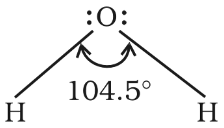
Some typical average bond lengths for single, double and triple bonds are shown in Table 4.2. Bond lengths for some common molecules are given in Table 4.3.

The covalent radii of some common elements are listed in Table 4.4.

4.3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under :



4.3.3 Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$$H_2(g) \rightarrow H(g) + H(g);\ \Delta_a H^\ominus = 435.8 \text{ kJ mol}^{-1}$$

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under :

$$O_2\ (O = O)\ (g) \rightarrow O(g) + O(g);\quad \Delta_a H^\ominus = 498 \text{ kJ mol}^{-1}$$

$$N_2\ (N \equiv N)\ (g) \rightarrow N(g) + N(g);\quad \Delta_a H^\ominus = 946.0 \text{ kJ mol}^{-1}$$

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a heteronuclear diatomic molecules like HCl, we have

$$HCl\ (g) \rightarrow H(g) + Cl\ (g);\ \Delta_a H^\ominus = 431.0 \text{ kJ mol}^{-1}$$

In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O – H bonds is not the same.

Table 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds

Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

Table 4.3 Bond Lengths in Some Common Molecules

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

Table 4.4 Covalent Radii, $^*r_{cov}$/(pm)

H	37						
C	77(1)	N	74 (1)	O	66(1)	F	64
	67 (2)		65(2)		57 (2)	Cl	99
	60(3)		55(3)				
		P	110	S	104(1)	Br	114
					95(2)		
		As	121	Se	104	I	133
		Sb	141	Te	137		

* *The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 3 for periodic trends).*

$H_2O(g) \rightarrow H(g) + OH(g); \Delta_a H_1^\ominus = 502 \text{ kJ mol}^{-1}$

$OH(g) \rightarrow H(g) + O(g); \Delta_a H_2^\ominus = 427 \text{ kJ mol}^{-1}$

The difference in the $\Delta_a H^\ominus$ value shows that the second O – H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O – H bond in different molecules like C_2H_5OH (ethanol) and water. Therefore in polyatomic molecules the term **mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

$$\text{Average bond enthalpy} = \frac{502 + 427}{2}$$

$$= 464.5 \text{ kJ mol}^{-1}$$

4.3.4 Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^\ominus$ is 946 kJ mol^{-1}; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

A general correlation useful for understanding the stablities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

4.3.5 Resonance Structures

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:

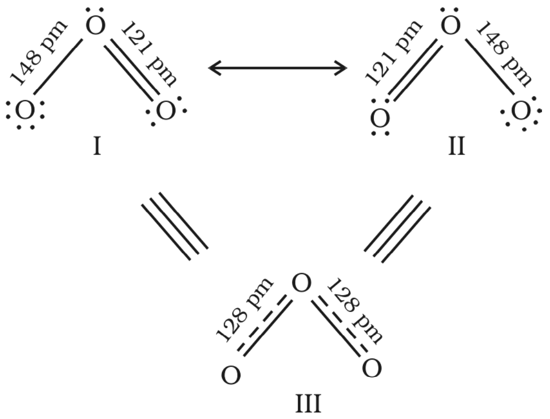


***Fig. 4.3** Resonance in the O_3 molecule*

(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 pairs of 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.**

Problem 4.3

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.

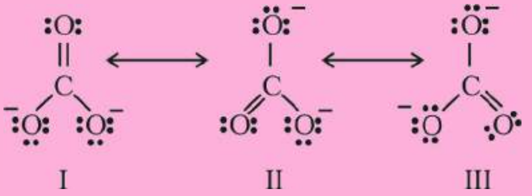


Fig.4.4 *Resonance in CO_3^{2-}, I, II and III represent the three canonical forms.*

Problem 4.4

Explain the structure of CO_2 molecule.

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond ($C=O$) and carbon to oxygen triple bond ($C\equiv O$) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for $C=O$ and $C\equiv O$. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.

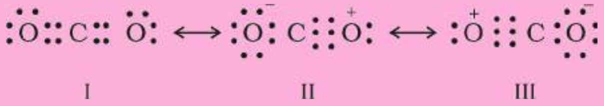


Fig. 4.5 *Resonance in CO_2 molecule, I, II and III represent the three canonical forms.*

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and,
- Resonance averages the bond characteristics as a whole.

Thus the energy of the O_3 resonance hybrid is lower than either of the two cannonical froms I and II (Fig 4.3).

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

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

4.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2, the shared pair of electrons is equally attracted by the two atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows :

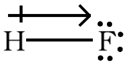
Dipole moment (μ) = charge (Q) × distance of separation (r)

Dipole moment is usually expressed in Debye units (D). The conversion factor is

$$1\ \text{D} = 3.33564 \times 10^{-30}\ \text{C m}$$

where C is coulomb and m is meter.

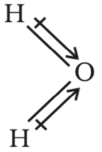
Further dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre. But in chemistry presence of dipole moment is represented by the crossed arrow (⟼) put on Lewis structure of the molecule. The cross is on positive end and arrow head is on negative end. For example the dipole moment of HF may be represented as :



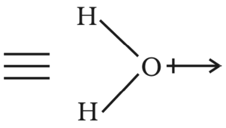
This arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opposite to the conventional direction of dipole moment vector.

Peter Debye, the Dutch chemist received Nobel prize in 1936 for his work on X-ray diffraction and dipole moments. The magnitude of the dipole moment is given in Debye units in order to honour him.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in H_2O molecule, which has a bent structure, the two O–H bonds are oriented at an angle of 104.5^0. Net dipole moment of 6.17 × 10^{-30} C m (1D = 3.33564 × 10^{-30} C m) is the resultant of the dipole moments of two O–H bonds.



(a)
Bond dipole



(b)
Resultant
dipole moment

Net Dipole moment, μ = 1.85 D

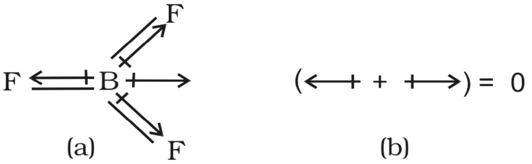
$$= 1.85 \times 3.33564 \times 10^{-30}\ \text{C m} = 6.17 \times 10^{-30}\ \text{C m}$$

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.

Bond dipoles in BeF_2

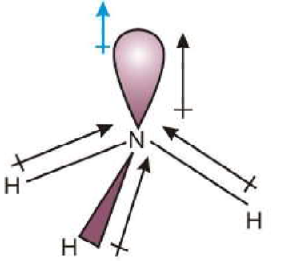
Total dipole moment in BeF_2

In tetra-atomic molecule, for example in BF_3, the dipole moment is zero although the B – F bonds are oriented at an angle of 120^o to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.

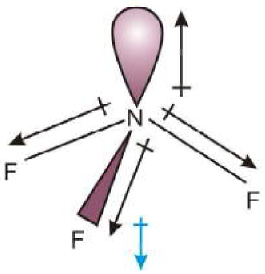


BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

Let us study an interesting case of NH_3 and NF_3 molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3 (4.90×10^{-30} C m) is greater than that of NF_3 (0.8×10^{-30} C m). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented below :



Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m



Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ C m

Dipole moments of some molecules are shown in Table 4.5.

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^{n}ns^{o}$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\,np^6$, typical of alkali and alkaline earth metal cations.

The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

4.4 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick

Table 4.5 Dipole Moments of Selected Molecules

Type of Molecule	Example	Dipole Moment, μ(D)	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)	NH_3	1.47	trigonal-pyramidal
	NF_3	0.23	trigonal-pyramidal
	BF_3	0	trigonal-planar
Molecule (AB_4)	CH_4	0	tetrahedral
	$CHCl_3$	1.04	tetrahedral
	CCl_4	0	tetrahedral

and Powell 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:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 4.6 (page114) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 4.6, in the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangement of electron pairs and the B atoms around the central atom A are : **linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral,** respectively. Such arrangement can be seen in the molecules like BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) as depicted below by their ball and stick models.

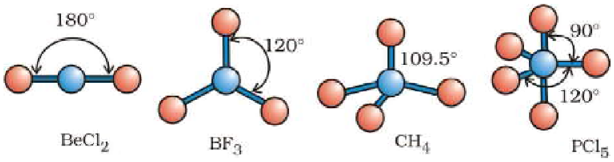


Fig. 4.6 *The shapes of molecules in which central atom has no lone pair*

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. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons

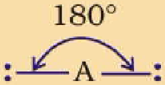
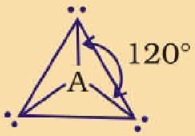
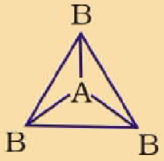
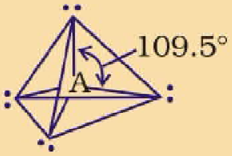
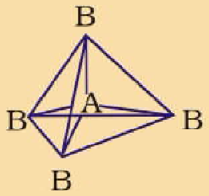
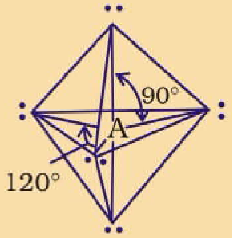
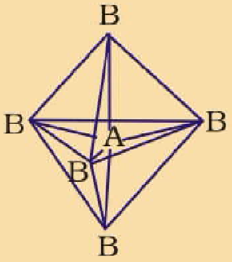
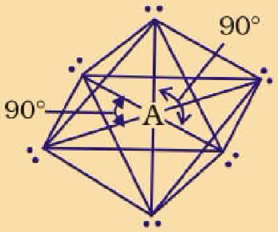
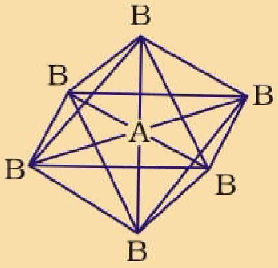
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

Table 4.7 Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).

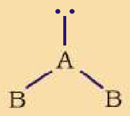
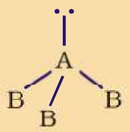
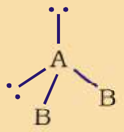
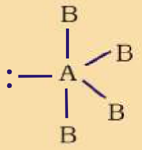
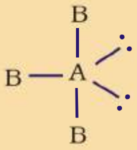
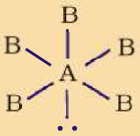
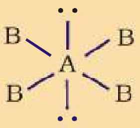
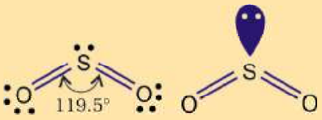
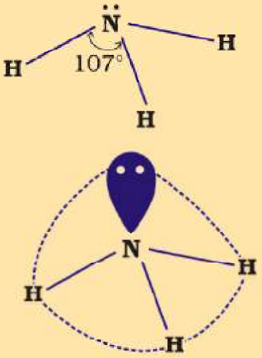
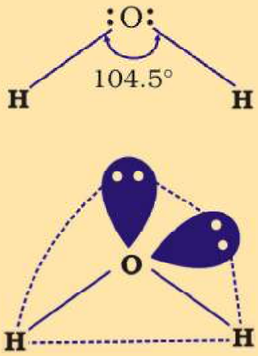
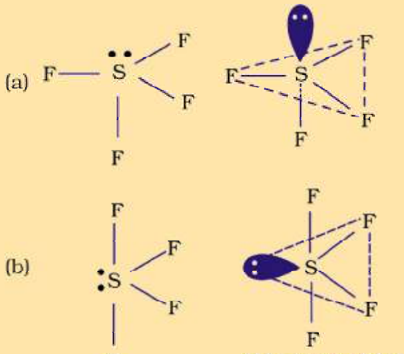
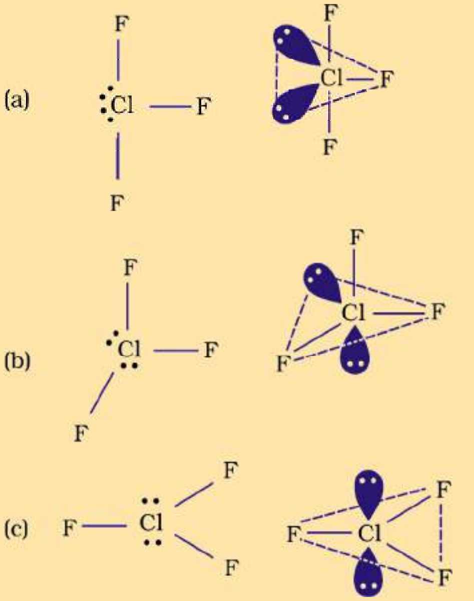
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planer	Bent	SO^2O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3
AB_3E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	 Octahedral	Square planer	XeF_4

Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB_4E	4	1	 (More stable)	See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at 90°. In(b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_3E_2	3	2		T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

4.5 VALENCE BOND THEORY

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 (435.8 kJ mol^{-1}, 74 pm) and F_2 (155 kJ mol^{-1}, 144 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.

Valence bond theory 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 (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

(i) nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.

(ii) nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly repulsive forces arise between (i) electrons of two atoms like $e_A - e_B$, (ii) nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 4.7).

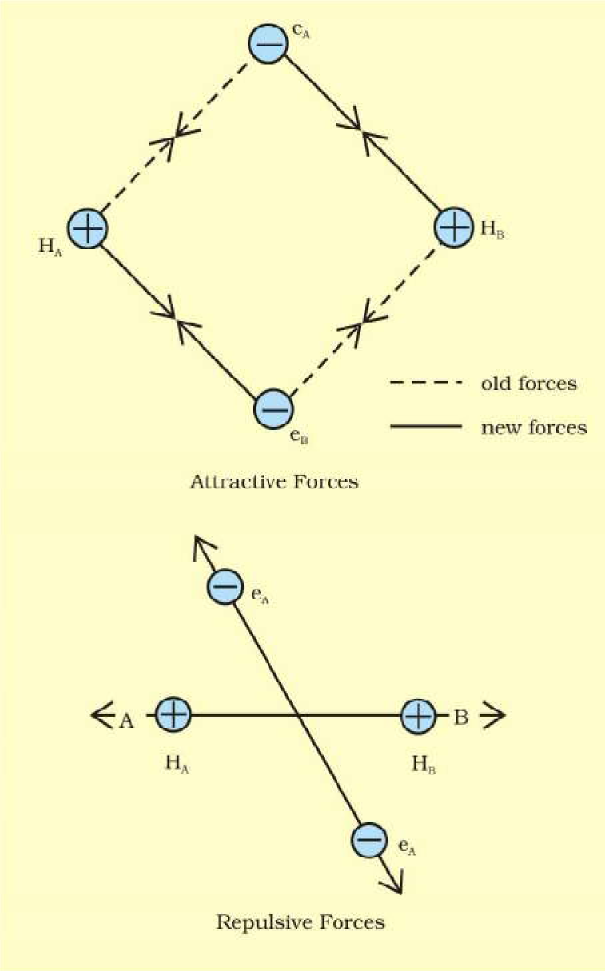


Fig. 4.7 *Forces of attraction and repulsion during the formation of H_2 molecule.*

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and 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. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 4.8. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_2(g) + 435.8 \text{ kJ mol}^{-1} \rightarrow H(g) + H(g)$$

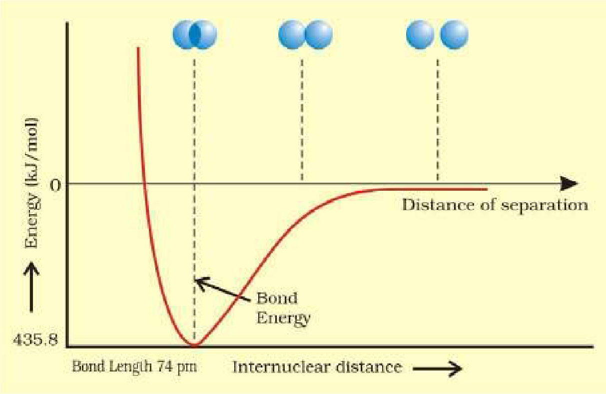


Fig. 4.8 *The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.*

4.5.1 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 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.

4.5.2 Directional Properties of Bonds

As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1*s*-orbitals of two H atoms.

In case of polyatomic molecules like CH_4, NH_3 and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH_4 molecule has tetrahedral shape and HCH bond angles are 109.5°? Why is the shape of NH_3 molecule pyramidal ?

The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

4.5.3 Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of *s* and *p* orbitals are depicted in Fig. 4.9.

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. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

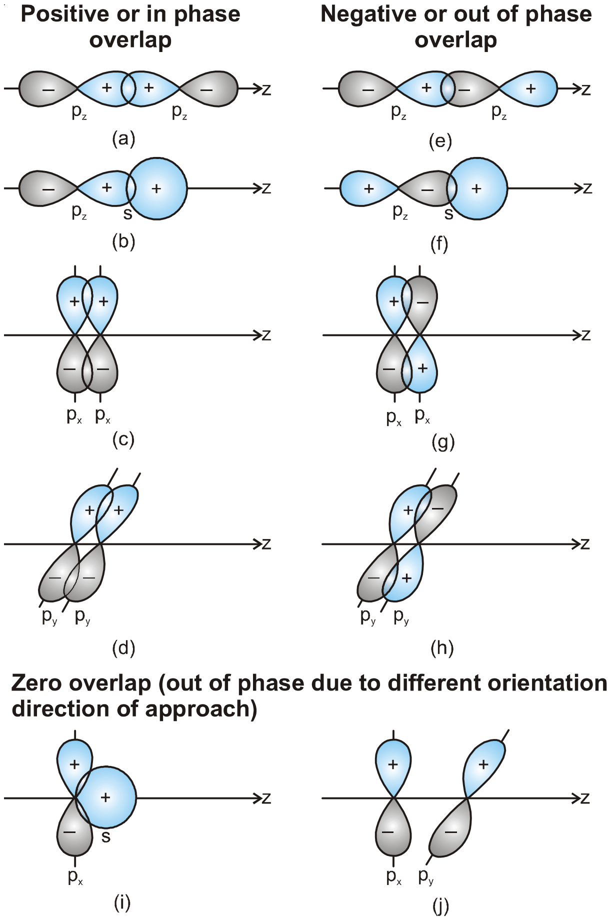


Fig.4.9 *Positive, negative and zero overlaps of s and p atomic orbitals*

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is $[He]2s^2\,2p^2$ which in the excited state becomes $[He]\,2s^1\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the hydrogen.The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90° to one another, the HCH angle for these will also be 90°. That is three C-H bonds will be oriented at 90° to one another. The 2*s* orbital of carbon and the 1*s* orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5°. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the case of NH_3 and H_2O molecules, the HNH and HOH angles should be 90°. This is in disagreement with the actual bond angles of 107° and 104.5° in the NH_3 and H_2O molecules respectively.

4.5.4 Types of Overlapping and Nature of Covalent Bonds

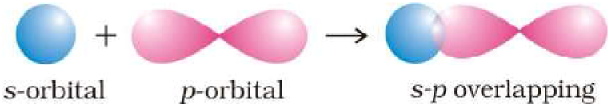
The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma(σ) bond, and (ii) pi(π) bond

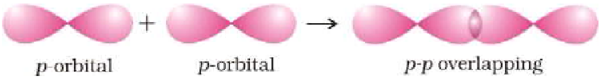
(i) Sigma(σ) bond : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

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

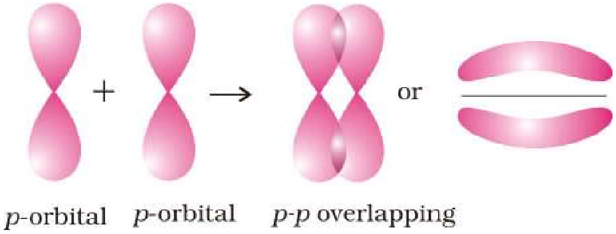
- ***s-p* overlapping:** This type of overlap occurs between half filled *s*-orbitals of one atom and half filled *p*-orbitals of another atom.



- ***p–p* overlapping :** This type of overlap takes place between half filled *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 axes 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.



4.5.5 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 in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

4.6 HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3 and H_2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2*s* and three 2*p*-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.

3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

4.6.1 Types of Hybridisation

There are various types of hybridisation involving *s*, *p* and *d* orbitals. The different types of hybridisation are as under:

(I) *sp* hybridisation: This type of hybridisation involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals. The suitable orbitals for *sp* hybridisation are *s* and p_z, if the hybrid orbitals are to lie along the z-axis. Each *sp* hybrid orbitals has 50% *s*-character and 50% *p*-character. Such a molecule in which the central atom is *sp*-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two *sp* hybrids point in the opposite direction along the z-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having *sp* hybridisation

$BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2*s*-electrons is promoted to vacant 2*p* orbital to account for its bivalency. One 2*s* and one 2*p*-orbital gets hybridised to form two *sp* hybridised orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the *sp* hybridised orbital overlaps with the 2*p*-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig. 4.10.

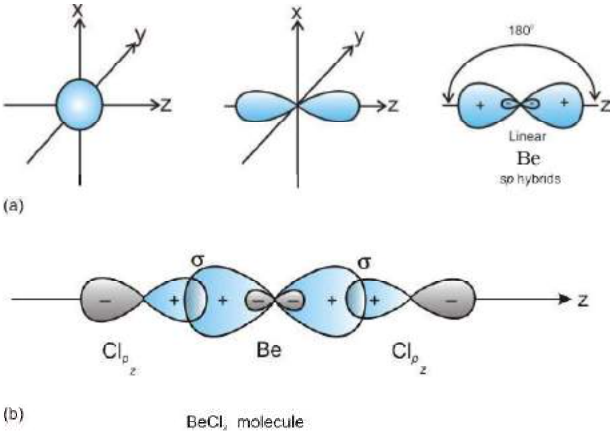


Fig.4.10 *(a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule*

(II) *sp*² *hybridisation* : In this hybridisation there is involvement of one *s* and two *p*-orbitals in order to form three equivalent sp^2 hybridised orbitals. For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2*s* electrons is promoted to vacant 2*p* orbital as

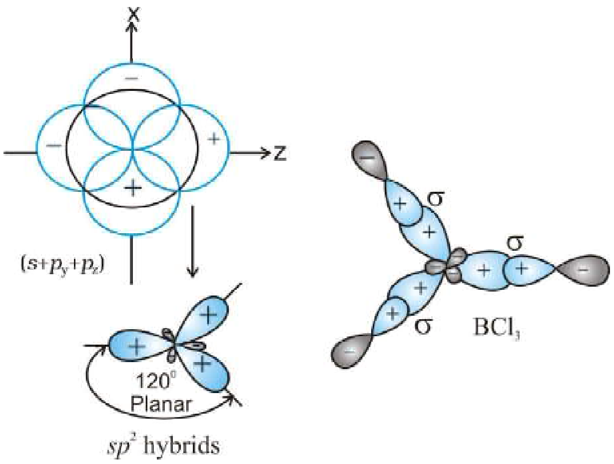


Fig.4.11 *Formation of sp^2 hybrids and the BCl_3 molecule*

a result boron has three unpaired electrons. These three orbitals (one 2*s* and two 2*p*) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2*p* orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl_3 (Fig. 4.11), the geometry is trigonal planar with ClBCl bond angle of 120°.

(III) *sp^3 hybridisation:* This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one *s*-orbital and three *p*-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% *s*-character and 75% *p*-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5° as shown in Fig. 4.12.

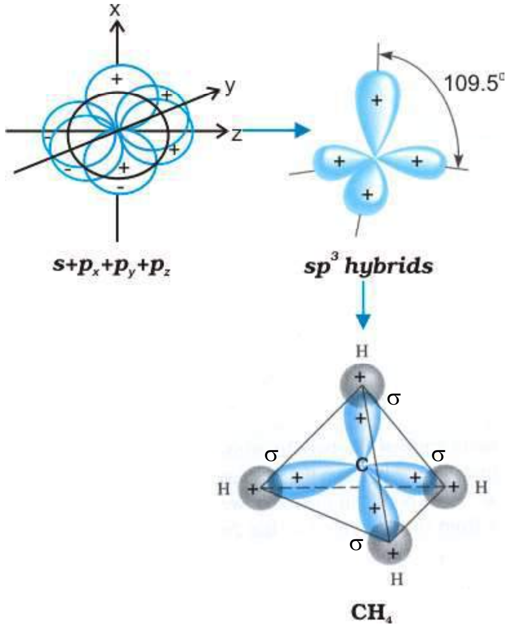


Fig.4.12 *Formation of sp^3 hybrids by the combination of s , p_x , p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule*

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2S^2 2p_x^1 2p_y^1 2p_z^1$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1*s* orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107° from 109.5°. The geometry of such a molecule will be pyramidal as shown in Fig. 4.13.

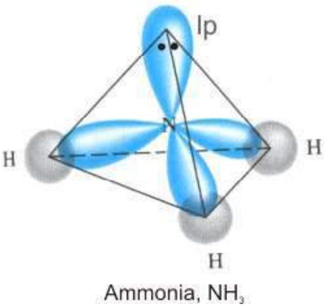


Fig.4.13 *Formation of NH_3 molecule*

In case of H_2O molecule, the four oxygen orbitals (one 2*s* and three 2*p*) undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.

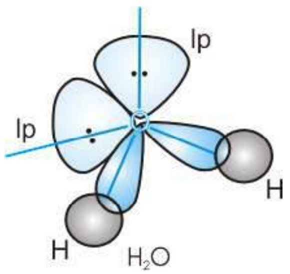


Fig.4.14 *Formation of H_2O molecule*

4.6.2 Other Examples of sp^3, sp^2 and sp Hybridisation

sp^3 Hybridisation in C_2H_6 molecule: In ethane molecule both the carbon atoms assume sp^3 hybrid state. One of the four sp^3 hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp^3-sp^3 sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp^3–s sigma bonds with hydrogen atoms as discussed in section 4.6.1(iii). Therefore in ethane C–C bond length is 154 pm and each C–H bond length is 109 pm.

sp^2 Hybridisation in C_2H_4: In the formation of ethene molecule, one of the sp^2 hybrid orbitals of carbon atom overlaps axially with sp^2 hybridised orbital of another carbon atom to form C–C sigma bond. While the other two sp^2 hybrid orbitals of each carbon atom are used for making sp^2–s sigma bond with two hydrogen atoms. The unhybridised orbital ($2p_x$ or $2p_y$) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak π bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

Thus, in ethene molecule, the carbon-carbon bond consists of one sp^2–sp^2 sigma bond and one pi (π) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C–H bond is sp^2–s sigma with bond length 108 pm. The H–C–H bond angle is 117.6° while the H–C–C angle is 121°. The formation of sigma and pi bonds in ethene is shown in Fig. 4.15.

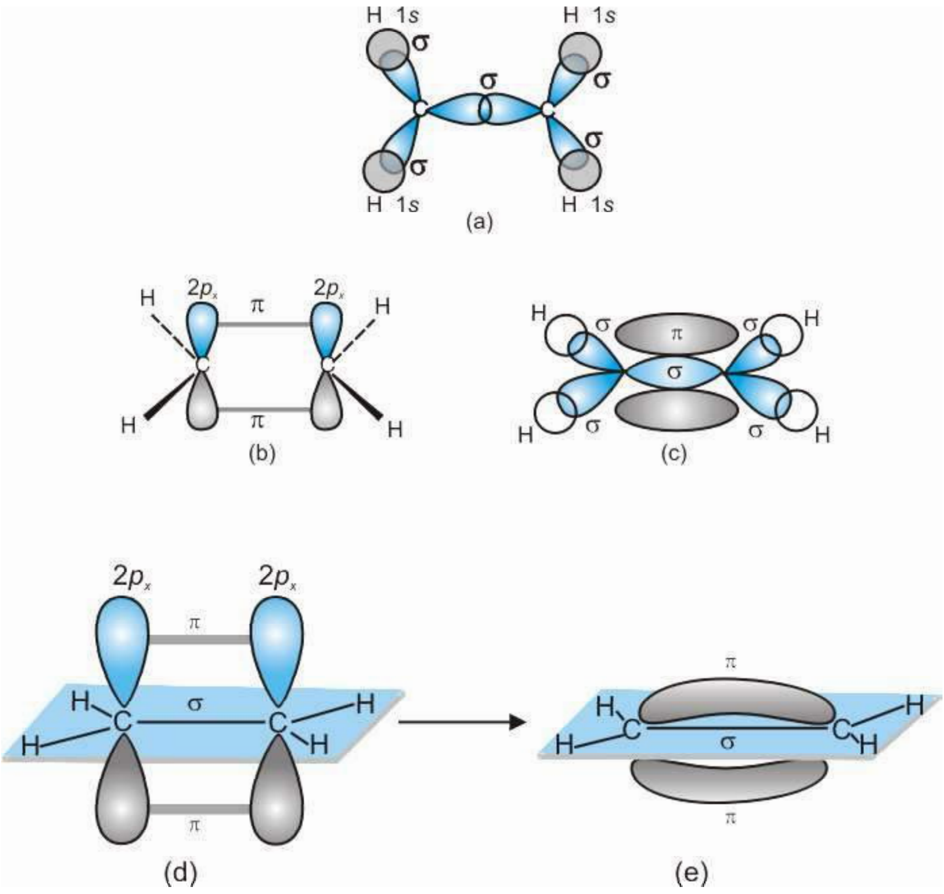


Fig. 4.15 *Formation of sigma and pi bonds in ethene*

***sp* Hybridisation in C_2H_2 :** In the formation of ethyne molecule, both the carbon atoms undergo *sp*-hybridisation having two unhybridised orbital *i.e.*, $2p_y$ and $2p_x$.

One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled *s* orbital of hydrogen atoms forming σ bonds. Each of the two unhybridised *p* orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two pi bonds as shown in Fig. 4.16.

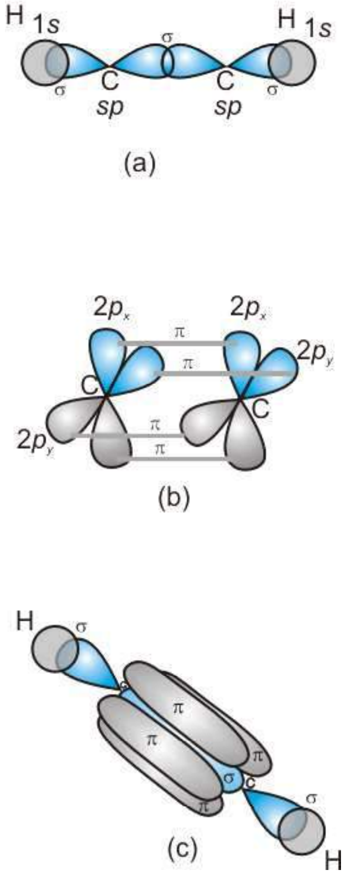


Fig.4.16 *Formation of sigma and pi bonds in ethyne*

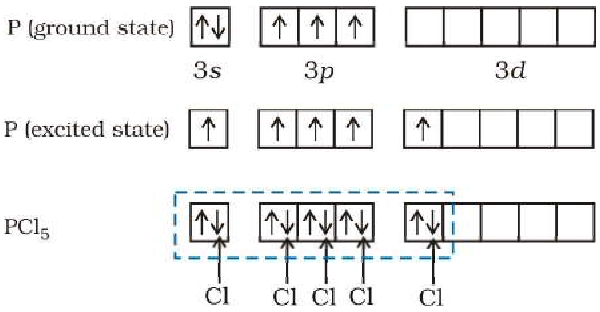
4.6.3 Hybridisation of Elements involving *d* Orbitals

The elements present in the third period contain *d* orbitals in addition to *s* and *p* orbitals. The energy of the 3*d* orbitals are comparable to the energy of the 3*s* and 3*p* orbitals. The energy of 3*d* orbitals are also comparable to those of 4*s* and 4*p* orbitals. As a consequence the hybridisation involving either 3*s*, 3*p* and 3*d* or 3*d*, 4*s* and 4*p* is possible. However, since the difference in energies of 3*p* and 4*s* orbitals is significant, no hybridisation involving 3*p*, 3*d* and 4*s* orbitals is possible.

The important hybridisation schemes involving *s*, *p* and *d* orbitals are summarised below:

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s+p(3)+d(2)$	BrF_5
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

(i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.



sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Now the five orbitals (*i.e.*, one *s*, three *p* and one *d* orbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 4.17.

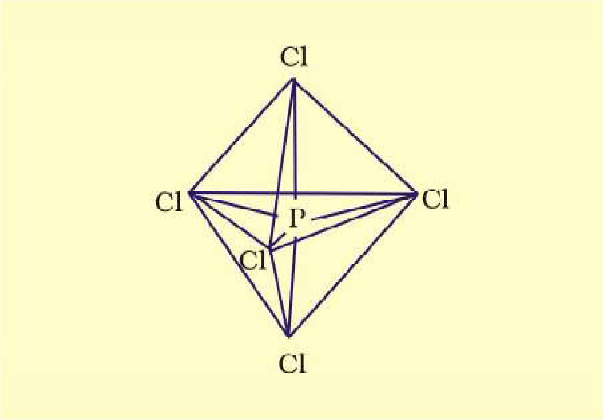
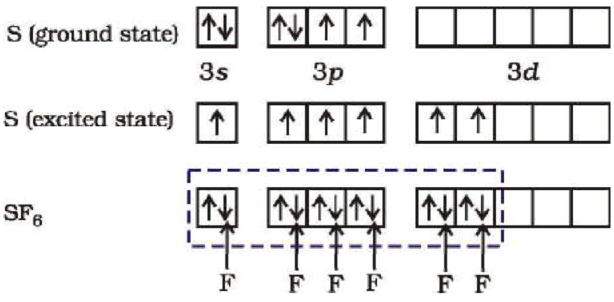


Fig. 4.17 *Trigonal bipyramidal geometry of PCl_5 molecule*

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In PCl_5 the five sp^3d orbitals of phosphorus overlap with the singly occupied *p* orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5 molecule more reactive.

(ii) Formation of SF_6 (sp^3d^2 hybridisation): In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^23p^4$. In the exited state the available six orbitals *i.e.*, one *s*, three *p* and two *d* are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry as shown in Fig. 4.18.



sp^3d^2 hybridisation

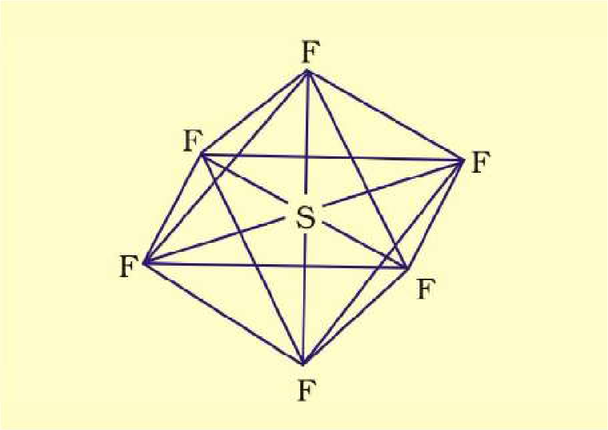


Fig. 4.18 *Octahedral geometry of SF_6 molecule*

4.7 MOLECULAR ORBITAL THEORY

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

(i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

(ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

(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 atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital**.

(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 a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the *aufbau* principle obeying the Pauli's exclusion principle and the Hund's rule.

4.7.1 Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1*s* orbital. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B.

Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and σ* are formed as :

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital σ* formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in Fig. 4.19.

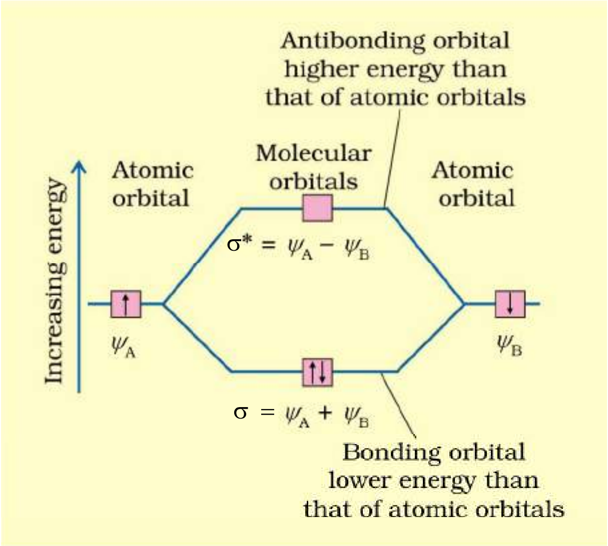


Fig.4.19 *Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.*

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 due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilise a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilise the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

4.7.2 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:

1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1*s* orbital can combine with another 1*s* orbital but not with 2*s* orbital because the energy of 2*s* orbital is appreciably higher than that of 1*s* orbital. This is not true if the atoms are very different.

2. 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.

3. 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.

4.7.3 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 orbitals are of the σ type and are designated as σ1*s* and σ*1*s* [Fig. 4.20(a),page 124]. **If internuclear axis is taken to be in the *z*-direction, it can be seen that a linear combination of $2p_z$- orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$**. [Fig. 4.20(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 above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and π* [Fig. 4.20(c)]. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

4.7.4 Energy Level Diagram for Molecular Orbitals

We have seen that 1*s* atomic orbitals on two atoms form two molecular orbitals designated as σ1*s* and σ*1*s*. In the same manner, the 2*s* and 2*p* atomic orbitals (eight atomic orbitals

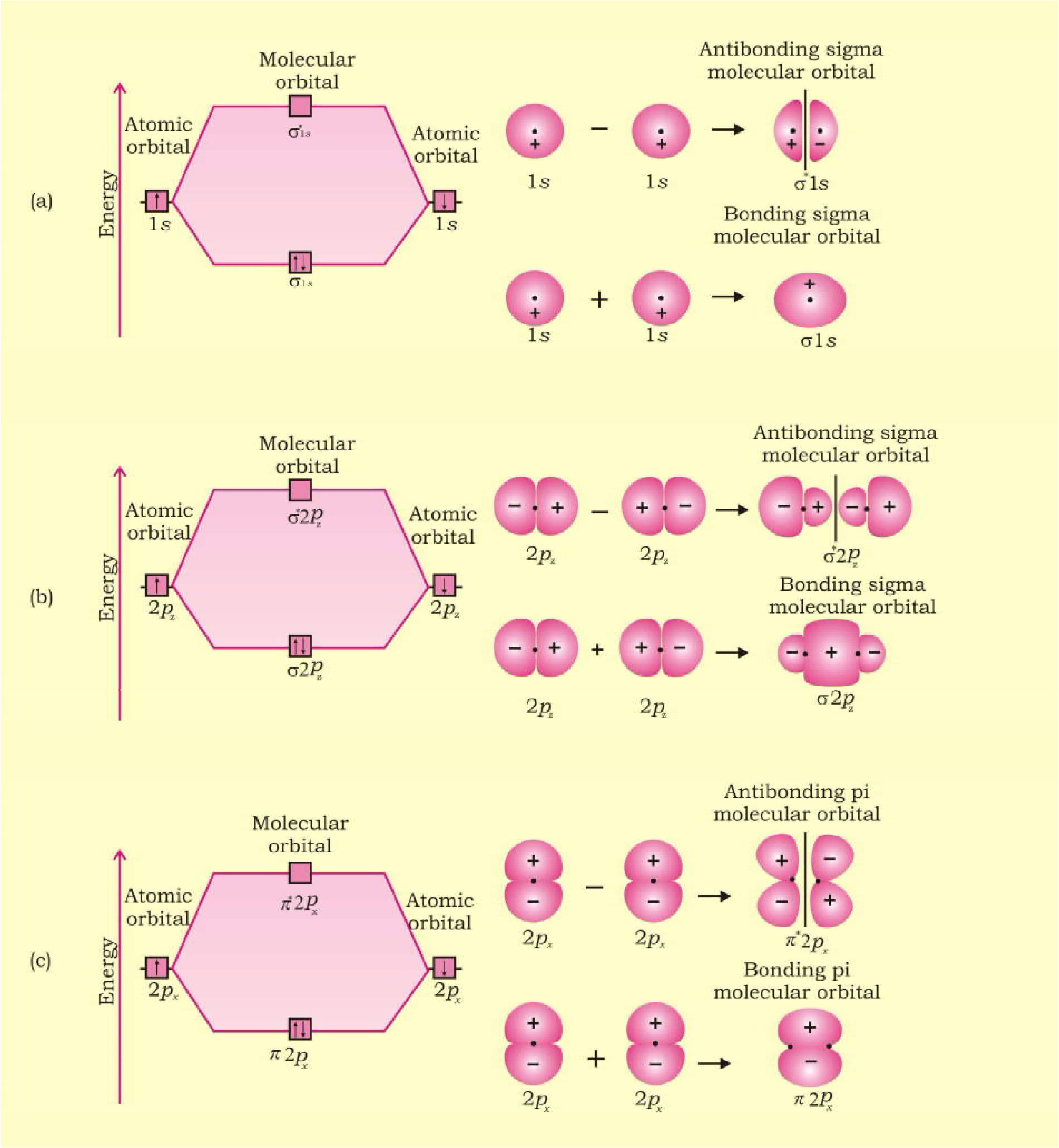


Fig. 4.20 *Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.*

on two atoms) give rise to the following eight molecular orbitals:

Antibonding MOs σ^*2s σ^*2p_z π^*2p_x π^*2p_y
Bonding MOs $\sigma 2s$ $\sigma 2p_z$ $\pi 2p_x$ $\pi 2p_y$

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 O_2 and F_2 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 Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2, etc. the increasing order of energies of various molecular orbitals is

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

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.**

4.7.5 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.

Stability of Molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then

(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.

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 orbitals i.e.,

Bond order (b.o.) = ½ $(N_b - N_a)$

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.

4.8 BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

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

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

$H_2 : (\sigma 1s)^2$

The bond order of H_2 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.

2. Helium molecule (He_2): The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals leading to electronic configuration:

He_2 : $(\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of He_2 is ½(2 – 2) = 0

He_2 *molecule is therefore unstable and does not exist.*

Similarly, it can be shown that Be_2 *molecule* $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ *also does not exist.*

3. Lithium molecule (Li_2): The electronic configuration of lithium is $1s^2, 2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2 molecule, therefore, is

Li_2 : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

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

From the electronic configuration of Li_2 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 ½ (4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

4. Carbon molecule (C_2): The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

$$C_2 : (\sigma 1s)^2 (\sigma * 1s)^2 (\sigma * 2s)^2 \left(\pi 2p_x^2 = \pi 2p_y^2\right)$$

or $KK(\sigma 2s)^2 (\sigma * 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

The bond order of C_2 is ½ (8 – 4) = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 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. In a similar fashion the bonding in N_2 molecule can be discussed.

5. Oxygen molecule (O_2): The electronic configuration of oxygen atom 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

$$O_2:\ (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$$
$$\left(\pi 2p_x{}^2 \equiv \pi 2p_y{}^2\right)\ \left(\pi^* 2p_x{}^1 \equiv \pi^* 2p_y{}^1\right)$$

$$O_2 : \left[\begin{matrix} KK\ (\sigma 2s)^2 (\sigma * 2s)^2 (\sigma 2p_z)^2 \\ \left(\pi 2p_x^2 \equiv \pi 2p_y^2\right), \left(\pi * 2p_x^1 \equiv \pi * 2p_y^1\right) \end{matrix}\right]$$

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.4.21 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.

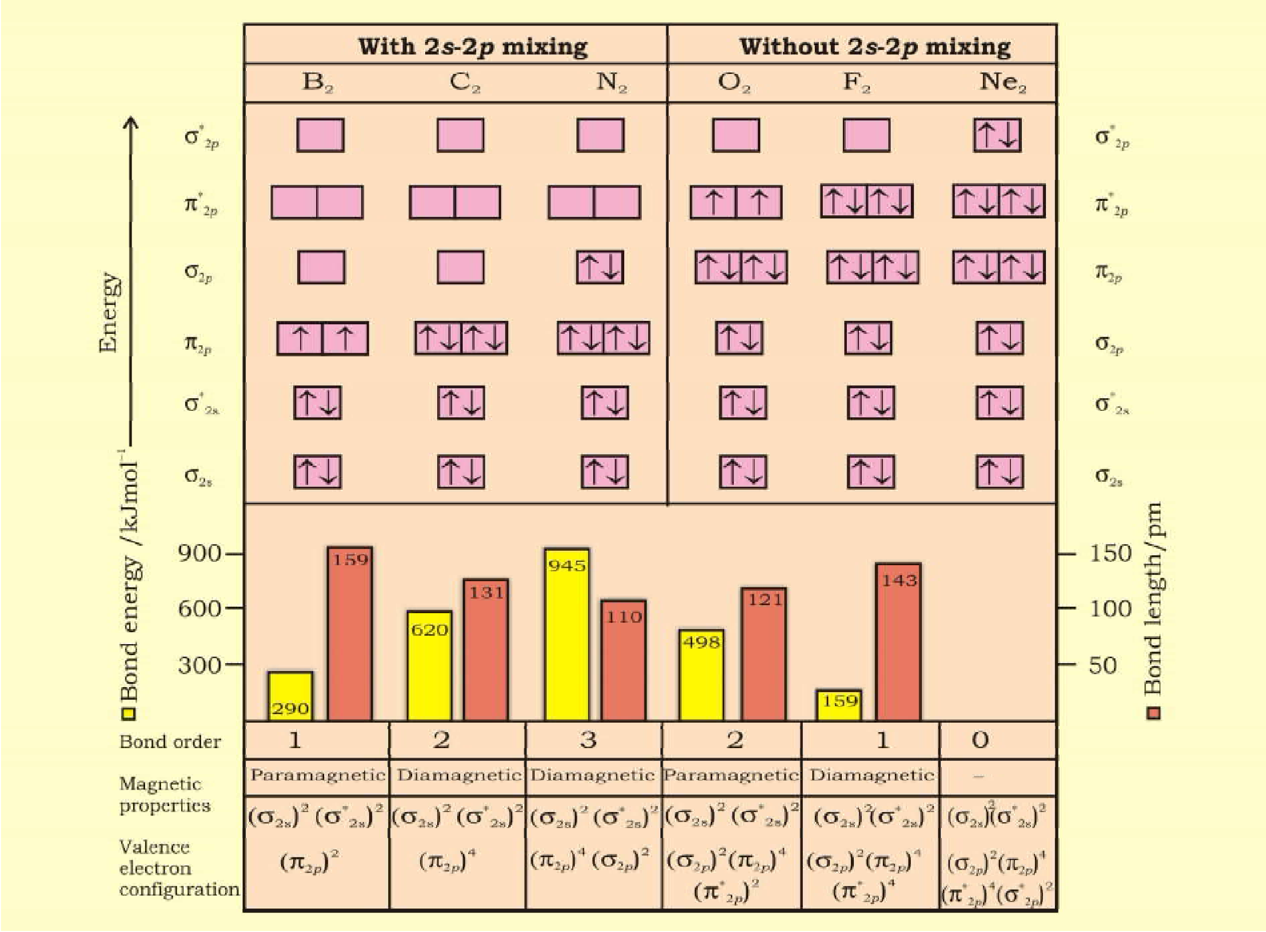


Fig. 4.21 *MO occupancy and molecular properties for B_2 through Ne_2.*

4.9 HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the higly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the 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 :

$$---H^{\delta+} - F^{\delta-} --- H^{\delta+} - F^{\delta-} --- H^{\delta+} - F^{\delta-}$$

Here, hydrogen bond acts as a bridge between two 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.**

4.9.1 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 (δ^+) 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 :

$$H^{\delta+} - X^{\delta-} --- H^{\delta+} - X^{\delta-} --- H^{\delta+} - X^{\delta-}$$

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.

4.9.2 Types of H-Bonds

There are two types of H-bonds

(i) Intermolecular hydrogen bond

(ii) Intramolecular hydrogen bond

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in *o*-nitrophenol the hydrogen is in between the two oxygen atoms.

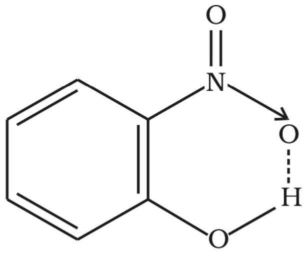


Fig. 4.22 *Intramolecular hydrogen bonding in o-nitrophenol molecule*

SUMMARY

Kössel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of **electrovalency**.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. **Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.**

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion.

The ***VSEPR model*** used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, *molecular geometry is determined by repulsions between lone pairs and lone pairs* ; *lone pairs and bonding pairs* and *bonding pairs and bonding pairs*. The order of these repulsions being : lp-lp > lp-bp > bp-bp

The **valence bond (VB) approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the 1*s* orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridisation of atomic orbitals**. sp, sp^2, sp^3 hybridizations of atomic orbitals of Be, B,C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O. They also explain the formation of multiple bonds in molecules like C_2H_2 and C_2H_4.

The **molecular orbital (MO) theory** describes bonding in terms of the combination and arrangment of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of elctrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.

Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.

EXERCISES

4.1 Explain the formation of a chemical bond.

4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

4.3 Write Lewis symbols for the following atoms and ions:
S and S^{2-}; Al and Al^{3+}; H and H^-

4.4 Draw the Lewis structures for the following molecules and ions :
H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

4.5 Define octet rule. Write its significance and limitations.

4.6 Write the favourable factors for the formation of ionic bond.

4.7 Discuss the shape of the following molecules using the VSEPR model:
$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

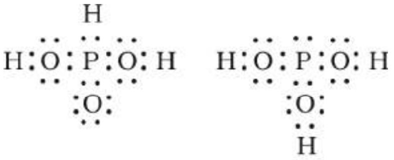
4.8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

4.9 How do you express the bond strength in terms of bond order ?

4.10 Define the bond length.

4.11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

4.12 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.



(1) (2)

4.13 Write the resonance structures for SO_3, NO_2 and NO_3^- .

4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N.

4.15 Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

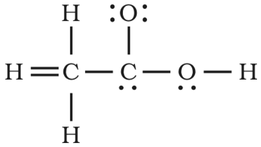
4.16 Write the significance/applications of dipole moment.

4.17 Define electronegativity. How does it differ from electron gain enthalpy ?

4.18 Explain with the help of suitable example polar covalent bond.

4.19 Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

4.20 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



4.21 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar ?

4.22 Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

4.23 Which out of NH_3 and NF_3 has higher dipole moment and why ?

4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of *sp*, *sp*^{2}, *sp*^{3} hybrid orbitals.

4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction?

$$BF_3 + NH_3 \rightarrow F_3B.NH_3$$

4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

4.28 What is the total number of sigma and pi bonds in the following molecules?

(a) C_2H_2 (b) C_2H_4

4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) $1s$ and $1s$ (b) $1s$ and $2p_x$; (c) $2p_y$ and $2p_y$ (d) $1s$ and $2s$.

4.30 Which hybrid orbitals are used by carbon atoms in the following molecules?

CH_3–CH_3; (b) CH_3–CH=CH_2; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH

4.31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one exmaple of each type.

4.32 Distinguish between a sigma and a pi bond.

4.33 Explain the formation of H_2 molecule on the basis of valence bond theory.

4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

4.35 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

4.36 Compare the relative stability of the following species and indicate their magnetic properties;

O_2, O_2^+, O_2^- (superoxide), O_2^{2-} (peroxide)

4.37 Write the significance of a plus and a minus sign shown in representing the orbitals.

4.38 Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

4.40 What is meant by the term bond order? Calculate the bond order of : N_2, O_2, O_2^+ and O_2^-.

UNIT 5

STATES OF MATTER

Objectives

After studying this unit you will be able to

- explain the existence of different states of matter in terms of balance between intermolecular forces and thermal energy of particles;
- explain the laws governing behaviour of ideal gases;
- apply gas laws in various real life situations;
- explain the behaviour of real gases;
- describe the conditions required for liquifaction of gases;
- realise that there is continuity in gaseous and liquid state;
- differentiate between gaseous state and vapours; and
- explain properties of liquids in terms of intermolecular attractions.

> *“The snowflake falls, yet lays not long*
> *Its feath'ry grasp on Mother Earth*
> *Ere Sun returns it to the vapors Whence it came,*
> *Or to waters tumbling down the rocky slope.”*
>
> *Rod O' Connor*

INTRODUCTION

In previous units we have learnt about the properties related to single particle of matter, such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity, etc. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, *i.e.,* the properties associated with a collection of a large number of atoms, ions or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. Collection of water molecules have wetting properties; individual molecules do not wet. Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam. Physical properties of ice, water and steam are very different. In all the three states of water chemical composition of water remains the same i.e., H_2O. Characteristics of the three states of water depend on the energies of molecules and on the manner in which water molecules aggregate. Same is true for other substances also.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical laws which govern the behaviour of matter in different states. In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states. To begin with, it is necessary to understand the nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles because a balance between these determines the state of a substance.

5.1 INTERMOLECULAR FORCES

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

Attractive intermolecular forces are known as **van der Waals forces**, in honour of Dutch scientist Johannes van der Waals (1837-1923), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this unit. van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. **Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.** We have already learnt about this interaction in Unit 4.

At this point, it is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces. We will now learn about different types of van der Waals forces.

5.1.1 Dispersion Forces or London Forces

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 (Fig. 5.1a). 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 (Fig. 5.1 b and c). 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 dipoles 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

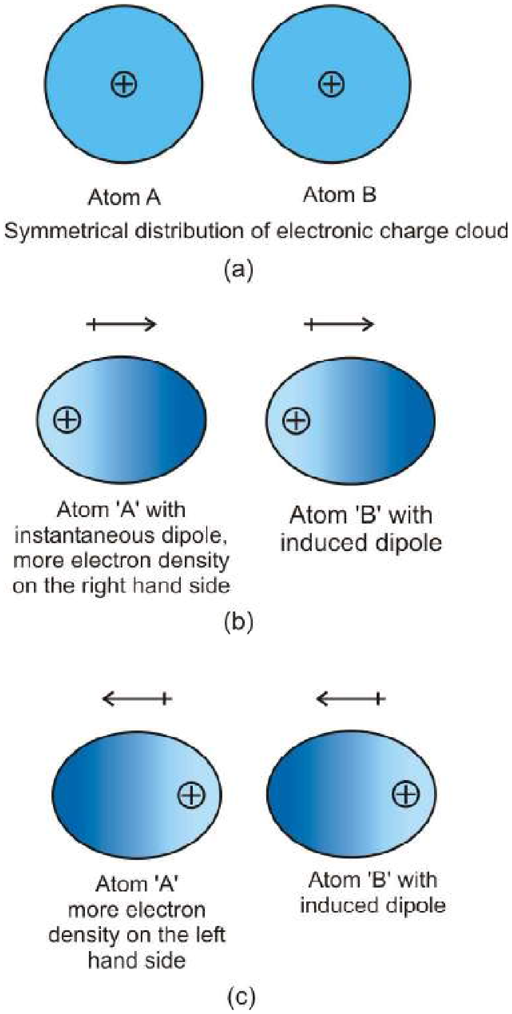


Fig. 5.1 *Dispersion forces or London forces between atoms.*

dipoles is known as **London force**. Another name for this force is **dispersion force**. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where r is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

5.1.2 Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter *delta* (δ). Partial charges are always less than the unit electronic charge (1.6×10^{-19} C). The polar molecules interact with neighbouring molecules. Fig 5.2 (a) shows electron cloud distribution in the dipole of hydrogen chloride and Fig. 5.2 (b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) 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 molecules increase.

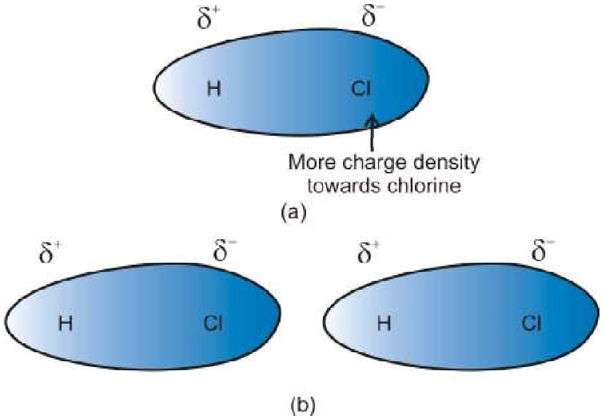


Fig. 5.2 *(a) Distribution of electron cloud in HCl – a polar molecule, (b) Dipole-dipole interaction between two HCl molecules*

5.1.3 Dipole–Induced Dipole Forces

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to $1/r^6$ where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. We have already learnt in Unit 4 that molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

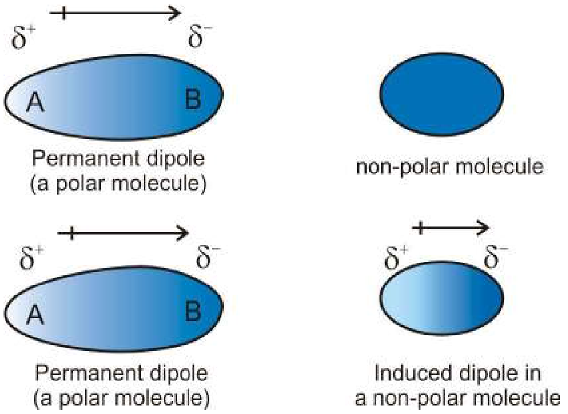


Fig. 5.3 *Dipole - induced dipole interaction between permanent dipole and induced dipole*

In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

5.1.4 Hydrogen bond

As already mentioned in section (5.1); this is special case of dipole-dipole interaction. We have already learnt about this in Unit 4. This is found in the molecules in which highly polar N–H, O–H or H–F bonds are present. Although hydrogen bonding is regarded as being limited to N, O and F; but species such as $\bar{\mathrm{Cl}}$ may also participate in hydrogen bonding. Energy of hydrogen bond varies between 10 to 100 kJ mol^{-1}. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids. Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule. Following diagram shows the formation of hydrogen bond.

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\cdots\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}$$

Intermolecular forces discussed so far are all attractive. **Molecules also exert repulsive forces** on one another. When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

5.2 THERMAL ENERGY

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.

5.3 INTERMOLECULAR FORCES *vs* THERMAL INTERACTIONS

We have already learnt that 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.

When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified. Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows :

Predominance of intermolecular interactions

Predominance of thermal energy

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about gaseous and liquid states and the laws which govern the behaviour of matter in these states. We shall deal with the solid state in class XII.

5.4 THE GASEOUS STATE

This is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. We spend our life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force. The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc.

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven elements

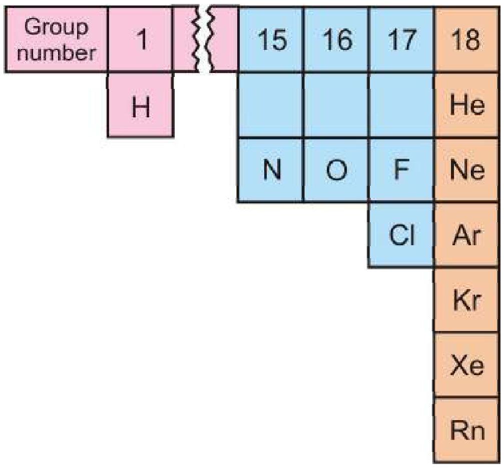


Fig. 5.4 *Eleven elements that exist as gases*

exist as gases under normal conditions (Fig 5.4).

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour 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. Interdependence of these variables leads to the formulation of gas laws. In the next section we will learn about gas laws.

5.5 THE GAS LAWS

The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. 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.

5.5.1 Boyle's Law (Pressure - Volume Relationship)

On the basis of his experiments, Robert Boyle reached to the conclusion that **at constant temperature, the pressure of a fixed amount** (i.e., number of moles *n*) **of gas varies inversely with its volume**. This is known as **Boyle's law**. Mathematically, it can be written as

$$p \propto \frac{1}{V} \quad (\text{at constant } T \text{ and } n) \qquad (5.1)$$

$$\Rightarrow p = k_1 \frac{1}{V} \qquad (5.2)$$

where k_1 is the proportionality constant. The value of constant k_1 depends upon the amount of the gas, temperature of the gas and the units in which *p* and *V* are expressed.

On rearranging equation (5.2) we obtain

$$pV = k_1 \qquad (5.3)$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2, then according to Boyle's law :

$$p_1V_1 = p_2V_2 = \text{constant} \qquad (5.4)$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1} \qquad (5.5)$$

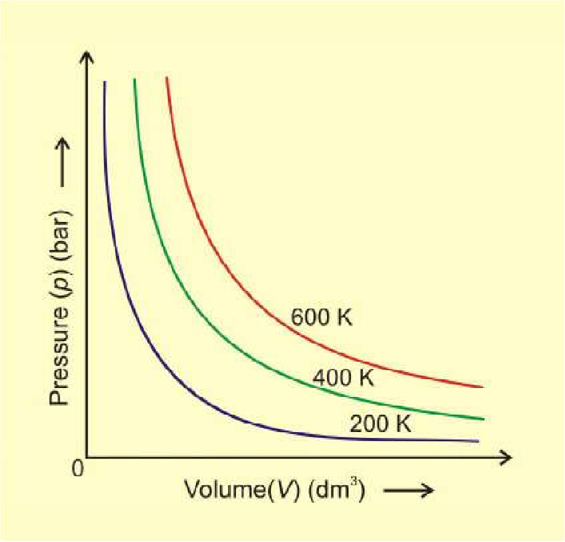


Fig. 5.5(a) *Graph of pressure, p vs. Volume, V of a gas at different temperatures.*

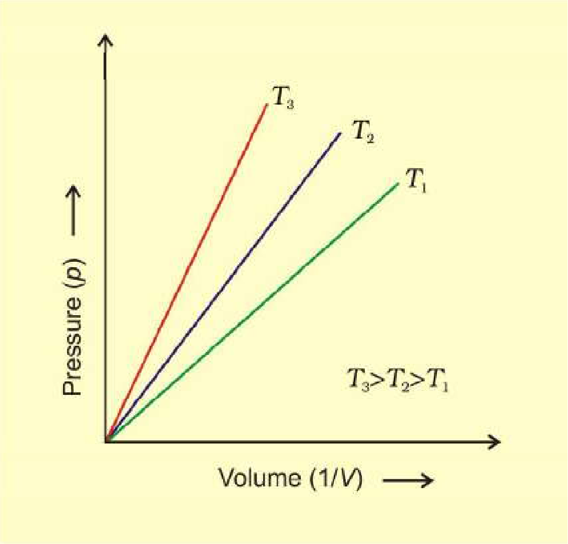


Fig. 5.5 (b) *Graph of pressure of a gas, p vs.* $\frac{1}{V}$

Figure 5.5 shows two conventional ways of graphically presenting Boyle's law. Fig. 5.5 (a) is the graph of equation (5.3) at different temperatures. The value of k_1 for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an **isotherm** (constant temperature plot). Higher curves correspond to higher temperature. It should be noted that volume of the gas doubles if pressure is halved. Table 5.1 gives effect of pressure on volume of 0.09 mol of CO_2 at 300 K.

Fig 5.5 (b) represents the graph between p and $\frac{1}{V}$. It is a straight line passing through origin. However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.

Experiments of Boyle, in a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law:

By definition, density '*d*' is related to the mass '*m*' and the volume '*V*' by the relation $d = \frac{m}{V}$. If we put value of V in this equation from Boyle's law equation, we obtain the relationship.

Table 5.1 Effect of Pressure on the Volume of 0.09 mol CO_2 Gas at 300 K.

Pressure/10^4 Pa	Volume/10^{-3} m^3	$(1/V)$/m^{-3}	pV/10^2 Pa m^3
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

$$d = \left(\frac{m}{k_1}\right) p = k' p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Problem 5.1

A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded ?

Solution

According to Boyle's Law $p_1V_1 = p_2V_2$

If p_1 is 1 bar, V_1 will be 2.27 L

If $p_2 = 0.2$ bar, then $V_2 = \frac{p_1V_1}{p_2}$

$$\Rightarrow V_2 = \frac{1\,\text{bar} \times 2.27\,\text{L}}{0.2\,\text{bar}} = 11.35\ \text{L}$$

Since balloon bursts at 0.2 bar pressure, the volume of balloon should be less than 11.35 L.

5.5.2 Charles' Law (Temperature - Volume Relationship)

Charles and Gay Lussac performed several experiments on gases independently to improve upon hot air balloon technology. Their investigations showed that for a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling. They found that for each degree rise in temperature, volume of a gas increases by $\frac{1}{273.15}$ of the original volume of the gas at 0 °C. Thus if volumes of the gas at 0 °C and at t °C are V_0 and V_t respectively, then

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$\Rightarrow V_t = V_0\left(1 + \frac{t}{273.15}\right)$$

$$\Rightarrow V_t = V_0\left(\frac{273.15 + t}{273.15}\right) \qquad (5.6)$$

At this stage, we define a new scale of temperature such that t °C on new scale is given by $T = 273.15 + t$ and 0 °C will be given by $T_0 = 273.15$. This new temperature scale is called the **Kelvin temperature scale** or **Absolute temperature scale**.

Thus 0°C on the celsius scale is equal to 273.15 K at the absolute scale. Note that degree sign is not used while writing the temperature in absolute temperature scale, i.e., Kelvin scale. Kelvin scale of temperature is also called **Thermodynamic scale** of temperature and is used in all scientific works.

Thus we add 273 (more precisely 273.15) to the celsius temperature to obtain temperature at Kelvin scale.

If we write $T_t = 273.15 + t$ and $T_0 = 273.15$ in the equation (5.6) we obtain the relationship

$$V_t = V_0\left(\frac{T_t}{T_0}\right)$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0} \qquad (5.7)$$

Thus we can write a general equation as follows.

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \qquad (5.8)$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{constant} = k_2 \qquad (5.9)$$

Thus $V = k_2 T$ (5.10)

The value of constant k_2 is determined by the pressure of the gas, its amount and the units in which volume V is expressed.

Equation (5.10) is the mathematical expression for **Charles' law**, which states that **pressure remaining constant, the volume**

of a fixed mass of a gas is directly proportional to its absolute temperature. Charles found that for all gases, at any given pressure, graph of volume *vs* temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 °C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 °C (Fig. 5.6).

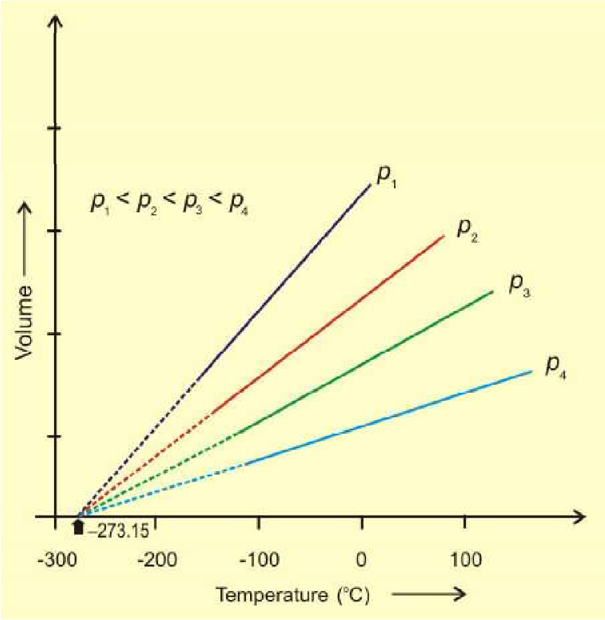


Fig. 5.6 *Volume vs Temperature (°C) graph*

Each line of the volume *vs* temperature graph is called **isobar**.

Observations of Charles can be interpreted if we put the value of t in equation (5.6) as – 273.15 °C. We can see that the volume of the gas at – 273.15 °C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero**.

All gases obey Charles' law at very low pressures and high temperatures.

Problem 5.2

On a ship sailing in Pacific Ocean where temperature is 23.4°C, a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C ?

Solution

$V_1 = 2$ L $\qquad T_2 = 26.1 + 273$

$T_1 = (23.4 + 273)$ K $\qquad = 299.1$ K

$= 296.4$ K

From Charles law

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

$$\Rightarrow V_2 = \frac{V_1 T_2}{T_1}$$

$$\Rightarrow V_2 = \frac{2\,\mathrm{L} \times 299.1\,\mathrm{K}}{296.4\,\mathrm{K}}$$

$$= 2\mathrm{L} \times 1.009$$

$$= 2.018\mathrm{L}$$

5.5.3 Gay Lussac's Law (Pressure-Temperature Relationship)

Pressure in well inflated tyres of automobiles is almost constant, but on a hot summer day this increases considerably and tyre may burst if pressure is not adjusted properly. During winters, on a cold morning one may find the pressure in the tyres of a vehicle decreased considerably. The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law. It states that **at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.** Mathematically,

$$p \propto T$$

$$\Rightarrow \frac{p}{T} = \text{constant} = k_3$$

This relationship can be derived from Boyle's law and Charles' Law. Pressure *vs* temperature (Kelvin) graph at constant molar volume is shown in Fig. 5.7. Each line of this graph is called **isochore.**

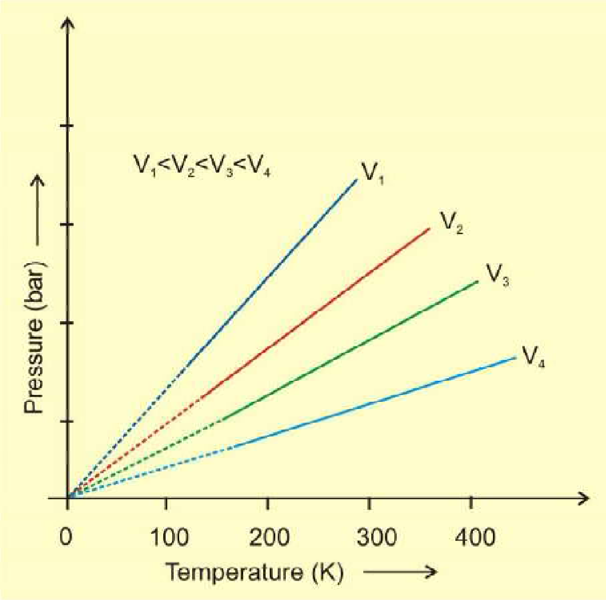


Fig. 5.7 *Pressure vs temperature (K) graph (Isochores) of a gas.*

5.5.4 Avogadro Law (Volume - Amount Relationship)

In 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes (Unit 1) which is now known as Avogadro law. **It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.** This means that as long as the temperature and pressure remain constant, the volume depends upon number of molecules of the gas or in other words amount of the gas. Mathematically we can write

$V \propto n$ where n is the number of moles of the gas.

$$\Rightarrow V = k_4 n \qquad (5.11)$$

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and is known as **Avogadro constant**. You will find that this is the same number which we came across while discussing definition of a 'mole' (Unit 1).

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. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.**

Molar volume of some gases is given in (Table 5.2).

Table 5.2 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

Number of moles of a gas can be calculated as follows

$$n = \frac{m}{M} \qquad (5.12)$$

Where m = mass of the gas under investigation and M = molar mass

Thus,

$$V = k_4 \frac{m}{M} \qquad (5.13)$$

Equation (5.13) can be rearranged as follows :

$$M = k_4 \frac{m}{M} = k_4 d \qquad (5.14)$$

---

* *The previous standard is still often used, and applies to all chemistry data more than decade old. In this definition STP denotes the same temperature of 0°C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa). One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.*

Standard ambient temperature and pressure *(SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e., exactly 10^5 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}.*

Here '*d*' is the density of the gas. We can conclude from equation (5.14) that the density of a gas is directly proportional to its molar mass.

A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called **an ideal gas**. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour. You will learn about the deviations later in this unit.

5.6 IDEAL GAS EQUATION

The three laws which we have learnt till now can be combined together in a single equation which is known as **ideal gas equation**.

At constant T and n; $V \propto \frac{1}{p}$ **Boyle's Law**

At constant p and n; $V \propto T$ **Charles' Law**

At constant p and T; $V \propto n$ **Avogadro Law**

Thus,

$$V \propto \frac{nT}{p} \tag{5.15}$$

$$\Rightarrow \quad V = \mathrm{R}\frac{nT}{p} \tag{5.16}$$

where R is proportionality constant. On rearranging the equation (5.16) we obtain

$$pV = n\mathrm{R}T \tag{5.17}$$

$$\Rightarrow \quad \mathrm{R} = \frac{pV}{nT} \tag{5.18}$$

R is called gas constant. It is same for all gases. Therefore it is also called **Universal Gas Constant**. Equation (5.17) is called **ideal gas equation.**

Equation (5.18) shows that the value of R depends upon units in which p, V and T are measured. If three variables in this equation are known, fourth can be calculated. From this equation we can see that at constant temperature and pressure n moles of any gas will have the same volume because $V = \frac{n\mathrm{R}T}{p}$ and n, R, T and p are constant. This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol^{-1}. Value of R for one mole of an ideal gas can be calculated under these conditions as follows :

$$\mathrm{R} = \frac{(10^5\ \mathrm{Pa})(22.71 \times 10^{-3}\mathrm{m}^3)}{(1\,\mathrm{mol})(273.15\ \mathrm{K})}$$

$$= 8.314\ \mathrm{Pa\ m^3\ K^{-1}\ mol^{-1}}$$

$$= 8.314 \times 10^{-2}\ \mathrm{bar\ L\ K^{-1}\ mol^{-1}}$$

$$= 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

At STP conditions used earlier (0 °C and 1 atm pressure), value of R is 8.20578 × 10^{-2} L atm K^{-1} mol^{-1}.

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.

Let us now go back to the ideal gas equation. This is the relationship for the simultaneous variation of the variables. If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

$$\frac{p_1V_1}{T_1} = n\mathrm{R} \quad \text{and} \quad \frac{p_2V_2}{T_2} = n\mathrm{R}$$

$$\Rightarrow \quad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \tag{5.19}$$

Equation (5.19) is a very useful equation. If out of six, values of five variables are known, the value of unknown variable can be calculated from the equation (5.19). This equation is also known as **Combined gas law**.

Problem 5.3

At 25°C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10°C and volume of the gas is 640 mL.

Solution

p_1 = 760 mm Hg, V_1= 600 mL

T_1 = 25 + 273 = 298 K

V_2 = 640 mL and T_2 = 10 + 273 = 283 K

According to Combined gas law

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\Rightarrow p_2 = \frac{p_1V_1T_2}{T_1V_2}$$

$$\Rightarrow p_2 = \frac{(760 \text{ mm Hg}) \times (600 \text{ mL}) \times (283 \text{ K})}{(640 \text{ mL}) \times (298 \text{ K})}$$

$$= 676.6 \text{ mm Hg}$$

5.6.1 Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows:

$$\frac{n}{V} = \frac{p}{RT}$$

Replacing n by $\frac{m}{M}$, we get

$$\frac{m}{MV} = \frac{p}{RT} \qquad (5.20)$$

$$\frac{d}{M} = \frac{p}{RT} \text{ (where } d \text{ is the density)} \qquad (5.21)$$

On rearranging equation (5.21) we get the relationship for calculating molar mass of a gas.

$$M = \frac{dRT}{p} \qquad (5.22)$$

5.6.2 Dalton's Law of Partial Pressures

The law was formulated by John Dalton in 1801. It states that **the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases** i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called **partial pressure**. Mathematically,

$$p_{\text{Total}} = p_1+p_2+p_3+......\text{(at constant } T, V) \qquad (5.23)$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2 , p_3 etc. are partial pressures of gases.

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called **aqueous tension**. Aqueous tension of water at different temperatures is given in Table 5.3.

$$p_{\text{Dry gas}} = p_{\text{Total}} - \text{Aqueous tension} \qquad (5.24)$$

Table 5.3 Aqueous Tension of Water (Vapour Pressure) as a Function of Temperature

Temp./K	Pressure/bar	Temp./K	Pressure/bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1, p_2 and p_3 respectively, then,

$$p_1 = \frac{n_1RT}{V} \qquad (5.25)$$

$$p_2 = \frac{n_2RT}{V} \qquad (5.26)$$

$$p_3 = \frac{n_3 RT}{V} \qquad (5.27)$$

where n_1 n_2 and n_3 are number of moles of these gases. Thus, expression for total pressure will be

$$p_{\text{Total}} = p_1 + p_2 + p_3$$

$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V} \qquad (5.28)$$

On dividing p_1 by p_{total} we get

$$\frac{p_1}{p_{\text{total}}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right) \frac{RTV}{RTV}$$

$$= \frac{n_1}{n_1 + n_2 + n_3} = \frac{n_1}{n} = x_1$$

where $n = n_1 + n_2 + n_3$

x_1 is called mole fraction of first gas.

Thus, $p_1 = x_1\, p_{\text{total}}$

Similarly for other two gases we can write

$p_2 = x_2\, p_{\text{total}}$ and $p_3 = x_3\, p_{\text{total}}$

Thus a general equation can be written as

$$p_i = x_i\, p_{\text{total}} \qquad (5.29)$$

where p_i *and* x_i are partial pressure and mole fraction of i^{th} gas respectively. If total pressure of a mixture of gases is known, the equation (5.29) can be used to find out pressure exerted by individual gases.

Problem 5.4

A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5 g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture ?

Number of moles of dioxygen

$$= \frac{70.6 \text{ g}}{32 \text{ g mol}^{-1}}$$

$$= 2.21 \text{ mol}$$

Number of moles of neon

$$= \frac{167.5 \text{ g}}{20 \text{ g mol}^{-1}}$$

$$= 8.375 \text{ mol}$$

Mole fraction of dioxygen

$$= \frac{2.21}{2.21 + 8.375}$$

$$= \frac{2.21}{10.585}$$

$$= 0.21$$

Mole fraction of neon $= \dfrac{8.375}{2.21 + 8.375}$

$= 0.79$

Alternatively,

mole fraction of neon = 1– 0.21 = 0.79

Partial pressure of a gas = mole fraction × total pressure

⇒ Partial pressure of oxygen = 0.21 × (25 bar) = 5.25 bar

Partial pressure of neon = 0.79 × (25 bar) = 19.75 bar

5.7 KINETIC ENERGY AND MOLECULAR SPEEDS

Molecules of gases remain in continuous motion. While moving they collide with each other and with the walls of the container. This results in change of their speed and redistribution of energy. So the speed and energy of all the molecules of the gas at any instant are not the same. Thus, we can obtain only average value of speed of molecules. If there are n number of molecules in a sample and their individual speeds are u_1, u_2, ...u_n, then average speed of molecules u_{av} can be calculated as follows:

$$u_{av} = \frac{u_1 + u_2 + \ldots\ldots\ldots u_n}{n}$$

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. Maxwell derived a formula for calculating the number of molecules possessing a particular speed. Fig. 5.8 shows schematic plot of number of molecules vs. molecular speed at two different temperatures T_1 and T_2 (T_2 is higher than T_1). The distribution of speeds shown in the plot is called Maxwell-Boltzmann distribution of speeds.

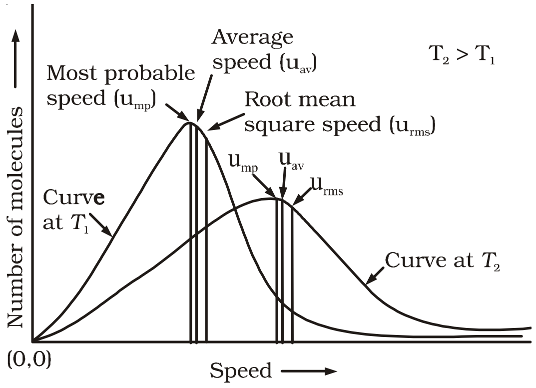


Fig. 5.8: *Maxwell-Boltzmann distribution of speeds*

The graph shows that number of molecules possessing very high and very low speed is very small. The maximum in the curve represents speed possessed by maximum number of molecules. This speed is called **most probable speed, u_{mp}**. This is very close to the average speed of the molecules. On increasing the temperature most probable speed increases. Also, speed distribution curve broadens at higher temperature. Broadening of the curve shows that number of molecules moving at higher speed increases. Speed distribution also depends upon mass of molecules. At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules. For example, at the same temperature lighter nitrogen molecules move faster than heavier chlorine molecules. Hence, at any given temperature, nitrogen molecules have higher value of most probable speed than the chlorine molecules. Look at the molecular speed distribution curve of chlorine and nitrogen given in Fig. 5.9. Though at a particular temperature the individual speed of molecules keeps changing, the distribution of speeds remains same.

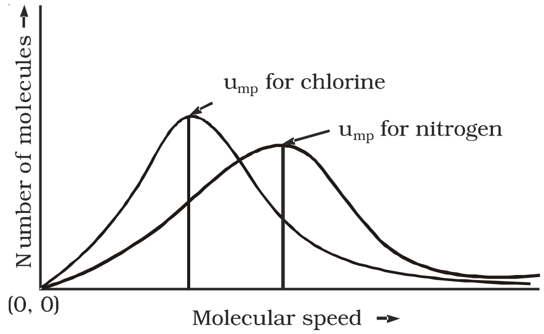


Fig. 5.9: *Distribution of molecular speeds for chlorine and nitrogen at 300 K*

We know that kinetic energy of a particle is given by the expression:

$$\text{Kinetic Energy} = \frac{1}{2}mu^2$$

Therefore, if we want to know average translational kinetic energy, $\frac{1}{2}m\overline{u^2}$, for the movement of a gas particle in a straight line, we require the value of mean of square of speeds, $\overline{u^2}$, of all molecules. This is represented as follows:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \ldots\ldots\ldots u_n^2}{n}$$

The mean square speed is the direct measure of the average kinetic energy of gas molecules. If we take the square root of the mean of the square of speeds then we get a value of speed which is different from most probable speed and average speed. This speed is called **root mean square speed** and is given by the expression as follows:

$$u_{rms} = \sqrt{\overline{u^2}}$$

Root mean square speed, average speed and the most probable speed have following relationship:

$$u_{rms} > u_{av} > u_{mp}$$

The ratio between the three speeds is given below :

$$u_{mp} : u_{av} : u_{rms} : : 1 : 1.128 : 1.224$$

5.8 KINETIC MOLECULAR THEORY OF GASES

So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However, once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases but we would like to know what happens at molecular level when a gas is compressed ? A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently, the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory, it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently, thus, exerting more pressure.

Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

5.9 BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

Our theoritical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV *vs* p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV *vs* p graph at all pressures will be a straight line parallel to x-axis. Fig. 5.10 shows such a plot constructed from actual data for several gases at 273 K.

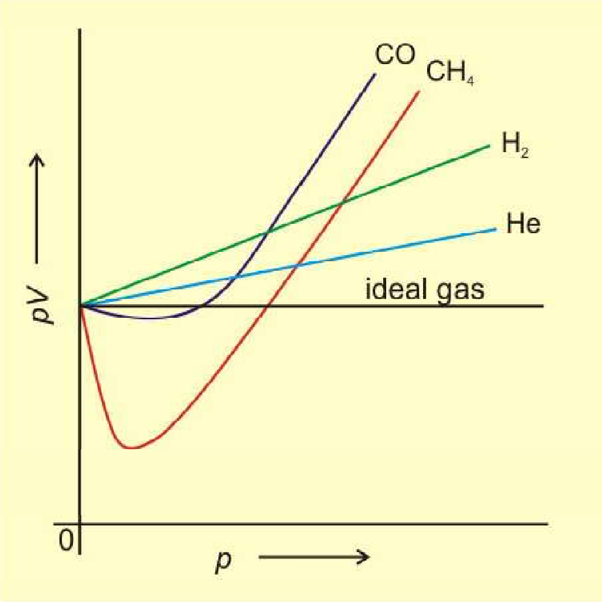


Fig. 5.10 *Plot of pV vs p for real gas and ideal gas*

It can be seen easily that at constant temperature pV *vs* p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus, found that real gases do not follow ideal gas equation perfectly under all conditions.

Deviation from ideal behaviour also becomes apparent when pressure *vs* volume plot is drawn. The pressure *vs* volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 5.11 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

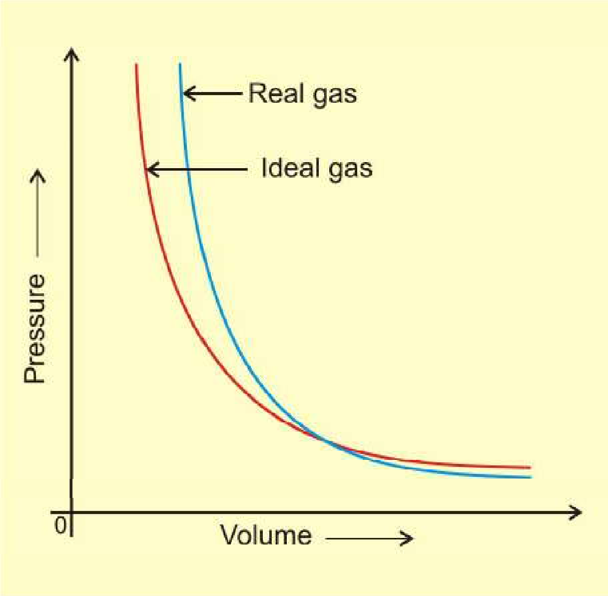


Fig. 5.11 *Plot of pressure vs volume for real gas and ideal gas*

It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

(i) Why do gases deviate from the ideal behaviour?

(ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

(a) There is no force of attraction between the molecules of a gas.

(b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure *vs* volume graph of experimental data (real gas) and that theoritically calculated from Boyles law (ideal gas) should coincide.

Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = \underset{\text{observed pressure}}{p_{real}} + \underset{\text{correction term}}{\frac{an^2}{V^2}} \qquad (5.30)$$

Here, a is a constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume *V*, these are now restricted to volume (*V*–*n*b) where *n*b is approximately the total volume occupied by the molecules themselves. Here, b is a constant. Having taken into account the corrections for pressure and volume, we can rewrite equation (5.17) as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (5.31)$$

Equation (5.31) is known as van der Waals equation. In this equation *n* is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of **compressibility factor** *Z*, which is the ratio of product *pV* and *nRT*. Mathematically

$$Z = \frac{pV}{n\,RT} \qquad (5.32)$$

For ideal gas *Z* = 1 at all temperatures and pressures because *pV* = *n* R*T*. The graph of *Z vs p* will be a straight line parallel to pressure axis (Fig. 5.12, page 152). For gases which deviate from ideality, value of *Z* deviates from unity. At very low pressures all gases shown have Z ≈1 and behave as ideal gas. At high pressure all the gases have Z > 1. These are more difficult to compress. At intermediate pressures, most gases have Z < 1. **Thus gases show ideal behaviour when the volume**

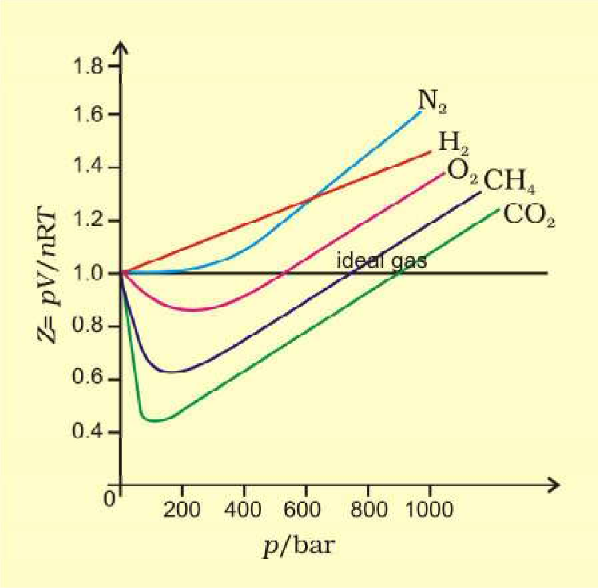


Fig. 5.12 *Variation of compressibility factor for some gases*

occupied is large so that the volume of the molecules can be neglected in comparison to it. In other words, the behaviour of the gas becomes more ideal when pressure is very low. Upto what pressure a gas will follow the ideal gas law, depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.** Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

More insight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{pV_{real}}{nRT} \qquad (5.33)$$

If the gas shows ideal behaviour then $V_{ideal} = \frac{nRT}{p}$. On putting this value of $\frac{nRT}{p}$ in equation (5.33) we have $Z = \frac{V_{real}}{V_{ideal}}$ (5.34)

From equation (5.34) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

In the following sections we will see that it is not possible to distinguish between gaseous state and liquid state and that liquids may be considered as continuation of gas phase into a region of small volumes and very high molecular attraction. We will also see how we can use isotherms of gases for predicting the conditions for liquifaction of gases.

5.10 LIQUIFACTION OF GASES

First complete data on pressure-volume-temperature relations of a substance in both gaseous and liquid state was obtained by Thomas Andrews on Carbon dioxide. He plotted isotherms of carbon dioxide at various temperatures (Fig. 5.13). Later on it was found that real gases behave in the same manner as carbon dioxide. Andrews noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure. As the temperature is lowered, shape of the curve changes and data show considerable deviation from ideal behaviour. At 30.98°C carbon dioxide remains gas upto 73 atmospheric pressure. (Point E in Fig. 5.13). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98°C is called **critical temperature (T_C)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed. Above this temperature it is gas. Volume of one mole of the gas at critical temperature is called **critical volume (V_C)** and pressure at this temperature is called **critical pressure (p_C)**. The critical temperature, pressure and volume are called critical constants. Further increase in pressure simply compresses the

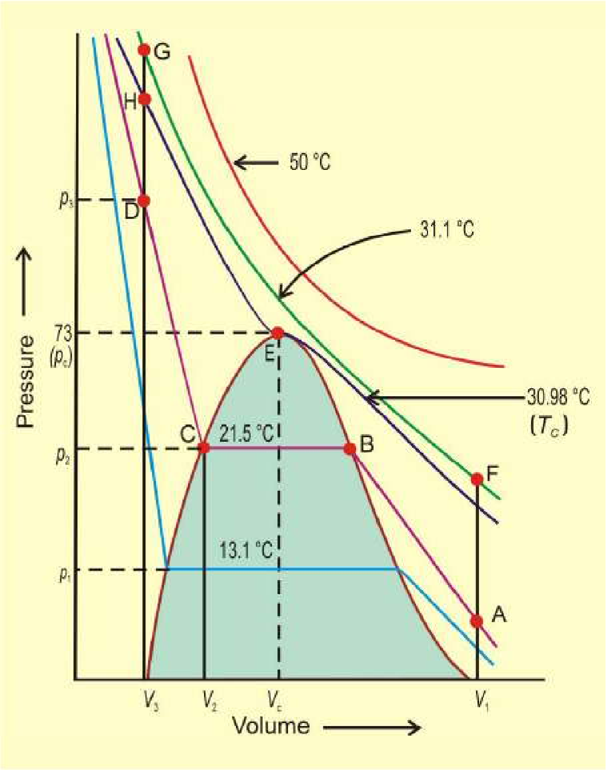


Fig. 5.13 *Isotherms of carbon dioxide at various temperatures*

liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid. Below 30.98 °C, the behaviour of the gas on compression is quite different. At 21.5 °C, carbon dioxide remains as a gas only upto point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. A slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3 (Fig. 5.13). Below 30.98 °C (critical temperature) each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures. At critical point horizontal portion of the isotherm merges into one point. Thus we see that a point like A in the Fig. 5.13 represents gaseous state. A point like D represents liquid state and a point under the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium. All the gases upon compression at constant temperature (isothermal compression) show the same behaviour as shown by carbon dioxide. Also above discussion shows that gases should be cooled below their critical temperature for liquification. Critical temperature of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

It is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example in Fig. 5.13 we can move from point A to F vertically by increasing the temperature, then we can reach the point G by compressing the gas at the constant temperature along this isotherm (isotherm at 31.1°C). The pressure will increase. Now we can move vertically down towards D by lowering the temperature. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region. If process is carried out at the critical temperature, substance always remains in one phase.

Thus there is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears (Section 5.11.1). A gas below the critical temperature can be liquified by applying pressure, and is called **vapour** of the substance. Carbon dioxide gas below its critical temperature is called carbon dioxide vapour. Critical constants for some common substances are given in Table 5.4.

Table 5.4 Critical Constants for Some Substances

Substance	T_c /K	p_c /bar	V_c/dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Problem 5.5

Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the gas particles. Critical temperatures of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquify first when you start cooling from 500 K to their critical temperature ?

Solution

Ammonia will liquify first because its critical temperature will be reached first. Liquifaction of CO_2 will require more cooling.

5.11 LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

5.11.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as **equilibrium vapour pressure or saturated vapour pressure.**. Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 5.14, page 155). At 1 atm pressure boiling temperature is called **normal boiling point**. If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because

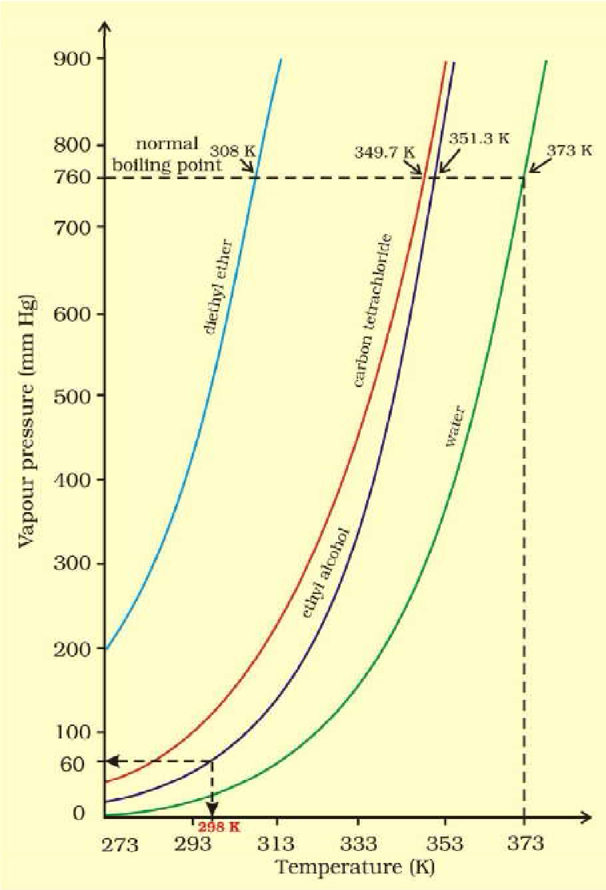


Fig. 5.14 *Vapour pressure vs temperature curve of some common liquids.*

1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature** about which we have already discussed in section 5.10.

5.11.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface. Why do particles of soil at the bottom of river remain separated but they stick together when taken out ? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid ? All these phenomena are caused due to the characteristic property of liquids, called **surface tension**. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 5.15), due to the molecules below it. Since there are no molecules above it.

Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than

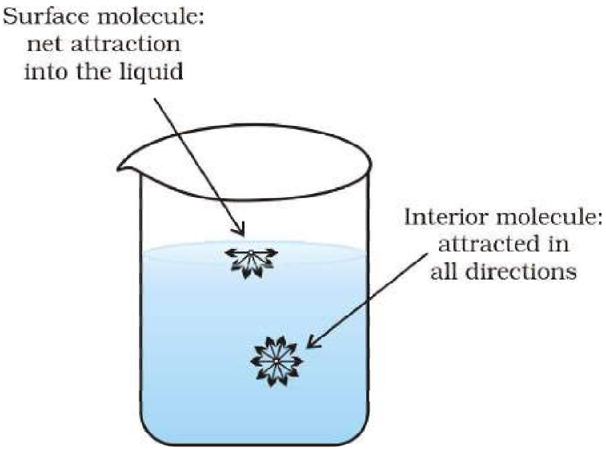


Fig. 5.15 *Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m^{-2}. Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1}. The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

5.11.3 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 increases 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 (Fig.5.16), the layer above it accelerates its flow and the layer below this retards its flow.

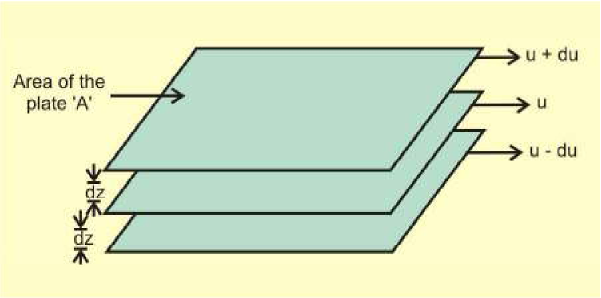


Fig. 5.16 *Gradation of velocity in the laminar flow*

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)

$$F \propto A.\frac{du}{dz}$$

$$\Rightarrow F = \eta A\frac{du}{dz}$$

'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 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ($N\ s\ m^{-2}$) = pascal second ($Pa\ s = 1kg\ m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = $1\ g\ cm^{-1}s^{-1} = 10^{-1}kg\ m^{-1}s^{-1}$

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.

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.

SUMMARY

Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of matter. "Bulk" properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. Chemical properties of a substance do not change with change of state, but the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases. **Boyle's law** states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. **Charles' law** is a relationship between volume and absolute temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature $(V \propto T)$. If state of a gas is represented by p_1, V_1 and T_1 and it changes to state at p_2, V_2 and T_2, then relationship between these two states is given by combined gas law according to which $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$. Any one of the variables of this gas can be found out if other five variables are known. **Avogadro law** states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules. **Dalton's law of partial pressure** states that total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus $p = p_1+p_2+p_3+ \ldots$. Relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is $pV=nRT$, where R is a gas constant and its value depends upon units chosen for pressure, volume and temperature.

At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volume and very strong molecular attractions. Some properties of liquids *e.g.*, surface tension and viscosity are due to strong intermolecular attractive forces.

EXERCISES

5.1 What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C?

5.2 A vessel of 120 mL capacity contains a certain amount of gas at 35 °C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 °C. What would be its pressure?

5.3 Using the equation of state $pV=nRT$; show that at a given temperature density of a gas is proportional to gas pressure p.

5.4 At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

5.5 Pressure of 1 g of an ideal gas A at 27 °C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

5.6 The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20 °C and one bar will be released when 0.15g of aluminum reacts?

5.7 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27 °C ?

5.8 What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C?

5.9 Density of a gas is found to be 5.46 g/dm^3 at 27 °C at 2 bar pressure. What will be its density at STP?

5.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?

5.11 A student forgot to add the reaction mixture to the round bottomed flask at 27 °C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477 °C. What fraction of air would have been expelled out?

5.12 Calculate the temperature of 4.0 mol of a gas occupying 5 dm^3 at 3.32 bar. ($R = 0.083$ bar dm^3 K^{-1} mol^{-1}).

5.13 Calculate the total number of electrons present in 1.4 g of dinitrogen gas.

5.14 How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second ?

5.15 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. $R = 0.083$ bar dm^3 K^{-1} mol^{-1}.

5.16 Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and $R = 0.083$ bar dm^3 K^{-1} mol^{-1}).

5.17 Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083$ bar L K^{-1} mol^{-1}.

5.18 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C, at the same pressure. What is the molar mass of the gas?

5.19 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

5.20 What would be the SI unit for the quantity pV^2T^2/n ?

5.21 In terms of Charles' law explain why –273 °C is the lowest possible temperature.

5.22 Critical temperature for carbon dioxide and methane are 31.1 °C and –81.9 °C respectively. Which of these has stronger intermolecular forces and why?

5.23 Explain the physical significance of van der Waals parameters.

UNIT 7

EQUILIBRIUM

Objectives

After studying this unit you will be able to

- identify dynamic nature of equilibrium involved in physical and chemical processes;
- state the law of equilibrium;
- explain characteristics of equilibria involved in physical and chemical processes;
- write expressions for equilibrium constants;
- establish a relationship between K_p and K_c;
- explain various factors that affect the equilibrium state of a reaction;
- classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;
- classify acids and bases as weak or strong in terms of their ionization constants;
- explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;
- describe pH scale for representing hydrogen ion concentration;
- explain ionisation of water and its duel role as acid and base;
- describe ionic product (K_w) and pK_w *for water;*
- appreciate use of buffer solutions;
- calculate solubility product constant.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O_2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an *equilibrium* in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached **equilibrium state** at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at *equilibrium*, the rate of evaporation is equal to the rate of condensation. It may be represented by

$$H_2O\ (l) \rightleftharpoons H_2O\ (vap)$$

The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture.**

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the **dynamic equilibrium** and the rates of the forward and reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed to reach the state of **chemical equilibrium,** these may be classified in three groups.

(i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.

(ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

(iii) The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as **ionic equilibrium**.

7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, *e.g.*,

$$\text{solid} \rightleftharpoons \text{liquid}$$
$$\text{liquid} \rightleftharpoons \text{gas}$$
$$\text{solid} \rightleftharpoons \text{gas}$$

7.1.1 Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.

It is obvious that ice and water are in equilibrium only at particular temperature and pressure. *For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.* The system here is in dynamic equilibrium and we can infer the following:

(i) Both the opposing processes occur simultaneously.

(ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

7.1.2 Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water