1 STATE OF AGGREGATION OF MATTER INTERMOLECULAR FORCES

1.1 Matter: States of Aggregation

Under ordinary conditions all material bodies exist in one of the three states of aggregation–solid, liquid or gaseous. Apart from these well known states matter is also found to exist in three other states, e.g. liquid crystals, glass and an unusual state under special conditions called the plasma state. Each state is characterized by some specific properties. For example, solids have definite shape and size and these are incompressible. On the other hand, liquids do not possess any definite shape or size. It takes the shape of the container in which it is placed. Liquids are also only slightly compressible. Gases are highly compressible. When placed in a container a gas completely fills it, that is to say, gases do not have a definite volume. A common characteristic of solids, liquids and gases is that these expand when heated at constant pressure, but the amount of expansion is much more in the case of a gas than in the case of a liquid or a solid.

In describing the nature of matter the atomic molecular theory of matter has been universally accepted. According to this theory the smallest particle of all elements is called atom. Atoms of the same element have the same characteristic structure and properties. The structures and properties of atoms of different elements are different. The molecule is defined as the smallest particle of matter which can exist independently.

Molecules of most substances are composed of two or more atoms of the same or different elements. Examples are molecules of nitrogen, N_2, or carbon dioxide, CO_2. Molecules of the rare gases like helium, argon etc. and those of mercury are made up of one atom and hence are called monatomic. The physical and chemical properties of a substance are the sum of the properties of all the molecules of which it is composed.

A substance may exist in all the three states of aggregation under different conditions of temperature and pressure, but it has the same molecules. The effect of heat on a piece of ice may be taken as an example. When heated, ice melts to form liquid water. On heating further liquid water is converted into steam or water vapour. Heat is a form of energy and ever since the days of Count Rumford heat energy has been related to motion. When motion is increased more heat is produced or, conversely, when heat energy is added to a substance, i.e., the substance is heated motion increases. The question is motion of what increases as a result of heating? In trying to answer this question it was soon realized that it must be the motion of the molecules that increases on heating a body. The kinetic molecular theory of matter

took its birth. The molecules may execute any one or more of the three possible types of motion, namely, translational, rotational and vibrational (Figure 1.1). Translational motion consists in movement from one position to another. For rotational and vibrational motion displacement of the molecule is not necessary. Rotation of the molecule may take place around any of the different axes, whereas vibration of the molecule may take place around a mean position.

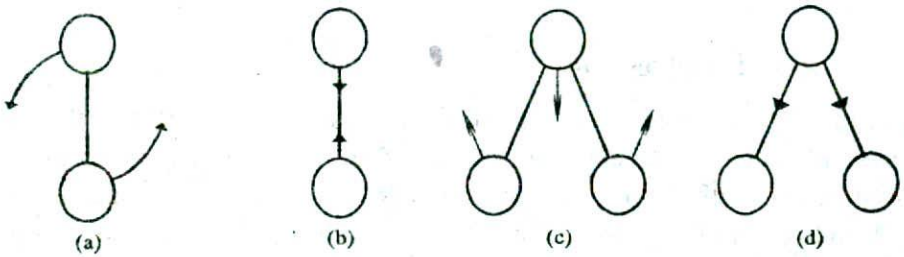


Figure 1.1 (a) Rotation of molecules; (b), (c) and (d) Different types of vibration

Based on the atomic molecular and kinetic molecular theory of matter the characteristics of the three states of matter may be summarized as follows.

In the solid state the molecules or ions are fixed in a uniform manner in definite mean positions in the solid state. There are strong intermolecular (or inter-ionic) forces which keep the molecules (ions) in their positions in the lattice. The only type of movement that the molecules may undergo is vibration around their fixed mean positions. The resulting structure is a fairly rigid one, having a definite shape and a definite volume, which strongly resists compression, expansion and distortion.

In the liquid state the molecules or ions have more energy. They have sufficient energy to overcome the forces which hold the particles in their positions in the solid state. As a result the molecules or ions possess translational motion but within a limited range, as the energy is not so high as to enable them to overcome the attractive forces altogether. The liquid state is, therefore, such that in this state it has a definite volume but not a definite shape. As the molecules (or ions) cannot escape far from each other the compressibility of a liquid is high. In the liquid state the molecules (ions) also possess rotational and vibrational energy.

When the molecules have sufficient energy which enables them to completely overcome the attractive forces the molecules form the gaseous state of matter. In the absence of the attractive forces molecules can move about in a random manner within the container at high speeds. As a result, they distribute themselves uniformly throughout the whole volume of the container. A gas, therefore, has no definite shape or volume. In the gaseous state the molecules are far apart from one another, and the volume within which the gas is confined is almost empty space. This explains why the gases are so highly compressible. When pressure is exerted the volume of the gas decreases, i.e., the molecules get closer. In addition to translational energy molecules in the gaseous state also possess rotational and vibrational motion.

The conversion of solid to liquid and that of liquid to gas takes place on the application of heat. The reverse process of converting a gas into a liquid may be accomplished by compressing the gas (so that the molecules are very close) and cooling so that the molecules have lesser energy than required to overcome the forces of repulsion. On further cooling, the translational energy may be decreased to such an extent that the attractive forces will hold the molecules in fixed positions, i.e., the solid state is reached. In solids, therefore, the particles are very close to each other, in liquids they are close but not very close, but in gas they are widely apart. This is shown in Figure 1.2 as a pictorial representation.

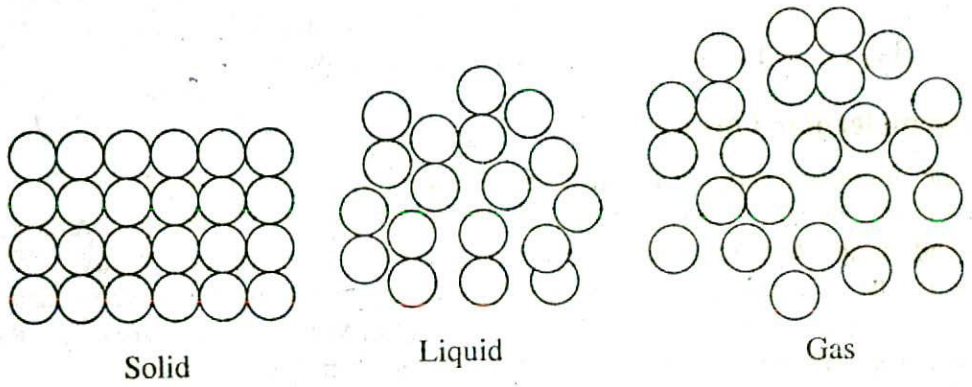


Figure 1.2 Schematic representation of gas, liquid and solid

It should be noted that solids may also be converted to the gaseous state without passing through the intermediate liquid state by application of heat. Such a process is known as sublimation. The above arguments may be given for such transformation. Changes of states are, therefore, reversible processes as shown in Figure 1.3.

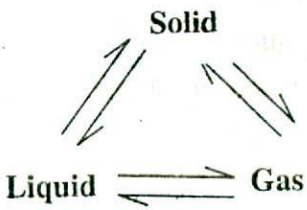


Figure 1.3 Reversibility between three states of matter

When solids are converted into liquids, intermediate phases possessing some of the molecular order characteristic of crystalline solids are sometimes obtained. These intermediate phases are called ***liquid crystals*** (*Section 4.14.1*) because they possess some of the properties of both solids and liquids.

Glasses are amorphous substances which have the properties of a solid but the structure of a liquid. Although apparently solid, structurally they resemble liquids as their constituent particles are found to be randomly arranged. Glasses are amorphous, meaning 'without shape'. These are, in fact, liquids cooled below their freezing points without crystallization taking place. These are regarded as supercooled liquids and are considered as intermediate between liquid and solid.

Plasma is an ionized gas formed when high temperature strips electrons from atoms. Plasma is an electrically neutral mixture of electrons and positive ions. It exists in the sun where nuclear fusion takes place. Over 99% of the matter in the universe, in stars and galaxies, seems to exist in the form of plasma. The sun and stars consist of matter in the form of highly ionized plasmas formed at very high temperatures.

1.2 Intermolecular Forces

In the above paragraphs mention has been made of intermolecular (or inter-ionic) forces. One might ask 'what is the origin of these forces'? We have to remember that atoms and molecules are made up of only protons, electrons and neutrons. Of these, protons in the nucleus are positively charged, electrons are negatively charged and neutrons do not carry any charge. These are particles with very small mass. As the effect of gravitational attraction between particles of such small mass is extremely small and negligible, one can only think that the forces between particles must be electrical in nature. The melting point and the boiling point of a substance are measures of the strength of such forces. The higher the melting and boiling points stronger must be the attractive forces between particles, i.e. ions or molecules.

From the study of the nature of these forces it has emerged that there are different types of forces between particles. These forces are listed below :

(a) Ionic interactions

(b) van der Waals forces

(i) Dipole –dipole interactions

(ii) Dipole-induced dipole interactions

(iii)Dispersion forces (instantaneous dipole-induced – induced dipole interaction)

(iv)Hydrogen bonding.

As an approximation the relative strengths of these forces can be summarized as follows:

Table 1.1 Relative strengths of inter-particle forces

Type of interaction	Relative strength
Ionic bonds	1000
Hydrogen bonds	100
Dipole-dipole	10
Dispersion	1

(a) Ionic Interactions

Electrostatic interactions occur between ions resulting in the formation of strong ionic bonds. These bonds are formed when metals atoms transfer their valence electrons to non-metal atoms forming positively charged metal ions (cations) and negatively charged non-metal ions (anions). The oppositely charged ions attract each other forming a three dimensional giant rigid structure in the solid state. Ionic compounds have high melting and boiling points as large amount of energy is required to overcome the electrostatic forces of attraction between the charged ions. In the molten state they are good conductors of electricity as the ions become free and mobile.

In cases where a small cation with large charge combines with an anion having a large size the resulting compound may have some covalent characters. Examples are, $MgBr_2$, $FeCl_3$, AlI_3 etc. There are examples (anhydrous ferric chloride, anhydrous aluminum chloride) of compounds between metals and non-metals which are completely covalent.

Metal atoms are held together by strong *metallic bonds.*

(b) van der Waals Forces

(i) Dipole – dipole interactions : Dipole-dipole interactions were first described by Willem Hendrick Keesom in 1921.

These are the forces that occur between two polar molecules with permanent dipole moments. Dipole-dipole attractions are electrostatic in nature like the ionic bonds, but are weaker because only partial charges are involved. An example of this type of interactions can be seen in the hydrogen chloride molecules. In a *HCl* molecule there is large difference in electronegativity between *H* atom and *Cl* atom (*Cl* is much more electronegative than *H*) and the electron pair between these two atoms in *HCl* molecule is attracted more strongly by *Cl* atom than by the *H* atom. This unsymmetrical (unequal) distribution of the electron pair between the combining atoms give rise to partial positive charge (δ^+) on the *H* atom and partial negative charge (δ^-) on the *Cl* atom. As a result a *dipole* is formed, and the molecule is called *polar*. When two polar *HCl* molecules are close together a structure similar to the one shown below is formed.



In a polyatomic molecule if the bond polarities do not cancel each other then the molecule has an overall polarity. This can happen because the symmetry in shape of the

molecule. Examples are H_2O and BF_3 molecules. Water is polar, but BF_3 is non-polar as shown below :

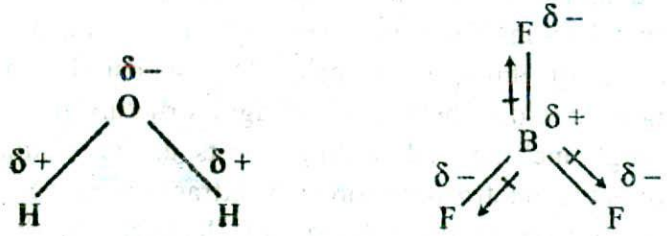


Figure 1.4 Shapes of H_2O and BF_3 molecules

As can be seen, the bond polarities in BF_3 cancel each other, because of the symmetrical planar shape of the molecule. In water, however, $O - H$ bond polarities do not cancel as the molecule has a bent shape.

(ii) Dipole-induced dipole interactions : Dipole-induced dipole interaction involve the attraction between temporarily induced dipoles in non-polar molecules. This polarization can be induced either (a) by a polar molecule or (b) by the repulsion of the negatively charged electron clouds in a non-polar molecule. An example of the former is chlorine dissolving in water.

$$[\textit{Permanent dipole}]\ \overset{(\delta+)}{H} - \overset{(\delta-)}{O} - \overset{(\delta+)}{H} - - - - \overset{(\delta-)}{Cl} - \overset{(\delta+)}{Cl}\ [\textit{Induced dipole}]$$

This is an example of interaction between the permanent dipole of water molecule and an induced dipole on chlorine molecule. The dipole in non-polar chlorine molecule is induced by the electric field offered by the permanent dipole of water molecule. This permanent dipole –induced dipole interaction is referred to as *induction* (*or polarization*) interaction and is to be distinguished from *London dispersion interaction.*

(iii) Induced dipole-induced dipole force (London forces or dispersion forces)

The above ideas of intermolecular force are unable to explain why molecules which do not have dipoles and noble gases like argon, xenon etc. can be liquefied and solidified. Strong attractive forces must exist between the molecules or atoms (in case of noble gases) to keep the particles together in these states.

Let us take the example of a Xenon atom. The electron distribution about the nucleus of a *Xe* atom is perfectly spherical. However, the electrons are constantly in motion and it is possible that at any given instant in some of the *Xe* atoms all the electrons may be positioned on one side of the nucleus, temporarily giving rise to partial positive charge at one end of the atoms and a partially negative charge on the other side. As a result an *instantaneous* dipole is formed in these *Xe* atoms. During this transitory existence the instantaneous dipole is likely to induce a dipole in a

neighbouring atom and the two instantaneous dipoles attract each other. A schematic diagram of this situation is depicted in Figure 1.5.

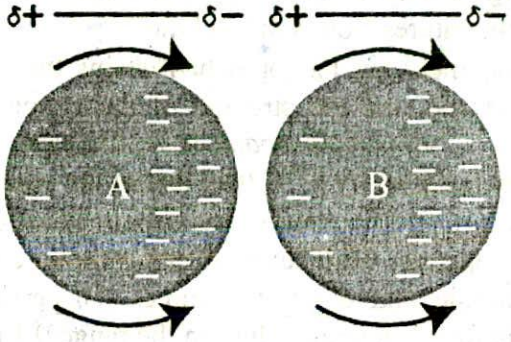


Figure 1.5 London forces as the instantaneous dipole in *A* forms, it induces a dipole in atom *B*

Forces between transitory dipoles are called *instantaneous dipole-induced dipole forces*, or alternately, *London forces or dispersion forces* after Fritz London who first proposed them. We will refer to them as *dispersion forces*. It should be realized that in a one gram sample of any substance the number of particles (atoms or molecules) is so large that if a small fraction of such particles are oriented in the manner described the attractive force between the particles will be significant. It is these forces that are responsible for the liquefaction and/or solidification of substances whose molecules do not possess permanent dipole moments. For example, dry ice or solid carbon dioxide. The carbon dioxide molecule is linear and has no overall dipole moment. Similarly, carbon tetrachloride, with perfectly tetrahedral molecules and no net dipole moment, is a liquid at room temperature, and iodine, which consists of iodine molecules, is a solid at room temperature.

Dispersion forces depend on two aspects of molecular (or atomic) structure.

- First, they increase in magnitude with the size and number of electrons and protons in the interacting particles and hence with their molecular masses (or atomic masses). Examples are: (a) the boiling points of the noble gases increase from helium to xenon; (b) fluorine and chlorine are gases at room temperature and 1 atm pressure, bromine is a liquid, and iodine is a solid; (c) large polymers which are electrically neutral are solids with low transition temperatures from solid to liquid. Only dispersion forces are operative in these substances.

- Second, dispersion forces depend upon molecular shape via the surface area over which two molecules can be in contact. When the molecules are close to each other lying side by side there are more sites of interaction; the molecules are able to come in contact over a large portion of their length. At each region of contact of the surface of a molecule distortion of the electron distribution may take place

and temporary dipoles may be created which will lead to dispersion forces in each region. The larger the surface area of contact the stronger the dispersion forces. Examples are: large polymers with linear structure which are neutral solids have low transition temperatures from solid to liquid.

If the molecule is not linear but has branched chains the number of contact points between the molecules is less and the strength of dispersion forces is also less. For example, *n- pentane* and *2,2-dimethylpropane* have the same molecular mass but the boiling point of *n-pentane* is higher by 27°C than that of the other isomer.

It is important to realize that dispersion forces operate between all molecules, whether or not other forces also operate. Molecules of chloroform, $CHCl_3$, are attracted by a combination of dipole-dipole and dispersion forces. Dispersion forces are generally weaker than dipole-dipole forces, having values in the range 0.1 to 5.0 kJ mol^{-1}.

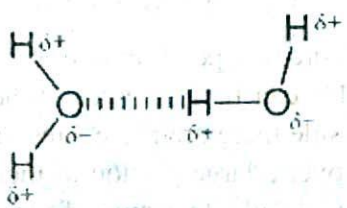
1.3 Hydrogen bonding

Strong forces of attraction exist between molecules containing a hydrogen atom bonded to a highly electronegative element such as nitrogen, oxygen or fluorine. This can be deduced by comparing the boiling point of water (H_2O) with that of hydrogen sulphide (H_2S). Water boils at 100°C while at room temperature H_2S is a gas. The attractive forces between H_2O molecules must be much stronger than that between H_2S molecules. *Water is a highly polar molecule and the strong attraction between water molecules is attributed to dipole-dipole interaction.* Such attractive forces are named ***hydrogen bonding*** because of the strength of such attractions as compared to other dipole-dipole attractions (Table 1.1). Hydrogen bond is defined as follows:

In compounds where a hydrogen atom is covalently bonded to a highly electronegative atom such as nitrogen, oxygen or fluorine the strong attrative force between a hydogen atom of one molecule for the electronegative atom of another molecule is called the ***hydrogen bond.***

The large electronegativity difference between the hydrogen atom and the electronegative atom gives rise to a partial positive charge on the hydrogen atom and a partial negative charge on the other atom joined by a covalent bond. *HCl* is an example as shown before.

As a result a stabilizing interaction between two or more molecules is developed that binds the molecules together. A common example of *H-bonding* is found in water:



It should be understood that hydrogen bond is an intermolecular force and not a bond as is understood in the cases of ionic or covalent bond. No transfer or sharing of electrons occur.

Evidences of hydrogen bonding are found throughout nature. Hydrogen bonding explains why the density of ice is less than that of liquid water. In the liquid state the water molecules joined by hydrogen bonds constantly change partners. When water starts freezing the hydrogen bonds between the molecules get fixed and in the solid state, as the molecules can not move, the hydrogen bonds between molecules get fixed in position. In the solid state (ice) each oxygen atom is surounded tetrahedrally by four hydrogen atoms: two forming covalent bonds with the O atom and are close to it to form H_2O molecule and two from other H_2O molecules farther away from it forming two hydrogen bonds. The result is a three-dimensional structure with empty space. This is why ice is less dense than water. When ice melts and liquid is formed again hydrogen bonds are constantly breaking and forming so that molecules can get close to each other giving rise to the liquid. This is a unique property of water and is very important to life on earth.

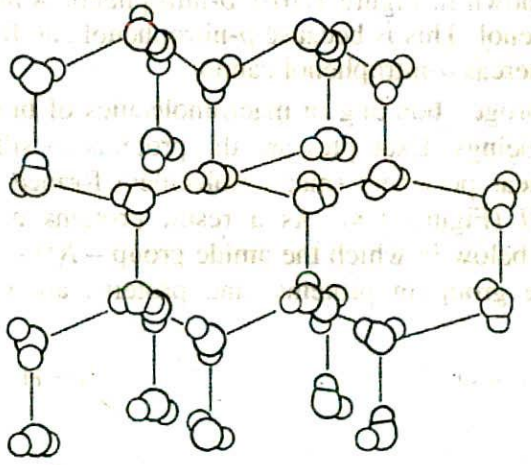


Figure 1.6 Structure of ice

Intramolecular hydrogen bonding (i.e. hydrogen bonding between the hydrogen atom in one part of the molecule with an electronegative atom like oxygen or nitrogen in another part of the same molecule) can also take place. For example, in *0- nitrophenol* the hydrogen atom of the $O - H$ group forms a hydrogen bond with one O- atom of the NO_2 group of the same molecule as shown below:

H-Bonding



o-Nitrophenol

Figure 1.7(a)
T.N.R. Intramolecular hydrogen bonding

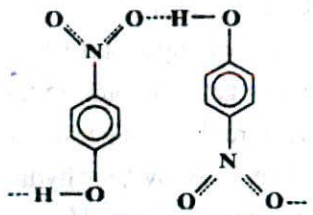


Figure 1.7(b)
T.N.R. Intermolecular hydrogen bonding in *p*-nitrophenol

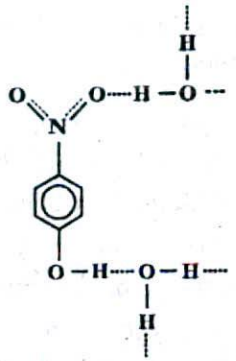


Figure 1.7(c)
T.N.R. Hydrogen bonding with water

Intramolecular hydrogen bonding in *o*-nitrophenol causes this compound to have a lower boiling point than *p*-nitrophenol where intermolecular hydrogen bonding (hydrogen bonding between two or more molecules) is present. In *p*-nitrophenol intramolecular hydrogen bonding is not possible because of the distance between the atoms which form such a bond. This is shown in Figure 1.7(b). *o*-nitrophenol is much less soluble in water compared to *p*-nitrophenol. This is because *p*-nitrophenol can form hydrogen bonds with water Figure 1.7(c) whereas *o*-nitrophenol cannot.

Intramolecular hydrogen bonding in macromolecules of biological origin is of great importance in living beings. Examples are the proteins in silk, hair, DNA, RNA etc. Many proteins are linear polymers (macromolecules) formed by reactions of α-amino acid $RCH(NH_2)COOH$ (Figure 1.8). As a result proteins consist of long chains of repeating units shown below in which the amide group – *NH* – *CO* – is repeated. This is known as the peptide group in proteins, and proteins are sometimes referred to as polypeptides.

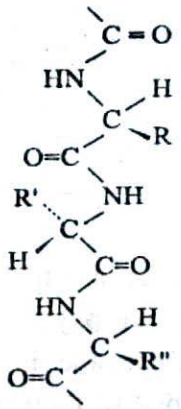


Figure 1.8 A part of protein molecule showing NH-CO bond formation

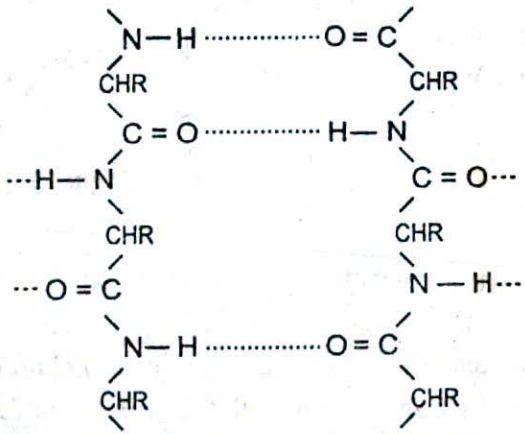


Figure 1.9 Two linear polymers joined by H-bonds

In some naturally occurring proteins two or more linear polymer molecules are joined together by hydrogen bonding (Figure 1.9). This creates secondary structures of proteins. In many proteins, including those in silk, hair, wool and nails hydrogen bonding causes the polypeptide chains to become twisted into tightly coiled helices (a *helix* is a spiral structure).

Intramolecular hydrogen bonding is important in the formation of the double helix structure of DNA (deoxyribonucleic acid). DNA is present in the nuclei of living cells and carry genetic information. The DNA molecule consists of two helical nucleic acid chains. Each nucleic acid is made up of 3 (three) components : a sugar, a phosphoric acid unit and a nitrogen-containing heterocyclic base – adenine (A), cytosine (C), guanine (G) or thymine (T). The two nucleic acid chains are held together by hydrogen bonding.

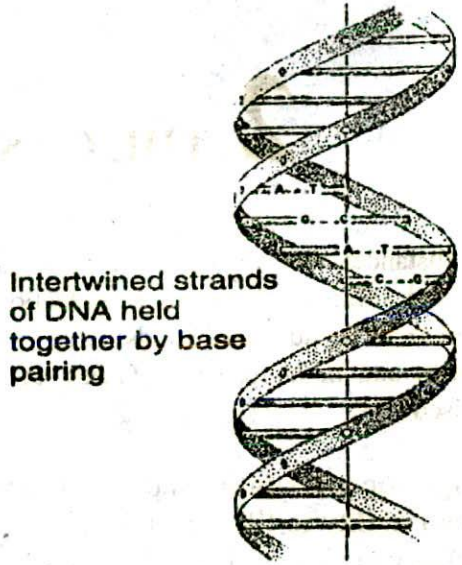


Figure 1.10 Two Nucleic acid chains held together by hydrogen bonding between two base pairs A ..... T or C ..... G

These hydrogen bonds are formed between specific pairs of bases in the two chains. The two strands coil tightly around each other (Figure 1.10).

QUESTIONS AND PROBLEMS

1. Describe from the kinetic theory point of view the arrangement of particles in the solid, liquid and gas states.
2. In the gaseous state what type movements the molecules can make?
3. What types of forces are responsible for keeping the particles together in the solid state and the liquid state? Do these forces operate in the gaseous phase?
4. What is the origin of the inter-particle forces?
5. Name the different types of intermolecular forces. Give example of each type.
6. With the help of a suitable sketch show how London force arise. Explain why F_2 and Cl_2 are gases at room temperature, while under the same condition Br_2 is a liquid and I_2 is a solid.
7. Define hydrogen bonding. With an appropriate example show the nature of hydrogen bonding.
8. Hydrogen chloride and hydrogen iodide are both gases at room temperature. Both consist of polar molecules. Hydrogen chloride has a boiling point of – 45°C whereas hydrogen iodide boils at – 35°C. In terms of types of intermolecular forces explain why this is so.
9. Xenon has a much higher boiling point than Neon. Explain the origin of intermolecular forces in these elements and the fact stated above.

2 THE GASEOUS STATE

All substances that we ordinarily call gases (e.g. nitrogen, hydrogen etc.) have been liquefied and solidified by suitable reduction of temperature and application of pressure. Many common liquids and solids have been converted into the gaseous state at low temperatures and high pressures. Gases, therefore, represent a state of matter. Gases are characterised by

(a) high compressibility and low density
(b) their ability to fill a container irrespective of the quantity of gas present in it
(c) large capacity of thermal expansion
(d) miscibility in all proportions of a gas with one or more different gases.

As pointed out in Chapter 1, from the molecular point of view these properties can be accounted for if one remembers that in the gaseous state the molecules have sufficient translational energy to overcome the attractive forces which tend to keep them in fixed positions as in a solid or in random movement as in a liquid.

2.1 Ideal Gases: The Gas Laws

The great compressibility and large capacity of thermal expansion of gases were described in the form of experimentally established laws a long time ago. Mathematical relationship between volume, pressure and temperature of a fixed mass of gas are known as *gas laws*. The relationship between mass and volume of a gas at fixed temperature was known. All gases, irrespective of their chemical nature, obey these laws provided the pressure is not too high or the temperature is not too low.

2.2 Boyle's Law

The effect of pressure on the volume of a gas was extensively studied by Robert Boyle in 1662. He enclosed some gas at the short end of a J-shaped tube and poured mercury at the other end. He found that the volume of the gas decreased (Figure 2.1). Each addition of mercury meant increase of pressure and this resulted in decrease of volume of the gas. The volume of a given mass of gas is 100 mL at atmospheric pressure. The volume is halved when the pressure is doubled by adding Hg. The volume is decreased to 33 mL by tripling the pressure to 1520 mm Hg. From such experiments he formulated a law of gases, known as Boyle's law. According to this law,

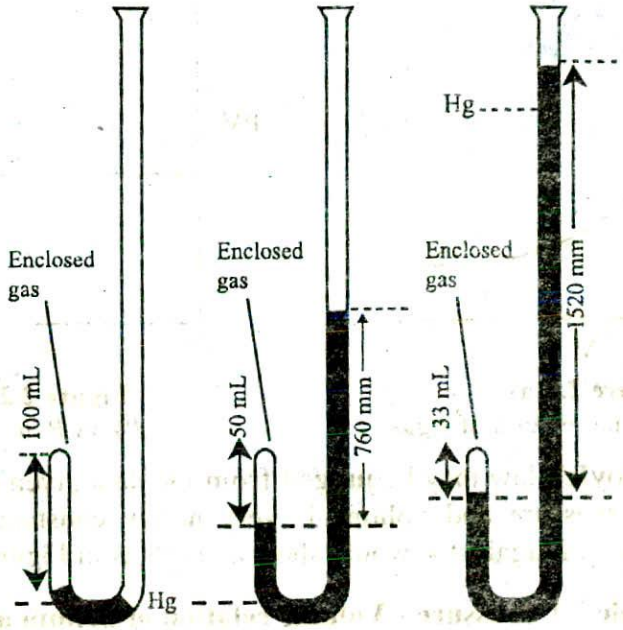


Figure 2.1 Boyle's experiment.

At constant temperature a fixed mass of gas occupies a volume which is inversely proportional to the pressure exerted on it.

If the pressure is doubled the volume becomes one-half of the original. Expressed mathematically the law states that

$$V \propto \frac{1}{P} \quad (n \text{ and } T \text{ constant}) \tag{2.1}$$

Or

$$PV = Constant \quad (n \text{ and } T \text{ constant}) \tag{2.2}$$

Here n is the number of moles of gas and T is the temperature.
It says that if a given mass of gas occupies a volume V_1 at a pressure of P_1 and a volume V_2 at a pressure of P_2 at a constant temperature then

$$P_1V_1 = P_2V_2 \tag{2.3}$$

Figure 2.2(a) shows the relation between volume and pressure at constant temperature. A plot of P against V at constant temperature is shown in Figure 2.2(a).

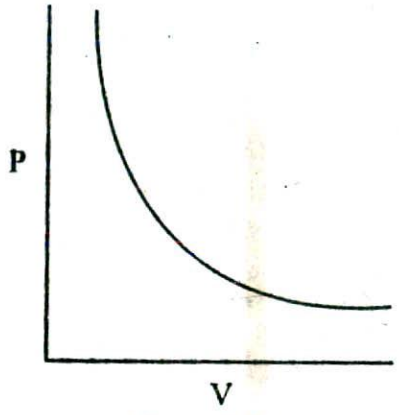


Figure 2.2(a)
Pressure-volume relation of a gas

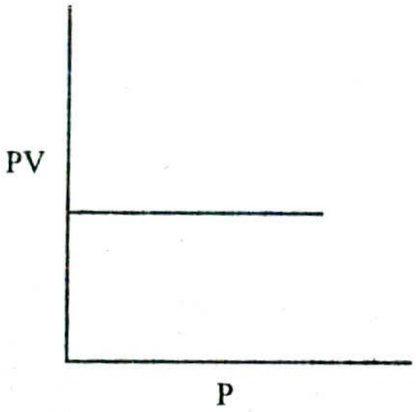


Figure 2.2(b)
PV vs P of a gas

The validity of Boyle's law may be judged from the data given in Table 2.1. Note that the product of pressure and volume is very nearly constant as suggested by equation (2.3). A plot of P against P would show a graph as in Figure 2.2(b).

Table 2.1 Pressure - Volume relation of helium at 0°C

Pressure (P) mm of Hg	Volume(V) mL	$PV \times 10^{-3}$ mm Hg-mL.
837.63	67.547	56.579
794.81	71.191	56.583
761.56	74.293	56.579
732.17	77.278	56.581
613.09	92.279	56.575
520.37	108.720	56.515
310.31	182.341	56.582
169.48	333.881	56.586

The use of the equation (2.3) is illustrated in the following example.

Example 2.1: 30 L of a gas exerts a pressure of 710 mm Hg at a temperature of 25°C. What will be the volume of the gas at the same temperature if the pressure is reduced to 600 mm Hg?

Solution: Substituting the values of pressure and temperature in equation (2.3)

$$P_1V_1 = P_2V_2$$

$$710 \times 30 = 600 \times V_2$$

Hence, $$V_2 = \frac{710 \times 30}{600} = 35.5 \text{ L}$$

2.3 Charles' Law or Gay-Lussac's Law

All gases increase in volume when their temperature is raised. If numerical data of volume of a given quantity of gas held at constant pressure are plotted against temperature in the centigrade scale (as shown in Figure 2.3) it is found that the points fall on a straight line. This indicates a linear relationship between volume and temperature when the pressure is kept constant.

If the temperature is sufficiently lowered, the gas liquefies and no more experimental points can be obtained. However, if the straight line joining the experimental points is extended as shown by the dotted line, it cuts the point of zero volume at a temperature of –273.16°C. Experiments have shown that this temperature, i.e. – 273·16°C does not depend on the nature of the gas provided it is stable, nor does it depend on the pressure at which the experiment is performed. This temperature is known as the *absolute zero of temperature* (^{0}A) and is the lowest temperature theoretically possible. 0°C would be the same as 273.16 °A. Similarly 100°C would be (100 + 273.16 =) 373.16 °A.

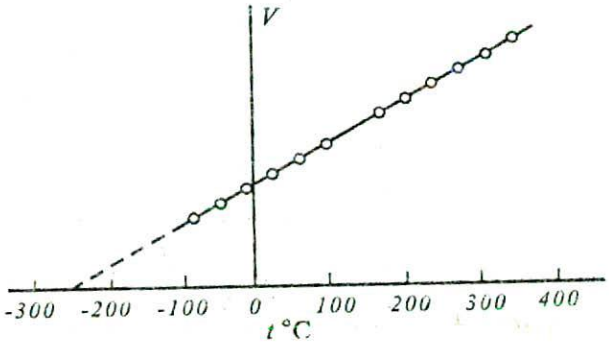


Figure 2.3 Volume of a given mass of gas *vs* temperature in °C

Temperatures below absolute zero would correspond to negative volume, which does not have any physical meaning. In the absolute scale temperature is also recorded as °K (degree Kelvin) or just K in honour of Lord Kelvin who first deduced this scale of temperature from theoretical considerations. The expression for the relation between the volume of a gas and temperature is known as *Charles' law* in honour of the French physicist whose experiments established it (1787). The law may now be stated as follows:

The volume of a given quantity of gas is directly proportional to the absolute temperature, the pressure remaining constant

Mathematically it may be expressed as

$$V \propto T \quad (n \text{ and } P \text{ constant}) \tag{2.4}$$

or

$$\frac{V}{T} = k \quad (n \text{ and } P \text{ constant}) \tag{2.5}$$

(k is a constant at constant pressure)

The value of the constant k depends on the pressure and on the quantity of gas. Figure 2.4 shows some plots of V against T (°K) at different P.

3-A

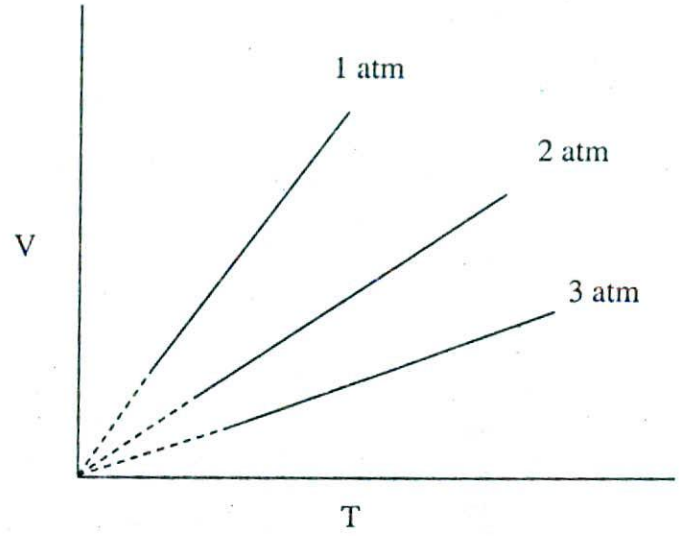


Figure 2.4 Volume of a fixed quantity of gas against temperature (K) at different pressures.

It follows from this expression that if a given quantity of gas at a particular pressure has volume V_1 at temperature T_1 and volume V_2 at temperature T_2 then we should have

$$\frac{V_1}{T_1}=\frac{V_2}{T_2} \tag{2.6}$$

This law is also sometimes known as *Gay-Lussac's Law (1802).* Gay-Lussac studied the effect of temperature on the pressure of gases keeping the volume constant. Gay-Lussac's law may now be expressed in the following form :

The pressure exerted by a fixed mass of a gas is directly proportional to absolute temperature or the Kelvin temperature

According to this law by following the same argument as in the case of Charles' law we can write

$$\frac{P_1}{T_1}=\frac{P_2}{T_2} \tag{2.7}$$

Example 2.2: A given mass of gas at a pressure of 1.0 atm pressure occupies a volume of 20.0 L at a temperature of 25.0 ^{0}C. When the temperature is raised to 50.0 ^{0}C keeping the pressure at 1.0 atm what will be the volume of the gas?

Solution: 25.0°C = 273.16 + 25.0 = 298.16 K
and 50.0°C = 273.16 + 50.0 = 323.16 K

3-B

Using equation (2.6) $\frac{20.0}{298.16} = \frac{V_2}{323.16}$

Hence $V_2 = \frac{20.0 \times 323.16}{298.16} = 21.7$ L

Like Boyle's law, Charles' law represents the behaviour of *ideal or perfect gases.* At high pressures and temperatures near the liquefaction point any real gas shows deviation from Charles' law.

2.4 The Absolute Zero of Temperature

At –273.16°C or 0°K the volume of any gas would theoretically be zero. In reality most gases become liquid long before the absolute zero is reached. A temperature as low as absolute zero has never been reached but low temperature scientists have been able to reach within a temperature of about 10^{-5} K. As the temperature of a substance is lowered the energy of its molecules also decreases. Consequently the movements of the molecules become less vigorous. At the absolute zero all movements of the molecules will cease or will be minimum. It has been shown theoretically by quantum mechanics that the only type of energy that the molecules may possess at 0°K is the energy due to *vibrational motion* and this energy at 0°K is known as the *zero-point energy.*

Although Figure 2.4 shows that at 0°K the volume of a gas is zero, in reality it is not so. At this temperature the molecules would be compressed so close to each other that they would not have space to move. This volume, however, would be very small compared to the volume occupied by the substance in the gaseous state under ordinary temperatures.

2.5 Avogadro's Law

In describing the behaviour of gases Avogadro(1811), an Italian physicist, proposed that *equal volumes of all gases at the same temperature and pressure contain equal number of molecules.* This is known as Avogadro's hypothesis or *Avogadro's law.*

Experimentally it was found that one gram molecular mass (one mole) of some gases at 0°C and 1 atmosphere pressure occupied a volume of 22.414 L. From Avogadro's law it follows that one gram molecular mass (one mole) of any gas at 0°C and 1 atmosphere pressure (STP, i.e., standard temperature and pressure) will occupy a volume of 22.414 L, since one mole of all gases contains the same number of molecules. Mathematically the law may then be stated as,

$$V \propto n \qquad (P \text{ and } T \text{ constant}) \tag{2.8}$$

Here n is the number of moles of the gas present. The molecular mass expressed in grams is known as the gram molecular mass. One gram mole or one mole signifies that quantity of the substance whose mass is equal to one gram molecular mass.

The volume occupied by one mole of gas is its molar volume and the number of molecules in one mole of a substance is known as the *Avogadro number(or Avogadro Constant).*

2.6 The Ideal Gas Equation

Boyle's, Charles' and Avogadro's laws may be combined to give a general relation between the V, P, T and n of a gas. Such a general relation is known as an *equation of state.* The equation of state shows how P, V, T and n are interrelated.

The equation of state for an ideal gas may be deduced as follows:

Let P = pressure, V = volume, T = absolute temperature and n = number of moles of any gas. We have seen that

$V \propto \frac{1}{P}$ at constant T and n (Boyle's law)

$V \propto T$ at constant P and n (Charles' law)

$V \propto n$ at constant P and T (Avogadro's law)

From the laws of variation it follows that

$$V \propto \left(\frac{1}{P}\right)(T)(n) \tag{2.9}$$

or $$V = R.\frac{nT}{P} \quad \text{where } R \text{ is a constant,} \tag{2.10}$$

Rearranging equation (2.10) we get,

$$PV = nRT \tag{2.11}$$

Equation (2.11) is the equation of state for an ideal gas. It applies to all gases. The word `*ideal*' is used because there is no actual gas whose behaviour follows this equation strictly under all conditions of temperature and pressure. The relationship is, however, useful in most calculations involving gases where high precision is not necessary.

2.7 The Significance of R

When one mole of gas is considered it follows from equation (2.11) that

$$PV = RT \tag{2.12}$$

or, $$R = \frac{PV}{T} \tag{2.13}$$

R is called the *universal gas constant or molar gas constant.* It follows from equation (2.13) that for one mole of any gas if the pressure is P_1,volume is V_1 at temperature T_1 then at temperature T_2 the pressure P_2 and volumeV_2 would be such that

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \qquad (2.14)$$

This relation is true for a known quantity of any gas.

The numerical value of R may be calculated by determining the volume occupied by 1 mole of a gas at a given pressure and a given temperature. The dimensions of R may be easily deduced from the equation (2.13).

Example 2.3: A 1.00 L flask was filled up with a gas at pressure of 751 mm Hg at temperature 26°C. What volume would this gas occupy at STP?

Solution: The information given are as follows:

P_1 = 751 mm Hg	P_2 = 760 mm Hg
V_1= 1.00 L	V_2 = Unknown
T_1 = 299 K	T_2 = 273 K

Substituting these data in equation (2.14) and solving for V_2 we get,

$$V_2=\frac{P_1V_1}{T_1}\left(\frac{T_2}{P_2}\right)=\frac{751\times1.00}{299}\left(\frac{273}{760}\right)=0.90\,L$$

2.8 The Numerical Value of *R*

The numerical value of R may be calculated by determining the volume occupied by 1 mole of a gas at a given pressure and a given temperature. The dimension of R may be easily deduced from the equation (2.13),

$$R=\frac{P\times V\,mol^{-1}}{T}$$

$$=\frac{force}{area}\times\frac{volume\,mol^{-1}}{temperature}\quad\left(\text{since pressure}=\frac{\text{force}}{\text{area}}\right)$$

$$=\frac{force}{(length)^2}\times\frac{(length)^3\,mol^{-1}}{temperature}$$

$$=force\times length\times\frac{mol^{-1}}{temperature}$$

$$=\frac{work\times mol^{-1}}{temperature}\text{, i.e., energy mol}^{-1}\text{ K}^{-1} \qquad (2.15)$$

Thus, the product PV has the dimension of work, and R may be expressed in any energy unit per mole per degree Kelvin. The constant R appears in many formulas in chemistry. The numerical value of R to be used depends on the system of units employed in the equation under consideration.

(a) *Litre-atmosphere units: In Section 2.5* it was pointed out that the molar volume at S.T.P., i..e, at 1 atmosphere pressure and 0°C or 273.16°K is 22.414 L. If these values are substituted in equation (2.13) one obtains,

$$R = \frac{1 \times 22.414}{273.16} = 0.0820 \text{ L-atm } K^{-1} \text{ mol}^{-1}$$

(b) *C.G.S. units*: In these units pressure is expressed in dynes per square centimetre and volume in cubic centimetres.

$P = 1$ atm $= 76$ cm of Hg

$$= 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$V = 22.414\ L = 22{,}414 \text{ cm}^3\text{mol}^{-1}$

$$R = \frac{76 \times 13.6 \times 981 \times 22{,}414}{273.16} = 8.316 \times 10^7 \text{ ergs } K^{-1} \text{ mol}^{-1}$$

(c) *Calories*: It is known that 1 calorie $= 4.184 \times 10^7$ ergs

$$\therefore \quad R = \frac{8.316 \times 10^7}{4.184 \times 10^7} = 1{\cdot}987 \text{ calories } K^{-1} \text{ mol}^{-1}$$

(d) Joules: We know 1 calorie = 4.184 J

So, 1.987 calories K^{-1} mol^{-1} $= 1.987 \times 4.184 = 8.314$ J K^{-1} mol^{-1}

and $R = 8.134$ J $K^{-1}mol^{-1}$

2.9 The Use of the Gas Equation in Calculations Involving Gases

Various types of calculations using the ideal gas equation are possible. For this purpose the equation may be used in different forms as shown below. Here g is the mass of a given quantity of gas, M is the molecular mass and ρ is the density of the gas.

(a) $PV = nRT$ (2.11)

(b) $PV = \frac{g}{M}RT$ (2.16)

(c) $P = \frac{g}{V} \times \frac{RT}{M} = \rho \frac{RT}{M}$ (2.17)

(d) $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (2.14)

2.10 Diffusion and Effusion: Graham's Law of Diffusion

One characteristic of gases is that it mixes readily with other gases until the mixture is uniform. This mixing happens as a result of diffusion of one gas in to another. *Diffusion is the process in which one gas spreads out through another gas to occupy the space uniformly.* One can find diffusion in liquids also. If sugar is placed in a glass of unstirred water it will be found after some time that sugar distributes itself throughout the liquid and the mixture becomes uniformly sweet. As can be seen, sugar molecules have moved from a region of high concentration to a region where there was no sugar until the concentration becomes equal.

Graham found by experiment that gases diffuse through a porous diaphragm and that a light gas diffuses more rapidly than a heavy gas. He described the diffusion of gases quantitatively in the form of a law which states that

'The rate of diffusion of a gas at constant pressure and temperature is inversely proportional to the square root of its density.

This is known as *'Graham's law of diffusion'*.

A related phenomenon is the process in which a gas flows out of a container through a small hole. This is called *effusion*. Experimentally it is simpler to measure effusion than diffusion. Graham studied the effusion of different gases through small holes and expressed his results in the form:

'The rate of effusion of gas molecules from a particular hole is inversely proportional to the square root of its density at constant temperature and pressure'. This is known as Graham's law of effusion. Mathematically

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\rho}} \text{ (constant } T \text{ and } P) \qquad (2.18)$$

$$\text{Or,} \quad r_{\text{effusion}} = \frac{k}{\sqrt{\rho}} \text{ where k is constant}$$

But from equation (2.17) we see

$$\rho = \frac{PM}{RT}$$

Hence

$$r_{\text{effusion}} = \frac{k}{\sqrt{\frac{PM}{RT}}}$$

If we compare the rates of effusion of two gases through the same hole at the same temperature and pressure it follows that

$$\frac{r_{effusion\ of\ gas\ A}}{r_{effusion\ of\ gas\ B}} = \frac{\sqrt{PM_B / RT}}{\sqrt{PM_A / RT}} = \sqrt{\frac{M_B}{M_A}} \qquad (2.19)$$

Example 2.4: A gas of unknown molecular mass was allowed to effuse through a small opening under constant pressure and temperature conditions. It required 60 seconds for 1 L of gas to effuse. Under identical conditions it required 97 seconds for 1 L of oxygen to effuse. Calculate the molecular mass of the unknown gas.

Solution: The rates of effusion of the two gases are

$$\text{For the unknown gas} = \left(\frac{1000}{60}\right) \text{mL s}^{-1}$$

$$\text{For oxygen} = \left(\frac{1000}{97}\right) \text{mL s}^{-1}$$

From equation (2.19)

$$\frac{\textit{Rate for } O_2}{\textit{Rate for the gas}} = \frac{\frac{1000}{97}}{\frac{1000}{60}} = \sqrt{\frac{M_2}{M_1}}$$

or $$\left(\frac{60}{97}\right)^2 = \frac{M_2}{32}$$

or $$M_2 = \left(\frac{60}{97}\right)^2 \times 32 = 12 \; g \; \text{mol}^{-1}$$

2.11 Equation of State of a Gas Mixture: Dalton's Law of Partial Pressure

When two or more gases are placed in the same container it is experimentally observed that the pressure of the gas mixture is related to the volume of the container and the temperature by the same expression as in the case of a single gas, i.e.,

$$PV = n\,R\,T \tag{2.11}$$

Here n stands for the total number of moles of gases in the container.

The behaviour of a mixture of gases is summarized in Dalton's law of partial pressures (1801). Dalton's law of partial pressure states that,

'The total pressure exerted by a mixture of gases is the sum of the partial pressures of the individual gases'.

The **partial pressure** of a component gas in a mixture is defined as

'The pressure that the gas would exert if it were present alone in the container at the same temperature, i.e., if it occupied the same volume'.

The total pressure P for a mixture of gases would, therefore, be equal to the sum of the partial pressures p_1, p_2, p_3 etc. of these gases.

$$P = p_1 + p_2 + p_3 + \text{--------} \tag{2.20}$$

If the volume in which the gas mixture is placed is V, then according to the definition of partial pressure,

$$p_1 = n_1 \frac{RT}{V}, \quad p_2 = n_2 \frac{RT}{V}, \quad p_3 = n_3 \frac{RT}{V} \tag{2.21}$$

Hence, $P = (n_1 + n_2 + n_3 + \ldots\ldots) \frac{RT}{V} = n \frac{RT}{V}$

This result shows that the expression $PV = nRT$ can be used for a mixture of gases as well as for pure gases.

It must be realized that the Dalton's law has the same limitations as the equation of state for gases.

Sometimes it is convenient to express partial pressure of a component in terms of the total pressure. It follows from equations (2.11) and (2.21) that

$$\frac{p_1}{P} = \frac{n_1}{n}, \text{ or } p_1 = \frac{n_1}{n} \times P \tag{2.22}$$

The fraction n_1/n i.e., the number of moles of component 1 divided by the total number of moles in the mixture, is known as the *mole fraction* and is given the symbol x. Hence equation (2.22) takes the form

$$p_1 = x_1 P \tag{2.23}$$

where x_1 is the mole fraction of component 1 in the mixture. In general if p_i is the partial pressure of a component whose mole fraction in the mixture is x_i and the total pressure of the mixture is P, then

$$p_i = x_i P \tag{2.24}$$

Example 2.5 : 4.00 L of N_2 at a pressure of 4.0 atm pressure and 1.00 L of O_2 at a pressure of 2.0 atm are introduced into a container of volume 2.0 L. Calculate the total pressure of the gas mixture in the container.

Solution: The partial pressure p_2 of N_2 in the container can be obtained from the relation

$$p_2 V_1 = p_2 V_2$$

$$p_2 = p_1 V_1 / V_2 = \frac{(4.00 \times 4.0)}{2.0} = 8.0 \text{ atm}$$

Similarly the partial pressure p_3 of O_2 in the container $= \frac{2.00 \times 1.00}{2.0} = 1.0$ atm

Adding p_2 and p_3 we obtain the total pressure $= 8.0 + 1.0 = 9.0$ atm.

Example 2.6: A mixture of gases at a pressure of 1.0 atm has the volume composition of 30% O_2, 50% N_2 and 20% CO_2.

(a) What is the partial pressure of each gas?

(b) If the carbon dioxide is removed by the addition of some pellets of sodiumhydroxide, what will be the partial pressures of O_2 and N_2?

Solution: (a) Since at constant temperature and pressure the volume of a gas is proportional to the number of moles, volume per cent is equal to mol per cent.

Hence the mol fractions of the *gases in the mixture are*

$$O_2 = 0.30; \quad N_2 = 0.50 \quad \text{and} \quad CO_2 = 0.20$$

The partial pressures are

$$p_{O_2} = 0.30 \times 1.0 \text{ atm} = 0.30 \text{ atm}$$

$$p_{N_2} = 0.50 \times 1.0 \text{ atm} = 0.50 \text{ atm}$$

$$p_{CO_2} = 0.20 \times 1.0 \text{ atm} = 0.20 \text{ atm}$$

(b) From the law of partial pressures we know that the gases exert pressure independently of each other. So removal of CO_2 does not have any effect on the partial pressures of the remaining gases.

2.12 The Kinetic Theory of Gases

Gases are nature's simplest substances. As in most scientific investigations, attempts have been made from ancient times to explain the behaviour of gases in terms of a simple model. The ideas of atoms and molecules as constituents of matter had been gradually developing. These ideas were extended by Maxwell, Boltzmann, Clausius and others to formulate a model of the gaseous state. The kinetic theory of gases represents this model. Elementary calculations using the laws of mechanics and statistics, when applied to this model, yield results which are in excellent agreement with experiment under certain conditions. The following are the basic postulates of the kinetic theory of gases:

1. A gas consists of tiny particles called molecules (atoms in few cases).
2. Molecules are treated as points, having no volume.
3. Molecules move continuously and randomly.
4. Molecules collide with each other, changing direction and velocity.
5. Collisions with the walls of the container exert a force, which is pressure.
6. The collisions are elastic (no loss of kinetic energy).
7. In the perfect gas there are no attractive or repulsive forces between molecules.

2.13 Root-mean-square (r.m.s.) Velocity

A result of the molecular collisions is that the speeds of all the molecules are not the same. Some have very high velocities, while others have lower velocities. In using the kinetic theory of gases it is convenient to assume a common value for all the molecules. An average velocity could be used, but theoretically it is more exact to use what is known as the root-mean-square (r.m.s.) velocity. If n_1 molecules have velocity c_1, n_2 molecules have velocity c_2, n_3 molecules have velocity c_3 and n_n molecules have velocity c_n, then

$$c = (\bar{c}^2)^{\frac{1}{2}} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ----- + n_nc_n^2}{n}} \qquad (2.25)$$

where $n = n_1 + n_2 + n_3 + ----- + n_n$ = total number of molecules.

$$\text{The average velocity} = \bar{c} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + ----- + n_nc_n}{n} \qquad (2.26)$$

It may be seen that the average velocity and the r.m.s. velocity do not have the same magnitude.

Example 2.7: In a system of 50 molecules, 15 have velocity 2.0×10^2 m s^{-1}, 30 have velocities 4.0×10^2 m s^{-1} and 5 have velocities 8.0×10^2 m s^{-1}. Calculate the r.m.s. velocity of the molecules.

Solution: From equation (2.25) we have,

$$(\bar{c}^2) = \left[\frac{15(2.0\times10^2)^2 + 30(4.0\times10^2)^2 + 5(8.0\times10^2)^2}{15+30+5}\right]$$

$$= \frac{15\times4\times10^4 + 30\times16\times10^4 + 5\times64\times10^4}{50}$$

$$= 17.2 \times 10^4 \text{ m}^2 \text{ s}^{-2}$$

Hence, $(\bar{c}^2)^{\frac{1}{2}} = 4.15 \times 10^2$ m s^{-1}.

2.14 Derivation of the Kinetic Equation

The pressure exerted by a gas is the total effect of the impacts of the gas molecules on the walls of the container. The expression for the pressure of a gas in terms of the molecular velocity may be derived as follows:

Consider a cube (Figure 2.5) with sides l cm each, which contains n molecules of a gas, the mass of each molecule being m.

Let the root-mean-square velocity of the molecules be c. This may be resolved into three mutually perpendicular components u, v and w along the x, y and z axes respectively. c and its components (which are vector quantities) are related by the expression

$$c^2 = u^2 + v^2 + w^2 \qquad (2.27)$$

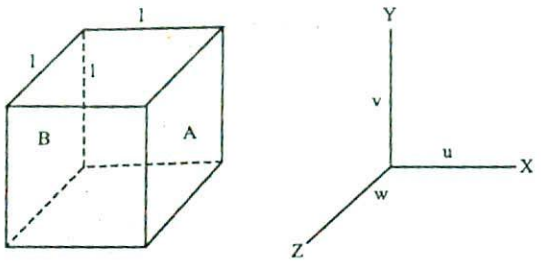


Figure 2.5 A cube with side l cm each

The molecules are moving at random within the container and are colliding with each other and the walls of the container. Consider one molecule starting from the wall B and moving in a straight line perpendicularly to the wall A opposite to it, and rebounds.

The momentum of the molecule before impact with the wall $A = mu$
The momentum of the molecule after the impact with the wall $A = -mu$.
Therefore, the change in momentum $= mu - (-mu) = 2mu$

This will be the momentum imparted to the wall by each impact. Before the molecule can strike the wall A again it has to travel a distance $2l$ to the face B and back.

The time required to travel from A to B and back to $A = 2l/u$ seconds.
Hence the number of impacts on the wall A by one molecule in one second will be $u/2l$.
The total change in momentum per second for one molecule due to impacts with wall $A = 2mu.u/2l = mu^2/l$.

As the number of molecules is n the total change of momentum in one second for all the molecules $= mnu^2/l$.

The rate of change of momentum is equal to the force on the wall A. Hence force is given by

$$f = \frac{mnu^2}{l} \qquad (2.28)$$

Experiment shows that the force exerted on the walls is the same for all the walls. Hence the velocities resolved along three axes must be equal, i.e.,

$$u^2 + v^2 + w^2 = c^2 = 3u^2$$

$$\text{or } u^2 = \frac{c^2}{3}$$

Therefore, $$\text{force} = f = \frac{mnc^2}{3l} \tag{2.29}$$

Dividing both sides by l^2 one obtains

$$\frac{f}{l^2} = \frac{mnc^2}{3l^3} \tag{2.30}$$

But $\frac{f}{l^2}$ is force per unit area, which is equal to the pressure, P, and l^3 is the volume, V, of the container cube.

Hence $$P = \frac{mnc^2}{3V} \tag{2.31}$$

or $$PV = \frac{1}{3}mnc^2 \tag{2.32}$$

This is the kinetic equation for gases. Although the above deduction has been made for a cubical vessel the equation is valid for a vessel of any shape as the vessel can be divided into a large number of small cubes for each of which this equation is valid.

2.15 Deduction of the Gas Laws from the Kinetic Equation

All the gas laws may be deduced from equation (2.32).

(a) Boyle's law: Temperature is a measure of the kinetic energy of the molecules. The higher the temperature higher is the kinetic energy of the molecules. Equation (2.32) may be written in the form,

$$PV = \frac{2}{3} \times \frac{1}{2}\ mnc^2 = \frac{2}{3} \times \text{total kinetic energy} \tag{2.33}$$

since the kinetic energy of a moving body is $\frac{1}{2}mc^2$. For a given quantity of gas, when the temperature is constant, the kinetic energy is constant. Hence,

PV = constant, (at constant T), which is Boyle's law.

(b) *Charles' or Gay-Lussac's law:* The total kinetic energy of the molecules is proportional to the absolute temperature, i.e. $K.E. = \text{const} \times T$. Hence, from equation (2.33)

$$PV = const \times T \tag{2.34}$$

At constant volume for a given quantity of gas $P \propto T$. This is Charles' or Gay-Lussac's law.

(c) *Avogadro's law:* Consider that two gases are at the same pressure, P, and contained in vessels of equal volume, V. Both the vessels are at the same temperature. For the first gas, from the kinetic equation (2.32)

$$PV = \frac{1}{3} n_1 m_1 c_1^2 \tag{2.35}$$

where n_1 is the number of molecules, m_1, is the mass of each molecule and c_1 is the r.m.s. velocity. Similarly, for the second gas,

$$PV = \frac{1}{3} n_2 m_2 c_2^2 \tag{2.36}$$

where n_2,, m_2 and c_2 have the same significance as for the first gas. Since P, V and T of the two gases are same, according to equation (2.3)

$$\frac{1}{3} m_1 n_1 c_1^2 = \frac{1}{3} m_2 n_2 c_2^2 \tag{2.37}$$

At the same temperature the kinetic energies of the molecules of both the gases are the same ; that is,

$$\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2 \tag{2.38}$$

If equation (2.37) is divided by equation (2.38) one obtains

$$n_1 = n_2$$

That is, the number of molecules in equal volumes of the two gases under the same conditions of T and P is the same. This is Avogadro's hypothesis or Avogadro's law.

(d) *Graham's law of diffusion:* Graham's law states that *the rate of diffusion of* a *gas at constant pressure and temperature is inversely proportional to the square root of its density.* This law may be easily deduced from the kinetic equation (2.31) which can be written in the form,

$$c^2 = \frac{3PV}{mn}$$

Since the density ρ of a gas is equal to the mass divided by the volume, $\rho = \frac{mn}{V}$

Hence, $$c^2 = \frac{3P}{\rho} \quad \text{or} \quad c = \sqrt{\frac{3P}{\rho}} \tag{2.39}$$

The rate of diffusion of a gas depends on the velocity of the molecules when the pressure is kept constant. Since c is proportional to $1/\sqrt{\rho}$ at constant P the rate of diffusion will also be inversely proportional to the square root of density, which is Graham's law of diffusion.

2.15 Molecular Velocities

The kinetic equation (2.32) may be used directly for calculating the r.m.s. velocity of a molecule of any gas. One can rearrange equation (2.32) as,

$$c = \sqrt{\frac{3PV}{mn}}$$

For one mole of gas mn=M, so that,

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} \quad \text{(since } PV=RT\text{)} \tag{2.40}$$

Example 2.8: Calculate the r.m.s. velocity of hydrogen gas (RMM = 2.016) at 25°C.

Solution: The r.m.s. velocity of a hydrogen molecule is given by

$$c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.314\times 10^7 \times 298}{2.016}} \text{ cm s}^{-1}.$$

$$= 1.92 \times 10^5 \text{ cm s}^{-1}$$

Any of the following forms of the kinetic equation may be used for calculating molecular velocities:

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M}}$$

It must, however, be remembered that if the velocity is to be obtained in the c.g.s, units, i e., in centimeter per second, all the quantities P, V, ρ, M and R have to be expressed in c.g.s. units.

As may be seen from above, the velocity of a hydrogen molecule at ordinary temperature is very high – more than a mile a second. The velocity is inversely proportional to the square root of the molecular mass; heavier molecules like those of carbon dioxide or uranium hexafluoride will have lower velocity than that of hydrogen.

2.17 Distribution of Velocities

A result of the chaotic movement of molecules in the gaseous state is that in addition to their collisions with the walls of the container they collide with each other. Collisions with other molecules continually change the speed of a particular molecule. A particular molecule may move along a given direction until it hits another, to which it loses a part of its kinetic energy. In the next collision with a third particle it may gain some kinetic energy and change its direction of movement. The path of each molecule is completely haphazard. The exchange of kinetic energy between colliding molecules goes on continually. The total kinetic energy of a given mass of gas, however, remains constant as long as the temperature remains the same. The total kinetic energy of a gas is made up of the contributions of all the molecules, each of which may be moving with different speed. At any instant some of the molecules may be moving with very high velocities, some may have very low velocities (may even be standing still), while the majority will have velocities near the average.

Since the velocities are determined by chance collisions and a large number of molecules are involved, Maxwell and Boltzmann applied the laws of probability to the situation obtaining in a gas and derived the following expression for the distribution of velocities among gas molecules:

$$\frac{dn}{n} = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} e^{-\frac{Mc^2}{2RT}} c^2 dc \qquad (2.41)$$

where M is the molecular mass, c is the velocity, n is the total number of molecules, dn/n is the fraction of molecules having velocity between c and $c + dc$ (dc being infinitesimally small increment), T is the absolute temperature and R is the universal gas constant. This is known as the Maxwell-Boltzmann distribution equation. Figure 2.6. is a graph representing equation (2.41). Such a graph is known as Maxwell-Boltzmann distribution curve.

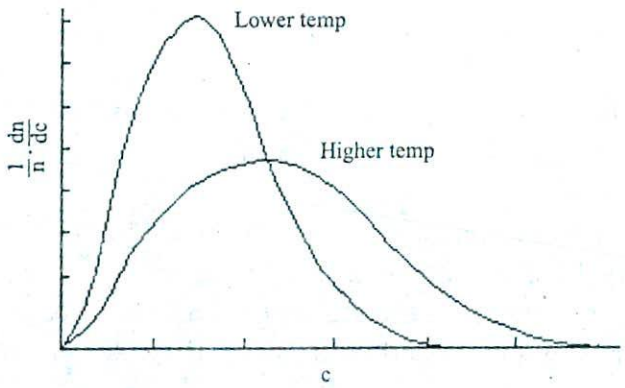


Figure 2.6 Distribution of velocities at two different temperatures

The values of *dn/n* have been calculated from the right side of the equation (2.41) by putting different values of *c*. Each point in the curve tells what fraction of the molecules has velocity specified by the value of the abscissa at the point.

It is evident from the distribution equation that the value of *dn/n* is profoundly influenced by temperature. The distribution at the higher temperature takes the form shown in Figure 2.6. At the higher temperature the molecules have higher average kinetic energy, i.e., higher velocity than at the lower temperature. Thus, temperature serves to measure the average kinetic energy.

2.18 Average Velocity, r.m.s. Velocity and Most Probable Velocity

The distribution equation (2.41) may be used to obtain the average velocity, $\bar{c}$, of the molecules. This is given by the relation

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} \qquad (2.42)$$

If we compare the average velocity with r.m.s. velocity it may be seen that the values are not the same.

$$\text{Average velocity, } \bar{c} = \sqrt{\frac{8}{3\pi}} \times \text{r. m. s. velocity} \qquad (2.43)$$

$$= 0.9213 \times \text{r. m. s. velocity}$$

Most probable velocity is the velocity possessed by the largest number of molecules in gas. Maxwell showed that the most probable velocity is given by the expression

$$c_{mpv} = \sqrt{\frac{2RT}{M}}$$

A value of the most probable velocity may be calculated from the values of *R*, *T* and *M*. A relation between the r.m.s. velocity and the most probable velocity can be established as follows:

$$\frac{c_{mpv}}{c_{r.m.s.}} = \frac{\sqrt{\frac{2RT}{M}}}{\sqrt{\frac{3RT}{M}}} = \sqrt{\frac{2}{3}} = 0.8165$$

Hence, $$c_{mpv} = 0.8165 \times c_{r.m.s.}$$

Example 2.9: Calculate, (a) r.m.s, (b) average and (c) most probable velocity for SO_2 gas at 25 ^{0}C.

Solution: (a) $c_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3\times8.314\times10^7\times298}{64}\right)^{\frac{1}{2}} = 3.4\times10^4 \text{ cm s}^{-1}$

(b) $\bar{c} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8\times8.314\times10^7\times298}{3.142\times64}\right)^{\frac{1}{2}} = 3.14\times10^4 \text{ cm s}^{-1}$

(c) $c_{mpv} = \left(\frac{2RT}{M}\right)^{\frac{1}{2}} = \left(\frac{2\times8.314\times10^7\times298}{64}\right)^{\frac{1}{2}} = 2.78\times10^4 \text{ cm s}^{-1}$

2.19 Mean Free Path

Mean free path of a gas molecule is defined as *the average distance a molecule travels between two successive collisions*. The actual distance travelled by a molecule between consecutive collisions may vary considerably from time to time. Sometimes it may move a long distance before hitting another molecule, at other times two consecutive collisions may take place within a very short distance. It may be shown that the mean free path, l, of a gas is given by

$$l = \frac{1}{\sqrt{2}} \frac{1}{\pi\sigma^2 n} \tag{2.44}$$

where n is the number of molecules in unit volume and σ is known as the collision diameter, i.e., the distance between the centres of molecules at the time of their closest approach. This value is slightly larger than the molecular diameter as shown in Figure 2.7. During collision the molecules do not actually touch each other because of mutual repulsion when they come very close to each other. Since σ is not very much different for ordinary gases (see Table 2.2) the mean free path of a gas depends mainly on n.

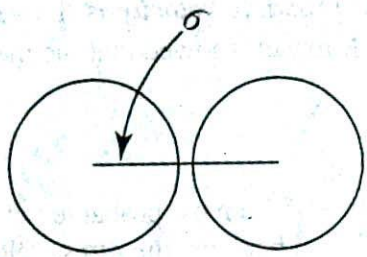


Figure 2.7 Collision diameter

2.19.1 Effect of pressure and temperature on the value of mean free path

(a) *Effect of pressure:* For a given quantity of gas n, i.e., the number of molecules per unit volume, the mean free path decreases with increase of volume (i.e., decrease of pressure) so that l increases with decrease of pressure.

(b) *Effect of temperature:* Again for a given quantity of gas when the temperature is increased at constant pressure the volume increases. Hence the n, the number of molecules in unit volume, decreases. From the expression above with decrease of n the value of l increases.

Example 2.10: Calculate the mean free path of nitrogen molecules at 1.0 atm pressure and 25°C. Collision diameter for nitrogen is 3.50×10^{-8} cm.

Solution: It is necessary first to calculate the number of molecules per cubic centimetre.

Volume of 1 mole of gas at 25 ^{0}C $= \frac{22,414}{273.16} \times 298.16 mL = 24474 mL$

$$n = \frac{6.02 \times 10^{23}}{24474} = 2.46 \times 10^{19}$$

$$l = \frac{1}{\sqrt{2}} \frac{1}{\pi \sigma^2 n} = \frac{1}{(\sqrt{2})} \frac{1}{(3.142)(3.50 \times 10^{-8})^2 (2.46 \times 10^{19})} = 7.5 \times 10^{-6} \text{ cm}$$

At 1 atm pressure and 25°C the value of l is of the order of 10^{-5} cm. At a pressure of 10^{-5} atm, therefore, the mean free path becomes about 1 cm.

2.20 Viscosity of Gases

When a mass of gas is caused to stream or flow in any given direction there is transfer of momentum from one layer of gas to neighbouring layer due to random movement of the molecules. This transfer of momentum causes frictional or dragging force trying to retard the motion of the fast moving layers giving rise to viscosity of gases. Viscosity, or the co-efficient of viscosity, is defined as the force per unit area exerted between two parallel layers one cm apart, when the velocity of streaming differs by unity in the two layers. (A more detailed treatment of viscosity is given in *Section 3.11*).

The mean free path of a gas may be determined from measurements of its viscosity. Viscosity of gas may be measured in the same way as for a liquid (*Section 3.13*).With the help of the kinetic theory a relation between the coefficient of viscosity, η, and the mean free path, l, has been deduced. The relation is

$$\eta = \frac{1}{2} mn\bar{c}l \qquad (2.45)$$

where m is the mass of one molecule, n is the number of molecules in 1 ml, $\bar{c}$ is the average velocity and l is the mean free path..

2.21 Molecular Diameter

Substituting the value for l, as given in equation (2.44), in equation (2.45) it follows that

$$\eta = \frac{\frac{1}{2} m\bar{c}}{(\sqrt{2}\pi\sigma^2)} \qquad (2.46)$$

This equation may be used to calculate σ from a knowledge of η, the coefficient of viscosity. As the repulsive forces operate only when the molecules are very close, σ may be taken as a measure of the molecular diameter of gases. Some values of σ are given in Table 2.2.

Table 2.2 Molecular diameter

Gases	$\sigma \times 10^8$ cm
Helium	2.18
Argon	3.36
Chlorine	4.96
Nitrogen	3.50
Carbon dioxide	4.18
Hydrogen	2.47

Molecular diameter calculated by other methods, e.g., X-ray and electron diffraction are in close agreement with those calculated from viscosity of gases.

2.22 Frequency of Collisions of Gas Molecules

The number of collisions undergone by a molecule of gas in one second, i.e., the frequency of collisions, may be calculated from the mean free path and the average velocity. If a molecule travels, on an average, a distance l cm before being hit by another molecule and its average velocity is $\bar{c}$, then the number of collisions that this particular molecule will undergo in one second in a volume of 1 mL is given by,

$$\frac{\bar{c}}{l} = \frac{\sqrt{8RT/\pi M}}{1/(\sqrt{2}\,\pi\sigma^2 n)} = 4\sigma^2 n\sqrt{\frac{\pi RT}{M}} \qquad (2.47)$$

Since there are n molecules in unit volume, the total number of collisions undergone by all the molecules in 1 mL is the product of the right hand side of equation (2.47) and n. But in this calculation each collision has been counted twice – once when the molecule hits another molecule and again when it is hit by another molecule. The correct number of collisions is obtained by introducing a factor $\frac{1}{2}$ in the product, so that the frequency of collisions, Z, is given by

$$Z = \left(\frac{1}{2}n\right) 4\sigma^2 n\sqrt{\frac{\pi RT}{M}}$$

$$= 2\sigma^2 n^2\sqrt{\frac{\pi RT}{M}} \qquad (2.48)$$

Example 2.11: Calculate the frequency of collisions for oxygen molecules at 0°C and 1 atm pressure. Collision diameter = 3.64×10^{-8} cm.

Solution: $n = \dfrac{6.02\times10^{23}}{22{,}414} = 2.58 \times 10^{19}$

$$Z = 2(3.64 \times 10^{-8})^2 (2.58 \times 10^{19})^2 \sqrt{\frac{(3.14)(8.32\times10^{7})(273.16)}{32}}$$

$$= 9.02 \times 10^{28}\ mL^{-1}\ s^{-1}.$$

It may be seen from the example that the frequency of collisions between molecules is rather high, about 10^{28} collisions in 1 mL in one second even at ordinary temperature. When the temperature increases the frequency of collisions also increases.

2.23 Number of Molecules Striking a Surface

The kinetic theory of gases may be used to deduce the number of molecules striking 1 sq cm of surface in one second. The expression obtained for this number is $nc/4$ where n is the number of molecules in 1 mL and c is the average velocity. The number of molecules striking unit area of a surface is useful in calculating the rate of evaporation of liquids or the rate of sublimation of solids, and other properties.

2.24 Avogadro Number

According to Avogadro's hypothesis equal volumes of all gases under the same conditions or temperature and pressure contain the same number of molecules. This number, i.e., the number of molecules in 1 mole of a gas, is called *Avogadro number.* It is a fundamental constant of physical chemistry. The number of atoms in 1 mole of atoms or the number of ions in 1 mole of ions has also the same value. The best value of this number is 6.023×10^{23})

The basis for accepting this as fundamental constant in physical chemistry is that different types of accurate measurements based on different principles yield the same value. Some of the experiments which have established the value of the Avogadro number are given below,

(i) Distribution of very small solid particles in different layers when these are suspended in a liquid medium.

(ii) Microscopic observation of the random displacement of small particles.

Both (i) and (ii) were carried out by Perrin with different particles and at various temperatures.

(iii) Determination of the charge of an electron by the oil-drop experiment of Millikan and the value of the Faraday constant of electrolysis.

(iv) From the determination of the charge on the *alpha* particles from radium by Rutherford.

(v) From a determination of the constants of radiation by Planck.

(vi) Direct determination of the wave-length of X-rays.

The usefulness and applications of the Avogadro number are numerous. For example, the mass of a single atom or molecule of a substance may be obtained by dividing the respective atomic or molecular mass by the Avogadro number. Thus, the mass of an atom of helium is $4.003/(6.023 \times 10^{23}) = 6.65 \times 10^{-24}$ *g*; the mass of a molecule of oxygen is $32.000 / (6.023 \times 10^{23}) = 5.32 \times 10^{-23}$ *g*.

Avogadro number also enables one to calculate the number of molecules in a given volume of gas or a given mass of substance. For example, the number of molecules

in 1 mL of hydrogen at 1 atm and 0°C = $(6.023 \times 10^{23}) / 22{,}414 = 2.63 \times 10^{19}$;

in 1 g of water is $(6.023 \times 10^{23}) / 18 = 3.34 \times 10^{22}$.

2.25 The Kinetic Theory – a review: Brownian Movement

The kinetic theory presupposes the existence of molecules. We have just seen that, the behaviour of gases can be explained in a more or loss satisfactory manner with the help of the kinetic theory. The question arises as to whether this agreement of experiment with theory is the only basis of the acceptance of the existence of the kinetic theory of matter or is there any direct evidence of the existence of molecules and their erratic movement. The molecules are too small to be seen under the most powerful microscope. An attempt at direct observation of molecules and their movement would, therefore, be futile. It is important, however, to consider other evidences which will justify the assumptions of the kinetic theory. One such evidence was provided by the experiments of the botanist Robert Brown.

Brown, while experimenting with pollen grains, observed that when suspended in a liquid these extremely small particles were in continuous irregular zigzag motion. This motion of suspended particles which was later observed for emulsions of mastic or gamboge and also of minute colloidal particles is known as the *Brownian movement*. The cause of this movement has been the subject of much investigation. It was established that the motion is not due to thermal or mechanical agitation, for it persists when placed in underground cellers for years. It is also not due to light used in observing the particles under the microscope, as the same movement was observed even when the intensity of light was decreased thousand-fold. The nature of the particles has very little influence upon their movement, but their size has considerable effect– the smaller the particles, more violent the movement. In all cases the movement was found to go on indefinitely.

The explanation of the phenomenon of Brownian movement is that the violent *zigzag* motion of the particles is caused by the collision of the suspended particles with the molecules of the medium which are in continuous irregular motion themselves. The movement of the particles is, therefore, a reflection of the movements of the molecules. This qualitative explanation was put on a firm experimental basis by Perrin who determined Avogadro's number from consideration of Brownian movement. As pointed out in *Section. 2.24* the value of the Avogadro number is in remarkable agreement with that obtained from experiments based on totally different principles.

It has been pointed out earlier that the gas laws, e.g., Boyle's law, Charles' law etc. are valid only under conditions of low pressures and/or high temperatures. At high pressures and/or low temperatures real gases show deviations from these laws. This means that the predictions of the kinetic theory are not in agreement with the experiments with real gases under these conditions. As experiment has the upper hand in cases of such disagreements, it must be concluded that there is something wrong with the assumptions made in the kinetic theory.

2.26 Behaviour of Real Gases: The Amagat's Curves

The ideal gas law equation $PV = nRT$ is not obeyed by most gases, particularly at high pressures or low temperatures. This was experimentally established by Regnault, Amagat and others. During the nineteenth century Amagat showed that the product of P and V, i.e., PV, is not quite independent of P, even for gases like H_2, O_2, N_2 etc. This is contrary to Boyle's law. The nature and magnitude of the deviation are clearly demonstrated from a plot of PV against P as in Figure 2.8. These curves are known as *Amagat's curves*. In these curves PV is arbitrarily taken as unity at 1 atmosphere and at the temperature of the experiment. If a gas obeyed Boyle's law the curves would be horizontal lines with a constant ordinate equal to RT.

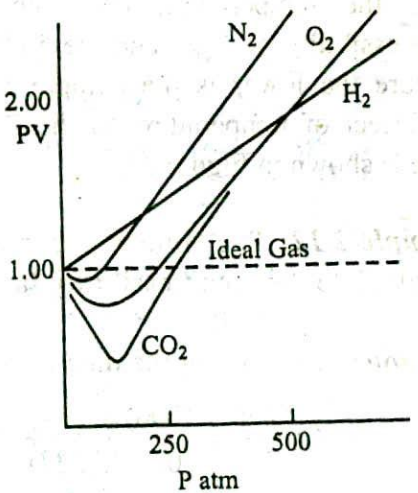


Figure 2.8 Amagat's curves

It will be observed that the curve for hydrogen shows steady rise in the value of PV as P increases; for the other gases shown it first passes through a minimum and then rises for still higher values of P. Based on these experiments the following conclusions were made:

(a) the inert gases give curves exactly like hydrogen,

(b) gases which are most easily liquefied deviate to a greater extent from the ideal behaviour and
(c) at relatively high temperatures most gases follow curves of the type obtained for hydrogen.

The behaviour of real gases may also be described in terms of a compressibility factor Z which is defined as,

$$Z = \frac{PV}{RT} \tag{2.49}$$

For one mole of an ideal gas $Z = 1$, and is independent of temperature and pressures. At high pressures the real gases are less compressible, i.e., they have large volume than what is expected from the Boyle's law. At low temperature the gases, particularly the easily liquefiable ones, show more compressibility, i.e., the volume is less than that predicted by Boyle's law. In general, one may roughly say that the lower the temperature, the higher the compressibility of a gas and the higher the pressure the lower is the compressibility. The effect of temperature on the *Z vs. P* curve is shown in Figure 2.9.

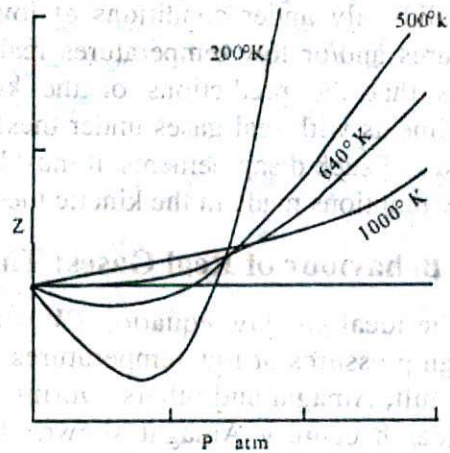


Figure 2.9 *Z* vs *P* at different temperature

Example 2.12: The volume occupied by a certain gas at 60°C and 200 atm. is 0.124 L. Calculate the compressibility factor of the gas.

Solution: Substituting the data in equation (2.48) and solving for Z,

$$Z = \frac{PV}{RT} = \frac{(200)(0.124)}{(0.082)(333)} = 0.908$$

2.27 Modification of the Ideal Gas Equation: van der Waals' Equation of State

It has been pointed out (*Section 2.25*) that in the event of a genuine conflict between theory and experiment the conclusion is generally made that there must be something wrong with the theory. The ideal gas equation has been derived from the kinetic theory of gases with the help of some simplifying assumptions. van der

Waals (1873), a Dutch physicist, pointed out that the following two assumptions of the kinetic theory of gases (*Section 2.12*) may not be correct, particularly at high pressures and at low temperatures:

(a) the volume of the gas molecules is negligible compared to the volume of the container,

(b) the molecules do not exert any force of attraction on each other.

van der Waals introduced corrections into the ideal gas equation to account for the above assumptions.

(a) Volume correction: The molecules, being incompressible themselves, will have a certain volume of their own. This volume may not be negligible when the pressure is very high. A simple calculation will prove this point. Taking the average molecular diameter as 4×10^{-8} cm, the volume of one molecule $= \frac{4}{3}\pi (2 \times 10^{-8})^3$ mL. The volume of one mole (i.e., Avogadro number of molecules) of the gas is,

$$\frac{4}{3}\pi (2 \times 10^{-8})^3 \times 6.023 \times 10^{23} \text{ mL} = 19.8 \text{ mL}.$$

The molar volume of a gas, i.e., the volume occupied by one mole of a gas at 1 atm pressure and 0°C, is 22,414 mL. At 1.0 atmosphere pressure the volume of the molecules themselves, 19.8 mL, is negligible compared to the volume of the container in which the gas is contained. But when the pressure is 1000 atmosphere the latter value becomes 22.414 mL. Compared to this value the volume 19.8 mL of the gas molecules themselvescannot be negligible.

The volume of the gas, by which is meant the free space available to the gas molecules for free movement, is not V, the volume of the vessel, but less than V by a quantity b. At constant temperature $(V - b)$, and not V, will vary with pressure according to Boyle's law. It can be seen that b is related to the size of the gas molecules and hence a rough idea of the molecular size may be obtained if b can be evaluated. b is not, however, the actual volume of the molecules, but is about 4 times the actual volume of the molecules.

(b) Pressure correction: The fact that gases can be liquefied, and the existence of the Joule-Thomson effect, i.e., the cooling of a gas when forced through a porous plug (*Section 5.14*), indicate that molecules possess attractive forces for one another. These forces, known as *van der Waals' forces*, arise from the attractive forces of electrons and protons in one atom or molecule for these in other atoms or molecules. The magnitude of these forces depends, besides other factors, on the distances between the molecules and their masses. When a gas is compressed the molecules get closer to each other and the effect of these forces becomes noticeable. As the temperature is

lowered, the molecules become sluggish as their kinetic energy decreases and they have less ability to overcome the attractive forces. At higher temperature the molecules move at higher speeds in a random fashion; although the attractive forces try to draw the molecules together, they stay away from each other because of the motion.

The effect of the attractive forces is that the real pressure P of the gas molecules is less than the pressure they would exert if there were no attraction for one another. Consider a molecule in the interior of the vessel. As this is being acted upon by forces from all directions the total effect is nil. On the other hand, a molecule about to strike the wall has its momentum reduced by an unbalanced force trying to pull the molecules towards the interior and away from the wall. The measured pressure is thus lower by a quantity p_a than the pressure the gas would exert if it were ideal. The pressure of the gas, if it were ideal, would then be $P + p_a$. This is the quantity that is calculated from the kinetic theory.

The quantity p_a may be evaluated as follows: A molecule about to strike the wall will be pulled back by attraction from all the other molecules in the neighbourhood; the attractive force will then be proportional to the density ρ, i.e., the number of molecules per unit volume. Again, the average number of molecules which will strike the wall is also proportional to ρ. The total force trying to pull the molecules about to hit the wall will be proportional to ρ^2 or $1/V^2$. Hence $p_a = a/V^2$, where a is a constant for the gas.

With the introduction of volume correction and pressure correction the gas equation, $PV = RT$, takes the form

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{2.50}$$

This is known as the van der Waals' equation of state for 1 mole of gas. For n moles the equation becomes

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{2.51}$$

The values of a and b in the van der Waals' equation may be calculated by solving the simultaneous equations obtained from measurements of pressure or volume at two different temperatures for a given mass of gas and substituting the values in equation (2.50) or (2.51). These constants may also be calculated in other ways (*Section 2.33*). Values of a and b for some gases are given in Table 2.3.

Table 2.3 van der Waals constants for few gases

Gas	a (L^2-atm-mol^{-2})	b(L mol^{-1})
He	0.034	0.0234
H_2	0.244	0.0266
O_2	1.360	0.0318
CO_2	3.610	0.0429
H_2O	5.720	0.0319
Cl_2	6.490	0.0562
NH_3	4.000	0.0360
C_3H_8	8.660	0.0845
n-C_5H_{12}	19.010	0.1460

It may be noticed that gases like hydrogen and helium which are difficult to liquefy have low values of a, whereas the easily liquefiable gases like ammonia, steam etc. have high values of a. The constant a is thus a measure of the magnitude of intermolecular attraction. The value of b is lowest for helium and highest for n-pentane in this Table indicating that b is a measure of the size of the molecule. The units in which a and b are expressed are to be noted.

Example 2.13; Calculate by using van der Waals equation the pressure exerted by 1 mol of CH_4 in a 250 mL container at 300K. For CH_4 a = 2.253 L^2- atm-mol^{-2} and b= 0.0428 L mol^{-1} . Repeat the calculation assuming that CH_4 behaves as an ideal gas.

Solution: Equation (2.51) can be written as, $P=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}$

Substituting the given data we get, $P=\frac{1\times0.0821\times300}{0.250-(1\times0.0428)}-\frac{1^2\times2.253}{(0.250)^2}=82.8\ atm$

According to ideal gas equation,

$$P=\frac{nRT}{V}=\frac{1\times0.0821\times300}{0.250}=98.5\ atm$$

We see that the discrepancy is very large, since the van der Waals constants a and b vary somewhat with pressure and temperature.

2.28 Significance and Limitations of van der Waals Equation

The success of the van der Waals equation lies in the fact that it can explain the variation of PV with P in Amagat's curves. At very low pressures both a and b may be neglected as the molecules are far apart and b is an insignificant fraction of V. The equation takes the form $PV = RT$. When the pressure is slightly greater, b may be neglected compared to V and the van der Waals' equation may be written as

$$(P+\frac{a}{V^2})V = RT$$

or
$$PV = RT - \frac{a}{V} \qquad (2.52)$$

PV is less than RT by a/V, i.e. PV decreases with increase of P.
The van der Waals' equation (2.50) may also be written as,

$$P(V-b) + \frac{a}{V^2}(V-b) = RT$$

or
$$P(V-b) + a(\frac{1}{V} - \frac{b}{V^2}) = RT$$

At high pressures $\frac{1}{V} - \frac{b}{V^2}$ becomes negligible as the two terms are not very much different from one another. Neglecting the second term on left hand side one obtains

$$P(V-b) = RT$$

or
$$PV = RT + Pb \qquad (2.53)$$

According to equation (2.53), PV increases with increase of P. These deductions are in agreement with Amagat's observations that for real gases with the increase of P the value of PV first decreases, passes through a minimum and then gradually increases. It may be observed that at low pressures the pressure correction has prominence, while when the pressure is high the volume correction predominates.

In the case of hydrogen and helium the values of a are smaller than those of b so that the volume correction predominates all along the range of pressures; PV increases as P is increased at ordinary temperatures (Figure 2.8). A point of considerable importance is that the van der Waals' equation is also applicable to gas-liquid transitions and liquids as will be seen in *Section 2.30*. The agreement of PV values calculated from van der Waals equation with experimental results are shown in Table 2.4 for ethylene at 20^0C. It is evident that over a wide range of pressures PV varies considerably but the values are in agreement with those calculated from van der Waals' equation.

Table 2.4 Change of PV with P for ethylene at 20°C

P(atmosphere)	PV (observed) in arbitrary units	PV (calculated) from van der Waals equation
1.0	1000	1000
31.6	914	895
84.2	399	392
110.5	454	456
233.6	807	805
329.1	1067	1067
398.7	1248	1254

The success of van der Waals equation should not, however, overshadow its limitations. At very high pressure the equation is inadequate for calculating the properties of gases. Moreover, experiment shows that the values of a and b, which were regarded as constants by van der Waals, change when the temperature is varied. Also b is not constant at all pressures.

Example 2.14: Calculate the pressure exerted by one mole of carbon dioxide in a 500 mL container at 300 K using van der Waals' equation. For CO_2 the values of the constants are: $a = 3.61$ L^2-atm-mol^{-1}, $b = 0.0429$ L mol^{-1}, and $R = 0.082$ L-atm mol^{-1} K^{-1}. Compare this value with the value obtained by using the ideal gas equation.

Solution: $V = 500$ mL $= 0.50$ L
Substitution in equation (2.49) gives

$$\left(P + \frac{3.61}{(0.50)^2}\right)(0.50 - 0.0429) = 0.082 \times 300$$

(On calculation we find $P = 39.4$ atm
Ideal gas equation gives $P = RT/V = (0.082 \times 300)/0.50 = 49.2$ atm

2.29 Other Equations of State

Many other equations of state have been proposed at different times. None of those were, however, entirely satisfactory; neither did these have better theoretical foundation than the equation of van der Waals and consequently have not found general acceptance. The most general equation relating P, V and T of a gas is that due to the Dutch physicist, H. Kammerling Onnes (1901), and is written as,

$$PV = RT\left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \quad \ldots\ldots\ldots\right] \tag{2.54}$$

where $B(T)$, $C(T)$, etc. which are functions of the temperature, are called the *virial coefficients*. This equation is superior in the sense that other equations of state may be derived from this equation by suitable replacement of the values of the virial coefficients.

2.30 Change of State: Gas-Liquid Transition

The kinetic theory of matter suggests that when a gas is subjected to high pressure the molecules will be brought closer to one another enabling them to exert attractive forces on each other. When the temperature is decreased the kinetic energy of the molecules would decrease so that the molecules would be sluggish and will not have enough energy to get away from each other after collisions. Either one or both of the operations of increasing pressure and decreasing temperature would, therefore, bring about liquefaction of gases. Long before the kinetic theory of matter was accepted

scientists were able to liquefy most gases by application of pressure or by decrease of temperature or both. Some gases like H_2, N_2, He etc. escaped attempts at liquefaction even at the very low temperatures that could be attained at the time. These gases were called *permanent* gases. It was soon to be realized, however, that all gases can be liquefied under proper conditions of T and P.

2.31 Andrews' Experiments with CO_2

From 1861 to 1870 Andrews carried out his famous experiments on the effect of temperature and pressure on the volume of carbon dioxide. He used a simple apparatus (Figure 2.10) for the purpose. The apparatus consists of a thick-walled glass capillary tube T containing the gas which is enclosed with a drop of mercury. The capillary tube T is sealed into the metal compression chamber, M, by means of liquid-tight joint. The chamber, M, contained water and is connected through C to an exactly similar chamber with a glass tube of the type T but containing air. This latter tube served as manometer. The experimental gas is contained in the capillary tube T. The pressure applied on the water by screwing up the screw, S, is hydraulically transmitted from water to the volume of the air. The upper part of the carbon dioxide tube was surrounded by a heating bath so that the temperature could be varied.

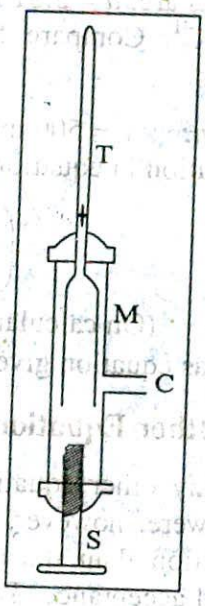


Figure 2.10 Andrew's apparatus for liquefaction of carbon dioxide

The volumes of the same mass of carbon dioxide at different pressures and at different constant temperatures were plotted by Andrews to obtain the curves shown in Figure 2.11. These curves are known as *isothermals* as each curve represents P-V data at a given temperature.

Consider the isothermal corresponding to the temperature T_1°C. When the pressure is low the volume is large as at A. As the pressure is increased the volume decreases nearly in accordance with Boyle's law. When a certain volume B is reached liquefaction starts, the volume decreases rapidly but the pressure remains constant. The isothermal is horizontal until all of the gas is liquefied and the

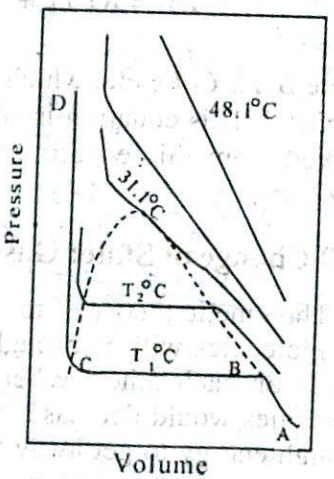


Figure 2.11 P-V isothermals for carbon dioxide

point *C* is reached. The portion *CD* of the isothermal represents the effect of pressure on the volume of liquid carbon dioxide. This part is steep, almost vertical, indicating that the liquid is much less compressible than the gas. *AB* represents the behaviour of carbon dioxide gas. Along *BC* both liquid and gas exist side by side (co-exist) and are in equilibrium, the pressure remaining the same. The pressure is not dependent on the relative quantities of liquid and gas. It will be seen later that *the pressure at which a liquid and its vapour are in equilibrium at a given temperature, and known as the vapour pressure of the liquid,* is an important quantity. The isothermal at T_2°C shows the same characteristic as that for T_1°C except that the horizontal portion showing the range of co-existence of liquid and gas is shorter than that for T_1°C. At higher temperature the horizontal portion gets rapidly shorter and, in fact, at 31.1°C and above there is no horizontal portion at all. At 31.1°C there is just a slight hump, showing a very short range of co-existence of liquid and gas. Andrews found that in the liquefaction of carbon dioxide the temperature 31.1°C was critical in the sense that at any temperature above this value carbon dioxide gas could not be liquefied even at a pressure of 300 to 400 atmospheres, whereas below this temperature a much lower pressure would be sufficient to liquefy the gas. Subsequently it was found that for all gases this is a common phenomenon, the temperature depending on the nature of the gas. The following critical phenomena can, therefore, be defined

(i) *This temperature above which a gas cannot be liquefied, however high the pressure may be, is called the* ***critical temperature*** *of the gas.*

(ii) *The pressure which is just sufficient to bring about liquefaction of the gas at the critical temperature is known as the* ***critical pressure.***

(iii) *The volume occupied by 1 mole of the substance at the critical pressure and temperature is called the* ***critical volume.***

(iv) *The pressure-volume curve at the critical temperature is like-wise referred to as the* ***critical isotherm.***

It has been found that the ends of the horizontal portion of the isotherm approximately fall on a parabola and the apex of the parabola is on the critical isotherm. Table 2.5 shows the critical constants of some substances. It may be seen that the values vary greatly for different gases.

Table 2.5 Critical constants (*T*, *P* and *V*) of gases

Substance	Temp (°K)	Press (atm)	Vol (L mol^{-1})
He	5.20	2.26	0.0574
H_2	33.20	12.80	0.0650
N_2	126.00	33.50	0.0901
O_2	154.30	49.70	0.0901
CO_2	304.20	72.90	0.0942
NH_3	405.50	111.50	0.0720
CH_4	190.20	45.60	0.0990

The case of the so-called permanent gases now becomes clear. These could not be liquefied because they were not cooled below their critical temperatures before applying pressure. At that time the techniques of obtaining very low temperatures had not been developed. All known gases have since been obtained in the liquid state.

2.32 Determination of Critical Constants

Long before Andrews performed his experiments with carbon dioxide, Caignard de La Tour (1822) observed that when ether was heated in a sealed tube, the surface of separation between liquid and its vapour disappeared at a particular temperature; but on cooling the surface reappeared at about the same temperature. The significance of these observations was not realized until Andrews correlated this with his work on carbon dioxide. He observed that the temperature at which the surface of separation between liquid and its vapour disappears is the same at which he observed the critical phenomenon.

These observations have been utilized for the determination of the critical constants. Critical pressure and temperature may be determined fairly easily by using an apparatus as shown in Figure 2.12, similar to Caignard de La Tour's apparatus.

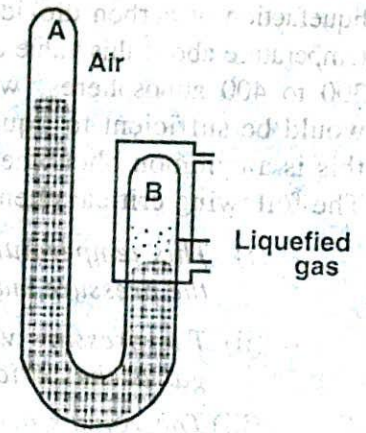


Figure 2.12 Caignard de La Tour's apparatus

It consists of a thick-walled glass *U-tube* one limb of which is longer than the other. The shorter end containing liquid in contact with its saturated vapour is sealed and is surrounded by a heating jacket. The other limb of the *U-tube*, which serves as manometer, has air at its upper end *A*, the rest of the tube being filled with mercury.

The end *B* is gradually heated by passing hot air or vapour through the jacket and the temperature at which the meniscus separating liquid and vapour just disappears and at which it reappears on cooling is noted. The average of the two is the *critical temperature*. The volume of the air in the limb *A* is also noted at this temperature and the critical pressure is calculated from this.

When the liquid and its vapour are gradually heated the density of the liquid decreases, but the density of the vapour increases because of compression until at the critical temperature and pressure the densities of both liquid and vapour become equal, and the liquid and vapour become indistinguishable from each other. This is the reason why at the critical point the surface of separation vanishes.

The critical volume is more difficult to determine. It is obtained with the help of a rule known as the *law of rectilinear diameter* discovered by Cailletet and Mathias (1886). The law states that the mean value of the densities of liquid and saturated vapour for a stable substance, measured at the same temperature, is a linear function of the temperature. If ρ_m is the mean of the densities at a temperature T, then

$$\rho_m = \rho_o + \alpha T \tag{2.55}$$

where ρ_o = density at $T = 0$ and α is a constant.

This law holds fairly accurately for a number of substances but is not strictly true in all cases. The applicability of the law of Cailletet and Mathias is illustrated in Figure 2.13 for CO_2 (from Amagat's data). The curves AC and BC represent densities of the liquid and vapour respectively at different temperatures. The two curves when extended meet at C which is the critical temperature.The mean densities fall on the line CD, which shows the validity of the law.

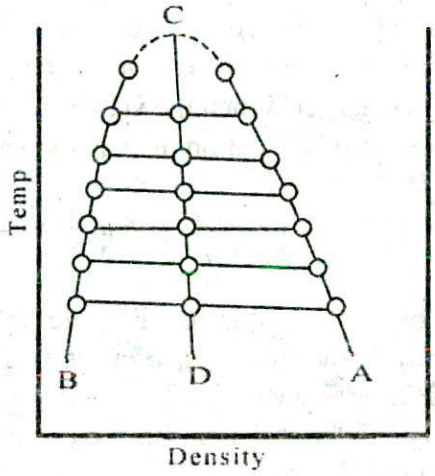


Figure 2.13 *T vs* ρ showing the validity of the law of *rectilinear diameter*

To determine the critical volume of the substance the densities of liquid and vapour are measured at different temperatures near the critical temperature. These are then plotted as in Figure 2.13. The mean of the densities at the same temperature is then calculated and the mean values at different temperatures are joined by a straight line. The straight line is now extended and the mean density at the critical temperature is obtained from the graph. The critical volume (V_c) per gram of the substance is equal to the reciprocal of the mean density (ρ_c) at the critical temperature, i.e.

$$V_c = \frac{1}{\rho_c} \tag{2.56}$$

The densities of the liquid and the vapour at a given temperature are obtained as follows: A known mass of liquid is taken in a graduated sealed tube and its temperature raised to the desired value. The mass is given by

$$m = \rho_l V_l + \rho_g V_g \tag{2.57}$$

where ρ_l and V_l are the density and volume of the liquid phase and ρ_g and V_g are the corresponding values for the vapour phase, the volumes being read off the

graduations. A different mass of liquid is similarly heated to the same temperature and the corresponding volumes of liquid and vapour measured. From the two simultaneous equations obtained by substituting the experimental quantities in the above equation, ρ_l and ρ_g at that temperature may be obtained.

2.33 van der Waals Equation and the Critical Phenomena

The isotherms obtained by plotting the curve $PV = nRT$ are rectangular hyperbolas. Gases approximate to this isotherm at low pressures and high temperatures. The behaviour of real gases, however, is better represented by the van der Waals' equation as pointed out earlier. When the van der Waals' equation for one mole is suitably rearranged, we obtain a cubic equation in V as shown below:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \qquad (2.58)$$

If one plots this equation graphically in the form of a $P-V$ isotherm, a curve of the type $ABCFDGE$ (Figure 2.14) is obtained. Such curves may be termed as van der Waals isotherms.

This equation has three roots, i.e., three values of V for any given value of P and T. All three roots may be real, or one or two roots real and the others imaginary. When the roots are real and different, three different values of V (for a given P and T) are shown by the points B, F and G in curve I. As T increases the three points get closer until they are identical, as in the critical isotherm, curve *II*. At higher temperatures the curve approximates a rectangular hyperbola, curve *III*, there being one real root and two imaginary roots.

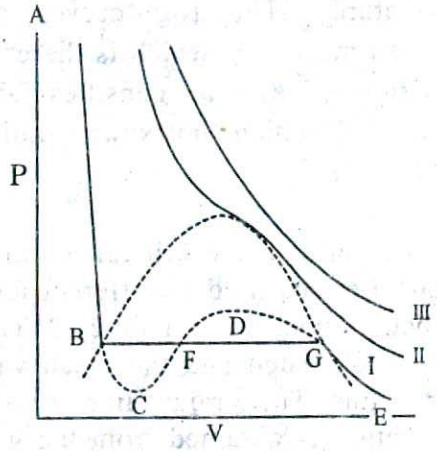


Figure 2.14 Isotherms for CO_2 according to van der Waals' equation

Andrews' experiments with carbon dioxide are in agreement with the deduction from the van der Waals equation except for the ~ shaped portion. Andrews obtained the horizontal portion representing condensation of the gas, i.e., the equilibrium between gas and liquid. Since three roots of the equation (2.58) are identical at the critical temperature, there is only one value of V, namely, the *critical volume*, V_c, which will satisfy this equation when the pressure and temperature have the critical values, P_c and T_c.

5-B

It is possible to express the critical constants in terms of the van der Waals constants in the following way:

A cubic equation in V, which has three identical roots, V_c, may be written in the form

$$(V - V_c)^3 = 0 \tag{2.59}$$

Expanding this we obtain

$$V^3 - 3V^2.\ V_c + 3V.\ V_c^2 - V_c^3 = 0 \tag{2.60}$$

Under the same conditions equation (2.58) becomes

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}.V - \frac{ab}{P_c} = 0 \tag{2.61}$$

Since equations (2.60) and (2.61) are simply different ways of writing the same equation, the co-efficient of V^3, V^2, V etc. must, therefore, be the same in both the equations. Equating the co-efficients one obtains,

$$3V_c = b + \frac{RT_c}{P_c};\ 3V_c^2 = \frac{a}{P_c};\ V_c^3 = \frac{ab}{P_c} \tag{2.62}$$

From these equations one can obtain the following values for P_c, V_c, and T_c :

$$V_c = 3b\ ;\ P_c = \frac{a}{27b^2}\ ;\ T_c = \frac{8a}{27Rb} \tag{2.63}$$

If the values of a and b are known, the critical constants may be calculated. Conversely, the equations may be rearranged to obtain the expressions

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \text{ and } \quad b = \frac{RT_c}{P_c} \tag{2.64}$$

so that one can calculate a and b from the critical temperature and pressure. The critical volume, V_c, has been eliminated from this expression as this is generally less accurately known than the values of P_c and T_c. By combining the equations (2.62) one may obtain the relation

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} \text{ or } 2.67 \tag{2.65}$$

This relation indicates that the ratio RT_c/P_cV_c should be equal to 2.67 for all substances irrespective of its nature. Experimental data in Table 2.6, however, show that though RT_c/P_cV_c is almost constant for a large number of substances, elements or compounds, the value is always higher than 2.67. This is a serious discrepancy and no satisfactory explanation of it is known.

Table 2.6 Values of the ratio RT_c/P_cV_c

Substance	RT_c/P_cV_c	Substance	RT_c/P_cV_c
H_2	3.05	CO_2	3.64
He	3.13	CCl_4	3.68
A	3.35	C_2H_4	3.64
Xe	3.60	$n\text{-}C_6H_{14}$	3.83
O_2	3.42	$CH_3COOC_2H_5$	3.88
N_2	3.42	$ZnCl_2$	3.74

The whole trouble lies in the fact that the van der Waals' equation is not very accurate near the critical state. This means that the van der Waals' equation, although an improvement over the ideal gas equation, cannot be used for a precision calculation of the gas properties, as has been pointed out earlier. One great virtue of the van der Waals' equation, however, lies in the fact that it predicts the existence of a critical state for all substances, and a study of its prediction gives an excellent insight into the relation between gases and liquids and the phenomena of liquefaction.

2.34 Continuity of State

At the critical temperature the boundary between the liquid phase and gas phase disappears and the densities of the substance in the two phases are the same. These observations led Andrews to believe that there is no difference between the liquid and the gas at the critical temperature. He went on further to state that the ordinary gaseous and liquid states are only widely separated states of matter and that one state may be made to pass to the other by a course of continuous physical changes representing nowhere any break of the continuity. In other words, transfor-mation from the gaseous state to the liquid state, or vice versa, may be made gradually, without passing through the phenomenon of conden-sation, i.e., nowhere during the transformation two phases will co-exist. This is Andrews *'theory of the continuity of state'*.

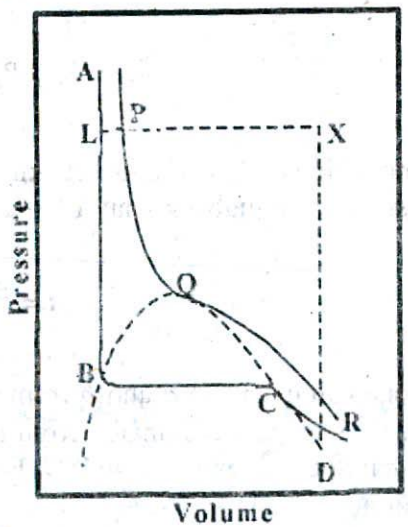


Figure 2.15 Continuity of state

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The idea of the continuity of state may be understood more clearly with reference to Figure 2.14 where the parts *BC* and *GD* of curve I (and of similar curves below the critical temperature) can be realized experimentally. If a gas is compressed isothermally in a perfectly clean and smooth vessel the volume decreases along the isothermal *EG* until the point *G* is reached, when liquefaction should start. However, it may so happen that liquid does not form and further increase in pressure produces a decrease in volume along the line *GD*. Along *GD* the gas may be termed as supersaturated or supercooled vapour. Any attempt at increase of pressure beyond *D* results in sudden liquefaction. Similarly, the section *BC* of the isotherm may be realized, i.e. with the reduction of pressure the volume of the liquid increases along *BC* without vaporization starting at *B*. The system is unstable along *BC* in the sense that a slight disturbance would be sufficient to cause the system to revert spontaneously to the stable state, with the liquid and vapour in equilibrium. The part *CFD cannot* be realized experimentally as this represents the impossible situation that the volume increases when the pressure is increased.

In spite of this there is an element of continuity from the gaseous state to the liquid state as the continuous curve *ABCFDGE* represents the *P-V* relation of the substance in both the states. We have seen earlier that the van der Waals' equation mathematically represents curve *I*, whereas it is impossible to get an analytical expression which will correspond to the isothermals below the critical temperature as obtained by Andrews.

The essential feature of the idea of the continuity of state may be demonstrated from yet another point of view. Consider Andrews isothermal for a gas, Figure 2.15. If the gas is heated, keeping the volume constant, pressure will rise along *DX*. Now decrease the temperature keeping the pressure constant; the volume will decrease along *XL*. The point *L* is on that portion of the isothermal *ABCD* which represents the liquid state. Thus the substance which was gaseous at *D* has been converted into a liquid at *L*, but at no time there was more than one phase. Somewhere along the line *XL*, most probably at *P*, the gas has turned into liquid; to the left of the critical isotherm *PQR* it is all liquid but to the right it is gaseous. The change from the gaseous to the liquid state has been gradual and transition may be regarded as continuous.

2.35 The Equation of the Corresponding States

Using the values of *a* from equation (2.62), *b* from equation (2.63) and *R* from equation (2.65) in terms of the critical constants the van der Waals' equation may be written in the form

$$\left(P+\frac{3V_c^2 P_c}{V^2}\right)\left(V-\frac{V_c}{3}\right)=\frac{8}{3}\frac{P_c V_c T}{T_c} \qquad (2.66)$$

This can be rearranged to the form by dividing by P_cV_c.

$$\left(\frac{P}{P_c}+\frac{3V_c^2}{V^2}\right)\left(\frac{V}{V_c}-\frac{1}{3}\right)=\frac{8}{3}\frac{T}{T_c} \qquad (2.67)$$

If the pressure, volume and temperature of a gas are expressed in terms of their critical values such that

$$\frac{P}{P_c}=\pi;\ \frac{V}{V_c}=\varnothing \text{ and } \frac{T}{T_c}=\theta, \text{ then equation (2.67) becomes}$$

$$(\pi+\frac{3}{\varnothing^2})\,(\varnothing-\frac{1}{3})=\frac{8}{3}\theta$$

$$\text{or } (\pi+\frac{3}{\varnothing^2})\,(3\varnothing-1)=8\theta \qquad (2.68)$$

Here π *is called the reduced pressure,* $\varnothing$ *the reduced volume and* θ *the reduced temperature.* Equation (2.68) is called *the reduced equation of state or the equation of corresponding states.*

The important thing about this equation is that it does not contain any constant which is peculiar to the individual gas; therefore, it should be capable of describing all gases. In this respect the reduced equation is perfectly general unlike van der Waals equation which has the constants, *a* and *b*, both depending on the individual gas. Otherwise, the reduced equation has the same properties as the van der Waals equation, e.g., it has three roots and represents the behaviour of substances both in the liquid and gaseous states.

If two or more substances are at the same reduced temperature and under the same reduced pressure then according to equation (2.68) their reduced volumes should also be equal. When these conditions are fulfilled the substances are said to be in *corresponding states* and the above statement is taken as the expression for *the law of corresponding states.* For many substances the law is in agreement with experimental results but there are also considerable discrepancies, particularly in the case of alcohols etc. In fact the reduced equation of state has been found to have the same limitations as the van der Waals equation from which it is derived.

2.36 Liquefaction of Gases – the Basic Principles

Liquefaction of gases is an exercise which had attracted the attention of scientists from very early times. As pointed out at the beginning of this chapter, increased pressure and lowering of temperature are used together or singly for the purpose. In many cases the investigators succeeded in liquefying easily liquefiable gases like NH_3, SO_2, Cl_2, HCl etc. Notable among the early work is due to Faraday (1823) who used a very simple device and was able to liquefy SO_2, H_2S, CO_2, N_2O and NH_3. He used an inverted *U-tube* (Figure 2.16) in one limb of which the gas was prepared from suitable

reagents and in the other the gas was liquefied under its own pressure with the help of cooling by immersion in a freezing mixture of ice and salt.

Thilorier (1834) used Faraday's apparatus, but made of wrought iron instead of glass, to liquefy CO_2 in large quantities, and even to obtain solid CO_2 by allowing partial evaporation of the liquid. He obtained the lowest temperature (−110°C) attainable at the time by using a freezing mixture of solid CO_2 and ether. The so-called permanent gases were not liquefied until Andrews discovered the critical phenomenon. His conclusion was that all gases could be liquefied provided these were *cooled below their respective critical temperatures*; but as long as the temperature was above the critical value no amount of pressure would bring the gas to the liquid state. Obviously, gases like H_2, N_2, O_2 etc. had critical temperatures lower than the lowest temperature attainable at the time. Thus followed an intense attempt at attaining very low temperature by the application of different physical principles.

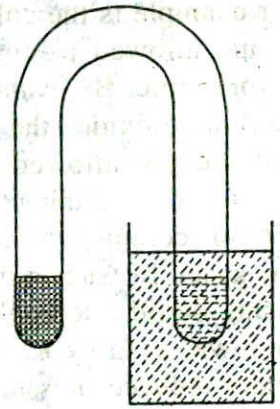


Figure 2.16 Faraday's apparatus for liquefaction of gases

2.37 Methods of Attaining Low Temperature

The methods used for producing low temperatures may be summarized as follows:

(1) Use of freezing mixtures.
(2) Rapid evaporation of volatile liquids.
(3) Adiabatic expansion of cold compressed gas.
(4) Application of the Joule-Thomson effect.
(5) Adsorption of a gas by activated charcoal and then rapid desorption by pumping it under adiabatic conditions.
(6) Application of the principle of adiabatic demagnetization.
(7) Use of the principle of nuclear demagnetization.

Brief description of each one of these methods will only be presented here.

(1) *Freezing mixtures* are useful for producing temperature below 0°C but their use is limited because it is difficult to prepare freezing mixtures which will produce very low temperatures. Solid carbon dioxide and ether could be used to attain a temperature of −110°C.

(2) *Cooling by rapid evaporation of volatile liquids* depends on the fact that when the liquid evaporates it takes up its latent heat of evaporation from the liquid itself. A familiar example is the cold felt when a few drops of ether or acetone is taken in the hand and allowed to evaporate. Pictet (1877) was able to liquefy oxygen by using this principle. By evaporation of liquid sulfur dioxide under reduced pressure around carbon dioxide, the latter was liquefied in large quantity. When liquid carbon dioxide was allowed to evaporate under reduced pressure, a temperature of about −130°C was obtained and this temperature was sufficient to bring about liquefaction of compressed oxygen. This process of attaining low temperatures and liquefying gases by successive evaporation (under reduced pressure) of different liquids, using liquid *A* to cool the gas *B* and so on, is known as the *cascade* method. The method was used by Keesom to attain a temperature of 0.71°K by boiling liquid helium under reduced pressure, but helium could not be liquefied by the use of this method alone.

(3) *Adiabatic expansion of cold compressed gas* for liquefying gases enjoyed considerable popularity at one time for producing liquid air. The principle is that when a gas expands and does work against the external pressure, the process being carried out adiabatically (no heat is allowed to enter or leave the system), the temperature of the gas falls. It will be shown later that for adiabatic expansion

$$\left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{T_1}{T_2}\right)$$

where P_1 and P_2 are the initial and final pressures, T_1 and T_2 are the respective temperatures at the two pressures and γ is the ratio of heat capacities of the gas at constant pressure and at constant volume. Thus T_2 will be much lower than T_1 if P_2 is much lower than P_1, i.e., the fall in temperature is large if the difference in initial and final pressures is large.

G. Claude (1900) made use of this principle for commercial production of liquid air. The apparatus is shown diagrammatically in Figure 2.17. The air was purified, compressed to about 40 atm pressure and passed through the tube *A* into an apparatus *B* where it was allowed to expand so that the pressure fell to about 1 atm.

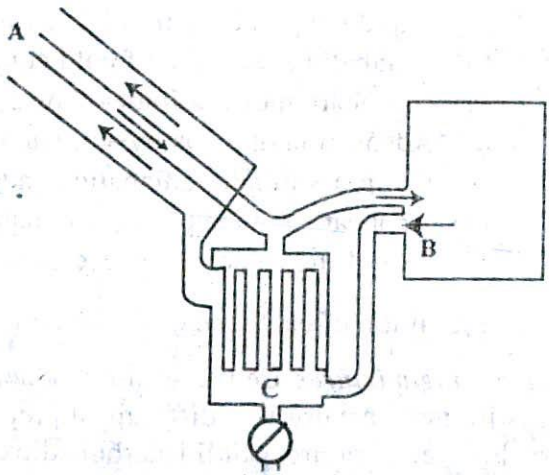


Figure 2.17 Claude's apparatus

The expanding air was used to do work, such as to drive a dynamo. The expanded and cooled air passed through the vessel *C* and around the tube *A* in the direction of the arrows to the compressor. The incoming compressed air was thus cooled and its temperature further reduced by expansion. When this cycle is repeated several times, the effect is cumulative and the temperature falls sufficiently so as to produce air in the liquid state which collects in the vessel *C*. In other forms of the Claude's process air was compressed to about 200 atm and then allowed to expand.

(4) *Joule-Thomson effect* was utilized to liquify gases. When a highly compressed gas is allowed to expand through a valve or throttle into a region of low pressure so that no work is done against external pressure, the temperature of the gas falls. This is called the **Joule-Thomson effect** *(Section 5.14)* after the famous porous-plug experiment of J. P. Joule and W. Thomson (Lord Kelvin). For an ideal gas there should be no external work done when a gas expands from a higher pressure to a lower pressure. The cooling observed was, therefore, attributed to molecular attraction in real gases. When the gas expands the molecules get away from each other's spheres of attractive forces. The energy necessary for this purpose is taken from the gas itself so that its temperature falls. *Joule-Thomson effect is to be carefully distinguished from cooling by adiabatic expansion.* Whereas in the former the expanding gas performs no external work, in adiabatic expansion the gas is made to do external work.

Under ordinary conditions H_2 and *He*, however, show an increase of temperature in the Joule-Thomson experiment. If these gases were cooled below certain temperatures (e.g. – 80°C for H_2 and – 240°C for *He*) the cooling effect was observed. In fact, for each gas there exists a temperature, known as the *inversion temperature,* above which the gas warms up when used in the Joule-Thomson experiment.

W. Hampson (1895) in England and C. von Linde (1895) in Germany employed the Joule-Thomson cooling effect for the manufacture of liquid air on a large scale. Of these the process of Linde is more widely used now-a-days because of its simplicity. Figure 2.18 shows the apparatus of Linde diagrammatically. The air to be liquefied is first freed from carbon dioxide and moisture as these, when condensed to solid, will block the apparatus. It is then cooled by passing through a freezing mixture, compressed to about 200 atmospheres and forced through the inner tube of the concentric pipes at *A*. These pipes are several hundred yards long and coiled spirally to save space.

The compressed air is allowed to expand suddenly into the vessel *D* to a pressure of about 50 atmospheres or less. The entry of the air into *D* is regulated by the throttle valve

at T operated by the handle H. This sudden expansion causes the temperature of the air to fall due to the Joule-Thomson effect. The cooled air passes through the annular space surrounding the inner tube A and thus cools the incoming compressed air. The temperature of this air on expansion through the valve T falls further. The expanded air, after passing through the annular space, is led to the compressor, again compressed to 200 atmospheres and then passed through the tube A. The process is repeated, the temperature of the air falling at each expansion step, and ultimately air is liquefied and collected in the vessel D. The tubes are all surrounded by insulating materials like wool, felt, feather etc. in order to minimise absorption of heat from the surroundings.

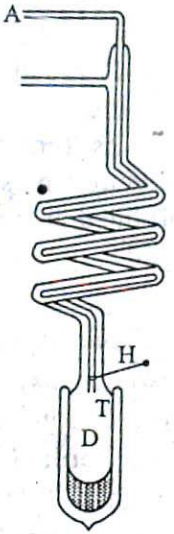


Figure 2.18 Linde apparatus for liquefaction of gases

H_2 and He were liquefied in quantity by applying the Joule-Thomson effect, after being cooled to below their respective inversion temperatures. Helium was first solidified at moderately high pressure in the Leyden cryogenic laboratory in Holland.

(5) When a gas is adsorbed by charcoal, heat is evolved and *when the adsorbed gas is pumped off, the temperature falls*. If the adsorption takes place at low temperature desorption lowers the temperature further. This principle has been used to obtain very low temperature and even to liquefy helium.

(6) The principle of cooling by *adiabatic demagnetization* was suggested by P. Debye (1926) and W. F. Giauque (1927). When a substance is placed in a strong magnetic field, the magnetic dipoles are oriented or ordered. If the substance is insulated and the magnetic field is removed, the magnetic dipoles return to a random arrangement. Since the system is insulated the energy necessary for the return to the random state is taken from the system itself. As a result the temperature falls. At ordinary temperatures the cooling effect of adiabatic demagnetization is not observed. But when the temperature is 1°K or less, the cooling effect becomes prominent. Salts of rare-earths, e.g. gadolinium, cerium and dysprosium, and ferric ammonium alum, potassium chrome alum etc. have been used in the cooling by adiabatic demagnetization process. Temperature as low as 0.003°K has thus been achieved.

(7) In recent years the principle of *nuclear demagnetization* has been utilized to attain such low temperature as 10^{-5} K.

2.38 Uses of Liquefied Gases

Liquefied gases have found wide application, particularly in producing low temperature. Oxygen and nitrogen gases are produced commercially by fractional evaporation of liquid air. Inert gases like *Ar, Ne* etc. which are used in commercial Neon signs are manufactured from liquid air. Liquid *He* finds application as an agent for producing intense cold. Liquid H_2 is used in the space industry.

2.39 Density of Gases and Molecular Mass

The density of a gas is defined in Physical Chemistry as the mass in *g* of 1 L of gas. As the volume depends on the pressure and temperature these must also be specified while making statement about density. Normal density of a gas is the mass of 1 L of gas measured at 0°C and 1atm pressure, i.e., at S.T.P. Under ordinary conditions gases are about 1/100 times as dense as liquids. Thus 1 mL of water at 4°C weighs 1 *g*, whereas the same volume of air weighs only about 0·0013 *g*. It is, therefore, evident that the experimental determination of densities is difficult and the methods used have necessarily to be delicate if good results are to be obtained.

Densities of gases are useful in calculating molecular masses. The ideal gas law equation is used for the purpose. We have seen that (*Section* 2.9)

$$PV = n\,R\,T = \frac{g}{M}\,R\,T$$

From this one can readily deduce that

$$P = \rho.\,\frac{RT}{M}$$

where ρ is the density of the gas. In using this equation for obtaining molecular mass, the value of R used will depend on the unit in which P and V are expressed. Thus if pressure is in atmosphere and volume in L, R is to be expressed in L-atm units.

If a liquid can be conveniently converted into the vapour state, the measurement of the density of vapour will yield the molecular mass of the liquid in the vapour state. The molecular masses of gases and vapours will be approximate as the equation from which the molecular mass is derived is not strictly obeyed by real gases. The following methods are used for the determination of gas density: (i) Regnault's method, (ii) Dumas method, (iii) Hofmann's method, (iv) Victor Meyer's method, (v) the buoyancy method and (vi) the method of limiting density.

(i) Regnault's method

The method is based on the measurement of mass of a known volume of gas under definite condition of temperature and pressure. Two glass bulbs, each of 2 L capacity, are first dried, evacuated and suspended from the two arms of a balance (Figure 2.19).

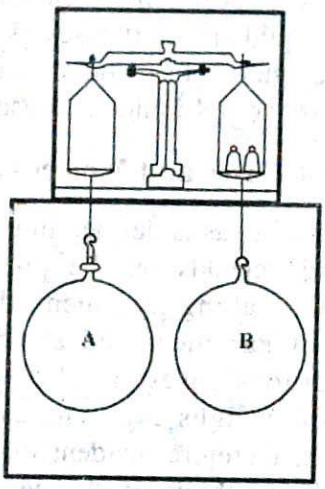


Figure 2.19 Regnault's apparatus for determination of density of a gas

The bulbs are counterpoised in the balance. One of the bulbs, say *A*, is then filled with gas under known pressure and again counterpoised against bulb *B*, adding necessary weights on the pan from which *B* is suspended. This additional weight necessary for balancing the arms is the mass of gas taken in bulb *A*. The temperature of the surroundings is kept uniform. The volume of bulb *A* is obtained from the mass of water necessary to fill the bulb and the density of water at the temperature of the experiment. From the mass and volume of the gas the density may be calculated and knowing the pressure and temperature the molecular mass of the gas is obtained.The bulb *B* is used as a counterpoise in order to minimize troublesome corrections for air buoyancy and moisture adhering to the surface. Even then a small buoyancy correction is required because the volumes of the evacuated bulbs differ somewhat from that when filled with water. This correction is, however, very small.

(ii) Dumas' method

It is used for substances which are liquid at room temperature. The apparatus is shown in Figure 2.20. It consists of a bulb with capacity of about 400 mL and a drawn-out neck. The bulb is first dried and weighed. A few mL of the liquid whose density in the vapour state is to be determined is introduced into the bulb. It is then placed in a bath as shown in the figure so that only the tip of the neck projects out of the liquid in the bath. The bath is then heated to a temperature about 20°C above the boiling point of the liquid in the bulb. The liquid boils, expels air from inside the bulb and then vapour comes out of the neck. When all the liquid is vaporized, and the pressure of the vapour within the bulb is, therefore, equal to the atmospheric pressure, the tip is sealed off with a blow torch. The pressure of the atmosphere and the temperature are immediately noted. The bulb is removed, cooled, its outside cleaned and dried, and re-weighed. The difference between this

mass and the mass of the bulb when empty gives the mass of the vapour. The volume of the bulb is determined from the density of water and the mass of the water required to fill the bulb after breaking the tip of the neck. As the mass and volume of the vapour and the pressure and temperature are known, the molecular mass may be easily calculated.

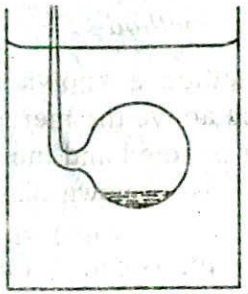


Figure 2.20 Dumas method for determination of density of a gas

Only extremely pure substances may be used in Dumas' method. Since most of the liquid is boiled off, the presence of a small quantity of high boiling impurity may cause a serious error in the results. The method may be used for the determination of densities of vapour of relatively easily volatilized metals (e.g. mercury, zinc etc.) by replacing the glass bulb by bulbs made of porcelain or silica because of the high temperatures required for volatilization.

Example 2.16: In a determination of the density of a gas by the Dumas' method the following data were obtained:

Mass of bulb + air = 50.274 *g*
Mass of bulb + vapour = 50.436 *g*
Mass of bulb + water = 261.3 *g*

The bulb was sealed off at 100°C and the room temperature and barometric pressure were respectively 20.5°C and 753 mm Hg.
Given that the density of air at S.T.P. is 0.001293 $g\ mL^{-1}$, calculate the molecular mass of the gas.

Solution: Volume of air filling the bulb at 20.5°C and 753 mm Hg pressure
= 261.3 – 50.274 = 211.0 *mL*.(assuming density of water is 1 $g\ mL^{-1}$)

$$\text{Volume of this air at S.T.P.} = \frac{(273.16)(753)(211.0)}{(760)293.6} = 194.5\,mL$$

The mass of this volume of air at S.T.P. = (0.001293)(194.5) *g* = 0.251 *g*
True mass of vapour which fills the bulb = (50.436–50.274) + 0.251 (after buoyancy correction)

= 0.162 + 0.251 = 0.413 *g*

But this mass of vapour filled the bulb at 100°C and 753 mm Hg pressure.

$$\text{Hence, molecular mass, } M = \frac{gRT}{PV} = \frac{(0.413)(0.082)(373)}{\left(\frac{753}{760}\right)\left(\frac{211.0}{1000}\right)} = 60.4$$

(iii) Hofmann's method

In this method a known mass of the liquid is allowed to evaporate in the vacuous space above the mercury column in a barometer. The pressure and volume of the vapour is noted and the molecular mass calculated from these data.

The apparatus is shown diagrammatically in Figure 2.21. The graduated barometer tube, *B*, about one metre long and filled with pure mercury, is inverted over a trough of mercury, *T*, with its end below the mercury level in *T*. Mercury stands at a height corresponding to the atmospheric pressure. The space, *V*, above the mercury level in the tube is the *Torricellian vacuum*. The barometer tube is surrounded by a jacket, *J*, through which hot vapour from the liquid boiling in the flask, *F*, may be passed so as to keep the space *V* at the desired temperature.

A small bottle fitted with a ground stopper, called Hofmann's bottle, or a small bulb with a neck drawn out into a fine capillary is dried and filled with about 0.1 g - 0.2 g of the liquid. The mass of the liquid should be accurately known.

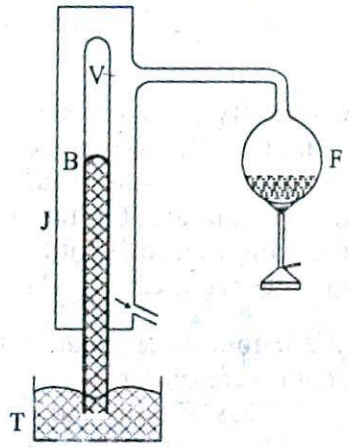


Figure 2.21 Hofmann's apparatus

The height of mercury level is noted and the bottle or bulb is introduced into the space, *V*, simply by holding it at the open end of the tube below mercury level, as mercury is much denser than the bulb. The liquid in the bulb evaporates or hot vapour may be passed through the heating jacket to facilitate evaporation. The pressure of the vapour will depress the mercury level and when the new level has become steady the height of mercury level and the temperature in the jacket are noted. The difference of mercury levels before and after introduction of the vapour is the pressure of the vapour. Since the volume of the vapour may be easily read off from the graduation in the tube and the mass of the liquid introduced is known, the density and hence the molecular mass of the vapour may be calculated.

Accurate results may be obtained with this method but the apparatus is cumbersome and difficult to arrange. Another disadvantage is that the method cannot be used for determining densities above 250°C because of the volatility of mercury above this temperature. Correction for vapour pressure of mercury has to be applied for measurements above 100°C.

(iv) *Victor Meyer's method*

This is perhaps the most common method for the determination of the molecular mass of substances which are liquid or solid at ordinary temperature. In this method

the volume of a known mass of the substance is determined by measuring the volume of air displaced by it. The apparatus is shown in Figure 2.22.

A long tube, usually made of glass, with a bulb at one end and a side tube near the open end, is the main part. This is known as the Victor Meyer tube, *T*, in which the substance is vaporized. This tube is surrounded by an outer jacket, J, made of glass, or more conveniently, copper. The outer jacket contains some liquid which boils at a temperature 20°-30°C higher than the experimental substance to be placed in the V.M. tube. There is an outlet of the jacket to allow the escape of hot vapour. The side tube is bent as shown in Figure 2.22 and passes under water in a trough. A graduated tube, *G*, completely filled with water, is inverted over the open end of this side tube.

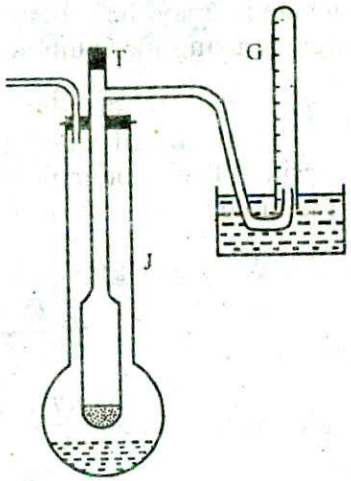


Figure 2.22 Victor Meyer's apparatus

The V. M. tube is first dried thoroughly, and a small quantity of dry sand or glasswool is placed at the bottom to prevent it from cracking when the bulb containing the experimental substance is allowed to fall into it. The tube is then placed in position and the liquid in the jacket is boiled; the hot vapour heats the V. M. tube, air inside it expands and excess air bubbles come out through the end of the side tube, the end being under water.

While this is going on a bulb with drawn out ends is prepared from a piece of glass tubing, one end of the bulb being sealed and the longer end open. This is dried by holding over a flame, cooled and then filled with a known quantity (0.1 *g* - 0.2 *g*) of the substance under investigation, the open end being sealed before the final weighing.

When no more air bubble escapes through the side tube of the V.M. tube, the temperature of the air in the inner tube is constant. The graduated tube is filled with water and placed over the side tube as shown in the diagram. The long stem of the bulb is broken at the tip, then it is dropped into the V. M. tube through the top end and the tube stoppered. These operations should be carried out as quickly as possible. The substance vaporizes immediately and the vapour displaces some of the air which is collected in the graduated tube. When all the displaced air has been collected the graduated tube is removed and placed in a tall cylinder filled with water and the volume of the air noted after making the water level outside and inside the tube the same. The temperature of water in the tall jar and the barometric pressure are noted. The total volume of the air displaced is the volume which the vapour would occupy if it were possible to have it as a gas at the room temperature and the atmospheric pressure. It is not necessary to know the temperature of the

bulb so long as we are sure that it is well above the boiling point of the experimental liquid. The pressure is corrected for the vapour pressure of water at the room temperature. The density of the vapour is calculated and hence the molecular mass of the substance may be obtained. The method can be used up to very high temperatures by using platinum vessels and electric heating.

Example 2.17: In a Victor Meyer experiment when 0.110 g of a substance was evaporated 27.0 mL of air was displaced and collected over water at 27°C and 750 mm Hg pressure. The vapour pressure of water at this temperature is 25.1 mm Hg. Calculate the molecular mass of the substance.

Solution: The pressure of the gas in the tube

$$= \frac{750-25.1}{760} = 0.954 \text{ atm}$$

The molecular mass, $M = \frac{gRT}{PV} = \frac{(0.110)(0.082)(300.1)}{(0.954)\left(\frac{27}{1000}\right)} = 105$

(v) The buoyancy method

This is a very accurate method of determining gas density. A very small quantity of the gas is sufficient for measurement by this method. It uses a form of a microbalance constructed entirely of good quartz. The apparatus is shown in Figure 2.23. The buoyancy bulb, *A*, having a capacity of about 8 mL is evacuated and suspended from one end of the beam, *B*, the other end of the beam is fixed to the plate, P, whose area is equal to that of the bulb, *A*.

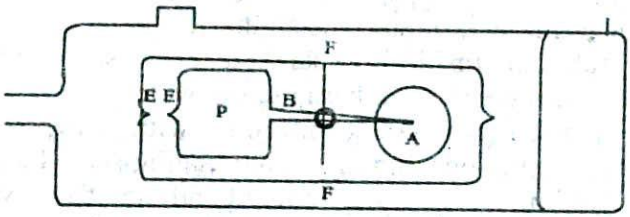


Figure 2.23 Buoyancy balance

The beam is attached to a frame by means of quartz fibre, *FF*, around which it can swing. The whole is enclosed within a tube 2 to 3 cm wide and 8 to 10 cm long. Arrangements for keeping the tube at constant temperature are provided and the tube may be evacuated and filled with gas at any pressure.

The tube is first evacuated and a gas, whose density is accurately known, is slowly introduced; the buoyancy bulb, *A*, rises until the pointers, *EE*, are on the same level. The pressure of the gas is noted. The tube is evacuated again and the gas under investigation is slowly introduced until the pointers are again at the same level. The pressure is noted. If P_1 and P_2 are the pressures of the two gases when the pointers are at the same level, the densities of the gases must be equal at these pressures. If ρ is the density of the reference gas at pressure P_1, then $P_2 = \rho RT/M_2$ from which the molecular mass M_2 of the gas under investigation may be calculated.

(vi) Method of limiting density

The above methods [(i) – (v)] are based on the assumption that the vapours behave as ideal gases. Since the equation is not strictly valid for real gases the results obtained are not very accurate. It will be seen that the behaviour of real gases approximates to that of ideal gases as the pressure is reduced. This approach towards ideal state refers only to *PV* relationships. If the density of a gas could be measured at very low pressures, preferably at zero pressure, accurate molecular masses could be obtained. Measurements at very low pressures are beset with experimental difficulties and the error will be large as the densities are so small at low pressures. However, the method of graphical extrapolation may be used to obtain accurate values of molecular masses.

In this method the density (ρ) of a gas is determined at various pressures (P) at constant temperature (T). The values of ρ/P are then plotted against P as shown in Figure 2.24. However, the pressure of the gas must be much below the atmospheric pressure.

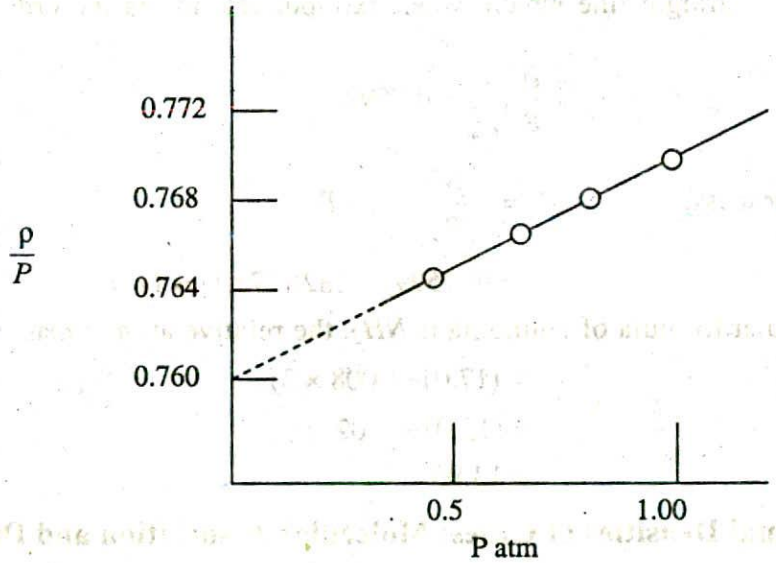


Figure 2.24 A plot of ρ/P *vs* P for NH_3 gas

The straight line is extrapolated to the ρ/P axis at zero pressure, the value at this point being designated as $(\rho/P)_o$. The ideal gas equation then becomes

$$M = \left(\frac{\rho}{P}\right)_0 RT \qquad (2.69)$$

This is valid for any gas. The molecular mass of the gas may be calculated from the value of $(\rho/P)_0$. In most cases the plot of ρ/P against P is linear. If the plot shows a curvature at higher pressure the straight line portion may be extrapolated to obtain $(\rho/P)_0$. This method of extrapolation to obtain accurate molecular mass is known is the *method of limiting density*. The limiting density, ρ_0, i.e., density at zero pressure, however, cannot be obtained by extrapolation of a plot of ρ *vs* P since the

density of the gas vanishes at zero pressure. The method which may also be used to determine atomic masses is illustrated in the following example.

Example2.18: The densities, ρ, of NH_3 in $g\ L^{-1}$ at various pressures, P, and at 0°C are measured. The ratio ρ/P calculated from the data are :

P atm	1.00	0.67	0.50	0.33
ρ/P	0.77169	0.76873	0.76586	0.76385

Calculate the molecular mass of NH_3 by the method of limiting density. If the relative atomic mass of hydrogen is taken as 1.008 what is the relative atomic mass of nitrogen?

Solution: A graph is drawn with ρ/P as ordinate and P as abscissa (Figure 2.24). The points lie on a straight line which, when extrapolated, meets the ordinate at 0.7599. Hence

$$\left(\frac{\rho}{P}\right)_{P\to 0} = 0.7599$$

The molecular mass, $$M = \left(\frac{\rho}{P}\right)_{P\to 0} . RT$$

$$= (0.7599)(0.082)(273.1) = 17.01$$

As the molecular formula of ammonia is NH_3, the relative atomic mass of nitrogen

$$= (17.01 - 1.008 \times 3)$$

$$= (17.01 - 3.024)$$

$$= 13.99$$

2.40 Abnormal Densities of Gases: Molecular Association and Dissociation

Measurements of densities of vapours have served to determine the molecular masses of a great many substances. In most cases the results are in agreement with the values obtained from the sum of the atomic masses of elements in the molecular formula. A few cases were, however, found where the molecular masses as determined from vapour density seemed abnormal. These abnormal values were attributed to association or dissociation of the molecules in the vapour state.

2.40.1 Molecular association

Compounds like HF, CH_3COOH etc. were found to have molecular masses higher than those represented by their simple chemical formula just above their boiling points. Molecules of HF and CH_3COOH were found to correspond to $(HF)_6$ and $(C_2H_4O_2)_2$ respectively. Such a phenomenon in which two or more molecules of the same substance combine to give larger molecules is known as ***association***.

6-B

Molecular association explains the experimental values of molecular masses of aluminium halides as Al_2Cl_6 and Al_2Br_6, of ferric chloride as Fe_2Cl_6, of sulphur as S_8, of oxides of phosphorus as P_4O_{10} and P_4O_6 etc. Many of these, particularly the metallic halides, are believed to exist in the associated form even in the solid state.

2.40.1 Molecular dissociation

Upon heating, the density of aluminium chloride vapour decreases and at 800°C the density corresponds to the formula $AlCl_3$, i.e., one molecule of Al_2Cl_6 has broken down to form 2 molecules of $AlCl_3$. This phenomenon in which a molecule breaks down to form two or more molecules is known as ***dissociation***. As the dissociation here is caused by heat the phenomenon is called *thermal dissociation* to distinguish it from *electrolytic dissociation*.

Dissociation is not the same as decomposition. In thermal decomposition the molecular species formed from breakdown do not combine upon cooling, but in dissociation the separated parts recombine upon cooling provided these are not removed from the vessel in which they are heated. $CuCO_3$ yields CuO and CO_2 upon heating. This is a case of decomposition as CuO and CO_2 will not recombine to form $CuCO_3$ upon cooling. When $AlCl_3$ vapour heated to 800°C is cooled to 200°C or below Al_2Cl_6 is formed again as shown by density measurements.

Thermal dissociation explains abnormally low molecular mass obtained for many elements and compounds. Well known examples are the dissociation of N_2O_4, NH_4Cl, PCl_5, PCl_3, I_2, S_8, Hg_2Cl_2 etc. Experimental evidence of such dissociation was first obtained by L. Pebal (1862) and K. Than (1864) in the case of NH_4Cl. They were able to achieve a partial separation of the dissociated products, e.g., NH_3 and HCl as in the equation

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

by allowing the gaseous products to diffuse through a porous plug. On one side of the plug the gas was alkaline and on the other side it was acidic. The rates of diffusion of the two gases are different as their molecular masses are widely different. This causes the presence of excess NH_3 on one side, and excess HCl on the other side, giving the characteristic reaction of base and acid on the two sides respectively.

The phenomenon of dissociation is clearly shown in the case of N_2O_4. The boiling point of the liquid is 22°C. Slightly above this temperature the vapour is pale reddish-brown in colour and the density of the gas corresponds to molecular formula N_2O_4. When the temperature is gradually increased the vapour darkens in colour until it is almost black at about 140°C; the molecular mass of the vapour is about 46, indicating almost complete dissociation into NO_2 molecules:

$$N_2O_4 \rightleftharpoons 2NO_2$$

When the temperature is raised further the colour of the vapour fades, at first slowly and then rapidly, until at 620°C it becomes almost colourless. The molecular mass of the vapour is about 30. This may be explained by dissociation of the NO_2 molecules as follows:

$$2NO_2 \rightleftharpoons 2NO + O_2$$

Both NO and O_2 are colourless. The dissociation is almost complete at 620°C. When the vapour is cooled the reverse reaction, i.e., association takes place. At 140°C, NO_2 is formed completely and at about 22°C the vapour again corresponds to the formula N_2O_4.

2.40.3 Degree of dissociation

Measurement of the density of vapour may be used for calculating the degree of dissociation (α) of substances, i.e., the extent to which the substance dissociates. The *degree of dissociation* of a vapour may be defined as, *'the fraction of the total number of molecules or moles which have dissociated'*.

Consider 1 mole of the substance in the vapour and let α be the degree of dissociation or the fraction of 1 mole dissociated. Then $(1 - \alpha)$ moles will remain undissociated. If each of the dissociated molecules form n molecules of the gaseous products then α moles will yield $n\alpha$ moles of product. The total number of moles present in the vapour under the conditions of temperature is then $1 - \alpha + n\alpha$ or, $1 + (n - 1)\alpha$.

If the pressure is kept constant then the volume occupied by the gas is directly proportional to the number of moles. If V_o is the volume the vapour would have occupied if there was no dissociation, i.e., the value calculated from the ideal gas equation, and V is the volume actually occupied due to dissociation, then

$$\frac{V}{V_0} = \frac{1+(n-1)\alpha}{1} = \frac{\rho_0}{\rho} \qquad (2.70)$$

since density, ρ, is inversely proportional to V. Here ρ_0 = density of the vapour assuming no dissociation and ρ = observed density, both at the same pressure and temperature. The equation (2.70) may be rearranged to

$$1 + (n - 1)\alpha = \frac{\rho_0}{\rho}$$

$$\text{or} \quad \alpha = \frac{\rho_0 - \rho}{\rho(n-1)} \qquad (2.71)$$

Since the molecular mass is proportional to the density it follows that

$$\alpha = \frac{M_0 - M}{M(n-1)} \qquad (2.72)$$

where M_o is the molecular mass calculated from the formula.

When dissociation is studied in a closed vessel, i.e., at constant volume, the increase of pressure is inversely proportional to the density at constant temperature. So, one can also write

$$\frac{P}{P_0} = 1 + (n-1)\,\alpha$$

$$\alpha = \frac{P - P_0}{P_0\,(n-1)} \qquad (2.73)$$

where P and P_0 are the pressures with and without dissociation.

Any of the above three equations (2.71), (2.72) and (2.73) may be used to determine the degree of dissociation of molecules upon heating.

Thermal dissociation is not accompanied by change in density or volume unless there is a change in the number of molecules due to dissociation.

The applications of these equations are illustrated in the following examples.

Example 2.19: Calculate the degree of dissociation of phosphorus pentachoride gas at 250°C if 1.0 L of the partially dissociated gas at 1 atm has mass 2.865 g.

Solution: The apparent molecular mass, $M = \frac{gRT}{PV}$

$$= \left(\frac{2.865}{1}\right)\left(\frac{0.082}{1}\right) \times (273.1 + 250)$$

$$= 122.9$$

Calculated molecular mass, $M_0 = 208{\cdot}5$

The degree of dissociation, $\alpha = \frac{M_0 - M}{M(n-1)} = \frac{208.5 - 122.9}{122.9\,(2-1)}$

$$= \frac{85.6}{122.9} = 0.697$$

i.e., $\alpha = 69.7\ \%$

Example2.20: At 525°C and 749 mm Hg pressure 0.0886 g of sulphur chloride (S_2Cl_2) occupies a volume of 47.7 mL. Calculate the degree of dissociation of S_2Cl_2 at this temperature.

Solution: The apparent molecular mass,

$$M = \frac{g}{P} \times \frac{RT}{V} = \frac{(0.0886)\,(0.082)\,(273.1+525)}{\left(\frac{749}{760}\right)\left(\frac{47.7}{1000}\right)}$$

$$= 123.4$$

Calculated molecular mass, $M_o = 135$

$$\alpha = \frac{M_o - M}{M(n-1)} = \frac{135-123.4}{(123.4)(2-1)}$$

$$= 0.0940$$

i.e., $\alpha = 9.40\%$

2.41 Heat Capacities of Gases: Definitions

Heat capacity of a substance is defined as *the heat necessary to raise the temperature of a given quantity of the substance through 1 °C.* **Specific heat capacity or specific heat** of a substance may be defined *as the amount of heat necessary to raise the temperature of 1 g of the substance through 1°C.* The specific heat of water at 15°C is just 1 calorie or 4.18 joule. If the temperature of a body is raised from T_1 to T_2 by adding an amount Q of heat, the heat capacity, C, of the body is given by

$$C = \frac{Q}{T_2 - T_1} \tag{2.74}$$

Another quantity, *molar heat capacity*, is also defined as, *the amount of heat necessary to raise the temperature of 1 mole of the substance through 1 °C.*
The value of the heat capacity will depend on whether heat has been added under constant pressure or constant volume conditions. This is particularly important in the case of gases as the heat capacity values at constant pressure (C_p) and constant volume (C_v) differ considerably.

2.42 Heat Capacity and Kinetic Theory

When a gas is heated at constant volume the heat supplied is used to, (a) increase the translational kinetic energy of the gas molecules and (b) to increase the intra-molecular energy, e.g., vibrational or rotational energy within the molecules.
According to the kinetic theory of gases

$$PV = \frac{2}{3} \times K.E. \tag{2.33}$$

or $$K.E. = \frac{3}{2} PV$$

But $PV = RT$ for one mole of gas.

Therefore, the K. E. of one mole = $\frac{3}{2} RT$.

For an increase of temperature from T_1 to T_2 the increase of kinetic energy of one mole of gas is

$$\frac{3}{2} R (T_2 - T_1)$$

When the increase of temperature is 1°C, i.e., $(T_2-T_1) = 1°C$, the increase in K. E. is equal to $\frac{3}{2}R$. But the molar heat capacity C_v = Increase of K. E. for increase of temperature by 1°C + increase in intra-molecular energy.

Hence, $$C_v = \frac{3}{2}R + x \qquad (2.75)$$

where x = contribution to the molar heat capacity for increase of intra-molecular energy. If the gas is monatomic there is no rotational or vibrational motion and $x = 0$. So, for monatomic gases

$$C_v = \frac{3}{2}R$$

When the gas is heated at constant pressure the gas expands and *does work* against the external pressure. Heat is required for this work to be done and also to raise the temperature. This work is equal to $(PV_2 - PV_1)$ or $P(V_2 - V_1)$ where V_2 and V_1 are the volumes at temperature T_2 and T_1 respectively.

When one mole of gas is considered, V_2 and V_1 are the molar volumes. If $T_2 - T_1 = 1°C$, then for a monatomic gas the molar heat capacity at constant pressure C_p, is given by

$$\begin{aligned} C_p &= C_v + P(V_2 - V_1) \\ &= C_v + R(T_2 - T_1) \\ &= C_v + R \end{aligned} \qquad (2.76)$$

or $$C_p - C_v = R \qquad (2.77)$$

In the general case where contribution from increase in intra-molecular energy is also to be taken into account,

$$\begin{aligned} C_p &= C_v + R + x \\ &= \frac{3}{2}R + R + x \\ &= \frac{5}{2}R + x \end{aligned} \qquad (2.78)$$

2.4.1 Ratio of C_P and C_v

For any gas the ratio C_p/C_v, which is denoted by γ, is given by the expression,

$$\gamma = \frac{C_P}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x} \qquad (2.79)$$

In the case of monatomic gases, $x = 0$, and

$$\gamma = \frac{5}{3} = 1.667$$

For diatomic molecules in many cases $x = R$,

$$\text{Hence, } \gamma = \frac{\frac{5}{2}R + R}{\frac{3}{2}R + R} = \frac{7}{5} = 1.40$$

For triatomic molecules, in many cases, $x = \frac{3}{2}$R, and $\gamma = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{3}{2}R + \frac{3}{2}R} = \frac{4}{3} = 1.33$

In the case of polyatomic molecules the value of x is large so that γ becomes less.

It is seen, therefore, that valuable information of a qualitative nature about the constitution of the molecules of different gases may be obtained from the values of γ. Table 2.7 shows a collection of data of γ for various gases.

Table 2.7 Molar heat capacities of gases

Gas	C_p	C_p	γ	Molecular constitution
He	4.97	2.98	1.67	Monatomic
Ar	4.97	2.98	1.67	Monatomic
Mg	4.97	2.98	1.67	Monatomic
O_2	7.05	5.05	1.40	Di-atomic
H_2	6.90	4.91	1.41	Di-atomic
N_2	6.94	4.95	1.40	Di-atomic
NO	7.11	5.11	1.39	Di-atomic
CO	6.97	4.97	1.40	Di-atomic
CO_2	9.75	6.71	1.30	Tri-atomic
SO_2	9.71	7.70	1.29	Tri-atomic
H_2S	8.62	6.53	1.32	Tri-atomic
NH_3	8.77	6.70	1.31	Tetra-atomic
CH_4	----	----	1.31	Penta-atomic
C_2H_4	10.23	8.19	1.25	Hexa-atomic

Cl_2, Br_2, I_2 etc. in the gaseous state constitute exception to such simple calculations. These have high C_p and C_v values compared to other diatomic gases and the value of γ is considerably less than 1.40.

2.43 Experimental Determination of γ of a Gas

(a) F. Clement and C. B. Desormes used the principle of adiabatic expansion to determine the value of γ. The gas at a pressure greater than one atmosphere is placed in a large vessel (capacity 30–40 L) fitted with a rubber stopper and a water or an oil manometer (Figure 2.25).

The pressure P_1 is measured. The stopper is suddenly opened and then closed again. The pressure of the gas momentarily becomes equal to that of the atmosphere and during the expansion, which is virtually adiabatic, the gas is cooled. As it warms up again and attains the temperature of the surrounding, the pressure rises to P_2. Let V_1 be the volume of one mole of gas at pressure P_1 and V be the volume after adiabatic expansion when the pressure is P. For an ideal gas *(Section 5.15)*

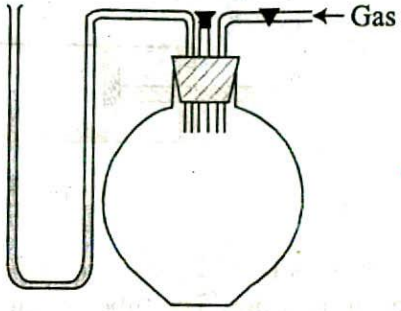


Figure 2.25 Clement and Desormes' apparatus

$$P_1V_1^{\gamma} = PV^{\gamma} \tag{2.80}$$

The initial and final temperatures are the same; the final pressure is P_2 and the corresponding volume of one mole of gas is V. It follows, by Boyle's law, that

$$P_1V_1 = P_2V \tag{2.81}$$

From equations (2.80) and (2.81) one obtains,

$$\left(\frac{P_1}{P_2}\right)^{\gamma} = \frac{P_1}{P}$$

or

$$\gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2} \tag{2.82}$$

The ratio of the specific heats may thus be calculated.

(b) In the method devised by Kundt the velocity of sound in a gas of pressure, P, and density, ρ, is measured in a simple apparatus. The velocity, v, of the gas is given by the expression

$$v = \sqrt{\gamma . \frac{P}{\rho}} \tag{2.83}$$

The value of γ may be calculated from a knowledge of v.

The apparatus (Figure 2.26) consists of a glass tube, T, about a metre long. A thin layer of lycopodium or other fine powder is spread along the tube, which is closed at both ends by corks.

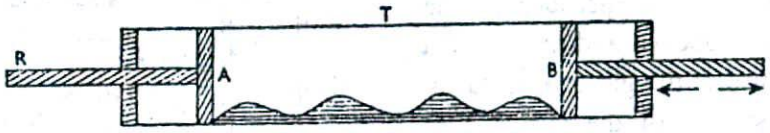


Figure 2.26 Kundt's apparatus

The piston, A, is fixed firmly in place and is attached to a glass rod, R. The piston, B, can be moved in and out. The tube is filled with the gas at atmospheric pressure. By gentle strokes on the rod, R, with damp chamois leather the rod is set vibrating. Sound waves are produced which travel in the tube between *A* and *B*. The powder forms itself in small heaps at the position of the vibration nodes. The piston, *B*, is moved in and out to get the best results. The distance between the two heaps is one half the wave length of sound. The tube is now filled with air at the same pressure and the experiment is repeated. We then have

$$\frac{\text{Velocity in the gas}}{\text{Velocity in air}} = \frac{\lambda_{gas}}{\lambda_{air}}$$

λ_{gas} and λ_{air} are the wavelengths of sound in the gas and air respectively.

Thus, knowing the velocity of sound in air the velocity in the gas is calculated.

Again,
$$\frac{\lambda\, gas}{\lambda\, air} = \sqrt{\frac{\gamma_1 \rho_2}{\gamma_2 \rho_1}} \qquad (2.84)$$

So, from the ratio of $\frac{\lambda_{gas}}{\lambda_{air}}$ and knowing γ_2 and *density* ρ_2 for air and density ρ_1 of the gas, γ for the gas may be determined.

2.44 The Principle of Equipartition of Energy

The principle of equipartition of energy states that the total energy of a molecule is divided equally among the different degrees of freedom. A degree of freedom is defined as an independent mode in which a body may be displaced. As seen in *Section 2.13,* the translational motion of a body may be resolved into three components along three mutually perpendicular directions. Thus, a body may have three translational degrees of freedom, one for displacement or motion along each direction. It has been seen in *Section 2.13* that the velocities of molecules along the three directions may be taken as equal so that one can write, for a molecule of mass *m*, the following for the K.E. of the molecule,

$$\frac{1}{2}mu^2 = \frac{1}{2}mv^2 = \frac{1}{2}mw^2$$

Again, the K.E. of an Avogadro number of molecules $= \frac{3}{2}RT$

Or for one molecule K.E. $=\frac{3}{2}T.\left(\frac{R}{N}\right)$, i.e., $=\frac{3}{2}kT$, where k is known as the Boltzmann constant. According to the principle of equipartition of energy the contribution from each degree of freedom to the total K.E. of one molecule is $\frac{1}{2}kT$ or that of one mole is $\frac{1}{2}RT$.

Consider now rotational motion of molecules. It can be easily visualized that a polyatomic molecule may have three rotational degrees of freedom for rotation around three mutually perpendicular axes. For a diatomic molecule or a linear polyatomic molecule there are only two rotational degrees of freedom as rotation around the axis of a molecule does not contribute to the total energy of the molecule. Each of the degrees of freedom for rotational motion will contribute $\frac{1}{2}kT$ molecule^{-1} or $\frac{1}{2}RT$ mol^{-1} to the total energy of the molecules. Monatomic molecules do not have rotational contribution to energy.

Molecules containing more than one atom have vibrational motion along the bonds as well as bending vibrations as shown in Figure1.1. Energy due to each vibrational motion has two components – one kinetic and one potential. Each component contributes $\frac{1}{2}kT$ molecule^{-1} or $\frac{1}{2}RT$ mol^{-1} to the energy of the molecules. Hence each vibrational degree of freedom contributes

$$2\times\frac{1}{2}kT \text{ molecule}^{-1} \text{ or } 2\times\frac{1}{2}RT \text{ mol}^{-1}.$$

It may be shown that a molecule containing N atoms has a total of $3N$ degrees of freedom. For a diatomic or a linear polyatomic molecule there are three translational degrees cf freedom and two rotational degrees of freedom. Hence the number of vibrational degrees of freedom is $(3N - 5)$. For a non-linear polyatomic molecule there are three rotational degrees of freedom and hence $(3N - 6)$ vibrational degrees of freedom.

These results are of great importance as they allow the calculation of the total energy and hence the molar heat capacity of the molecules.

It should be mentioned that complicating factors must be taken into account for obtaining correct value of molar heat capacities from the energy values obtained with the help of the principle of equipartition of energy.

QUESTIONS AND PROBLEMS

1. What is an ideal gas and a real gas? Explain with reference to Amagat's curves.
2. Show that the molar gas constant '*R*' has the dimension of work. Deduce the value of '*R*' in three different units.
3. What are meant by the terms:
   (a) Mean free path; (b) root mean square speed; (c) Avogadro number; (d) diffusion?
4. State the fundamental assumptions of the kinetic theory of gases and show how the theory supports (a) Avogadro's law and (b) Graham's law of diffusion.
5. The relative densities of two gases, A and B, are 1 and 1.06 respectively. Calculate the volume of B which would diffuse in the same time in which 150 mL of A would diffuse through a porous partition.
6. Deduce Boyle's law, Avogadro's law and Gay-Lussac's law on the basis of the kinetic theory of gases.
7. Calculate the kinetic energy (a) in ergs and (b) joules of the molecules of an ideal gas in a container of volume 250 mL measured at 25°C and 750 mm Hg pressure.
   [Ans.(a) 3.075×10^8 ergs; (b) 37.45 joules]
8. The co-efficient of viscosity of gaseous oxygen at 0°C and 1 atm pressure is 1.92×10^{-4} poise. Calculate (a) the mean free path and (b) the collision diameter of the molecules at this temperature.
   [Ans.(a) 6.34×10^{-6} cm; (b) 3.64×10^{-8} cm.]
9. Calculate (a) the number of moles and (b) the number of molecules contained in 0.5 litres of hydrogen at a temperature of 120°C and a pressure of 1 mm Hg assuming ideal behaviour.
   [Ans. (a) 2.04×10^{-8}; (b) 1.231×10^{16}]
10. Calculate the root-mean-square velocity of hydrogen at 0°C. [Ans. 1.84×10^5 cm s^{-1}]
11. State the assumptions of the kinetic theory of gases and deduce the relation $PV = \frac{1}{3} mnc^2$. What are the two main causes of deviation of real gases from ideal behaviour?
12. (a) Discuss the principles underlying the Victor Meyer's method for the determination of molecular mass of a volatile liquid. Draw a neat sketch of the apparatus and give a brief description of the procedure.
    (b) How do you explain the abnormal vapour density of NH_4Cl between 350° and 1000°C?
13. Explain the essential conditions for the liquefaction of a gas. Give an outline of the various methods which have been used for the liquefaction of gases. What is the importance of liquefaction of gases?
14. What considerations led van der Waals to modify the gas law equation, $PV = nRT$? Explain the significance of '*a*' and '*b*' in the equation.
15. 0.250 g of a volatile liquid when vaporized in a Victor Meyer's apparatus displaced 30.0 mL of air collected over water at 27°C. The pressure was 755 mm Hg and vapour pressure of water at 27°C is 2.67 mm Hg. Calculate the molecular mass of the liquid. [Ans. 213.9]
16. Discuss Andrews' isothermals for carbon dioxide. What fundamental information on liquefaction of gases do you obtain from the isothermals? What is Joule-Thomson effect?
17. (a) What is meant by the `degree of dissociation' of a substance in the vapour state? Deduce an expression for the degree of dissociation of PCl_5 as related to density. (b) 4.5 gm of PCl_5 were completely vaporized at 250°C; the vapour occupied 1700 mL at one atmosphere. Calculate the degree of dissociation at this temperature. (RMM of $PCl_5 = 208.5$) [Ans. 0.84]
18. Give an account of Andrews' experiments on the liquefaction of carbon dioxide and the conclusions derived there from. Discuss how these findings and Joule and Thomson's work on adiabatic expansion helped in developing practical methods for liquefaction of gases. Add a note on the behaviour of hydrogen and helium.
19. Calculate the volume occupied by 85.0 g of nitrogen tetroxide (N_2O_4) when 27% is dissociated at 35°C and under one atmosphere pressure. [Ans. 29.6 litres.]

20. Define critical temperature and critical pressure of a gas. Describe one method of determining critical temperature or critical pressure.
21. The vapour density of PCl_5 at 250°C was found to be 57.6. Calculate the percentage dissociation of PCl_5 at this temperature (density of oxygen =16). [Ans. 81%]
22. Explain how van der Waals' equation accounted for the deviation of real gases from the ideal gas laws. Discuss the limitations of van der Waals equation of state.
23. What is meant by the law of corresponding states? Deduce the reduced equation of state.
24. Describe the Dumas' method of determining vapour densities.
25. At 220°C and a pressure of 747 mm Hg 1.3852 g of a certain organic substance in vapour form occupies a volume of 420 mL. Elementary chemical analysis of the substance is; C = 70.60 per cent, H = 5.88 per cent and O = 23.52 per cent. What is the molecular mass of the substance and what is its chemical formula? [Ans. 136; $C_8H_8O_2$]
26. The following values were obtained for the density of carbon dioxide at a temperature of 0°C: Pressure (atm) 1 2/3 1/2 1/3 Density (g/l) 1.97676 1.31485 0.94505 0.65596 Calculate the molecular mass of carbon dioxide by the method of limiting densities. [Ans. 44·021]
27. 3.062 g of a gas occupies a volume of 1.224 litres at a temperature of 10°C and a pressure of 2 atm. At what pressure will 0.436 g of the same gas occupy a volume of 300 mL at a temperature of 25°C?
28. The molecular mass of iodine vapour at a temperature of 842°C and pressure of 1 atm was found to be 231. Calculate the degree of dissociation of iodine vapour under these conditions. [Ans. 9.88 per cent]
29. Calculate the pressure at which 1 mole of NH_3 occupies 1 litre at 25°C assuming (a) ideal behaviour and (b) a van der Waals gas with $a = 4.170$ L^2-atm-mol^{-1} and $b = 0.037$ L mol^{-1}. [Ans. (a) 24.47 atm; (b) 21.24 atm]
30. If 5.0 g of ammonium carbamate $(NH_4CO_2NH_2)$ evaporates at 200°C, the substance occupies a volume of 7.66 L at a pressure of 740 mm Hg. Calculate the degree of dissociation if dissociation takes place according to the equation $NH_4CO_2NH_2 \rightleftharpoons 2NH_3 + CO_2$ [Ans. 99·9%]
31. On the basis of the kinetic theory of gases calculate the ratio of the molar heat capacity at constant pressure to that at constant volume, C_p/C_v, in the case of a monatomic gas. How does C_p/C_v vary with the molecular complexity of a gas?
32. Explain the difference between the specific heats at constant pressure and at constant volume of a gas. What information concerning the atomicity of a molecule can be obtained from a knowledge of its specific heats?
33. State and explain Dalton's law of partial pressures. Show that in a mixture of gases the total pressure is equal to the sum of the partial pressure of the components.
34. A mixture, composed of 0.15 gm of hydrogen, 0.70 gm of nitrogen and 0.34 g of ammonia, exerts a total pressure of 1 atm at 27°C. Calculate (a) the partial pressure of each gas and (b) the mole fraction of each gas. [Ans. $P_{H_2} = 0.625$ atm; $P_{N_2} = 0.207$ atm; $P_{NH_3} = 0166$ atm. $X_{NH_3} = 0.625$; $X_{N_2} = 0.208$; $X_{NH_3} = 0.166$]
35. A quantity of gas occupies a volume of 2 L at 630 mm Hg. What will be its volume at 760 mm Hg pressure? [Ans. 1.66 L]
36. Calculate the molecular mass of the gas if 0.057 g of it occupies a volume of 50 mL at 760 mm Hg pressure and 27°C. [Ans. 28·1]
37. 40.0 g of oxygen and 6.0 g of hydrogen are contained in a 6 L flask at 127°C. Calculate the total pressure of the mixture. [Ans. 23.2 atm]

38. Calculate the partial pressures of N_2, O_2 and *He* in a mixture whose total pressure is 2 atm if there are 20 *g* of N_2, 10 *g* of O_2 and 4 *g* of *He* present in a 2.0 L flask.
[Ans. $P_{N_2} = 1.53$ atm; $P_{O_2} = 1.33$ atm ; $P_{He} = 2.14$ atm]

39. The density of nitrogen peroxide gas is 248 at 90°C. Calculate the degree of dissociation into NO_2 molecules at this temperature. [Ans. 85.5 %]

40. At 1000°C the vapour density of bromine is 76.94. Calculate the degree of dissociation of bromine molecules into atoms at this temperature. (RAM of bromine = 80) [Ans. 40%]

41. How would you distinguish between electrolytic dissociation and gaseous dissociation? Deduce an expression for the calculation of degree of dissociation from vapour density.
At 90°C the vapour density of nitrogen peroxide (N_2O_4) is 24.8. Calculate the degree of dissociation into NO_2 molecules at this temperature. [Ans. 85·5%]

42. Describe in details the Victor Meyer method of determining the molecular mass of a volatile liquid. The following observations were made in a Victor Meyer determination: mass of liquid used = 0.0572 g; volume of dry air displaced = 15.3 mL; room temperature = 23.5°C; barometric pressure = 763.2 mm Hg. Calculate the molecular mass and density at N.T.P. of the vapour.
[Ans. RMM=90.5; density = 4·0 g L^{-1}]

43. Discuss the deviation of gases from ideal gas laws. Deduce the van der Waals equation and state its limitations.

44. Discuss the critical phenomena in the light of van der Waals equation. What is the principle of corresponding state? How would you determine experimentally the critical constants?

45. What factors cause the real gases to deviate from ideal behaviour Y Show how van der Waals equation may be used to explain these deviations.

46. What are the assumptions of the kinetic theory of gases and how far are they valid for real gases? Deduce an expression for the mean free path of a gas. What is its magnitude?

47. By means of a mercury vapour pump a vacuum of 10.7 mm Hg is obtained within a certain apparatus. Calculate the number of molecules which still remain in 1 mL of the apparatus at 27°C.
[Ans. 3.24×10^9]

48. (a) Using the van der Waals equation calculate the pressure developed by 100 *g* of CO_2 contained in a volume of 5 L at 40°C. (b) Compare this value with that calculated using the simple gas law.
[Ans. (a) 11.17 atm; (b) 11.67 atm]

49. In a Victor Meyer experiment for the determination of the molecular mass of a volatile organic compound the following data were obtained:
Mass of liquid taken = 0.1901 gm.
Volume of air displaced = 30.4 mL
Temperature = 27°C
Atmospheric pressure = 758.4 mm Hg
Vapour pressure of water at 27°C = 27.4 mm Hg
Calculate the molecular mass of the liquid. [Ans. 160]

50. If a 2.0 L flask of N_2, at 25°C and 750 mm Hg pressure is connected with a 3.0 L flask of CO_2 at the same temperature and 1000 mm Hg pressure, what will be the final pressure after the gases have thoroughly mixed and reached a temperature of 25°C? [Ans. 900 mm Hg]

3 THE LIQUID STATE

Liquids are characterised by very small compressibility. Unlike solids, liquids have no definite shape. Liquids, however, have definite volumes under given conditions. They have high densities relative to gases, and consequently the intermolecular distance in the liquids is much less than that in a gas. For example, at 0°C and 1 atmosphere pressure a gas occupies about 22,400 mL mol^{-1} , while the majority of liquids occupy 10 to 100 mL mol^{-1}.

In a liquid the molecules are held close together by strong attractive forces. The molecules do, however, possess translational motion in the liquid state. This motion acts against the attractive forces but it is not sufficient to overcome these forces. Because of this motion the molecules do not remain fixed in positions as will be found in a solid. These properties of the molecules in the liquid phase explain why a liquid has a definite volume but not a definite shape. Other characteristic properties of liquids such as vapour pressure, surface tension, viscosity etc., may also be explained in terms of the properties of the molecules.

It must, however, be pointed out that the nature of the forces between molecules is not easily understood. The result is that the theoretical treatment of liquid state is much less satisfactory than in the case of gases. Our knowledge about the structure of liquids is inadequate although efforts are constantly being made to understand the complexities.

3.1 Vapour Pressure of Liquids

The vapour pressure of a liquid at a given temperature is defined as *the pressure exerted by the saturated vapour in equilibrium with the liquid at that temperature*. This definition will be clear from experiments with a barometer tube (Figure 3.1).

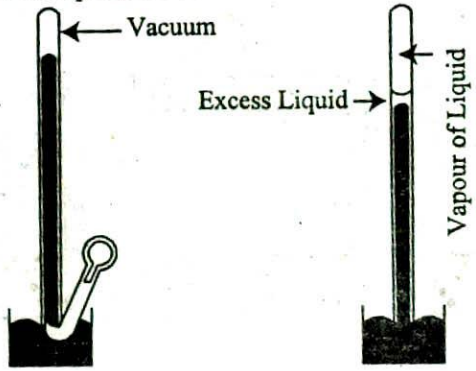


Figure 3.1 Vapour pressure of liquids

A tube filled with mercury is inverted over a trough of mercury. The level of mercury in the tube stands at a certain height above the level of mercury in the trough, the difference between the heights of the levels gives a measure of the atmospheric pressure. The space above the mercury level in the tube is empty and is known as the *Toricellian vacuum*. If a drop of water is introduced into this space by means of a dropper this will immediately vaporize and the level of mercury will be depressed. This depression of the mercury level is due to the pressure exerted by the water vapour. If more water is introduced it will vaporize and the mercury level will be depressed further. If one goes on introducing water into this space a state will be reached when no more water will vaporize but will collect on top of the mercury surface and the level of mercury will remain the same. (The small pressure effect due to the excess water will be negligible.)

At this stage water and its vapour are in equilibrium and pressure exerted by the vapour is known as the saturation vapour pressure, or simply vapour pressure. If the barometer tube is surrounded at the top portion by a hot air-jacket so that the temperature inside the tube may be raised, on performing the same experiment as above it will be found that the vapour pressure increases with the rise in temperature.

3.2 Kinetic Theory of Vapour Pressure

Consider a liquid placed in a closed vessel which it fills partially, the remainder being evacuated. The molecules of the liquid, like those of a gas, are in continual motion. There is a distribution of velocities of these molecules just as there is in a gas, the average velocity having a definite value depending on the temperature. Although in a liquid the molecules are held together by attractive forces some of these molecules, near the surface, may have sufficiently high velocities to overcome the attractive forces and escape into the evacuated space above the liquid surface. Again, some of the molecules in the vapour phase, during their haphazard movements, may have low velocities and come within the sphere of influence of the attractive forces of the molecules in the liquid phase so that these will return to the liquid phase (Figure 3.2). In general, as there are many more molecules per unit area of the liquid surface than there are in unit volume of vapour

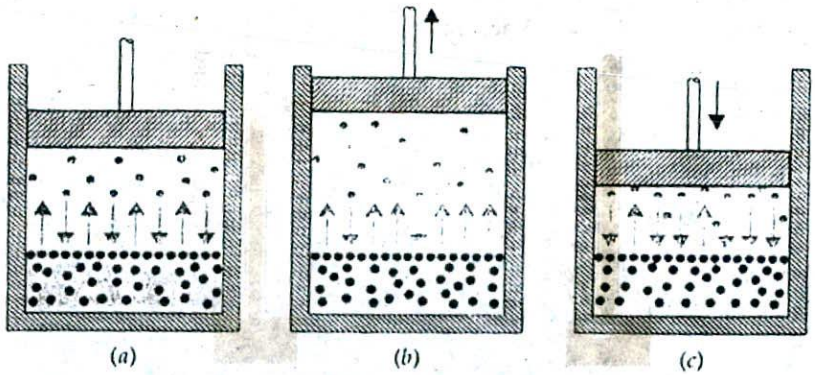


Figure 3.2 Molecules leaving the surface and returning to it

phase, more and more molecules will escape into the vapour phase. The pressure exerted by the molecules in the vapour phase will increase, but the number of molecules in this phase increases and there will be a greater tendency for them to return to the liquid phase. Eventually a state will be reached when the number of molecules leaving the unit area of the liquid surface in unit time is equal to the number of molecules returning to it from the vapour in the same time. This is the state of *dynamic equilibrium* and the pressure exerted by the vapour under such condition is the saturation vapour pressure at the given temperature. Since the number of molecules that can escape from the liquid surface in a given time is proportional to the area of the free surface of the liquid and since the number that returns to the liquid phase is also proportional to the area of this surface, the vanour pressure will be independent of the relative amounts of the liquid and vapour. Only the fraction of the molecules which have high velocity can escape and this fraction increases with increase of temperature. Vapour pressure may also be regarded as a measure of *escaping tendency* of the liquid molecules. The higher the escaping tendency the higher is the vapour pressure.

It is significant to note that liquids with a low vapour pressure have relatively large values of the van der Waals' constant *'a'*.

3.3 Vapour Pressure and Temperature

The general behaviour of the vapour pressure of liquids *at* different temperatures is shown in Figure 3.3. It may be seen that vapour pressure rises rather sharply at higher temperatures. The curves continue to the critical temperature beyond which these cannot be extended because liquids cannot exist above the critical temperature. When logarithms of vapour pressure are plotted against the reciprocals of absolute temperatures straight lines, shown in Figure 3.4, and represented by the equation, where A and B are constants,

$$\log p = -\frac{B}{T} + A \qquad (3.1)$$

are obtained. As will be seen in *Section 7.15*, the slope B is equal to ΔH_{vap} /2·303 R where ΔH_{vap} is the molar heat of vaporization. Hence the molar heat of vaporization may be determined from measurements of vapour pressure at several temperatures.

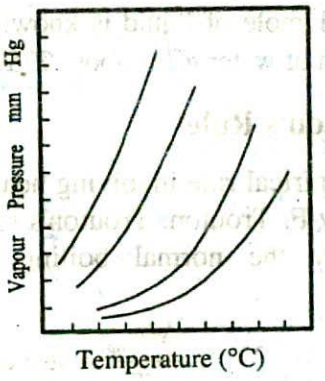


Figure 3.3 Vapour pressure vs temperature

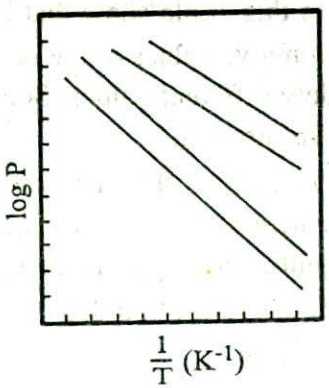


Figure 3.4 log of vapour pressure vs 1/T

3.4 Boiling Point of a Liquid: Enthalpy of Vaporization

The temperature at which the vapour pressure of a liquid equals the atmospheric pressure is called the *boiling point* of the liquid. Boiling is characterized by the state in which stable bubbles of vapour formed within the body of the liquid rises to the surface and then break. Once boiling of the liquid starts, the temperature of the liquid remains constant at its boiling point, and the liquid continues to change to vapour. If, however, the external pressure is higher than 1.0 atmosphere the boiling point will be higher. In dealing with organic liquids which decompose at the normal boiling point, it is sometimes necessary to boil or distil at a lower temperature. This is accomplished by reducing the external pressure and the process is known as *distillation under reduced pressure*.

The fact that liquid at its boiling point is converted into vapour by continued heating but without increase of temperature indicates that the process of conversion of liquid into vapour is accompanied by absorption of heat. This energy goes to supply the extra energy to the molecules so that they can escape from the sphere of attraction of other molecules and go to the vapour state. The heat absorbed when a definite quantity of liquid, e.g., 1 *g* or 1 mole, is converted into vapour is known as the *Latent Heat of Vaporization*. The heat necessary to evaporate 1 mole of liquid is known as the *molar heat of vaporization*. The latent heat of evaporation of water g^{-1} is about 2259.4 J while that of benzene is about 393.30 J.

3.5 Trouton's Rule

An empirical rule involving heats of vaporization at the normal boiling point was put forward by F. Trouton. Trouton's rule states that the heat of vaporization in Joule mol^{-1} divided by the normal boiling point in Kelvin is approximately 88 for most liquids, i.e.,

$$\frac{\Delta H_{vap}}{T} \approx 88\, J\, \text{deg}^{-1}\, mol^{-1} \qquad (3.2)$$

Trouton's rule is obeyed by a number of liquids as shown in Table 3.1.

Data in this Table show that liquids with wide ranges of boiling points and heats of vaporization give values of the ratio $\Delta H_{vap}/T$ close to 88, although some of the substances show widely different values. Some sort of explanation may be given for such deviation from the Trouton's rule.

It may be noted that the heat of vaporization divided by the temperature in Kelvin gives the increase in entropy (*Section 7.91*) when a liquid is converted into vapour. For many liquids, then, the increase of entropy during vaporization or the entropy of vaporization is about $88\, J\, \text{deg}^{-1}\, mol^{-1}$ i.e.,

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} \approx 88\, J\, \text{deg}^{-1}\, mol^{-1} \qquad (3.3)$$

7-B

Table 3.1 Heats and entropies of vaporization of liquids at the normal boiling points.

Liquid	Normal b.p. (K)	ΔH_{vap} J mol^{-1}	$\Delta S_{vap} = \Delta H_{vap}/T$ J deg^{-1} $mole^{-1}$
Oxygen	90.2	6820.0	75.6
Nitrogen	77.8	5564.7	71.5
Chlorine	239.1	20410	85.4
Acetic acid	391.5	24393	62.31
Formic acid	374.0	24100	64.45
Ethane	184.6	14715	79.7
n-Butane	271.4	22393	82.5
Benzene	353.3	30765	87.09
Cyclohexane	353.9	30083	85.01
Naphthalene	491.2	40460	82.37
Carbon tetrachloride	349.9	30000	85.74
Stannic chloride	385.2	33054	85.82
Ammonia	239.8	23347	97.4
Ethyl alcohol	351.7	38576	109.70
Water	373.2	40656	108.95

This means that the increase in disorder mol^{-1} due to vaporization is the same for a large number of liquids. The liquids which have entropies of vaporization appreciably higher than the average value of 88 $J\ deg^{-1}\ mol^{-1}$ are those which are known to be associated in the liquid state due to hydrogen bonding. Extra energy would be required to separate the molecules from each other, which makes the entropy of vaporization high. Acetic acid and other carboxyl acids show lower values of ΔS_{vap}. This is to be expected as these acids exist as double molecules even in the vapour state.

A usefulness of the Trouton's rule is that an approximate value of the boiling point of the liquid may be calculated from this rule if the heat of vaporization is known. The latter quantity may be derived, as has been said earlier (*Section 3.1*), from measurement of vapour pressure of the liquid at two or more temperatures.

3.6 Measurement of Vapour Pressure

A number of methods are known for the determination of vapour pressure of liquids. Barometer tubes may be used, as described in *Section 3.1.* A second barometer tube is used for comparison.

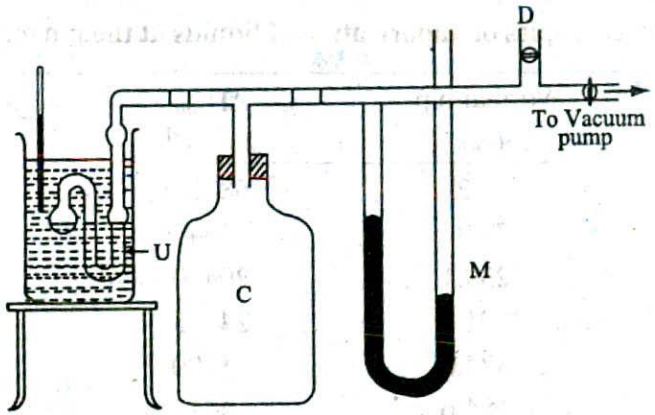


Figure 3.5 Isoteniscope for measuring vapour pressure

In one method described by A. Smith and A. W. C. Menzies a device, known as isoteniscope (Figure 3.5) is used. A bulb, about 3 cm in diameter, is about half-filled with the experimental liquid; liquid is introduced into the two limbs of tube. The isoteniscope is placed in a constant temperature bath, and is connected to a vacuum pump. There is a manometer, M, in the line and a large bottle, C, for regulating the pressure. The air in the liquid is first boiled out. The pressure is reduced and then adjusted with the help of the regulator bottle until the level of the liquid is the same in both the limbs of the U-tube. The pressure registered by the manometer at this point is the vapour pressure of the liquid at this temperature.

In the procedure devised by Ramsay and Young the external pressure is fixed and the temperature at which the liquid boils is then measured. The external pressure is equal to the vapour pressure of the liquid at this temperature. The apparatus is shown in Figure 3.6.

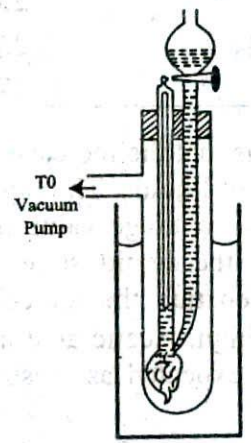


Figure 3.6 Ramsay and Young's apparatus for vapour pressure measurement

It consists of a boiling tube fitted with a rubber stopper through which passes a thermometer. The bulb of the thermometer is covered with absorbent cotton which is kept moist with the liquid to be studied. This is achieved by dropping a slow stream of the liquid from a dropping funnel as shown in the figure. The boiling tube is provided with a side tube which is connected to a vacuum system as in Figure 3.5. The liquid film in contact with thermometer bulb is warmed by placing the boiling tube in a liquid bath, the temperature of which is maintained 10°-20°C above that indicated by the thermometer.

For making a measurement the pressure is maintained at a given low value by adjusting the air inlet in the vacuum system. The temperature of the tube and its contents are then raised until the thermometer reading does not change when a drop of liquid is allowed to flow into the cotton. The reading of the thermometer and the pressure reading are taken. At this temperature the liquid is in equilibrium with the vapour. Hence the pressure recorded is the vapour pressure of the liquid at this temperature.

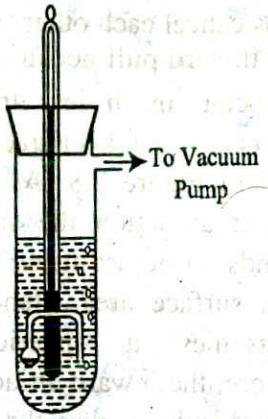


Figure 3.7 Apparatus of Smith and Menzies

Smith and Menzies devised a very simple apparatus for measuring vapour pressures of liquids. It consists of a bulb-tube with a narrow and bent outlet, which is tied to the bulb of a thermometer as shown in Figure 3.7. The bulb is partly filled with the liquid under investigation. The thermometer bulb is then introduced into a boiling tube containing a liquid of high boiling point, e.g., paraffin; the boiling tube is connected to pressure reservoir, pressure gauge and a vacuum system as in Figure 3.5. The paraffin in the boiling tube is brought to a convenient temperature in a thermostat and the tube is evacuated. After some time the liquid in the bulb starts boiling as is indicated by the escape of a stream of bubbles. Air is allowed to enter the system very slowly through D (Figure 3.5) until the bubbles just cease to come out of the tube. The temperature and pressure are recorded. The pressure is corrected for the pressure of the column of paraffin above the bulb-tube. The corrected pressure reading is the vapour pressure of the liquid at this temperature. In a similar way vapour pressures at other temperatures may be measured.

The gas saturation or transpiration method is more suitable for determining lowering of vapour pressure in dealing with dilute solutions *(Section 9.5)* but may be adapted for measurement of vapour pressure of pure liquids.

3.7 Surface Tension

It is a matter of common experience that drops of liquid tend to assume a spherical shape. When a steel needle is placed carefully on the surface of water it floats, although its density is much higher than that of water and the buoyancy effect is practically nil. The cause of this property of the surface of liquids is what is known as *surface tension.*

The surface tension of liquids arises from the unbalanced forces of molecular attraction on the surface. Consider a molecule in the interior of a liquid. The molecule is being attracted in all directions by the surrounding molecules and, on an average, these

attractions cancel each other. A molecule on the surface, on the other hand, experiences a resultant inward pull because there are practically no molecules on the vapour side (density being much less than that of liquid) to counteract this attraction. This is illustrated in Figure 3.8. As a result of this inward attraction the surface of a liquid tends to adjust itself to give the minimum surface area. Hence a liquid drop assumes a spherical shape. Furthermore, the inward attraction on the surface molecules makes the surface act as if it consisted of an elastic membrane.

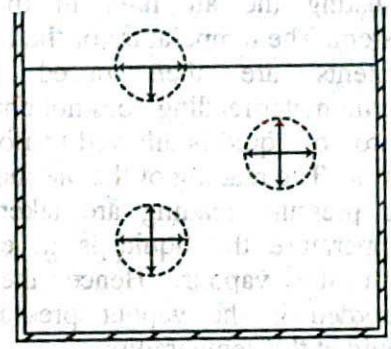


Figure 3.8 Attraction on molecules in a liquid.

The surface tension of a liquid may be defined with reference to Figure 3.9. A liquid film is formed, like a soap film, in a wire frame, three sides of which are fixed while the fourth is movable. The film may be expanded by applying a force to the movable side. If the force is withdrawn the film contracts. The force required to stretch the film is found to be proportional to the length, l, of the movable side. Since there are two surfaces to the films the total length of the film is $2l$ and one can write

$$Force = \gamma(2l) \tag{3.4}$$

The proportionality constant, γ, is known as the surface tension. Hence surface tension may be defined as

'The force in dynes, which acts at right angles to a line of 1 cm length on the surface, opposing the expansion of the surface area'.

In order to increase the area of the surface it is necessary to do work to bring the molecules from the interior to the surface against the force of attraction. The liquid surface may, therefore, be thought to possess free energy. *Surface free energy may be defined as the work (in ergs) required to increase the area by 1 sq cm.* The tendency of a liquid surface to reduce its area may be regarded as another example of a system tending toward a state of minimum free energy.

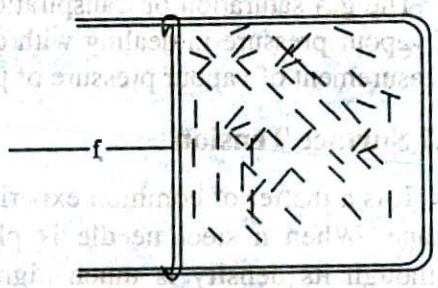


Figure 3.9 Surface tension of a liquid

3.8 Adhesion and Cohesion

Attractive force operating between like molecules, as in a pure liquid, is termed the force of cohesion. The term adhesion is used if the attraction is between unlike molecules, namely, between water and a clean metal surface. When adhesion is relatively strong the water molecules will spread on the clean metal surface. This is known as *wetting*. The forces have decisive influence in choosing a correct detergent for cleaning purposes.

3.9 Measurement of Surface Tension

A number of methods are available for the measurement of surface tension of liquids. Of these a few are described below.

(a) Capillary rise method : This method is the most convenient, simple and gives the most accurate result. The method is based on the fact that when a clean capillary tube, which is wetted by the liquid, is dipped in to a liquid the liquid rises in the capillary. The rise of the liquid in the capillary may be understood if it is assumed that a thin film of the liquid adheres to the wall of the capillary. In order to reduce its surface area the liquid rises in the tube. The height to which the liquid column rises is dependent on the surface tension pulling the liquid upward. Equilibrium is reached when the force of surface tension is balanced by the force of gravity on the column of liquid. The experimental procedure may be illustrated with reference to Figure 3.10.

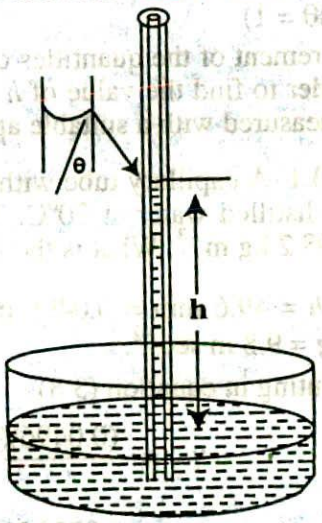


Figure 3.10 Measurement of surface tension by capillary rise method.

Let r be the radius of the capillary and d be the density of the liquid. At equilibrium let the height of the liquid column above the level in the container be h. The surface of the liquid in the capillary, i.e., the liquid meniscus, makes an angle θ with the wall of the capillary. Consequently the average height (h) of the column is to be taken and is computed as the height of the column up to the bottom of the meniscus *plus* one-third of the radius of the capillary.

Then the downward force = (h)(area of cross section of the capillary) (d) (g)

$$= (h)(\pi r^2)(d)(g) \tag{3.5}$$

where g is the gravitational constant

As the surface makes an angle θ with the walls and only the vertical component of the force is effective in holding up the liquid column,

$$\text{The upward force} = 2\pi r\gamma\cos\theta \tag{3.6}$$

At equilibrium, upward force = downward force.

$$\text{So,} \quad 2\pi r\gamma\cos\theta = h\pi r^2 dg$$

$$\text{or} \quad \gamma = \frac{hdgr}{2\cos\theta} \tag{3.7}$$

For many liquids, including water, θ is very close to 0 in glass capillary so that we have

$$\gamma = \frac{1}{2}hdgr \tag{3.8}$$

(as $\cos\theta = 1$)

Measurement of the quantities on the right hand side of equation (3.8) gives the value of γ. In order to find the value of h a travelling microscope is used and the density of the liquid is measured with a suitable apparatus.

Example 3.1: A capillary tube with inside diameter of 0.06 cm is dipped vertically into a beaker of distilled water at 20°C. The water rises 49.6 mm in the tube. The density of water is 998.2 kg m^{-3}. What is the surface tension of the water?

Solution: h = 49.6 mm = 0.0496 m; r = 0.06/2 cm = 0.0006/2m = 0.0003m; d = 998.2 kg m^{-3}; g = 9.8 m sec^{-2}.

Substituting in equation (3.8)

$$\gamma = \frac{(0.0496)(998.2)(9.8)(0.0003)}{2}$$

$$= 0.0728 \text{ N m}^{-1}$$

If the liquid does not adhere to the glass, i.e., does not wet it, for example, mercury in a glass capillary, a condition as shown in Figure 3.11 results. Here the liquid column is depressed in the tube. At equilibrium the downward pull of the force due to surface tension is equal to the effect of gravity in the liquid outside the capillary tending to restore the original level in the tube.

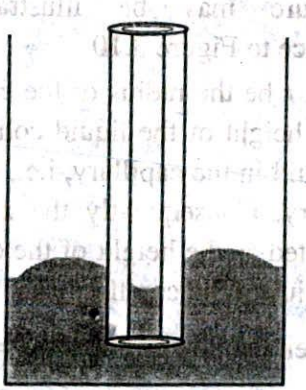


Figure 3.11 Mercury meniscus

(b) Drop formation method : Figure 3.12 shows a drop of liquid forming at the end of a capillary tube of radius *r*.

As the liquid slowly extends from the tip of the tube, the excess liquid is held to the tip of the tube by the surface tension forces. As the volume of the extended mass of the liquid increases, the drop finally breaks off when the surface force can no longer support the mass of the drop. At the instant the drop breaks, the gravitational force on a drop of mass *m* equals the surface tension force.

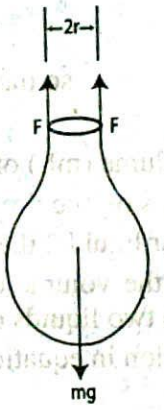


Figure 3.12 A drop forming at the tip of capillary tube of radius *r*

$$mg = 2\pi r\gamma \qquad (3.9)$$

In practice the mass of a number of drops are taken from which the average value for one drop is calculated.

Example 3.2: A drop pipette of radius 0.40 cm was used to slowly drop a liquid at 25°C in the form of small drops which were collected in a weighing bottle. If the mass of 20 drops of the liquid was 1.052 *g*, calculate the surface tension of the liquid at this temperature. ($g = 980$ cm sec^{-2}).

Solution: Substituting the values of the different quantities in equation (3.9) we obtain

$$\frac{1.052}{20} \times 980 = (2 \times 3.14 \times 0.4)\gamma$$

Hence $\gamma = 20.5$ *dyne* cm^{-1}

Another way of using the drop formation on the tip of a capillary for surface tension measurement is the drop volume method. A drop pipette (Figure 3.13) is filled with one liquid whose surface tension is known. The liquid is allowed to drop slowly and the number of drops counted until the lower meniscus travels from A to B. The experiment is repeated with the test liquid and again the number of drops when the meniscus travels from A to B is counted. For the two liquids the surface tension equation (3.9) may be written as

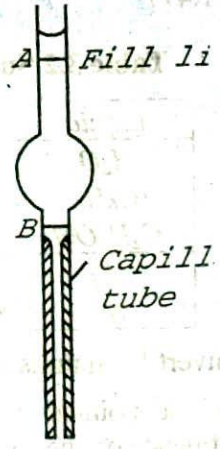


Figure 3.13 A drop pipette

$$m_1 g = 2\pi r\gamma_1$$
$$m_2 g = 2\pi r\gamma_2$$

so that $$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \qquad (3.10)$$

Now the volume (mL) of one drop of liquid 1= V/n_1
And the mass of one drop of liquid 1 $= m_1 = (V/n_1)d_1$
Similarly for liquid 2 the mass of one drop = $m_2 = (V/n_2)d_2$
where V is the volume of liquid dropped in each case and n_2 and n_1 are the number of drops of the two liquids of densities d_2 and d_1 respectively.

Substitution in equation (3.10) gives

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} = \frac{\frac{V}{n_1}\cdot d_1}{\frac{V}{n_2}\cdot d_2} = \frac{n_2 d_1}{n_1 d_2}$$

Example 3.3: In a drop volume method of measuring surface tension 10.5 mL of water dropped between the two lines and the number of drops was 40. When the same volume of another liquid was allowed to fall the number of drops was found to be 52. If the density of the second liquid is 0.88 g mL^{-1} find the surface tension of the liquid. (surface tension of water = 72 dynes cm^{-1} and density of water = 1.0 g mL^{-1})

Solution: $$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2} = \frac{52\times 1.0}{40\times 0.88} = 1.477$$

$$\gamma_2 = \frac{72}{1.477} = 48.7 \text{ dynes cm}^{-1}$$

Table 3.2 Surface tension (dynes/cm) of some liquids

Liquid	20°C	50°C	75°C
H_2O	72.75	67.91	63.5
C_6H_6	28.2	25.0	21.9
C_2H_5OH	21.8	19.8	—
Hg	480 (at 0 °C)	—	—
Ag	800 (at 970 °C)	—	—

(To convert from units of dynes cm^{-1} to SI unit Nm^{-1} multiply by 10^{-3})

It should be pointed out that the phase in immediate contact with the surface has profound influence on the surface tension of a liquid. The values quoted in the table are those for measurements in air. The surface tension of molten metals is seen to be quite large.

3.10 Surface Tension and Temperature

Surface tensions of all substances vary with temperature. For most liquids the value usually decreases with increase of temperature and becomes zero at the critical temperature (*Section 2.30 and Section 20.2*).

3.11 The Viscosity of Liquids

Liquids flow when placed in an inclined surface or a tube. Some liquids flow more readily than others. Those that flow slowly, namely coal-tar, lubricating oil, glycerine etc., are said to be viscous. On the other hand, those which flow easily, namely water, kerosene oil, benzene etc. are said to be liquids of low viscosity. In general, it may be stated that liquids possess a certain resistance to flow. Viscosity is a measure of this resistance to flow.

Viscosity is really a frictional effect experienced by one layer of a liquid in moving past another in much the same way as an object experiences frictional resistance when dragged an a surface. The frictional force, *f*, resisting the flow of one layer of fluid past the adjacent layer is proportional to the area, A, of the interface between the layers and to *du/dr*, the velocity gradient. This is Newton's law and is given by

$$f = \eta A \frac{du}{dr} \tag{3.10}$$

where η, (eta, a Greek letter), the constant of proportionality, is called the *co-efficient of viscosity*. When the velocity gradient is unity and the area is 1 sq cm, η is equal to the force. Hence *the co-efficient of viscosity, η, may be defined as the force per sq cm required to maintain a difference of velocity of 1 cm per second between two parallel layers 1 cm apart.* It is evident that the dimensions of η are $g\ cm^{-1}\ s^{-1}$. When the force is 1 dyne, η is called the poise after the French scientist Poiseuille. For most liquids η is much smaller than one poise and the viscosity is usually expressed in millipoise or centipoise. In the SI unit viscosity is $kg\ m^{-1}\ s^{-1}$.

One poise = $1\ g\ cm^{-1}\ s^{-1} = 0.1\ kg\ m^{-1}\ s^{-1}$.

The reciprocal of the co-efficient of viscosity is known as the fluidity, $\varnothing$, or

$$\varnothing = \frac{1}{\eta} \tag{3.11}$$

Fluidity is a measure of the ease with which a liquid can flow.

3.12 The Poiseuille Equation

Poiseuille studied the flow of liquids through capillaries and derived an expression for the co-efficient of viscosity. Although the correct version of the formula, which is widely used in measurement of viscosity, was derived by Hagenbach the formula is known as *Poiseuille equation.* Consider a liquid flowing through a tube of length, *l*, and

of circular cross-section with radius, R. The velocity of flow becomes uniform when the pressure drop, $P = P_1 - P_2$, along the length, l, balances the viscous drag of the liquid. The viscous drag results from the thin film of liquid that adheres to the wall of the tube. This thin film is assumed to be stationary, and the rate of flow increases to a maximum at the centre of the tube. If the volume of liquid flowing in t seconds is V, then according to Poiseille

$$\eta = \frac{\pi P R^4 t}{8 V l} \tag{3.12}$$

This is Poiseuille equation. This equation has been verified quite accurately for flow of liquids through tubes. The kind of flow consistent with this equation is called laminar or streamline flow. At high rates of flow or flow in tubes of large diameter the flow type changes to what is known as turbulent flow. In turbulent flow the imaginary layers of liquid do not flow parallel to each other.

3.13 Measurement of Viscosity

There are a number of diverse methods for determining the co-efficient of viscosity; for example, (a) by determining the volume of liquid flowing through a capillary of known dimensions under a given pressure, i.e., using Poiseuille's equation, (b) from the rate of fall of spherical balls through the liquid (c) from the torsion in a standard wire supporting a cylinder immersed in a liquid moving at a known speed.

The method most useful for ordinary liquids is that based on Poiseuille's equation (3.12).

It is difficult to determine the absolute viscosity by Poiseuille's method. The usual procedure is to determine the viscosity of a given liquid relative to another liquid whose viscosity is accurately known. Such relative measurement is a common practice in the determination of many physico-chemical quantities.

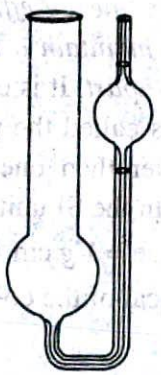


Figure 3.15 Simple viscometer

A relatively simple viscometer, as shown in Figure 3.15, may be used for the determination of relative viscosities. For a given viscometer the radius, R, and length, l, are constants. The pressure difference that causes the liquid to flow through the capillary is the difference, h, between the levels of liquid in the bulbs. If d is the density of the liquid this pressure will be $h.\ g.\ d.$

For a liquid of density, d_1, and viscosity, η_1, if the time of flow through the capillary is t_1 seconds, equation (3.12) takes the form

$$\eta_1 = \left(\frac{hg\pi R^4}{8Vl}\right) d_1 t_1 \tag{3.13}$$

If the same volume of another liquid of viscosity, η_2, and density, d_2, flows through the capillary in the same viscometer in t_2 seconds, then

$$\eta_2 = \left(\frac{hg\pi R^4}{8Vl}\right) d_2 t_2 \tag{3.14}$$

The ratio of viscosities is then given by

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \tag{3.15}$$

Water is usually taken as the standard substance. It is obvious that if the viscosity of one liquid is known, that of the other may be calculated from the measured values of the densities and times of flow of the two liquids.

The viscometer shown in Figure 3.15 is known as the Ostwald viscometer. A known appropriate volume of the liquid under examination is first placed in the wider limb and sucked up the capillary to a level beyond the upper mark in the capillary. The liquid is then allowed to fall and the time taken for the liquid level to fall from the upper to the lower mark in the capillary is noted. The liquid is then replaced by an equal volume of the second liquid and the procedure is repeated. Use of equation (3.15) will give the required viscosity value. There are a number of other viscometers in use which are simple modifications of the Ostwald viscometer.

Example 3.4: The flow time for water in a viscometer is140 seconds while that for a liquid of unknown viscosity in the same viscometer is 80 seconds. The density of water is 1.0 $g\ mL^{-1}$ and that of the other liquid is 0.82 $g\ mL^{-1}$. All measurements are done at 20°C. The viscosity coefficient of water is 1 centipoise at 20°C. Calculate the viscosity coefficient of the experimental liquid.

Solution: Taking liquid 1 as water and the other liquid (viscosity η) as 2 and substitution in equation (3.15) yields

$$\frac{1}{\eta} = \frac{1\times140}{0.82\times82} = \frac{140}{65.6}$$

Hence $$\eta = \frac{65.6}{140} = 0.469 \text{ centipoise}$$

3.14 Viscosity and Temperature

The viscosity of liquids usually decreases with increasing temperature. For many liquids the variation of viscosity with temperature may be represented by

$$log\ \eta = \frac{A}{T} + B \qquad (3.16)$$

where A and B are constants for a given liquid (Figure 3.16). This is not, however, valid for all liquids.

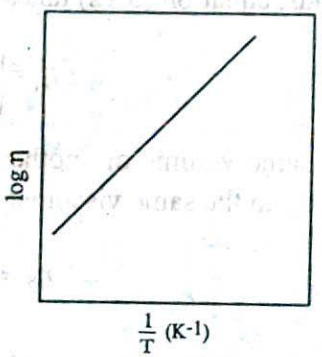


Figure 3.16 log η plotted against 1/T

Viscosity measurements should, therefore, be carried out in constant temperature baths.

3.15 Viscosity and Its Importance

Viscosity is an important property in both theoretical and practical work. Viscosities of lubricating oils play an important role in their use in machines. In the manufacture of paint, rubber, glue and synthetic polymers extensive use of viscosity measurements is made in control operation.

In theoretical work, particularly in determining molecular masses of high polymers viscosity measurements have found very wide applications.

3.16 Structure of Liquids

During the past decades much progress has been made in the understanding of the gaseous and solid state of matter. Our knowledge about the liquids is still very meagre.

X-ray diffraction studies of liquids, study of the phenomenon of fusion, viscosity of liquids etc. have led to several approaches to a theory of liquid.

Close to the critical temperature a liquid may be regarded as an imperfect gas, as at the critical point there is no distinction between liquid and vapour. On the other hand, near the freezing point the liquid may be considered as similar to a crystal except that the well ordered arrangement of units does not extend beyond a number of molecules. This view is supported by X-ray studies. The situation is called short-range order and long-range disorder.

A model of a liquid in which a molecule moves in some small volume or "cell", or "cage" and that it is generally confined to this cell by the neighbouring molecules has been advanced. The molecules are also moving about, and the cell is, therefore, not of a fixed geometry. The volume in which the centre of molecule is free to move is called the free volume. This can be related to some of the thermodynamic properties of the liquid,

such as the entropy of vaporization. In another approach the free volume that is distributed throughout the liquid 'cells' is replaced by 'holes' or 'vacancies' in the liquid structure. The 'holes' or 'vacancies' can move about within the liquid volume. Molecules close to such a vacancy would have the properties of a gas, whereas molecules far from a vacancy would have solid-like properties. None of these approaches, however, explains all the known facts about liquids and attempts are constantly being made to formulate a satisfactory theory of liquids.

QUESTIONS AND PROBLEMS

1. Explain what is meant by the vapour pressure of a liquid. How does vapour pressure change with temperature?
2. What is meant by the normal boiling point of a liquid? What is meant by distillation under reduced pressure?
3. Liquid sodium has the following vapour pressures at the indicated temperatures;

t°C	439	549	701
p mm Hg	1.0	10.0	100

By plotting these data appropriately determine (a) the boiling point of liquid sodium, and (b) the heat of vaporization at the boiling point. [Ans.(a) 880°C;(b) 102 kJ mol^{-1}]

4. What is meant by molar latent heat of vaporization? How can this quantity for a liquid be determined?
5. (a) From the boiling point T_b of a liquid and the assumption that the liquid follows Trouton's rule, calculate the value of the vapour pressure at any temperature T. [Ans. $ln\ P_{atm} = 0.5\ (1—T_b/T)$]

(b) The boiling point of diethyl ether at 1.0 atm pressure is 34.6°C. Calculate the vapour pressure at 25°C. [Ans. 0.715 atmosphere]

6. Describe a method of making accurate measurements of vapour pressure of liquids.
7. Explain the phenomenon of surface tension of liquids. How is surface tension of liquids measured?
8. Ethanol rises to a height of 5.20 cm at 20°C in a capillary tube of radius 0.110 mm. From these data calculate the surface tension of ethanol at this temperature. Density of ethanol at 20°C is 0.741 g per mL. [Ans. 22.2 dynes per cm]
9. Give a detailed derivation of the expression relating surface tension to capillary rise.
10. Explain what is meant by the viscosity of a liquid. Give an exact definition of viscosity. In what units is viscosity expressed?
11. Discuss the experimental determination of viscosity by means of an Ostwald viscometer. How is viscosity affected by temperature?

4 THE SOLID STATE

Solids are characterized by their definite shapes and fixed volumes. The rigid structure is indicative of the fact that the atoms, molecules or ions in solids are held together by strong forces of attraction and the constituents are placed in fixed positions from which they cannot move appreciably. As a result the solid substances assume rigidity and mechanical strength and have definite shapes. The forces holding the constituent atoms, molecules or ions are different and give rise to differences in physical properties of the solids.

The solid state of matter is broadly classified into two types: *crystalline and amorphous*. The crystalline state is characterized by, (i) definite geometric shapes, (ii) rigidity, (iii) incompressibility and (iv) definite melting point. The atoms, molecules or ions are arranged in completely regular fashion in a crystal. The arrangement of the constituent atoms, molecules or ions is not regular in amorphous solids, and they do not have sharp melting points. Glasses or plastics are amorphous in nature, and they may be regarded as super cooled liquids. Upon heating, the amorphous solids gradually become soft and then become mobile over a wide range of temperature. There are, however, substances in the solid state which have regions in which orderly arrangement of the constituents predominates, but in other parts there is completely random arrangement. Examples are cotton, jute, silk, wool, rubber, hair and many of the synthetic fibres. These considerations have led some people to restrict the term solid state to purely crystalline substances. In the subsequent sections the treatment will be concentrated on solids of crystalline form.

4.1 Preparation of Crystals

Crystals of solid substances are formed when saturated solutions of solids are cooled slowly. The process is called *crystallization*. The size and purity of crystals depend to a large extent on the rate at which they are formed. Formation of the crystals is accompanied by evolution of a large amount of heat (heat of fusion). The slower the rate of formation the purer and larger is the crystal, because the atoms and molecules have time to find their proper positions in the crystal lattice. Crystals of different substances and of varying sizes have been prepared by a good number of ingenious methods. Some of the commonly used methods are: (a) Ceramic method, (b) Microwave synthesis, (c) Sol-Gel method, (d) Precursor method, (e) Hydrothermal method, (f) Chemical Vapour Deposition (CVD) method. A brief description only of each of these methods will be discussed here.

(a) Ceramic method : In this method two solids which react to form the required product are heated together either in an ambient condition or in an evacuated vessel. Evacuated vessels are required when the reactant or product is air or water sensitive and volatile.

(b) Microwave synthesis : In some cases microwave ovens rather than conventional heating is used to speed up the reactions. Solid state materials such as mixed oxides have been synthesized by this method. Microwave heating offers better control over the reaction conditions. A number of superconductors have been prepared by this method.

(c) Sol-Gel method : A sol is a colloidal dispersion of small (1-1000 nm diameter) particles. In the Sol-Gel method a sol of reactants in a suitable solvent is first prepared. The sol is then either treated or simply left to form gel. The gel is finally heated to obtain the desired product. The main steps in Sol-Gel method is schematically shown in Figure 4.1.

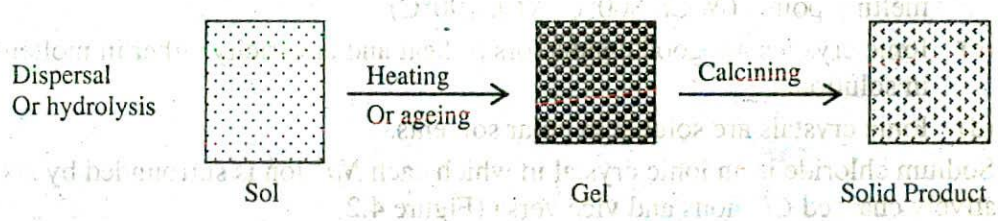


Figure 4.1 Schematic diagram of Sol-Gel method

The heating of the gel helps to remove the solvent and allows the rearrangement in the structure of the solid. It also allows crystallization.

(d) Precursor method : The precursor method is a novel synthesis method for the preparation of solid substances of correct stoichiometry from a single source solid precursor. For example, an oxide MM'_2O_4 can be prepared if a mixed salt of an acetate containing M and M' in the ratio 1:2 is formed, which upon heating decomposes to produce the desired compound. Doped semiconductor, nanocrystals encapsulated within oxide-shells, coating metal oxide film on titanium, ultrafine *Ni-Zn* ferrites etc. have been prepared by the precursor method.

(e) Hydrothermal method : When water is heated in a closed vessel (autoclave) the pressure inside is increased and water remains as liquid above its normal boiling point. This condition is called *hydrothermal*. The heating of reactants in *'super-heated water'* , (also known as supercritical water; >373 K) has received much attention in synthesising crystals, particularly in mineralogy.

(f) Chemical Vapour Deposition (CVD) method : This method is based on the crystallization of reactants in the vapour or gas phase. In this method volatile starting materials are mixed at a suitable temperature and the solid products are crystallized out. Sometime the volatile compounds are passed through the reaction vessels with an inert carrier gas. Typical volatile materials include among others, hydrides, halides, organometallic compounds etc.

4.2 Bonding in Crystals and their Characteristic

Depending on the forces that hold the atoms, molecules or ions together in crystal lattice crystals are classified into four main types. These are:

(i) *Ionic crystal*, (ii) *Molecular crystal*, (iii) *Network covalent crystal* and (v) *Metallic crystal.*

(i) Ionic crystal: The ionic crystals are made up of positive and negative ions held together by electrostatic forces of attractions. The bonds between the oppositely charged ions are *ionic bonds*. The important features of ionic crystals are:

(a) The ionic forces are non-directional,

(b) Since the electrostatic forces between ions are strong the ions are closely packed in ionic crystals and it is difficult to remove the ions from their respective positions in the lattice. As a result ionic crystals are very hard and have high melting points (*NaCl*, 800°C; *KCl*, 790°C).

(c) Ionic crystals are good conductors of heat and electricity either in molten state or in solution.

(d) Ionic crystals are soluble in polar solvents.

Sodium chloride is an ionic crystal in which each Na^+ ion is surrounded by six negatively charged Cl^- ions and vice versa (Figure 4.2)

(ii) Molecular crystal: The lattice points in molecular crystals are occupied by molecules which are held together either by relatively weak van der Waal's force or hydrogen bonding. As a result the molecular crystals are soft and have low melting points. Solid sulfur dioxide (SO_2) is an example of molecular crystal. The predominant force in solid sulfur dioxide is dipole-dipole interaction. Ice is another example of molecular crystal which has a three dimensional lattice structure. Intermolecular hydrogen bonding is responsible for maintaining this three dimensional network in ice. Other examples of molecular crystals are I_2, P_4, S_8, CCl_4 etc.

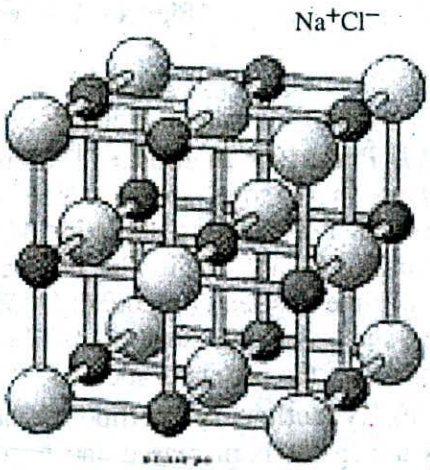


Figure 4.2 Structure of *NaCl* crystal

(iii) Network covalent crystal: Network covalent crystals are made up of atoms held together by covalent bonds arranged in an extensive three dimensional network. Such crystals are strong and hard. They have very high melting points. A good example is the diamond structure (Figure 4.3). In diamond each carbon atom of the lattice is tetrahedrally bonded to four neighbours. Germanium and silicon have diamond like crystal structure. Similar structure is assumed by compounds such as *ZnS* (Zinc blende), *SiC* etc.

8-B

In crystals having diamond like lattice the covalent bonds are arranged in three dimensions. Graphite is an example of the class of crystals which have a two dimensional array of covalent bonds. As shown in Figure 4.4, graphite has layers of hexagonal networks as in the aromatic series of compounds. In each layer the carbon atoms are held by strong covalent forces but the forces between layers are weaker. This is why graphite is an excellent lubricant as one layer can slip over another.

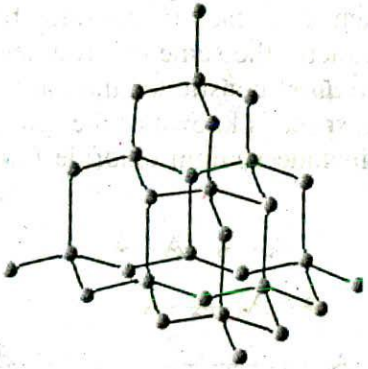


Figure 4.3 Structure of diamond

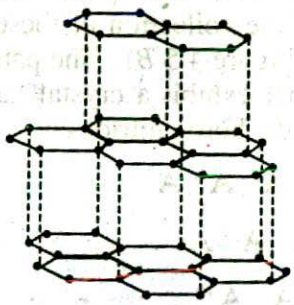


Figure 4.4 Structure of graphite

(iv) Metallic crystal: The bonding in metals is quite different from other types of crystals. In a metal the outer electrons of the atoms are *delocalized* over the entire crystal. The lattice consists of arrays of cations immersed in a sea of valence electrons. Strong electrostatic forces between the cations and the cloud of delocalized electrons are responsible for the greater strength of the metals. The delocalized electrons occupy a series of energy levels. These energy levels are generally very close so as to form a discrete energy band. There are gaps between the energy bands and electrons are forbidden to occupy these gaps. The bands and gaps are characteristic of a solid. The high electrical conductivity of metals may be understood in terms of the Band Model (*Section 4.11*). The ease with which the delocalized electrons move makes the metals good conductors of heat and electricity. Metals are lustrous (reflectivity), ductile and malleable. All these properties of metal can be explained by considering delocalization of electrons in metallic crystals.

4.3 Internal Structure of a Crystal

It has already been stated at the beginning of this chapter that solid substances can either be *crystalline or amorphous*. The crystalline solids are composed of one or more smaller crystals each having a well-ordered structure. In order to study the structure of crystalline solids certain terms commonly used in crystallography should be well understood.

4.3.1. Crystal lattice, space lattice and lattice Points

The definite geometric shape of the crystals results from complete regular arrangements of atoms, molecules or ions in three dimensions. This three dimensional ordered arrangement of one or more smaller units of crystals is conveniently described in

terms of a *crystal lattice*. The lattice is divided into a number of identical blocks or cells that are repeated in all directions to form a particular geometric pattern. Lattices are classified according to their dominant symmetries. These are trigonal, hexagonal, tetrahedral, orthorhombic, monoclinic, and triclinic. However, the concept of crystal lattice can be best understood by considering two-dimensional repeating units as shown in Figure 4.5 (A). It can be seen from the figure that a pattern of *A*'s has been demonstrated which consists of *basic repeating units.* A *lattice point* is obtained by selecting the same point (a ***dot*** at the crossbar of each *A)* in each of the same basic unit (in this case each *A*). Each point in the lattice has exactly the same environment as any similar point. The collection of these points (i.e. the ***dots***) constitutes the pattern of the lattice points (Figure 4.5 *B*). The pattern of points in space is known as the *space lattice.* Compounds that exhibit a crystal lattice structure include sodium chloride (table salt), caesium chloride, boron nitride etc.

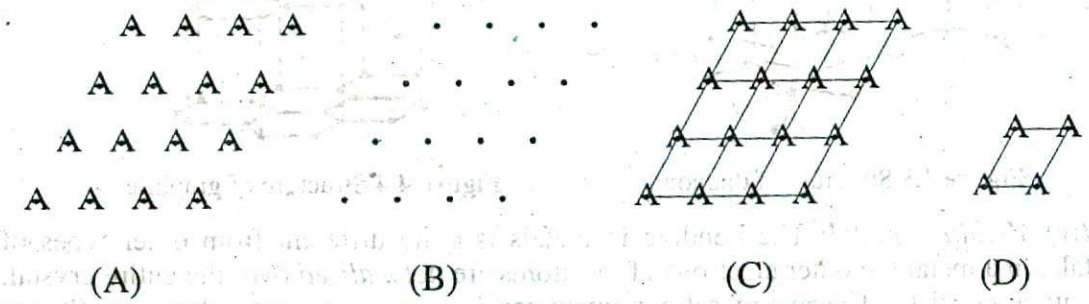


Figure 4.5 A two dimensional representation of a crystal lattice. (A) A pattern of A's (A's may be an atom, molecule or ion), (B) The pattern of lattice points, (C) Subdivision of crystal lattice into unit cells and (D) A single unit cell

Let us consider the space lattice of *NaCl* (Figure 4.6). Each of the points corresponds to the position of the *centre* of an ion. • indicates Na^+ ions and ○ indicates Cl^- ions. The points do not represent sodium ions or chloride ions but the positions occupied by their centres. In fact in sodium chloride the ions are of different sizes and are practically touching as shown in Figure 4.7.

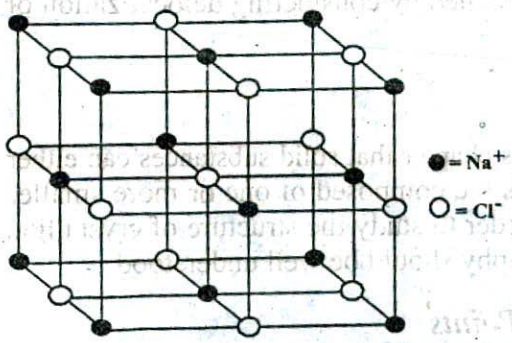


Fig 4.6 The sodium chloride lattice



Figure 4.7 Actual crystal lattice of sodium chloride : black spheres, sodium ions; hollow spheres, chloride ions.

The arrangement of the • is the space lattice for Na^+ ions and that of ○ is the space lattice for Cl^- ions. The space lattice of *NaCl* is, therefore, made up of two identical inter-penetrating space lattices. In other compounds the inter-penetrating space lattices may not be identical, as in CaF_2. In crystals of monatomic elements, namely of a metal or of inert gases, there is only one space lattice.

4.3.2 Unit cell

The repeating units or cells in the crystal lattice are called *unit cells* (Figure 4.8). The lengths of the edges of a unit cell and the angles between them are called the *lattice parameters*. The unit cell will have the same symmetry as the crystal. If each point in a *space lattice* is replaced by an identical atom, ion or group of atoms a crystal structure is obtained. The unit cells can have seven possible shapes (Figure 4.8). Each unit cell has

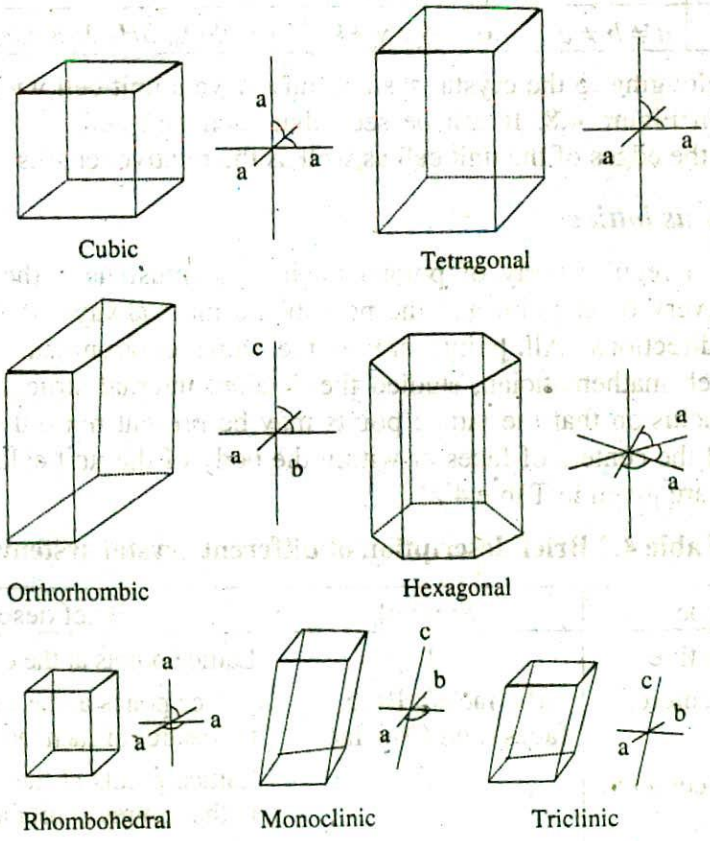


Figure 4.8 The crystal systems

characteristic parameters. A particular crystal may be formed from one of these unit cells, and the seven different crystal structures thus formed are called *crystal systems*. The characteristics of the crystal system are summarized in Table 4.1.

Table 4.1 The seven crystal systems

Crystal System	Length of each edge	Angles between edges	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	*NaCl, Cu*
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2 (rutile), *Sn* (white)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	*S*(rhombic), $CaCO_3$(aragonite), $BaSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90°$ $\gamma \neq 90°$	*S*(monoclinic), $PbCrO_4$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$(calcite)
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	*C*(graphite), *ZnO*
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4$, $5H_2O$; $K_2Cr_2O_7$

A crystal belonging to the crystal system must have a unit cell with one of the seven shapes shown in Figure 4.8. It can be seen that each unit cell is characterized by the angles between the edges of the unit cell as well as the relative lengths of the edges.

4.3.3 The Bravais lattices

A lattice is a regular array of points. Each point must have the same number of neighbours as every other point and the neighbours must always be found at the same distances and directions. All points are in the same environment. In 1850, August Bravais, a French mathematician, studied the detailed internal structure of crystals and came to the conclusion that the lattice points may be present not only at the corners of unit cells, but at the centers of faces or within the body of the unit cells. The description of these lattices are given in Table 4.2

Table 4.2 Brief description of different crystal systems

No	Type	Symbol	Brief description
1	Primitive	P	Lattice points at the corners only
2	Face-centered	A(bc faces), B(ac faces) and C(ac faces)	Lattice points at the corners as well as at the centres of each face of the unit cell
3	All face-centered	F	Lattice points at the corners as well as in the centres of all faces of the unit cell
4	Body-centered	I	Lattice points at the corners as well as within the body of each unit cell

Bravais identified different types of lattices corresponding to seven crystallographic systems. There are 14 ways in which this can be accomplished. These 14 types of lattices are called *Bravais lattices*. The fourteen Bravais lattices are shown in Table 4.3.

Table 4.3 The fourteen Bravais lattices

Crystal systems	Bravais lattices	Number of Bravais lattices
Triclinic	P,	1
Monoclinic	P, C	2
Orthorhombic	P, C, I, F	4
Tetragonal	P, I	2
Rhombohedral	R	1
Hexagonal	P	1
Cubic	P, I, F	3

The cubic crystal system has three possible cubic unit cells (a) the simple (also known as primitive) cube, (b) the body-centered cubic and (c) the face-centered cubic. These are illustrated in Figure 4.9.

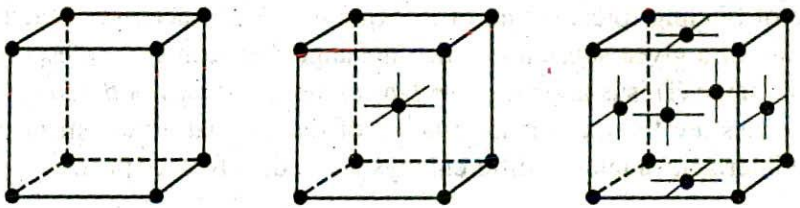


Figure 4.9 (a) Simple cubic, (b) body-centered cubic and (c) face-centered cubic

Information about the structure of crystals is derived from X-ray diffraction studies as discussed in *Section* 4.6.

4.4 Symmetry in Crystals

Symmetry is an important property of crystals. Symmetry in crystals indicates the various ways in which the crystal may be rotated, reflected in a plane, or inverted through a point without changing its appearance. Crystals may have :

(i) Plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.

These are called the *elements of symmetry.*

(i) Plane of symmetry: When a crystal can be divided by an imaginary plane into two equal parts, each of which is a mirror image of the other, the crystal is said to have *a plane of symmetry.* A cube has several planes of symmetry, namely those perpendiculars to the faces of the cube and those bisecting the angles of the upper and lower faces.

(ii) Axis of symmetry: An axis of *symmetry* is an imaginary line drawn through the crystal about which the crystal may be rotated so that the crystal shows identical appearance more than once during the rotation through 360°. Such identical appearances may be presented twice, thrice, four times or six times. Accordingly the crystal is said to possess two-fold, three-fold, four-fold and six-fold symmetry respectively.

(iii) Centre of symmetry: It is a point at the centre of a crystal. A crystal is said to have a *centre of symmetry* when any line drawn through this point will intersect the opposite and identical faces, edges or corners of the crystal at equal distances.

A crystal may have more than one plane of symmetry and axis of symmetry but never more than one centre of symmetry. All the three types of symmetry are not presented by all crystals. In fact, some crystals do not have any centre of symmetry at all.

The cube has the greatest symmetry. One can examine a cube and find that there are altogether 23 elements of symmetry – thirteen axes of symmetry (three four-fold, four three-fold and six two-fold), nine planes of symmetry and one centre of symmetry. Unless the crystal is perfectly grown it is not always easy to recognize the elements of symmetry but the interfacial angles of a particular crystal system are the same whether the crystal is perfect or imperfect.

4.5 The Crystal Systems

Crystalline solids exhibit different forms depending on the relative sizes of the ions or atoms, type of binding force, nature of stacking etc. A characteristic feature of the crystals, large or small, of a given substance is that the angle between the corresponding faces of the crystals is the same. This is known as the *Law of the Constancy of the Interfacial Angles.* The interfacial angles are the outer manifestation of the internal arrangement of the crystals. A study of the interfacial angles of different crystals is, therefore, of primary importance.

4.5.1 The law of rational indices

The faces of crystals and also planes within crystals can be characterized by means of a suitable set of co-ordinates. Let us consider the three axes OX, OY, OZ (Figure 4.10) which are cut by a crystal face ABC at distances OA, OB and OC from the origin. These distances are called intercepts. It is found that if the axes are suitably chosen, the intercepts of different faces upon them bear a simple ratio to each other or a given face may cut an axis at infinity. This is called the *Law of Rational Intercepts* (or Indices).

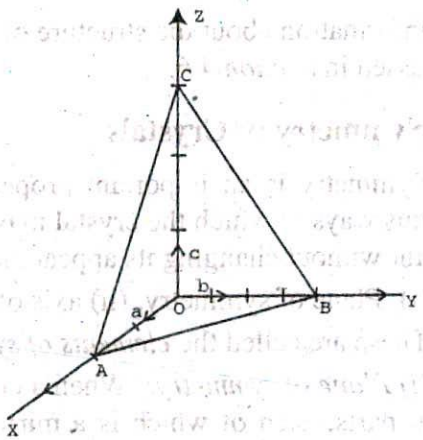


Figure 4.10 The intercepts of a crystal plane

4.5.2 Miller indices

The Miller indices may be defined 'as *the reciprocals of the co-efficients of the intercepts of a given plane on the crystallographic axes, expressed as integers*'. The Miller indices may be explained with reference to Figure 4.10. If *a, b, c* are chosen as unit lengths on the three axes, the lengths of the intercepts may be expressed as OA/*a*, OB/*b* and OC/*c*.

The reciprocal of these lengths will then be a/OA, b/OB and c/OC. A consequence of the law of rational indices is that reciprocal intercepts of crystal faces are small whole numbers. Thus if h, k, l are small integers then

$$\frac{a}{OA} = h, \quad \frac{b}{OB} = k, \quad \frac{c}{OC} = l$$

The reciprocal numbers, hkl, are known as the *Miller indices*. If a face is parallel to any one axis, that is, the length of the intercept is α, the Miller index is reciprocal of α, i.e., 0. The notation is also applicable to planes drawn within the crystal. It is clear that for the standard plane, i.e. the plane which makes intercepts of length a, b and c on the axis, the value of h, k and l are unity. It is often described as a (111) plane. If the intercept of any plane has a negative value it is represented by placing a bar over the Miller index. For example, $(1\bar{1}\bar{1})$ plane represents a plane which cuts the OZ axis at a distance of $-c$. The use of the Miller indices may be illustrated with the help of Figure 4.11 for cubic crystals.

The crystal forms of almost all crystals may be described with the help of seven different sets of co-ordinates. Crystals belonging to any one set are said to form a crystal system. The seven different crystal systems have been illustrated in Table 4.1 and Figure 4.8.

The property which determines to which system a crystal belongs is *symmetry*. Once a suitable set of axes has been fixed for a given crystal the crystal planes can be described.

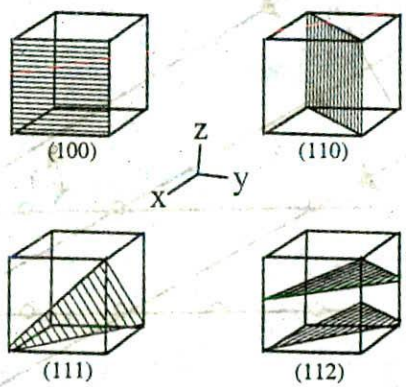


Figure 4.11 Crystal planes in a cubic crystal

4.6 X-rays and Diffraction of X-rays by Crystals

X-rays are electromagnetic radiation of high penetrating power and short wavelength, which are emitted from a target when it is bombarded with high-energy electrons as illustrated in Figure 4.12. These high-energy electrons knock out the tightly bound electrons in the K or L electronic shells of the target material. The low-energy empty levels thus created are filled by falling back of the electrons from higher energy levels to the inner levels. The energy liberated during this process is in the form of X-rays.

Max von Laue (1912) suggested that the wavelengths of X-rays are of the same order of magnitude as the spacing between ions or atoms in a crystal such as that of *NaCl*. The crystals would, therefore, act as a three dimensional diffraction grating for X-rays in much the same way as a grating diffracts visible light. These predictions were soon found to be essentially correct.

The diffraction effect occurs when radiation is disturbed from its direction of propagation so that some of the waves of the radiation are shifted out of phase with other waves due to scattering. As a result interference will occur. When the waves are *in phase* at a point the intensity there will increase due to constructive interference, while if the waves meet when they are *out of phase* destructive interference decreases the intensity of the radiation at these points. The final effect is a diffraction pattern.

W. H. Bragg and his son Lawrence considered the phenomenon of diffraction of X-rays by crystals and pointed out that it is convenient to think of the X-rays as being 'reflected' from successive planes of ions or atoms in the crystal when a beam of X-rays falls on such a crystal. Consider, in Figure 4.12, a set of parallel planes in the crystal structure and a beam of X-rays of wavelength, λ, incident on the planes at an angle θ.

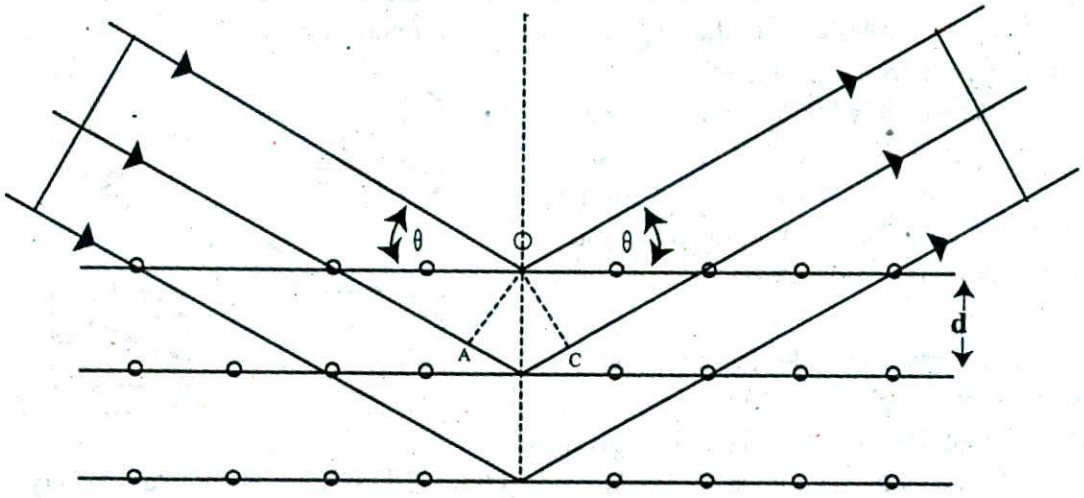


Figure 4.12 Reflection of X-rays from crystal planes

The planes are separated by a distance *d*. The X-rays will be reflected from different planes. The beam reflected from the first plane will reinforce the beam reflected from any other plane when the two beams are in phase, i.e., when the difference in path of the two beams is in integral multiple of the wavelength. This happens when the relation

$$n\lambda = 2d \sin\theta, \text{ where } n = 1, 2, 3... \qquad (4.1)$$

holds. This is the famous Bragg equation. The experimental arrangement which Bragg set up for making use of equation (4.1) is shown in Figure 4.13.

An X-ray beam generated in the X-ray tube is made monochromatic and parallel as far as possible by optical means, and then allowed to fall on to a known face of the crystal, mounted on a rotating table. The position of the table is read off the scale over

which the arm of the rotating table moves. The radiation reflected from the crystal is led into a detecting device which is usually an ionization chamber. The current produced by the ionization of an easily ionizable gas, such as methyl bromide, in this chamber is measured by means of an electrometer. The current is a measure of the intensity of radiation. The ionization chamber may also be rotated around the same axis as the crystal. This chamber is rotated at twice the rate of the rotation of the table carrying the crystal. The intensity of ionization produced at different angles are measured by the electrometer and these are plotted against 2θ.

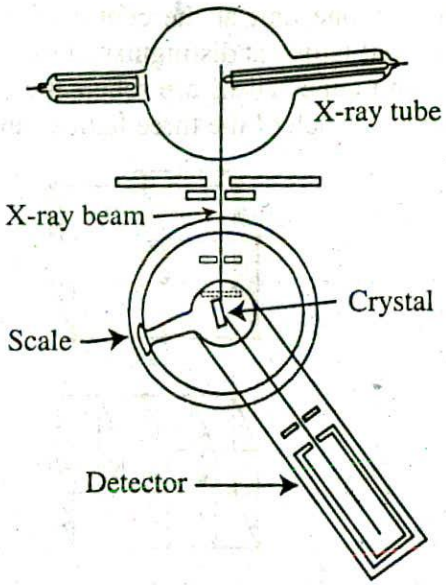


Figure 4.13 X-ray diffraction apparatus

There were maxima in the graphs and these must coincide with the angles for which the Bragg equation, $n\lambda = 2d \sin\theta$, holds. The maxima corresponding to $n = 1$, 2, 3--- are known as first-order, second-order, third-order etc. reflections. The curves obtained for sodium chloride and potassium chloride crystals are shown in Figure 4.14.

In order to determine d, the spacing of the planes of atoms or ions in the crystal, from X-ray measurements the wavelength of the incident X-ray beam must be known, Now-a-days X-ray tubes are available which give a monochromatic X-ray beam of known wavelength. X-ray tubes with a copper target which gives off a beam with wavelength equal to 15.40 nm are in common use.

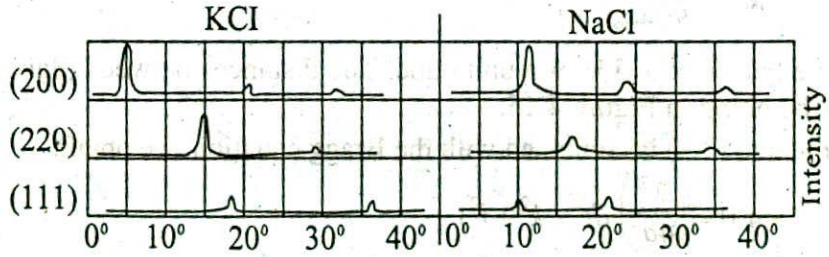


Figure 4.14 Graph of intensity against 2θ for *NaCl* and *KCl*

4.7 Cubic Lattices

In the cubic lattice system the three different space lattices are called the simple cubic, the face-centred cubic and the body-centred cubic lattices. In the simple cubic lattice the structural units are at each corner of the unit cube. In the face-centered lattice

there is one unit at the centre of each face, in addition to those at the corners. Body-centered lattice is distinguished by having one unit at the centre and one at each corner of the unit cube. These are schematically shown in Figure 4.9. The three types of reflecting planes in each of the three lattices are shown in Figure 4.15.

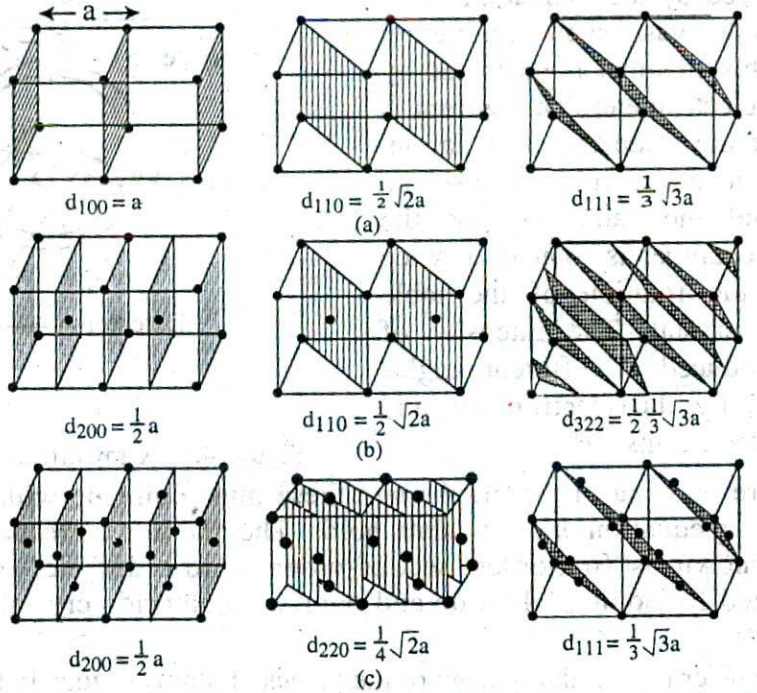


Figure 4.15 Plane through cubic lattices (a) simple cubic, (b) body-centred cubic and (c) face-centred cubic.

The distance between the planes *(hkl)* in a cubic lattice may be shown to be given by

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \tag{4.2}$$

where a is the length of a side of a unit cube. The distances between planes in the three lattices may be noted in Figure 4.15.

When equation (4.2) is combined with the Bragg equation, we obtain

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2) \tag{4.3}$$

Thus the angle at which reflections from different planes ($h\ k\ l$) and hence maxima in the plot of intensity vs. 2θ would be obtained may be calculated from equation (4.3). Conversely, the maxima obtained experimentally may be used to determine the planes from which the reflections are obtained. For a cubic lattice the following spacings are allowed :

(hkl)	100	110	111	200	210	211	220	etc.
$(h^2+k^2+l^2)$	1	2	3	4	5	6	8	etc.

It should be noticed that the term 7 is missing since there is no set of integers such that $h^2 + k^2 + l^2 = 7$.

The ratios of d_{hkl} values of each cubic structure are given in Table 4.4.

Table 4.4 Ratio of d_{hkl} values for different structures

Simple cubic	$d_{100} : d_{110} : d_{111}$	$= 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$
Face-centred cubic	$d_{200} : d_{220} : d_{111}$	$= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$
Body-centred cubic	$d_{200} : d_{110} : d_{222}$	$= 1 : \sqrt{2} : \frac{1}{\sqrt{3}}$

4.8 The Structure of Sodium Chloride Crystals

It is known from the external geometry of sodium chloride crystal that it belongs to the cubic system. X-ray diffraction studies with palladium target ($\lambda = 5.81$ nm) as X-ray source shows that maxima occur from the (200), (220) and (111) faces of sodium chloride at angles 11.8°, 16.8° add 10.4° respectively (Figure 4.14). These correspond to θ =5.9°, 8.4° and 5.2° respectively. If these are considered as first order reflections n =1, then the ratio of the spacings for these planes may be written from Bragg equation as

$$d_{200} : d_{220} : d_{111} = \frac{\lambda}{2 \sin \theta_{200}} : \frac{\lambda}{2 \sin \theta_{200}} : \frac{\lambda}{2 \sin \theta_{111}}$$

$$= \frac{1}{\sin \theta_{200}} : \frac{1}{\sin \theta_{220}} : \frac{1}{\sin \theta_{111}}$$

$$= \frac{1}{\sin 5.9^0} : \frac{1}{\sin 8.4^0} : \frac{1}{\sin 5.2^0}$$

$$= \frac{1}{0.1028} : \frac{1}{0.1461} : \frac{1}{0.0906}$$

$$= 1 : 0.704 : 1.136 \qquad (4.4)$$

It is seen in Table 4.4 from purely geometric consideration that for a face-centred cubic lattice

$$d_{200} : d_{220} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$$

$$= 1 : 0.707 : 1.155 \qquad (4.5)$$

As values in equations (4.4) and (4.5) are in close agreement one must conclude that sodium chloride crystallizes in this lattice. The crystal lattice of sodium chloride is shown in Figure 4.6. From the difference in intensity of reflections of alternate orders it was concluded that sodium chloride lattice consists of interpenetrating face-centred cubic

lattice of sodium and chloride ions. In the lattice each sodium ion is surrounded by six chloride ions and vice versa (co-ordination number is six). In Figure 4.6 the sodium ions are represented by small black circles and chloride ions are shown as open large circles. This is a schematic representation of the lattice. In the actual crystal the ions are probably almost touching each other so that very little free space is left (Figure 4.7). It will be noted that there are no discrete molecules of sodium chloride in the lattice.

From the X-ray diffraction data the length of a the unit cell may be computed. For example, for the d_{200} and d_{220} plane one obtains from the angle θ for reflection and the Bragg equation using a λ(Pd) = 5.84 nm,

$$d_{200} = \frac{5.84\,nm}{2\sin 5.90} = \frac{5.84\,nm}{2(0.1028)} = 28.2\,nm$$

Hence, $a = d_{200}\sqrt{4+0+0} = 2d_{200} = 56.4$ nm

One can readily see that the d_{200} and d_{220} planes have alternate sodium ion and chloride ions; the d_{111} plane consists of alternating planes containing sodium ions or chloride ions only.

4.9 The Powder Method

P. Debye and P. Scherrer devised a very simple technique for obtaining X-ray diffraction data. Their technique, known as the powder method, depends on the use of a powder of the crystalline sample instead of a single crystal. The powder is usually placed in a fine capillary or made into a rod. The experimental arrangement is shown in Figure 4.16.

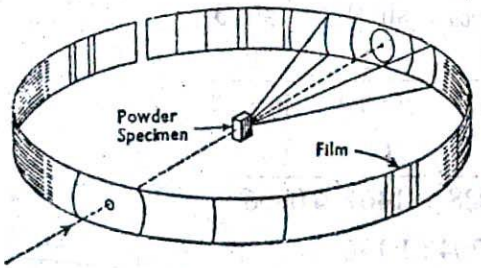


Figure 4.16 Experimental arrangement for X-ray powder photograph

The little crystals constituting the powder will be oriented in all directions. There will be some oriented at the proper angle for X-ray reflection from each set of planes. The diffraction pattern will be just like the one which would be obtained by mounting a single crystal and turning it through all possible angles. Since the orientations of the little crystals are random there will be reflections from a large number of planes and consequently the X-ray pattern will show scattering at a large number of angles. On a flat plate film the observed pattern consists of a series of concentric circles. Bragg's law may be applied to these lines to obtain the plane spacing. In order to derive the dimensions of the unit cell from the inter-planar spacing we must know the crystal

system to which the specimen belongs. This can sometimes be determined from microscopic examination.

The X-ray powder photograph is a characteristic property of a crystal. The method may, therefore, be used for identification of the components of a solid mixture.

4.10 Application of X-ray Diffraction

The most important application of X-ray diffraction is in the field of determination of crystal structure. X-ray diffraction technique has enabled scientists to obtain deep insight into the structures of alloys and intermetallic compounds. Many metallurgical operations, which were until recently a matter of art, can now be studied by means of X-rays.

The X-ray pattern of an unknown substance may be used to identify it. Quantitative determination of impurities in crystals has also been made possible.

X-ray diffraction studies of such substances as rubber, fibres, silk, hair etc. have revealed the existence of regions of ordered arrangements as in a crystal.

At present the technique of X-ray diffraction studies of single crystals have developed to a stage where the structures of complex organic molecules have been established from such measurements.

4.11 Conductors, Insulators and Semiconductors

The electrical conductivity of solids was first demonstrated by Stephen Gray in 1729. Conductivity is the ability of a material to conduct electricity. Accordingly, the solid materials can be classified as (i) *conductors*, (ii) *semiconductors* or (iii) *insulators* depending on their ability to conduct electricity. The electrical conductivity of semiconductors ranges from about 10^{2} to 10^{-9} ohm^{-1} cm^{-1} at 25 °C, while the maximum conductivity of a good conductor is about 10^{-4} ohm^{-1} cm^{-1} at 25 °C. Substances having conductivity of the order of about 10^{22} ohm^{-1} cm^{-1} at 25 °C are known as insulators.

Some solids, particularly metals, are good conductors of electricity because they have free mobile electron. These are also known as *electronic conductors*, since electrons are the carriers of electricity. Metallic elements, their alloys, graphite and some organic solids fall in this category. The electrical conductivity of metallic conductors *decreases* with rise of temperature. Semiconductors are also electronic conductors. The conductivity of semiconductors *increases* with temperature. Silicon, diamond and gallium arsenide are examples of semiconductors. Semiconductors have generally very low conductivity, but their conductivities may be significantly enhanced by incorporating impurities into the structure. Materials with very low electrical conductivities are known as *insulators*. Glass, wood etc. are insulators. There is another class of solids known as *super-conductors*. They have almost zero resistance to the flow of electricity. Certain metals and alloys exhibit *superconductivity* when cooled to sufficiently low temperatures. It was discovered in 1911 by Kamerlingh Onnes. Superconductors find applications in superconducting magnets, energy technology, telecommunications, computing and medicine. Detail consideration of superconductivity is beyond the scope of this text.

The conducting and insulating properties of solids can be explained by considering the '*Band Theory*' of metals. According to this theory, in a metallic crystal the atoms are closely packed together in such a way that the energy levels of electrons of each atom are affected by the energy levels of electrons of the immediate neighbours. As a result the atomic orbitals of neighbouring atoms overlap with each other. According to the molecular orbital theory the overlapping of atomic orbitals lead to the formation of *bonding* and *antibonding* molecular orbitals. Since the number of atoms even in a small piece of metal is very large, the number of molecular orbitals thus formed must also be very large. These molecular orbitals are so closely *spaced* on the energy scale that they are described as '*Bands*'. The highest filled energy band is called '*valence band*', and the next higher one is called the '*conduction band*' (Figure 4.17). The conduction band is separated from the valence band by an *energy gap*, also known as *forbidden band*. The Fermi level lies between the valence band and the conduction band. The concept of *Fermi energy* or *Fermi level* comes from statistical consideration which is beyond the scope of this text.

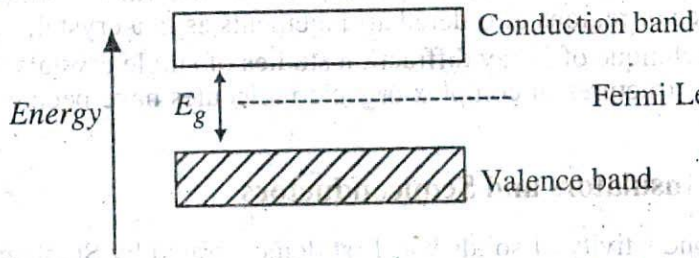


Figure 4.17 Schematic diagram of conduction band, valence band and Fermi level

The important energy bands are (a) the topmost valence bands, i.e., the energy levels of the valence electrons, and (b) the conduction band which is at a higher energy level than the valence bands.

4.11 1 Conductors

The conductors are characterized by overlapping of either (i) partially filled valence band and the conduction band (Figure 4.18a) or (ii) completely filled valence band and empty conduction band (Figure 4.18b). Case (b) is a metal, but not a good conductor as in case (a).

Under the influence of an applied electric field the vacant levels within the topmost valence band are to receive electrons from the originally filled levels giving a 'drift' of charge through the lattice. This corresponds to the conduction of electricity. The conduction may also result from the promotion of electrons from the valence band to the conduction band by the applied electric field.

4.11.2 Insulators

A non-conductor or insulator has completely occupied lower band separated from the conduction band by a wide energy gap as schematically shown in Figure 4.18(c). At sufficiently high temperature the excitation of electrons from the valence band to the conduction band is negligible for insulators.

4.11.3 Semiconductors

The term semiconductor refers to those which have weak conductivity at low temperatures but show increased conductivity as the temperature is raised. In such solids the topmost filled valence band is separated from empty conduction band by a small energy gap. Since the energy gap is smaller an appreciable number of electrons can be promoted from the top of the valence band into the bottom of the conduction band and the material behaves like a conductor.

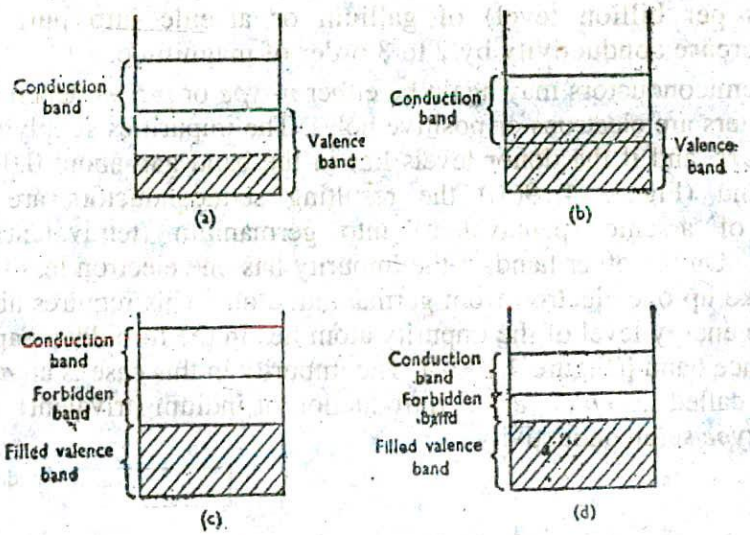


Figure 4.18 Schematic energy band diagrams: (a) overlap between a conduction band and a partly filled valence band; (b) overlap between a conduction band and a filled band; (c) energy bands in an insulator; note large forbidden band; (d) energy bands in a semiconductor (forbidden band is small).

Based on their origin the semiconductors are broadly divided into two classes :

(i) intrinsic semiconductor and

(ii) extrinsic semiconductor.

A semiconductor in which the concentration of charge carriers, electrons or holes (*Section 4.11.4*), is characteristic of the material itself rather than of the presence of any impurities or structural defects of the crystal is called an *intrinsic semiconductor*. The carrier concentration, and hence the conductivity of *intrinsic semiconductor*, is very sensitive to temperature and depends strongly on the energy gap. The energy gap ranges from a fraction of 1.0 eV to several eV. Silicon and germanium are typical intrinsic semiconductors. At 300°K the thermal energy of the valence band electrons is not sufficient to allow many of them to cross the forbidden energy gap and go to the conduction band. These have poor conducting power. When the temperature is raised, many electrons will move up to the conduction band and give rise to the conductivity. Such excitation of the electrons to the conduction band may also be achieved by allowing radiation of short wavelength (i.e., of high frequency or energy) to be incident on the solid.

9-A

Sometimes the conductivity of a pure semiconductor may be significantly enhanced by incorporating a trace amount of impurity into the crystal structure to produce what is known as *extrinsic semiconductivity*. This type of semiconductor is also known as *impurity semiconductors*. The impure atoms exist at lattice sites in the crystal in place of the atoms in the crystal. The effect of the impure atoms is to introduce new energy levels. These levels may lie in a gap between a filled band and an empty band. Electrons may be excited to the conduction band and these will contribute significantly to the conduction. For example, incorporation of a trace amount (parts per billion level) of gallium or arsenic into pure silicon and/or germanium increase conductivity by 2 to 3 order of magnitude.

Extrinsic semiconductors may again be either *n-type* or *p-type* depending on whether the charge carriers are electrons or positive holes. The impurities supplying the electrons are called *donors*, and if the donor levels lies in the band gap about 0.01 eV below the conduction band (Figure 4.19(a)) the resulting semiconductors are called *n-type.* Incorporation of arsenic (pentavalent) into germanium (tetravalent) gives *n-type* semiconductor. On the other hand, if the impurity has one electron less than germanium atom, it can take up one electron from germanium atom. This requires about 0.01 eV of energy, and the energy level of the impurity atom lies in the forbidden gap about 0.01 eV above the valence band [(Figure 4.19(b)]. The impurity in this case is an *acceptor* and the energy state is called *acceptor level.* Introduction of indium (trivalent) into germanium gives rise to *p-type* semiconductivity.

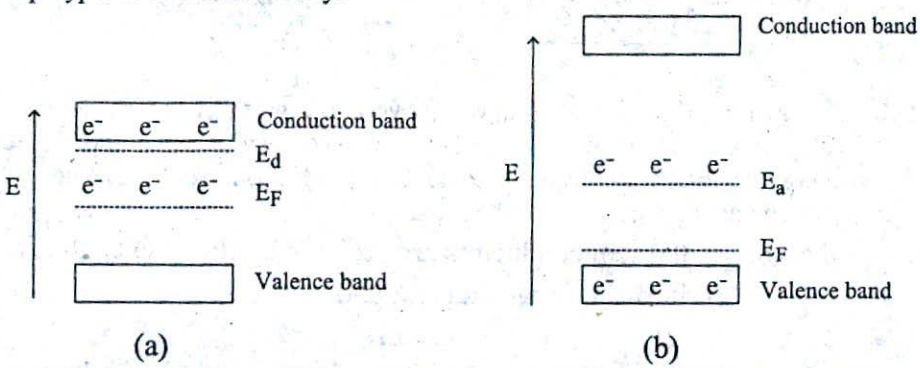


Figure 4.19 Impurity semiconductors. (a) *n-type*, E_d is the donor level and (b) *p-type*, E_a is the acceptor level. In both cases E_F is the Fermi level.

4.11.4 The 'hole' concept and conductance

At sufficiently high temperature a significant number of electrons in the valence band may gain enough thermal energy and promoted to the conduction band. The magnitude of the *energy gap* will, of course, determine the number of electrons thus promoted. These electrons in an unfilled conduction band can easily participate in conduction. However, there is now a corresponding number of vacancies left in the electron population of the valence band. These vacancies, or *holes* as they are called, have the effect of carriers of positive charge, by means of which the valence band makes a contribution to the conduction of the crystal.

9-B

Transistors, which are used so widely in many fields, are ultra-pure silicon or germanium crystals into which are introduced very small amounts of impurities like arsenic or indium or other elements to give these crystals the semiconducting property.

4.12 Defects in Solids

A crystal is considered to be ideal or perfect if there is regular arrangement of lattice points, and there is no irregularities of any kind in the crystal lattice. Real crystals, however, feature defects or irregularities in the arrangements of atoms, molecules or ions in the lattice points. Any deviation from a chemically pure, stoichiometric perfect crystal is called an imperfection or a defect. However, depending on how these defects arise in crystal lattice, there are basically two types of defects: (i) *intrinsic* (also called *thermodynamic* defect) and (ii) *extrinsic* (also called *non-equilibrium* defect).

(i) Intrinsic defect: The intrinsic defects occur when certain configurational disorder is introduced into the crystal lattice spontaneously at an elevated temperature. This is a direct consequence of the laws of thermodynamics.

(ii) Extrinsic defect: The extrinsic defects are deliberately introduced into the crystal lattice to manipulate the properties of a particular crystal system.

The presence of defects in crystal lattice may profoundly influence the mechanical, electrical and optical properties of crystals. Reactivity of the solids may also be explained by considering the defect structure. Crystal defects are broadly divided into three classes: *(a) Point defect, (b) Line defect* and (c) *Plane defect*. Each one of these defects are subdivided into the following class

es depending on their formation:

(a) Point defects: (i) Vacancy, (ii) Substitutional, (iii) Interstitial, (iv) Frenkel, (v) Schottky, (vi) Non-stoichiometric and (vii) Colour centres.

(b) Line defects: (i) Edge defect and (ii) Screw dislocation

(c) Plane defect: (i) Grain boundary faults and (ii) Stacking faults.

A brief description of point defects will only be considered in this text.

(a) Point defects

(i) Vacancy defects: Vacancy defects arise when some of the lattice points usually occupied by metal atoms are vacant (Figure4.20). This can happen only at an elevated temperature.

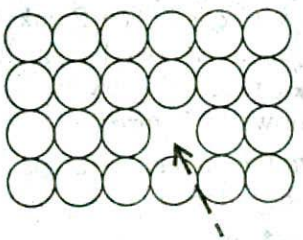


Figure 4.20 Vacancy defect

(ii) Substitutional defect: An impurity atom or an ion may be substituted for another atom or ion. The substitution of an atom or an ion is dependent on the ionic radius and electronic structure. Two cases may be considered:

(a) A monovalent cation may be substituted by a divalent cation. For example, a Ag^+ ion from $AgCl$ may be substituted by a Cd^{2+} ion. A Ag^+ ion must also be removed for charge balance. This will lead to *cation vacancy* as shown in Figure 21(a).

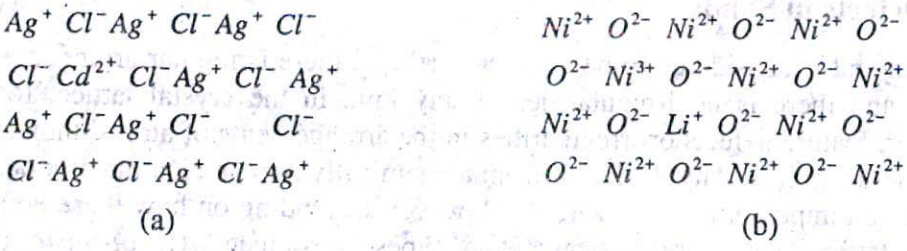


Figure 4.21 (a) Vacancy defect. A monovalent cation is substituted by a divalent cation and (b) Valence defect caused by Li^+ substitution.

(b) Alternatively, a divalent cation may be substituted by a monovalent cation. Substitution of Ni^{2+} by Li^+ in NiO lattice will give rise to this kind of defect as shown in Figure 21(b). The defect thus produced is known as valency defect.

(iii) Interstitial defect : An atom or an ion may be introduced into an interstitial position.

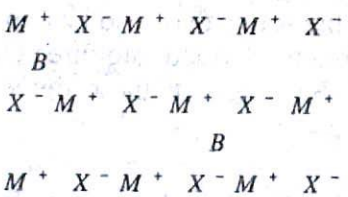


Figure 4.22 Interstitial defect

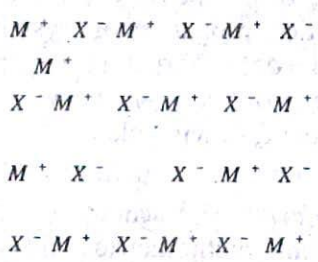


Figure 4.23 Frenkel defect

Thus a foreign atom B is incorporated at interstitial positions of an ionic crystal MX. The introduction of the impurity is critically determined by the relative sizes of the *host* (parent lattice) and the *guest* (impurity).

(iv) Frenkel defect: The Frenkel defect is also a kind of point defect. In this case an atom or an ion is removed from its normal lattice site and is placed at an interstitial position. As a result the crystal structure has a vacancy as well as an interstitial. An example is shown in Figure 23.

(v) Schottky defect: This is another kind of vacancy defect. If the number of anion vacancies in a crystal is equal to the number of cation vacancies, the combination is called *Schottky defect.* The formation of *Schottky defect* is shown in Figure 4.24.

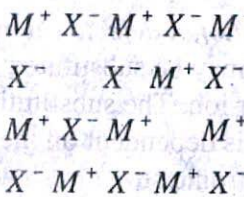


Figure 4.24 Schottky defect

(vi) Non-stoichiometric: The Law of Definite Proportion, put forward by Berthollet at the beginning of the nineteenth century, states that the composition of a chemical compound must be constant. In other words elements must always combine in a definite ratio by mass. For example chemical formulas such as *FeO or ZnO* suggest that the constituent atoms/ions are present in stoichiometric ratio in these compounds. However, with the applications of sophisticated technique it became clear that there are deviations from stoichiometry in seemingly stoichiometric compounds. This deviation from stoichiometry in predominantly binary ionic solids implies that one of the constituent elements is in excess compared to the other. Thus in metal oxide MO_{1-x} this may arise due to the presence of excess metal atom at the interstitial position or due to the presence of oxygen vacancies in excess of metal vacancies. Usually elements exhibiting variable valencies tend to form non- stoichiometric compounds. There are plenty of examples of non-stoichiometric compounds. For example the composition of *CuS* may range from $Cu_{1.7}S$ to Cu_2S; *TiO* may exist in the range $TiO_{1.35}$ to $TiO_{0.60}$ etc.

(vii) Colour centres: This is a kind of defect in which a colourless compound becomes coloured. For example if *NaCl* (a colourless compound) is heated in an atmosphere of *Na* or *K* vapours and then quenched rapidly it becomes coloured. The colour appears due to the incorporation of electrons in vacant sites created by removal of chlorine atoms. Detail consideration of this type of defects is beyond the scope of this text.

However, the presence of these lattice defects gives rise to special electrical and optical properties. The strength and hardness of metals also depend markedly on defects in their crystal structure.

4.14 Liquid Crystals

In a liquid the molecules have no orderly arrangement. The molecules can move with respect to each other in a random manner, so liquids are able to flow. In a solid the particles are present in a highly ordered pattern, but they can not move from their positions as they are held rigidly in place. Particles in the solid state can not flow.

Certain organic compounds, exhibit properties characteristic of both liquid and solid in a temperature range just above their melting points. These are called *liquid crystals.* They are fluids but their molecules are arranged in a highly ordered way. At temperatures above this range the order is lost and they become like any other liquid.

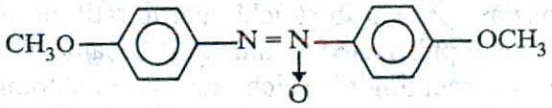
Liquid crystal displays (LCD's) are found in calculators, wrist watches, TV screens and a host of other objects in use.

Three types of molecular arrangements, known as *nematic, smectic and cholesteric* liquid crystals have been identified. Several unsymmetrical molecules that have approximately rod-like shapes behave as liquid crystals. Some examples are shown below along with their chemical fomulas: *4, 4'–Dimethoxyazoxybezene, 4–Butyloxy-4'–ethanoylazobenzene, Cholesterylbenzoate.*

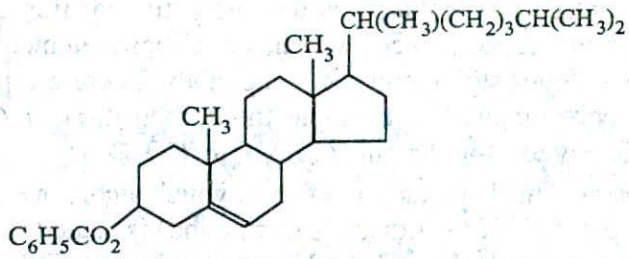
All are organic compounds and end in a polar group, e.g. $-CN$, $-OR$ (R is an alkyl group), $-NO_2$, $-NH_2$ etc. Many have flat parts such as a benzene ring.

(a) 

4-Butyloxy-4' -ethanoylazobenzene

(b) 

4,4'-Dimethoxyazoxybenzene

(c) 

Cholesteryl benzoate (the first to be discovered)

Fig. 4.25 Compounds which for liquid crystals

The three types of liquid crystals differ in the kind of order of the molecules within the crystals. In the *nematic liquid crystals* the molecules are arranged parallel to each other but can slide or roll over each other, but their centres are oriented randomly.

Smectic liquid crystals show greater order. The molecules are parallel to each other and are arranged in layers that are one molecule thick. These are able to slide readily over each other. Liquid crystals of this type are turbid and viscous.

In *cholesteric liquid crystals* the molecules are arranged in thin layers but they are aligned parallel to the layers in the *nematic* fashion, with slightly different orientations from one layer to the next.



(a) *(b)* *(c)*

Figure 4.26 Arrangements of molecules in liquid crystals. (a) Packing in a *nematic* liquid crystal; (b) Packing in a *smectic* liquid crystal and (c) Packing in a *cholesteric* liquid crystal.

The use of liquid crystals is based on their special electrical and optical properties. In liquid crystal displays (LCD's) a thin layer of *nematic* liquid crystal is placed between two electrodes (at least one of which is transparent) that are arranged on glass in special

pattern. In the absence of any electric signal across the electrodes the molecules are uniformly oriented. In this configuration light passes readily through the cell. When a particular electrode segment is energized, the orientations of the molecules in the liquid crystal are changed and the substance becomes opaque. By activating appropriate segments in this way various numbers and letters can be formed and displayed. One advantage of the liquid crystal devices is that they use very little power.

In cholesteric liquid crystals the presence of smectic-like layers give rise to colours in the light scattered from them. The spacing of the layers depends on the temperature; consequently different colours are observed at different temperatures. This effect is used to make *liquid crystal thermometers*. In medical science small difference of temperature on different parts of the skin of a patient due to abnormalities can be detected from the colour change of liquid crystals. The technique is called *thermography*.

4.15 The Specific Heats of Solids

Dulong and Petit in 1819 observed that at room temperature and atmospheric pressure the product of the specific heats, C_p, and the relative atomic masses of solid elements, mostly metals, are approximately 26.8 J deg^{-1}. This is known as Dulong and Petit's law. The product is also known as atomic heat or heat capacity, C_p. There are, however, many exceptions to the rule, e.g., boron and carbon (diamond) for which this product is 10.5 and 5.6 respectively.

Dulong and Petit's law was extended by Kopp and others to compounds. They observed that *the product of the specific heat of a compound and its molecular mass is approximately equal to the sum of atomic heats of the constituent atoms.*

In spite of their limitations Dulong and Petit's law and Kopp's rule were very useful in determining the atomic masses of many elements, e.g., uranium, indium, mercury etc.

Data in Table 4.5 shows the approximate constancy of atomic heats of many solids.

Table 4.5 Atomic heats of solid elements

Element	Atomic mass.	Sp. heat	Atomic heat (J)
Lithium	7	3.84	26.9
Sodium	23	1.17	26.9
Aluminium	27	0.88	23.8
Calcium	40	0.63	25.2
Iran	56	0.46	25.8
Copper	63.5	0.39	24.8
Arsenic	75	0.35	26.3
Silver	108	0.23	24.8
Iodine	127	0.22	27.9
Lead	207	0.13	26.9

Dulong and Petit's law received some theoretical support as the value of approximately 25.06 joules for atomic heat at constant volume could be derived by considering the atoms in the solids to execute vibrational motion about their fixed positions in the crystal lattice. For solids C_p and C_v do not vary to any great extent. According to this treatment C_v should be independent of temperature. Measurements of heat capacities at low temperatures showed, however, that C_v, decreases with the decrease of temperature and approaches zero at 0°K as shown in Figure 4.26. Explanation for the low values of C_v at very low temperatures was given by Einstein and Debye in terms of Planck's quantum theory. According to Debye's theory of specific heats, at low temperatures C_v is given by

$$C_v = 77.93 \times 3R \left(\frac{T}{\theta}\right)^3$$

i.e., the specific heat is proportional to T^3. θ is called the characteristic temperature and is characteristic of the solid. The equation is valid below temperatures of about 15 K where measurements do not yield accurate results. The relation is very useful in calculating specific heats at such low temperatures. Predictions of Debye's theory are in excellent agreement with experimental results. The theory also predicts that heat capacities of all solids will approximate to about 25.1 $J\ deg^{-1}$ at sufficiently high temperatures, which may be different for different elements. In fact those elements which deviate from Dulong and Petit's law at room temperature are found to have atomic heats in agreement with the law at sufficiently high temperature.

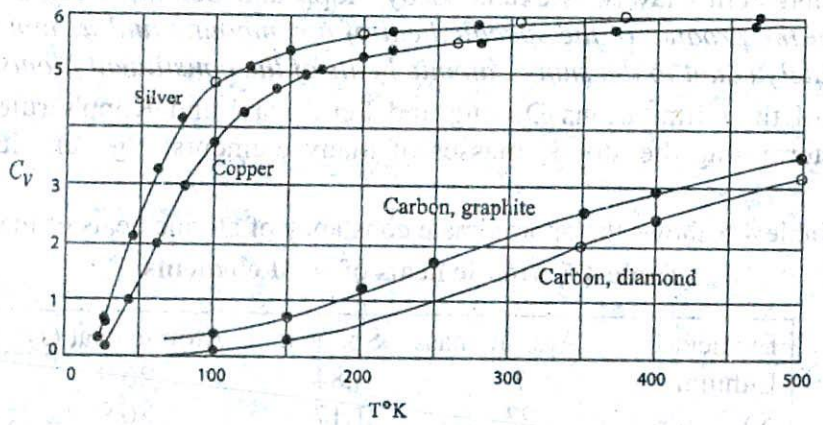


Figure 4.27 Molar heat capacities of solid elements at different temperatures

4.16 Isomorphism

It was recognized early in the study of crystals that crystals of similar constitution but containing different atoms have similar crystalline forms. These observations were summarized in the form of a law by Mitscherlich (1819). The law states that *substances possessing an equal number of atoms combined in the same manner produce the same crystalline form.* This law is known as Mitscherlich's *law of isomorphism.* Substances

crystallizing in the same crystalline form are said to be isomorphous with each other. For example, ferrous sulphate ($FeSO_4.7H_2O$), magnesium sulphate ($MgSO_4.7H_2O$) and zinc sulphate ($ZnSO_4.7H_2O$) are isomorphous. The alums such as ferric alum and chrome alum are isomorphous.

Tests of isomorphism : For two substances to be isomorphous with each other the following three criteria are to be satisfied :

(a) The crystalline form should be similar. This is not a good criterion as there are crystals which have similar crystalline constants but they are not isomorphous.

(b) The two substances should give mixed crystals, i.e., when two substances are crystallized from a solution containing both the solids, the crystals should contain both the substances and be homogeneous. Copper sulphate and ferrous sulphate give mixed crystals and the crystals of the two substances are isomorphous. It must, however, be recognized that all isomorphous crystals do not form mixed crystals.

(c) If one crystal grows in a supersaturated solution of another, the two crystals may be isomorphous. Such growth of a crystal is called overgrowth. For example, when green crystals of nickel sulphate are placed in a supersaturated solution of zinc sulphate, the green crystals are covered with colourless zinc sulphate crystals. There are exceptions to this criterion also, as it is found that crystals which are not isomorphous form overgrowths.

QUESTIONS AND PROBLEMS

1. Discuss the characteristics of solids and their classifications?
2. What are the binding forces in crystals? Discuss briefly the different types of crystals in which different types of binding forces are operative.
3. What is isomorphism? Discuss the tests of isomorphism.
4. State Dulong and Petit's law. What are its limitations and how have these been explained?
5. Give an account of the specific heats of solids.
6. Discuss crystal systems and the classification of crystals into different systems.
7. Explain what is meant by (a) crystal lattice, (b) space lattice and (c) unit cell.
8. Give an account of the use of X-ray diffraction studies in the determination of the structure of crystals.
9. The intercept of a certain plane on the x axis is 2a/3; on the y axis is 2b; and on z axis it is 1c/3. (a) Sketch the plane. What are the Miller indices of this plane? (b) What will be the Miller indices of such a plane if the intercept is zero? [Ans. (a) (316); (b) (306)]
10. Calculate the wavelength of X-rays that will give a reflection from the d_{100} planes in KBr at an angle of 19°20'. The length of a unit cell in KBr is 0.329 nm. [Ans.0.154 nm]
11. Draw sketches showing the different cubic lattices together with the reflecting planes in each of the different types of cubic lattices..
12. What are semiconductors? How does semiconductivity arise? Discuss some of the uses of semiconductors.

5 THERMODYNAMICS I : THE FIRST LAW

5.1 The Nature of Thermodynamics

Thermodynamics is an important discipline in physical science. It deals with the relationship between thermal energy and other forms of energy. The science of thermodynamics was developed in the nineteenth century and is based on innumerable observations and experiments over many years. The deductions from these observations and experiments are summarized in the form of three fundamental laws: *the first, the second and the third law of thermodynamics*. The laws of thermodynamics are accepted as laws because no exception to these has ever been found by experiments. There are two approaches to the study of thermodynamics:

- *Classical thermodynamics* – deals with the *macroscopic views of matter*, i.e., the properties of matter in bulk. It does neither consider the internal constitution of matter, nor does it require any theory of matter.
- *Statistical thermodynamics* – deals with the study of the *microscopic behaviours* of thermodynamic systems using probability theory. Statistical thermodynamics provides a molecular level interpretation of thermodynamic quantities such as work, heat, energy and entropy. The development of this branch of thermodynamics was initiated by an Austrian physicist *Ludwig Boltzmann* in 1870. Discussion of *statistical thermodynamics* is beyond the scope of this text.

The great usefulness of thermodynamics to chemists can be summarized as follows:

- The laws of thermodynamics are not based on any assumption about the existence or nature of atoms, molecules or ions. Thus, if future experiments reveal that the accepted theories of the structure of atoms and molecules are inadequate, the laws of thermodynamics would still be valid.
- It can predict the *feasibility* as well as *direction* of thermodynamic processes.
- It can explain why reactions can reach equilibrium position and what their compositions at equilibrium are.
- It can explain how reactions in electrochemical cells as well as in biological cells can be used to generate electricity.
- Applications of thermodynamic principles to colligative properties of solutions, Distribution Law, Phase Rule etc. led to the deductions of important relationships and better understanding of these and other phenomenon in physical sciences.

The principles of thermodynamics have few limitations as well. These are,

- *Time* is never a *variable* in thermodynamics. It does not give any indication of the *rate* of any process.

- The principles of thermodynamics are interested only in the *initial* and *final* states of the system. It does not give any information about how the final condition is attained or how long it takes to reach this condition. In other words, it does not give any idea about the *mechanism* of any process.
- *Classical thermodynamics* deals with macroscopic systems, and does not give any idea about the role of individual atoms, molecules and ions on overall properties of a system.

5.2 Important Concepts in Thermodynamics

The laws of thermodynamics and many quantitative relationships deduced therefrom are based on some fundamental concepts. It is imperative to understand these concepts before discussing the principles of thermodynamics.

5.2.1 System, boundary and surroundings

The portion of the physical universe which is under thermodynamic consideration is called a *system*. It usually consists of some form of matter undergoing a change. The *system* is confined to a definite place in space by the *boundary* which separates it from the rest of the universe, *the surroundings*. The *boundary* is actually the interface between the system and the surrounding. The boundary may be real or imaginary. For example, let us consider a beaker containing water. In this case the beaker with water is the *system*. The rest of the universe outside the beaker is the *surroundings*. The wall of the beaker is the *boundary*. However, in practice the immediate vicinity of the *system* is considered as the *surroundings*. There are three types of systems depending on the nature of the boundary: *open*, *closed* and *isolated*.

Open System : The system is called *open* when both energy and mass can pass between the system and the surroundings across the boundary.

Closed System : If mass cannot pass between the system and the surroundings across the boundary, but energy can be exchanged with the surroundings, it is called a *closed* system. Energy may pass through the boundary either as heat or as some form of work. A sealed beaker containing water is an example of *closed system*.

Isolated System : A *system* is said to be *isolated* when the boundary prevents the exchange of both energy and mass with the surroundings. A sealed flask thermally, mechanically and electrically isolated from the surroundings is an example of *closed system*. The boundary in this case must be thermally and electrically insulated

A system can be either *homogeneous* or *heterogeneous*. If the composition of the system is uniform throughout, it is called homogeneous. Pure liquid, pure gas, pure solid, mixture of gases or a true solution – are few examples of homogeneous systems. If the composition of the system is not uniform throughout and consists of two or more phases, it is called a heterogeneous system. Mixture of insoluble liquids, mixture of solids, mixture of liquid and its vapour – are few examples of heterogeneous systems. There are phase boundaries between different phases or components in heterogeneous systems.

5.2.2 State of a thermodynamic system and state functions (variables)

A thermodynamic system is considered to be in a definite *state* when each of the macroscopic properties of the system has a definite value. The state of a thermodynamic system is completely defined by four measurable macroscopic properties: *pressure, volume, temperature and composition*. These properties upon which the state of a system is dependent are called *state variables* or *state functions*. It is not necessary to know all the *state functions* to clearly define the *state of a system*. For example, if the composition of a given mass of an ideal gas is fixed, the remaining variables are related by an *equation of state*, $PV = RT$. If any two of the three variables P, T and V are known, the third is automatically calculated. In this case the two known variables are designated as *independent state variable*, while the third unknown variable is called *dependent state variable*.

5.2.3 Intensive and extensive thermodynamic properties

Thermodynamic properties of a system may be classified into two groups:

(i) *Intensive properties* and

(ii) *Extensive properties*

Any property of a system *that does not depend on the actual quantity of matter contained in the system is called intensive property*. Pressure, temperature, boiling point, melting point, density, concentration etc. are examples of *intensive properties*. On the other hand, the property of a system *that is dependent upon the actual quantity of matter contained in the system is called extensive property*. Mass, volume, enthalpy, internal energy, entropy, number of moles etc are examples of *extensive properties*. Extensive properties are additive, while the intensive properties are non-additive.

5.2.4 Heat, energy and work

Heat: Heat is an important form of energy. It is difficult to define heat energy by a simple statement but the feeling of hotness or coldness is a common experience of all. Heat energy is capable of raising the temperature of a body. Temperature gives a feeling of how hot or how cold an object is. Temperature also determines the tendency of an object either to lose or gain heat. If an object A feels hotter than B, then object A has higher temperature than object B. If A and B are placed in contact with each other, heat will flow from object A to object B until the two objects are in thermal equilibrium and are at the same temperature. We say that heat can flow from a system at higher temperature to another system at lower temperature. From our experience we know that heat never flows from a body at a lower temperature to a body at a higher temperature. Heat energy can be *partially* converted into work. Other forms of energy can be *completely* converted into heat.

Unit of heat: The unit of heat is the calorie. *A calorie is defined as the quantity of heat required to raise the temperature of 1.0 g of water through 1.0 °C.* 1 calorie = 4.18 Joules. Sometimes heat is expressed in kilocalories (kcal), where 1 kcal = 1000 calories.

In the SI unit Joule is used as the unit of heat. In this book in all cases JOULE will be used as the unit of heat or work. 1000 Joules = 1 kilo Joule (kJ).

Heat energy can either be gained oy the system or lost from it whenever there is a change in the state of the system. The amount of heat (q) gained or lost is directly proportional to the mass, m, of the system and the change in temperature.

$$q \propto m\,(T_f - T_i)$$

The constant of proportionality is called the specific heat of the substance.

Here T_i and T_f are the initial and final temperatures respectively of the system. So

$$\Delta T = (T_f - T_i).$$

Hence
$$q = (\text{sp heat})\, m\, \Delta T \qquad (5.1)$$

If ΔT is positive, q is positive. This means heat energy has been gained by the system, and the process is *endothermic*. If, however, ΔT is negative, q is also negative. In other words heat energy has been lost by the system. The process is *exothermic*.

Example 5.1: 25.0 g of iron was heated from 25°C to 75°C. Calculate the amount of heat required, given that specific heat of iron is 0.4476 J $g^{-1}deg^{-1}$.

Solution : Using equation (5.1),

$$q = (0.4476)\,(25.0)\,[(75 - 25)]$$
$$= 559.5 \text{ J}$$

Energy : Energy of a system is defined as *'its capacity to do work'*. There are various forms of energy and conversion of energy from one form into another is possible. Electrical energy is converted into mechanical energy with the help of an electric motor. Chemical energy is transformed into mechanical energy in an internal combustion engine, such as that of a motor car or an aeroplane. In a flashlight battery chemical energy of a cell is converted into light energy *via* electrical energy. Broadly speaking, energy may be classified into two types :

(i) *Kinetic Energy and*

(ii) *Potential Energy.*

Kinetic Energy : Energy possessed by a system by virtue of its mass and speed is called kinetic energy. The kinetic energy of a body is measured by the amount of work that the body can do.

Potential Energy : An object possesses potential energy by virtue of its position in a *force field* (*an object above the surface of the earth is under the influence of gravitational force; or when an atom is bonded in a molecule it is under the influence of binding force*). An atom bonded with other atoms in a molecule has potential energy. If the atom is bonded to a different atom, its potential energy will be different. An object above the surface of the earth has potential energy equal to mgh (m = mass, h = height above the surface of the earth and g = acceleration due to gravity). Similarly, a coiled spring has potential energy and can do mechanical work, such as drive the minute and second hands in a watch. There are innumerable examples like this.

Internal Energy : In thermodynamics the total energy possessed by a system is termed its internal energy (U), [*older books use* E]. Internal energy is the sum of all possible forms of energy contained in a body. Internal energy of a system is a function of temperature, chemical nature of the system and sometimes also pressure and volume of the system. In a given system the magnitude of the internal energy depends on the way the molecules are put together and the nature of the individual atoms. The energy possessed by the molecules, the arrangement and number of electrons in the molecules, all contribute to U. In addition, the energy due to the *vibrational*, *rotational* and *translational* motions of the molecules is also included in U. Chemical and physical changes are accompanied by rearrangements in the relative positions of the atoms. This leads to changes in internal energy.

At the present time it is impossible to determine the absolute value of the internal energy of a system. Fortunately, however, it is the change in internal energy accompanying a chemical or physical change that is of interest to chemists. Absorption or release of heat which accompany chemical or physical changes are manifestations of the change in internal energy. The difference between the internal energy when a system changes from state A to state B is expressed as ΔU, so that

$$\Delta U = U_B - U_A \tag{5.2}$$

where U_B is the internal energy in the final state and U_A is the energy in the initial state. *The symbol Δ always indicates the difference between the values of the property of a system in the final state and in the initial state.*

Work : In thermodynamics *work* has a broader meaning. It includes mechanical work, electrical work, surface work etc. Mechanical work (w) is said to be done when an object is moved a distance Δl by an applied force F. Accordingly,

$$w = F \times \Delta l \tag{5.3}$$

If as a result of application of the force F the object moves an infinitesimally small distance dl then the infinitesimally small work done dw would be given by

$$dw = F \times dl \tag{5.4}$$

Unit of work :The unit of force in the cgs units is dyne and that of length is centimetre. Work in the same unit is expressed in ergs. So, dyne × cm = erg; erg is the work done when a force of 1 dyne acts and causes a displacement of 1 cm. Since an erg of work is a small quantity, a larger unit, **joule**, is often used; **1 joule = 10^7 ergs.**

Characteristics of heat and work :

(a) Both appear at the boundary of the system

(b) Both cause changes in the system

(c) Both produce equivalent and opposite effects in the surroundings.

5.2.5 Sign convention for heat and work

It is necessary to follow a systematic sign convention in calculations involving heat, energy and work. In this book sign convention recommended by the *International Union of Pure and Applied Chemistry (IUPAC)* will be followed. Thus the sign convention is

- If heat is supplied to a system, q is +ve, and ΔU is +ve
- If heat is lost by the system, q is –ve, and ΔU is –ve
- If work is done *on* the system, w is +ve, and ΔU is +ve
- If work is done *by* the system, w is –ve, and ΔU is –ve

5.3 The First Law of Thermodynamics

The first law of thermodynamics is also known as *the law of conservation of energy.* The first law may be stated in different forms:

(1) Energy can neither be created nor destroyed; it can only be converted from one form into another.

(2) The total energy of an isolated system is constant.

(3) It is impossible to construct a perpetual motion machine which will create energy out of nothing.

(4) The sum of all of the energy changes for all systems participating in a process must be zero.

(5) *If work is produced during a cyclic process, an equivalent amount of heat must also be consumed.*

This law has been accepted as valid after a long period of skepticism about its inviolability. Numerous attempts were made by scientists to construct a machine by means of which energy could be created. All such attempts to design a "*perpetual motion machine*" have failed. This is an indirect experimental evidence for the first law of thermodynamics. It is possible to convert matter into energy, as in a nuclear reaction, and under some circumstances to reverse this process. The law of conservation of matter by itself, therefore, does not hold. One may thus consider matter as a form of energy and the law of conservation of energy and the law of conservation of matter are essentially the same. Such transformations of matter into energy then fall under the first law of thermodynamics.

A corollary of the first law is that the internal energy of a system is a function of the state of the system and is independent of the path by which the state has been reached. Consider that a system can exist either in state A or in state B (Figure 5.1). The internal energy at A is U_A and that at B is U_B. When the system goes from state A to state B the change in the internal energy is $U_B - U_A$. If now the system is brought back to state A by a different path the change in the internal energy will be

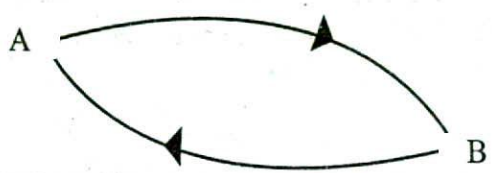


Figure 5.1 Internal energy as a state property.

$U_A - U_B$. According to the first law $U_B - U_A$ must be equal to $U_A - U_B$ in magnitude. If it were not so, creation of energy would be possible, which is against experience. It follows, therefore, that $\Delta U = U_B - U_A$ depends on the internal energies U_B and U_A at state B and state A, and not on how the system passed from state A to B. The internal energy is said to be a property of state, or *a state function*. Consequently, in a cyclic process there is no change in internal energy. Or mathematically

$$\oint dU = 0 \tag{5.5}$$

A cyclic process is one in which a system returns exactly to its original state after undergoing different changes. The symbol $\oint$ indicates integration over the whole cycle.

5.4 Mathematical Formulation of the First Law

When heat is applied to a system, the internal energy of the system will increase if no work is done. Similarly, the energy of a system may be increased by doing work on the system in absence of heat, e.g. by rubbing two objects together, or passing electricity though a resistor. If heat and work processes occur simultaneously, the net change in internal energy of a system is equal to the algebraic sum of the energy *gained* or *lost* as heat, and energy *gained or lost* due to work done *on* or *by* the system, w. In other words,

$$\Delta U = q + w \tag{5.6}$$

For infinitesimally small changes equation (5.6) may be written as

$$dU = dq + dw \tag{5.7}$$

(where dU represents an infinitesimally small change in internal energy, and similarly for q and w). It must, however, be pointed out that dq and dw do not represent differences between final and initial states. Whereas for two given states ΔU or dU is fixed and is always equal to $dq + dw$, the values of dq and dw depend on the manner in which the change from one state to another is brought about. The terms dq and dw are not regarded as *perfect* or *exact differentials*. So we should not indicate heat absorbed and work done as dq and dw respectively, and these are simply represented by q and w respectively. It is only the state properties or the state functions which are regarded as exact differentials. Equation (5.7) should, therefore, be written as

$$dU = q + w \tag{5.8}$$

If the work done ***by*** the system is simply mechanical, i.e., work of expansion, then $w = P.dV$, where P is the pressure and dV is the infinitesimal increase in volume. Equation (5.8) then becomes

$$dU = q - P.dV \tag{5.9}$$

In equation (5.9), the work done by the system $P.dV$ is represented by a negative sign (*Section 5.2.5*), because work of expansion is done *by* the system.

5.5 Thermodynamic Processes

When the state of a system is changed by changing any of the variables on which it is dependent, the operation is called a *thermodynamic process*. Different types of thermodynamic process are:

(i) Reversible and irreversible, (ii) Isothermal and adiabatic,
(iii) Isochoric and isobaric and (iv) Cyclic process.

5.5.1 Reversible and irreversible processes

One of the most important concepts in thermodynamics is that of reversibility. A thermodynamically reversible process is defined as, *'A process that takes place infinitesimally slowly in infinite number of small steps and requires infinite time to reach the final state. The process takes place in such a way that each step is at equilibrium with the preceding step. The reversible process can be made to go in the reverse direction by infinitesimal change in the state of the system'.*

In contrast, *'the irreversible process takes place at finite time and the system is at equilibrium only at the initial and final state. Irreversible processes are real and can be performed in real world'.*

One of the major requirements for carrying out a reversible process involving gases is the availability of a weightless and frictionless piston which is not feasible in practice. In order to better understand the concept of reversible and irreversible processes two examples are given.

Example 1: Let us consider that a liquid is placed in a cylinder fitted with a weightless and frictionless piston. The cylinder with the liquid is placed in a large reservoir maintained at the boiling temperature of the liquid. The vapour pressure of the liquid will be equal to the atmospheric pressure and the system will be in equilibrium at this temperature. If the pressure on the piston is now increased by an infinitesimally small amount dP, small quantity of the vapour condenses and the heat given up will be dissipated in the reservoir so that the temperature does not rise. As the increase in pressure is infinitesimally small the condensation will take place very slowly and the system will be in equilibrium at all times. If the temperature of the reservoir is raised by an infinitesimal amount dT, the vapour pressure of the liquid will be slightly greater, and the piston will be raised by a small amount. More liquid will evaporate and the pressure of the vapour in the cylinder is maintained constant. The temperature in the cylinder tends to decrease due to expansion of the vapour but is maintained constant by flow of heat from the reservoir. On the other hand, if the external pressure is decreased by a very small amount dP, the liquid will evaporate at a slow rate. The system will remain at equilibrium and the process will be reversible. If, however, the pressure change is made appreciable, sudden evaporation or condensation will take place rapidly, and since the system is not at equilibrium during the process, it is irreversible

Example 2 : Another example of a reversible process is an electrolytic cell. Let us consider a Daniel cell. If the electrodes of the cell are connected externally, current will flow in one direction. If an external source of e.m.f. is connected to the Daniel cell such

that the e.m.f. of the external is in opposite direction and is slightly higher than that of the Daniel cell, current in the latter will flow in the opposite direction, i.e., from the external cell to the Daniel cell. If the e.m.f. of the external source is slightly smaller, current will flow from the Daniel cell into the external source. In this sense the process is reversible as it may be reversed by small changes one way or the other of the voltage.

A reversible process is a hypothetical one since infinite number of steps is required to complete the process. Infinitesimally small changes are impossible to carry out in practice. All processes that occur in nature are more or less irreversible. It should, however, be mentioned that reversible processes yield the maximum work as will be shown in *Section 5.8.*

Examples of irreversible processes are abundant in Nature, e.g. flowing of rivers down stream, blooming of flowers in the gardens or evolution of hydrogen when a piece of zinc is placed in acid etc.

5.5.2 Isothermal and adiabatic processes

A process in which the temperature is maintained constant during the change is called an *isothermal process.* In an isothermal process $dT = 0$. In such a case heat is allowed to flow from the surrounding into the system during expansion of the gas, and taken out from the system to the surrounding during compression of the gas. An isothermal process is usually carried out by placing the system in a thermostat (constant temperature bath).

On the other hand, in an *adiabatic process* heat is not allowed into or out of the system during a change. The system is completely isolated from the surroundings by an insulated boundary. In an adiabatic process $dq = 0$.

5.5.3 Isochoric and isobaric processes

A thermodynamic process in which the volume is kept constant is known as an *isochoric process.* For an isochoric process $dV = 0$.

A process which takes place at constant pressure is called an *isobaric process.* For an isobaric process $dP=0$. The four thermodynamic processes involving a gas can be diagrammatically shown in Figure 5.2.

It can be seen from Figure 5.2 that the curve for an adiabatic process is steeper than that for an isothermal process. The reason for this is that in an isothermal expansion process heat is absorbed to make up for the work done by the gas. In an adiabatic expansion, on the other hand, the energy for the work of expansion is taken from the system itself so that its temperature falls. At this lower temperature but at the same pressure the volume is less.

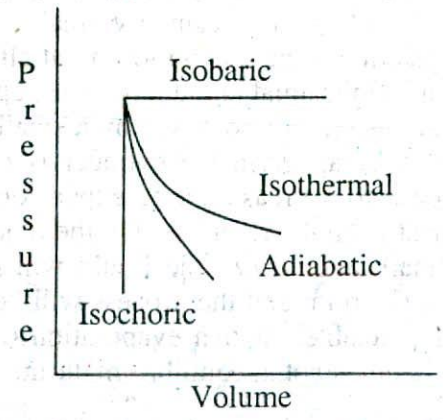


Figure 5.2 Four thermodynamic processes

5.5.4 The cyclic process

A process in which a system goes from an initial state to a final state and returns back to the initial state is called a *cyclic process*. The net energy change in a cyclic process is zero. Let us consider that a system changes from state A to state B, and then back to state A again. For the change from A to B, $\Delta U_1 = U_B - U_A$ and for the change from B to A, $\Delta U_2 = U_A - U_B$. The total energy change,

$$\Delta U_{total} = \Delta U_1 + \Delta U_2 = (U_B - U_A) + (U_A - U_B) = 0.$$

For a cyclic process, ΔH must also be zero as H is a state function.

5.6 Work of Expansion

The work involved in the change of volume of a gas against an external pressure is of considerable interest to chemists. The work done as a result of expansion of the gas is the work of expansion. Consider a gas contained in a cylinder (Figure 5.3) of cross-sectional area, a, fitted with a weightless and frictionless piston.

When the pressure on the piston is P it comes to an equilibrium position. The force on the piston is $P \times a$, i.e., the pressure multiplied by the area. Let the gas in the cylinder expand, when the piston is raised by a distance, h. As the point of application of the force has been displaced by h the work done against the force is $P \times a \times h$. But $a \times h$ is equal to the change in volume, ΔV. Hence the work of expansion will be,

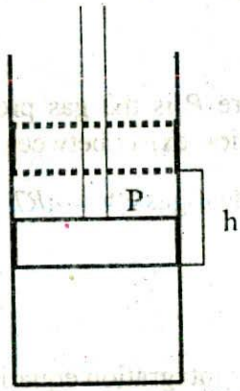


Figure 5.3 Expansion of gas

$$w = -P \times \Delta V \qquad (5.10)$$

The negative sign in equation (5.10) indicates that the work is done by the gas on the surrounding (*Section 5.5.2*). In equation (5.10) ΔV $(=V_f - V_i)$ is the change in volume, where V_f and V_i are the final and initial volume of the gas respectively. For expansion of gas $\Delta V > 0$ and $P \times \Delta V$ is a negative quantity. For compression (work done on the system) $\Delta V < 0$, and $P \times \Delta V$ is a positive quantity. If the gas is an ideal one, $P\Delta V$ may be replaced by RT for one mole and work of expansion equals RT. The units in which work is expressed will depend on the units of P and V.

5.7 Isothermal Reversible Expansion of an Ideal Gas: Maximum Work

The work done in an isothermal reversible expansion of a gas may be obtained by using a similar apparatus as shown in Figure 5.2. Let us consider that a definite quantity of an ideal gas is placed in a cylinder fitted with a weightless and frictionless piston, the cylinder itself being *placed in a large heat reservoir whose temperature is maintained constant at T*. Let the pressure on the piston be P and the initial volume of the gas V. If

the pressure is decreased by an infinitesimally small amount dP to a value of $P - dP$, the volume of the gas at this pressure increases by an amount dV. As the temperature is maintained constant, the work done in this infinitesimally small change is given by

$$w = -(P - dP)\, dV \tag{5.11}$$

The negative sign indicates that work is done by the system due to expansion against an external pressure. The product $dPdV$ is very small and one can write

$$w = -PdV \tag{5.12}$$

If the pressure is again decreased by an amount dP, the volume increases by dV and a small amount of work given by equation (5.12) is done. The total work done in expanding the gas from the initial volume, V_1, to the final volume, V_2, in such small steps is equal to the sum of the work done in each step and may be expressed by the integral

$$w = -\int_{V_1}^{V_2} PdV \tag{5.13}$$

where P is the gas pressure at any instant. The integration can be performed only if a relation exists between the pressure of the gas and the volume it occupies. For n mole of an ideal gas $PV = nRT$ or $P = \frac{nRT}{V}$. Equation (5.13) can, therefore, be written as

$$w = -\int_{V_1}^{V_2} P\, dV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \tag{5.14}$$

After integration equation (5.14) can be written as,

$$w = -nRT \ln \frac{V_2}{V_1} \tag{5.15}$$

Again, $P_1V_1 = P_2V_2$

So, $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

and equation (5.15) may also be written in the form

$$w = -nRT \ln \frac{P_1}{P_2} \tag{5.16}$$

This work done in an isothermal reversible expansion of an ideal gas is maximum as can be shown in the following manner:

Equation (5.16) may be written in the form,

$$-w = nRT \ln \left(1 + \frac{P_1 - P_2}{P_2}\right) \tag{5.17}$$

It is known that when x is small $\ln (1 + x) \approx x$.

So when $(P_1 - P_2)$ is small compared to P_2

$$ln\left(1+\frac{P_1-P_2}{P_2}\right) \approx \frac{P_1-P_2}{P_2} \tag{5.18}$$

and equation (5.17) becomes

$$-w = nRT\,\frac{P_1-P_2}{P_2} \tag{5.19}$$

If the expansion process is carried out irreversibly so that P_1 is rapidly changed to P_2 and *one mole* of the gas is allowed to expand from a volume V_1 to V_2 the work done is given by

$$-w_{irr} = P_2\,(V_2 - V_1) \tag{5.20}$$

By adding and subtracting P_1V_1 equation (5.20) may be rearranged to yield,

$$\begin{aligned} -w_{irr} &= P_2V_2 - P_2V_1 + P_1V_1 - P_1V_1 \\ &= P_2V_2 - P_1V_1 + V_1(P_1 - P_2) \\ &= V_1(P_1 - P_2) \qquad (\text{since } P_1V_1 = P_2V_2) \\ &= RT\frac{P_1-P_2}{P_1} \end{aligned} \tag{5.21}$$

for 1 mole of an ideal gas. For n mole of an ideal gas equation (5.21) becomes,

$$-w_{irr} = nRT\frac{P_1-P_2}{P_1} \tag{5.21a}$$

Comparing equations (5.19) and (5.21a) if we look at the denominator we find that as $P_1 > P_2$, w must be larger than w_{irr}.

Thus it can be concluded that the work done in a reversible process is greater than that done in an irreversible process. In other words, the work done in a reversible process is maximum.

It must be remembered that the negative sign before the work done w (reversible or irreversible) merely indicate that the work is done by the system on the surrounding.

Example 5.2: Calculate the work done when 1 mole of an ideal gas expands isothermally and reversibly at 27°C from a pressure of 10 atm to 1 atm.

Solution: From equation (5.16) work done, $w = -RT\,ln\frac{P_1}{P_2}$

$$\begin{aligned} &= -(8.314)(273.16+27)(2.303)\log\frac{10}{1} \\ &= -5747.2\ \text{J} \end{aligned}$$

Example 5.3: Calculate the work done if 2.0 moles of an ideal gas, initially occupying a volume of 30.0 L at 280 K, is allowed to expand isothermally and reversibly until the final volume is 50.0 L.

Solution: According to equation (5.15),

$$w = -nRT\ ln\frac{V_2}{V_1}$$

$$= -(2.0)(8.314)(280)\ (ln\frac{50.0}{30.0})$$

$$= -\ 2.38\ \text{kJ}$$

5.8 Constant Volume Processes

If the thermodynamic process is carried out at constant volume, $w = 0$, since dV = zero. Hence the first law equation takes the form

$$q = dU \tag{5.22}$$

The heat absorbed or evolved directly changes the internal energy. For example, if a chemical reaction is carried out in a stainless-steel pressurized container the heat produced must increase the internal energy by raising the temperature since the volume is fixed.

5.9 Partial Differential Notation

If a property X of a system depends on several variables such as pressure, volume, temperature and the number of moles of the constituents of the system then one can write,

$$X = f(V,T,\ n_1, n_2\ \text{etc.}) \tag{5.23}$$

If all the variables change by infinitesimal amounts then the change in the property X is given by

$$dX = \left(\frac{\partial X}{\partial V}\right)_{T,n_1,n_2\cdots} dV + \left(\frac{\partial X}{\partial T}\right)_{V,n_1,n_2\cdots} dT + \left(\frac{\partial X}{\partial n_1}\right)_{V,T,n_2,n_3\cdots} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{V,T,n_1,n_3\cdots} dn_2 + \cdots \tag{5.24}$$

according to the method of partial differentiation.

Here, $\left(\frac{\partial X}{\partial V}\right)_{T,n_1,n_2}$ indicates that only the variable V is allowed to change, and other variables such as T, n_1, n_2 etc. are kept constant.

5.10 Constant Pressure Processes and Enthalpy

In chemistry constant pressure processes are more common than constant volume processes since most reactions are usually carried out in open vessels under atmospheric pressure. A convenient thermodynamic function *enthalpy, or heat content* is used to

describe a constant pressure process. This function is represented by the letter H and is defined by,

$$H = U + PV \tag{5.25}$$

Like any other thermodynamic state function it is impossible to determine the absolute value of enthalpy of a system. The enthalpy of a system depends only on the state of the system and is in no way affected by the way in which the state is reached. When a system changes from state 1 to state 2 the value of ΔH, i.e., $(H_2 - H_1)$, is constant, no matter how the system undergoes change in going from the initial state to the final state. In thermodynamic treatments we are concerned with ΔH. As will be seen, for solids and liquids ΔH values are usually almost equal to the change in internal energy, ΔU. This is because solids and liquids are only slightly compressible, i.e., their volume changes only to a small extent when the pressure is changed.

Under constant pressure conditions equation (5.9) may be written as,

$$dU = q_p - P.dV$$

$$q_p = \Delta U + P\Delta V \qquad (\text{as } w = P\Delta V) \tag{5.26}$$

$$= U_2 - U_1 + P(V_2 - V_1)$$

$$= (U_2 + PV_2) - (U_1 + PV_1) \tag{5.26a}$$

q_p being the heat absorbed at constant pressure.

As $H = U + PV$, equation (5.26a) takes the form

$$q_p = H_2 - H_1 = \Delta H \tag{5.27}$$

In other words, the heat absorbed under constant pressure conditions is equal to the increase in enthalpy or heat content, if the only work done is the pressure-volume work.

Example 5.4: What will be the change in enthalpy when 5.0 mol of iron is heated from 90°C to 140°C at atmospheric pressure?

(specific heat of Fe is 0.4476 J $g^{-1}deg^{-1}$).

Solution: We know, $\Delta H = q_p = (\text{sp. heat})\ m\ \Delta T$

$$\Delta H = (5.0 \times 55.8)(0.4776)[(140 - 90)] = 6.25 \text{ kJ}$$

5.11 Relationship between U and H

Using equation (5.25), $H = U + PV$, for the general case in which neither U nor P is constant we can write,

For final state $H_{(final)} = U_{(final)} - PV_{(final)}$

For initial state $H_{(initial)} = U_{(initial)} - PV_{(initial)}$

For a change of the system between two states,

$$\Delta H = H_{(final)} - H_{(initial)}$$

$$= U_{(final)} - PV_{(final)} - [U_{(initial)} - PV_{(initial)}]$$
$$= [U_{(final)} - U_{(initial)}] - [PV_{(final)} - PV_{(initial)}].$$
$$= \Delta U - \Delta(PV) \quad (5.28)$$

Considering that the system is composed of an ideal gas, we can replace nRT for PV in equation (5.28). Thus,

$$\Delta H = \Delta U + R\,\Delta(nT) \quad (5.29)$$

At constant n, $\Delta H = \Delta U + R\,n\,\Delta T$ (5.30)

And at constant temperature, $\Delta H = \Delta U + R\,T\,\Delta n$ (5.31)

Equation (5.31) can be applied to chemical reactions, where

$$\Delta n = \Sigma n(gas, products) - \Sigma n(gas, reactants) \quad (5.32)$$

Example 5.5: Calculate the difference between ΔU and ΔH at 1000°C for the reaction :

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

assuming that the gaseous substances behave ideally.

Solution: *At constant temperature* rearrangement of equation (5.31)gives

$$\Delta H - \Delta U = R\,T\,\Delta n$$

and from equation (5.32) we have $\Delta n = 2 - 3 = -1$

Therefore, $\Delta H - \Delta U = (8.314)\,(1273)\,(-1) = -1.058 \times 10^4$ J

Example 5.6: Calculate ΔH of the reaction, $H_2F_2(g) \rightarrow H_2(g) + F_2(g)$ at 298K, given that ΔU at this temperature is – 59.41 kJ mol^{-1}.

Solution: We know, $\Delta H = \Delta U + RT\,\Delta n$

$$= (-59.41) + (8.314)\,(298)(2-1)/(1000)$$
$$= (-59.41) + (2.48)$$
$$= -56.93 \text{ kJ mol}^{-1}$$

5.12 Heat Capacity and Molar Heat Capacity

It is a common experience that the temperature of a substance (a system) increases when heat is supplied to it. The resulting temperature increase, however, depends on the 'heat capacity' of the substance. The heat capacity C is defined as,

$$C = \frac{q}{\Delta T} \quad (5.33)$$

where, q is the amount of heat absorbed by the system and ΔT $(=T_f - T_i)$ is the temperature change. The heat capacity, C, is defined as, '*the amount of heat energy required to raise the temperature of a system by one degree*'. If the temperature is expressed in Kelvin and q is in joule, C is expressed as J K^{-1}; or in J per degree Celsius, if the temperature is in degree Celsius. Calculation of the amount of heat energy absorbed or released by a system is a simple operation by rearranging equation (5.33). Thus,

$$q = C \times \Delta T \quad (5.34)$$

C is an *extensive property* since it is dependent on the amount of substance present. It is, however, convenient to express the heat capacity as an *intensive property* when it is

independent of the amount of substance present. Two other terms, specific heat capacity (C_s), or molar heat capacity (C_m) are used for this purpose. By definition,

$$C_s = \frac{C}{m} = \frac{JK^{-1}}{g} = JK^{-1}g^{-1} \tag{5.35}$$

and $$C_m = \frac{C}{n} = \frac{JK^{-1}}{mol} = JK^{-1}mol^{-1} \tag{5.36}$$

Here, m is the mass in g and n is the number of moles of the substance of which the heat capacity is C. Now heat energy can be supplied to the system at constant volume as well as at constant pressure. Accordingly the heat capacities are distinguished as C_v, specific heat at constant volume, or C_p, specific heat at constant pressure.

5.12.1 Thermodynamic definition of C_v

Rearranging equation (5.9), we get

$$q = dU + PdV$$

Dividing both sides by dT we get,

$$\frac{q}{dT} = \frac{dU + PdV}{dT} = \frac{dU}{dT} + \frac{PdV}{dT} \tag{5.37}$$

At constant volume, $dV = 0$. Equation (5.37) then becomes $\frac{q}{dT} = \frac{dU}{dT}$

Since $C_v = \frac{q}{dT}$, we can write $$C_v = \frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_v \tag{5.38}$$

Thus, the heat capacity at constant volume is defined as, '*the rate of change of internal energy with temperature at constant volume*'. Equation (5.38) is sometimes written as,

$$dU = C_v\,dT \quad \text{or more accurately, } \Delta U = C_v \Delta T \tag{5.38a}$$

Example 5.7: 2.0 moles of NH_3 were heated from 300 K to 370 K at constant volume. Calculate ΔU, given that the molar heat capacity of NH_3 at constant volume, $C_{v,m}$, is equal to 24.8 J K^{-1} mol^{-1}.

Solution: Integration of equation (5.38) between the two temperatures gives

$$\int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} C_v dT = C_v \int_{T_1}^{T_2} dT$$

For n moles we get, $\Delta U = n\,C_{v,m}(T_2 - T_1)$

$= (2.0)\,(24.8)(370 - 300) = 3472$ J

5.12.2 Thermodynamic definition of C_p

Equation (5.37) may be written as,

$$\left(\frac{q}{dT}\right)_p = \left(\frac{dU}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p \tag{5.39}$$

We know, $H = U + PV$.

Differentiating this equation with respect to T at constant pressure we get,

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \tag{5.40}$$

Comparing equation (5.39) with equation (5.40) one can write,

$$C_p = \left(\frac{q}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{5.41}$$

Thus, the heat capacity at constant pressure is defined as, *'the rate of change of enthalpy with temperature at constant pressure'*. Equation (5.41) is sometimes written as,

$$dH = C_p\, dT \quad \textit{or less accurately} \quad \Delta H = C_p \Delta T \tag{5.41a}$$

Problem 5.8: 3000 J of heat was added to1.0 mole of CO_2 at 400 K at constant pressure. What will be the final temperature if $C_{p,m}$ for CO_2 is 41.0 J $K^{-1}mol^{-1}$.

Solution: From equation (5.41a) we get,

$$\int_{H_1}^{H_2} dH = nC_p \int_{T_1}^{T_2} dT = nC_p (T_2 - T_1)$$

$$\Delta H = n\, C_p (T_2 - T_1)$$

$$\text{Or, } T_2 - T_1 = \frac{\Delta H}{nC_{p,m}} = \frac{3000}{(1.00)(41.0)} = 73.2$$

Hence $T_2 = 73.2 + 400 = 473.2$ K

5.12.3 Relationship between C_v and C_p

When heat is supplied to a system at constant volume no pressure-volume work is done by the system, and the energy is used up completely in increasing the internal energy of the system. If, however, the heat is supplied to the system at constant pressure, some pressure-volume work is done by the system. In addition, the internal energy of the system will also be increased. It is, therefore, quite reasonable that extra heat energy must be supplied to the system at constant pressure for work of expansion as well as to raise the temperature of the system through the same value as at constant volume process. Thus $C_p > C_v$. This can also be proved from the thermodynamic definitions of C_P and C_V as shown below.

Let us consider equations (5.25) and (5.41),

$$H = U + PV; \quad C_p = \left(\frac{dH}{dT}\right)_p$$

Combining these two equations and introducing the concept of total differential (*Section 5.10*) we get,

$$C_P = \left[\frac{\partial(U+PV)}{\partial T}\right]_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \tag{5.42}$$

The internal energy U of a pure homogeneous substance is a function of two variables; and it is convenient to choose T and V and consider that,

$$U = f(V,T) \tag{5.43}$$

Hence, $$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{5.44}$$

On dividing both sides of equation (5.44) by dT and imposing the conditions of constant pressure it follows that,

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{5.45}$$

$$= C_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{5.45a}$$

Substituting equation (5.45a) into equation (5.42) and rearranging we get,

$$C_p - C_v + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{5.46}$$

Or $$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{5.47}$$

Equation (5.47) is one form of relationship between molar heat capacities $C_{m,p}$ and $C_{m,v}$. It will be shown that the quantity on the right hand side is always positive. Thus $C_p > C_v$.

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$, so that, $C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_p$ (5.48)

For 1.0 mole of an ideal gas, $PV = RT$. Differentiating both sides of this equation of state with respect to temperature and imposing the condition of constant pressure one can obtain,

$$P\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial(RT)}{\partial T} = R \tag{5.49}$$

Thus, combining equation (5.48) and (5.49) we obtain,

$$C_p - C_v = R \tag{5.50}$$

More appropriately, $$C_{m,p} - C_{m,v} = R \tag{5.50a}$$

where $C_{m,p}$ *and* $C_{m,v}$ are the molar heat capacities at constant pressure and constant volume respectively.

5.13 The Internal Energy of an Ideal Gas: Joule's Experiments

In an adiabatic expansion the work is done by the system on the surrounding at the expense of the internal energy. This was experimentally demonstrated by J. P. Joule in 1844. The experiments were performed in an apparatus described in Figure 5.4. Two similar copper vessels, one filled with an 'ideal gas' at a high pressure and the other evacuated, were used.

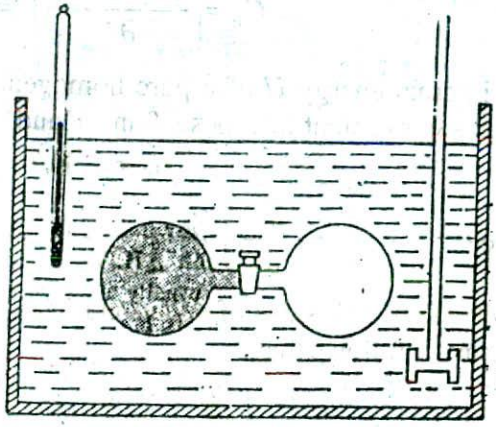


Figure 5.4 Joule's Experiment

The vessels were connected by means of a stop-cock. These were then placed in a water bath, the temperature of which was recorded. When the stop-cock was opened gas rushed from the high pressure vessel to the evacuated vessel. As a result the temperature of the vessel containing the gas under pressure fell, but that of the originally evacuated vessel rose by an equal amount. When equilibrium was established the temperature of the water bath was again recorded. There was no change in the temperature of the bath which means that there was neither absorption nor evolution of heat in the system. Since the total volume of the system consisting of the two vessels had not changed, no external work was done against the atmosphere. Since $q = 0$ and $w = 0$ it follows from equation (5.9) that ΔU must be zero. In other words, for an ideal gas the internal energy is independent of volume, i.e.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{5.51}$$

This is regarded as a thermodynamic criterion for an ideal gas.

5.14 Joule-Thomson Porous Plug Experiments

A more refined and sensitive experiment was carried out by Joule in conjunction with William Thomson (later, Lord Kelvin) in order to detect any possible heat effect as a result of free expansion of a gas. In these experiments gas at a high pressure P_1 was forced through a throttle valve (originally porous plug) into a space of lower pressure P_2. The system was thermally insulated so that, as the gas passed through the plug, no heat could be absorbed or given off, i.e., $q = 0$. The pressure and temperature on both sides of

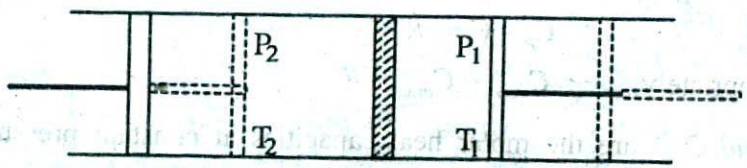


Figure 5.5 Joule-Thomson experiment

the plug were measured. It was observed that there was a fall in temperature on the low pressure side when the gas was forced through the plug, i.e. the gas expanded. This cooling effect is known as the *Joule-Thomson effect.* It may be defined as,

'The cooling effect observed when a gas is adiabatically expanded from a high pressure region to a low pressure region through a throttle valve, or porous plug is called Joule-Thomson effect'.

The cooling effect in the Joule-Thomson experiment is attributed to intermolecular attractions of the molecules. An expanding gas has to do work in order to overcome the attractive force so that the molecules may move further apart. The work is done at the cost of internal energy since the process is adiabatic: As a result the temperature of the expanding gas will fall.

Subsequent experiments demonstrated that under ordinary conditions the cooling effect was observed with most gases except hydrogen and helium which registered an increase of temperature in the Joule-Thomson experiment. If, however, the experiment with these gases were performed at a very low temperature the cooling effect was observed as with other gases. It was, thus, established that for each gas there is a temperature above which heating is observed in a Joule-Thomson experiment, whereas below this temperature cooling is noticed. This temperature is known as the *Joule-Thompson inversion temperature (or simply, inversion temperature).* For hydrogen and helium the inversion temperatures are considerably below the room temperature; hence these gases undergo heating on adiabatic expansion under ordinary conditions of temperature.

It can be shown that the enthalpy of gas on the two sides of the porous plug in the Joule-Thompson experiment is the same, i.e. to say that the Joule-Thomson experiment is *isenthalpic*. If P_1 and V_1 are the pressure and volume of the gas before passage through the plug and P_2 and V_2 are the corresponding quantities after passing through the porous plug the work of expansion is given by

$$w = P_2V_2 - P_1V_1 \tag{5.52}$$

Using equation (5.9)

$$\Delta U = q - (P_2V_2 - P_1V_1) \tag{5.53}$$

But $\Delta U = U_2 - U_1$ and $q = 0$, so equation (5.53) becomes

$$U_2 - U_1 = 0 - (P_2V_2 - P_1V_1)$$

$$= -(P_2V_2 - P_1V_1)$$

or $$U_2 + P_2V_2 = U_1 + P_1V_1$$

and $$H_2 = H_1 \tag{5.54}$$

The results of the Joule-Thomson experiments are expressed in terms of the Joule-Thomson co-efficient defined by

$$\mu_{J,T} = \left(\frac{\partial T}{\partial P}\right)_H \tag{5.55}$$

The quantity $\mu_{J,T}$ is thus defined as, '*the change in temperature in degrees when the pressure is changed by one atmosphere under conditions of constant enthalpy.*' Three cases may be considered:

(i) $\mu_{J,T}$ is positive, then T decreases when P decreases, and the gas cools upon expansion.

(ii) $\mu_{J,T}$ is negative, then T increases when P decreases, the gas is heated up upon expansion.

(iii) $\mu_{J,T} = 0$, the gas is neither heated nor cooled upon adiabatic expansion. $\mu_{J,T} = 0$ only when $dT = 0$ for any value of dP.

Most common gases, except *He* and H_2, have positive $\mu_{J,T}$ at room temperature (Table 5.1), and thus will cool during Joule-Thompson expansion that starts at room temperature.

Table 5.1 Joule-Thomson co-efficient at 1.0 atm for gases (Unit: K atm^{-1})

Gas	0 °C	100 °C
He	– 0.0616	– 0.0638
H_2	– 0.013	– 0.039
N_2	0.2655	0.1291
O_2	0.366	0.193
Ar	0.430	0.230
CO_2	1.369	0.729
C_2H_5Cl	5.220	2.430
Air	0.2751	0.1371

As shown in *Section 2.35* the Joule-Thomson effect is of considerable importance in the liquefaction of gases.

It may be shown by applying van der Waals' equation that the $\mu_{J,T}$ is related to a and b by the expression

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\left(\frac{2a}{RT} - b\right)}{C_p} \tag{5.56}$$

At the inversion temperature $\left(\frac{\partial T}{\partial P}\right)_H = 0$, from which it follows that

$$T_I = \frac{2a}{Rb} \tag{5.57}$$

Example 5.9: Show that $\mu_{J,T}\, C_p = -\left(\frac{\partial H}{\partial P}\right)_T$

Solution: Let us consider that $H = f(P,T)$. The total differential of H as a function of P and T can, therefore, be written as,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

For constant H, $dH = 0$. Then dividing by dP, we have

$$0 = \left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H$$

We know, $\left(\frac{\partial H}{\partial T}\right)_P = C_p$ and $\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J,T}$

Substituting these and rearranging the above equation we get,

$$\mu_{J,T}\, C_p = -\left(\frac{\partial H}{\partial P}\right)_T$$

5.15 Adiabatic Processes

An adiabatic process is one in which there is no loss or gain of heat from the system, i.e. for an adiabatic change $q = 0$. So when a gas expands adiabatically its temperature falls as some energy of the system is used up in doing the work of expansion. Adiabatic compression results in a rise of temperature of the gas. This can be clearly seen as follows:

From the first law of thermodynamics

$$dU = -w \quad (\text{since } q = 0)$$
$$= -PdV \tag{5.58}$$

and since for an ideal gas $dU = C_v dT$ (from equation 5.38a)

$$C_v dT = -PdV \tag{5.59}$$

For one mole of an ideal gas, $P = \frac{RT}{V}$; hence

$$C_v dT = -RT\frac{dV}{V}$$

$$C_v \frac{dT}{T} = -R\frac{dV}{V} \tag{5.60}$$

If V_1 is the volume of the gas at temperature T_1, and V_2 is the volume at temperature T_2, it follows by integration within these limits that,

$$\int_{T_1}^{T_2} C_v \frac{dT}{T} = -\mathrm{R}\int_{V_1}^{V_2} \frac{dV}{V} \tag{5.61}$$

Since C_v is constant,

$$C_v \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1} \tag{5.62}$$

Again, $C_p - C_v = R$ and for 1 mole of gas $R/C_v = \gamma - 1$, where $\gamma = C_p/C_v$, the ratio of molar heat capacities. This value of R/C_v, reduces equation (5.62) to

$$\ln\frac{T_2}{T_1} = -(\gamma - 1)\ln\frac{V_2}{V_1} \tag{5.63}$$

Equation (5.63) can be written in the form,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

or $$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad (5.64)$$

As the gas is ideal $P_1V_1 = RT_1$ and $P_2V_2 = RT_2$, so that

$$\frac{T_1}{T_2} = \frac{P_1V_1}{P_2V_2} \quad (5.65)$$

From equations (5.64) and (5.65) it follows that

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

or $$PV^{\gamma} = \text{constant} \quad (5.66)$$

Since C_p is always greater than C_v the ratio C_p/C_v is larger than unity. When pressure is plotted against volume it will be noted that the curve for an adiabatic process is steeper than that for an isothermal process (Figure 5.3), which has already been explained (*Section 5.5.3*).

QUESTIONS AND PROBLEMS

1. Discuss the nature of thermodynamics, its power and limitations.
2. Explain the following terms:
   (a) Reversible and irreversible processes; (b) internal energy; (c) inversion temperature;
   (d) isothermal and adiabatic processes.
3. Derive an expression for the work done in an isothermal reversible expansion of an ideal gas. Prove that the work done in such a process is the maximum.
4. Write explanatory notes on : (a) Joule-Thomson effect; (b) Heat capacities of gases;
5. One mole of nitrogen is heated from 0°C to 10°C under a pressure of 2 atm. Calculate (a) the change in enthalpy, (b) the change in internal energy assuming that nitrogen behaves as an ideal gas. The mean specific heat at constant pressure is 1.02 J deg^{-1} g^{-1}. [Ans. (a) 3143 J; (b) 2224 J]
6. 20 L of hydrogen at 27°C and 50 atm pressure expands isothermally and reversibly to 100 L. Calculate (a) the work done during the expansion; (b) the final pressure after expansion and (c) heat absorbed during the process. [Ans. (a) 162.5 kJ; (b) 10 atm; (c) 160.4 kJ]
7. Describe the Joule-Thomson experiments and discuss what important deductions were made from the results.
8. Show that the work done in an adiabatic process is less than that in an isothermal process, both being carried out reversibly.
9. One mole of argon gas is expanded reversibly and adiabatically from 22.4 L at 25°C to 44.8 L. Calculate (a) the final temperature and (b) pressure of the gas if it is assumed to be ideal.
   [Ans. (a) 8.4°K; (b) 0.345 atm]
10. State whether the following statement are correct or not. Justify your answer in brief:–
    (a) $C_p - C_v = R$
    (b) When an ideal gas expands into a vacuum, $\left(\frac{\partial U}{\partial V}\right)_T = 0$
11. Deduce an expression for the efficiency of an engine operating thermodynamically reversibly.
12. One mole of an ideal gas at 27°C expands isothermally and reversibly from 1.0 L to 5.0 L. Calculate w and each of the thermodynamic quantities ΔU, and ΔH. [Ans. $w = q = 4004$ J; $\Delta H = \Delta U = 0$]