UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to

- understand Kössel-Lewis approach to chemical bonding;
- explain the octet rule and its limitations, draw Lewis structures of simple molecules;
- explain the formation of different types of bonds;
- describe the VSEPR theory and predict the geometry of simple molecules;
- explain the valence bond approach for the formation of covalent bonds;
- predict the directional properties of covalent bonds;
- explain the different types of hybridisation involving *s*, *p* and *d* orbitals and draw shapes of simple covalent molecules;
- describe the molecular orbital theory of homonuclear diatomic molecules;
- explain the concept of hydrogen bond.

> ***“Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts.”***

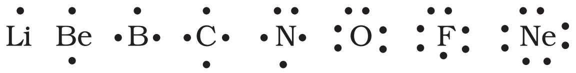
Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. **The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.** Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature’s way of lowering the energy of the system to attain stability.

4.1 KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. **Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.** In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Kössel, in relation to chemical bonding, drew attention to the following facts:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$$\begin{array}{lcl} Na & \rightarrow & Na^+ + e^- \\ [Ne]\,3s^1 & & [Ne] \\ Cl + e^- & \rightarrow & Cl^- \\ [Ne]\,3s^2\,3p^5 & & [Ne]\,3s^2\,3p^6 \text{ or } [Ar] \\ Na^+ + Cl^- & \rightarrow & NaCl \text{ or } Na^+Cl^- \end{array}$$

Similarly the formation of CaF_2 may be shown as:

$$\begin{array}{lcl} Ca & \rightarrow & Ca^{2+} + 2e^- \\ [Ar]4s^2 & & [Ar] \\ F + e^- & \rightarrow & F^- \\ [He]\,2s^2\,2p^5 & & [He]\,2s^2\,2p^6 \text{ or } [Ne] \\ Ca^{2+} + 2F^- & \rightarrow & CaF_2 \text{ or } Ca^{2+}(F^-)_2 \end{array}$$

The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as

the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

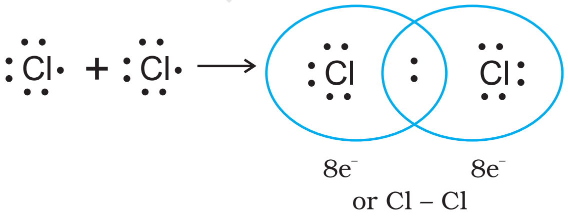
Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts.

4.1.1 Octet Rule

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory** of **chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

4.1.2 Covalent Bond

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule,Cl_2. The Cl atom with electronic configuration, $[Ne]3s^2\,3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

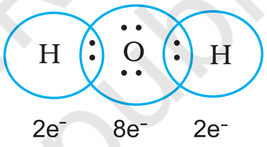


Covalent bond between two Cl atoms

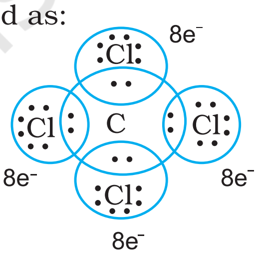
The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

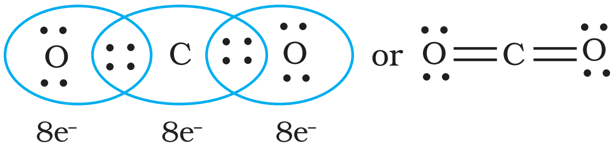


H atoms attain a duplet of electrons and O, the octet

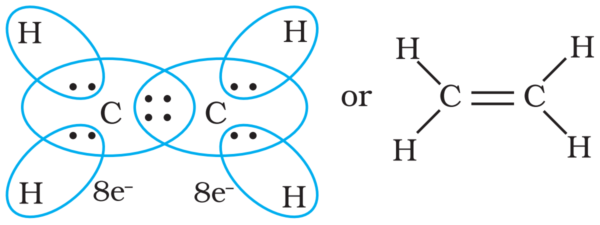


Each of the four Cl atoms along with the C atom attains octet of electrons

Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

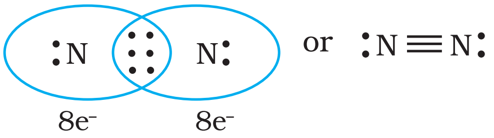


Double bonds in CO_2 molecule

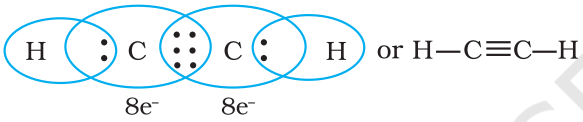


C_2H_4 *molecule*

When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



N_2 *molecule*



C_2H_2 *molecule*

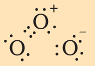
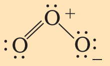
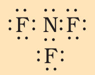
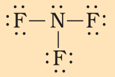
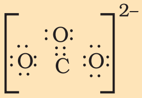
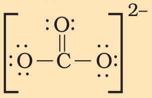
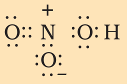
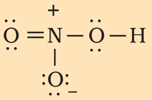
4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in Table 4.1.

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion		Lewis Representation
H_2	H : H*	H – H
O_2	:Ö::Ö:	:Ö=Ö:
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

* *Each H atom attains the configuration of helium (a duplet of electrons)*

Problem 4.1

Write the Lewis dot structure of CO molecule.

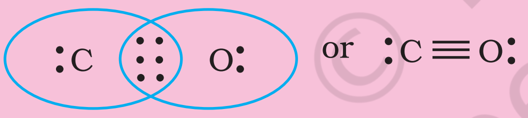
Solution

Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2\ 2p^2$ and $2s^2\ 2p^4$, respectively. The valence electrons available are 4 + 6 =10.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.

This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Problem 4.2

Write the Lewis structure of the nitrite ion, NO_2^-.

Solution

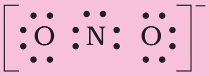
Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

$N(2s^2\ 2p^3)$, $O\ (2s^2\ 2p^4)$

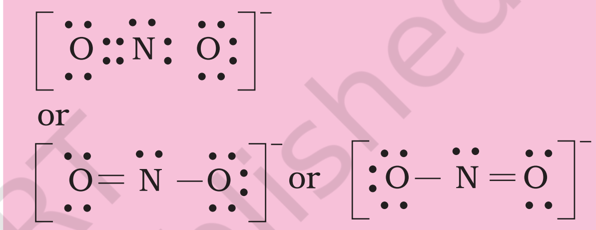
5 + (2 × 6) +1 = 18 electrons

Step 2. The skeletal structure of NO_2^- is written as : O N O

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.



Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.



4.1.4 Formal Charge

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

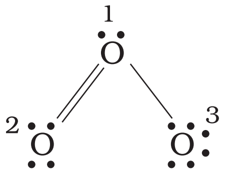
Formal charge (F.C.) on an atom in a Lewis structure =

[total number of valence electrons in the free atom] — [total number of non bonding (lone pair) electrons]

— (1/2) [total number of bonding(shared) electrons]

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on:

- The central O atom marked 1

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

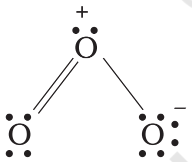
- The end O atom marked 2

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

- The end O atom marked 3

$$= 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we represent O_3 along with the formal charges as follows:



We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.**

4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.

Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

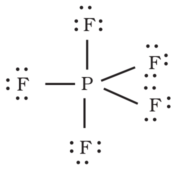
Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms

The expanded octet

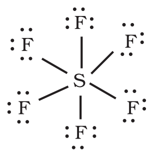
Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



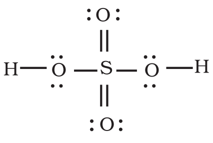
PF_5

10 electrons around the P atom



SF_6

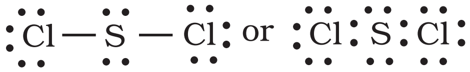
12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

4.2 IONIC OR ELECTROVALENT BOND

From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$$M(g) \rightarrow M^+(g) + e^- \;; \quad \text{Ionization enthalpy}$$

$$X(g) + e^- \rightarrow X^-(g) \;; \quad \text{Electron gain enthalpy}$$

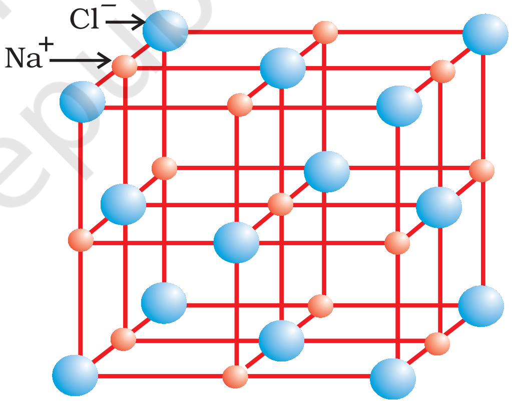
$$M^+(g) + X^-(g) \rightarrow MX(s)$$

The **electron gain enthalpy, $\Delta_{eg}H$,** is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.



Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $Na^+(g)$ formation from Na(g) is 495.8 kJ mol^{-1} ; while the electron gain enthalpy for the change $Cl(g) + e^- \rightarrow Cl^-(g)$ is, – 348.7 kJ mol^{-1} only. The sum of the two, 147.1 kJ mol^{-1} is more than compensated for by the enthalpy of lattice formation of NaCl(s) (–788 kJ mol^{-1}). Therefore, the energy released in the processes is more than the energy absorbed. **Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.**

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

4.2.1 Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^+ (g) and one mole of Cl^- (g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

4.3 BOND PARAMETERS

4.3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 4.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. **The van der Waals radius represents the overall size of the atom which includes its valence shell in a nonbonded situation.** Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in Fig.4.2

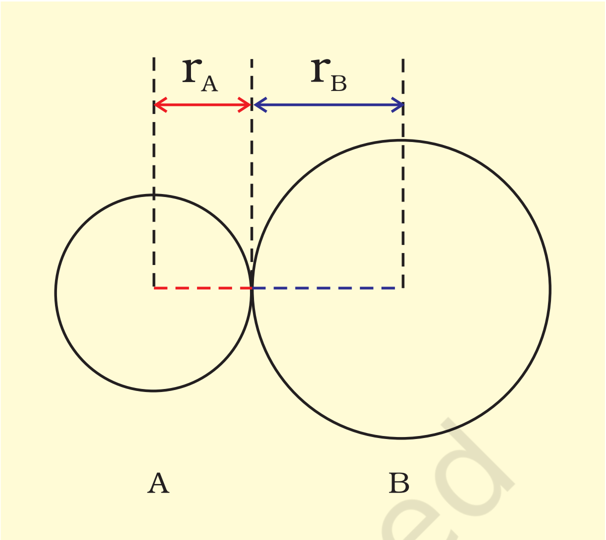


Fig. 4.1 *The bond length in a covalent molecule AB.*
R = $r_A + r_B$ *(R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)*

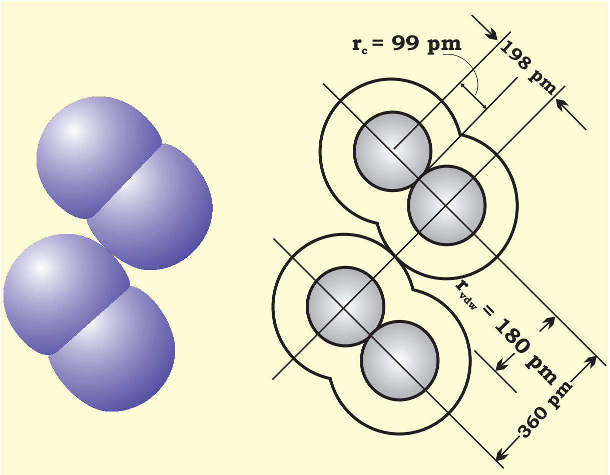


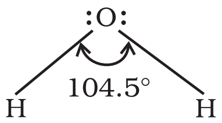
Fig. 4.2 *Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).*

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 :

$O_2 \text{ (O = O) } (g) \rightarrow O(g) + O(g);$

$\Delta_a H^\ominus = 498 \text{ kJ mol}^{-1}$

$N_2 \text{ (N} \equiv \text{N) } (g) \rightarrow N(g) + N(g);$

$\Delta_a H^\ominus = 946.0 \text{ kJ mol}^{-1}$

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:

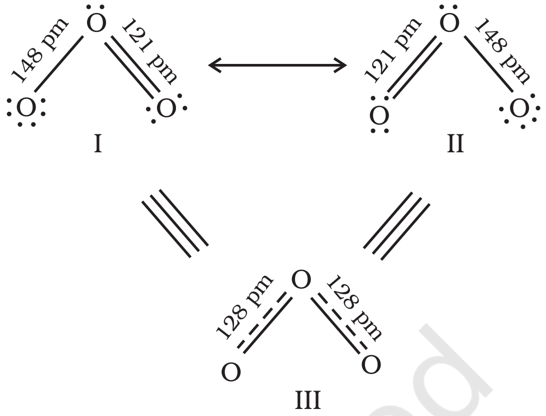


Fig. 4.3 *Resonance in the O_3 molecule*

(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.

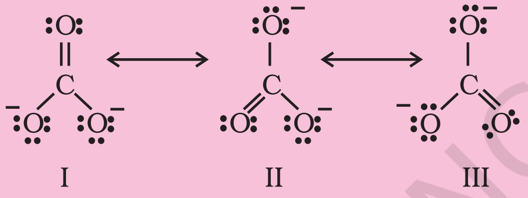


Fig.4.4 *Resonance in CO_3^{2-}, I, II and III represent the three canonical forms.*

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≡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≡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.

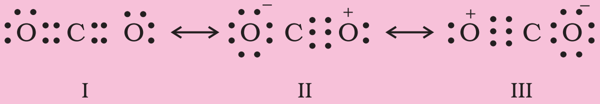


Fig. 4.5 *Resonance in CO_2 molecule, I, II and III represent the three canonical forms.*

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

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

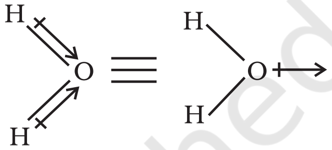
where C is coulomb and m is meter.

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

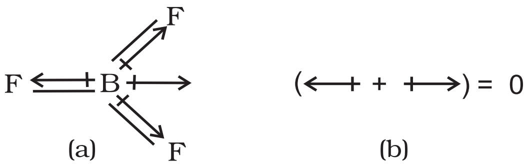
$$= 1.85 \times 3.33564 \times 10^{-30}\ \text{C m} = 6.17 \times 10^{-30}\ \text{C m}$$

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

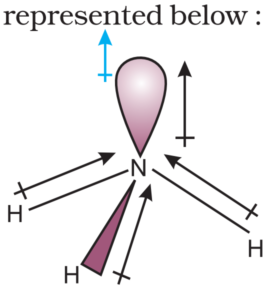
Total dipole moment in BeF_2

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.

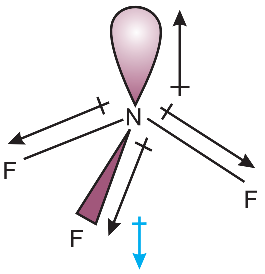


BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

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 × 10^{-30} C m



Resultant dipole moment in NF_3 = 0.80 × 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.

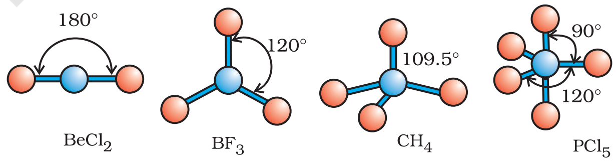


Fig. 4.6 *The shapes of molecules in which central atom has no lone pair*

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

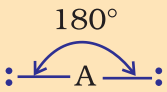
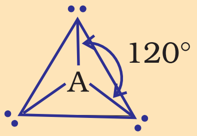
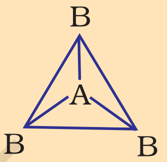
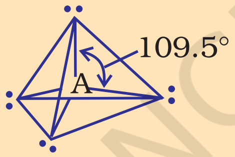
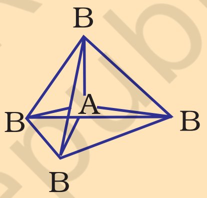
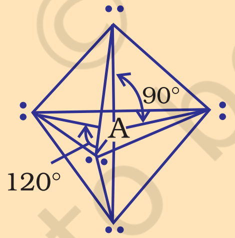
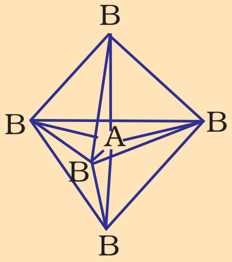
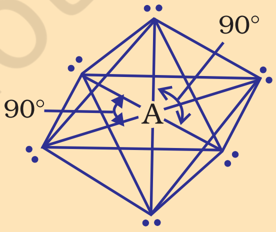
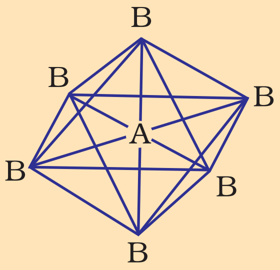
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

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

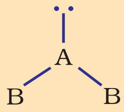
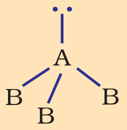
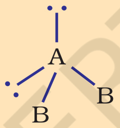
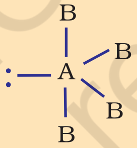
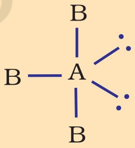
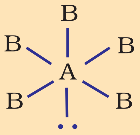
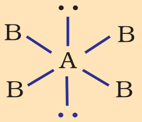
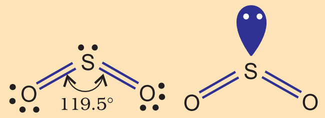
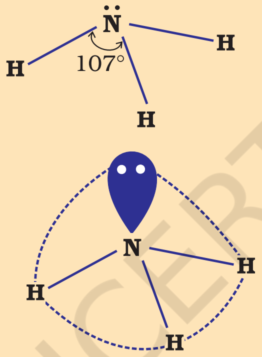
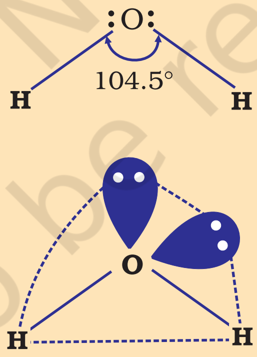
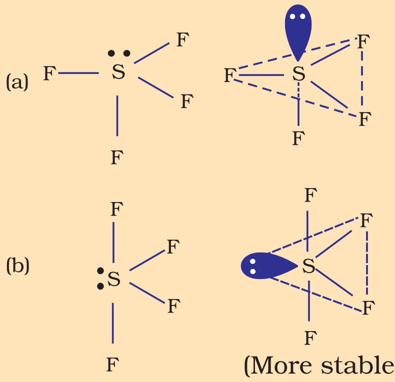
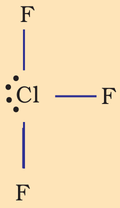
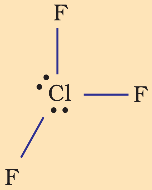
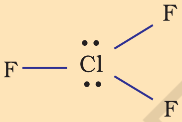
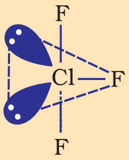
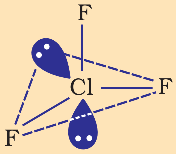
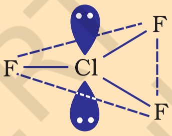
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planer	Bent	SO^2O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3
AB_3E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	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	(a)  (b)  (c) 	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).

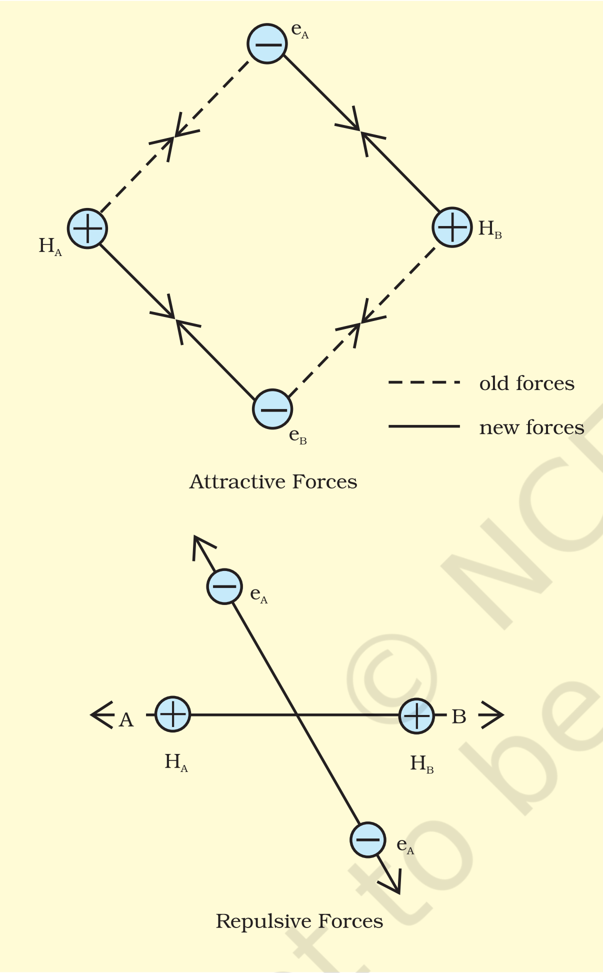


Fig. 4.7 *Forces of attraction and repulsion during the formation of H_2 molecule.*

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.

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

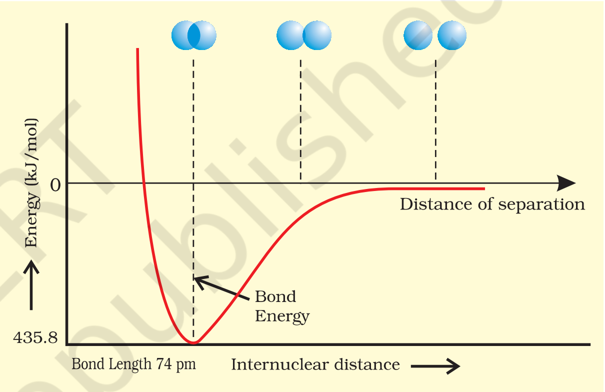


Fig. 4.8 *The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.*

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.

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

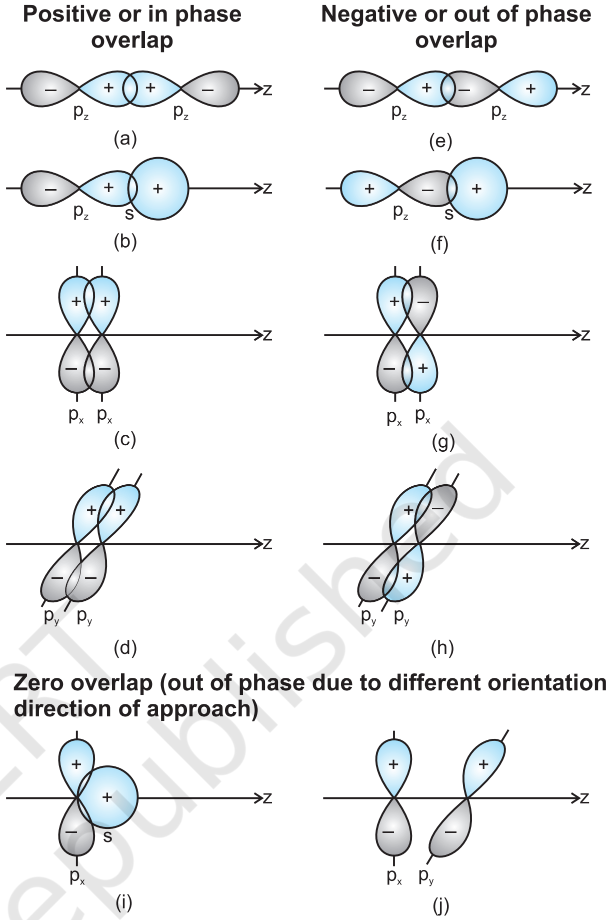


Fig.4.9 *Positive, negative and zero overlaps of s and p atomic orbitals*

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.

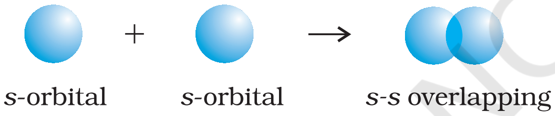
4.5.4 Types of Overlapping and Nature of Covalent Bonds

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

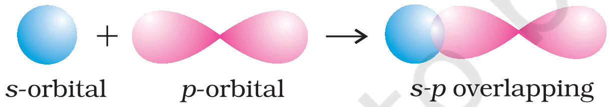
(i) Sigma(σ) bond, and (ii) pi(π) bond

(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.

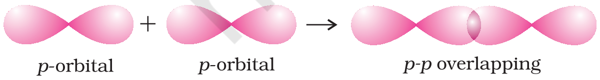
- ***s-s* overlapping :** In this case, there is overlap of two half filled *s*-orbitals along the internuclear axis as shown below :



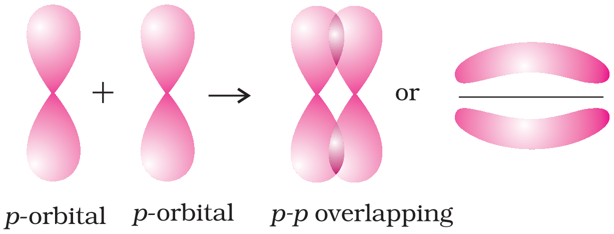
- ***s-p* overlapping:** This type of overlap occurs between half filled *s*-orbitals of one atom and half filled *p*-orbitals of another atom.



- ***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 $1s^22s^2$. 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.

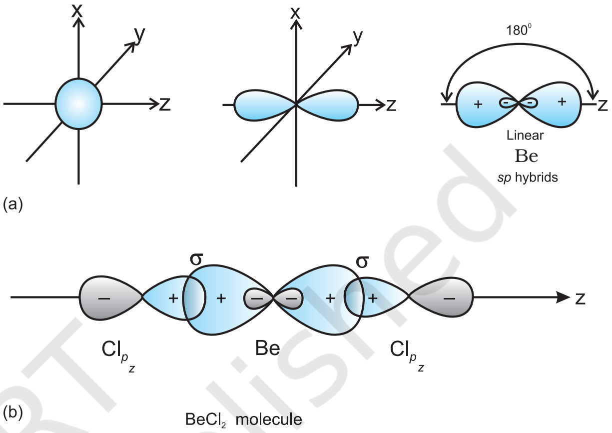


Fig.4.10 *(a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule*

(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 $1s^22s^22p^1$. In the excited state, one of the 2*s* electrons is promoted to vacant 2*p* orbital as

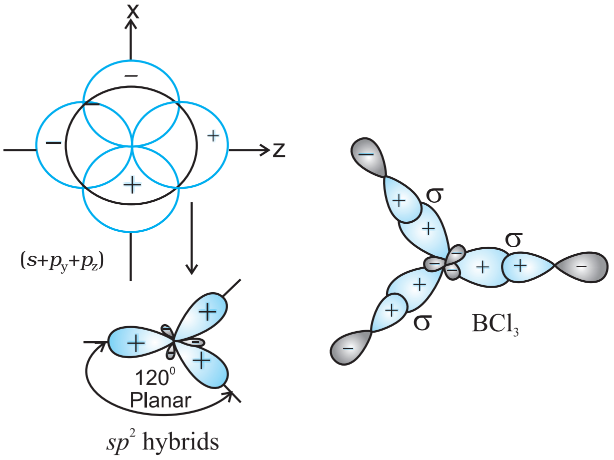


Fig.4.11 *Formation of sp^2 hybrids and the BCl_3 molecule*

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.

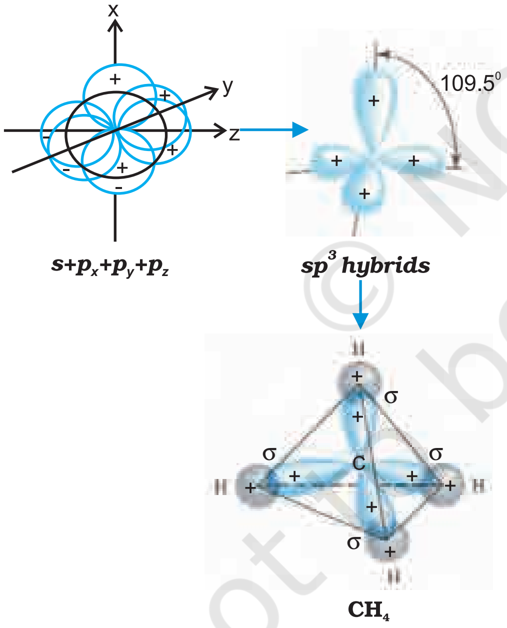


Fig.4.12 *Formation of sp^3 hybrids by the combination of s , p_x , p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule*

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.

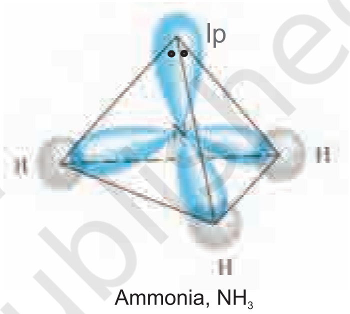


Fig.4.13 *Formation of NH_3 molecule*

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.

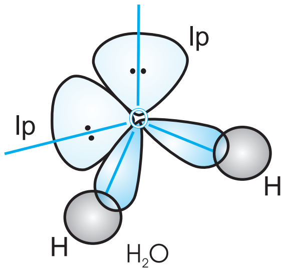


Fig.4.14 *Formation of H_2O molecule*

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.

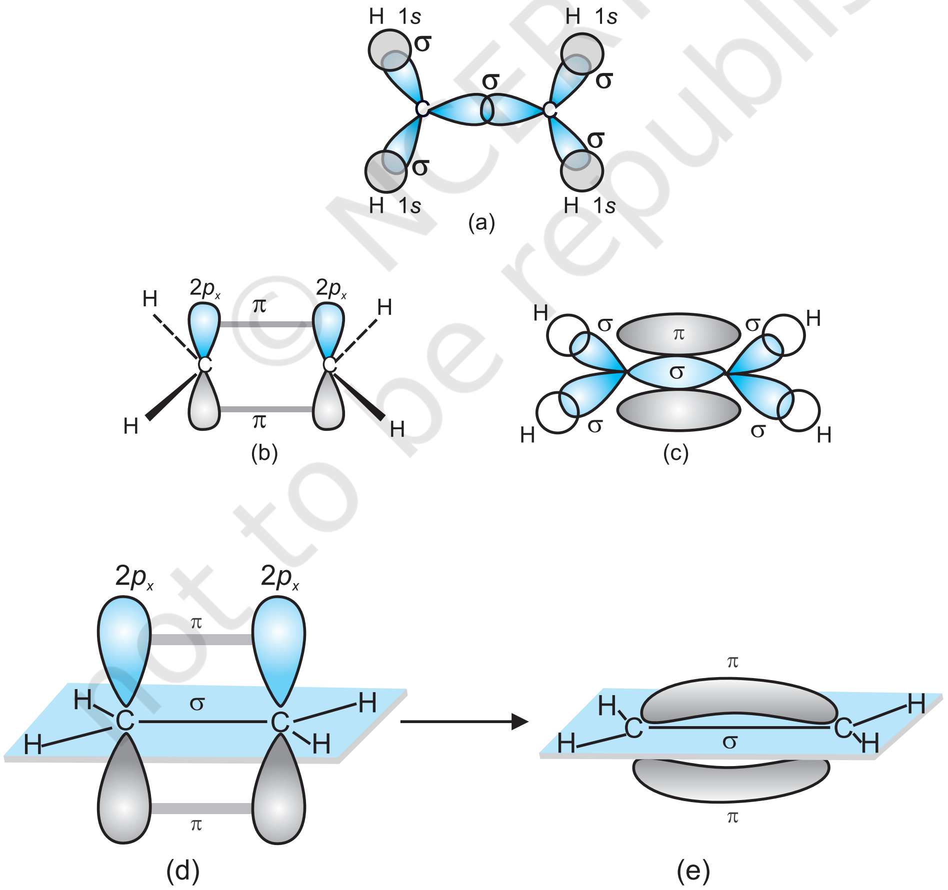


Fig. 4.15 *Formation of sigma and pi bonds in ethene*

***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.

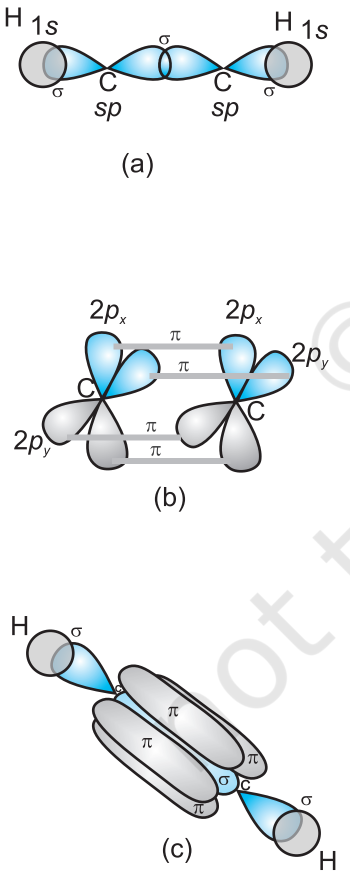


Fig.4.16 *Formation of sigma and pi bonds in ethyne*

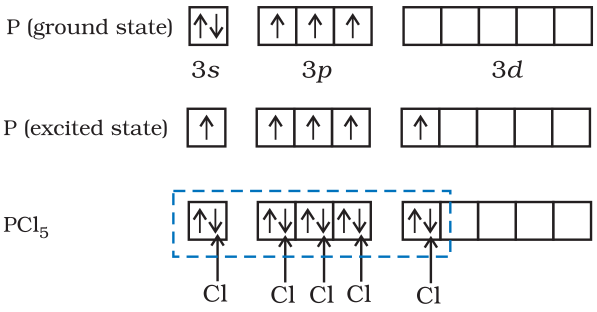
4.6.3 Hybridisation of Elements involving *d* Orbitals

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.

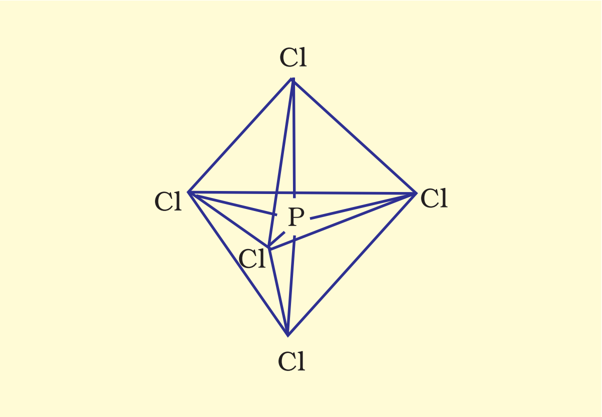
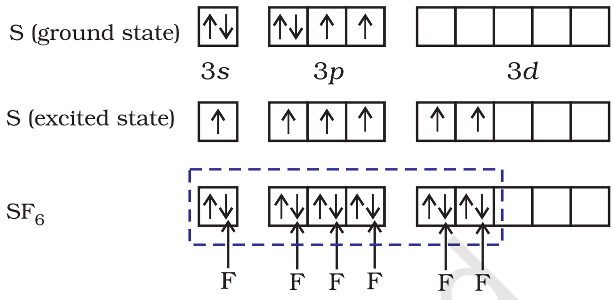


Fig. 4.17 *Trigonal bipyramidal geometry of PCl_5 molecule*

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

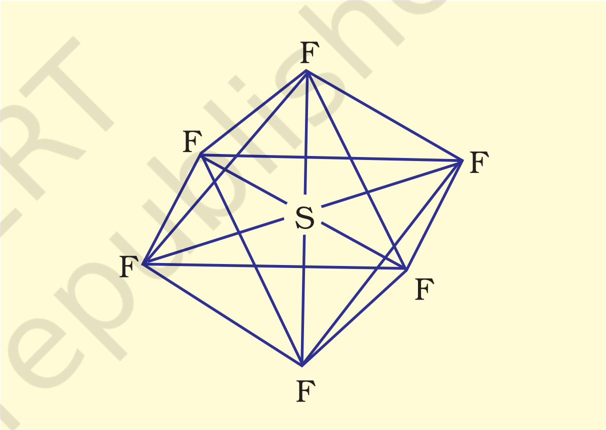


Fig. 4.18 *Octahedral geometry of SF_6 molecule*

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.

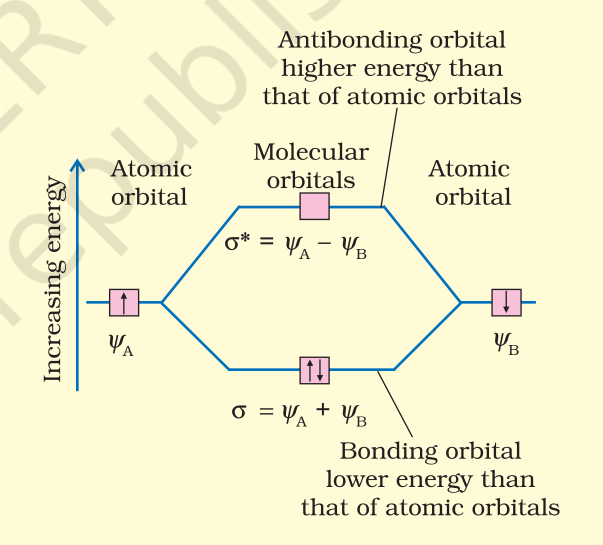


Fig.4.19 *Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.*

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 $\sigma 1s$ and $\sigma^* 1s$ [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 $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2*s* and 2*p* atomic orbitals (eight atomic orbitals

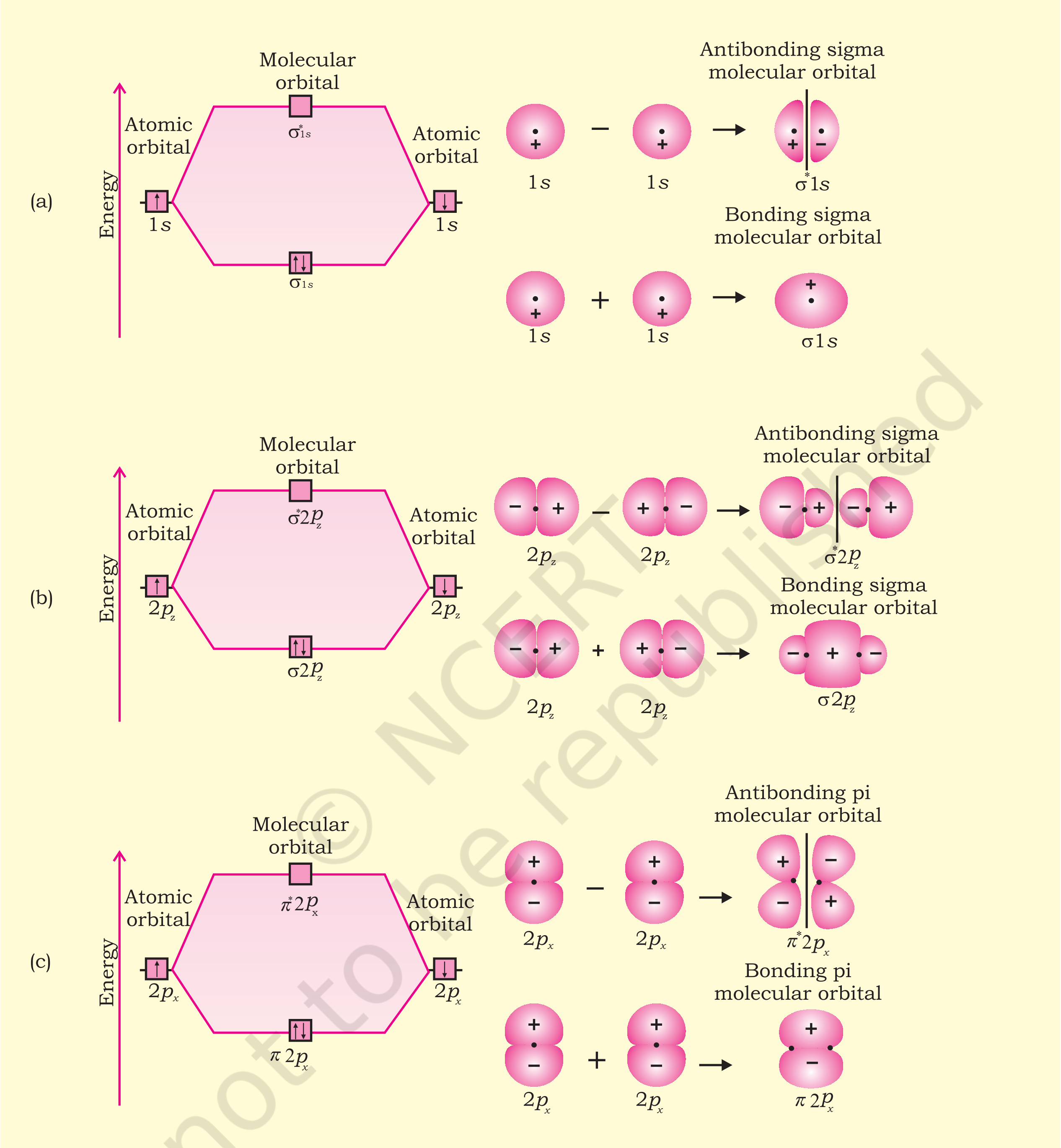


Fig. 4.20 *Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.*

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 σ1*s* 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

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

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

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

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

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

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.

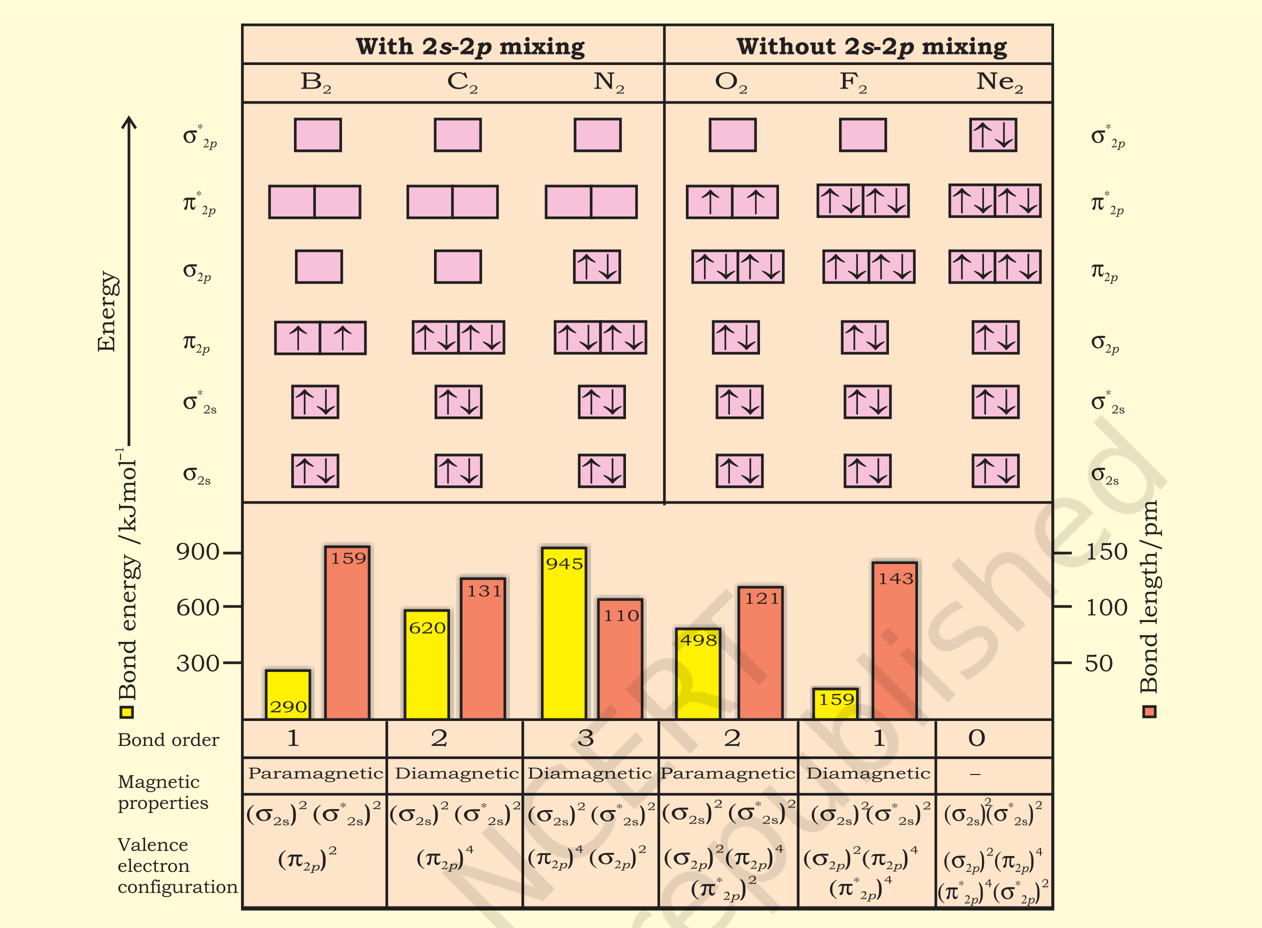


Fig. 4.21 *MO occupancy and molecular properties for B_2 through Ne_2.*

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.

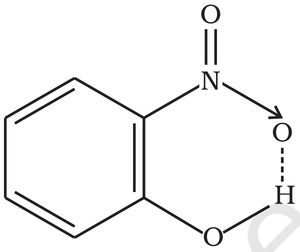


Fig. 4.22 *Intramolecular hydrogen bonding in o-nitrophenol molecule*

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

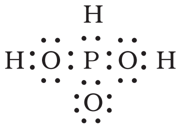
4.8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

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

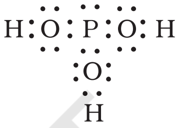
4.10 Define the bond length.

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.

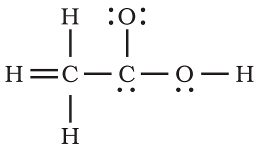
4.16 Write the significance/applications of dipole moment.

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

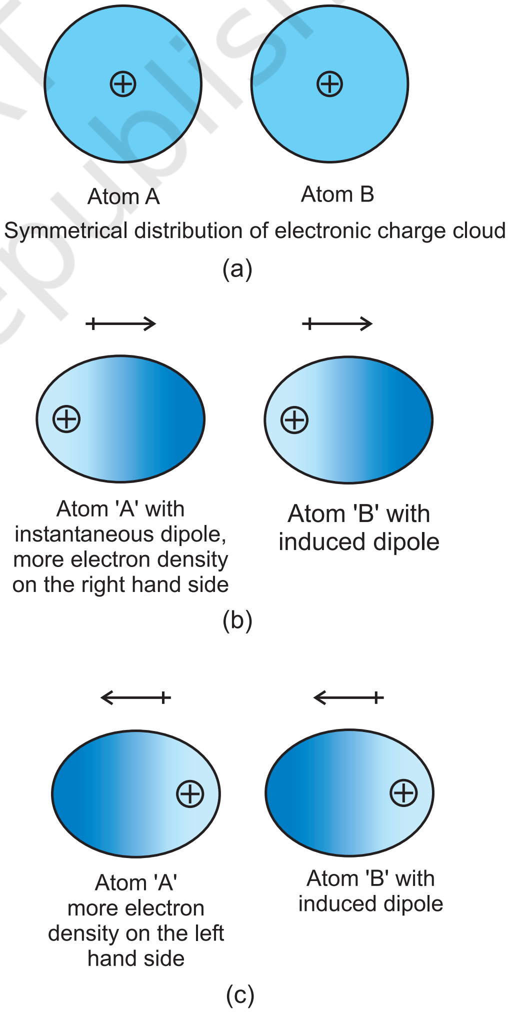


Fig. 5.1 *Dispersion forces or London forces between atoms.*

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.

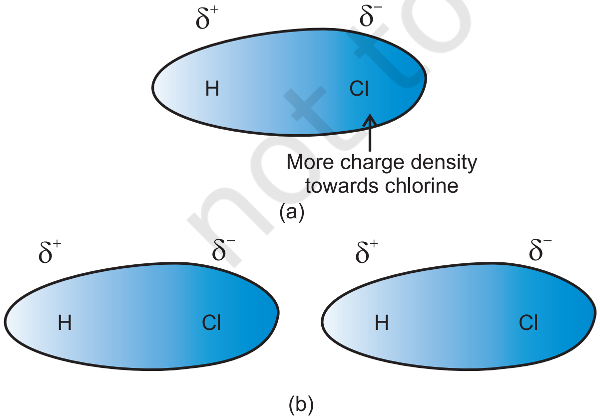


Fig. 5.2 *(a) Distribution of electron cloud in HCl – a polar molecule, (b) Dipole-dipole interaction between two HCl molecules*

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.

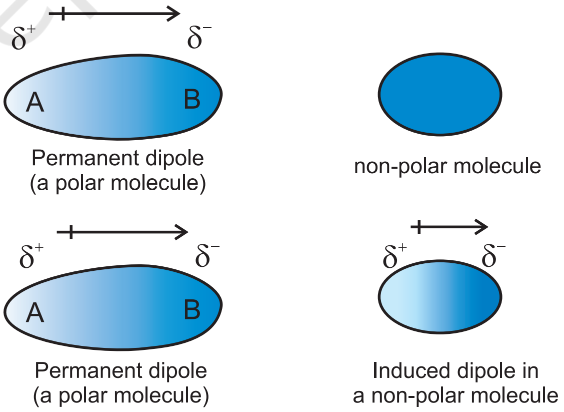


Fig. 5.3 *Dipole - induced dipole interaction between permanent dipole and induced dipole*

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 $\overset{-}{\text{Cl}}$ 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.

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

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.

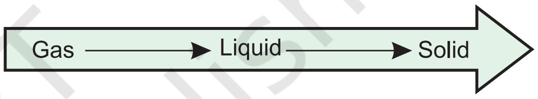
5.2 THERMAL ENERGY

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.

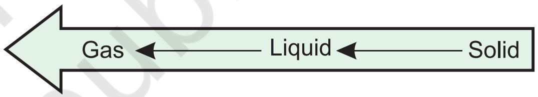
5.3 INTERMOLECULAR FORCES *vs* THERMAL INTERACTIONS

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

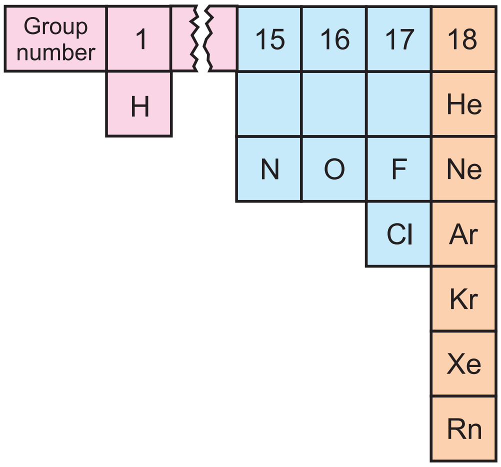


Fig. 5.4 *Eleven elements that exist as gases*

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

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

$$\Rightarrow p = \mathrm{k}_1 \frac{1}{V} \qquad (5.2)$$

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

$$pV = \mathrm{k}_1 \qquad (5.3)$$

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 :

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

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

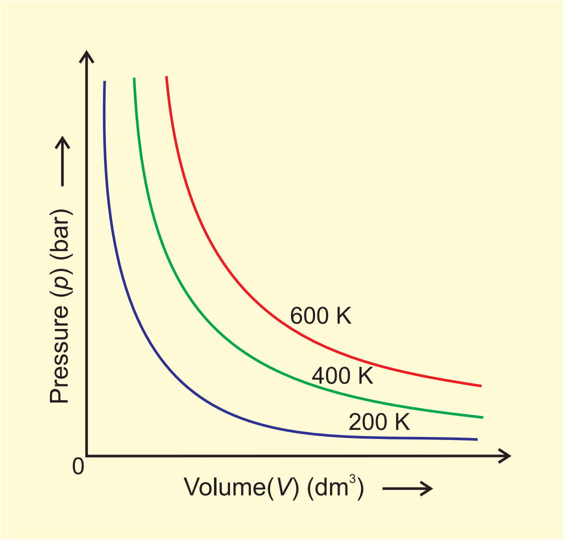


Fig. 5.5(a) *Graph of pressure, p vs. Volume, V of a gas at different temperatures.*

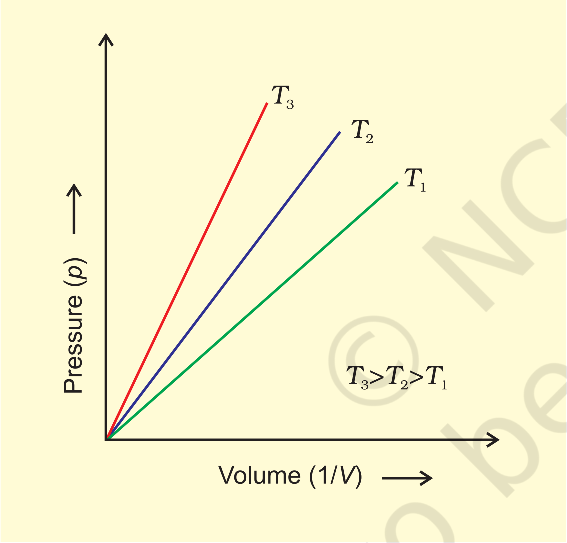


Fig. 5.5 (b) *Graph of pressure of a gas, p vs.* $\frac{1}{V}$

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).

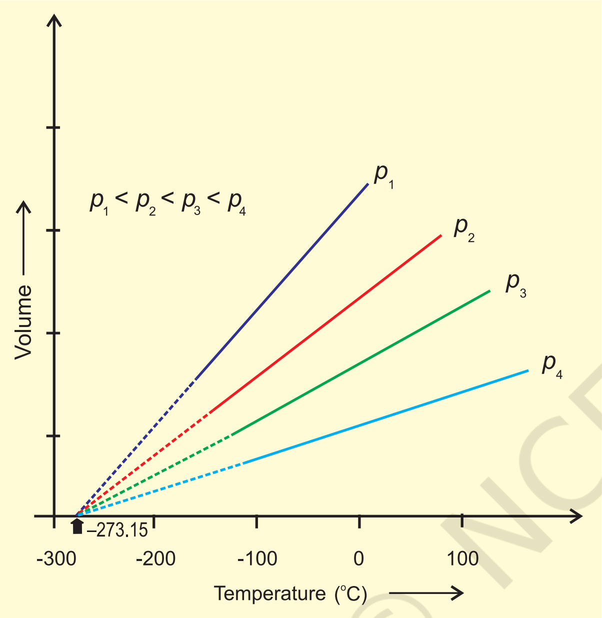


***Fig. 5.6** Volume vs Temperature (°C) graph*

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

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

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

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

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

$$= 2.018\text{L}$$

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,

$$p \propto T$$

$$\Rightarrow \frac{p}{T} = \text{constant} = \text{k}_3$$

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.**

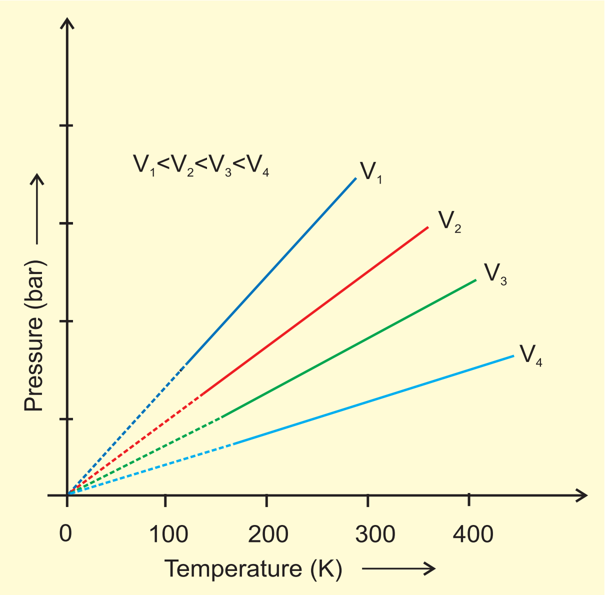


Fig. 5.7 *Pressure vs temperature (K) graph (Isochores) of a gas.*

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,

$$V \propto \frac{nT}{p} \qquad (5.15)$$

$$\Rightarrow \quad V = \mathrm{R}\frac{nT}{p} \qquad (5.16)$$

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

$$pV = n\mathrm{R}T \qquad (5.17)$$

$$\Rightarrow \quad \mathrm{R} = \frac{pV}{nT} \qquad (5.18)$$

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

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

$$\Rightarrow \quad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad (5.19)$$

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

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

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

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

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

5.6.1 Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows:

$$\frac{n}{V} = \frac{p}{\mathrm{R}T}$$

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

$$\frac{m}{\mathrm{M}\;V} = \frac{p}{\mathrm{R}\,T} \qquad (5.20)$$

$$\frac{d}{\mathrm{M}} = \frac{p}{\mathrm{R}\,T} \quad \text{(where } d \text{ is the density)} \qquad (5.21)$$

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

$$\mathrm{M} = \frac{d\,\mathrm{R}T}{p} \qquad (5.22)$$

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,

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

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,

$$p_1 = \frac{n_1\mathrm{R}T}{V} \qquad (5.25)$$

$$p_2 = \frac{n_2\mathrm{R}T}{V} \qquad (5.26)$$

$$p_3 = \frac{n_3 RT}{V} \tag{5.27}$$

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

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

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

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

On dividing p_1 by p_{total} we get

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

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

where $n = n_1+n_2+n_3$

x_1 is called mole fraction of first gas.

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

Similarly for other two gases we can write

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

Thus a general equation can be written as

$$p_i = x_i\ p_{total} \tag{5.29}$$

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

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

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

$$= 0.21$$

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

$$= 0.79$$

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.

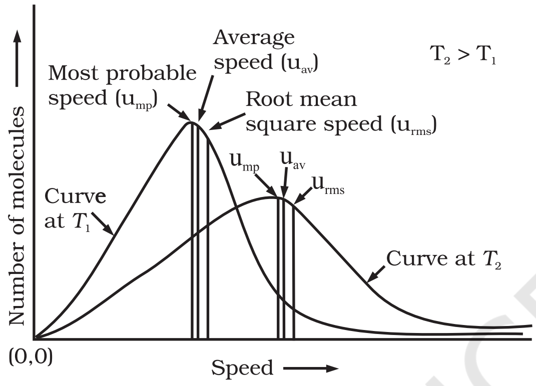


Fig. 5.8: *Maxwell-Boltzmann distribution of speeds*

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.

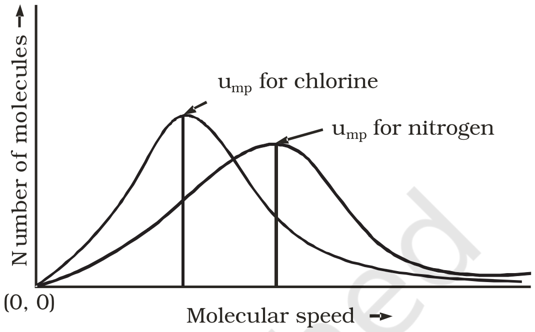


Fig. 5.9: *Distribution of molecular speeds for chlorine and nitrogen at 300 K*

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:

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

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.

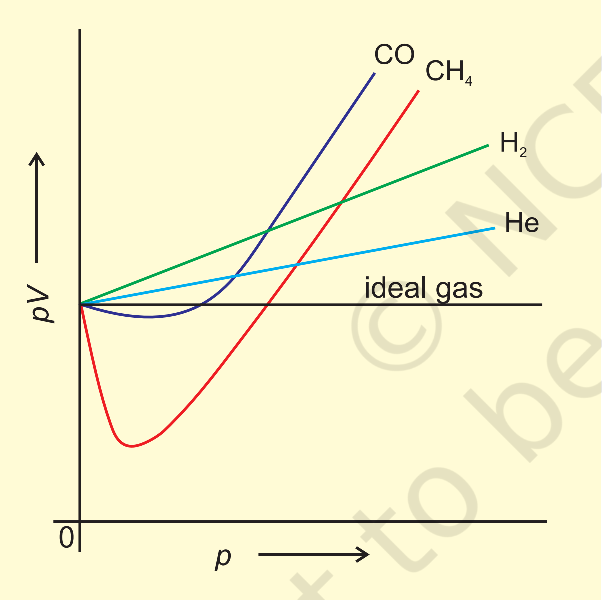


Fig. 5.10 *Plot of pV vs p for real gas and ideal gas*

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.

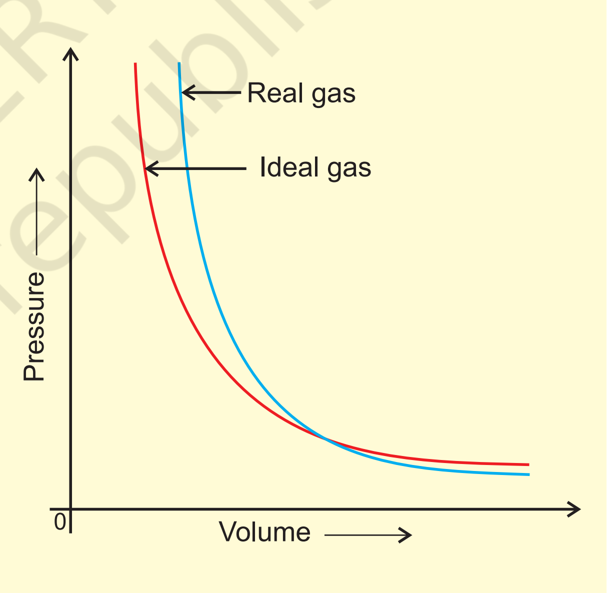


Fig. 5.11 *Plot of pressure vs volume for real gas and ideal gas*

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.

$$p_{ideal} = \underbrace{p_{real}}_{\text{observed pressure}} + \underbrace{\frac{\mathrm{a}n^2}{V^2}}_{\text{correction term}} \quad (5.30)$$

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

$$\left(p + \frac{\mathrm{a}n^2}{V^2}\right)(V - n\mathrm{b}) = n\mathrm{R}T \quad (5.31)$$

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 *n*R*T*. Mathematically

$$Z = \frac{pV}{n\,\mathrm{R}T} \quad (5.32)$$

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**

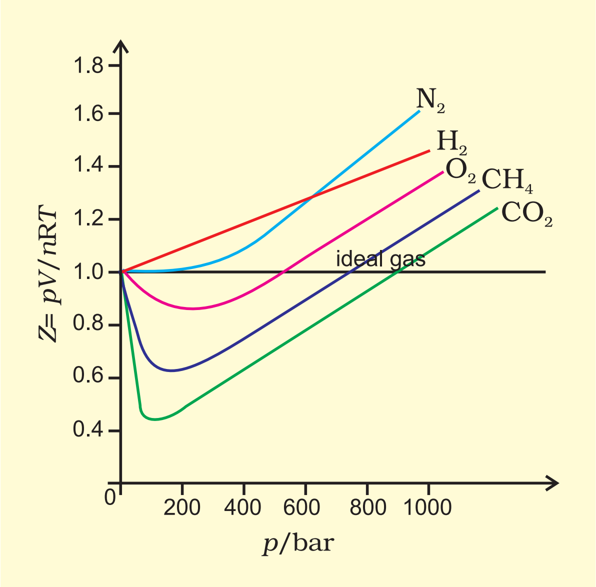


Fig. 5.12 *Variation of compressibility factor for some gases*

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

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

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

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \qquad (5.34)$$

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

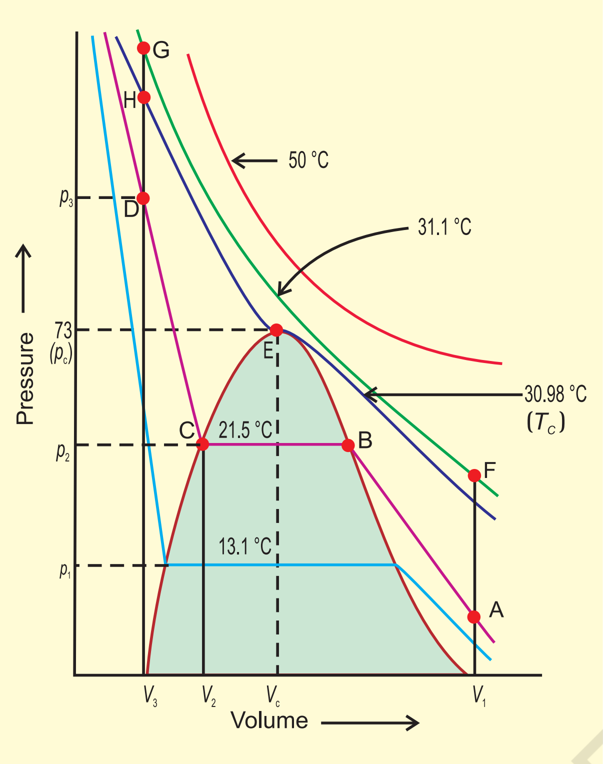


Fig. 5.13 *Isotherms of carbon dioxide at various temperatures*

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

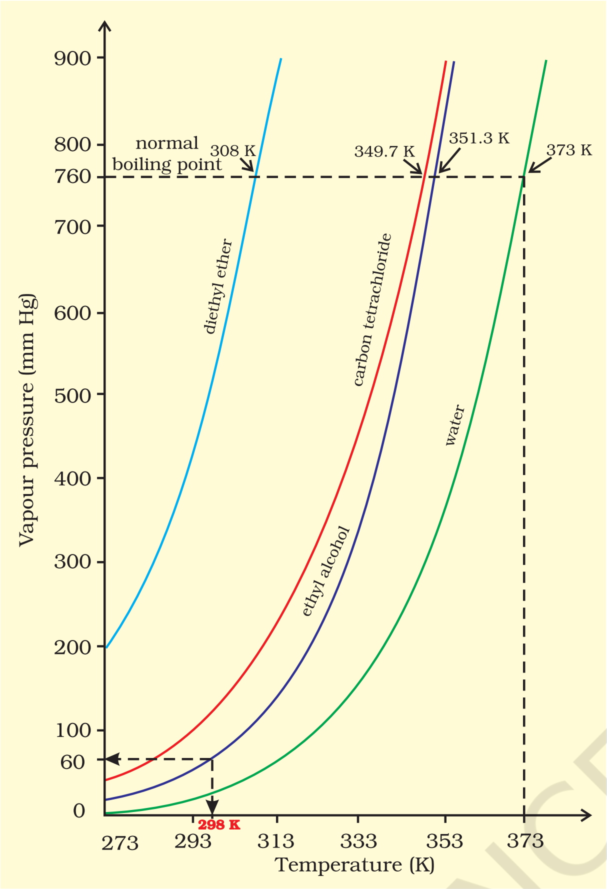


Fig. 5.14 *Vapour pressure vs temperature curve of some common liquids.*

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

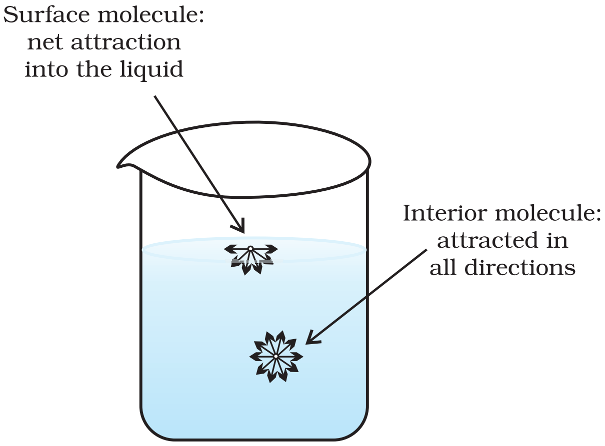


Fig. 5.15 *Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

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.

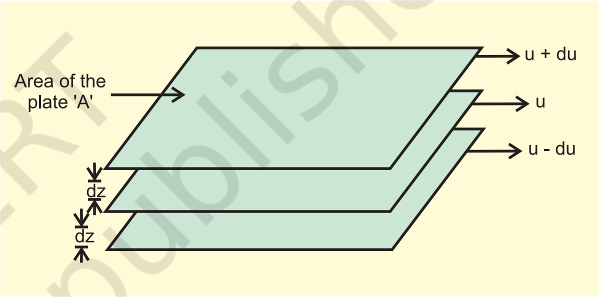


Fig. 5.16 *Gradation of velocity in the laminar flow*

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 ‘ ’ 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.

η

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 $\left(V \propto T\right)$. 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 $pV=n\mathrm{R}T$, 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 6

THERMODYNAMICS

Objectives

After studying this Unit, you will be able to

- explain the terms : system and surroundings;
- discriminate between close, open and isolated systems;
- explain internal energy, work and heat;
- state first law of thermodynamics and express it mathematically;
- calculate energy changes as work and heat contributions in chemical systems;
- explain state functions: U, H.
- correlate ΔU and ΔH;
- measure experimentally ΔU and ΔH;
- define standard states for ΔH;
- calculate enthalpy changes for various types of reactions;
- state and apply Hess's law of constant heat summation;
- differentiate between extensive and intensive properties;
- define spontaneous and non-spontaneous processes;
- explain entropy as a thermodynamic state function and apply it for spontaneity;
- explain Gibbs energy change (ΔG); and
- establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.

> ***"It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."***
>
> ***Albert Einstein***

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?

What drives a chemical reaction/process?

To what extent do the chemical reactions proceed?

6.1 THERMODYNAMIC TERMS

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

6.1.1 The System and the Surroundings

A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings.** The surroundings include everything other than the system. System and the surroundings together constitute the universe .

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).

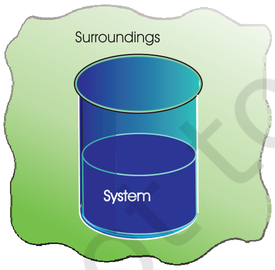


Fig. 6.1 *System and the surroundings*

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates the system from the surroundings is called **boundary**. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

6.1.2 Types of the System

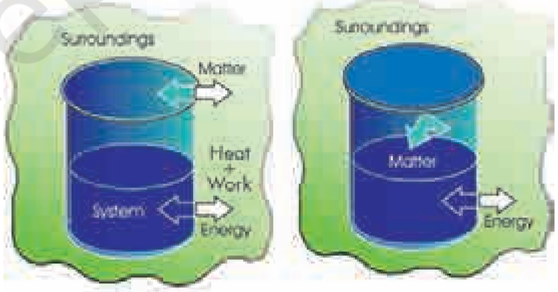
We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 6.2 (a)]. The presence of reactants in an open beaker is an example of an open system*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 6.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.



(a) Open System (b) Closed System

(c) Isolated System

Fig. 6.2 *Open, closed and isolated systems.*

---

* *We could have chosen only the reactants as system then walls of the beakers will act as boundary.*

3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

6.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (*p*), volume (*V*), and temperature (*T*) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by **state functions** or **state variables**.

The **state** of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (*p*), volume (*V*), temperature (*T*), amount (*n*) etc. Variables like *p*, *V*, *T* are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

6.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, *U* of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

These systems are classified accordingly as you have already studied in section 6.1.2.

(a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as **adiabatic**. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 6.3).

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A. Let the internal energy of the system in state A be called U_A. We can change the state of the system in two different ways.

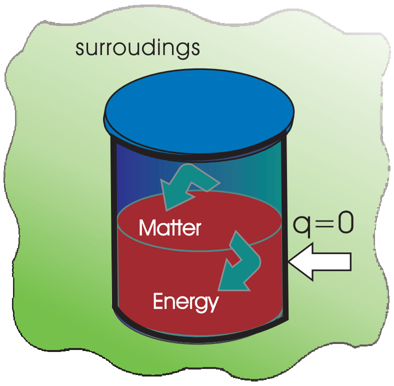


Fig. 6.3 *An adiabatic system which does not permit the transfer of heat through its boundary.*

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

Second way: We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So, it seems appropriate to define a quantity, the internal energy *U*, whose value is characteristic of the state of a system, whereby the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of *U* in one state and that in another state, ΔU *i.e.,*

$$\Delta U = U_2 - U_1 = w_{ad}$$

Therefore, internal energy, *U*, of the system is a state function.

By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that w_{ad} is positive when work is done **on** the system and the internal energy of system increases. Similarly, if the work is done **by** the system, w_{ad} will be negative because internal energy of the system decreases.

Can you name some other familiar state functions? Some of other familiar state functions are *V*, *p*, and *T*. For example, if we bring a change in temperature of the system from 25°C to 35°C, the change in temperature is 35°C–25°C = +10°C, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, *T* is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both.

(b) Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, *q*. Let us consider bringing about the same change in temperature (the same initial and final states as before in section 6.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).

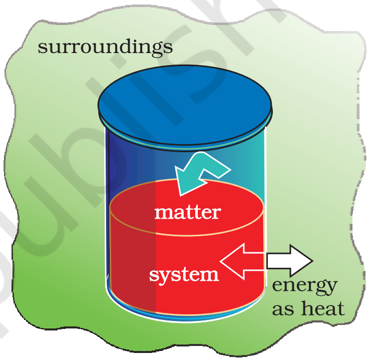


Fig. 6.4 *A system which allows heat transfer through its boundary.*

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, T_B. The heat absorbed by the system (water), *q* can be measured in terms of temperature difference, $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system..

---

* *Earlier negative sign was assigned when the work is done on the system and positive sign when the work is done by the system. This is still followed in physics books, although IUPAC has recommended the use of new sign convention.*

(c) The general case

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + \mathrm{w} \qquad (6.1)$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + \mathrm{w} = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if $\mathrm{w} = 0$ and $q = 0$, then $\Delta U = 0$.

The equation 6.1 i.e., $\Delta U = q + \mathrm{w}$ is mathematical statement of the **first law of thermodynamics**, which states that

> ***The energy of an isolated system is constant.***

It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system.

Problem 6.1

Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Solution

(i) $\Delta U = \mathrm{w}_{\mathrm{ad}}$, wall is adiabatic

(ii) $\Delta U = -q$, thermally conducting walls

(iii) $\Delta U = q - \mathrm{w}$, closed system.

6.2 APPLICATIONS

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

6.2.1 Work

First of all, let us concentrate on the nature of work a system can do. We will consider only mechanical work i.e., pressure-volume work.

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change

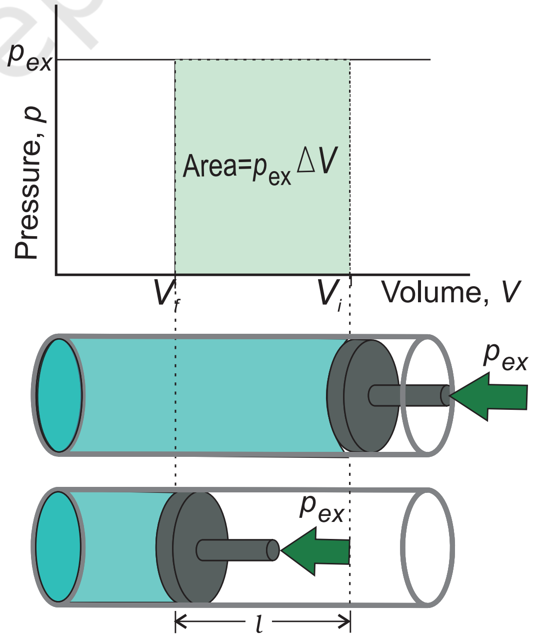


Fig. 6.5(a) *Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.*

be achieved in a single step and the final volume be V_f. During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A [Fig. 6.5(a)].

then, volume change = $l \times A = \Delta V = (V_f - V_i)$

We also know, $\text{pressure} = \dfrac{\text{force}}{\text{area}}$

Therefore, force on the piston = $p_{ex} \cdot A$

If w is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l$$

$$= p_{ex} \cdot (-\Delta V) = -p_{ex}\,\Delta V = -p_{ex}(V_f - V_i) \qquad (6.2)$$

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$ [Fig. 6.5 (b)]

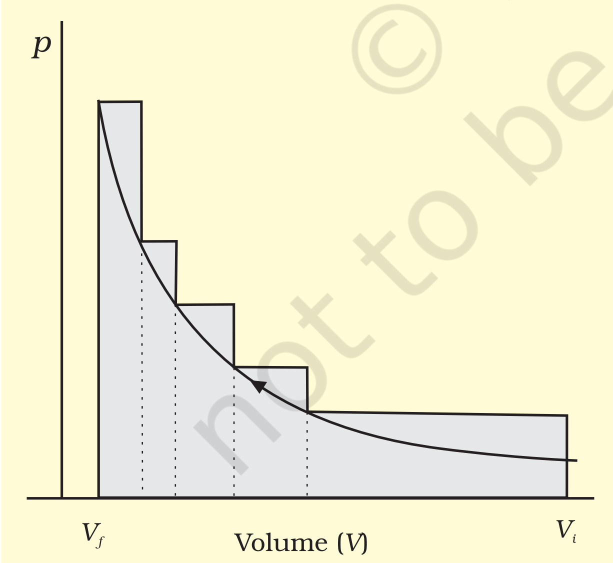


Fig. 6.5 (b) *pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex}\,dV \qquad (6.3)$$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression [Fig. 6.5(c)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} - dp)$. In general case we can write, $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes

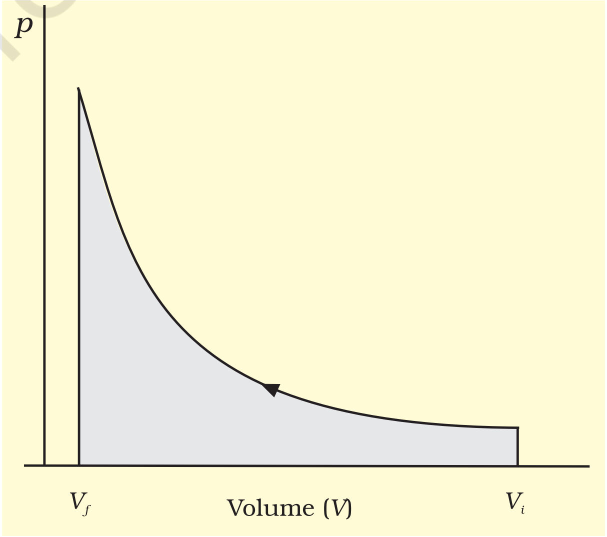


Fig. 6.5 (c) *pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

other than reversible processes are known as irreversible processes.

In chemistry, we face problems that can be solved if we relate the work term to the **internal pressure of the system.** We can relate work to internal pressure of the system under **reversible conditions** by writing equation 6.3 as follows:

$$\mathrm{w}_{rev} = -\int_{V_i}^{V_f} p_{ex} dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\, dV$$

Since $dp \times dV$ is very small we can write

$$\mathrm{w}_{rev} = -\int_{V_i}^{V_f} p_{in} dV \qquad (6.4)$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., $pV = n\mathrm{R}T$

$$\Rightarrow p = \frac{n\mathrm{R}T}{V}$$

Therefore, at constant temperature (isothermal process),

$$\mathrm{w}_{\mathrm{rev}} = -\int_{V_i}^{V_f} n\mathrm{R}T \frac{dV}{V} = -n\mathrm{R}T \ln \frac{V_f}{V_i}$$

$$= -2.303\ n\mathrm{R}T \log \frac{V_f}{V_i} \qquad (6.5)$$

Free expansion: Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation 6.2 and 6.3).

Now, we can write equation 6.1 in number of ways depending on the type of processes.

Let us substitute $\mathrm{w} = -\,p_{ex}\Delta V$ (eq. 6.2) in equation 6.1, and we get

$$\Delta U = q - p_{ex}\Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_V$$

the subscript V in q_V denotes that heat is supplied at constant volume.

Isothermal and free expansion of an ideal gas

For isothermal (T = constant) expansion of an ideal gas into vacuum ; $\mathrm{w} = 0$ since $p_{ex} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$

Equation 6.1, $\Delta U = q + \mathrm{w}$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

   $q = -\mathrm{w} = p_{ex}(V_f - V_i)$
2. For isothermal reversible change

   $$q = -\mathrm{w} = n\mathrm{R}T \ln \frac{V_f}{V_i}$$

   $$= 2.303\ n\mathrm{R}T \log \frac{V_f}{V_i}$$
3. For adiabatic change, $q = 0$,

   $\Delta U = \mathrm{w}_{\mathrm{ad}}$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = -\mathrm{w} = p_{ex}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

Problem 6.3

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -\mathrm{w} = p_{ex}(8) = 8$ litre-atm

Problem 6.4

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solution

$$\text{We have } q = -\mathrm{w} = 2.303\ \mathrm{nRT} \log \frac{V_f}{V_s}$$

$$= 2.303 \times 1 \times 0.8206 \times 298 \times \log \frac{10}{2}$$

$= 2.303 \times 0.8206 \times 298 \times \log 5$

$= 2.303 \times 0.8206 \times 298 \times 0.6990$

$= 393.66$ L atm

6.2.2 Enthalpy, *H*

(a) A Useful New State Function

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation (6.1) as $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$$U_2 - U_1 = q_p - p\,(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \qquad (6.6)$$

Now we can define another thermodynamic function, the enthalpy *H* [Greek word *enthalpien*, to warm or heat content] as :

$$H = U + pV \qquad (6.7)$$

so, equation (6.6) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although *q* is a path dependent function, *H* is a state function because it depends on *U*, *p* and *V*, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation 6.7 as

$$\Delta H = \Delta U + \Delta pV$$

Since *p* is constant, we can write

$$\Delta H = \Delta U + p\Delta V \qquad (6.8)$$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

At constant volume ($\Delta V = 0$), $\Delta U = q_V$, therefore equation 6.8 becomes

$$\Delta H = \Delta U = q_V$$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

and $$pV_B = n_B RT$$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $p\,(V_B - V_A) = (n_B - n_A)\,RT$

or $$p\,\Delta V = \Delta n_g RT \qquad (6.9)$$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation 6.9 in equation 6.8, we get

$$\Delta H = \Delta U + \Delta n_g RT \qquad (6.10)$$

The equation 6.10 is useful for calculating ΔH from ΔU and *vice versa*.

Problem 6.5

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol^{-1}. Calculate the internal energy change, when

1 mol of water is vapourised at 1 bar pressure and 100°C.

Solution

(i) The change $H_2O(l) \rightarrow H_2O(g)$

$$\Delta H = \Delta U + \Delta n_g RT$$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$$\Delta U = 41.00 \text{ kJ mol}^{-1} - 1$$
$$\times 8.3 \text{ J mol}^{-1}\text{K}^{-1} \times 373 \text{ K}$$

$= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1}$
$= 37.904 \text{ kJ mol}^{-1}$

(b) Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property, χ_m, is the value of an extensive property χ of the system for 1 mol of the substance. If n is the amount of matter, $\chi_m = \frac{\chi}{n}$ is independent of the amount of matter. Other examples are molar volume, V_m and molar heat capacity, C_m. Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume V and at temperature T [Fig. 6.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 6.6 (b)] now has one half of the original volume, $\frac{V}{2}$, but the temperature will still remain the same i.e., T. It is clear that volume is an extensive property and temperature is an intensive property.

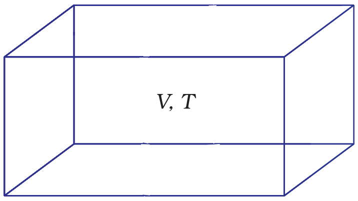


Fig. 6.6(a) *A gas at volume V and temperature T*

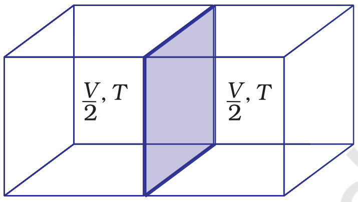


Fig. 6.6 (b) *Partition, each part having half the volume of the gas*

(c) Heat Capacity

In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system.

The increase of temperature is proportional to the heat transferred

$$q = coeff \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as $q = C\,\Delta T$

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance. The molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$, is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as

$$q = c \times m \times \Delta T = C \Delta T \qquad (6.11)$$

(d) The Relationship between C_p and C_V for an Ideal Gas

At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p. Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as $q_V = C_V \Delta T = \Delta U$

at constant pressure as $q_p = C_p \Delta T = \Delta H$

The difference between C_p and C_V can be derived for an ideal gas as:

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\therefore\ \Delta H = \Delta U + R\,\Delta T \qquad (6.12)$$

On putting the values of ΔH and ΔU, we have

$$C_p \Delta T = C_V \Delta T + R\Delta T$$

$$C_p = C_V + R$$

$$C_p - C_V = R \qquad (6.13)$$

6.3 MEASUREMENT OF ΔU AND ΔH: CALORIMETRY

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

i) at constant volume, q_V

ii) at constant pressure, q_p

(a) ΔU Measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 6.7). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter with the help of equation 6.11.

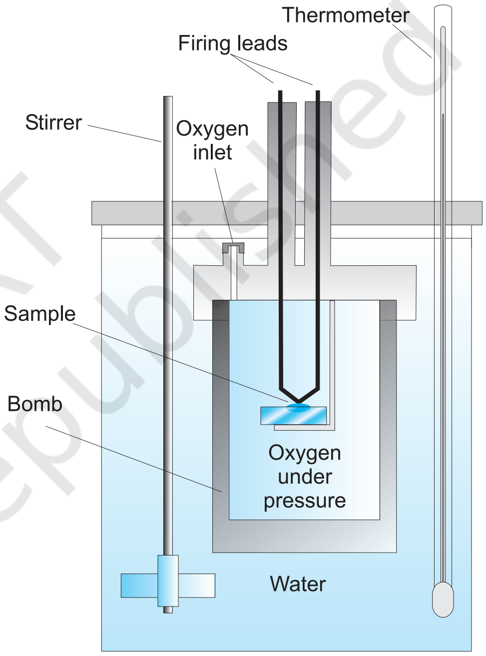


Fig. 6.7 *Bomb calorimeter*

(b) ΔH Measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 6.8. We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.

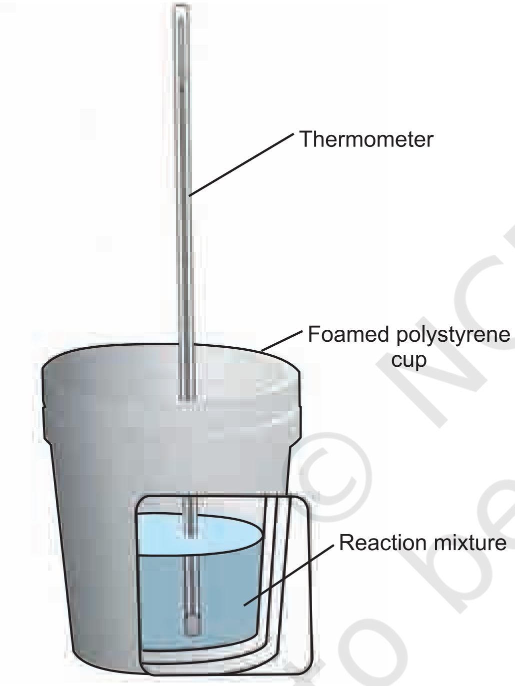


Fig. 6.8 *Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).*

Problem 6.6

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

C (graphite) + O_2 (g) $\rightarrow$ CO_2 (g)

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Solution

Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$q = C_V \times \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_V \times \Delta T = -20.7\,\text{kJ/K} \times (299 - 298)\,\text{K}$$
$$= -20.7\,\text{kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite = – 20.7 kJK^{-1}

For combustion of 1 mol of graphite,

$$= \frac{12.0\ \text{g mol}^{-1} \times (-20.7\,\text{kJ})}{1\,\text{g}}$$

$= -2.48 \times 10^2\,\text{kJ mol}^{-1}$, Since $\Delta n_g = 0$,

$\Delta H = \Delta U = -2.48 \times 10^2\,\text{kJ mol}^{-1}$

6.4 ENTHALPY CHANGE, $\Delta_r H$ OF A REACTION – REACTION ENTHALPY

In a chemical reaction, reactants are converted into products and is represented by,

Reactants $\rightarrow$ Products

The enthalpy change accompanying a reaction is called the **reaction enthalpy**. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$= \sum_i a_i H_{products} - \sum_i b_i H_{reactants} \quad (6.14)$$

Here symbol $\sum$ (sigma) is used for summation and a_i and b_i are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

$$\Delta_r H = \sum_i a_i H_{Products} - \sum_i b_i H_{reactants}$$

$$= [H_m\,(CO_2,g) + 2H_m\,(H_2O,l)] - [H_m\,(CH_4,g) + 2H_m\,(O_2,g)]$$

where H_m is the molar enthalpy.

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

(a) Standard Enthalpy of Reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH, e.g., $\Delta H^{\ominus}$

(b) Enthalpy Changes during Phase Transformations

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).

$$H_2O(s) \rightarrow H_2O(l);\ \Delta_{fus}H^{\ominus} = 6.00\ \text{kJ mol}^{-1}$$

Here $\Delta_{fus}H^{\ominus}$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^{\ominus}$.

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires

Table 6.1 Standard Enthalpy Changes of Fusion and Vaporisation

Substance	T_f/K	$\Delta_{fus}H^{\ominus}$/(kJ mol^{-1})	T_b/K	$\Delta_{vap}H^{\ominus}$/(kJ mol^{-1})
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

(T_f and T_b are melting and boiling points, respectively)

heat for evaporation. At constant temperature of its boiling point T_b and at constant pressure:
$H_2O(l) \rightarrow H_2O(g)$; $\Delta_{vap}H^\ominus = +40.79$ kJ mol^{-1} $\Delta_{vap}H^\ominus$ is the standard enthalpy of vaporisation.

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^\ominus$.

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H^\ominus$=25.2 kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H^\ominus = 73.0$ kJ mol^{-1} .

Standard enthalpy of sublimation, $\Delta_{sub}H^\ominus$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transfomations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 6.1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

Problem 6.7

A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K.

$\Delta_{vap}H^\ominus$ for water

at 298K= 44.01kJ mol^{-1}

Solution

We can represent the process of evaporation as

$$\underset{1\text{mol}}{H_2O(1)} \xrightarrow{\text{vaporisation}} \underset{1\text{mol}}{H_2O(g)}$$

No. of moles in 18 g $H_2O(l)$ is

$$= \frac{18\text{g}}{18\,\text{g mol}^{-1}} = 1\,\text{mol}$$

Heat supplied to evaporate18g water at 298 K $= n \times \Delta_{vap}H^\ominus$

$= (1 \text{ mol}) \times (44.01 \text{ kJ mol}^{-1})$

$= 44.01$ kJ

(assuming steam behaving as an ideal gas).

$$\Delta_{vap}U = \Delta_{vap}H^\ominus - p\Delta V = \Delta_{vap}H^\ominus - \Delta n_g RT$$

$$\Delta_{vap}H^{\vee} - \Delta n_g RT = 44.01 \text{ kJ}$$

$$-(1)(8.314 \text{ JK}^{-1}\text{mol}^{-1})(298\text{K})(10^{-3}\text{kJ J}^{-1})$$

$$\Delta_{vap}U^{\vee} = 44.01\,\text{kJ} - 2.48\,\text{kJ}$$

$$= 41.53\,\text{kJ}$$

Problem 6.8

Assuming the water vapour to be a perfect gas, calculate the internal energy change when 1 mol of water at 100°C and 1 bar pressure is converted to ice at 0°C. Given the enthalpy of fusion of ice is 6.00 kJ mol^{-1} heat capacity of water is 4.2 J/g°C

The change take place as follows:

Step - 1 1 mol H_2O (l, 100°C) → 1 mol (l, 0°C) Enthalpy change ΔH_1

Step - 2 1 mol H_2O (l, 0°C) → 1 mol H_2O(S, 0°C) Enthalpy change ΔH_2

Total enthalpy change will be -

$\Delta H = \Delta H_1 + \Delta H_2$

$\Delta H_1 = -(18 \times 4.2 \times 100)$ J mol^{-1}

$= -7560$ J mol^{-1} $= -7.56$ k J mol^{-1}

$\Delta H_2 = -6.00$ kJ mol^{-1}

Table 6.2 Standard Molar Enthalpies of Formation ($\Delta_f H^\ominus$) at 298K of a Few Selected Substances

Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})	Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})
$Al_2O_3(s)$	-1675.7	$HI(g)$	+26.48
$BaCO_3(s)$	-1216.3	$KCl(s)$	-436.75
$Br_2(l)$	0	$KBr(s)$	-393.8
$Br_2(g)$	+30.91	$MgO(s)$	-601.70
$CaCO_3(s)$	-1206.92	$Mg(OH)_2(s)$	-924.54
C (diamond)	+1.89	$NaF(s)$	-573.65
C (graphite)	0	$NaCl(s)$	-411.15
$CaO(s)$	- 635.09	$NaBr(s)$	-361.06
$CH_4(g)$	-74.81	$NaI(s)$	-287.78
$C_2H_4(g)$	52.26	$NH_3(g)$	-46.11
$CH_3OH(l)$	-238.86	$NO(g)$	+ 90.25
$C_2H_5OH(l)$	-277.69	$NO_2(g)$	+33.18
$C_6H_6(l)$	+ 49.0	$PCl_3(l)$	-319.70
$CO(g)$	-110.53	$PCl_5(s)$	-443.5
$CO_2(g)$	-393.51	$SiO_2(s)$ (quartz)	-910.94
$C_2H_6(g)$	-84.68	$SnCl_2(s)$	-325.1
$Cl_2(g)$	0	$SnCl_4(l)$	-511.3
$C_3H_8(g)$	-103.85	$SO_2(g)$	-296.83
$n-C_4H_{10}(g)$	-126.15	$SO_3(g)$	-395.72
HgS(s) red	-58.2	$SiH_4(g)$	+ 34
$H_2(g)$	0	$SiCl_4(g)$	-657.0
$H_2O(g)$	-241.82	$C(g)$	+716.68
$H_2O(l)$	-285.83	$H(g)$	+217.97
$HF(g)$	-271.1	$Cl(g)$	+121.68
$HCl(g)$	-92.31	$Fe_2O_3(s)$	–824.2
$HBr(g)$	-36.40		

Therefore,

$$\Delta H = - 7.56 \text{ kJ mol}^{-1} + (-6.00 \text{ kJ mol}^{-1})$$
$$= -13.56 \text{ kJ mol}^{-1}$$

There is negligible change in the volume during the change form liquid to solid state.

Therefore, $p\Delta v = \Delta ng\, RT = 0$

$\Delta H = \Delta U = - 13.56 \text{kJ mol}^{-1}$

(c) Standard Enthalpy of Formation

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^\ominus$, where the subscript 'f' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are as follows.

$H_2(g) + ½O_2(g) \rightarrow H_2O(1)$;

$\Delta_f H^\ominus = –285.8\ kJ\ mol^{-1}$

$C\ (graphite, s) + 2H_2(g) \rightarrow Ch_4\ (g)$;

$\Delta_f H^\ominus = –74.81\ kJ\ mol^{-1}$

$2C\ (graphite, s)+3H_2\ (g)+ ½O_2(g) \rightarrow C_2H_5OH(1)$;

$\Delta_f H^\ominus = – 277.7 kJ\ mol^{-1}$

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:

$CaO(s) + CO_2(g) \rightarrow CaCo_3(s)$;

$\Delta_r H^\ominus = – 178.3 kJ\ mol^{-1}$

is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H^\ominus$ for HBr(g).

$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$;

$\Delta_r H^\ominus = – 178.3 kJ\ mol^{-1}$

Here two moles, instead of one mole of the product is formed from the elements, i.e., .
$\Delta_r H^\ominus = 2\Delta_f H^\ominus$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as

$½H_2(g) + ½Br_2(1) \rightarrow HBr(g)$;

$\Delta_f H^\ominus = – 36.4\ kJ\ mol^{-1}$

Standard enthalpies of formation of some common substances are given in Table 6.2.

By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g);\ \Delta_r H^\ominus = ?$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$$\Delta_r H^\ominus = \sum_i a_i \Delta_f H^\ominus(\text{products}) - \sum_i b_i \Delta_f H^\ominus(\text{reactants}) \qquad (6.15)$$

where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1 each. Therefore,

$\Delta_r H^\ominus = \Delta_f H^\ominus = [CaO(s)] + \Delta_f H^\ominus [CO_2(g)]$

$– \Delta_f H^\ominus = [CaCO_3(s)]$

$=1\ (–635.1\ kJ\ mol^{-1}) + 1(–393.5\ kJ\ mol^{-1})$

$–1(–1206.9\ kJ\ mol^{-1})$

$= 178.3\ kJ\ mol^{-1}$

Thus, the decomposition of $CaCO_3$ (s) is an endothermic process and you have to heat it for getting the desired products.

(d) Thermochemical Equations

A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation. We specify the physical state (alongwith allotropic state) of the substance in an equation. For example:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$;

$\Delta_r H^\ominus = – 1367\ kJ\ mol^{-1}$

The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

It would be necessary to remember the following conventions regarding thermochemical equations.

1. The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.
2. The numerical value of $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ will have units as kJ mol^{-1}.

To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction :

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l),$$

From the Table (6.2) of standard enthalpy of formation ($\Delta_f H^\ominus$), we find :

$\Delta_f H^\ominus$ (H_2O,l) = –285.83 kJ mol^{-1};

$\Delta_f H^\ominus$ (Fe_2O_3,s) = – 824.2 kJ mol^{-1};

Also $\Delta_f H^\ominus$ (Fe, s) = 0 and

$\Delta_f H^\ominus$ (H_2, g) = 0 as per convention

Then,

$$\Delta_f H_1^\ominus = 3(-285.83 \text{ kJ mol}^{-1}) - 1(-824.2 \text{ kJ mol}^{-1})$$

$$= (-857.5 + 824.2) \text{ kJ mol}^{-1}$$

$$= -33.3 \text{ kJ mol}^{-1}$$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for $\Delta_r H^\ominus$ is kJ mol^{-1}, which means *per mole of reaction.* Once we balance the chemical equation in a particular way, as above, this defines the *mole of reaction*. If we had balanced the equation differently, for example,

$$\frac{1}{2}Fe_2O_3(s) + \frac{3}{2}H_2(g) \rightarrow Fe(s) + \frac{3}{2}H_2O(l)$$

then this amount of reaction would be one mole of reaction and $\Delta_r H^\ominus$ would be

$$\Delta_f H_2^\ominus = \frac{3}{2}(-285.83 \text{ kJ mol}^{-1})$$

$$- \frac{1}{2}(-824.2 \text{ kJ mol}^{-1})$$

$$= (-428.7 + 412.1) \text{ kJ mol}^{-1}$$

$$= -16.6 \text{ kJ mol}^{-1} = ½ \, \Delta_r H_1^\ominus$$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of $\Delta_r H^\ominus$ is reversed in sign. For example

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$;

$\Delta_r H^\ominus$ = – 91.8 kJ. mol^{-1}

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$;

$\Delta_r H^\ominus$ = + 91.8 kJ mol^{-1}

(e) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function, therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law.

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example.

Consider the enthalpy change for the reaction

$$C(\text{graphite,s}) + \frac{1}{2}O_2(g) \rightarrow CO(g); \ \Delta_r H^\ominus = ?$$

Although CO(g) is the major product, some CO_2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

$$C(\text{graphite,s}) + O_2(g) \rightarrow CO_2(g); \quad \Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1} \quad \text{(i)}$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\ominus = -283.0 \text{ kJ mol}^{-1} \quad \text{(ii)}$$

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of $\Delta_r H^\ominus$ value

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g); \quad \Delta_r H^\ominus = +283.0 \text{ kJ mol}^{-1} \quad \text{(iii)}$$

Adding equation (i) and (iii), we get the desired equation,

$$C(\text{graphite, s}) + \frac{1}{2}O_2(g) \rightarrow CO(g);$$

for which $\Delta_r H^\ominus = (-393.5 + 283.0)$

$= -110.5\ \text{kJ mol}^{-1}$

In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route, then we have

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots \qquad (6.16)$$

It can be represented as:

$$\begin{tikzcd}
\boxed{A} \arrow[r, "\Delta_r H"] \arrow[d, dash, "\Delta H_1"'] & \boxed{B} \\
\boxed{C} \arrow[r, "\Delta_r H_2"'] & \boxed{D} \arrow[u, "\Delta_r H_3"']
\end{tikzcd}$$

6.5 ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

It is convenient to give name to enthalpies specifying the types of reactions.

(a) Standard Enthalpy of Combustion (symbol : $\Delta_c H^\ominus$)

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane (C_4H_{10}). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$$

$$\Delta_c H^\ominus = -2658.0\ \text{kJ mol}^{-1}$$

Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :

$$C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);$$

$$\Delta_c H^\ominus = -2802.0\ \text{kJ mol}^{-1}$$

Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

Problem 6.9

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_2(g)$ and H_2O (1) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\ominus$ of benzene. Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are –393.5 kJ mol^{-1} and – 285.83 kJ mol^{-1} respectively.

Solution

The formation reaction of benezene is given by :

$$6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l);$$

$$\Delta_f H^\ominus = ? \ldots (i)$$

The enthalpy of combustion of 1 mol of benzene is :

$$C_6H_6(l) + \frac{15}{2}O_2 \rightarrow 6CO_2(g) + 3H_2O(l);$$

$$\Delta_c H^\ominus = -3267\ \text{kJ mol}^{-1} \ldots (ii)$$

The enthalpy of formation of 1 mol of $CO_2(g)$:

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);$$

$$\Delta_f H^\ominus = -393.5\ \text{kJ mol}^{-1} \ldots (iii)$$

The enthalpy of formation of 1 mol of $H_2O(l)$ is :

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);$$

$$\Delta_c H^\ominus = -285.83\ \text{kJ mol}^{-1} \ldots (iv)$$

multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

$$6C(\text{graphite}) + 6O_2(g) \rightarrow 6CO_2(g);$$
$$\Delta_f H^{\ominus} = -2361 \text{ kJ mol}^{-1}$$

$$3H_2(g) + \frac{3}{2}O_2(g) \rightarrow 3H_2O(l);$$
$$\Delta_f H^{\ominus} = -857.49 \text{ kJ mol}^{-1}$$

Summing up the above two equations :

$$6C(\text{graphite}) + 3H_2(g) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l);$$
$$\Delta_f H^{\ominus} = -3218.49 \text{ kJ mol}^{-1} \ldots \text{(v)}$$

Reversing equation (ii);

$$6CO_2(g) + 3H_2O(l) \rightarrow C_6H_6(l) + \frac{15}{2}O_2;$$
$$\Delta_f H^{\ominus} = -3267.0 \text{ kJ mol}^{-1} \ldots \text{(vi)}$$

Adding equations (v) and (vi), we get

$$6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l);$$
$$\Delta_f H^{\ominus} = -48.51 \text{ kJ mol}^{-1} \ldots \text{(iv)}$$

(b) Enthalpy of Atomization (symbol: $\Delta_a H^{\ominus}$)

Consider the following example of atomization of dihydrogen

$H_2(g) \rightarrow 2H(g)$; $\Delta_a H^{\ominus} = 435.0 \text{ kJ mol}^{-1}$

You can see that H atoms are formed by breaking H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, $\Delta_a H^{\ominus}$. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

In case of diatomic molecules, like dihydrogen (given above), the enthalpy of atomization is also the bond dissociation enthalpy. The other examples of enthalpy of atomization can be

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H^{\ominus} = 1665 \text{ kJ mol}^{-1}$

Note that the products are only **atoms** of C and H in gaseous phase. Now see the following reaction:

$Na(s) \rightarrow Na(g)$; $\Delta_a H^{\ominus} = 108.4 \text{ kJ mol}^{-1}$

In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

(c) Bond Enthalpy (symbol: $\Delta_{bond} H^{\ominus}$)

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy
(ii) Mean bond enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules.

Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H_2) are broken:

$H_2(g) \rightarrow 2H(g)$; $\Delta_{H-H} H^{\ominus} = 435.0 \text{ kJ mol}^{-1}$

The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

$Cl_2(g) \rightarrow 2Cl(g)$; $\Delta_{Cl-Cl} H^{\ominus} = 242 \text{ kJ mol}^{-1}$

$O_2(g) \rightarrow 2O(g)$; $\Delta_{O=O} H^{\ominus} = 428 \text{ kJ mol}^{-1}$

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$$CH_4(g) \rightarrow C(g) + 4H(g);$$
$$\Delta_a H^{\ominus} = 1665 \text{ kJ mol}^{-1}$$

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$CH_4(g) \rightarrow CH_3(g)+H(g); \Delta_{bond}H^\ominus = +427\ kJ\ mol^{-1}$

$CH_3(g) \rightarrow CH_2(g)+H(g); \Delta_{bond}H^\ominus = +439\ kJ\ mol^{-1}$

$CH_2(g) \rightarrow CH(g)+H(g); \Delta_{bond}H^\ominus = +452\ kJ\ mol^{-1}$

$CH(g) \rightarrow C(g)+H(g); \Delta_{bond}H^\ominus = +347\ kJ\ mol^{-1}$

Therefore,

$CH_4(g) \rightarrow C(g)+4H(g); \Delta_a H^\ominus = 1665\ kJ\ mol^{-1}$

In such cases we use **mean bond enthalpy of C – H bond**.

For example in CH_4, $\Delta_{C-H}H^\ominus$ is calculated as:

$$\Delta_{C-H}H^\ominus = ¼\ (\Delta_a H^\ominus) = ¼\ (1665\ kJ\ mol^{-1})$$
$$= 416\ kJ\ mol^{-1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in CH_3CH_2Cl, CH_3NO_2, etc, but it does not differ in a great deal*. Using Hess's law, bond enthalpies can be calculated. Bond enthalpy values of some single and multiple bonds are given in Table 6.3. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, $\Delta_r H^\ominus$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^\ominus = \sum \text{bond enthalpies}_{reactants} - \sum \text{bond enthalpies}_{products} \quad (6.17)^{**}$$

This relationship is particularly more useful when the required values of $\Delta_f H^\ominus$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is

Table 6.3(a) Some Mean Single Bond Enthalpies in kJ mol^{-1} at 298 K

H	C	N	O	F	Si	P	S	Cl	Br	I	
435.8	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272	-	209	-	201	243	-	N
			138	184	368	351	-	205	-	201	O
				155	540	490	327	255	197	-	F
					176	213	226	360	289	213	Si
						213	230	331	272	213	P
							213	251	213	-	S
								243	218	209	Cl
									192	180	Br
										151	I

Table 6.3(b) Some Mean Multiple Bond Enthalpies in kJ mol^{-1} at 298 K

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

---

* *Note that symbol used for bond dissociation enthalpy and mean bond enthalpy is the same.*

** *If we use enthalpy of bond formation, ($\Delta_f H^\ominus_{bond}$), which is the enthalpy change when one mole of a particular type of bond is formed from gaseous atom, then* $\Delta_f H^\ominus = \sum \Delta_f H^\ominus_{\text{bonds of products}} - \sum \Delta_f H^\ominus_{\text{bonds of reactants}}$

approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

(d) Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g);$$

$$\Delta_{lattice}H^{\ominus} = +788 \text{ kJ mol}^{-1}$$

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle** (Fig. 6.9).

Let us now calculate the lattice enthalpy of $Na^+Cl^-(s)$ by following steps given below :

1. $Na(s) \rightarrow Na(g)$, *sublimation of sodium metal*, $\Delta_{sub}H^{\ominus} = 108.4 \text{ kJ mol}^{-1}$

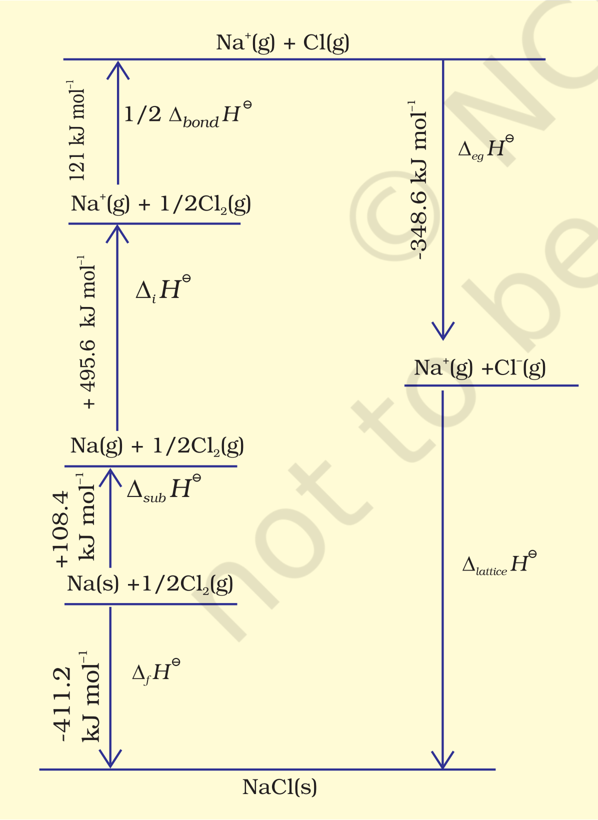


Fig. 6.9 *Enthalpy diagram for lattice enthalpy of NaCl*

2. $Na(g) \rightarrow Na^+(g) + e^{-1}(g)$, the *ionization of sodium atoms*, ionization enthalpy $\Delta_i H^{\ominus} = 496 \text{ kJ mol}^{-1}$

3. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$, the *dissociation of chlorine*, the reaction enthalpy is half the bond dissociation enthalpy.

$$\frac{1}{2}\Delta_{bond}H^{\ominus} = 121 \text{ kJ mol}^{-1}$$

4. $Cl(g) + e^{-1}(g) \rightarrow \bar{Cl}(g)$ *electron gained* by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H^{\ominus} = -348.6 \text{ kJ mol}^{-1}$.

You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification).

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

$M(g) \rightarrow M^+(g) + e^-$ (for ionization)

$M(g) + e^- \rightarrow M^-(g)$ (for electron gain)

at temperature, T is

$$\Delta_r H^{\ominus}(T) = \Delta_r H^{\ominus}(0) + \int_0^T \Delta_r C_p^{\ominus} dT$$

The value of C_p for each species in the above reaction is 5/2 R (C_V = 3/2R)

So, $\Delta_r C_p^{\ominus}$ = + 5/2 R (for ionization)

$\Delta_r C_p^{\ominus}$ = – 5/2 R (for electron gain)

Therefore,

$\Delta_r H^{\ominus}$ (ionization enthalpy)

= E_0 (ionization energy) + 5/2 RT

$\Delta_r H^{\ominus}$ (electron gain enthalpy)

= – A(electron affinity) – 5/2 RT

5. $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$

The sequence of steps is shown in Fig. 6.9, and is known as a Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero. Applying Hess's law, we get,

$$\Delta_{lattice}H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{lattice}H^\ominus = +788 \text{kJ}$$

for $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

Internal energy is smaller by 2RT (because $\Delta n_g = 2$) and is equal to + 783 kJ mol^{-1}.

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$$

For one mole of NaCl(s),

lattice enthalpy = + 788 kJ mol^{-1}

and $\Delta_{hyd}H^\ominus$ = – 784 kJ mol^{-1}(from the literature)

$$\Delta_{sol}H^\ominus = +788 \text{ kJ mol}^{-1} - 784 \text{ kJ mol}^{-1}$$
$$= +4 \text{ kJ mol}^{-1}$$

The dissolution of NaCl(s) is accompanied by very little heat change.

(e) Enthalpy of Solution (symbol : $\Delta_{sol}H^\ominus$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)

$$\begin{tikzcd}
AB\,(s) \arrow[r, "\Delta_{sol}H^\ominus"] \arrow[d, "\Delta_{lattice}H^\ominus"'] & A^+(aq) + B^-(aq) \\
A^+(g) + B^-(g) \arrow[ur, "\Delta_{hyd}H^\ominus"'] &
\end{tikzcd}$$

The enthalpy of solution of AB(s), $\Delta_{sol}H^\ominus$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H^\ominus$ and enthalpy of hydration of ions, $\Delta_{hyd}H^\ominus$ as

$$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$$

For most of the ionic compounds, $\Delta_{sol}H^\ominus$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies).

(f) Enthalpy of Dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water

$$HCl(g) + 10 \text{ aq.} \rightarrow HCl.10 \text{ aq.} \qquad \Delta H = -69.01 \text{ kJ / mol}$$

Let us consider the following set of enthalpy changes:

(S-1) $HCl(g) + 25 \text{ aq.} \rightarrow HCl.25 \text{ aq.}$ $\quad \Delta H = -72.03$ kJ / mol

(S-2) $HCl(g) + 40 \text{ aq.} \rightarrow HCl.40 \text{ aq.}$ $\quad \Delta H = -72.79$ kJ / mol

(S-3) $HCl(g) + \infty \text{ aq.} \rightarrow HCl.\infty \text{ aq.}$ $\quad \Delta H = -74.85$ kJ / mol

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain–

$$\text{HCl.25 aq.} + \text{15 aq.} \rightarrow \text{HCl.40 aq.}$$
$$\Delta H = [-72.79 - (-72.03)] \text{ kJ / mol}$$
$$= -0.76 \text{ kJ / mol}$$

This value (–0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

6.6 SPONTANEITY

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means *'having the potential to proceed without the assistance of external agency'*. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

> ***A spontaneous process is an irreversible process and may only be reversed by some external agency.***

(a) Is Decrease in Enthalpy a Criterion for Spontaneity ?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g) \; ; \qquad \Delta_r H^{\ominus} = -46.1 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g) \; ; \qquad \Delta_r H^{\ominus} = -92.32 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \; ; \qquad \Delta_r H^{\ominus} = -285.8 \text{ kJ mol}^{-1}$$

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.10(a).

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far !

Now let us examine the following reactions:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \qquad \Delta_r H^{\ominus} = +33.2 \text{ kJ mol}^{-1}$$

$$C(\text{graphite, s}) + 2\,S(l) \rightarrow CS_2(l); \qquad \Delta_r H^{\ominus} = +128.5 \text{ kJ mol}^{-1}$$

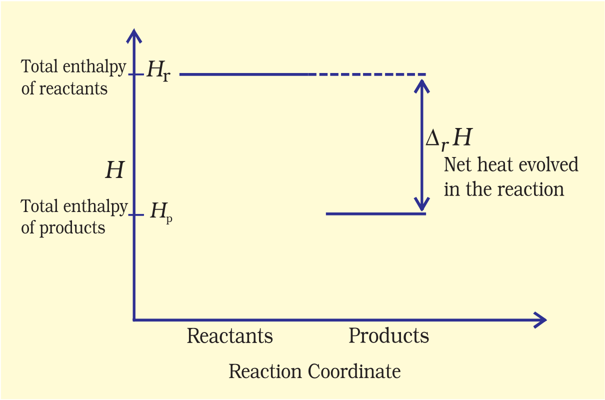


Fig. 6.10 (a) *Enthalpy diagram for exothermic reactions*

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.10(b).

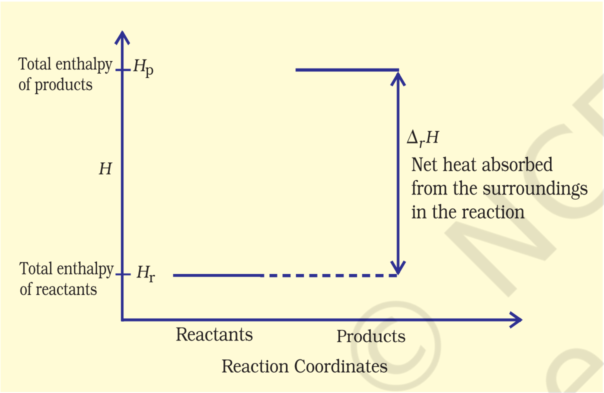


Fig. 6.10 (b) *Enthalpy diagram for endothermic reactions*

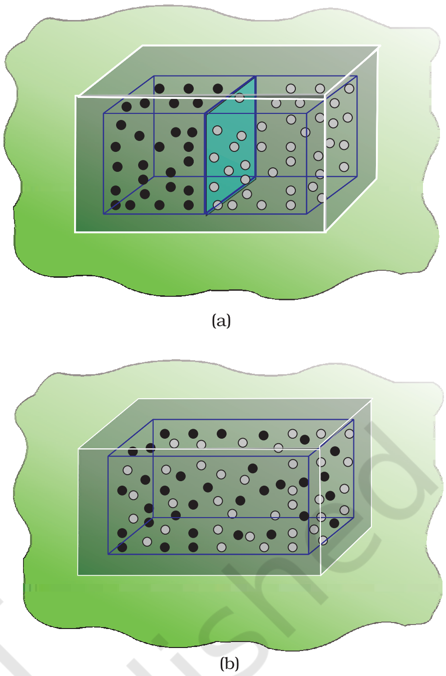
Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and Spontaneity

Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 6.11.

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 6.11 (a)]. When the partition is withdrawn [Fig.6.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.


(a)

(b)

Fig. 6.11 *Diffusion of two gases*

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !

At this point, we introduce another thermodynamic function, **entropy** denoted as S. The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (*q*) has randomising influence** on the system. Can we then equate ΔS with q? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average chaotic motion of particles in the system**. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \qquad (6.18)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \qquad (6.19)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Problem 6.10

Predict in which of the following, entropy increases/decreases :

(i) A liquid crystallizes into a solid.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.

(iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(iv) $H_2(g) \rightarrow 2H(g)$

Solution

(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Problem 6.11

For oxidation of iron,

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

entropy change is – 549.4 $JK^{-1}mol^{-1}$at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^\ominus$for this reaction is -1648×10^3 J mol^{-1})

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total}\left(\Delta S_{sys} + \Delta S_{surr}\right)$. For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^\ominus}{T}\ (\text{at constant pressure})$$

$$= -\frac{\left(-1648 \times 10^3\ \text{J mol}^{-1}\right)}{298\ \text{K}}$$

= 5530 $JK^{-1}mol^{-1}$

Thus, total entropy change for this reaction

$$\Delta_r S_{total} = 5530\text{JK}^{-1}\text{mol}^{-1} + \left(-549.4\text{JK}^{-1}\text{mol}^{-1}\right)$$

= 4980.6 JK^{-1} mol^{-1}

This shows that the above reaction is spontaneous.

(c) Gibbs Energy and Spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, *G*, as

$$G = H - TS \qquad (6.20)$$

Gibbs function, *G* is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \qquad (6.21)$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S$ = (K) (J/K) = J.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -\left(\Delta H_{sys} - T\Delta S_{sys}\right) > 0$$

Using equation 6.21, the above equation can be written as

$-\Delta G > 0$

$$\Delta G = \Delta H - T\Delta S < 0 \qquad (6.22)$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous.

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.4 summarises the effect of temperature on spontaneity of reactions.

(d) *Entropy and Second Law of Thermodynamics*

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

(e) *Absolute Entropy and Third Law of Thermodynamics*

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. **The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.** This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing $\frac{q_{rev}}{T}$ increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

6.7 GIBBS ENERGY CHANGE AND EQUILIBRIUM

We have seen how a knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium

$A + B \rightleftharpoons C + D$; is

$\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

or $\Delta_r G^\ominus = -RT \ln K$

or $\Delta_r G^\ominus = -2.303\, RT \log K$ (6.23)

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K \quad (6.24)$$

For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G^\ominus$ also depends upon $\Delta_r S^\ominus$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected,

Table 6.4 Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
–	+	–	Reaction spontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

---

* *The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

depending upon whether $\Delta_r S^\ominus$ is positive or negative.

Using equation (6.24),

(i) It is possible to obtain an estimate of $\Delta G^\ominus$ from the measurement of $\Delta H^\ominus$ and $\Delta S^\ominus$, and then calculate *K* at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of $\Delta G^\ominus$ at any other temperature can be calculated.

Using equation (6.24),

Problem 6.12

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. if K_p for this conversion is 2.47×10^{-29}.

Solution

We know $\Delta_r G^\ominus = -\ 2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$

Therefore, $\Delta_r G^\ominus =$

$$-\ 2.303\ (8.314\ J\ K^{-1}\ mol^{-1}) \times (298\ K)\ (\log 2.47 \times 10^{-29})$$

$= 163000\ J\ mol^{-1}$

$= 163\ kJ\ mol^{-1}$.

Problem 6.13

Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3(g) + CO_2(g) \leftrightharpoons NH_2CONH_2(aq) + H_2O(l)$$

Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is $-13.6\ kJ\ mol^{-1}$.

Solution

We know, $\log K = \dfrac{-\Delta_r G^\ominus}{2.303\,RT}$

$$= \frac{\left(-13.6 \times 10^3\ J\ mol^{-1}\right)}{2.303\left(8.314\ JK^{-1}\ mol^{-1}\right)(298\,K)}$$

$= \ 2.38$

Hence K = antilog $2.38 = 2.4 \times 10^2$.

Problem 6.14

At 60°C, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1-0.5}{1+0.5} : x_{NO_2} = \frac{2 \times 0.5}{1+0.5}$$

$$p_{N_2O_4} = \frac{0.5}{1.5} \times 1\ \text{atm},\ p_{NO_2} = \frac{1}{1.5} \times 1\ \text{atm}.$$

The equilibrium constant K_p is given by

$$K_p = \frac{\left(p_{NO_2}\right)^2}{p_{N_2O_4}} = \frac{1.5}{(1.5)^2\ (0.5)}$$

$= \ 1.33$ atm.

Since

$\Delta_r G^\ominus = -RT \ln K_p$

$$\Delta_r G^\ominus = (-\ 8.314\ JK^{-1} mol^{-1}) \times (333\ K) \times (2.303) \times (0.1239)$$

$= -\ 763.8\ kJ\ mol^{-1}$

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + \mathrm{w}$. ΔU, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $\mathrm{w} = -p_{ex}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{ex} = p$ for infinitesimal changes in the volume making $\mathrm{w}_{\mathrm{rev}} = -p\,\mathrm{d}V$. In this condition, we can use gas equation, $pV = n\mathrm{R}T$.

At constant volume, $\mathrm{w} = 0$, then $\Delta U = q_V$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function **enthalpy**. Enthalpy change, $\Delta H = \Delta U + \Delta n_g \mathrm{R}T$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f \left(a_i \Delta_f H_{\text{products}}\right) - \sum_i \left(b_i \Delta_f H_{\text{reactions}}\right)$$

and in gaseous state by

$\Delta_r H^{\ominus} = \Sigma$ *bond enthalpies of the reactants* – Σ *bond enthalpies of the products*

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S, **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation $\Delta S = \dfrac{q_{\mathrm{rev}}}{T}$ for a reversible process. $\dfrac{q_{\mathrm{rev}}}{T}$ is independent of path.

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G, which is related to entropy and enthalpy changes of the system by the equation:

$\Delta_r G = \Delta_r H - T\,\Delta_r S$

For a spontaneous change, $\Delta G_{\mathrm{sys}} < 0$ and at equilibrium, $\Delta G_{sys} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$\Delta_r G^{\ominus} = -\mathrm{R}T \ln K$.

K can be calculated from this equation, if we know $\Delta_r G^{\ominus}$ which can be found from $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

EXERCISES

6.1 Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only.

6.2 For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

6.3 The enthalpies of all elements in their standard states are:

(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

6.4 $\Delta U^{\ominus}$ of combustion of methane is – X kJ mol^{-1}. The value of $\Delta H^{\ominus}$ is

(i) $= \Delta U^{\ominus}$

(ii) $> \Delta U^{\ominus}$

(iii) $< \Delta U^{\ominus}$

(iv) $= 0$

6.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol^{-1} –393.5 kJ mol^{-1}, and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of CH_4(g) will be

(i) –74.8 kJ mol^{-1} (ii) –52.27 kJ mol^{-1}

(iii) +74.8 kJ mol^{-1} (iv) +52.26 kJ mol^{-1}.

6.6 A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(v) possible at any temperature

6.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

6.8 The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$$NH_2CN(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$$

6.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

6.10 Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at –10.0°C. $\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C.

$C_p\,[H_2O(l)] = 75.3$ J mol^{-1} K^{-1}

$C_p\,[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}

6.11 Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

6.12 Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, – 393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

6.13 Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta_r H^\ominus = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of NH_3 gas?

6.14 Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$$CH_3OH\,(l) + \frac{3}{2}\,O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ ;\ \Delta_r H^\ominus = -726\ \text{kJ mol}^{-1}$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta_c H^\ominus = -393\ \text{kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(l)\ ;\ \Delta_f H^\ominus = -286\ \text{kJ mol}^{-1}.$$

6.15 Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4\,Cl(g)$

and calculate bond enthalpy of C – Cl in CCl_4(g).

$\Delta_{vap}H^\ominus(CCl_4) = 30.5$ kJ mol^{-1}.

$\Delta_f H^\ominus\,(CCl_4) = -135.5$ kJ mol^{-1}.

$\Delta_a H^\ominus$ (C) = 715.0 kJ mol^{-1}, where $\Delta_a H^\ominus$ is enthalpy of atomisation

$\Delta_a H^\ominus\,(Cl_2) = 242$ kJ mol^{-1}

6.16 For an isolated system, $\Delta U = 0$, what will be ΔS ?

6.17 For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

6.18 For the reaction,

$2\,Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

6.19 For the reaction

$2\,A(g) + B(g) \rightarrow 2D(g)$

$\Delta U^\ominus = -10.5$ kJ and $\Delta S^\ominus = -44.1$ JK^{-1}.

Calculate $\Delta G^\ominus$ for the reaction, and predict whether the reaction may occur spontaneously.

6.20 The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^\ominus$? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

6.21 Comment on the thermodynamic stability of NO(g), given

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g) \quad ; \quad \Delta_r H^\ominus = 90 \text{ kJ mol}^{-1}$$

$$NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g) \quad : \quad \Delta_r H^\ominus = -74 \text{ kJ mol}^{-1}$$

6.22 Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^\ominus$ = –286 kJ mol^{-1}.

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

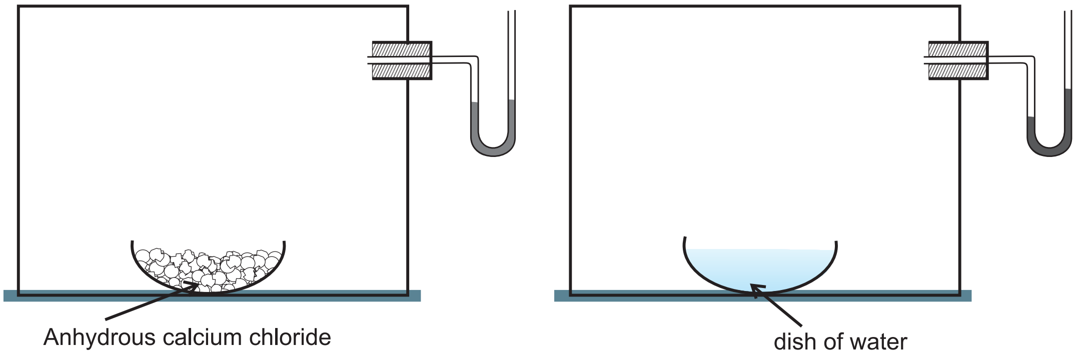


Fig.7.1 *Measuring equilibrium vapour pressure of water at a constant temperature*

molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e.,

rate of evaporation= rate of condensation

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

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

7.1.3 Solid – Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$I_2(solid) \quad I_2\ (vapour)$$

Other examples showing this kind of equilibrium are,

$$Camphor\ (solid) \rightleftharpoons Camphor\ (vapour)$$

$$NH_4Cl\ (solid) \rightleftharpoons NH_4Cl\ (vapour)$$

7.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution:

Sugar (solution) $\rightleftharpoons$ Sugar (solid), and

the rate of dissolution of sugar = rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,

$$CO_2 \text{ (gas)} \rightleftharpoons CO_2 \text{ (in solution)}$$

This equilibrium is governed by Henry's law, **which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.** This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that:

(i) For solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.

(ii) For liquid $\rightleftharpoons$ vapour equilibrium, the vapour pressure is constant at a given temperature.

(iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.

(iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 7.1

Table 7.1 Some Features of Physical Equilibria

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour H_2O (l) $\rightleftharpoons$ H_2O (g)	p_{H_2O} constant at given temperature
Solid $\rightleftharpoons$ Liquid H_2O (s) $\rightleftharpoons$ H_2O (l)	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) CO_2(g) $\rightleftharpoons$ CO_2(aq)	[gas(aq)]/[gas(g)] is constant at a given temperature [CO_2(aq)]/[CO_2(g)] is constant at a given temperature

7.1.5 General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant.

(iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 7.1 lists such quantities.

(v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

7.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

$$A + B \rightleftharpoons C + D$$

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in he rate of the reverse reaction,

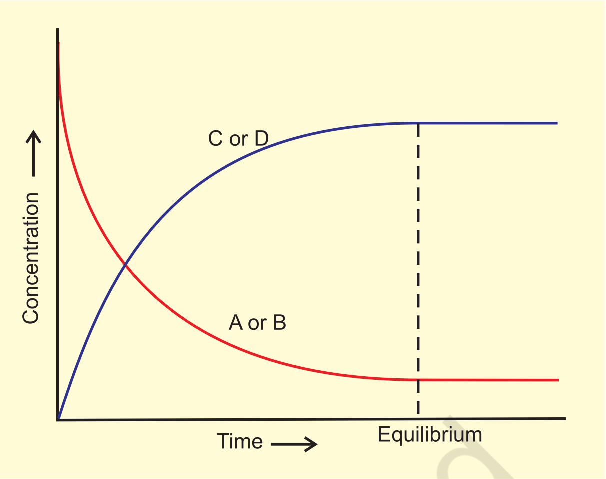


Fig. 7.2 *Attainment of chemical equilibrium.*

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.4 (page 191) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2. The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures

Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students.

Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty.

Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the coloured water contained in its lower portion to cylinder 2. Using second tube, kept in 2nd cylinder, transfer the coloured water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant.

If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning.

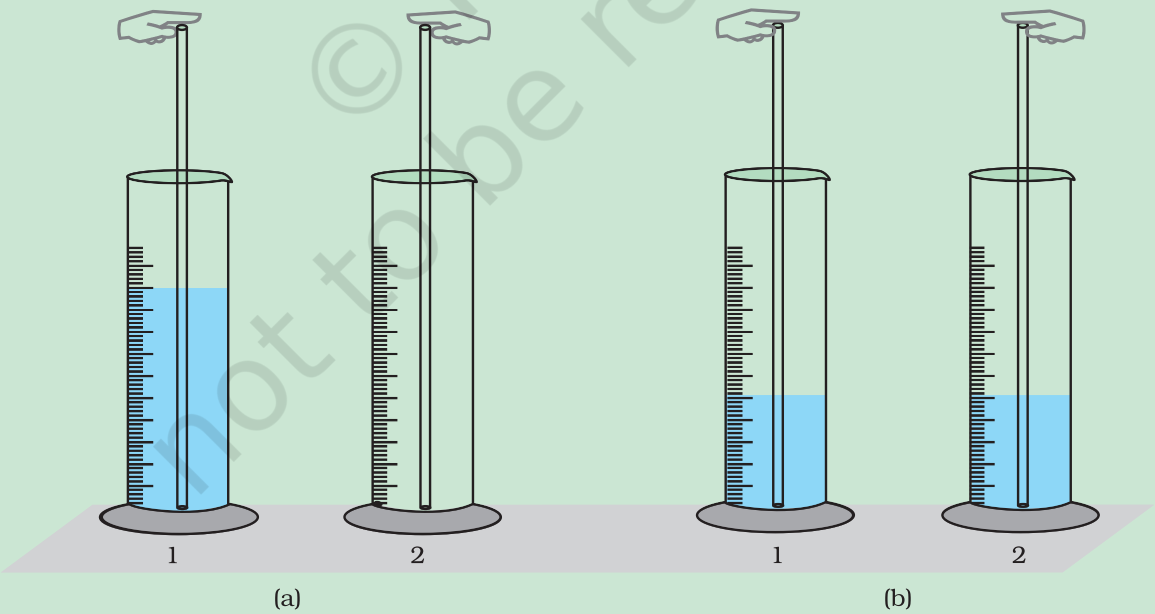


Fig.7.3 *Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.*

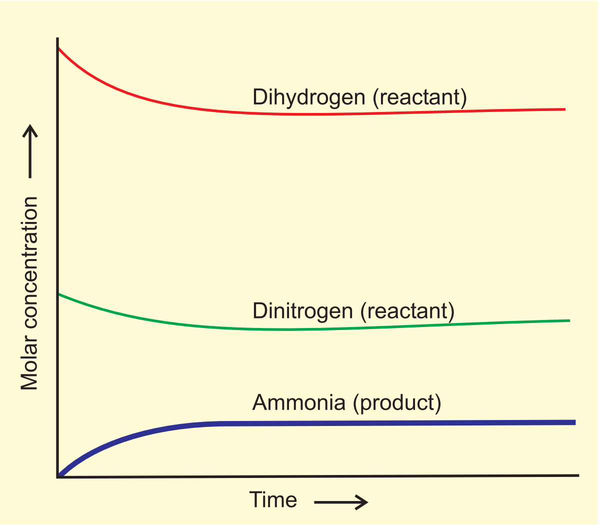


Fig 7.4 *Depiction of equilibrium for the reaction*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and dihydrogen and its deutrated forms (H_2, HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

Equilibrium can be attained from both sides, whether we start reaction by taking, $H_2(g)$ and $N_2(g)$ and get $NH_3(g)$ or by taking $NH_3(g)$ and decomposing it into $N_2(g)$ and $H_2(g)$.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Similarly let us consider the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 7.5). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig.7.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

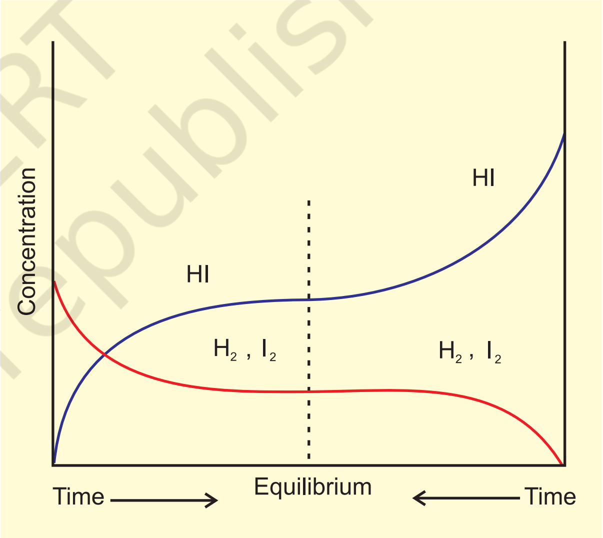


Fig.7.5 *Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction*

7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations?

What factors can be exploited to alter the composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H_2, NH_3, CaO etc.

To answer these questions, let us consider a general reversible reaction:

$$A + B \rightleftharpoons C + D$$

where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following **equilibrium equation,**

$$K_c = \frac{[C][D]}{[A][B]}$$

(7.1) where K_c is the *equilibrium constant* and the expression on the right side is called the *equilibrium constant expression*.

The equilibrium equation is also known as the *law of mass action* because in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider reaction between gaseous H_2 and I_2 carried out in a sealed vessel at 731K.

$$\begin{array}{ccccc} H_2(g) & + & I_2(g) & \rightleftharpoons & 2HI(g) \\ 1\text{ mol} & & 1\text{ mol} & & 2\text{ mol} \end{array}$$

Six sets of experiments with varying initial conditions were performed, starting with only gaseous H_2 and I_2 in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of H_2 and / or I_2, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 7.2.

It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted = ½ (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$[H_2(g)]_{eq} = [I_2(g)]_{eq}$$

Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$[HI(g)]_{eq} \;/\; [H_2(g)]_{eq}\,[I_2(g)]_{eq}$$

It can be seen from Table 7.3 that if we put the equilibrium concentrations of the reactants and products, the above expression

Table 7.2 Initial and Equilibrium Concentrations of H_2, I_2 and HI

Experiment number	Initial concentration/mol L^{-1}			Equilibrium concentration/mol L^{-1}		
	[H_2 (g)]	[I_2 (g)]	[HI (g)]	[H_2 (g)]	[I_2 (g)]	[HI (g)]
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

Table 7.3 Expression Involving the Equilibrium Concentration of Reactants
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Experiments Number	$\dfrac{[HI(g)]_{eq}}{[H_2(g)]_{eq}\,[I_2(g)]_{eq}}$	$\dfrac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}\,[I_2(g)]_{eq}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

is far from constant. However, if we consider the expression,

$$[HI(g)]^2_{eq} / [H_2(g)]_{eq}\,[I_2(g)]_{eq}$$

we find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, following equation 7.1, the equilibrium constant K_c is written as,

$$K_c = [HI(g)]^2_{eq} / [H_2(g)]_{eq}\,[I_2(g)]_{eq} \qquad (7.2)$$

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write,

$$K_c = [HI(g)]^2 / [H_2(g)]\,[I_2(g)] \qquad (7.3)$$

The subscript '*c*' indicates that K_c is expressed in concentrations of mol L^{-1}.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

The equilibrium constant for a general reaction,

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

is expressed as,

$$K_c = [C]^c[D]^d / [A]^a[B]^b \qquad (7.4)$$

where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction, $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ is written as

$$K_c = [NO]^4[H_2O]^6 / [NH_3]^4\,[O_2]^5$$

Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.

Let us write equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (7.5)

as, $K_c = [HI]^2 / [H_2]\,[I_2] = x$ (7.6)

The equilibrium constant for the reverse reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, at the same temperature is,

$$K_c' = [H_2]\,[I_2] / [HI]^2 = 1/x = 1 / K_c \qquad (7.7)$$

Thus, $K_c' = 1 / K_c$ (7.8)

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (7.5) is written as,

$$\tfrac{1}{2} H_2(g) + \tfrac{1}{2} I_2(g) \rightleftharpoons HI(g) \qquad (7.9)$$

the equilibrium constant for the above reaction is given by

$$K_c'' = [HI] / [H_2]^{1/2}[I_2]^{1/2} = \{[HI]^2 / [H_2][I_2]\}^{1/2}$$
$$= x^{1/2} = K_c^{1/2} \qquad (7.10)$$

On multiplying the equation (7.5) by n, we get

$$nH_2(g) + nI_2(g)\ \mathrm{D} \rightleftharpoons 2nHI(g) \qquad (7.11)$$

Therefore, equilibrium constant for the reaction is equal to $K_c^{\,n}$. These findings are summarised in Table 7.4. It should be noted that because the equilibrium constants K_c and K'_c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 7.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.

Chemical equation	Equilibrium constant
$a\,A + b\,B \rightleftharpoons c\,C + d\,D$	K_c
$c\,C + d\,D \rightleftharpoons a\,A + b\,B$	$K'_c = (1/K_c)$
$na\,A + nb\,B \rightleftharpoons ncC + ndD$	$K''_c = (K_c^n)$

Problem 7.1

The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}M$. $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}M$. Calculate equilibrium constant.

Solution

The equilibrium constant for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as,

$$K_c = \frac{\left[NH_3(g)\right]^2}{\left[N_2(g)\right]\left[H_2(g)\right]^3}$$

$$= \frac{\left(1.2 \times 10^{-2}\right)^2}{\left(1.5 \times 10^{-2}\right)\left(3.0 \times 10^{-2}\right)^3}$$

$$= 0.106 \times 10^4 = 1.06 \times 10^3$$

Problem 7.2

At equilibrium, the concentrations of N_2=3.0 × 10^{-3}M, O_2 = 4.2 × 10^{-3}M and NO= 2.8 × 10^{-3}M in a sealed vessel at 800K. What will be K_c for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Solution

For the reaction equilibrium constant, K_c can be written as,

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{\left(2.8 \times 10^{-3}M\right)^2}{\left(3.0 \times 10^{-3}M\right)\left(4.2 \times 10^{-3}M\right)}$$

$$= 0.622$$

7.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, reactants and products are in the homogeneous phase. Similarly, for the reactions,

$$CH_3COOC_2H_5\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COOH\,(aq) + C_2H_5OH\,(aq)$$

and, $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT$$

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

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin

Therefore,

n/V is concentration expressed in mol/m³

If concentration c, is in mol/L or mol/dm^3, and p is in bar then

$p = cRT,$

We can also write $p = [\text{gas}]RT$.

Here, R= 0.0831 bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$p \propto [\text{gas}]$

For reaction in equilibrium

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

We can write either

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$\text{or } K_c = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} \qquad (7.12)$$

$$\text{Further, since } p_{HI} = [HI(g)]RT$$

$$p_{I_2} = [I_2(g)]RT$$

$$p_{H_2} = [H_2(g)]RT$$

Therefore,

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$= \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = K_c \qquad (7.13)$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

$$= \frac{[NH_3(g)]^2[RT]^2}{[N_2(g)]RT.[H_2(g)]^3(RT)^3}$$

$$= \frac{[NH_3(g)]^2[RT]^{-2}}{[N_2(g)][H_2(g)]^3} = K_c(RT)^{-2}$$

$$\text{or } K_p = K_c(RT)^{-2} \qquad (7.14)$$

Similarly, for a general reaction

$aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{(a+b)}}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n} = K_c(RT)^{\Delta n} \qquad (7.15)$$

where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

It is necessary that while calculating the value of K_p, pressure should be expressed in bar because standard state for pressure is 1 bar. We know from Unit 1 that :

1pascal, Pa=1Nm^{-2}, and 1bar = 10^5 Pa

K_p values for a few selected reactions at different temperatures are given in Table 7.5

Table 7.5 Equilibrium Constants, K_p for a Few Selected Reactions

Reaction	Temperature/K	K_p
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	2.5×10^{10}
	700	3.0×10^4
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700

Problem 7.3

PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5.

Calculate K_c for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Solution

The equilibrium constant K_c for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$$

Problem 7.4

The value of $K_c = 4.24$ at 800K for the reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each.

Solution

For the reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

Initial concentration:

0.1M 0.1M 0 0

Let x mole per litre of each of the product be formed.

At equilibrium:

(0.1-x) M (0.1-x) M x M x M

where x is the amount of CO_2 and H_2 at equilibrium.

Hence, equilibrium constant can be written as,

$K_c = x^2/(0.1-x)^2 = 4.24$

$x^2 = 4.24(0.01 + x^2 - 0.2x)$

$x^2 = 0.0424 + 4.24x^2 - 0.848x$

$3.24x^2 - 0.848x + 0.0424 = 0$

$a = 3.24,\ b = -0.848,\ c = 0.0424$

(for quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a}$$

$x = 0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)}/(3.24 \times 2)$

$x = (0.848 \pm 0.4118)/\ 6.48$

$x_1 = (0.848 - 0.4118)/6.48 = 0.067$

$x_2 = (0.848 + 0.4118)/6.48 = 0.194$

the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

Hence the equilibrium concentrations are,

$[CO_2] = [H_2] = x = 0.067$ M

$[CO] = [H_2O] = 0.1 - 0.067 = 0.033$ M

Problem 7.5

For the equilibrium,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Solution

We know that,

$K_p = K_c(RT)^{\Delta n}$

For the above reaction,

$\Delta n = (2+1) - 2 = 1$

$K_p = 3.75 \times 10^{-6}\ (0.0831 \times 1069)$

$K_p = 0.033$

7.5 HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,

$$Ca(OH)_2\ (s) + (aq) \rightleftharpoons Ca^{2+}\ (aq) + 2OH^-(aq)$$

is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary to this, [X(g)] and [X(aq)] will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.

$$CaCO_3\,(s) \overset{\Delta}{\rightleftharpoons} CaO\,(s) + CO_2\,(g) \qquad (7.16)$$

On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since $[CaCO_3(s)]$ and [CaO(s)] are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K'_c = [CO_2(g)] \qquad (7.17)$$

$$\text{or } K_p = p_{CO_2} \qquad (7.18)$$

Units of Equilibrium Constant

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions,

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_c and K_p have no unit.

$N_2O_4(g) \rightleftharpoons 2NO_2\,(g)$, K_c has unit mol/L and K_p has unit bar

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1bar. Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state (c_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states.

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with CaO(s) and $CaCO_3(s)$. Experimentally it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_3(s)$ and CaO(s), is 2.0×10^5 Pa. Therefore, equilibrium constant at 1100K for the above reaction is:

$$K_p = P_{CO_2} = 2 \times 10^5\ \text{Pa}/10^5\ \text{Pa} = 2.00$$

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),

$$Ni\,(s) + 4\,CO\,(g) \rightleftharpoons Ni(CO)_4\,(g),$$

the equilibrium constant is written as

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4}$$

It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction,

$$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$$

$$K_c = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

Problem 7.6

The value of K_p for the reaction,

$CO_2\,(g) + C\,(s) \rightleftharpoons 2CO\,(g)$

is 3.0 at 1000 K. If initially $P_{CO_2} = 0.48$ bar and $P_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2.

Solution

For the reaction,

let 'x' be the decrease in pressure of CO_2, then

	$CO_2(g)$	+ C(s) ⇌	2CO(g)
Initial pressure:	0.48 bar		0

At equilibrium:

(0.48 – x)bar 2x bar

$$K_p = \frac{p^2_{CO}}{p_{CO_2}}$$

$K_p = (2x)^2/(0.48 – x) = 3$

$4x^2 = 3(0.48 – x)$

$4x^2 = 1.44 – x$

$4x^2 + 3x – 1.44 = 0$

$a = 4, b = 3, c = –1.44$

$$x = \frac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a}$$

$= [–3 \pm \sqrt{(3)^2 – 4(4)(–1.44)}]/2 \times 4$

$= (–3 \pm 5.66)/8$

$= (–3 + 5.66)/8$ (as value of x cannot be negative hence we neglect that value)

$x = 2.66/8 = 0.33$

The equilibrium partial pressures are,

$p_{CO_2} = 2x = 2 \times 0.33 = 0.66$ bar

$p_{CO_2} = 0.48 – x = 0.48 – 0.33 = 0.15$ bar

7.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

1. Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
2. The value of equilibrium constant is independent of initial concentrations of the reactants and products.
3. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
4. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
5. The equilibrium constant *K* for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Let us consider applications of equilibrium constant to:

- predict the extent of a reaction on the basis of its magnitude,
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

7.6.1 Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the *rate* at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of *K* is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:

(a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, $K_c = 2.4 \times 10^{47}$.

(b) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has $K_c = 4.0 \times 10^{31}$.

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ at 300 K, $K_c = 5.4 \times 10^{18}$

- If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely. Consider the following examples:

(a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, at 298 K has $K_c = 4.8 \times 10^{-31}$.

- If K_c is in the range of 10^{-3} to 10^3, appreciable concentrations of both reactants and products are present. Consider the following examples:

(a) For reaction of H_2 with I_2 to give HI, $K_c = 57.0$ at 700K.

(b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

These generarlisations are illustrated in Fig. 7.6

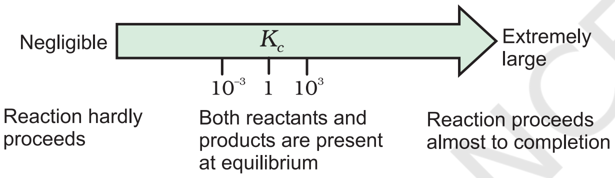


Fig.7.6 *Dependence of extent of reaction on* K_c

7.6.2 Predicting the Direction of the Reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient** ***Q***. The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values. For a general reaction:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \tag{7.19}$$

$$Q_c = [C]^c[D]^d / [A]^a[B]^b \tag{7.20}$$

Then,

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Consider the gaseous reaction of H_2 with I_2,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K_c = 57.0 \text{ at } 700\text{ K}.$$

Suppose we have molar concentrations $[H_2]_t$=0.10M, $[I_2]_t$ = 0.20 M and $[HI]_t$ = 0.40 M. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Thus, the reaction quotient, Q_c at this stage of the reaction is given by,

$$Q_c = [HI]_t^2 / [H_2]_t [I_2]_t = (0.40)^2 / (0.10)\times(0.20)$$
$$= 8.0$$

Now, in this case, Q_c (8.0) does not equal K_c (57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(g) and their concentrations will decrease till $Q_c = K_c$.

The reaction quotient, Q_c is useful in predicting the direction of reaction by comparing the values of Q_c and K_c.

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 7.7) :

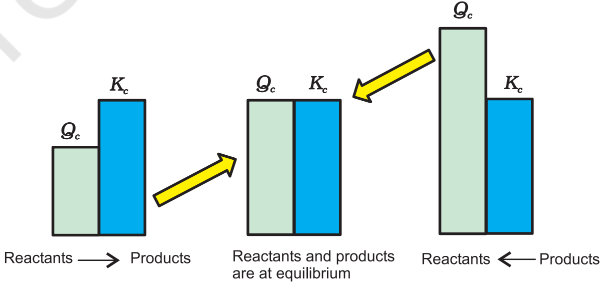


Fig. 7.7 *Predicting the direction of the reaction*

- If $Q_c < K_c$, net reaction goes from left to right
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs.

Problem 7.7

The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is [A] = [B] = [C] = 3×10^{-4} M. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Q_c is given by,

$Q_c = [B][C]/ [A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}M$

$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

7.6.3 Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) the initial concentration,
(b) the change in concentration on going to equilibrium, and
(c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

Problem 7.8

13.8g of N_2O_4 was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

The total pressure at equilbrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium.

Solution

We know $pV = nRT$

Total volume $(V) = 1$ L

Molecular mass of N_2O_4 = 92 g

Number of moles of the gas (n) = 13.8g/92 g = 0.15

Gas constant (R) = 0.083 bar L $mol^{-1}K^{-1}$

Temperature $(T) = 400$ K

$pV = nRT$

$p \times 1L = 0.15 \text{ mol} \times 0.083 \text{ bar L mol}^{-1}K^{-1} \times 400 \text{ K}$

$p = 4.98$ bar

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial pressure:	4.98 bar		0
At equilibrium:	(4.98 – x) bar		2x bar

Hence,

p_{total} at equilibrium $= p_{N_2O_4} + p_{NO_2}$

$9.15 = (4.98 - x) + 2x$

$9.15 = 4.98 + x$

$x = 9.15 - 4.98 = 4.17$ bar

Partial pressures at equilibrium are,

$p_{N_2O_4} = 4.98 - 4.17 = 0.81$bar

$p_{NO_2} = 2x = 2 \times 4.17 = 8.34$ bar

$$K_p = \left(p_{NO_2}\right)^2 / p_{N_2O_4}$$

$$= (8.34)^2/0.81 = 85.87$$

$K_p = K_c(RT)^{\Delta n}$

$85.87 = K_c(0.083 \times 400)^1$

$K_c = 2.586 = 2.6$

Problem 7.9

3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. $K_c = 1.80$

Solution

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial concentration:	3.0		0		0

Let x mol per litre of PCl_5 be dissociated,
At equilibrium:
(3-x) x x

$K_c = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/\ (3 - x)$

$x^2 + 1.8x - 5.4 = 0$

$x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2$

$x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [-1.8 \pm 4.98]/2$

$x = [-1.8 + 4.98]/2 = 1.59$

$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

7.7 RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT *K*, REACTION QUOTIENT *Q* AND GIBBS ENERGY *G*

The value of K_c for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit 6, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG. If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G^{\ominus} + RT \ln Q \qquad (7.21)$$

where, $G^{\ominus}$ is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (7.21) becomes,

$$\Delta G = \Delta G^{\ominus} + RT \ln K = 0$$

$$\Delta G^{\ominus} = -RT \ln K \qquad (7.22)$$

$$\ln K = -\Delta G^{\ominus} / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^{\ominus}/RT} \qquad (7.23)$$

Hence, using the equation (7.23), the reaction spontaneity can be interpreted in terms of the value of $\Delta G^{\ominus}$.

- If $\Delta G^{\ominus} < 0$, then $-\Delta G^{\ominus}/RT$ is positive, and $e^{-\Delta DG^{\ominus}/RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G^{\ominus} > 0$, then $-\Delta G^{\ominus}/RT$ is negative, and $e^{-\Delta G^{\ominus}/RT} < 1$, that is , $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Problem 7.10

The value of $\Delta G^{\ominus}$ for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.

Solution

$\Delta G^{\ominus}$ = 13.8 kJ/mol = 13.8×10^3 J/mol

Also, $\Delta G^{\ominus} = -RT \ln K_c$

Hence, $\ln K_c = -13.8 \times 10^3$ J/mol
(8.314 J $mol^{-1}K^{-1} \times 298$ K)

$\ln K_c = -5.569$

$K_c = e^{-5.569}$

$K_c = 3.81 \times 10^{-3}$

Problem 7.11

Hydrolysis of sucrose gives,

Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose

Equilibrium constant K_c for the reaction is 2×10^{13} at 300K. Calculate $\Delta G^{\ominus}$ at 300K.

Solution

$\Delta G^{\ominus} = -RT \ln K_c$

$\Delta G^{\ominus} = -8.314 \text{J mol}^{-1}\text{K}^{-1} \times$
$300\text{K} \times \ln(2 \times 10^{13})$

$\Delta G^{\ominus} = -7.64 \times 10^4$ J mol^{-1}

7.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilizers.

Equilibrium constant, K_c is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and *make a qualitative prediction* about the effect of a change in conditions on equilibrium we use ***Le Chatelier's principle***. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.** *This is applicable to all physical and chemical equilibria.*

We shall now be discussing factors which can influence the equilibrium.

7.8.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition/removal of any reactant/products, Le Chatelier's principle predicts that:

- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.

or in other words,

"*When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes*".

Let us take the reaction,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.7.8). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

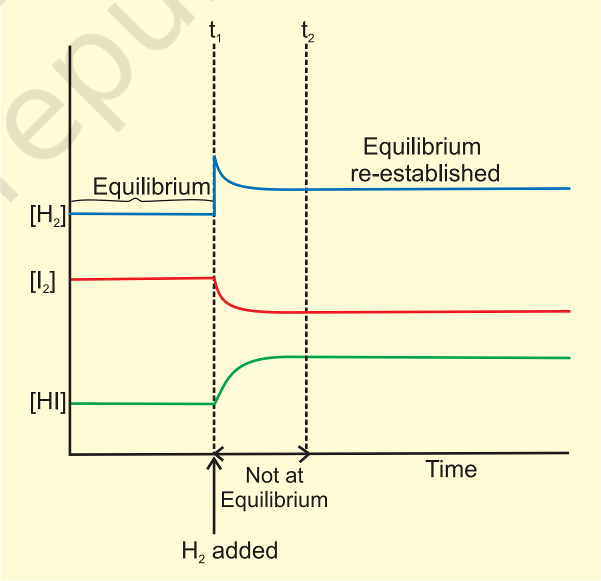


Fig. 7.8 *Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$*

The same point can be explained in terms of the reaction quotient, Q_c,

$Q_c = [HI]^2 / [H_2][I_2]$

Addition of hydrogen at equilibrium results in value of Q_c being less than K_c. Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

Effect of Concentration – An experiment

This can be demonstrated by the following reaction:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq) \qquad (7.24)$$

yellow colourless deep red

$$K_c = \frac{\left[Fe(SCN)^{2+}(aq)\right]}{\left[Fe^{3+}(aq)\right]\left[SCN^-(aq)\right]} \qquad (7.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocynate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^- ions. For example, oxalic acid ($H_2C_2O_4$), reacts with Fe^{3+} ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free $Fe^{3+}(aq)$. In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the Fe^{3+} ions. Because the concentration of $[Fe(SCN)]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aq. $HgCl_2$ also decreases red colour because Hg^{2+} reacts with SCN^- ions to form stable complex ion $[Hg(SCN)_4]^{2-}$. Removal of free SCN^- (aq) shifts the equilibrium in equation (7.24) from right to left to replenish SCN^- ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

7.8.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

Consider the reaction,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 + H_2O$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c. Let [CO], $[H_2]$, $[CH_4]$ and $[H_2O]$ be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

7.8.3 Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

7.8.4 Effect of Temperature Change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c. However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \ ;$$
$$\Delta H = -\ 92.38 \text{ kJ mol}^{-1}$$

is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

Effect of Temperature – An experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas (brown in colour) which dimerises into N_2O_4 gas (colourless).

$$2NO_2(g) \rightleftharpoons N_2O_4(g);\ \Delta H = -57.2 \text{ kJ mol}^{-1}$$

NO_2 gas prepared by addition of Cu turnings to conc. HNO_3 is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 7.9). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases. While in beaker 3, high temperature favours the reverse reaction of

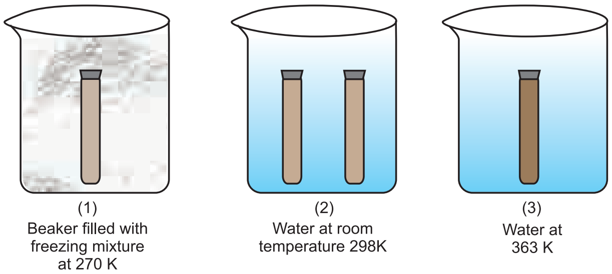


Fig. 7.9 *Effect of temperature on equilibrium for the reaction,* $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$

formation of NO_2 and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction,

$$[Co(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

pink colourless blue

At room temperature, the equilibrium mixture is blue due to $[CoCl_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[Co(H_2O)_6]^{3+}$.

7.8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500 °C and 200 atm.

Similarly, in manufacture of sulphuric acid by *contact process*,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ K_c = 1.7 \times 10^{26}$$

though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K, a catalyst would be of little help.

7.9 IONIC EQUILIBRIUM IN SOLUTION

Under the effect of change of concentration on the direction of equilibrium, you have incidently come across with the following equilibrium which involves ions:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other do not and are thus, referred to as *non-electrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

7.10 ACIDS, BASES AND SALTS

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "*acidus*" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.7.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules.

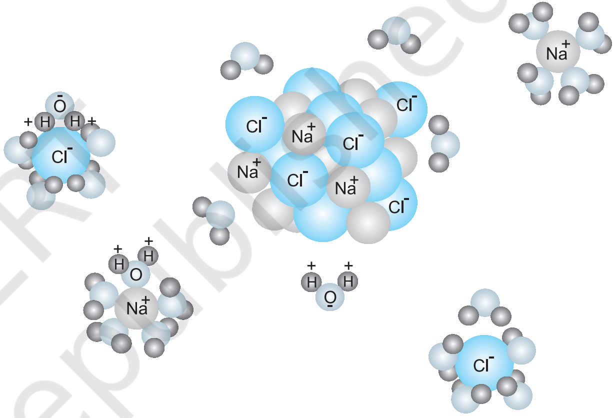
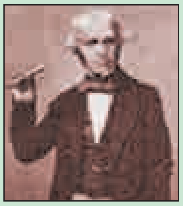


Fig.7.10 *Dissolution of sodium chloride in water. Na^+ and Cl^- ions are stablised by their hydration with polar water molecules.*

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent



Michael Faraday (1791–1867)

Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-4, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry. Faraday's first important work was on analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834. Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers.

molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

7.10.1 Arrhenius Concept of Acids and Bases

According to Arrhenius theory, *acids are substances that dissociates in water to give hydrogen ions* $H^+(aq)$ *and bases are substances that produce hydroxyl ions* $OH^-(aq)$. The ionization of an acid HX (aq) can be represented by the following equations:

$$HX\,(aq) \rightarrow H^+(aq) + X^-(aq)$$

or

$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$

A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal* **hydronium ion**, H_3O^+ $\{[H\,(H_2O)]^+\}$ (see box). In this chapter we shall use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to mean the same i.e., a hydrated proton.

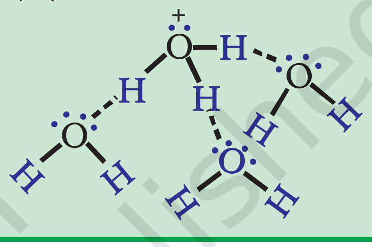
Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$$

The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

Hydronium and Hydroxyl Ions

Hydrogen ion by itself is a bare proton with very small size (~10^{-15} m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.

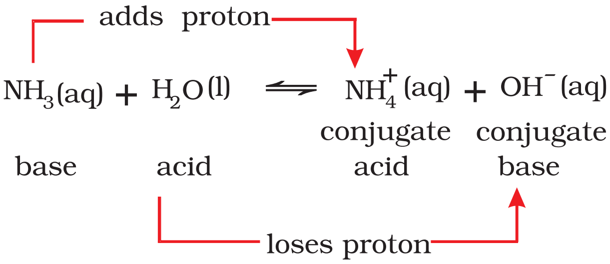


$H_9O_4^+$

7.10.2 The Brönsted-Lowry Acids and Bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion* H^+ *and bases are substances capable of accepting a hydrogen ion,* H^+. In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and

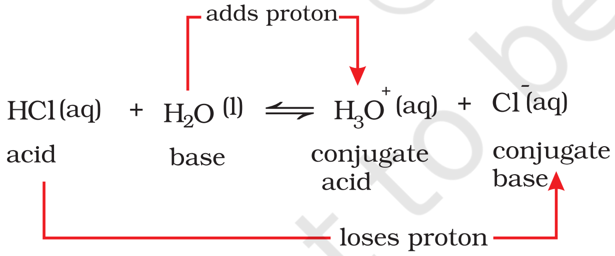
Svante Arrhenius
(1859-1927)

Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Brönsted acid is a strong acid then **its conjugate base is a weak base and *vice-versa.*** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Problem 7.12

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^-?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

Problem 7.13

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Problem 7.14

The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Solution

The answer is given in the following Table:

Species	**Conjugate acid**	**Conjugate base**
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

7.10.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an *acid as a species which accepts electron pair and base which donates an electron pair*. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3.

BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

Problem 7.15

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^- (b) F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:OH^-$).

(b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

7.11 IONIZATION OF ACIDS AND BASES

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^-. According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{A^-(aq)}$$

In section 7.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases.** Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl, Br^-, I^-, NO_3^- and HSO_4^-, which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.

Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

$HIn(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$In^-(aq)$
acid indicator colour A				conjugate acid		conjugate base colourB

Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

7.11.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 7.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

$H_2O(l)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$OH^-(aq)$
acid		base		conjugate acid		conjugate base

The dissociation constant is represented by,

$$K = [H_3O^+]\,[OH^-] \,/\, [H_2O] \qquad (7.26)$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[H_2O]$ is incorporated within the equilibrium constant to give a new constant, K_w, which is called the **ionic product of water**.

$$K_w = [H^+][OH^-] \qquad (7.27)$$

The concentration of H^+ has been found out experimentally as 1.0×10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH^- ions, the concentration of hydroxyl ions, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M. Thus, the value of K_w at 298K,

$$K_w = [H_3O^+][OH^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14}\ M^2 \qquad (7.28)$$

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as,

$$[H_2O] = (1000\ g\ /L)(1\ mol/18.0\ g) = 55.55\ M.$$

Therefore, the ratio of dissociated water to that of undissociated water can be given as:

$10^{-7} / (55.55) = 1.8 \times 10^{-9}$ or ~ 2 in 10^{-9} (thus, equilibrium lies mainly towards undissociated water)

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

7.11.2 The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity $\left(a_{H^+}\right)$ of hydrogen ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[H^+]$. It should be noted that activity has no units and is defined as:

$$= [H^+] / \text{mol L}^{-1}$$

From the definition of pH, the following can be written,

$$pH = -\log a_{H+} = -\log \{[H^+] / \text{mol L}^{-1}\}$$

Thus, an acidic solution of HCl (10^{-2} M) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH^-] = 10^{-4}$ M and $[H_3O^+] = 10^{-10}$ M will have a pH = 10. At 25 °C, pure water has a concentration of hydrogen ions, $[H^+] = 10^{-7}$ M. Hence, the pH of pure water is given as:

$$pH = -\log(10^{-7}) = 7$$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ M, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ M. thus, we can summarise that

Acidic solution has pH < 7
Basic solution has pH > 7
Neutral solution has pH = 7

Now again, consider the equation (7.28) at 298 K

$$K_w = [H_3O^+]\,[OH^-] = 10^{-14}$$

Taking negative logarithm on both sides of equation, we obtain

$$-\log K_w = -\log \{[H_3O^+]\,[OH^-]\}$$
$$= -\log [H_3O^+] - \log [OH^-]$$
$$= -\log 10^{-14}$$

$$pK_w = pH + pOH = 14 \qquad (7.29)$$

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 7.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.

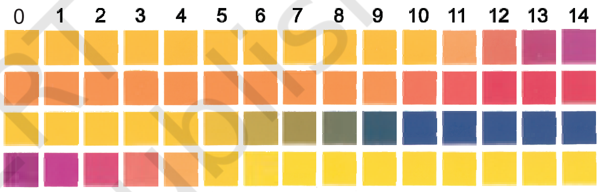


Fig.7.11 pH-*paper with four strips that may have different colours at the same* pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 7.5 (page 212).

Problem 7.16

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. what is its pH ?

Solution

$$pH = -\log[3.8 \times 10^{-3}]$$
$$= -\{\log[3.8] + \log[10^{-3}]\}$$
$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Problem 7.17

Calculate pH of a 1.0×10^{-8} M solution of HCl.

Table 7.5 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~–1.0
Human Saliva	6.4		

Solution

$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-(aq)$

$K_w = [OH^-][H_3O^+]$

$= 10^{-14}$

Let, $x = [OH^-] = [H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + Cl^-(aq)$,

and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{-8} + x$

$K_w = (10^{-8} + x)(x) = 10^{-14}$

or $x^2 + 10^{-8}\,x - 10^{-14} = 0$

$[OH^-] = x = 9.5 \times 10^{-8}$

So, pOH = 7.02 and pH = 6.98

7.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$

Initial
concentration (M)
c 0 0
Let α be the extent of ionization
Change (M)
-cα +cα +cα
Equilibrium concentration (M)
c-cα cα cα

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

$K_a = c^2\alpha^2 / c(1\text{-}\alpha) = c\alpha^2 / 1\text{-}\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$$K_a = [H^+][X^-] / [HX] \qquad (7.30)$$

At a given temperature *T*, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

The values of the ionization constants of some selected weak acids are given in Table 7.6.

Table 7.6 The Ionization Constants of Some Selected Weak Acids (at 298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HCIO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w, it has been extended to other species and quantities. Thus, we have:

$$pK_a = -\log(K_a) \qquad (7.31)$$

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate pH = $-\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.

Problem 7.18

The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

$$K_a = 3.2 \times 10^{-4}$$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K_w = 1.0 \times 10^{-14}$$

As $K_a >> K_w$, [1] is the principle reaction.

	HF +	H_2O ⇌	H_3O^+ +	F^-
Initial concentration (M)	0.02		0	0
Change (M)	−0.02α		+0.02α	+0.02α
Equilibrium concentration (M)	0.02 – 0.02 α		0.02 α	0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha)$

$= 0.02\,\alpha^2 / (1 - \alpha) = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

α = + 0.12 and – 0.12

The negative root is not acceptable and hence,

α = 0.12

This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12$

$= 2.4 \times 10^{-3}$ M

$[HF] = c(1 - \alpha) = 0.02\ (1 - 0.12)$

$= 17.6 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 7.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+,

A^- and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

$$pH = -\log [H^+]$$

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$$= 3.16 \times 10^{-5}$$

$[H^+] = [A^-] = 3.16 \times 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \simeq 0.1$

$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = -\log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$= [HA]_{dissociated}/[HA]_{initial} \times 100\%$ (7.32)

Problem 7.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)

0.08 0 0

Change to reach equilibrium concentration (M)

$-x$ $+x$ $+x$

equilibrium concentartion (M)

$0.08 - x$ x x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$= x^2 / (0.08 - x)$

As $x << 0.08$, therefore $0.08 - x \simeq 0.08$

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$

$[H^+] = 1.41 \times 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} / [HOCl]_{initial}\} \times 100$

$= 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76$ %.

$pH = -\log(1.41 \times 10^{-3}) = 2.85.$

7.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$$

In a weak base there is partial ionization of MOH into M^+ and OH^-, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$K_b = [M^+][OH^-] / [MOH]$ (7.33)

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$K_b = (c\alpha)^2 / c(1-\alpha) = c\alpha^2 / (1-\alpha)$

The values of the ionization constants of some selected weak bases, K_b are given in Table 7.7.

Table 7.7 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	1.3×10^{-14}

Many organic compounds like *amines* are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and nicotine all behave as very weak bases due to their very small K_b. Ammonia produces OH^- in aqueous solution:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The pH scale for the hydrogen ion concentration has been extended to get:

$$pK_b = -\log(K_b) \qquad (7.34)$$

Problem 7.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+] = \text{antilog}(-pH)$

$= \text{antilog}(-9.7) = 1.67 \times 10^{-10}$

$[OH^-] = K_w / [H^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10}$
$= 5.98 \times 10^{-5}$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

$= (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$

$pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04.$

Problem 7.22

Calculate the pH of the solution in which 0.2M NH_4Cl and 0.1M NH_3 are present. The pK_b of ammonia solution is 4.75.

Solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The ionization constant of NH_3,

$K_b = \text{antilog}(-pK_b)$ i.e.

$K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Initial concentration (M)

0.10 0.20 0

Change to reach equilibrium (M)

$-x$ $+x$ $+x$

At equilibrium (M)

$0.10 - x$ $0.20 + x$ x

$K_b = [NH_4^+][OH^-] / [NH_3]$

$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$

As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

$[OH^-] = x = 0.88 \times 10^{-5}$

Therefore, $[H^+] = 1.12 \times 10^{-9}$

$pH = -\log[H^+] = 8.95.$

7.11.5 Relation between K_a and K_b

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3 we see,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$$

$$\text{Net: } 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M$$

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

$$K_a \times K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \times \{[NH_4^+][OH^-] / [NH_3]\}$$

$$= [H_3O^+][OH^-] = K_w$$

$$= (5.6\text{x}10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}\ M$$

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**

$$K_{NET} = K_1 \times K_2 \times \ldots\ldots \qquad (3.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \qquad (7.36)$$

Knowing one, the other can be obtained. It should be noted that a *strong acid will have a weak conjugate base and vice-versa.*

Alternatively, the above expression $K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = [BH^+][OH^-] / [B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$$K_b = [BH^+][OH^-][H^+] / [B][H^+]$$

$$=\{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\}$$

$$= K_w / K_a$$

$$\text{or } K_a \times K_b = K_w$$

It may be noted that if we take negative logarithm of both sides of the equation, then p*K* values of the conjugate acid and base are related to each other by the equation:

$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

Problem 7.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

We use equation (7.33) to calculate hydroxyl ion concentration,

$$[OH^-] = c\,\alpha = 0.05\,\alpha$$

$$K_b = 0.05\,\alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$K_b = c\,\alpha^2 \text{ or } \alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$$

$$= 0.018.$$

$$[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4}\text{M}.$$

$$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4})$$

$$= 1.06 \times 10^{-11}$$

$$pH = -\log(1.06 \times 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \times K_b = K_w$$

using the value of K_b of NH_3 from Table 7.7.

We can determine the concentration of conjugate acid NH_4^+

$$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$$

$$= 5.64 \times 10^{-10}.$$

7.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$$

$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$$

And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[H^+][HX^-]\} / [H_2X] \text{ and}$$

$K_{a_2} = \{[H^+][X^{2-}]\} / [HX^-]$

Here, K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H_2X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 7.8.

Table 7.8 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionization constant (K_{a_1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-. Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-} anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A, and H_3O^+ in the solution comes mainly from the first dissociation step.

7.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

$$\xrightarrow{\text{Size increases}}$$
$$HF << HCl << HBr << HI$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

Similarly, H_2S is stronger acid than H_2O.

But, when we discuss elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

$$\xrightarrow{\text{Electronegativity of A increases}}$$
$$CH_4 < NH_3 < H_2O < HF$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

7.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$\text{or}\quad HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$

$$K_a = [H^+][Ac^-] / [HAc]$$

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of

common ion effect. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$

Initial concentration (M)

0.05 0 0.05

Let x be the extent of ionization of acetic acid.

Change in concentration (M)

–x +x +x

Equilibrium concentration (M)

0.05-x x 0.05+x

Therefore,

$K_a = [H^+][Ac^-]/[H\,Ac] = \{(0.05+x)(x)\}/(0.05-x)$

As K_a is small for a very weak acid, $x \ll 0.05$.

Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

$1.8 \times 10^{-5} = (x)\,(0.05 + x)\;/\;(0.05 - x)$

$= x(0.05)\;/\;(0.05) = x = [H^+] = 1.8 \times 10^{-5}M$

$pH = -\log(1.8 \times 10^{-5}) = 4.74$

Problem 7.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Solution

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$K_b = [NH_4^+][OH^-]\;/\;[NH_3] = 1.77 \times 10^{-5}$$

Before neutralization,

$[NH_4^+] = [OH^-] = x$

$[NH_3] = 0.10 - x \simeq 0.10$

$x^2\;/\;0.10 = 1.77 \times 10^{-5}$

Thus, $x = 1.33 \times 10^{-3} = [OH^-]$

Therefore, $[H^+] = K_w\;/\;[OH^-] = 10^{-14}\;/\;(1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$

$pH = -\log(7.5 \times 10^{-12}) = 11.12$

On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

2.5 2.5 0 0

At equilibrium

0 0 2.5 2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of uneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

0.033M – y y y

where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$[NH_4^+] = 0.033 + y$

As y is small, $[NH_4OH] \simeq 0.033$ M and $[NH_4^+] \simeq 0.033M$.

We know,

$K_b = [NH_4^+][OH^-]\;/\;[NH_4OH]$

$= y(0.033)/(0.033) = 1.77 \times 10^{-5}$ M

Thus, $y = 1.77 \times 10^{-5} = [OH^-]$

$[H^+] = 10^{-14}\;/\;1.77 \times 10^{-5} = 0.56 \times 10^{-9}$

Hence, pH = 9.24

7.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^-, Br^-, NO_3^-, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i) salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+(aq) + H_2O(1) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increased of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

CH_3COOH and NH_4OH, also remain into partially dissociated form:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their p*K* values:

$$pH = 7 + ½ (pK_a - pK_b) \qquad (7.38)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 7.25

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$$pH = 7 + ½ [pK_a - pK_b]$$
$$= 7 + ½ [4.76 - 4.75]$$
$$= 7 + ½ [0.01] = 7 + 0.005 = 7.005$$

7.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

7.12.1 Designing Buffer Solution

Knowledge of pK_a, pK_b and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, K_a of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water,

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

For which we can write the expression

$$K_a = \frac{[\text{H}_3\text{O}^+]\,[\text{A}^-]}{[\text{HA}]}$$

Rearranging the expression we have,

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking logarithm on both the sides and rearranging the terms we get —

$$\text{p}K_a = \text{pH} - \log\frac{[\text{A}^-]}{[\text{HA}]}$$

Or

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]} \qquad (7.39)$$

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Conjugate base, A}^-]}{[\text{Acid, HA}]} \qquad (7.40)$$

The expression (7.40) is known as **Henderson–Hasselbalch equation.** The quantity $\frac{[\text{A}^-]}{[\text{HA}]}$ is the ratio of concentration of conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A$^-$], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (7.40) takes the form:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

In the equation (7.39), if the concentration of [A$^-$] is equal to the concentration of [HA], then pH = pK_a because value of log 1 is zero. Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the pK_a of the acid. So for preparing the buffer solution of the required pH we select that acid whose pK_a is close to the required pH. For acetic acid pK_a value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]} \qquad (7.41)$$

pH of the buffer solution can be calculated by using the equation pH + pOH = 14.

We know that pH + pOH = pK_w and pK_a + pK_b = pK_w. On putting these values in equation (7.41) it takes the form as follows:

$$\text{p}K_w - \text{pH} = \text{p}K_w - \text{p}K_a + \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

or

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]} \qquad (7.42)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as pK_a for the base. pK_a value for ammonia is 9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (7.42) becomes:

$$\mathrm{pH} = 9.25 + \log \frac{[\text{Conjugate acid}, \mathrm{BH}^+]}{[\text{Base}, \mathrm{B}]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule , for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

7.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation:

$$\mathrm{BaSO_4(s)} \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} \mathrm{Ba^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)},$$

The equilibrium constant is given by the equation:

$$K = \{[\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]\} / [\mathrm{BaSO_4}]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[\mathrm{BaSO_4}] = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}] \qquad (7.43)$$

We call K_{sp} the *solubility product constant* or simply *solubility product*. The experimental value of K_{sp} in above equation at 298K is 1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then

$1.1 \times 10^{-10} = (\mathrm{S})(\mathrm{S}) = \mathrm{S}^2$

or $\qquad \mathrm{S} = 1.05 \times 10^{-5}$.

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol $\mathrm{L^{-1}}$.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula $(\mathrm{Zr^{4+}})_3(\mathrm{PO_4}^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$[\mathrm{Zr^{4+}}] = 3\mathrm{S}$ and $[\mathrm{PO_4^{3-}}] = 4\mathrm{S}$

and $K_{sp} = (3\mathrm{S})^3 (4\mathrm{S})^4 = 6912\ (\mathrm{S})^7$

or $\mathrm{S} = \{K_{sp} / (3^3 \times 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$

A solid salt of the general formula $M_x^{p+} X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$$M_xX_y(s) \rightleftharpoons xM^{p+}(aq) + yX^{q-}\ (aq)$$

(where $x \times p^+ = y \times q^-$)

And its solubility product constant is given by:

$$K_{sp} = [M^{p+}]^x[X^{q-}]^y = (xS)^x(yS)^y \qquad (7.44)$$

$$= x^x \,.\, y^y \,.\, S^{(x+y)}$$

$$S^{(x+y)} = K_{sp} \,/\, x^x \,.\, y^y$$

$$S = (K_{sp} \,/\, x^x \,.\, y^y)^{1\,/\,x+y} \qquad (7.45)$$

The term K_{sp} in equation is given by Q_{sp} (section 7.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 7.9.

Problem 7.26

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.

Solution

$A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = [A^{3+}]^2\ [X^{2-}]^3 = 1.1 \times 10^{-23}$

If S = solubility of A_2X_3, then

$[A^{3+}] = 2S;\ \ [X^{2-}] = 3S$

therefore, $K_{sp} = (2S)^2(3S)^3 = 108S^5$

$= 1.1 \times 10^{-23}$

thus, $S^5 = 1 \times 10^{-25}$

$S = 1.0 \times 10^{-5}$ mol/L.

Problem 7.27

The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×0^{-17} respectively. Which salt is more soluble? Explain.

Solution

$AgCN \rightleftharpoons Ag^+ + CN^-$

Table 7.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

Name of the Salt	Formula	K_{sp}
Silver Bromide	$AgBr$	5.0×10^{-13}
Silver Carbonate	Ag_2CO_3	8.1×10^{-12}
Silver Chromate	Ag_2CrO_4	1.1×10^{-12}
Silver Chloride	$AgCl$	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium Hydroxide	$Al(OH)_3$	1.3×10^{-33}
Barium Chromate	$BaCrO_4$	1.2×10^{-10}
Barium Fluoride	BaF_2	1.0×10^{-6}
Barium Sulphate	$BaSO_4$	1.1×10^{-10}
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}
Calcium Fluoride	CaF_2	5.3×10^{-9}
Calcium Hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium Oxalate	CaC_2O_4	4.0×10^{-9}
Calcium Sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium Hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous Bromide	$CuBr$	5.3×10^{-9}
Cupric Carbonate	$CuCO_3$	1.4×10^{-10}
Cuprous Chloride	$CuCl$	1.7×10^{-6}
Cupric Hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	$FeCO_3$	3.2×10^{-11}
Ferrous Hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric Hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous Chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous Iodide	Hg_2I_2	4.5×10^{-29}
Mercurous Sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium Fluoride	MgF_2	6.5×10^{-9}
Magnesium Hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Magnesium Oxalate	MgC_2O_4	7.0×10^{-7}
Manganese Carbonate	$MnCO_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	$PbBr_2$	4.0×10^{-5}
Lead Carbonate	$PbCO_3$	7.4×10^{-14}
Lead Chloride	$PbCl_2$	1.6×10^{-5}
Lead Fluoride	PbF_2	7.7×10^{-8}
Lead Hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead Iodide	PbI_2	7.1×10^{-9}
Lead Sulphate	$PbSO_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	$Sn(OH)_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	$SrCO_3$	1.1×10^{-10}
Strontium Fluoride	SrF_2	2.5×10^{-9}
Strontium Sulphate	$SrSO_4$	3.2×10^{-7}
Thallous Bromide	$TlBr$	3.4×10^{-6}
Thallous Chloride	$TlCl$	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	$ZnCO_3$	1.4×10^{-11}
Zinc Hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1^{\,2} = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)(2S_2)^2 = 2 \times 10^{-15}$, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

7.13.2 Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$. This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp}. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.

Problem 7.28

Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

Solution

Let the solubility of $Ni(OH)_2$ be equal to S.

Dissolution of S mol/L of $Ni(OH)_2$ provides S mol/L of Ni^{2+} and 2S mol/L of OH^-, but the total concentration of $OH^- = (0.10 + 2S)$ mol/L because the solution already contains 0.10 mol/L of OH^- from NaOH.

$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}]\,[OH^-]^2$

$= (S)\,(0.10 + 2S)^2$

As K_{sp} is small, $2S << 0.10$,

thus, $(0.10 + 2S) \approx 0.10$

Hence,

$2.0 \times 10^{-15} = S\,(0.10)^2$

$S = 2.0 \times 10^{-13}\ M = [Ni^{2+}]$

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously i.e.,

$K_{sp} = [M^+]\,[X^-]$,

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq);$$

$$K_a = \frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]}$$

$[X^-] / [HX] = K_a / [H^+]$

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [X^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

Now, again taking inverse, we get

$[X^-] / \{[X^-] + [HX]\} = f = K_a / (K_a + [H^+])$ and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

$K_{sp} = [S]\,[f\,S] = S^2\,\{K_a / (K_a + [H^+])\}$ and

$S = \{K_{sp}\,([H^+] + K_a) / K_a\}^{1/2}$ (7.46)

Thus solubility S increases with increase in $[H^+]$ or decrease in pH.

SUMMARY

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. **Equilibrium constant**, K_c is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient.

$$\text{For reaction, a A + b B} \rightleftharpoons \text{c C +d D}$$
$$K_c = [C]^c[D]^d/[A]^a[B]^b$$

Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as K_p and is written by replacing concentration terms by partial pressures in K_c expression. The direction of reaction can be predicted by reaction quotient Q_c which is equal to K_c at equilibrium. **Le Chatelier's principle** states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. **Catalyst** does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.

All substances that conduct electricity in aqueous solutions are called **electrolytes**. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the **dissociation or ionization of electrolytes** in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to **Arrhenius, acids** give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. **Brönsted-Lowry** on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a **conjugate pair of acid-base** differs only by one proton. **Lewis** further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion are discussed. The **pH scale** (pH = $-\log[H^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities (pOH = $-\log[OH^-]$) ; pK_a = $-\log[K_a]$; pK_b = $-\log[K_b]$; and pK_w = $-\log[K_w]$ etc.). The ionization of water has been considered and we note that the equation: pH + pOH = pK_w is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution.The definition of **buffer solutions**, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as **solubility product constant** (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.

SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT

(a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.
(b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases.
(c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper.
(d) They may be provided with different indicators to observe their colours in solutions of varying pH.
(e) They may perform some acid-base titrations using indicators.
(f) They may observe common ion effect on the solubility of sparingly soluble salts.
(g) If pH meter is available in their school, they may measure the pH with it and compare the results obtained with that of the pH paper.

EXERCISES

7.1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

a) What is the initial effect of the change on vapour pressure?

b) How do rates of evaporation and condensation change initially?

c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

7.2 What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]= 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90M$?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

7.3 At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms

$$I_2\,(g) \rightleftharpoons 2I\,(g)$$

Calculate K_p for the equilibrium.

7.4 Write the expression for the equilibrium constant, K_c for each of the following reactions:

(i) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$

(ii) $2Cu(NO_3)_2\,(s) \rightleftharpoons 2CuO\,(s) + 4NO_2\,(g) + O_2\,(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH\,(aq) + C_2H_5OH\,(aq)$

(iv) $Fe^{3+}\,(aq) + 3OH^-\,(aq) \rightleftharpoons Fe(OH)_3\,(s)$

(v) $I_2\,(s) + 5F_2 \rightleftharpoons 2IF_5$

7.5 Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$; $K_p= 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_p= 167$ at 1073 K

7.6 For the following equilibrium, $K_c= 6.3 \times 10^{14}$ at 1000 K

$NO\,(g) + O_3\,(g) \rightleftharpoons NO_2\,(g) + O_2\,(g)$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

7.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

7.8 Reaction between N_2 and O_{2-} takes place as follows:

$$2N_2\ (g) + O_2\ (g) \rightleftharpoons 2N_2O\ (g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

7.9 Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO\ (g) + Br_2\ (g) \rightleftharpoons 2NOBr\ (g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2 .

7.10 At 450K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3\ (g)$$

What is K_c at this temperature ?

7.11 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium ?

$$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$

7.12 A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

7.13 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4\,[O_2]^5}{[NO]^4\,[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

7.14 One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O\ (g) + CO\ (g) \rightleftharpoons H_2\ (g) + CO_2\ (g)$$

Calculate the equilibrium constant for the reaction.

7.15 At 700 K, equilibrium constant for the reaction:

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of H_2(g) and I_2(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

7.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$2ICl\ (g) \rightleftharpoons I_2\ (g) + Cl_2\ (g);\quad K_c = 0.14$

7.17 K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6\ (g) \rightleftharpoons C_2H_4\ (g) + H_2\ (g)$$

7.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

7.19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g)\ +\ Cl_2(g)$$

7.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO\ (s) + CO\ (g) \rightleftharpoons Fe\ (s) + CO_2\ (g)$; $K_p = 0.265$ atm at 1050K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: $p_{CO} = 1.4$ atm and = 0.80 atm?

7.21 Equilibrium constant, K_c for the reaction

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \text{ at 500 K is 0.061}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

7.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl\ (g) \rightleftharpoons Br_2\ (g) + Cl_2\ (g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

7.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with soild carbon has 90.55% CO by mass

$$C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g)$$

Calculate K_c for this reaction at the above temperature.

7.24 Calculate a) $\Delta G^\ominus$ and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

$$NO\ (g) + ½\ O_2\ (g) \rightleftharpoons NO_2\ (g)$$

where

$\Delta_f G^\ominus (NO_2) = 52.0$ kJ/mol

$\Delta_f G^\ominus (NO) = 87.0$ kJ/mol

$\Delta_f G^\ominus (O_2) = 0$ kJ/mol

7.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

(b) $CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s)$

(c) $3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

7.26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(i) $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

(ii) $CH_4\ (g) + 2S_2\ (g) \rightleftharpoons CS_2\ (g) + 2H_2S\ (g)$

(iii) $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

(iv) $2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)$

(v) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

(vi) $4\ NH_3\ (g) + 5O_2\ (g) \rightleftharpoons 4NO\ (g) + 6H_2O(g)$

7.27 The equilibrium constant for the following reaction is 1.6×10^5 at 1024K

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

7.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$CH_4\ (g) + H_2O\ (g) \rightleftharpoons CO\ (g) + 3H_2\ (g)$

(a) Write as expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

(i) increasing the pressure

(ii) increasing the temperature

(iii) using a catalyst ?

7.29 Describe the effect of :

a) addition of H_2
b) addition of CH_3OH
c) removal of CO
d) removal of CH_3OH

on the equilibrium of the reaction:

$$2H_2(g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)$$

7.30 At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g) \qquad \Delta_r H^\ominus = 124.0\ kJ\ mol^{-1}$

a) write an expression for K_c for the reaction.

b) what is the value of K_c for the reverse reaction at the same temperature ?

c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

7.31 Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

If a reaction vessel at 400 °C is charged with an equimolar mixture of CO and steam such that $p_{co} = p_{H_2O}$ = 4.0 bar, what will be the partial pressure of H_2 at equilibrium? K_p= 10.1 at 400°C

7.32 Predict which of the following reaction will have appreciable concentration of reactants and products:

a) Cl_2 (g) $\rightleftharpoons$ 2Cl (g) $K_c = 5 \times 10^{-39}$

b) Cl_2 (g) + 2NO (g) $\rightleftharpoons$ 2NOCl (g) $K_c = 3.7 \times 10^{8}$

c) Cl_2 (g) + $2NO_2$ (g) $\rightleftharpoons$ $2NO_2Cl$ (g) $K_c = 1.8$

7.33 The value of K_c for the reaction $3O_2$ (g) $\rightleftharpoons$ $2O_3$ (g) is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

7.34 The reaction, CO(g) + $3H_2$(g) $\rightleftharpoons$ CH_4(g) + H_2O(g)

is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

7.35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}

7.36 Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+

7.37 What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3^-?

7.38 Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

7.39 The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

7.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3 .

7.41 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. what is its pH?

7.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

7.43 The ionization constant of HF, HCOOH and HCN at 298K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

7.44 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

7.45 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1M solution. How will this concentration be affected if the solution is 0.1M in HCl also ? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

7.46 The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

7.47 It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

7.48 Assuming complete dissociation, calculate the pH of the following solutions:
(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

7.49 Calculate the pH of the following solutions:
a) 2 g of TlOH dissolved in water to give 2 litre of solution.
b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.
c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

7.50 The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

7.51 The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

7.52 What is the pH of 0.001M aniline solution ? The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

7.53 Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl ?

7.54 The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH?

7.55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:
(a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2
(c) Human blood, 7.38 (d) Human saliva, 6.4.

7.56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

7.57 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

7.58 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

7.59 The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

7.60 The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

7.61 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

7.62 A 0.02M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

7.63 Predict if the solutions of the following salts are neutral, acidic or basic:
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

7.64 The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

7.65 Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

7.66 Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

7.67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9. Determine also the molarities of individual ions.

7.68 The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

7.69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

7.70 The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

7.71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

7.72 What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

7.73 The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

Appendix I

Definitions of the SI Base Units

Metre (m): The metre is the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second (17th CGPM, 1983).

Kilogram (kg): The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram (3rd CGPM, 1901).

Second (s): The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom (13th CGPM, 1967).

Ampere (A): The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} Newton per metre of length (9th CGPM, 1948).

Kelvin (K): The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water (13th CGPM, 1967).

Mole (mol): The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles (14th CGPM, 1971).

Candela (cd): The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of (1/683) watt per steradian (16th CGPM, 1979).

(The symbols listed here are internationally agreed and should not be changed in other languages or scripts).

Appendix II

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

Appendix III

A. Specific and Molar Heat Capacities for Some Substances at 298 K and one Atmospheric Pressure

Substance	Specific Heat Capacity (J/g)	Molar Heat Capacity (J/mol)
air	0.720	20.8
water (liquid)	4.184	75.4
ammonia (gas)	2.06	35.1
hydrogen chloride	0.797	29.1
hydrogen bromide	0.360	29.1
ammonia (liquid)	4.70	79.9
ethyl alcohol (liquid)	2.46	113.16
ethylene glycol (liquid)	2.42	152.52
water (solid)	2.06	37.08
carbon tetrachloride (liquid)	0.861	132.59
chlorofluorocarbon (CCl_2F_2)	0.5980	72.35
ozone	0.817	39.2
neon	1.03	20.7
chlorine	0.477	33.8
bromine	0.473	75.6
iron	0.460	25.1
copper	0.385	24.7
aluminium	0.902	24.35
gold	0.128	25.2
graphite	0.720	8.65

B. Molar Heat Capacities for Some Gases (J/mol)

Gas	C_p	C_v	$C_p - C_v$	C_p / C_v
Monatomic*				
helium	20.9	12.8	8.28	1.63
argon	20.8	12.5	8.33	1.66
iodine	20.9	12.6	8.37	1.66
mercury	20.8	12.5	8.33	1.66
Diatomic†				
hydrogen	28.6	20.2	8.33	1.41
oxygen	29.1	20.8	8.33	1.39
nitrogen	29.0	20.7	8.30	1.40
hydrogen chloride	29.6	21.0	8.60	1.39
carbon monoxide	29.0	21.0	8.00	1.41
Triatomic†				
nitrous oxide	39.0	30.5	8.50	1.28
carbon dioxide	37.5	29.0	8.50	1.29
Polyatomic†				
ethane	53.2	44.6	8.60	1.19

*Translational kinetic energy only.
†Translational, vibrational and rotational energy.

Appendix IV

Physical Constants

Quantity	Symbol	Traditional Units	SI Units
Acceleration of gravity	g	980.6 cm/s	9.806 m/s
Atomic mass unit (1/12 the mass of ^{12}C atom)	amu or u	1.6606×10^{-24} g	1.6606×10^{-27} kg
Avogadro constant	N_A	6.022×10^{23} particles/mol	6.022×10^{23} particles/mol
Bohr radius	a_o	0.52918 Å 5.2918×10^{-9} cm	5.2918×10^{-11} m
Boltzmann constant	k	1.3807×10^{-16} erg/K	1.3807×10^{-23} J/K
Charge-to-mass ratio of electron	e/m	1.758820×10^{8} coulomb/g	1.7588×10^{11} C/kg
Electronic charge	e	1.602176×10^{-19} coulomb 4.8033×10^{-19} esu	1.60219×10^{-19} C
Electron rest mass	m_e	9.109382×10^{-28} g 0.00054859 u	9.10952×10^{-31} kg
Faraday constant	F	96,487 coulombs/eq 23.06 kcal/volt. eq	96,487 C/mol e^- 96,487 J/V.mol e^-
Gas constant	R	$0.8206 \frac{\text{L atm}}{\text{mol K}}$ $1.987 \frac{\text{cal}}{\text{mol K}}$	$8.3145 \frac{\text{kPa dm}^3}{\text{mol K}}$ 8.3145 J/mol.K
Molar volume (STP)	V_m	22.710981 L/mol	22.710981×10^{-3} m^3/mol 22.710981 dm^3/mol
Neutron rest mass	m_n	1.674927×10^{-24} g 1.008665 u	1.67495×10^{-27} kg
Planck constant	h	6.6262×10^{-27} ergs	6.6262×10^{-34} J s
Proton rest mass	m_p	$1.6726216 \times 10^{-24}$ g 1.007277 u	1.6726×10^{-27} kg
Rydberg constant	R_∞	3.289×10^{15} cycles/s 2.1799×10^{-11} erg	1.0974×10^{7} m^{-1} 2.1799×10^{-18} J
Speed of light (in a vacuum)	c	2.9979×10^{10} cm/s (186,281 miles/second)	2.9979×10^{8} m/s

$\pi = 3.1416$ $\quad$ $2.303\,R = 4.576$ cal/mol K = 19.15 J/mol K

$e = 2.71828$ $\quad$ $2.303\,RT$ (at 25°C) = 1364 cal/mol = 5709 J/mol

$\ln X = 2.303 \log X$

Appendix V

Some Useful Conversion Factors

Common Unit of Mass and Weight

1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centigrams
= 1000 milligrams
1 gram = 6.022 × 10^{23} atomic mass units or u
1 atomic mass unit = 1.6606 × 10^{-24} gram
1 metric tonne = 1000 kilograms
= 2205 pounds

Common Unit of Volume

1 quart = 0.9463 litre
1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre
1 millilitre = 1 cubic centimetre = 0.001 litre
= 1.056 × 10^{-3} quart
1 cubic foot = 28.316 litres = 29.902 quarts
= 7.475 gallons

Common Units of Energy

1 joule = 1 × 10^{7} ergs

1 thermochemical calorie**
= 4.184 joules
= 4.184 × 10^{7} ergs
= 4.129 × 10^{-2} litre-atmospheres
= 2.612 × 10^{19} electron volts
1 ergs = 1 × 10^{-7} joule = 2.3901 × 10^{-8} calorie
1 electron volt = 1.6022 × 10^{-19} joule
= 1.6022 × 10^{-12} erg
= 96.487 kJ/mol†
1 litre-atmosphere = 24.217 calories
= 101.32 joules
= 1.0132 ×10^{9} ergs
1 British thermal unit = 1055.06 joules
= 1.05506 ×10^{10} ergs
= 252.2 calories

Common Units of Length

1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres
1 yard = 36 inches = 0.9144 metre
1 metre = 100 centimetres = 39.37 inches
= 3.281 feet
= 1.094 yards
1 kilometre = 1000 metres = 1094 yards
= 0.6215 mile
1 Angstrom = 1.0 × 10^{-8} centimetre
= 0.10 nanometre
= 1.0 × 10^{-10} metre
= 3.937 × 10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere = 760 millimetres of mercury
= 1.013 × 10^{5} pascals
= 14.70 pounds per square inch
1 bar = 10^{5} pascals
1 torr = 1 millimetre of mercury
1 pascal = 1 kg/ms^{2} = 1 N/m^{2}

Temperature

SI Base Unit: Kelvin (K)

K = -273.15˚C
K = ˚C + 273.15
˚F = 1.8(˚C) + 32

$$°C = \frac{°F - 32}{1.8}$$

---

* Force: 1 newton (N) = 1 kg m/s^{2}, i.e.,the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.

** The amount of heat required to raise the temperature of one gram of water from 14.5^{0}C to 15.5^{0}C.

† Note that the other units are per particle and must be multiplied by 6.022 ×10^{23} to be strictly comparable.

Appendix VI

Thermodynamic Data at 298 K

INORGANIC SUBSTANCES

Substance	Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})	Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})
Aluminium			
Al(s)	0	0	28.33
Al^{3+}(aq)	– 524.7	–481.2	–321.7
Al_2O_3(s)	–1675.7	–1582.3	50.92
$Al(OH)_3$(s)	–1276	—	—
$AlCl_3$(s)	–704.2	–628.8	110.67
Antimony			
SbH_3(g)	145.11	147.75	232.78
$SbCl_3$(g)	–313.8	–301.2	337.80
$SbCl_5$(g)	–394.34	–334.29	401.94
Arsenic			
As(s), gray	0	0	35.1
As_2S_3(s)	–169.0	–168.6	163.6
AsO_4^{3-}(aq)	–888.14	–648.41	–162.8
Barium			
Ba(s)	0	0	62.8
Ba^{2+}(aq)	–537.64	–560.77	9.6
BaO(s)	–553.5	–525.1	70.42
$BaCO_3$(s)	–1216.3	–1137.6	112.1
$BaCO_3$(aq)	–1214.78	–1088.59	–47.3
Boron			
B(s)	0	0	5.86
B_2O_3(s)	–1272.8	–1193.7	53.97
BF_3(g)	–1137.0	–1120.3	254.12
Bromine			
Br_2(l)	0	0	152.23
Br_2(g)	30.91	3.11	245.46
Br(g)	111.88	82.40	175.02
Br^-(aq)	–121.55	–103.96	82.4
HBr(g)	–36.40	–53.45	198.70
BrF_3(g)	–255.60	–229.43	292.53
Calcium			
Ca(s)	0	0	41.42
Ca(g)	178.2	144.3	154.88
Ca^{2+}(aq)	–542.83	–553.58	–53.1

(continued)

Substance	**Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})**	**Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})**	**Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})**
Calcium (continued)			
CaO(s)	–635.09	–604.03	39.75
$Ca(OH)_2$(s)	–986.09	–898.49	83.39
$Ca(OH)_2$(aq)	–1002.82	–868.07	–74.5
$CaCO_3$(s), calcite	–1206.92	–1128.8	92.9
$CaCO_3$(s), aragonite	–1207.1	–1127.8	88.7
$CaCO_3$(aq)	–1219.97	–1081.39	–110.0
CaF_2(s)	–1219.6	–1167.3	68.87
CaF_2(aq)	–1208.09	–1111.15	–80.8
$CaCl_2$(s)	–795.8	–748.1	104.6
$CaCl_2$(aq)	–877.1	–816.0	59.8
$CaBr_2$(s)	–682.8	–663.6	130
CaC_2(s)	–59.8	–64.9	69.96
CaS(s)	–482.4	–477.4	56.5
$CaSO_4$(s)	–1434.11	–1321.79	106.7
$CaSO_4$(aq)	–1452.10	–1298.10	–33.1
*Carbon***			
C(s), graphite	0	0	5.740
C(s), diamond	1.895	2.900	2.377
C(g)	716.68	671.26	158.10
CO(g)	–110.53	–137.17	197.67
CO_2(g)	–393.51	–394.36	213.74
CO_3^{2-}(aq)	–677.14	–527.81	–56.9
CCl_4(l)	–135.44	–65.21	216.40
CS_2(l)	89.70	65.27	151.34
HCN(g)	135.1	124.7	201.78
HCN(l)	108.87	124.97	112.84
Cerium			
Ce(s)	0	0	72.0
Ce^{3+}(aq)	–696.2	–672.0	–205
Ce^{4+}(aq)	–537.2	–503.8	–301
Chlorine			
Cl_2(g)	0	0	223.07
Cl(g)	121.68	105.68	165.20
Cl^-(aq)	–167.16	–131.23	56.5
HCl(g)	–92.31	–95.30	186.91
HCl(aq)	–167.16	–131.23	56.5
Copper			
Cu(s)	0	0	33.15
Cu^+(aq)	71.67	49.98	40.6
Cu^{2+}(aq)	64.77	65.49	–99.6
Cu_2O(aq)	–168.6	–146.0	93.14
CuO(s)	–157.3	–129.7	42.63
$CuSO_4$(s)	–771.36	–661.8	109
$CuSO_4.5H_2O$(s)	–2279.7	–1879.7	300.4

(continued)

** For organic compounds, a separate table is provided in continuation.

Substance	**Enthalpy of formation, $\Delta_f H^\ominus$ / (kJ mol^{-1})**	**Gibbs Energy of formation, $\Delta_f G^\ominus$ / (kJ mol^{-1})**	**Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})**
Deuterium			
D_2(g)	0	0	144.96
D_2O(g)	–249.20	–234.54	198.34
D_2O(l)	–294.60	–243.44	75.94
Fluorine			
F_2(g)	0	0	202.78
F^-(aq)	–332.63	–278.79	–13.8
HF(g)	–271.1	–273.2	173.78
HF(aq)	–332.63	–278.79	–13.8
Hydrogen (see also Deuterium)			
H_2(g)	0	0	130.68
H(g)	217.97	203.25	114.71
H^+(aq)	0	0	0
H_2O(l)	–285.83	–237.13	69.91
H_2O(g)	–241.82	–228.57	188.83
H_2O_2(l)	–187.78	–120.35	109.6
H_2O_2(aq)	–191.17	–134.03	143.9
Iodine			
I_2(s)	0	0	116.14
I_2(g)	62.44	19.33	260.69
I^-(aq)	–55.19	–51.57	111.3
HI(g)	26.48	1.70	206.59
Iron			
Fe(s)	0	0	27.28
Fe^{2+}(aq)	–89.1	–78.90	–137.7
Fe^{3+}(aq)	–48.5	–4.7	–315.9
Fe_3O_4(s), magnetite	–1118.4	–1015.4	146.4
Fe_2O_3(s), haematite	–824.2	–742.2	87.40
FeS(s,α)	–100.0	–100.4	60.29
FeS(aq)	—	6.9	—
FeS_2(s)	–178.2	–166.9	52.93
Lead			
Pb(s)	0	0	64.81
Pb^{2+}(aq)	–1.7	–24.43	10.5
PbO_2(s)	–277.4	–217.33	68.6
$PbSO_4$(s)	–919.94	–813.14	148.57
$PbBr_2$(s)	–278.7	–261.92	161.5
$PbBr_2$(aq)	–244.8	–232.34	175.3
Magnesium			
Mg(s)	0	0	32.68
Mg(g)	147.70	113.10	148.65
Mg^{2+}(aq)	–466.85	–454.8	–138.1
MgO(s)	–601.70	–569.43	26.94
$MgCO_3$(s)	–1095.8	–1012.1	65.7
$MgBr_2$(s)	–524.3	–503.8	117.2

(continued)

Substance	**Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})**	**Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})**	**Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})**
Mercury			
$Hg(l)$	0	0	76.02
$Hg(g)$	61.32	31.82	174.96
$HgO(s)$	–90.83	–58.54	70.29
$Hg_2Cl_2(s)$	–265.22	–210.75	192.5
Nitrogen			
$N_2(g)$	0	0	191.61
$NO(g)$	90.25	86.55	210.76
$N_2O(g)$	82.05	104.20	219.85
$NO_2(g)$	33.18	51.31	240.06
$N_2O_4(g)$	9.16	97.89	304.29
$HNO_3(l)$	–174.10	–80.71	155.60
$HNO_3(aq)$	–207.36	–111.25	146.4
NO_3^- (aq)	–205.0	–108.74	146.4
$NH_3(g)$	–46.11	–16.45	192.45
$NH_3(aq)$	–80.29	–26.50	111.3
NH_4^+ (aq)	–132.51	–79.31	113.4
$NH_2OH(s)$	–114.2	—	—
$HN_3(g)$	294.1	328.1	238.97
$N_2H_4(l)$	50.63	149.34	121.21
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4ClO_4(s)$	–295.31	–88.75	186.2
Oxygen			
$O_2(g)$	0	0	205.14
$O_3(g)$	142.7	163.2	238.93
$OH^-(aq)$	–229.99	–157.24	–10.75
Phosphorus			
P(s), white	0	0	41.09
$P_4(g)$	58.91	24.44	279.98
$PH_3(g)$	5.4	13.4	210.23
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$H_3PO_3(aq)$	–964.8	—	—
$H_3PO_4(l)$	–1266.9	—	—
$H_3PO_4(aq)$	–1277.4	–1018.7	—
$PCl_3(l)$	–319.7	–272.3	217.18
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.6
Potassium			
$K(s)$	0	0	64.18
$K(g)$	89.24	60.59	160.34
$K^+(aq)$	–252.38	–283.27	102.5
$KOH(s)$	–424.76	–379.08	78.9
$KOH(aq)$	–482.37	–440.50	91.6
$KF(s)$	–567.27	–537.75	66.57

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$ / (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\ominus$ / (kJ mol^{-1})	Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})
Potassium (continued)			
KCl(s)	–436.75	–409.14	82.59
KBr(s)	–393.80	–380.66	95.90
KI(s)	–327.90	–324.89	106.32
$KClO_3$(s)	–397.73	–296.25	143.1
$KClO_4$(s)	–432.75	–303.09	151.0
K_2S(s)	–380.7	–364.0	105
K_2S(aq)	–471.5	–480.7	190.4
Silicon			
Si(s)	0	0	18.83
SiO_2(s,α)	–910.94	–856.64	41.84
Silver			
Ag(s)	0	0	42.55
Ag^+(aq)	105.58	77.11	72.68
Ag_2O(s)	–31.05	–11.20	121.3
AgBr(s)	–100.37	–96.90	107.1
AgBr(aq)	–15.98	–26.86	155.2
AgCl(s)	–127.07	–109.79	96.2
AgCl(aq)	–61.58	–54.12	129.3
AgI(s)	–61.84	–66.19	115.5
AgI(aq)	50.38	25.52	184.1
$AgNO_3$(s)	–124.39	–33.41	140.92
Sodium			
Na(s)	0	0	51.21
Na(g)	107.32	76.76	153.71
Na^+(aq)	–240.12	–261.91	59.0
NaOH(s)	–425.61	–379.49	64.46
NaOH(aq)	–470.11	–419.15	48.1
NaCl(s)	–411.15	–384.14	72.13
NaCl(aq)	–407.3	–393.1	115.5
NaBr(s)	–361.06	–348.98	86.82
NaI(s)	–287.78	–286.06	98.53
$NaHCO_3$(s)	–947.7	–851.9	102.1
Na_2CO_3(s)	–1130.9	–1047.7	136.0
Sulphur			
S(s), rhombic	0	0	31.80
S(s), monoclinic	0.33	0.1	32.6
S^{2-}(aq)	33.1	85.8	–14.6
SO_2(g)	–296.83	–300.19	248.22
SO_3(g)	–395.72	–371.06	256.76
H_2SO_4(l)	–813.99	–690.00	156.90
H_2SO_4(aq)	–909.27	–744.53	20.1
SO_4^{2-}(aq)	–909.27	–744.53	20.1
H_2S(g)	–20.63	–33.56	205.79
H_2S(aq)	–39.7	–27.83	121
SF_6(g)	–1209	–1105.3	291.82

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})	Entropy,* $S^\ominus$/(J K^{-1} mol^{-1})
Tin			
Sn(s), white	0	0	51.55
Sn(s), gray	–2.09	0.13	44.14
SnO(s)	–285.8	–256.9	56.5
SnO_2(s)	–580.7	–519.6	52.3
Zinc			
Zn(s)	0	0	41.63
Zn^{2+}(aq)	–153.89	–147.06	–112.1
ZnO(s)	–348.28	–318.30	43.64
Zn(g)	+130.73	+95.14	160.93

*The entropies of individual ions in solution are determined by setting the entropy of H^+ in water equal to 0 and then defining the entropies of all other ions relative to this value; hence a negative entropy is one that is lower than the entropy of H^+ in water.

ORGANIC COMPOUNDS

Substance	Enthalpy of combustion, $\Delta_c H^\ominus$/ (kJ mol^{-1})	Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})	Entropy, $S^\ominus$/(J K^{-1} mol^{-1})
Hydrocarbons				
CH_4(g), methane	–890	–74.81	–50.72	186.26
C_2H_2(g), ethyne (acetylene)	–1300	226.73	209.20	200.94
C_2H_4(g), ethene(ethylene)	–1411	52.26	68.15	219.56
C_2H_6(g), ethane	–1560	–84.68	–32.82	229.60
C_3H_6(g), propene (propylene)	–2058	20.42	62.78	266.6
C_3H_6(g), cyclopropane	–2091	53.30	104.45	237.4
C_3H_8(g), propane	–2220	–103.85	–23.49	270.2
C_4H_{10}(g), butane	–2878	–126.15	–17.03	310.1
C_5H_{12}(g), pentane	–3537	–146.44	–8.20	349
C_6H_6(l), benzene	–3268	49.0	124.3	173.3
C_6H_6(g)	–3302	—	—	—
C_7H_8(l), toluene	–3910	12.0	113.8	221.0
C_7H_8(g)	–3953	—	—	—
C_6H_{12}(l), cyclohexane	–3920	–156.4	26.7	204.4
C_6H_{12}(g),	–3953	—	—	—
C_8H_{18}(l), octane	–5471	–249.9	6.4	358
Alcohols and phenols				
CH_3OH(l), methanol	–726	–238.86	–166.27	126.8
CH_3OH(g)	–764	–200.66	–161.96	239.81
C_2H_5OH(l), ethanol	–1368	–277.69	–174.78	160.7
C_2H_5OH(g)	–1409	–235.10	–168.49	282.70
C_6H_5OH(s), phenol	–3054	–164.6	–50.42	144.0

(continued)

Substance	**Enthalpy of combustion, $\Delta_c H^\ominus$/ (kJ mol^{-1})**	**Enthalpy of formation, $\Delta_f H^\ominus$/ (kJ mol^{-1})**	**Gibbs Energy of formation, $\Delta_f G^\ominus$/ (kJ mol^{-1})**	**Entropy, $S^\ominus$/(J K^{-1} mol^{-1})**
Carboxylic acid				
HCOOH(l), formic acid	–255	–424.72	–361.35	128.95
CH_3COOH(l), acetic acid	–875	–484.5	–389.9	159.8
CH_3COOH (aq)	—	–485.76	–396.64	86.6
$(COOH)_2$(s), oxalic acid	–254	–827.2	–697.9	120
C_6H_5COOH(s), benzoic acid	–3227	–385.1	–245.3	167.6
Aldehydes and ketones				
HCHO(g), methanal (formaldehyde)	–571	–108.57	–102.53	218.77
CH_3CHO(l), ethanal (acetaldehyde)	–1166	–192.30	–128.12	160.2
CH_3CHO(g)	–1192	–166.19	–128.86	250.3
CH_3COCH_3(l), propanone (acetone)	–1790	–248.1	–155.4	200
Sugars				
$C_6H_{12}O_6$(s), glucose	–2808	–1268	–910	212
$C_6H_{12}O_6$(aq)	—	—	–917	—
$C_6H_{12}O_6$(s), fructose	–2810	–1266	—	—
$C_{12}H_{22}O_{11}$(s), sucrose	–5645	–2222	–1545	360
Nitrogen compounds				
$CO(NH_2)_2$(s), urea	–632	–333.51	–197.33	104.60
$C_6H_5NH_2$(l), aniline	–3393	31.6	149.1	191.3
NH_2CH_2COOH(s), glycine	–969	–532.9	–373.4	103.51
CH_3NH_2(g), methylamine	–1085	–22.97	32.16	243.41

Appendix VII

Standard potentials at 298 K in electrochemical order

Reduction half-reaction	$E^{\ominus}$/V	Reduction half-reaction	$E^{\ominus}$/V
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$F_2 + 2e^- \longrightarrow 2F–$	+2.87	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$2H^+ + 2e– \longrightarrow H_2$	0.0 by definition
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	–0.08
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$In^+ + e^- \longrightarrow In$	–0.14
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$AgI + e^- \longrightarrow Ag + I^-$	–0.15
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.23
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97	$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96	$Co^{2+} + 2e^- \longrightarrow Co$	–0.28
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92	$In^{3+} + 3e^- \longrightarrow In$	–0.34
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89	$Tl^+ + e^- \longrightarrow Tl$	–0.34
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86	$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	–0.36
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80	$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$Ag^+ + e^- \longrightarrow Ag$	+0.80	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79	$In^{2+} + e^- \longrightarrow In^+$	–0.40
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62	$In^{3+} + 2e^- \longrightarrow In^+$	–0.44
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60	$S + 2e^- \longrightarrow S^{2-}$	–0.48
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56	$In^{3+} + e^- \longrightarrow In^{2+}$	–0.49
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54	$U^{4+} + e^- \longrightarrow U^{3+}$	–0.61
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
		$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76

(continued)

Appendix continued

Reduction half-reaction	**$E^\ominus$/V**	**Reduction half-reaction**	**$E^\ominus$/V**
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83	$Na^+ + e^- \longrightarrow Na$	–2.71
$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$V^{2+} + 2e^- \longrightarrow V$	–1.19	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$U^{3+} + 3e^- \longrightarrow U$	–1.79	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09	$K^+ + e^- \longrightarrow K$	–2.93
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36	$Li^+ + e^- \longrightarrow Li$	–3.05
$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48		

Answer to Some Selected Problems

UNIT 1

1.17 ~ 15×10^{-4} g , 1.25×10^{-4} *m*
1.18 (i) 4.8×10^{-3} (ii) 2.34×10^{5} (iii) 8.008×10^{3} (iv) 5.000×10^{2}
(v) 6.0012
1.19 (i) 2 (ii) 3 (iii) 4 (iv) 3
(v) 4 (vi) 5
1.20 (i) 34.2 (ii) 10.4 (iii) 0.0460 (iv) 2810
1.21 (a) law of multiple proportion (b) (i) Ans : (10^{6} mm, 10^{15} pm)
(ii) Ans : (10^{-6} kg, 10^{6} ng)
(iii) Ans : (10^{-3} L, 10^{-3} dm^{3})
1.22 6.00×10^{-1} m =0.600 m
1.23 (i) B is limiting (ii) A is limiting
(iii) Stoichiometric mixture –No (iv) B is limiting
(v) A is limiting
1.24 (i) 2.43×10^{3} g (ii) Yes
(iii) Hydrogen will remain unreacted; 5.72×10^{2}g
1.26 Ten volumes
1.27 (i) 2.87×10^{-11}m (ii) 1.515×10^{-11} m (iii) 2.5365×10^{-2}kg
1.30 1.99265×10^{-23}g
1.31 (i) 3 (ii) 4 (iii) 4
1.32 39.948 g mol^{-1}
1.33 (i) 3.131×10^{25} atoms (ii) 13 atoms (iii) 7.8286×10^{24} atoms
1.34 Empirical formula CH, molar mass 26.0 g mol^{-1}, molecular formula C_2H_2
1.35 0.94 g $CaCO_3$
1.36 8.40 g HCl

UNIT 2

2.1 (i) 1.099×10^{27} electrons (ii) 5.48×10^{-7} kg, 9.65×10^{4}C
2.2 (i) 6.022×10^{24}electrons
(ii) (a) 2.4088×10^{21} neutrons(b) 4.0347×10^{-6} kg
(iii) (a) 1.2044×10^{22} protons (b) 2.015×10^{-5} kg
2.3 7,6: 8,8: 12,12: 30,26: 50, 38
2.4 (i) Cl (ii) U (iii) Be
2.5 5.17×10^{14} s^{-1}, $1.72 \times 10^{6}m^{-1}$
2.6 (i) 1.988×10^{-18} J (ii) 3.98×10^{-15} J

2.7 6.0×10^{-2} m, 5.0×10^{9} s^{-1} and 16.66 m^{-1}
2.8 2.012×10^{16} photons
2.9 (i) 4.97×10^{-19} J (3.10 eV); (ii) 0.97 eV (iii) 5.84×10^{5} m s^{-1}
2.10 494 kJ mol^{-1}
2.11 $7.18 \times 10^{19} s^{-1}$
2.12 $4.41 \times 10^{14} s^{-1}$, 2.91×10^{-19}J
2.13 486 nm
2.14 8.72×10^{-20}J
2.15 15 emission lines
2.16 (i) 8.72×10^{-20}J (ii) 1.3225 nm
2.17 1.523×10^{6} m^{-1}
2.18 2.08×10^{-11} ergs, 950 Å
2.19 3647Å
2.20 3.55×10^{-11}m
2.21 8967Å
2.22 Na^+, Mg^{2+}, Ca^{2+}; Ar, S^{2-} and K^+
2.23 (i) (a) $1s^2$ (b) $1s^2\ 2s^2\ 2p^6$; (c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^6$
2.24 n = 5
2.25 n = 3; l = 2; m_l = –2, –1, 0, +1, +2 (any one value)
2.26 (i) 29 protons
2.27 1, 2, 15
2.28 (i)

l	m_l
0	0
1	–1,0,+1
2	–2,–1,0,+1,+2

(ii) l = 2; m_1=–2, –1,0,+1,+2
(iii) 2*s*, 2*p*
2.29 (a) 1*s*, (b) 3*p*, (c) 4*d* and (d) 4*f*
2.30 (a), (c) and (e) are not possible
2.31 (a) 16 electrons (b) 2 electrons
2.33 *n* = 2 to n = 1
2.34 8.72×10^{-18}J per atom
2.35 1.33×10^{9}
2.36 0.06 nm
2.37 (a) 1.3×10^{2} pm (b) 6.15×10^{7} pm
2.38 1560
2.39 8
2.40 More number of K–particles will pass as the nucleus of the lighter atoms is small, smaller number of K–particles will be deflected as a number of positve charges is less than on the lighter nuclei.
2.41 For a given element the number of prontons is the same for the isotopes, whereas the mass number can be different for the given atomic number.
2.42 $^{81}_{35}Br$

2.43 $^{37}_{17}Cl^{-1}$

2.44 $^{56}_{26}Fe^{3+}$

2.45 Cosmic rays > X–rays > amber colour > microwave > FM

2.46 3.3×10^{6} J

2.47 (a) 4.87×10^{14} s^{-1} (b) 9.0×10^{9} m (c) 32.27×10^{-20} J

(d) 6.2×10^{18} quanta

2.48 10

2.49 8.28×10^{-10} J

2.50 3.45×10^{-22} J

2.51 (a) Threshold wave length 652.46 nm (b) Threshold frequency of radiation 4.598×10^{14} s^{-1}

(c) Kinetic energy of ejected photoelectron 9.29×10^{-20} J, Velocity of photoelectron 4.516×10^{5} ms^{-1}

2.52 530.9 nm

2.53 4.48 eV

2.54 7.6×10^{3} eV

2.55 infrared, 5

2.56 434 nm

2.57 455 pm

2.58 494.5 ms^{-1}

2.59 332 pm

2.60 1.516×10^{-38} m

2.61 Cannot be defined as the actual magnitude is smaller than uncertainity.

2.62 (v) < (ii) = (iv) < (vi) = (iii) < (i)

2.63 4*p*

2.64 (i) 2*s* (ii) 4*d* (iii) 3*p*

2.65 Si

2.66 (a) 3 (b) 2 (c) 6

(d) 4 (e) zero

2.67 16

UNIT 5

5.1 2.5 bar

5.2 0.8 bar

5.4 70 g/mol

5.5 $M_B = 4M_A$

5.6 203.2 mL

5.7 8.314×10^{4} Pa

5.8 1.8 bar

5.9 3g/dm^{3}

5.10 1249.8 g mol^{-1}

5.11 3/5

5.12 50 K

5.13 4.2154×10^{23} electrons
5.14 1.90956×10^{6} year
5.15 56.025 bar
5.16 3811.1 kg
5.17 5.05 L
5.18 40 g mol^{-1}
5.19 0.8 bar

UNIT 6

6.1 (ii)
6.2 (iii)
6.3 (ii)
6.4 (iii)
6.5 (i)
6.6 (iv)
6.7 q = + 701 J
w = – 394 J, since work is done by the system
$\Delta U = 307$ J
6.8 –743.939 kJ
6.9 1.067 kJ
6.10 $\Delta H = -7.151$ kJ mol^{-1}
6.11 – 314.8 kJ
6.12 $\Delta_r H = -778$ kJ
6.13 – 46.2 kJ mol^{-1}
6.14 – 239 kJ mol^{-1}
6.15 326 kJ mol^{-1}
6.16 $\Delta S > 0$
6.17 2000 K
6.18 ΔH is negative (bond energy is released) and ΔS is negative (There is less randomness among the molecules than among the atoms)
6.19 0.164 kJ, the reaction is not spontaneous.
6.20 –5.744 kJ mol^{-1}
6.21 NO(g) is unstable, but NO_2(g) is formed.
6.22 $q_{surr} = +286$ kJ mol^{-1}
$\Delta S_{surr} = 959.73$ J K^{-1}

UNIT 7

7.2 12.229
7.3 2.67×10^{4}
7.5 (i) 4.33×10^{-4} (ii) 1.90
7.6 1.59×10^{-15}
7.8 $[N_2] = 0.0482$ $molL^{-1}$, $[O_2] = 0.0933$ $molL^{-1}$, $[N_2O] = 6.6 \times 10^{-21}$ $molL^{-1}$

7.9 0.0352mol of NO and 0.0178mol of Br_2

7.10 7.47×10^{11} M^{-1}

7.11 4.0

7.12 $Q_c = 2.379 \times 10^3$. No, reaction is not at equilibrium.

7.14 0.44

7.15 0.068 $molL^{-1}$ each of H_2 and I_2

7.16 $[I_2] = [Cl_2] = 0.167$ M, $[ICl] = 0.446$ M

7.17 $[C_2H_6]_{eq} = 3.62$ atm

7.18 (i) $[CH_3COOC_2H_5][H_2O] / [CH_3COOH][C_2H_5OH]$
(ii) 3.92 (iii) value of Q_c is less than K_c therefore equilibrium is not attained.

7.19 0.02$molL^{-1}$ for both.

7.20 $[P_{CO}] = 1.739$atm, $[P_{CO2}] = 0.461$atm.

7.21 No, the reaction proceeds to form more products.

7.22 3×10^{-4} $molL^{-1}$

7.23 0.149

7.24 a) – 35.0kJ, b) 1.365×10^6

7.27 $[P_{H_2}]_{eq} = [P_{Br_2}]_{eq} = 2.5 \times 10^{-2}$bar, $[P_{HBr}] = 10.0$ bar

7.30 b) 120.48

7.31 $[H_2]_{eq} = 0.96$ bar

7.33 2.86×10^{-28} M

7.34 $5.85 x 10^{-2}$

7.35 NO_2^-, HCN, ClO_4, HF, H_2O, HCO_3^-, HS^-

7.36 BF_3, H^+, NH_4^+

7.37 F^-, HSO_4^-, CO_3^{2-}

7.38 NH_3, NH_4^+, HCOOH

7.41 2.42

7.42 $1.7 x 10^{-4}$M

7.43 $F^- = 1.5 x 10^{-11}$, $HCOO^- = 5.6 \times 10^{-11}$, $CN^- = 2.08 x 10^{-6}$

7.44 [phenolate ion]= 2.2×10^{-6}, $\alpha = 4.47 \times 10^{-5}$, α in sodium phenolate = 10^{-8}

7.45 $[HS^-] = 9.54 x 10^{-5}$, in 0.1M HCl $[HS^-] = 9.1 \times 10^{-8}$M, $[S^{2-}] = 1.2 \times 10^{-13}$M, in 0.1M HCl $[S^{2-}] = 1.09 \times 10^{-19}$M

7.46 $[Ac^-] = 0.00093$, pH= 3.03

7.47 $[A^-] = 7.08 x 10^{-5}$M, $K_a = 5.08 \times 10^{-7}$, $pK_a = 6.29$

7.48 a) 2.52 b) 11.70 c) 2.70 d) 11.30

7.49 a) 11.65 b) 12.21 c) 12.57 c) 1.87

7.50 pH = 1.88, $pK_a = 2.70$

7.51 $K_b = 1.6 \times 10^{-6}$, $pK_b = 5.8$

7.52 $\alpha = 6.53 \times 10^{-4}$, $K_a = 2.35 \times 10^{-5}$

7.53 a) 0.0018 b) 0.00018

7.54 $\alpha = 0.0054$

7.55 a) 1.48×10^{-7}M, b) 0.063 c) 4.17×10^{-8}M d) 3.98×10^{-7}

7.56 a) 1.5×10^{-7}M, b) 10^{-5}M, c) 6.31×10^{-5}M d) 6.31×10^{-3}M

7.57 $[K^+] = [OH^-] = 0.05$M, $[H^+] = 2.0 \times 10^{-13}$M

7.58 $[Sr^{2+}] = 0.1581M$, $[OH^-] = 0.3162M$, pH = 13.50

7.59 $\alpha = 1.63 \times 10^{-2}$, pH = 3.09. In presence of 0.01M HCl, $\alpha = 1.32 \times 10^{-3}$

7.60 $K_a = 2.09 \times 10^{-4}$ and degree of ionization = 0.0457

7.61 pH = 7.97. Degree of hydrolysis = 2.36×10^{-5}

7.62 $K_b = 1.5 \times 10^{-9}$

7.63 NaCl, KBr solutions are neutral, NaCN, $NaNO_2$ and KF solutions are basic and NH_4NO_3 solution is acidic.

7.64 (a) pH of acid solution= 1.9 (b) pH of its salt solution= 7.9

7.65 pH = 6.78

7.66 a) 12.6 b) 7.00 c) 1.3

7.67 Silver chromate S= 0.65×10^{-4}M; Molarity of Ag^+ = 1.30 x 10^{-4}M

Molarity of CrO_4^{2-} = 0.65×10^{-4}M; Barium Chromate S = 1.1×10^{-5}M; Molarity of Ba^{2+} and CrO_4^{2-} each is 1.1×10^{-5}M; Ferric Hydroxide S = 1.39×10^{-10}M;

Molarity of Fe^{3+} = 1.39×10^{-10}M; Molarity of $[OH^-]$ = 4.17×10^{-10}M

Lead Chloride S = 1.59×10^{-2}M; Molarity of Pb^{2+} = 1.59×10^{-2}M

Molarity of Cl^- = 3.18×10^{-2}M; Mercurous Iodide S = 2.24×10^{-10}M;

Molarity of Hg_2^{2+} = 2.24×10^{-10}M and molarity of I^- = 4.48×10^{-10}M

7.68 Silver chromate is more soluble and the ratio of their molarities = 91.9

7.69 No precipitate

7.70 Silver benzoate is 3.317 times more soluble at lower pH

7.71 The highest molarity for the solution is 2.5×10^{-9}M

7.72 2.43 litre of water

7.73 Precipitation will take place in cadmium chloride solution