}_4} = (U_{avg})_{\text{O}_2}$

$$\sqrt{\frac{8RT}{\pi \times 16}} = \sqrt{\frac{8 \times R \times 300}{\pi \times 32}}$$

$$T = 150 \text{ K}$$

Ex.35 At 27°C find the ratio of root mean square speeds of ozone to oxygen :-

$$\text{Sol. } \frac{U_{\text{rms}}(\text{O}_3)}{U_{\text{rms}}(\text{O}_2)} = \sqrt{\frac{\frac{3RT}{M.W_{\text{O}_3}}}{\frac{3RT}{M.W_{\text{O}_2}}}} = \sqrt{\frac{M.W_{\text{O}_2}}{M.W_{\text{O}_3}}} = \sqrt{\frac{32}{48}} = \sqrt{\frac{2}{3}}$$

Ex.36 The temperature at which U_{rms} of He becomes equal to U_{mp} of CH_4 at 500 K.

$$\text{Sol. } (U_{\text{rms}})_{\text{He}} = (U_{\text{mp}})_{\text{CH}_4}$$

$$\sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} = \sqrt{\frac{2RT_{\text{CH}_4}}{M_{\text{CH}_4}}}$$

$$\frac{3T}{4} = \frac{2 \times 500}{16}$$

$$T = \frac{250}{3} \text{ K}$$

Ex.37 Calculate the root mean square speed of H_2 molecules under following condition.

- (a) 2 mole of H_2 at 27°C.
- (b) 3 mole of H_2 in a 5 lit container at 10^5 Pa.
- (c) 4 mole of H_2 at the density of 1 gm/ml at 10^5 Pa.

$$\text{Sol. (a) } U_{\text{r.m.s.}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J/mol K} \times 300 \text{ K}}{2 \times 10^{-3} \text{ kg}}} = 1934.24 \text{ m/sec.}$$

$$\text{(b) } U_{\text{r.m.s.}} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3 \times 10^5 \text{ Pa} \times 5 \times 10^{-3} \text{ m}^3}{3 \text{ mol} \times 2 \times 10^{-3} \text{ kg}}} = 500 \text{ m/sec.}$$

$$\text{(c) } U_{\text{r.m.s.}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5 \text{ Pa}}{10^3 \text{ kg/m}^3}} = 17.32 \text{ m/sec.}$$

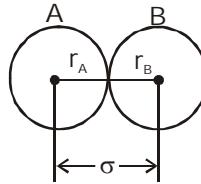
12. COLLISION PARAMETERS :

Assumption :

All the particles (molecules or atoms) have rigid, similar shape and size and are spherical in nature that will not change after collision.

12.1 Collision diameter : It is the closest distance between the centres of two molecules taking part in collision.

$$\text{Collision diameter } (\sigma) = r_A + r_B$$



12.2 Collision Frequency :

It is the total number of molecular collisions taking place per second per unit volume of the gas.

The no. of collisions made by a single molecule with other molecules per unit time (**collision number**) are given by

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{\text{avg}} N^*$$

The total number of bimolecular collision per unit time per unit volume is given as Z_{11} (**collision frequency**)

$$Z_{11} = \frac{1}{2} (Z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi \sigma^2 U_{\text{avg}} N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{\text{avg}} N^{*2}$$

(f) If the collisions involve two unlike molecules, the no. of bimolecular collision is given as Z_{12} .

$$Z_{12} = \pi \sigma_{12}^2 \left(\frac{8kT}{\pi \mu} \right)^{\frac{1}{2}} N_1^* N_2^*$$

Where N_1^* and N_2^* are the no. of molecules per unit volume of the two types of gases,

σ_{12} is the average diameter of two molecules, that is $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$ & μ is the reduced mass,

that is $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$, m_1 & m_2 are the mass of single molecule respectively 1 and 2.

12.3 Mean free path :

The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{distance travelled per unit time}}{\text{No. of collisions made by single molecule per unit time}}$$

$$= \frac{U_{\text{avg}}}{Z_1} = \frac{U_{\text{avg}}}{\sqrt{2}\pi\sigma^2 U_{\text{avg}} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

12.4 Wall collision :

It represents the total number of molecules colliding at the wall per unit area per unit time.

$$Z_w = \frac{1}{4} \cdot N^* \cdot u_{\text{av}} = \frac{P \cdot N_A}{\sqrt{2\pi MRT}}$$

12.5 Rate of effusion :

If the cross-section area of orifice in the vessel is 'A', then the number of molecules effusing out per unit time is

$$r_{\text{eff.}} = Z_w \cdot A = \frac{P \cdot N_A \cdot A}{\sqrt{2\pi MRT}}$$

Ex.38. Calculate λ , Z_1 and Z_{11} for oxygen at 298 K and 10^{-3} mm Hg. Given $\sigma = 3.61 \times 10^{-8}$ cm.

$$\text{Sol. } N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 0.324 \times 10^{20}$$

$$U_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8}{3.14} \times \frac{8.314 \times 298}{32 \times 10^{-3}}} = 444.138 \text{ m/sec}$$

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{\text{avg}} N^* = \sqrt{2} \times 3.14 \times 3.61 \times 10^{-10} \text{ m} \times 444.138 \text{ m} \times 0.324 \times 10^{20} \\ = 8.326 \times 10^3 \text{ sec}^{-1}$$

$$Z_{11} = \frac{1}{2} Z_1 N^* = \frac{1}{2} \times 8.326 \times 10^3 \text{ sec}^{-1} \times 0.324 \times 10^{20} = 13.488 \times 10^{22} \text{ m}^{-3} \text{ sec}^{-1};$$

$$\lambda = \frac{U_{\text{avg}}}{Z_1} = \frac{444.138 \text{ m/sec}}{8.326 \times 10^3 \text{ sec}^{-1}} = 5.334 \times 10^{-2} \text{ m}$$

Ex.39 Two flask A and B have equal volume. A is maintained at 300 K and B at 600 K while A contains H₂ gas, B has an equal mass of CH₄ gas. Assuming ideal behaviour for both the gases, find the following.

- (a) Flask containing greater number of moles
- (b) Flask in which pressure is greater
- (c) Flask in which U_{avg} of the molecules are greater
- (d) Flask with greater mean free path of molecules (Collision diameters of H₂ & CH₄ may be taken same)
- (e) Flask with greater molar kinetic energy.
- (f) Flask in which the total kinetic energy is greater
- (g) Flask in which Z₁ and Z₁₁ are greater

Sol.

(a) $N_{H_2} = \frac{m}{2} N_A ; N_{CH_4} = \frac{m}{16} N_A$

\therefore molecules of H₂ in flask A > molecules of CH₄ in flask B

(b) P_AV = n_ART_A ; P_BV = n_BRT_B

$$\Rightarrow \frac{P_A}{P_B} = \frac{n_A T_A}{n_B T_B} = \frac{m/2}{m/16} \times \frac{300}{600} = 4$$

\therefore pressure of H₂ in flask A > pressure of CH₄ in flask B

(c) $(U_{avg})_A = \sqrt{\frac{8 RT_A}{\pi M_A}} ; (U_{avg})_B = \sqrt{\frac{8 RT_B}{\pi M_B}}$

$$\frac{(U_{avg})_A}{(U_{avg})_B} = \sqrt{\frac{T_A}{T_B} \times \frac{M_B}{M_A}} = \sqrt{\frac{300}{600} \times \frac{16}{2}} = 2$$

$\therefore U_{avg}$ of H₂ in flask A > U_{avg} of CH₄ in flask B

(d) $\lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}} = \frac{1}{\sqrt{2\pi\sigma^2} \times P} \propto kT$ [where $N^* = P/kT$]

$$\frac{\lambda_A}{\lambda_B} = \frac{T_A}{T_B} \times \frac{P_B}{P_A} = \frac{300}{600} \times \frac{1}{4} = \frac{1}{8}$$

$$\therefore \lambda_B > \lambda_A$$

(e) molar K.E. = $\frac{3}{2}RT$

$$\therefore T_B > T_A$$

\therefore KE of CH_4 in flask B > KE of H_2 in flask A

(f) $(KE)_{\text{total}} = \frac{3}{2}RT \times n$

$$\frac{(KE)_{T,A}}{(KE)_{T,B}} = \frac{(300 \times \frac{m}{2})}{(600 \times \frac{m}{16})} = \frac{1}{2} \times 8 = 4$$

$$\therefore (KE)_{T,A} > (KE)_{T,B}$$

(g) (i) $Z_1 = \sqrt{2\pi\sigma^2} U_{\text{avg}} N^*$

$$\frac{(Z_1)_A}{(Z_1)_B} = \frac{(U_{\text{avg}})_A}{(U_{\text{avg}})_B} \times \frac{N_A^*}{N_B^*} = 2 \times \frac{N_A}{N_B} = 2 \times 8 = 16$$

$$\therefore (Z_1)_A > (Z_1)_B \quad (Z_1)_A > (Z_1)_B$$

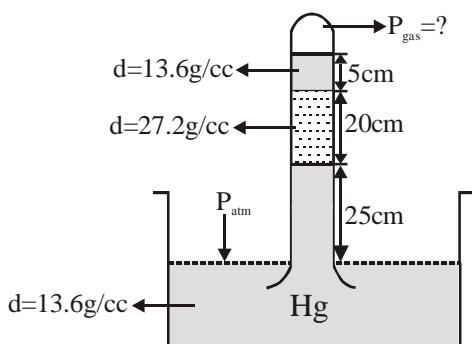
(ii) $Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{\text{avg}} N^{*2}$

$$\frac{(Z_{11})_A}{(Z_{11})_B} = \frac{(U_{\text{avg}})_A}{(U_{\text{avg}})_B} \times \frac{(N_A^*)^2}{(N_B^*)^2} = 2 \times \frac{N_A}{N_B} = 2 \times 8^2 = 128$$

$$\therefore (Z_{11})_A > (Z_{11})_B$$

EXERCISE (S-1)

1. In the following arrangement find the pressure of gas (in cm of Hg).
 (Assume that atmospheric pressure $P_{\text{atm}} = 75 \text{ cm of Hg}$)

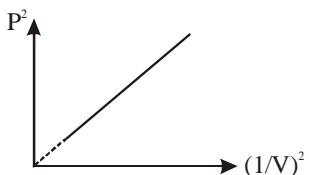


- 2.
-

Find pressure of gas in cm of Hg enclosed in tube.

BOYLE'S LAW

3. Consider the following graph



Graph is plotted for 1 mol of gas at 400K, find slope of curve.

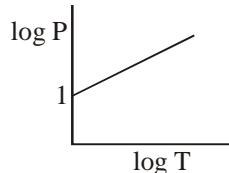
$$[\text{Take : } R = 0.08 \frac{\text{L} - \text{atm}}{\text{mol} - \text{K}}]$$

4. Two glass bulbs A and B are connected by a very small tube having a stop cock. Bulb A has a volume of 100 ml and contained the gas, while bulb B was empty on opening the stop cock, the pressure fell down to 40% at constant temperature. Find out the volume of bulb B in mL.

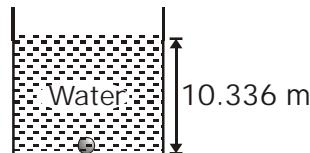
5. A glass bulb of 2 L capacity is filled by helium gas at 10 atm pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is 1 atm.

CHARLES LAW

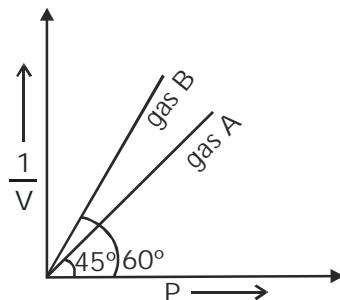
6. Calculate the volume which 4 litre of gas at 0°C will occupied at 100°C and the same pressure.
7. In constant volume container of 0.821 litre, log P vs log T is plotted as shown in graph. Calculate number of moles of ideal gas present in container :



8. A certain amount of a gas at 27°C and 1 bar pressure occupies a volume of 25 m³. If the pressure is kept constant and the temperature is raised to 77°C, what will be the volume of the gas ?
9. (a) Radius of a bubble at the bottom of the tank shown below was found to be 1 cm, then find the radius of the bubble at the surface of water considering the temperature at the surface & bottom being same.



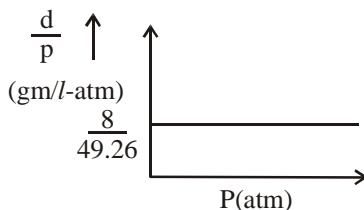
- (b) If absolute temperature at the surface is 4 times that at the bottom, then find radius of bubble at the surface.
10. (a) Plot the curve between PT vs T at const V & constant no. of moles.
- (b) Find the number of moles of gas taken when the volume of the vessel is 82.1 ml and $\frac{d}{dT} [PT] \text{ at } 300 \text{ K} = 300$ for the given curve.
11. At constant temperature of 273 K, $\left(\frac{1}{V}\right)$ v/s P are plotted for two ideal gases A and B as shown.
(V in litre & P in atm)



Find out the number of moles of gas A and B.

IDEAL GAS EQUATION

12. For an ideal gas, the following graph is obtained at constant temperature of 300 K.
 The molar mass of gas (in gm/mol) is -



13. The density of phosphorus vapours at 327°C and 1 atm is 2.52 gm/lit. If molecular formula of phosphorus is P_x , then calculate 'X'. (**Atomic weight of : P = 31**)
14. Density of ideal gas at 2.46 atm and 300 K is 0.8 gm/l. Hence gm-molar mass of gas is
 $[R = 0.082 \text{ L-atm/mol-K}]$
15. In a hospital respiratory unit the pressure gauge reads 4500 mm Hg for 10 L tank containing compressed O_2 , how many litres of O_2 can be delivered from tank at atmospheric pressure of 750 mm Hg. (Take temperature to be constant at TK)
16. While resting, the average human male use 0.2 dm³ of O_2 per hour at 1 atm & 300 K for each kg of body mass. Assume that all this O_2 is used to produce energy by oxidising glucose in the body . What is the mass of glucose required per hour by a resting male having mass 60 kg . What volume, at

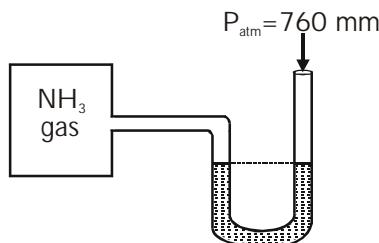
$$1 \text{ atm} \& 300 \text{ K of } CO_2 \text{ would be produced } (R = 0.08 \frac{L - atm}{mol - K})$$

17. A human adult breathes in approximately 0.50 dm³ of air at 1.00 bar with each breath. If an air tank holds 100 dm³ of air at 200 bar, how many breathes the tank will supply ?
18. A gas at a pressure of 5.0 bar is heated from 0°C to 546°C and simultaneously compressed to one third of its original volume. What will be the final pressure ?
19. 3.6 g of an ideal gas was injected into a bulb of internal volume of 8 L at pressure P atm and temp T K. The bulb was then placed in a thermostat maintained at (T + 15)K, 0.6 g of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

DALTON'S LAW OF PARTIAL PRESSURE

20. The partial pressures of N_2 , O_2 and CO_2 in a vessel are 38 cm of Hg, 190 torr and 0.5 atm, respectively . The total pressure of the mixture at the same temperature is.
21. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is.
22. A mixture of hydrogen and oxygen at one bar pressure contains 20% , by weight of hydrogen. The partial pressure of hydrogen will be.

23. A closed vessel contains equal number of nitrogen and oxygen molecules at pressure of P mm. If nitrogen is removed from the system, then the pressure will be.
24. If 2 lit. of gas A at 1.5 atm and 3 lit. of gas B at 2 atm are mixed in a 5 lit. container then find the final pressure, considering all are at same temperature.
25. One mole of N_2 and 3 moles of H_2 are taken in a container of capacity 8.21 lit. at 300 K to produce NH_3 . Find the partial pressures of N_2 and H_2 if partial pressure of NH_3 after sufficient time was found to be 3 atm.
26. A manometer attached to a flask contains NH_3 gas have no difference in mercury level initially as shown in diagram. After the sparking into the flask, it have difference of 19 cm in mercury level in two columns. Calculate % dissociation of ammonia.



27. A gaseous mixture at 760 mm in a cylinder has 65% N_2 , 15% O_2 and 20 % CO_2 by volume. Calculate the partial pressure of each gas.

CONTAINER PROBLEMS

28. A toy balloon originally held 1.0 gm of He gas and had a radius 10 cm. During the night, 0.875 gm of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant P and T conditions, what was the radius of the balloon the next morning.
29. The density of a mixture of O_2 and N_2 gases at 1 atm and 273K is 0.0013 gm/ml. If partial pressure of O_2 in the mixture is A then calculate value of 25A.
30. A containers contains air above liquid water. Total pressure was 800 torr. What will be the final pressure if volume is doubled. (Aqueous tension = 40 torr)
31. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mmHg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume that temperature to be 50°C. Aqueous tension at 50°C = 93 mmHg.

DIFFUSION / EFFUSION

32. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of rate of diffusion of helium to methane is.

33. At a particular fixed temperature the gas A_n is 52% dissociated according to the following reaction
 $A_n(g) \rightleftharpoons nA(g)$
 The equilibrium mixture effuses 1.25 times slower than pure oxygen gas under identical condition.
 If atomic wt. of A is 32, then find "n" ?
34. H_2 and O_2 are kept in mass ratio 1 : 8 respectively at 6 atm. If small orifice is made then relative rate of effusion of H_2 with respect to O_2 initially is.
35. A mixture of H_2 and O_2 in 2 : 1 mole ratio is allowed to diffuse through a orifice. Calculate the composition of gases coming out initially.
36. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.
37. A mixture of N_2 and H_2 has initially mass ratio of 196 : 1 then find after how many steps we can obtain a mixture containing 1 : 14 mole ratio of N_2 and H_2 .
38. Find the ratio of moles of SO_2 to CH_4 after fifth diffusion steps if their initially mole ratio is 8 : 1.

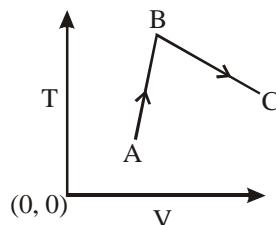
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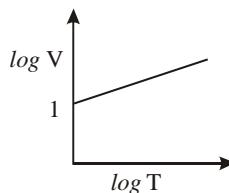
39. Calculate the root mean square speed of H_2 molecules under following conditions.
- 2 mole of H_2 at 27°C
 - 3 mole of H_2 in a 5 litre container at 10^5 Pa
 - 4 mole of H_2 at the density of 1gm / ml at 10^5 Pa
40. Root mean square speed of an unknown gas at 727°C is 10^5 cm/second. Calculate molar mass of unknown gas (in gram/mole) [Take $R = \frac{25}{3}$ J/mole-K].
41. How many times is the rms speed of molecules in 8 gm O_2 gas at 1200 K and 10 bar, relative to rms speed of molecules in 16 gm O_2 gas at 300K and 20 bar ?
42. Average translational kinetic energy of an ideal gas molecule at 27°C is 3.88×10^{-x} eV. Hence x is
 $(1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$
43. When the temperature of an ideal gas is increased from 27°C to 927°C the kinetic energy will be increased by x times. Find the value of x ?
44. Two flask A and B have equal volume at 100 K and 200 K and have pressure 4 atm and 1 atm respectively. The flask A contains H_2 gas and B contains CH_4 gas. The collision diameter of CH_4 is twice that of H_2 . Calculate ratio of mean free path of CH_4 to H_2 .
45. If the mean free path is 10 cm at one bar pressure then its value at 5 bar pressure, if temperature is kept constant.

EXERCISE (O-1)

Single Correct :

1. In the given isobaric process shown by graph between T & V.





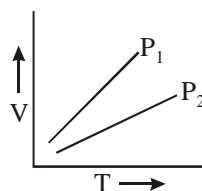
3. A gas at a pressure of 5.0 atm is heated from 0°C to 546°C and simultaneously compressed to one-third of its original volume. Hence final pressure is
(A) 10 atm (B) 30 atm (C) 45 atm (D) 0.1

4. A flask containing air (open to the atmosphere) is heated from 300 K to 500 K. Then % of air escaped to the atmosphere is -
(A) 20.0 (B) 40 (C) 60 (D) 80

5. 10 g of a gas at 1 atm, 273 K occupies 5 litres. The temp. at which the volume becomes double for the same mass of gas at the same pressure is ?
(A) 273K (B) -273°C (C) 273°C (D) 546°C

6. A gas is found to have a formula $[CO]_x$. If its vapour density is 70 the value of x is
(A) 2.5 (B) 3.0 (C) 5.0 (D) 6.0

7. V versus T curves at constant pressure P_1 and P_2 for an ideal gas are shown in Fig.
Which is correct

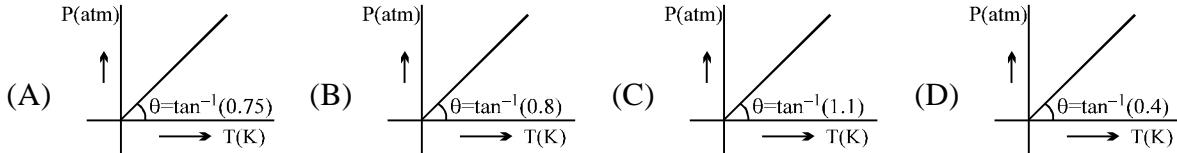


- (A) $P_1 > P_2$ (B) $P_1 < P_2$ (C) $P_1 = P_2$ (D) All of the above

8. A container when is empty weighs 50 gm. After certain liquid of density 25 gm/dm^3 is filled its mass becomes equal to 100 gm. The volume of the container will be :
- (A) 0.25 dm^3 (B) 0.5 dm^3 (C) 1 dm^3 (D) 2 dm^3
9. A vessel contains mono atomic 'He' at 1 bar and 300 K, determine its number density -
- (A) $2.4 \times 10^{25} \text{ m}^{-3}$ (B) $6.8 \times 10^{23} \text{ m}^{-3}$ (C) $4.8 \times 10^{26} \text{ m}^{-3}$ (D) $9.2 \times 10^{27} \text{ m}^{-3}$
10. A rigid container containing 10 gm gas at some pressure and temperature. The gas has been allowed to escape from the container due to which pressure of the gas becomes half of its initial pressure and temperature become $(2/3)^{\text{rd}}$ of its initial. The mass of gas (in gms) escaped is
- (A) 7.5 (B) 1.5 (C) 2.5 (D) 3.5
11. The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be
- (A) 1 : 6 (B) 7 : 8 (C) 6 : 1 (D) 1 : 4
12. In a rigid container NH_3 is kept at certain temperature, if on doubling the temperature it is completely dissociated into N_2 and H_2 . Find final pressure to initial pressure ratio :
- (A) 4 (B) 2 (C) $\frac{1}{2}$ (D) $\frac{1}{4}$
13. Gas A (1 mol) dissociates in a closed rigid container of volume 0.16 lit. as per following reaction.



If degree of dissociation of A is 0.4 and remains constant in entire range of temperature, then the correct P vs T graph is [Given R = 0.08 lit-atm/mol/K]



14. A gaseous reaction,



is carried out in a 0.0821 litre closed container initially containing 1 mole of gas A. After sufficient time a curve of P (atm) vs T (K) is plotted and the angle with x-axis was found to be 42.95° . The degree of association of gas A is [Given : $\tan 42.95 = 0.8$]

- (A) 0.4 (B) 0.6 (C) 0.5 (D) 0.8

- 15.** 4.0 g of argon has pressure P and temperature T K in a vessel. On keeping the vessel at 50° higher temperature, 0.8 g of argon was given out to maintain the pressure P. The original temperature was :
 (A) 73 K (B) 100 K (C) 200 K (D) 510 K

16. The total pressure exerted by a number nonreacting gases is equal to the sum of partial pressure of the gases under the same conditions is known as :
 (A) Boyle's law (B) Charle's law (C) Avogadro's law (D) Dalton's law

17. Dalton's law cannot be applied for which gaseous mixture at normal temperatures:
 (A) O₂ and N₂ (B) NH₃ and HCl (C) He and N₂ (D) CO₂ and O₂

18. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is - [AIEEE-2008]
 (A) 2/3 (B) $\frac{1}{3} \times \frac{273}{298}$ (C) $\frac{1}{3}$ (D) $\frac{1}{2}$

19. A closed vessel contains helium and ozone at a pressure of P atm. The ratio of He and oxygen atoms is 1 : 1. If helium is removed from the vessel, the pressure of the system will reduce to :
 (A) 0.5 P atm (B) 0.75 P atm (C) 0.25 P atm (D) 0.33 P atm

20. At constant temperature 200 cm³ of N₂ at 720 mm and 400 cm³ of O₂ at 750 mm pressure are put together in a one litre flask. The final pressure of mixture is
 (A) 111 mm (B) 222 mm (C) 333 mm (D) 444 mm

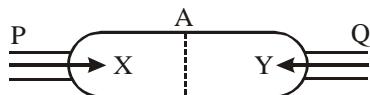
21. If saturated vapours are compressed slowly (temperature remaining constant) to half the initial volume, the vapour pressure will :
 (A) Become four times (B) become doubled
 (C) Remain unchanged (D) Become half

22. A box of 1L capacity is divided into two equal compartments by a thin partition which are filled with 2g H₂ and 16g CH₄ respectively. The pressure in each compartment is recorded as P atm. The total pressure when partition is removed will be :
 (A) P (B) 2P (C) P/2 (D) P/4

23. A vessel has N₂ gas and water vapours at a total pressure of 1 atm. The vapour pressure of water is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at the same temperature the total pressure of this system in the new vessel is -
 (A) 3.0 atm (B) 1 atm (C) 3.33 atm (D) 2.4 atm

24. Which gas effuses fastest under identical conditions -
 (A) N₂ (B) O₂ (C) Cl₂ (D) CH₄

34. 3 mole of gas "X" and 2 moles of gas "Y" enters from end "P" and "Q" of the cylinder respectively. The cylinder has the area of cross-section A, shown as under -



The length of the cylinder is 150 cm. The gas "X" intermixes with gas "Y" at the point A. If the molecular weight of the gases X and Y is 20 and 80 respectively, then what will be the distance of point A from Q?

- (A) 75cm (B) 50cm (C) 37.5 cm (D) 90 cm
35. Under identical experiment conditions which of the following pairs of gases will be most easy to separate by using effusion process -
 (A) H₂ and T₂ (B) SO₂ and SO₃ (C) NH₃ and CH₄ (D) U²³⁵O₂ and U²³⁸O₂
36. Certain volume of He gas takes 10 sec for its diffusion, how much time will be taken by CH₄ gas to disffuse it's same volume under identical conditions -
 (A) 5 sec (B) 10 sec (C) 20 sec (D) 40 sec
37. A football bladder contains equimolar proportions of H₂ and O₂. The composition by mass of the mixture effusing out of punctured football is in the ratio (H₂ : O₂)
 (A) 1 : 4 (B) 2 $\sqrt{2}$: 1 (C) 1 : 2 $\sqrt{2}$ (D) 4 : 1
38. Consider the following pairs of gases A and B.

	A	B
(a)	CO	N ₂
(b)	O ₂	O ₃
(c)	²³⁵ UF ₆	²³⁸ UF ₆

Relative rates of effusion of gases A to B under similar condition is in the order:

- (A) a < b < c (B) a < c < b (C) a > b > c (D) a > c > b
39. For the reaction

$$2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}),$$
 what is the % of NH₃ converted if the mixture diffuses twice as fast as that of SO₂ under similar conditions.
 (A) 3.125 % (B) 31.25 % (C) 6.25 % (D) 62.5 %
40. A 4 : 1 molar mixture of He & CH₄ kept in a vessel at 20 bar pressure. Due to a hole in the vessel, gas mixture leaks out. What is the composition of mixture effusing out initially -
 (A) 8 : 1 (B) 4 : 1 (C) 1 : 4 (D) 4 : 3

- 41.** Calculate the ratio of rate of effusion of O_2 and H_2 from a container containing 16gm O_2 and 2gm H_2
 (A) 1 : 8 (B) 8 : 1 (C) 1 : 4 (D) 4 : 1

42. The number of effusion steps required to convert a mixture of H_2 and O_2 from 240 : 1600 (by mass) to 3072 : 20 (by mass) is
 (A) 2 (B) 4 (C) 5 (D) 6

43. The density of the gaseous mixture in a vessel (CH_4 and He) at 2 atmosphere pressure and 300 K is 0.9756 g/lit. If a small pin-hole is made on the wall of the vessel, through which gases effuse, then which of the followings is the correct composition (by volume) of the gases CH_4 and He effusing out initially ?
 (A) 1 : 1 (B) 2 : 1 (C) 3 : 1 (D) 1 : 4

44. At STP, the order of root mean square speed of molecules H_2 , N_2 , O_2 and HBr is :
 (A) $H_2 > N_2 > O_2 > HBr$ (B) $HBr > O_2 > N_2 > H_2$
 (C) $HBr > H_2 > O_2 > N_2$ (D) $N_2 > O_2 > H_2 > HBr$

45. Four particles have speed 2, 3, 4 and 5 cm/s respectively. Their rms speed is :
 (A) 3.5 cm/s (B) $\left(\frac{27}{2}\right)$ cm/s (C) $\sqrt{54}$ cm/s (D) $\left(\frac{\sqrt{54}}{2}\right)$ cm/s

46. A flask has 10 molecules out of which four molecules are moving at 7ms^{-1} & the remaining are moving at same speed of $X\text{ ms}^{-1}$. If Urms of the gas is 5 ms^{-1} . The value of 'X' will be
 (A) 5 (B) 3 (C) 9 (D) 16

47. If the average velocity of N_2 molecules is 0.3 m/sec. at 27°C , then the velocity of 0.6 m/sec will take place at :
 (A) 273 K (B) 927 K (C) 1000 K (D) 1200 K

48. Which of the following expression does not give root mean square velocity –
 (A) $\left(\frac{3RT}{M_w}\right)^{\frac{1}{2}}$ (B) $\left(\frac{3P}{DM_w}\right)^{\frac{1}{2}}$ (C) $\left(\frac{3P}{D}\right)^{\frac{1}{2}}$ (D) $\left(\frac{3PV}{nM_w}\right)^{\frac{1}{2}}$

49. Which one of the following gases would have the highest R.M.S. velocity at 25°C ?
 (A) Oxygen (B) Carbon dioxide (C) Sulphur dioxide (D) Carbon monoxide

50. At what temperature would the rms speed of a gas molecule have twice its value at 100°C ?
 (A) 4192 K (B) 1492 K (C) 9142 K (D) 2491 K

51. Two flasks X and Y have capacity 1L and 2L respectively and each of them contains 1 mole of a gas. The temperature of the flask are so adjusted that average speed of molecules in X is twice as those in Y. The pressure in flask X would be
 (A) same as that in Y (B) half of that in Y (C) twice of that in Y (D) 8 times of that in Y

52. Temperature at which most probable speed of O_2 becomes equal to root mean square speed of N_2 is [Given : N_2 at $427^\circ C$]
(A) 732 K (B) 1200 K (C) 927 K (D) 800 K
53. The density ratio of O_2 and H_2 is 16 : 1. The ratio of their U_{rms} is :-
(A) 4 : 1 (B) 16 : 1 (C) 1 : 4 (D) 1 : 16
54. Which of the gas have highest fraction of molecules at $27^\circ C$ in most probable speed region -
(A) H_2 (B) N_2 (C) O_2 (D) CO_2
55. The av. K.E./mole of an ideal monoatomic gas at $27^\circ C$ is
(A) 900 cal (B) 1800 cal (C) 300 cal (D) None
56. The average kinetic energy of an ideal gas per molecule in SI units at $25^\circ C$ will be :
(A) $6.17 \times 10^{-21} \text{ kJ}$ (B) $6.17 \times 10^{-21} \text{ J}$
(C) $6.17 \times 10^{-20} \text{ J}$ (D) $7.16 \times 10^{-20} \text{ J}$
57. At what temperature will be total kinetic energy (KE) of 0.30 mole of He be the same as the total KE of 0.40 mole of Ar at 400 K :
(A) 400 K (B) 373 K (C) 533 K (D) 300 K
58. Average K.E. of CO_2 at $27^\circ C$ is E. The average kinetic energy of N_2 at the same temperature will be
(A) E (B) $22E$ (C) $E/22$ (D) $E/\sqrt{2}$
59. If a gas expands at constant temperature then :
(A) No. of gaseous molecule decreases
(B) kinetic energy of molecule decreases
(C) K.E. remain same
(D) K.E. increases
60. Total translational kinetic energy possessed by 8 gm methane at $273^\circ C$
($R = 2 \text{ Cal/mol-K}$)
(A) 819 calorie (B) 409.5 calorie (C) 1638 calorie (D) None of these
61. Ideal gas equation in terms of K.E. per unit volume E, is-
(A) $P = \frac{3}{2}RT$ (B) $P = \frac{2}{3}E$ (C) $P = \frac{2}{3}RT$ (D) $P = \frac{3}{2}RT$

- 62.** According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels - [AIEEE-2003]

(A) In a straight line path
(B) with an accelerated velocity
(C) In a circular path
(D) In a wavy path

63. What volume of hydrogen gas, at 273K and 1 atm pressure will be consumed in obtaining 21.6g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ? [AIEEE-2003]

(A) 44.8 L (B) 22.4 L (C) 89.6 L (D) 67.2 L

64. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by factor of which of the following ? [AIEEE-2004]

(A) 1/2 (B) $\sqrt{313/293}$ (C) 313/293 (D) 2

65. Three gases A, B and C are at same temperature. If their r.m.s. speed are in the ratio $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ then their molar masses will be in the ratio :
(A) $1 : 2 : 3$ (B) $3 : 2 : 1$ (C) $1 : \sqrt{2} : \sqrt{3}$ (D) $\sqrt{3} : \sqrt{2} : 1$

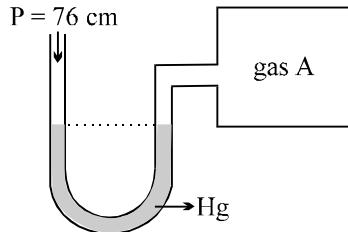
66. The following gases are present under similar condition of T, P & V. The longest mean free path stands for
(A) H_2 (B) N_2 (C) O_2 (D) Cl_2

67. At constant volume, Z_{11} is directly proportional to -
(A) \sqrt{P} (B) P (C) T^2 (D) T

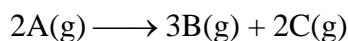
EXERCISE (O-2)

One or more may be correct :

1. An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.



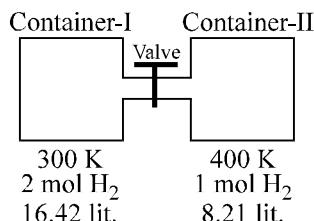
After sparking 'A' dissociates according to following reaction



If pressure of Gas "A" decreases to 0.8 atm. Then (Assume temperature to be constant and is 300 K)

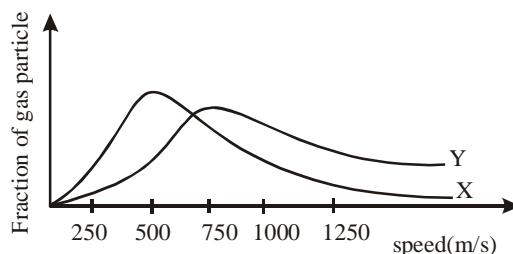
(A) total pressure increased by 1.3 atm (B) total pressure increased by 0.3 atm
 (C) total pressure increased by 22.3 cm of Hg (D) difference in mercury level is 228 mm.

2. Select the correct option(s) :



- (A) Pressure in container-I is 3 atm before opening the valve.
 (B) Pressure after opening the valve is 3.57 atm.
 (C) Moles in each compartment are same after opening the valve.
 (D) Pressure in each compartment are same after opening the valve.

3. The graph below shows the distribution of molecular speed of two ideal gases X and Y at 200K. on the basis of the below graph identify the correct statements -



- (A) If gas X is methane, then gas Y can be CO₂
 (B) Fraction of molecules of X must be greater than Y in a particular range of speed at 200K
 (C) Under identical conditions rate of effusion of Y is greater than that of X
 (D) The molar kinetic energy of gas X at 200K is equal to the molar kinetic energy of Y at 200K

4. Identify the correct statements when a fixed amount of ideal gas is heated in a container fitted with a movable piston always operating at constant pressure.
- (A) Average distance travelled between successive collisions will decreases.
(B) Collisions frequency increases since speed of the molecules increases with increase in temperature.
(C) Average relative speed of approach remains unaffected.
(D) Average angle of approach remains unaffected.
5. Choose the correct statement(s) among the following
- (A) Average molecular speed of gases increases with decrease in fraction of molecules moving slowly
(B) Rate of effusion of gases increases with increase in collision frequency at constant volume.
(C) Rate of effusion is inversely proportional to molecular weight of gas
(D) Mean free path does not change with change in temperature at constant pressure.
6. Which of the following quantities is the same for all ideal gases at the same temperature :
- (A) The kinetic energy of 1 mol
(B) The kinetic energy of 1 g
(C) The number of molecules in 1 mol
(D) The number of molecules in 1 g
7. Choose the correct statement(s) among the following -
- (A) The mean free path (λ) of gaseous molecules is directly proportional to temperature of gas at constant volume
(B) The mean free path (λ) of gaseous molecules is inversely proportional to pressure of gas at constant volume
(C) The mean free path (λ) of gaseous molecules is directly proportional to volume of gas at constant T
(D) The mean free path (λ) of gaseous molecules is directly proportional to volume of gas at constant P

- 8.** Which statement is/are correct for postulates of kinetic theory of gases -
- Gases are composed of molecules whose size is negligible compared with the average distance between them
 - Molecules moves randomly in straight lines in all directions and at various speeds.
 - When molecules collide with one another the collisions are elastic. In an elastic collision the loss of kinetic energy takes place
 - The average kinetic energy of a molecule is proportional to the absolute temperature.

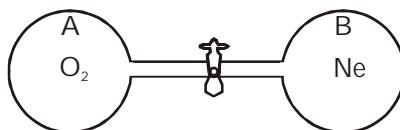
Paragraph for Question 9 to 11

The constant motion and high velocities of gas particles lead to some important practical consequences. One such consequence is that as minimum rapidly when they come in contact. The mixing of different gases by random molecular motion and with frequent collisions is called diffusion. A similar process in which gas molecules escape through a tiny hole into a vaccume is called effusion.

- 9.** Helium gas at 1 atm and SO_2 at 2 atm pressure, temperature being the same, are released separately at the same moment into 1 m long evacuated tubes of equal diameters. If helium reaches the other end of the tube in t sec, what distance SO_2 would traverse in the same time interval in the other tube ?
- 25 cm
 - 50 cm
 - 60 cm
 - 75 cm
- 10.** 4 g of H_2 effused through a pinhole in 10 sec at constant temperature and pressure. The amount of oxygen effused in the same time interval and at the same conditions of temperature and pressure would be :
- 4 g
 - 8 g
 - 16 g
 - 32 g
- 11.** For 10 min. each at 27°C , from two identical bulbs helium and an unknown gas X at equal pressures are leaked into a common vessel of 3 L capacity. The resulting pressure is 4.1 atm and the mixture contains 0.4 mol of helium. The molar mass of gas X is :
- 16
 - 32
 - 64
 - None of these

Paragraph for Question 12 to 13

Initially, flask A contained oxygen gas at 27°C and 950 mm of Hg, and flask B contained neon gas at 27°C and 900 mm. Finally, the two flasks were joined by means of a narrow tube of negligible volume equipped with a stopcork and gases were allowed to mix up freely. The final pressure in the combined system was found to be 910 mm of Hg.



12. What is the correct relationship between volumes of the two flasks ?
 (A) $V_B = 3V_A$ (B) $V_B = 4V_A$ (C) $V_B = 5V_A$ (D) $V_B = 4.5V_A$
13. How many moles of gas are present in flask A in the final condition, if volume of flask B is 304 litre ? ($R = 0.08 \text{ atm L mol}^{-1} \text{ K}^{-1}$)
 (A) 7.58 (B) 3.79 (C) 15.16 (D) None of these

TABLE TYPE QUESTION :
Column-I

(Gases at different conditions)

(A) CH_4 at 27°C

(B) SO_2 at 27°C

(C) 4 gm He at 1 atm and
24.6 litre

(D) 32 gm O_2 at 127°C

Column-II

(Value of speed (m/s))

(P) $U_{\text{rms}} = 342.5$

(Q) $U_{\text{mp}} = 1100$

(R) $U_{\text{rms}} = 685$

(S) $U_{\text{rms}} = 550$

Column-III

(I) Molar K.E. = 3750 Joule

(II) Molar K.E. = 5000 Joule

(III) Average K.E. per gram
= 937.5 Joule

(IV) Average K.E. per gram
= 234 Joule.

(Given : $R = \frac{25}{3} \frac{\text{J}}{\text{mol} \times \text{K}}$, $\sqrt{30} = 5.48$, $\sqrt{\frac{2}{3}} = 0.8$, $\sqrt{5} = 2.2$)

14. Which of the following is correct
 (A) A ; R ; 4 (B) A ; R ; 2 (C) A ; Q ; 4 (D) B ; R ; 1
15. Which of the following is correct
 (A) B ; Q ; 1 (B) B ; Q ; 2 (C) B ; P ; 1 (D) C ; S ; 3
16. Which of the following is correct
 (A) C ; Q ; 3 (B) D ; R ; 2 (C) D ; S ; 1 (D) D ; S ; 4

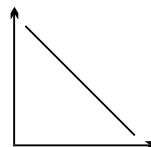
Match the column:

17. Match the entries in column I with entries in Column II and then pick out correct options.

Column I
Column II

(A) $\frac{1}{V^2}$ vs P for ideal gas at

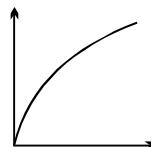
(P)



constant T and n.

(B) V vs $\frac{1}{T}$ for ideal gas at

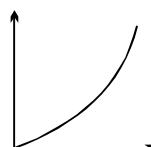
(Q)



constant P and n

(C) log P vs log V for ideal gas

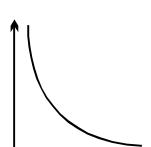
(R)



at constant T and n.

(D) V vs $\frac{1}{P^2}$ for ideal gas

(S)



at constant T and n.

EXERCISE (JM)

1. The molecular velocity of any gas is :- [AIEEE-2011]
- inversely proportional to the square root of temperature
 - inversely proportional to absolute temperature
 - directly proportional to square of temperature
 - directly proportional to square root of temperature
2. α , v and u represent most probable velocity, average velocity and root mean square velocity respectively of a gas at a particular temperature. The correct order among the following is - [JEE(Main)-2012]
- $\alpha > u > v$
 - $v > u > \alpha$
 - $u > v > \alpha$
 - $u > \alpha > v$
3. An open vessel at 300 K is heated till $\frac{2}{5}$ th of the air in it is expelled. Assuming that the volume of the vessel remains constant, the temperature to which the vessel is heated is :- [JEE(Main-online)-2012]
- 750 K
 - 400 K
 - 500 K
 - 1500K
4. For 1 mol of an ideal gas at constant temperature T, the plot of $(\log P)$ against $(\log V)$ is a (P : Pressure, V : Volume) :- [JEE(Main-online)-2012]
- Straight line parallel to x-axis
 - Curve starting at origin
 - Straight line with a negative slope
 - Straight line passing through origin
5. The relationship among most probable velocity, average velocity and root mean square velocity is respectively :- [JEE(Main-online)-2012]
- $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$
 - $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$
 - $\sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$
 - $\sqrt{8/\pi} : \sqrt{3} : \sqrt{2}$
6. Which one of the following is the wrong assumption of kinetic theory of gases ? [JEE(Main-online)-2013]
- All the molecules move in straight line between collision and with same velocity.
 - Molecules are separated by great distances compared to their sizes.
 - Pressure is the result of elastic collision of molecules with the container's wall.
 - Momentum and energy always remain conserved.
7. By how many folds the temperature of a gas would increase when the root mean square velocity of the gas molecules in a container of fixed volume is increased from 5×10^4 cm/s to 10×10^4 cm/s? [JEE(Main-online)-2013]
- Four
 - three
 - Two
 - Six

8. For gaseous state, if most probable speed is denoted by C^* , average speed by \bar{C} and mean square speed by C , then for a large number of molecules the ratios of these speeds are :-

[JEE(Main-offline)-2013]

- (1) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$ (2) $C^* : \bar{C} : C = 1.128 : 1.225 : 1$
 (3) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$ (4) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$

- 9.** A gaseous compound of nitrogen and hydrogen contains 12.5% (by mass) of hydrogen. The density of the compound relative to hydrogen is 16. The molecular formula of the compound is :

[JEE(Main-online)-2014]

- (1) NH_2 (2) NH_3 (3) N_3H (4) N_2H_4

- 10.** The initial volume of a gas cylinder is 750.0 mL. If the pressure of gas inside the cylinder changes from 840.0 mm Hg to 360.0 mm Hg, the final volume the gas will be

[JEE(Main-online)-2014]

- (1) 1.750 L (2) 7.50 L (3) 3.60 L (4) 4.032 L

11. The temperature at which oxygen molecules have the same root mean square speed as helium atoms have at 300 K is : (Atomic masses : He = 4 u, O = 16 u) [JEE(Main-online)-2014]

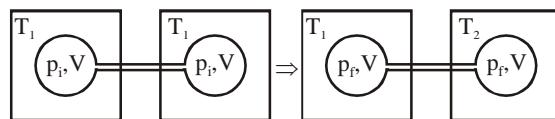
- (1) 1200 K (2) 600 K (3) 300 K (4) 2400 K

12. Which of the following is not an assumption of the kinetic theory of gases ?

 - (1) Gas particles have negligible volume. [JEE-Mains (online)-2015]
 - (2) A gas consists of many identical particles which are in continual motion.
 - (3) At high pressure, gas particles are difficult to compress.
 - (4) Collisions of gas particles are perfectly elastic.

13. Two closed bulbs of equal volume(V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2 . The final pressure p_f is :-

[JEE-Mains-2016]



- (1) $2p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$ (2) $p_i \left(\frac{T_1 T_2}{T_1 + T_2} \right)$ (3) $2p_i \left(\frac{T_1}{T_1 + T_2} \right)$ (4) $2p_i \left(\frac{T_2}{T_1 + T_2} \right)$

14. At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen (N_2) at 4 bar. The molar mass of gaseous molecule is:- [JEE-Mains-2017(ONLINE)]

(1) 28 g mol^{-1} (2) 56 g mol^{-1} (3) 224 g mol^{-1} (4) 112 g mol^{-1}

15. Assuming ideal gas behaviour, the ratio of density of ammonia to that of hydrogen chloride at same temperature and pressure is : (Atomic wt. of Cl = 35.5 u) [JEE-Mains-2018(ONLINE)]

(1) 0.64 (2) 1.64 (3) 1.46 (4) 0.46

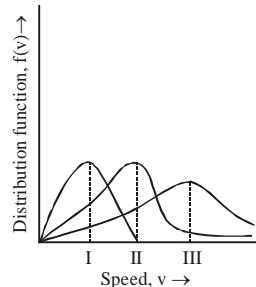
16. Points I, II and III in the following plot respectively correspond to. (V_{mp} : most probable velocity)

(1) V_{mp} of N_2 (300K); V_{mp} of H_2 (300K); V_{mp} of O_2 (400K) [JEE-Mains-2019(ONLINE)]

(2) V_{mp} of H_2 (300K); V_{mp} of N_2 (300K); V_{mp} of O_2 (400K)

(3) V_{mp} of O_2 (400K); V_{mp} of N_2 (300K); V_{mp} of H_2 (300K)

(4) V_{mp} of N_2 (300K); V_{mp} of O_2 (400K); V_{mp} of H_2 (300K)



17. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m^3 at 1000 K. Given R is the gas constant in $\text{JK}^{-1} \text{ mol}^{-1}$, x is : [JEE-Mains-2019(ONLINE)]

(1) $\frac{2R}{4+12}$

(2) $\frac{2R}{4-R}$

(3) $\frac{4-R}{2R}$

(4) $\frac{4+R}{2R}$

18. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is : [JEE-Mains-2019(ONLINE)]

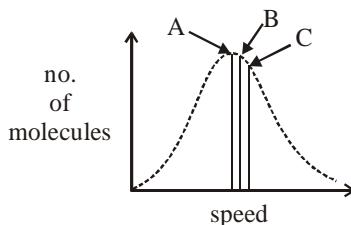
(1) 750°C

(2) 500°C

(3) 750 K

(4) 500 K

19. Identify the correct labels of A, B and C in the following graph from the options given below: [JEE(Main-online)-2020]



Root mean square speed (V_{rms}) ; most probable speed (V_{mp}) ; Average speed ($V_{av.}$)

(1) A – V_{rms} ; B – V_{mp} ; C – $V_{av.}$

(2) A – $V_{av.}$; B – V_{rms} ; C – V_{mp}

(3) A – V_{mp} ; B – V_{rms} ; C – $V_{av.}$

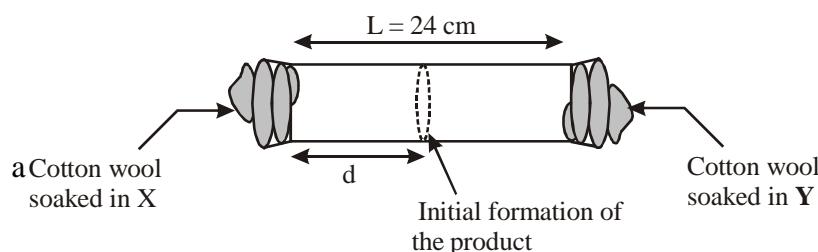
(4) A – V_{mp} ; B – $V_{av.}$; C – V_{rms}

EXERCISE (JA)

- 1.** To an evacuated vessel with movable piston under external pressure of 1 atm., 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to [JEE 2011]

Paragraph for Question 2 & 3

X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length $L = 24\text{ cm}$, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K . Vapours of X and Y react to form a product which is first observed at a distance $d\text{ cm}$ from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



4. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment A after the system attains equilibrium is _____. [JEE 2018]

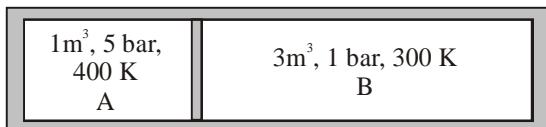


Figure 1

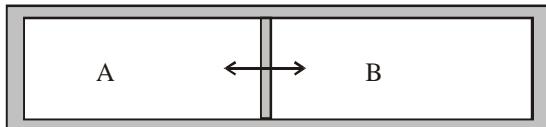


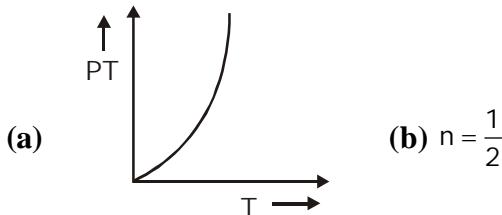
Figure 2

5. Which of the following statement(s) is (are) correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (ε_{av}) of a molecule in a gas at equilibrium ?
- (1) U_{rms} is doubled when its temperature is increased four times [JEE 2019]
 - (2) ε_{av} at a given temperature does not depend on its molecular mass
 - (3) U_{rms} is inversely proportional to the square root of its molecular mass
 - (4) ε_{av} is doubled when its temperature is increased four times

ANSWER KEY

EXERCISE (S-1)

1. Ans.(5) 2. Ans. (90) 3. Ans.(1024) 4. Ans. (150)
 5. Ans.(18) 6. Ans.(5.46) 7. Ans. (100) 8. Ans. 29.17 m^3
 9. Ans. (a) $2^{1/3} \text{ cm}$; (b) 2 cm
 10. Ans.



11. Ans. $n_A = \frac{1}{22.4}$, $n_B = \frac{1}{22.4\sqrt{3}}$
 12. Ans.(4) 13. Ans.(4) 14. Ans (8) 15. Ans. (50)
 16. 15 gm ; 12 dm³ 17. Ans.39,800 breaths. 18. Ans.45 bar
 19. Ans. T = 75 K , P = 0.062 atm
 20. Ans.(1.25 atm) 21. Ans.(15:16) 22. Ans.(0.8 bar) 23. Ans.(0.5 P mm)
 24. 1.8 atm 25. $P_{H_2} = 1.5 \text{ atm}$, $P_{N_2} = 4.5 \text{ atm}$ 26. 25 %
 27. $p_{N_2} = 494 \text{ mm}$, $p_{O_2} = 114 \text{ mm}$, $p_{CO_2} = 152 \text{ mm}$
 28. 5 cm. 29. Ans. (7) 30. Ans. (420) 31. P = 146.5 mm
 32. Ans. (2 : 1) 33. Ans. (4) 34. Ans. (8) 35. 8/1
 36. XeF₆. 37. n = 4 38. 1/4
 39. Ans.(a) 1934.24 m/sec. (b) 500 m/sec. (c) 17.32 m/sec.
 40. Ans. (25) 41. Ans.(2) 42. Ans. (2) 43. Ans. (4)
 44. Ans.(2) 45. Ans.(2)

EXERCISE (O-1)

- | | | | |
|-------------|-------------|-------------|-------------|
| 1. Ans.(C) | 2. Ans.(C) | 3. Ans.(C) | 4. Ans.(B) |
| 5. Ans.(C) | 6. Ans.(C) | 7. Ans.(B) | 8. Ans.(D) |
| 9. Ans.(A) | 10. Ans.(C) | 11. Ans.(C) | 12. Ans.(A) |
| 13. Ans.(B) | 14. Ans.(B) | 15. Ans.(C) | 16. Ans.(D) |
| 17. Ans.(B) | 18. Ans.(C) | 19. Ans.(C) | 20. Ans.(D) |
| 21. Ans.(C) | 22. Ans.(A) | 23. Ans.(D) | 24. Ans.(D) |
| 25. Ans.(A) | 26. Ans.(B) | 27. Ans.(B) | 28. Ans.(D) |
| 29. Ans.(A) | 30. Ans.(C) | 31. Ans.(D) | 32. Ans.(B) |
| 33. Ans.(D) | 34. Ans.(C) | 35. Ans.(A) | 36. Ans.(C) |
| 37. Ans.(A) | 38. Ans.(B) | 39. Ans.(C) | 40. Ans.(A) |
| 41. Ans.(A) | 42. Ans.(C) | 43. Ans.(A) | 44. Ans.(A) |
| 45. Ans.(D) | 46. Ans.(B) | 47. Ans.(D) | 48. Ans.(B) |
| 49. Ans.(D) | 50. Ans.(B) | 51. Ans.(D) | 52. Ans.(B) |
| 53. Ans.(C) | 54. Ans.(D) | 55. Ans.(A) | 56. Ans.(B) |
| 57. Ans.(C) | 58. Ans.(A) | 59. Ans.(C) | 60. Ans.(A) |
| 61. Ans.(B) | 62. Ans.(A) | 63. Ans.(D) | 64. Ans.(C) |
| 65. Ans.(A) | 66. Ans.(A) | 67. Ans.(A) | |
-

EXERCISE (O-2)

- | | | | |
|--------------|---------------------------------------|---------------|----------------|
| 1. Ans.(B,D) | 2. Ans.(A,D) | 3. Ans. (C,D) | 4. Ans.(D) |
| 5. Ans.(A,B) | 6. Ans.(A,C) | 7. Ans.(C,D) | 8. Ans.(A,B,D) |
| 9. Ans.(B) | 10. Ans.(C) | 11. Ans.(C) | 12. Ans.(B) |
| 13. Ans.(B) | 14. Ans.(A) | 15. Ans.(C) | |
| 16. Ans.(A) | 17. Ans.(A)→R ; (B)→S ; (C)→P ; (D)→Q | | |
-

EXERCISE (JM)

- | | | | |
|-------------|-------------|-------------|-------------|
| 1. Ans.(4) | 2. Ans.(3) | 3. Ans.(3) | 4. Ans.(3) |
| 5. Ans.(1) | 6. Ans.(1) | 7. Ans.(1) | 8. Ans.(3) |
| 9. Ans.(4) | 10. Ans.(1) | 11. Ans.(4) | 12. Ans.(3) |
| 13. Ans.(4) | 14. Ans.(4) | 15. Ans.(4) | 16. Ans.(4) |
| 17. Ans.(3) | 18. Ans.(4) | 19. Ans.(4) | |
-

EXERCISE (JA)

- | | | | |
|----------------|------------|------------|---------------|
| 1. Ans.(7) | 2. Ans.(C) | 3. Ans.(D) | 4. Ans.(2.22) |
| 5. Ans.(1,2,3) | | | |
-

CHAPTER 4

REAL GAS

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IMPORTANT NOTES

CHAPTER 4

REAL GAS

1. INTRODUCTION :

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

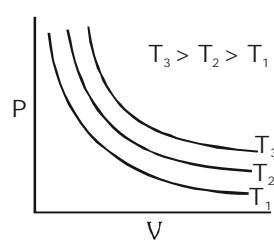
- (i) The volume of gas particle is negligible compared to volume of container (while the real gas particle may have some significant volume).
- (ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

1.1 Comparision between Real and Ideal gas :

IDEAL GAS

(i) $PV = nRT$

(ii) No liquifaction is possible.

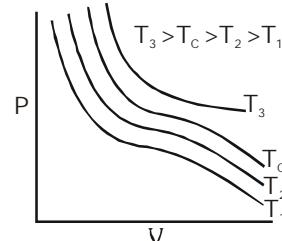


REAL GAS

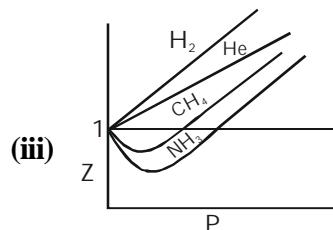
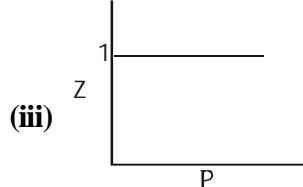
(i) $PV \neq nRT$

\Rightarrow If $PV > nRT$ (Gas is less compressible than ideal gas).
If $PV < nRT$ (Gas is more compressible than ideal gas).

(ii) Liquifaction is possible below a certain temperature.



\Rightarrow Follow critical phenomena and can not liquefy above T_c .



(iv) No interaction force is present between gas particles.

(v) Volume of gas particles is negligible w.r.t. volume of container.

(iv) Interaction force exist between gas particles which vary depending upon conditions.

(v) Volume of gas particles has significant value and can not be neglected normally w.r.t. volume of container.

1.2 Vander Waal Equation of real gases

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

Van der Waal corrected the ideal gas equation by taking the effect of

- (a) Molecular volume
- (b) Molecular attraction

(A) Volume correction :

In the ideal gas equation, $P_i V_i = nRT$, V_i represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume V_f is the total volume V minus the volume occupied by the gas molecules.

Real volume of gas = Actual volume of container – volume occupied by molecules in motion.

$$V_f = V - nb \text{ for } n \text{ mole of gas}$$

Where b is termed the 'excluded volume' or 'co-volume' per mole.

It is constant and characteristic for each gas.

$$b = 4 \times \text{volumes of one molecule} \times N_A$$

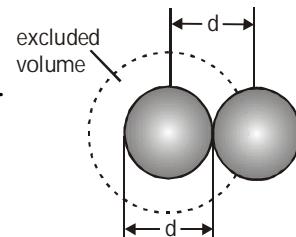
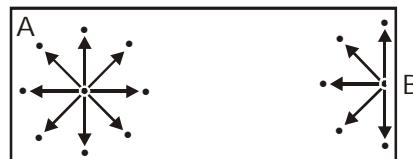


Illustration of excluded volume

(B) Pressure correction :

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A in the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.



Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only in one side of the vessel, i.e. towards its centre, with the result of that, this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V . However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V . Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas law by a factor proportional to n^2/V^2 . Letting a be the proportionality constant, we can write

$$P(\text{actual}) = P(\text{ideal}) - \frac{an^2}{V^2} \quad \text{or} \quad P(\text{ideal}) = P(\text{actual}) + \frac{an^2}{V^2}$$

'a' is a constant which depends upon the nature of the gas,
Combining the two corrections,
for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

and for n mole of gas $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

The constants 'a' and 'b' :

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

- (i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.
- (ii) The gas having higher value of 'a' can be liquefied easily and therefore H₂ and He are not liquefied easily.
- (iii) Unit of 'a' is atm lit² mole⁻² or dyne cm⁴ mole⁻² or Nm⁴mol⁻²
- (iv) Unit of 'b' is lit mole⁻¹ or cm³ mole⁻¹ or m³ mol⁻¹

The van der Walls constants for some common gases

Gas	a (atmL ² mol ⁻²)	b (L mol ⁻¹)
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

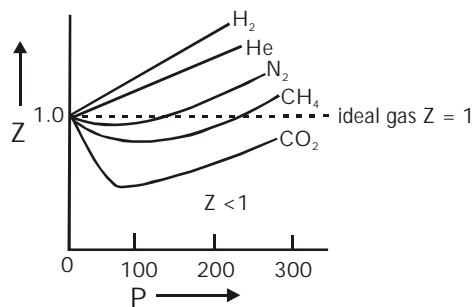
1.3 Compressibility factor (Z) :

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z),

$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

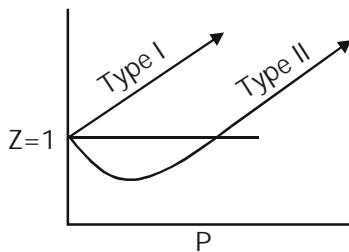
1.4 Plots of compressibility factor vs pressure :

- (i) For an ideal gas $Z = 1$ and is independent of temperature and pressure.
- (ii) Exceptional behaviour of H_2 and He :
For these gases $Z > 1$ at 0°C .
- (iii) Effect of pressure :
At very low P, $PV_m \approx RT$ i.e. $Z \approx 1$
At low P, $PV_m < RT$ i.e. $Z < 1 \Rightarrow$ attractive forces dominant
At high P, $PV_m > RT$ i.e. $Z > 1 \Rightarrow$ repulsive forces dominant
- (iv) For the gases which are easily liquefied (e.g. CO_2) Z dips sharply below the ideal line in the low pressure region.
- (v) Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours, Z approaches unity with increase in temperature.



1.5 Verification of compressibility factor using Van Der Waal's equation:

Variation of Z with P for real gas at any temperature is given by following graph.



Van der waal equation :

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

(i) At low pressure and constant temperature

At low pressure V_m will be high hence b can be neglected in comparison to V_m . But $\frac{a}{V_m^2}$ can't be neglected as pressure is low. Thus equation would be

$$\left(P + \frac{a}{V_m^2} \right) V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \Rightarrow Z < 1$$

Substituting $V_m = \frac{RT}{P}$ in above equation ; $Z = 1 - \frac{aP}{R^2 T^2}$

At low pressure, real gas is easily compressible as compared to an ideal gas.

(ii) At high pressure and constant temperature

At high pressure the V_m will be low. So b can't be neglected in comparison to V_m but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P .

Then van der Waals' equation will be

$$P(V_m - b) = RT$$

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1 \Rightarrow (Z > 1)$$

At high pressure, gas is more difficult to compress as compared to an ideal gas.

(iii) At low pressure and very high temperature.

V_m will be very large, hence ' b ' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large.

$$PV_m = RT \text{ (ideal gas condition)}$$

(iv) For H_2 or He $a \approx 0$ because molecules are smaller in size or vander Waal's forces will be very weak.

$$P(V_m - b) = RT$$

$$\text{So } Z = 1 + \frac{Pb}{RT}$$

This explains type I plot.

Ex.1. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that $a = 3.592 \text{ atm l}^2 \text{ mol}^{-2}$, $b = 0.0427 \text{ L/mol}$. Also, if the volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K.

Sol. Vander waal's equation

$$\left[p + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

$$n_{\text{CO}_2} = 5, V = 1 \text{ litre}, T = 320 \text{ K}, a = 3.592, b = 0.0427$$

$$\therefore \left[P + 25 \times \frac{3.592}{1} \right] [1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$$\therefore P = 77.218 \text{ atm}$$

For ideal behaviour of gas, $PV = nRT$

$$\therefore P \times 1 = 5 \times 0.0821 \times 320$$

$$\therefore P = 131.36 \text{ atm}$$

$$\text{For one mole } \left[P + \frac{a}{V^2} \right] [V - b] = RT$$

$$\therefore P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

$$\therefore P = 0.9922 \text{ atm}$$

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

Ex.2 One mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If vander waal's constants are $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.1383 \text{ L mol}^{-1}$, calculate compressibility factor Z under,

(a) low pressure region. (b) high pressure region.

Sol. (a) Under low pressure region, V is high

$$\therefore (V - b) \approx V$$

$$\left(P + \frac{a}{V^2} \right) V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV} \right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure region, P is high,

$$\left(P + \frac{a}{V^2} \right) \approx P$$

$$\therefore P(V - b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{b}{V-b} = 1 + \frac{0.1383}{35 - 0.1383} = 1 + 0.004 \approx 1.004 \quad \left(\because P = \frac{RT}{V-b} \right)$$

Ex.3 One way of writing the equation of state for real gases is $PV = RT \left[1 + \frac{B}{V} + \dots \right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

Sol. According to van der Waal's equation

$$\left[P + \frac{a}{V^2} \right] [V - b] = RT \text{ or } P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V} \quad \text{or} \quad PV = RT \left[\frac{V}{V-b} - \frac{a}{VRT} \right]$$

$$\text{or} \quad PV = RT \left[\left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\therefore \left[1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V} \right)^2 + \dots$$

$$\therefore PV = RT \left[1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[1 + \left(b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \dots \right]$$

$$\therefore B = b - \frac{a}{RT}$$

2. BOYLE TEMPERATURE :

(i) It is temperature at which a real gas behave ideally in a wide range of pressure.

(ii) (a) Temperature < Boyle temperature

Z < 1, low pressure range

Z > 1, high pressure range

(b) Temperature = Boyle temperature

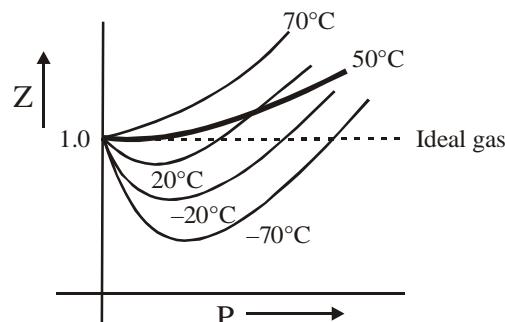
Z = 1, low pressure range

Z > 1, high pressure range

(c) At temperature > Boyle temperature

Z > 1, at all pressure

(d) $T \rightarrow \infty, Z \rightarrow 1$



On increasing the temperature, the thermal energy increases and simultaneously the attractive forces decreases. Hence a temperature comes at which the thermal energy become too high that it balances the effect of attraction and gas molecules becomes independent.

If at Boyle temperature, pressure is increased, molecules come more closer. Due to repulsive force, Z becomes greater than 1.

2.1 CALCULATION OF T_B :

(i) $PV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$ at low pressure.

At $T = T_B$, the second initial coefficient should be 0

$$B = 0$$

$$\text{or } b - \frac{a}{RT_B} = 0$$

$$\therefore T_B = \boxed{\frac{a}{Rb}}$$

(ii) Calculus method :

At Boyle temperature, $\left(\frac{\partial Z}{\partial P} \right)_T = 0$ at low pressure.

Ex.4 Derive the expression for compressibility factor of a vanderwaal gas at Boyle temperature.

Solution : $Z = \frac{V_m}{V_m - b} - \frac{a}{V_m - RT}$

At Boyle temperature,

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m R \times \frac{a}{Rb}}$$

$$Z = \frac{V_m}{V_m - b} - \frac{b}{V_m}$$

$$Z = \frac{V_m^2 - V_m b + b^2}{V_m (V_m - b)}$$

$$Z = 1 + \frac{b^2}{V_m (V_m - b)}$$

Ex.5 Calculate the volume occupied by 2 moles of a vanderwall gas at 5 atm 800 K.

Given : $a = 4.0 \text{ atm } \ell^2 \text{ mol}^{-2}$, $b = 0.0625 \text{ } \ell \text{ mol}^{-1}$, $R = 0.08 \text{ } \ell \text{-atm/K-mol}$

Solution : $T_B = \frac{a}{Rb} = 800\text{K}$

Gas behave ideally at given condition.

$$PV = nRT$$

$$5 \times V = 2 \times 0.08 \times 800$$

$$V = 25.6 \text{ litre}$$

3. LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they exist in liquid state.

A gas can be liquefied by :

- (a) **Increasing pressure :** An increase in pressure results decrease in intermolecular distance.
- (b) **Decreasing temperature :** A decrease in temperature results decrease in kinetic energy of molecules.

Note : Due to absence of intermolecular forces, ideal gases can never be liquified.

3.1 Andrews Isotherms :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO₂. The types of isotherms are shown in figure.

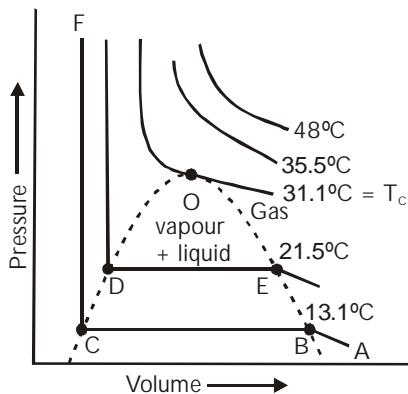


Fig : Isotherms for carbon dioxide

Observations from figure :

- (a) **At low temperatures** : For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B). At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density). At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium and CF represent liquid state.
The pressure corresponding to the line BC is vapour pressure of the liquid at that temperature.
- (b) **At lower temperatures** : Similar type of curve as in case (A) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.
- (c) **At high temperatures** : (say 48°C), the isotherms are like those of ideal gas. Gas does not liquify, even at very high pressure.
- (d) **At temperature (31.1°C)** : The horizontal portion is reduced to a point.
The isotherm at T_C is called **critical isotherm**.

$$\text{At point O, } \frac{dP}{dV} = 0.$$

The point O is called the **point of inflection**.

3.2 Critical parameters or critical constants :

Critical temperature (T_C) : The temperature above which a system can never be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exist is called the critical temperature T_C.

Critical pressure (P_C) : The minimum pressure required to liquefy the system at the temperature T_C is called the critical pressure P_C .

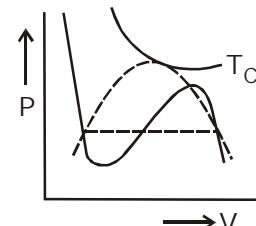
Critical volume (V_C) : The volume occupied by one mole of the system at critical temperature, T_C and critical pressure, P_C is called the critical volume (V_C) of the gas.

3.3 Determination of value of P_C , V_C and T_C :

The Vander waal's equation is

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

or $V_m^3 - \left(b + \frac{RT}{P} \right) V_m^2 + \frac{a}{P} V_m - \frac{ab}{P} = 0 \quad \dots \dots (1)$



This equation has three roots in V_m for given values of a , b , P and T . It is found that either all the three roots are real or one is real and the other two are imaginary.

At temperature lower than T_C , the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g., V_1 , V_2 and V_3 at pressure P_1 . On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as

$$(V_m - V') (V_m - V'') (V_m - V''') = 0$$

At the critical point $V' = V'' = V''' = V_C$

\therefore the equation becomes,

$$(V_m - V_C)^3 = 0$$

$$\text{or } V_m^3 - V_C^3 - 3V_C V_m^2 + 3 V_C^2 V_m = 0 \quad \dots \dots (2)$$

By comparing the coefficients in eq.(1) and eq(2)

$$3V_C = b + \frac{RT_c}{P_c}, \quad 3V_C^2 = \frac{a}{P_c}, \quad V_C^3 = \frac{ab}{P_c}$$

$$\text{By solving, } V_C = 3b, \quad P_c = \frac{a}{27b^2} \quad \text{and} \quad T_c = \frac{8a}{27Rb}$$

- The value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_c V_c}{R T_c} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{3}{8} = 0.375$$

If we compare the value of $\frac{P_c V_c}{R T_c} = 0.375$, with the experimental values, it has been found that the agreement is very poor.

Critical constants of gases

Gas	P _C (atm)	V _{m,c} (cm ³ mol ⁻¹)	T _C (K)
He	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
H ₂	12.8	65.5	33.3
O ₂	50.1	78.2	154.8
N ₂	33.5	90.1	126.2
CO ₂	72.8	94.0	304.2
H ₂ O	218.0	55.6	647.3
NH ₃	111.5	72.5	405.0
CH ₄	45.6	98.7	190.6
C ₂ H ₆	48.2	148.0	305.4

Ex.6 The critical temperature and pressure of CO₂ gas are 304.2 K and 72.9 atm respectively. What is the radius of CO₂ molecule assuming it to behave as vander Waal's gas ?

Sol. T_C = 304.2 K P_C = 72.9 atm

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

$$\therefore \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \quad \text{or} \quad b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

$$b = 4 N_A \times \frac{4}{3} \pi r^3 = 42.77 \text{ cm}^3$$

$$\text{or } r = (4.24)^{1/3} \times 10^{-8} \text{ cm} = 1.62 \times 10^{-8} \text{ cm}$$

$$\therefore \text{radius of CO}_2 \text{ molecule} = 1.62 \text{ \AA}$$

4. THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids posses fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The following general characteristics are exhibited by liquids :

(i) Shape :

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) Volume :

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong.

(iii) Density :

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL⁻¹ while that of water vapour under similar conditions as calculated from ideal gas law $\left(d = \frac{MP}{RT} \right)$ is 0.000588 g mL⁻¹.

(iv) Compressibility :

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little on increasing pressure. Thus, liquids are relatively incompressible compared to gases.

(v) Diffusion :

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi) Evaporation :

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules do not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation depends on the following factor.

(a) Nature of the liquid : The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :



→
Increasing extent of hydrogen bonding

(b) Surface area : Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

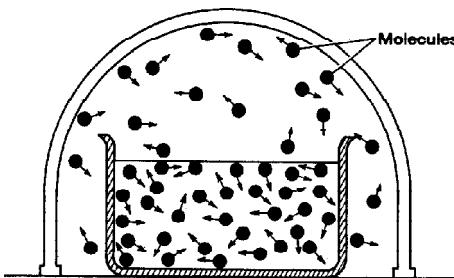
(c) **Temperature :** Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

(d) **Flow of air current over the surface :** Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation of liquid in open vessel.

(vii) Heat of vaporisation :

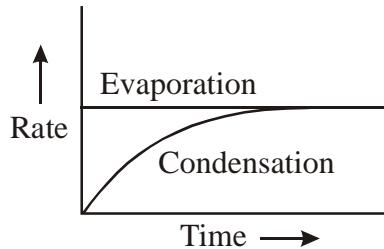
The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation. The heat of vaporisation depends on the strength of the intermolecular forces within the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

(viii) Vapour pressure :



When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they may be trapped. The return of the molecules from the vapour state of the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.



At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it may be given by ideal gas equation, assuming ideal behaviour.

$$P = \frac{n}{V} RT = CRT$$

where C is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporisable liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

Substance	Temperatures				
	0° C	20° C	40° C	80° C	100° C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	812.6	1693.3	
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

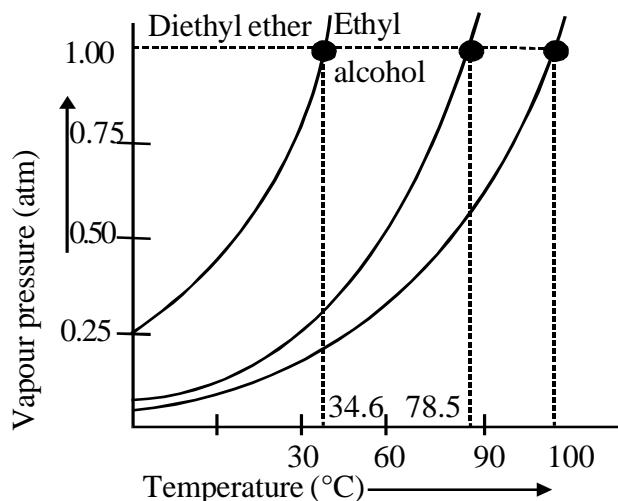
The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation**.

$$\log \times \frac{P_2}{P_1} = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Where ΔH is the latent heat of vaporisation and R is the molar gas constant.

(ix) Boiling point :

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.



The temperature of the liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

- (a) Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.
- (b) Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

Note. : Boiling does not occur when liquid is heated in a closed vessel.

(x) Freezing point :

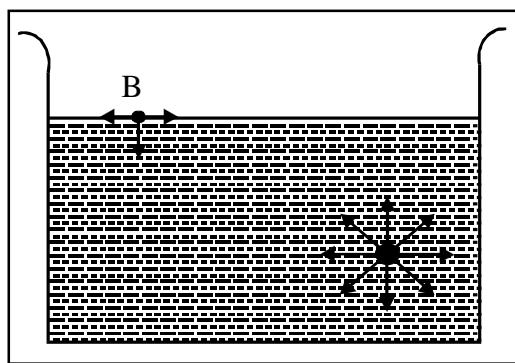
When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the rotational motion is seized. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point**.

Normal freezing point of a liquid is the temperature at which liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point, which is called the **heat of fusion**.

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls. But the effect of pressures is very small because solid as well as liquid are almost incompressible.

(xi) Surface tension :

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.



Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface. The unit of surface tension is dyne cm⁻¹. Surface tension is, thus, defined **as the force acting on the surface at right angles to any line of unit length.**

As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid may reduce its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

Many common phenomenon can be explained with the help of surface tension. Some are described here :

(a) Small droplets are spherical in shape :

The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) Insects can walk on the surface of water :

Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) Cleaning action of soap and detergents :

Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) Capillary action :

The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension.

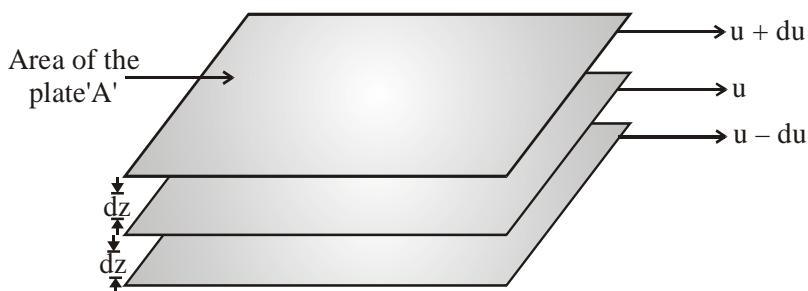
(e) Surface Energy :

The work required to be done to increase or extend surface area by unit area is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e. J m⁻² in S.I. system)

(xii) Viscosity :

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increase as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid, the layer above it accelerates its flow and the layer below this retards its flow.



Gradation of velocity in the laminar flow

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$ (A is the area of contact)

$F \propto A \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A \cdot \frac{du}{dz} \Rightarrow F = \eta A \frac{du}{dz}$$

' η ' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'h' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ($N \text{ s m}^{-2}$) = pascal second ($\text{Pa s} = 1 \text{ kg m}^{-1} \text{s}^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

$$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{s}^{-1} = 10^{-1} \text{ kg m}^{-1} \text{s}^{-1}$$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

SOME MISCELLANEOUS SOLVED EXAMPLES

1. Calculate the temperature of gas if it obeys vander waal's equation from the following data.
A flask of 25 litre contains 10 moles of a gas under 50 atm. Given $a = 5.46 \text{ atm litre}^{-2}$ and $b = 0.31 \text{ litre mol}^{-1}$.

Sol. Given, $P = 50 \text{ atm}$, $V = 25 \text{ litre}$, $n = 10$

$$a = 5.46 \text{ atm litre}^2 \text{mol}^{-2}, b = 0.031 \text{ litre mol}^{-1}$$

Now vander waal's equation for n mole of gas.

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

$$\left[50 + \frac{100 \times 5.46}{625} \right] [25 - 10 \times 0.031] = 10 \times 0.0821 \times T$$

$$\therefore T = 1529.93 \text{ K} = 1256.93^\circ\text{C}$$

2. The molar volume of He at 10.135 MPa and 273 K is 0.011075 of its molar volume of 101.325 kPa at 273K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.

Sol. For real gas : $\left[P + \frac{a}{V^2} \right] [V - b] = RT$

$$P [V - b] = RT \text{ (neglecting } a)$$

$$\therefore \frac{10.1325 \times 10^6}{101325} [V_1 - b] = 0.0821 \times 273$$

$$\text{or } 100 [V_1 - b] = 0.0821 \times 273 = 22.41 \quad \dots\dots(1)$$

$$\frac{101.325 \times 10^3}{101325} [V_2 - b] = 0.0821 \times 273$$

$$\text{or } [V_2 - b] = 22.41 \quad \dots\dots(2)$$

$$\text{by eq. (1)} \quad V_1 - = 0.2241 + b \quad \dots\dots(3)$$

$$\text{by eq. (2)} \quad V_2 - = 22.41 + b \quad \dots\dots(4)$$

$$\text{By eqs. (3) and (4), } \frac{V_1}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$\frac{0.011075 V_2}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$(V_1 = 0.011075 V_2 \text{ is given})$$

$$\therefore b = 0.024 \text{ litre mol}^{-1} = 24 \text{ cm}^3 \text{mol}^{-1}$$

$$\therefore b = 4N \times v = 4 \times 6.023 \times 10^{23} \times \frac{4}{3}\pi r^3$$

$$\text{or } 24 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$\therefore r = 1.33 \times 10^{-8} \text{ cm}$$

3. Calculate vander waal's constant a and b if critical temperature and critical pressure are 30°C and 72 atm respectively.

Sol. $T_C = \frac{8a}{27Rb}$ and $P_C = \frac{a}{27b^2}$

$$\therefore \frac{T_C}{P_C} = \frac{8b}{R} \text{ or } b = \frac{RT_C}{8P_C}$$

$$\therefore b = \frac{0.0821 \times 303}{8 \times 72} = 0.043 \text{ litre mol}^{-1}$$

$$\begin{aligned} a &= 27P_C \times b^2 = 27 \times 72 \times (0.043)^2 \\ &= 3.59 \text{ litre}^2 \text{atm mol}^{-2} \end{aligned}$$

4. Using vander waal's equation, calculate the constant, 'a' when two mole of a gas confined in a four litre temperature of 300K. The value of 'b' is 0.05 litre mol⁻¹.

Sol. Vander waal's equation for n mole of gas is

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

Given V = 4 litre ; P = 11.0 atm, T = 300 K

b = 0.05 litre mol⁻¹ ; n = 2

$$\text{Thus, } \left[11 + \frac{2^2 a}{4^2} \right] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300.$$

$$\therefore a = 6.46 \text{ atm litre}^2 \text{ mol}^2$$

5. One way of writing the equation for state for real gases is,

[JEE 1997]

$$P \bar{V} = RT \left[1 + \frac{B}{V} + \dots \right] \text{ where } B \text{ is a constant.}$$

Derive an approximate expression for 'B' in terms of van der Waals' constants 'a' & 'b'.

Ans. $B = \left(b - \frac{a}{RT} \right)$

Sol. $\left[P + \frac{a}{V_m^2} \right] [V_m - b]$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$Z = \left(1 - \frac{b}{V_m} \right)^{-1} - \frac{a}{V_m RT}$$

$$= 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \dots - \frac{a}{V_m RT}$$

$$= 1 + \left[b - \frac{a}{RT} \right] \frac{1}{V_m} + \frac{b^2}{V_m^2} \dots \dots \dots \quad \dots (1)$$

Also, $P\bar{V} = RT \left[1 + \frac{B}{V} + \dots \right]$

$$\Rightarrow \frac{P\bar{V}}{RT} = \left[1 + \frac{B}{V} + \dots \right] \quad \dots (2)$$

⇒ Comparing equation (1) & (2), we get

$$B = b - \frac{a}{RT}$$

6. Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is $0.05 \text{ litre mol}^{-1}$. [JEE 1998]

Ans. $6.52 \text{ atm L}^2 \text{ mol}^{-2}$

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

$$\left[11 + \frac{2^2 \times a}{4 \times 4} \right] [4 - 2 \times 0.05] = 2 \times 0.0821 \times 300$$

$$\Rightarrow a = 6.52 \text{ atm L}^2 \text{ mol}^{-2}$$

7. A gas will approach ideal behaviour at :
- low temperature and low pressure
 - low pressure and high temperature

[JEE 1999]

- low temperature and high pressure
- high temperature and high pressure .

Ans. (C)**Sol.** A gas approaches ideal behavior at High T & low P

8. The compressibility of a gas is less than unity at STP. Therefore ,

[JEE 2000]

- $V_m > 22.4 \text{ L}$
- $V_m < 22.4 \text{ L}$
- $V_m = 22.4 \text{ L}$
- $V_m = 44.8 \text{ L}$

Ans. (B)

Sol. $Z = \frac{(Vm)_{\text{real}}}{(Vm)_{\text{ideal}}} ; Z < 1$

$$\Rightarrow (Vm)_{\text{real}} < (Vm)_{\text{ideal}}$$

$$\therefore (Vm)_{\text{real}} < 22.4 \text{ L}$$

9. The compression factor (compressibility factor) for one mole of a Van der Waals' gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals' constant 'a'. [JEE 2001]

Ans. $1.256 \text{ atm L}^2 \text{ mol}^{-2}$

Sol. $Z = 1 - \frac{a}{VmRT}$

$$Z = \frac{PVm}{RT} \Rightarrow Vm = \frac{RTZ}{P}$$

$$Z = 1 - \frac{a}{(RT)^2} \times \frac{P}{Z}$$

$$0.5 = 1 - \frac{a \times 100}{(273 \times 0.0821)^2 \times .5}$$

$$a = 1.256 \text{ atm L}^2 \text{ mol}^{-2}$$

10. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3} . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

Determine

[JEE 2002]

- mol. wt.;
- molar volume;
- compression factor z of the vapour and
- which forces among the gas molecules are dominating, the attractive or the repulsive

Ans. (i) 18 g/mol , (ii) 50 L mol^{-1} , (iii) 1.218 , (iv) repulsive

Sol. (i) $\frac{r_{\text{gas}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{gas}}}}$

$$\Rightarrow \frac{4}{3} = \sqrt{\frac{32}{M_{\text{gas}}}}$$

$$\Rightarrow M_{\text{gas}} = 18$$

(ii) $V_m = \frac{18}{0.36} 50 \text{ L mol}^{-1}$

(iii) $Z = \frac{PVm}{RT} = \frac{1 \times 50}{0.0821 \times 500} = 1.218$

(iv) since, $Z > 1$ = Repulsive forces are operative

11. Positive deviation from ideal behaviour takes place because of

[JEE 2003]

(A) molecular attractions between atoms and $\frac{PV}{nRT} > 1$

(B) molecular attractions between atoms and $\frac{PV}{nRT} < 1$

(C) finite size of atoms and $\frac{PV}{nRT} > 1$

(D) finite size of atoms and $\frac{PV}{nRT} < 1$

Ans. (C)

- Sol.** Positive deviation from ideal behavior takes place because of finite size of atoms & compressibility factor $Z > 1$.

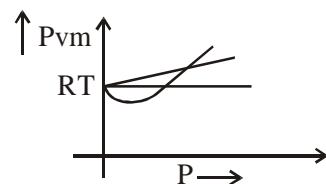
12. For a real gas obeying van der Waals' equation a graph is plotted between PV_m (y-axis) and $P(V_m)$ (x-axis) where V_m is molar volume. Find y-intercept of the graph.

[JEE 2004]

Ans. RT

Sol. $\lim_{P \rightarrow 0} PV_m = RT$

Since, at very low P, all gases behave ideally.



13. The given graph represents the variation of Z

(compressibility factor = $\frac{PV}{nRT}$) versus P, for three real

gases A, B and C. Identify the only **INCORRECT** statement.

- (A) for the gas A, $a = 0$ and its dependence on P is linear at all pressure
- (B) for the gas B, $b = 0$ and its dependence on P is linear at all pressure
- (C) for the gas C, which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated.
- (D) At high pressure, the slope is positive for all real gases A, B and C.

[JEE 2006]

Ans. (D)

Sol. (A) In case of A, repulsion dominate because $Z > 1$

$$\text{So, } Z = 1 + \frac{Pb}{RT} \Rightarrow a = 0$$

(B) In case of B, attraction dominate because $Z < 1$

$$\text{So, } z = 1 - \frac{a}{VmRT} \Rightarrow b = 0$$

(C) In case of C, a typical real gas :

We can calculate the minima of curve to given equation (1) in terms of a & b .

Similarly, at intersection point of the curve with $Z = 1$, we get another equation (2) in terms of a & b . Solving the two equation we can calculate a & b .

(D) At high P, a Slope is negative for gas B.

SO, (D) is incorrect.

14. Match gases under specific conditions listed in Column I with their properties / laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS.

Column I

- (A) Hydrogen gas ($P = 200$ atm, $T = 273$ K)
- (B) Hydrogen gas ($P \sim 0$, $T = 273$ K)
- (C) CO_2 ($P = 1$ atm, $T = 273$ K)
- (D) Real gas with very large molar volume

Column II

- (P) Compressibility factor $\neq 1$
- (Q) Attractive forces are dominant
- (R) $PV = nRT$
- (S) $P(V - nb) = nRT$

[JEE 2007]

Ans. (A) - P, S ; (B) - R ; (C) - P, Q ; (D) - R

Sol. (A) H₂ gas at high P,

Repulsions dominate

So, Z ≠ 1

& P(V-nb) = nRT

(B) H₂ gas at P → 0, will exhibit ideal behaviour PV = nRT

(C) CO₂ at P = 1 atm, T = 273 K

CO₂ is easily liquefiable gas.

Z < 1, So attraction forces dominate.

(D) If volume is very large, no intermolecular force exists. Moreover, molecular volume can also be neglected.

SO, PV = nRT

15. A gas described by van der Waals' equation

[JEE 2008]

(A) behaves similar to an ideal gas in the limit of large molar volumes

(B) behaves similar to an ideal gas in the limit of large pressures

(C) is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature

(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Ans. (A,C,D)

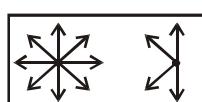
Sol. (A) PV_m → RT as V_m → ∞

(B) PV_m → RT as P → 0 So (B) is incorrect

$$(C) \left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

where, a & b are vander waals, coefficients independent of temperature

(D) P_{real} < P_{ideal}



EXERCISE (S-1)

1. Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm³ at 300 K using:
 - (a) the ideal gas law and
 - (b) Van der Waal's equation respectively.

Given : [a = 3.6 atm litre²mol⁻², b = 0.04 litre mol⁻¹, R = 0.08 L-atm/K-mol]
2. Calculate from the Van der Waals equation, the temperature at which 192 g of SO₂ would occupy a volume of 6 dm³ at 15 atm pressure.[a = 5.68 atm L² mol⁻², b = 0.06 L mol⁻¹]
3. The density of water vapour at 328.4 atm and 800 K is 135.0 g/dm³. Determine the molar volume, V_m and the compression factor of water vapour .
4. At 300 K and under a pressure of 10.1325 MPa, the compressibility factor of O₂ is 0.9. Calculate the mass of O₂ necessary to fill a gas cylinder of 45 dm³ capacity under the given conditions.
[R = 0.08L-atm/K-mol]
5. 1 mole of CCl₄ vapours at 27°C occupies a volume of 40 L. If Van der Waals constants are 24.6 L² atm mol⁻² and 0.125 Lmol⁻¹, then, calculate compressibility factor in
 - (a) Low pressure region
 - (b) High Pressure region [R = 0.082 L -atm/K-mol]
6. If at 200 K & 500 atm, density of CH₄ is 0.246 gm/ml then its compressibility factor (Z) is approx 2.0×10^x . 'x' is:
7. Certain mass of a gas occupy 500 ml at 2 atm and 27°C. Calculate the volume occupied by same mass of the gas at 0.3 atm and 227°C. The compressibility factors of gas at the given condition are 0.8 and 0.9, respectively.

BOYLE TEMPERATURE

8. The vander waal's constant for a gas are a = 1.92 atm L² mol⁻², b = 0.06L mol⁻¹. If R = 0.08 L atm K⁻¹mol⁻¹, what is the Boyle's temperatruue of this gas.
9. The Van der Waals constant for O₂ are a = 1.642 atm L² mol⁻² and b = 0.04 L mol⁻¹. Calculate the temperature at which O₂ gas behaves ideally for longer range of pressure.

LIQUIFICATION OF GASES, CRITICAL PHENOMENON

10. The Van der Waals constants for gases A, B and C are as follows

Gas	a/[atm L ² mol ⁻²]	b/[L mol ⁻¹]
A	8.21	0.050
B	4.105	0.030
C	1.682	0.040

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 500 K?

11. For a real gas, if at critical conditions molar volume of gas is 8.21 litre at 3 atm, then critical temperature (in K) will be :
12. An unknown gas behaves ideally at 540K in low pressure region, then calculate the temperature (in K) below which it can be liquified by applying pressure.

EXERCISE (O-1)

1. The correct expression for the Van der Waals equation of state is :

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

(B) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = \Delta nRT$

(C) $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$

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

2. At relatively high pressure, Van der Waals equation reduces to :

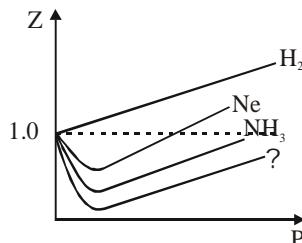
(A) $PV_m = RT$

(B) $PV_m = RT + \frac{a}{V_m}$

(C) $PV_m = RT + Pb$

(D) $PV_m = RT - \frac{a}{V_m^2}$

3. Observe the following Z vs P graph.



The missing gas in the above graph can be :

(A) He

(B) Ar

(C) C₅H₁₂

(D) All are correct

4. Correct option regarding a container containing 1 mol of a gas in 22.4 litre container at 273 K is

(A) If compressibility factor (Z) > 1 then 'P' will be less than 1 atm.

(B) If compressibility factor (Z) > 1 then 'P' will be greater than 1 atm.

(C) If 'b' dominates, pressure will be less than 1 atm.

(D) If 'a' dominates, pressure will be greater than 1 atm.

5. If 'V' is actual volume of 1 molecule of gas then, excluded volume (b) of 1 mole of gaseous molecule is -

(A) $4 N_A V$

(B) $N_A V$

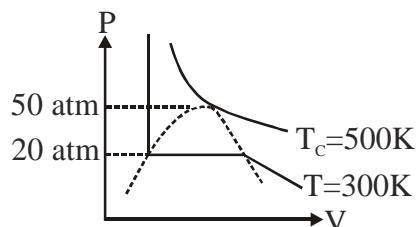
(C) V/N_A

(D) V

6. Consider the equation $Z = \frac{PV}{RT}$, Which of the following statements is correct :
- (A) When $Z > 1$ real gases are easier to compress
 - (B) When $Z = 1$ real gases are easier to compress
 - (C) When $Z > 1$ real gases are difficult to compress
 - (D) When $Z < 1$ real gases are difficult to compress
7. Compressibility factor of ideal gas is :-
- (A) $z > 1$
 - (B) $z > 1$
 - (C) $z = 1$
 - (D) $z = \infty$
8. The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lit. If the molecular weight of the substance is 27, the dominant forces existing among gas molecules is -
- (A) Attractive
 - (B) Repulsive
 - (C) Both (A) and (B)
 - (D) None of these
9. The third virial coefficient of a He gas is 4×10^{-2} (lit/mol)², then what will be volume of 2 mole He gas at 1 atm 273K ($273K > T_B$)
- (A) 22.0 lit
 - (B) 44.0 lit
 - (C) 44.8 lit
 - (D) 45.3 lit
10. At low pressure the vander waals equation is reduced to -
- | | |
|---|--|
| (A) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m}$ | (B) $Z = \frac{pV_m}{RT} = 1 + \frac{a}{RT} p$ |
| (C) $pV_m = RT$ | (D) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$ |
11. The values of Van der Waals constant 'a' for the gases O₂, N₂, NH₃ and CH₄ are 1.360, 1.390, 4.170 and 2.253 L atm mol⁻² respectively. The gas which can most easily be liquefied is :
- (A) O₂
 - (B) N₂
 - (C) NH₃
 - (D) CH₄
12. The values of critical temperatures of few gases are given gases :
- | | |
|--------------------|--|
| Gases : | H ₂ He O ₂ N ₂ |
| T _C (K) | 33.2 5.2 154.3 126 |
- From the above data arrange the given gases in the increasing order of ease of their liquification.
- (A) O₂, N₂, H₂, He
 - (B) He, N₂, O₂, H₂
 - (C) He, H₂, N₂, O₂
 - (D) H₂, N₂, O₂, He

EXERCISE (O-2)

1. For real gas the P–V curve was experimentally plotted and it had the following appearance.
With respect to liquification, choose the incorrect statement :



- (A) At $T = 500 \text{ K}$, $P = 40 \text{ atm}$, the state will be liquid
 - (B) At $T = 300 \text{ K}$, $P = 50 \text{ atm}$, the state will be gas
 - (C) At $T < 300 \text{ K}$, $P = 20 \text{ atm}$, the state will be gas
 - (D) At $300 \text{ K} < T < 500 \text{ K}$, $P > 50 \text{ atm}$, the state will be liquid
2. Select the incorrect statement (s)
- (A) The critical constant for a Vander Waal's gas is $V_c = 3b$, $P_c = \frac{a}{27b^2}$ and $T_c = \frac{a}{27Rb}$
 - (B) At 56 K a gas may be liquified if its critical temperature is -156°C .
 - (C) U_{avg} of gas in a rigid container can be doubled when the pressure is quadrupled by pumping in more gas at constant temperature
 - (D) At extremely low pressure, all real gases behave ideally.
3. A 1 litre vessel contains 2 moles of a vanderwaal's gas.

Given data : $a = 2.5 \text{ atm-L}^2 \text{ mole}^{-2}$ $T = 240 \text{ K}$
 $b = 0.4 \text{ L-mole}^{-1}$ $RT = 20 \text{ L-atm mole}^{-1}$

Identify the correct options about the gas sample :

- (A) Pressure of gas = 190 atm
 - (B) Compressibility factor = 4.75
 - (C) Attraction forces are dominant in the gaseous sample
 - (D) T_B (Boyle temperature) = 75 K
4. Choose the correct statement(s) among the following -
- (A) A gas having higher value T_c is easy to liquify
 - (B) The radius of molecules of gas having same value of T_c/P_c is same
 - (C) Hydrogen gas can be liquified at its boyle temperature by application of pressure.
 - (D) Real gas show negative deviation from ideal behaviour at low pressure condition.

5. Select the **INCORRECT** statement(s):

- (A) At Boyle's temperature a real gas behaves like an ideal gas irrespective of pressure.
- (B) At critical condition, a real gas behaves like an ideal gas.
- (C) On increasing the temperature four times, collision frequency (Z_1) becomes double at constant volume.
- (D) At high pressure Van der Waals constant 'b' dominates over 'a'.

Question No. 6 & 7 (2 questions)

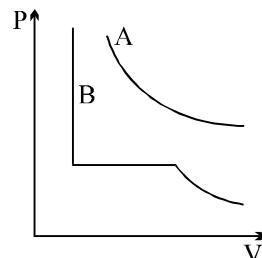
For two gases A and B, P v/s V isotherms are shown at same temperature, T K . T_A & T_B are critical temperatures of A & B respectively

6. Which of the following is true?

- | | |
|---------------------|---------------------|
| (A) $T_A < T < T_B$ | (B) $T_A > T > T_B$ |
| (C) $T_A > T_B > T$ | (D) none of above |

7. The correct statement(s) is/are

- (I) Pressure correction term will be more negligible for gas B at T K.
 - (II) The curve for gas 'B' will be of same shape as for gas A if $T > T_B$
 - (III) Gas 'A' will show same P v/s V curve as of gas 'B' if $T > T_A$
- | | | | |
|--------------|----------------|-------------|---------|
| (A) III only | (B) II and III | (C) II only | (D) All |
|--------------|----------------|-------------|---------|



Match the column:

8. Match the column :

Column-I	Column-II
(A) Boyle's temperature	(P) Depends on 'a' and 'b'
(B) Compressibility factor	(Q) Depends on identity of real gas
(C) Real gas with very large molar volume	(R) The temperature at which $\frac{dZ}{dP} = 0$ at low pressure region.
(D) Critical temperature	(S) $PV = nRT$
	(T) $\frac{8a}{27R.b}$

EXERCISE (JM)

1. 'a' and 'b' are Van der Waals constants for gases. Chlorine is more easily liquefied than ethane because :- [AIEEE-2011]
 - (1) a for $\text{Cl}_2 < a$ for C_2H_6 but b for $\text{Cl}_2 > b$ for C_2H_6
 - (2) a for $\text{Cl}_2 > a$ for C_2H_6 but b for $\text{Cl}_2 < b$ for C_2H_6
 - (3) a and b for $\text{Cl}_2 > a$ and b for C_2H_6
 - (4) a and b for $\text{Cl}_2 < a$ and b for C_2H_6
2. When does a gas deviate the most from its ideal behaviour ? [JEE-MAINS(ONLINE)-2015]
 - (1) At high pressure and low temperature
 - (2) At high pressure and high temperature
 - (3) At low pressure and low temperature
 - (4) At low pressure and high temperature
3. If Z is the compressibility factor, Van der Waals equation at low pressure can be written as : [JEE-MAINS-2014]

$$(1) Z = 1 - \frac{Pb}{RT} \quad (2) Z = 1 + \frac{Pb}{RT} \quad (3) Z = 1 + \frac{RT}{Pb} \quad (4) Z = 1 - \frac{a}{V_m RT}$$
4. Among the following, the incorrect statement is : [JEE-Mains-2017(ONLINE)]
 - (1) At low pressure, real gases show ideal behaviour
 - (2) At very large volume, real gases show ideal behaviour
 - (3) At Boyle's temperature, real gases show ideal behaviour
 - (4) At very low temperature, real gases show ideal behaviour
5. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are : [JEE-MAINS-2019]

$$(1) 2P_A = 3P_B \quad (2) P_A = 3P_B \quad (3) P_A = 2P_B \quad (4) 3P_A = 2P_B$$
6. At a given temperature T, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour.

Their equation of state is given as $P = \frac{RT}{V - b}$ at T.

[JEE-MAINS-2019]

Here, b is the van der Waals constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) vs p?

- (1) Ne
- (2) Ar
- (3) Xe
- (4) Kr

7. Consider the van der Waals constants, a and b , for the following gases.

Gas	Ar	Ne	Kr	Xe
-----	----	----	----	----

[JEE-MAINS-2019]

a/ (atm dm ⁶ mol ⁻²)	1.3	0.2	5.1	4.1
---	-----	-----	-----	-----

b/ (10 ⁻² dm ³ mol ⁻¹)	3.2	1.7	1.0	5.0
--	-----	-----	-----	-----

Which gas is expected to have the highest critical temperature?

(1) Kr	(2) Ne	(3) Ar	(4) Xe
--------	--------	--------	--------

8. Consider the following table :

[JEE-MAINS-2019]

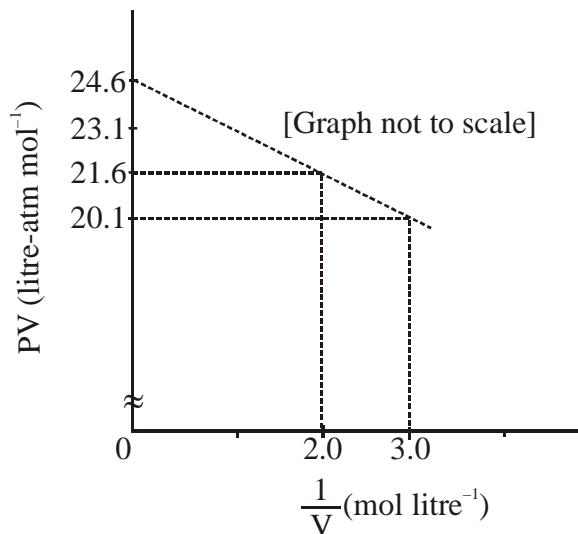
Gas	a/(k Pa dm ⁶ mol ⁻¹)	b/(dm ³ mol ⁻¹)
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and b are vander waals constant. The correct statement about the gases is :

- (1) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D
- (2) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D
- (3) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D
- (4) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D

EXERCISE (JA)

1. For one mole of a Van der Waals gas when $b = 0$ and $T = 300\text{ K}$, the PV vs. $1/V$ plot is shown below. The value of the Van der Waals constant a ($\text{atm. litre}^2 \text{ mol}^{-2}$) is [JEE 2012]



ANSWER KEY

EXERCISE (S-1)

- | | |
|---|----------------------------|
| 1. (a) 24.0 atm, (b) 21.4 atm | 2. 388 K |
| 3. Molar vol. = 0.1333 L/mol; Z = 0.667 | 4. 6.67 kg |
| 5. (a) 0.975 ; (b) 1.003 | 6. Ans. 0 |
| 7. 6.25 L | 8. Ans. 400 K |
| 9. 500 K | 10. (i) A, (ii) A, (iii) C |
| 11. Ans. 800 | 12. Ans. 160 K |

EXERCISE (O-1)

- | | | | |
|------------|-------------|-------------|-------------|
| 1. Ans.(D) | 2. Ans.(C) | 3. Ans.(C) | 4. Ans.(B) |
| 5. Ans.(A) | 6. Ans.(C) | 7. Ans.(C) | 8. Ans.(B) |
| 9. Ans.(D) | 10. Ans.(A) | 11. Ans.(C) | 12. Ans.(C) |

EXERCISE (O-2)

- | | | | |
|---|---------------|-----------------|-----------------|
| 1. Ans. (A,B,C) | 2. Ans. (A,C) | 3. Ans. (A,B,D) | 4. Ans. (A,B,D) |
| 5. Ans.(A,B) | 6. Ans.(A) | 7. Ans. (C) | |
| 8. (A) - P,Q,R,S ; (B) - P, Q ; (C) - S ; (D) - P, Q, T | | | |

EXERCISE (JM)

- | | | | |
|-------------|-------------|-------------|-------------|
| 1. Ans. (2) | 2. Ans. (1) | 3. Ans. (4) | 4. Ans. (4) |
| 5. Ans. (1) | 6. Ans.(3) | 7. Ans. (1) | 8. Ans.(3) |

EXERCISE (JA)

1. Ans.(C)