Adapted from NCERT textbook of class XI 2006 edition reprinted edition pre rationalization

STATES OF MATTER

INTRODUCTION

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

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical laws which govern the behaviour of matter in different states.

THE GASEOU STATE

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

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven elements exist as gases under normal conditions (Fig5.4).

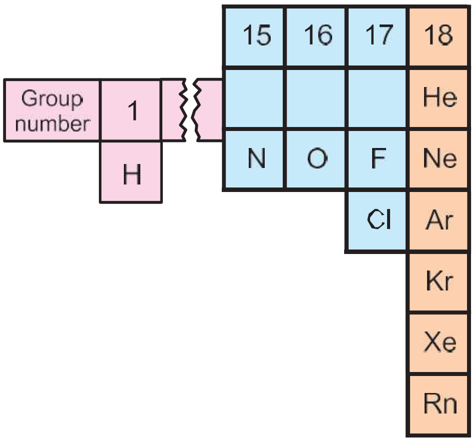


Fig. 5.4 *Eleven elements that exist as gases*

The gaseous state is characterized by the following physical properties.

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

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas. Interdependence of these variables leads to the formulation of gas laws. In the next section we will learn about gas laws.

THE GAS LAWS

The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as Boyle's Law. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.

Boyle's Law (Pressure - Volume Relationship)

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

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

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

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

On rearranging equation (5.2) we obtain

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

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

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

$$p_1 V_1 = p_2 V_2 = \text{constant} \qquad (5.4)$$

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

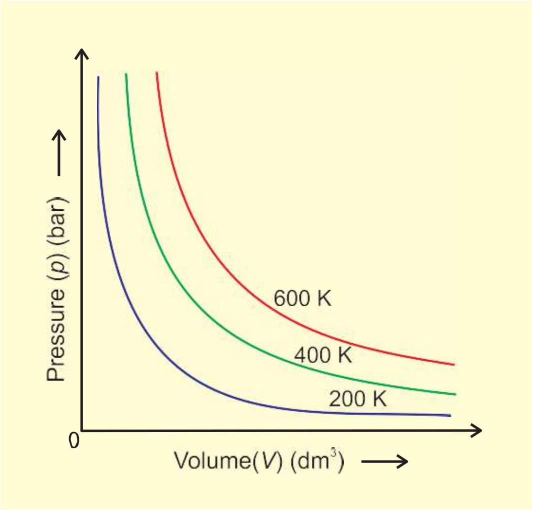


Fig. 5.5(a) *Graph of pressure, p vs. Volume, V of a gas at different temperatures.*

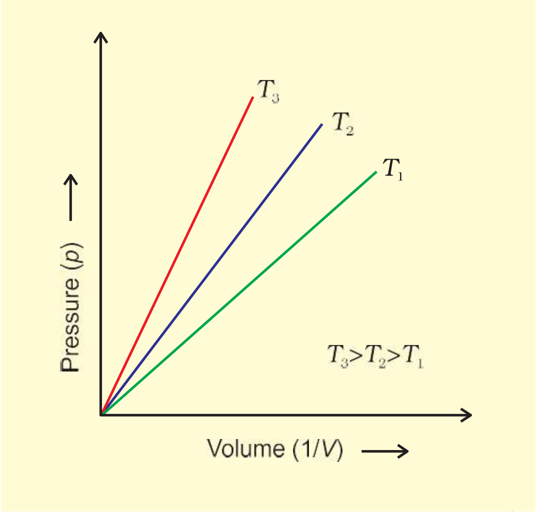


Fig. 5.5 (b) *Graph of pressure of a gas, p vs.* $\frac{1}{V}$

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

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

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

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

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

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

from Boyle's law equation, we obtain the relationship.

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

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

Problem 5.1

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

Solution

According to Boyle's Law $p_1V_1 = p_2V_2$

If p_1 is 1 bar, V_1 will be 2.27 L

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

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

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

Charles' Law (Temperature - Volume Relationship)

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

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

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

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

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

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

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

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

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

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

Thus we can write a general equation as follows.

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

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

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

$$\text{Thus } V = k_2 T \qquad (5.10)$$

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

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

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

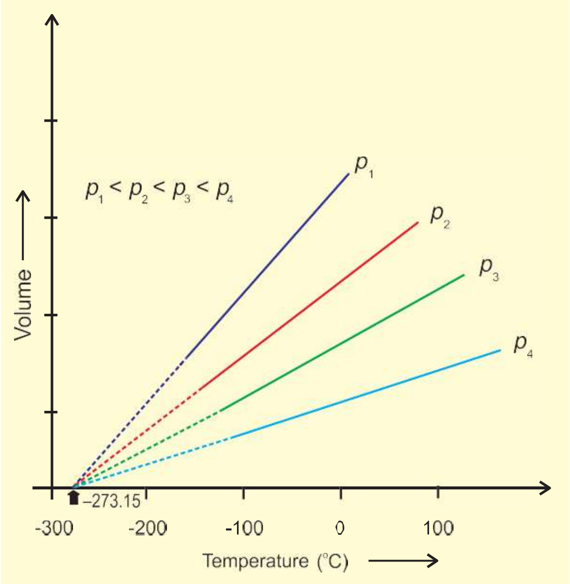


Fig. 5.6 Volume vs Temperature (°C) graph

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

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

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

Problem 5.2

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

Solution

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

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

$= 296.4$ K

From Charles law

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

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

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

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

$$= 2.018\,\text{L}$$

Gay Lussac's Law (Pressure-Temperature Relationship)

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

$$p \propto T$$

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

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

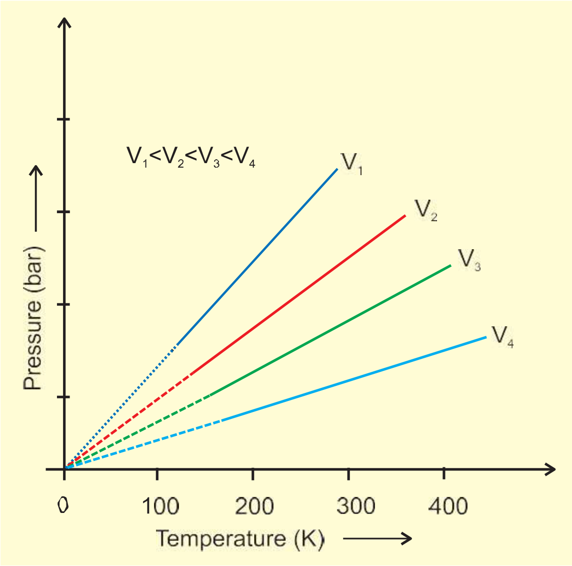


Fig. 5.7 *Pressure vs temperature (K) graph (Isochores) of a gas.*

Avogadro Law (Volume - Amount Relationship)

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

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

$$\Rightarrow V = k_4\, n \tag{5.11}$$

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

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at **standard temperature and pressure (STP)* will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.**

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

Table 5.2 Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

Number of moles of a gas can be calculated as follows

$$n = \frac{m}{M} \tag{5.12}$$

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

Thus,

$$V = k_4 \frac{m}{M} \tag{5.13}$$

Equation (5.13) can be rearranged as follows :

$$M = k_4 \frac{m}{V} = k_4 d \tag{5.14}$$

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

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

IDEAL GAS EQUATION

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

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

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

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

Thus,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Problem 5.3

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

Solution

p_1 = 760 mm Hg, V_1= 600 mL

T_1 = 25 + 273 = 298 K

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

According to Combined gas law

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

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

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

= 676.6 mm Hg

5.6.1 Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows:

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

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

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

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

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

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

5.6.2 Dalton's Law of Partial Pressures

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

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

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

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

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

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

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

Partial pressure in terms of mole fraction

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

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

$$p_2 = \frac{n_2 RT}{V} \qquad (5.26)$$

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

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

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

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

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

On dividing p_1 by p_{total} we get

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

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

where $n = n_1 + n_2 + n_3$

x_1 is called mole fraction of first gas.

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

Similarly for other two gases we can write

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

Thus a general equation can be written as

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

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

Problem 5.4

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

Number of moles of dioxygen

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

$$= 2.21\text{ mol}$$

Number of moles of neon

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

$$= 8.375\text{ mol}$$

Mole fraction of dioxygen

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

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

$$= 0.21$$

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

$$= 0.79$$

Alternatively,

mole fraction of neon = 1– 0.21 = 0.79

Partial pressure of a gas = mole fraction total pressure

$\Rightarrow$ Partial pressure of oxygen = 0.21 (25 bar) = 5.25 bar

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

KINETIC MOLECULAR THEORY OF GASES

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

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

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

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

BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

Our theoritical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV *vs* p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV *vs* p graph at all pressures will be a straight line parallel to x-axis. Fig. 5.8 shows such a plot constructed from actual data for several gases at 273 K.

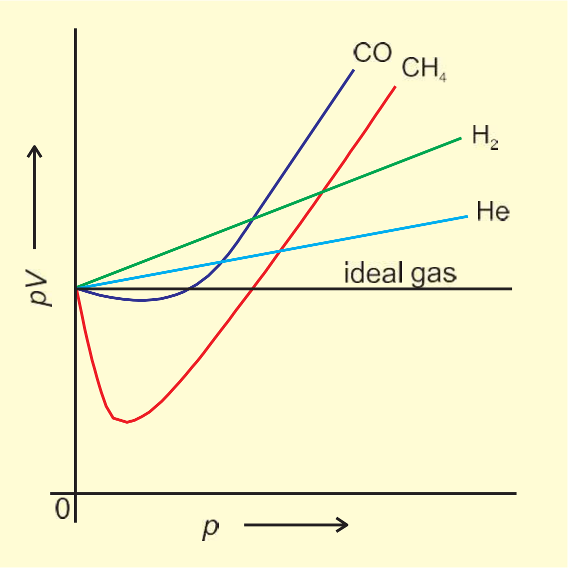


Fig. 5.8 *Plot of pV vs p for real gas and ideal gas*

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

Deviation from ideal behaviour also becomes apparent when pressure *vs* volume plot is drawn. The pressure *vs* volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 5.9 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

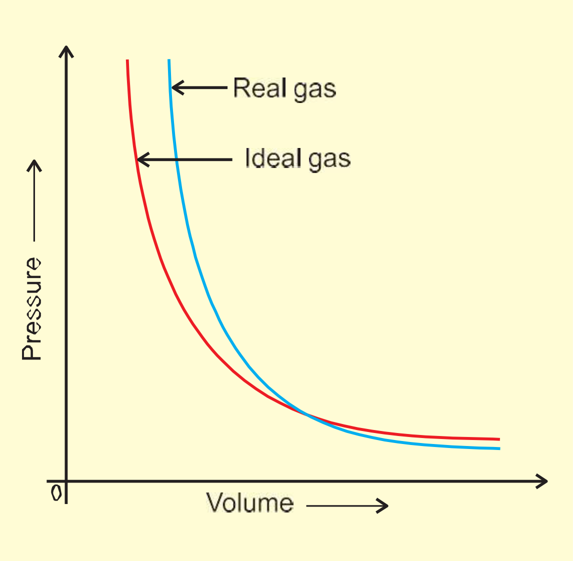


Fig. 5.9 *Plot of pressure vs volume for real gas and ideal gas*

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

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

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

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

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

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

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress.

This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure *vs* volume graph of experimental data (real gas) and that theoritically calculated from Boyles law (ideal gas) should coincide.

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

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

Here, a is a constant.

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

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

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

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

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

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

For ideal gas $Z = 1$ at all temperatures and pressures because $pV = n\,RT$. The graph of Z *vs* p will be a straight line parallel to pressure axis (Fig. 5.10). For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown

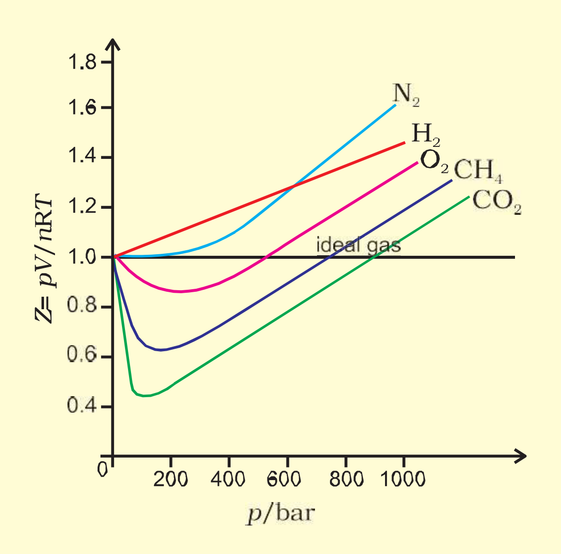


Fig. 5.10 Variation of compressibility factor for some gases

have Z ≈ 1 and behave as ideal gas. At high pressure all the gases have Z > 1. These are more difficult to compress. At intermediate pressures, most gases have Z < 1. **Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.** In other words, the behaviour of the gas becomes more ideal when pressure is very low. Upto what pressure a gas will follow the ideal gas law, depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.** Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

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

$$Z = \frac{pV_{\text{real}}}{n\,\mathrm{R}T} \qquad (5.33)$$

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

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

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

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

Adapted from NCERT textbook of class XI 2006 edition reprinted edition pre rationalization

THE *s* -BLOCK ELEMENTS

The s-block elements of the Periodic Table are those in which the last electron enters the outermost s-orbital. Asthe s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table.Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature.The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because theiroxides and hydroxides are alkaline in nature and thesemetal oxides are found in the earth's crust.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances (Table 10.1). Francium is highly radioactive; its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectivelyin the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10^{-10} per cent of igneous rocks[†] (Table 10.2).

The general electronic configuration of s-block elementsis [noble gas] ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

Lithium and beryllium, the first elementsof Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group.In these anomalous properties they resemblethe second element of the following group. Thus, lithium shows similarities to magnesiumand beryllium to aluminium in many of their properties. This type of diagonal similarity iscommonly referred to as *diagonal relationship*in the periodic table. The diagonal relationshipis due to the similarity in ionic sizes and /orcharge/radius ratio of the elements. Monovalent sodium and potassium ions anddivalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balanceand nerve impulse conduction.

10.1 GROUP 1 ELEMENTS: ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic,physical and chemical properties of alkali metals are discussed below.

10.1.1 Electronic Configuration

All the alkali metals have one valence electron,ns^1 (Table 10.1) outside the noble gas core. The loosely held *s*-electron in the outermost valence shell of these elements makes them themost electropositive metals. They readily loseelectron to give monovalent M^+ ions. Hence theyare never found in free state in nature.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or [Xe] $6s^1$
Francium	Fr	[Rn]$7s^1$

10.1.2 Atomic and Ionic Radii

The alkali metal atoms have the largest sizes in a particular period of the periodic table. With increase in atomic number, the atom becomes larger. The monovalent ions (M^+) are smaller than the parent atom. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

10.1.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

Table 10.1 Atomic and Physical Properties of the Alkali Metals

Property	**Lithium Li**	**Sodium Na**	**Potassium K**	**Rubidium Rb**	**Caesium Cs**	**Francium Fr**
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius /pm	152	186	227	248	265	–
Ionic radius M^+/pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials E^0/ V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	$\sim 10^{-18}$ *

*ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle*

10.1.5 Physical Properties

All the alkali metals are silvery white, soft andlight metals. Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium. The meltingand boiling points of the alkali metals are lowindicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impartcharacteristic colour to an oxidizing flame. Thisis because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back tothe ground state, there is emission of radiationin the visible region as given below:

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

Alkali metals can therefore, be detected bythe respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy. These elements when irradiated with light, the light energy absorbedmay be sufficient to make an atom lose electron. This property makes caesium and potassium useful as electrodes in photoelectric cells.

10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) ***Reactivity towards air:*** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals formsuperoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

2

$4\,Li + O_2 \rightarrow 2\,Li_2O$ (oxide)

$2\,Na + O_2 \rightarrow Na_2O_2$ (peroxide)

$M + O_2 \rightarrow MO_2$ (superoxide)

(M = K, Rb, Cs)

Problem 10.1

What is the oxidation state of K in KO_2?

Solution

The superoxide species is represented as O_2^-; since the compound is neutral, therefore, the oxidation state of potassium is +1.

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of their high reactivity towards air and water, alkali metals are normally kept in kerosene oil.

(ii) ***Reactivity towards water:*** The alkali metals react with water to form hydroxide and dihydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2 \qquad (M = \text{an alkali metal})$$

It may be noted that although lithium has most negative E^o value (Table 10.1), its reaction with water is less vigorous than that of sodium which has the least negative E^o value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) ***Reactivity towards dihydrogen:*** The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

(iv) ***Reactivity towards halogens:*** The alkali metals readily react vigorously with halogens to form ionic halides, M^+X^-. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li^+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) ***Reducing nature:*** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (Table 10.1). The standard electrode potential (E^0) which measures the reducing power represents the overall change :

$M(s) \rightarrow M(g)$ sublimation enthalpy

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

$M^+(g) + H_2O \rightarrow M^+(aq)$ hydration enthalpy

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative E^0 value and its high reducing power.

Problem 10.2

The E^0 for Cl_2/Cl^- is +1.36, for I_2/I^- is + 0.53, for Ag^+/Ag is +0.79, Na^+/Na is –2.71 and for Li^+/Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength:

I^-, Ag, Cl^-, Li, Na

Solution

The order is Li > Na > I^- > Ag > Cl^-

(vi) Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M+(x + y)\,NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_3\,(1) \rightarrow MNH_{2(am)} + \tfrac{1}{2}H_2$$ (where 'am' denotes solution in ammonia.)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

10.1.7 Uses

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also usedto make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds wereearlier used as anti-knock additives to petrol,but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells

10.2 ANOMOLOUS BEHAVIOUR OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents.

10.2.1 Points of Difference between Lithium and other alkali metals

i. Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.
ii. Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.
iii. LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.
iv. Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.
v. Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
vi. Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.
vii. LiF a nd Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3 GROUP 2 ELEMENTS: ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differ rs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table 10.2.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^22s^2$
Magnesium	Mg	$1s^22s^22p^63s^2$
Calcium	Ca	$1s^22s^22p^63s^23p^64s^2$
Strontium	Sr	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$
Barium	Ba	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^2$ or [Xe]$6s^2$
Radium	Ra	[Rn]$7s^2$

10.3.1 Electronic Configuration

These elements have two electrons in the *s* -orbital of the valence shell (Table 10.2). Their general electronic configuration may be represented as [noble gas] ns^2. Like alkalimetals, the compounds of these elements arealso predominantly ionic

10.3.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, theatomic and ionic radii increase with increase in atomic number.

Table 10.2 Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	− 2494	− 1921	−1577	− 1443	− 1305	-
Metallic radius / pm	111	160	197	215	222	-
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential E^0 / V for (M^{2+}/ M)	−1.97	−2.36	−2.84	−2.89	− 2.92	−2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6}*

**ppm (part per million); ** percentage by weight*

10.3.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 10.2). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

10.3.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

10.3.5 Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic. Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry. The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

10.3.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) Reactivity towards air and water:

Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

(ii) Reactivity towards the halogens: All the alkaline earth metals combine with halogenat elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \left(X = F, Cl, Br, l\right)$$

(iii) Reactivity towards hydrogen: All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH2.

BeH2, however, can be prepared by the reaction of BeCl2 with LiAlH4.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

(iv) Reactivity towards acids: The alkaline earth metals readily react with acids liberating dihydrogen.

$$M + 2HCl \rightarrow MCl_2 + H_2$$

(iv) Reducing nature: Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 10.2). However, their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of theatomization enthalpy of the metal.

(v) Solutions in liquid ammonia: Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x+y)\,NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2\,[e(NH_3)_y]^-$$

From these solutions, the ammoniates, $[M(NH_3)_x]^{2+}$ can be recovered.

10.4 USES

Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes. Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called milk of magnesia) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes. Radium salts are used in radiotherapy, for example, in the treatment of cancer.

10.5 ANOMOLOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behavior as compared to magnesium and rest of the members.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus not well with other members of group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The Remaining members of the group can have a coordination number of six by making use of d-orbitals.

(iii) The oxide and hydroxide of beryllium, unlike the hydroxides other elements in the group, are amphoteric in nature.

Adapted from NCERT textbook of class XII 2006 edition reprinted edition pre rationalization

THE *p*-BLOCK ELEMENTS

In *p*-block elements the last electron enters the outermost *p* orbital. As we know that the number of *p* orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of *p* orbitals is six. Consequently, there are six groups of *p*–block elements in the periodic table numbering from 13 to 18. Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell **electronic configuration is** ns^2np^{1-6} (except for He). The **inner core** of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of *p*-block is observed. The *maximum oxidation state* shown by a *p*-block element is equal to the total number of valence electrons (*i.e.,* the sum of the *s*- and *p*-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called *group oxidation state*, *p*-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by *p*-block elements are shown in Table 11.1. In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group. The occurrence of oxidation states two unit less than the group oxidation states is sometime attributed to the '**inert pair effect**'.

Table 11.1 General Electronic Configuration and Oxidation States of *p*-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8

Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, −2	+5, + 3, +1, −1	+6, +4, +2

The relative stabilities of these two oxidation states – group oxidation state and two units less than the group oxidation state – may vary from group to group and will be discussed at appropriate places.

It is interesting to note that the *non-metals* and *metalloids* exist only in the *p*-block of the periodic table. The non-metallic character of elements decreases down the group. In fact, the heaviest element in each *p*-block group is the most metallic in nature. This change from non- metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size. Thus, the lightest *p*-block elements show the same kind of differences as the lightest *s*-block elements, lithium and beryllium. The second important difference, which applies only to the *p*-block elements, arises from the effect of *d*- orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements. The second period elements of *p*-groups starting from boron are restricted to a maximum covalence of four (using 2*s* and three 2*p* orbitals). In contrast, the third period elements of *p*-groups with the electronic configuration $3s^2 3p^n$ have the vacant 3*d* orbitals lying between the 3*p* and the 4*s* levels of energy. Using these *d*-orbitals the third period elements can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion. The presence of these *d*-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of *d* orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form *p*π - *p*π multiple bonds to itself (e.g., C=C, C≡C N≡N) and to other second row elements (e.g., C=O, C=N, C≡N, N=O). This type of π - bonding is not particularly strong for the heavier *p*-block elements. The heavier elements do form π bonds but this involves *d* orbitals (*d*π − *p*π or *d*π −*d*π). As the *d* orbitals are of higher energy than the *p* orbitals, they contribute less to the overall stability of molecules than does pπ - pπ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions : NO_3^- (three-coordination with π – bond involving one nitrogen *p*-orbital) and PO_4^{3-} (four-coordination involving *s*, *p* and *d* orbitals contributing to the π – bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

GROUP 13 ELEMENTS: THE BORON FAMILY

This group element shows a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium, thallium and nihonium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax,

$Na_2B_4O_7\cdot10H_2O$, and kernite, $Na_2B_4O_7\cdot4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, Al_2O_3. $2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature. Nihonium has symbol Nh, atomic number 113, atomic mass 286 g mol^{-1} and electronic configuration [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^2$. So far it has been prepared isotope is 20 seconds. Due to these reasons its chemistry has not been established.

Nihonium is a synthetically prepared radioactive element. Here atomic, physical and chemical properties of elements of this group leaving nihonium are discussed below.

Electronic Configuration

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*- electrons plus 10 *d*-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increased in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between in and Tl are due to inability of *d*- and *f*-electrons, which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$. The sum of the

in small amount and half-life of its most stable first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties

Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally (Table 11.2). This is because of the discrepancies in atomic size of the elements.

Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

Chemical Properties

Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening *d* and *f* orbitals, the increased effective nuclear charge holds *ns* electrons tightly (responsible for *inert pair effect*) and thereby, restricting their participation in bonding. As a result of this, only *p*-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al<Ga<In<Tl. In thallium +1 oxidation state is predominant

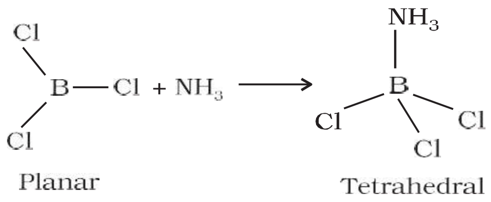
Table 11.2 Atomic and Physical Properties of Group 13 Elements

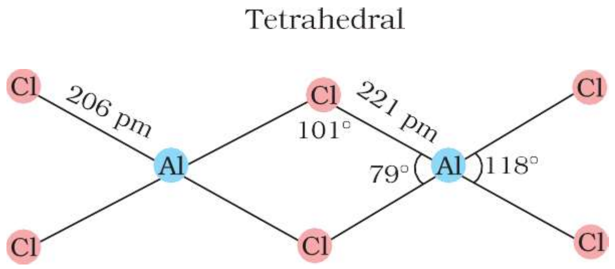
Property	Element				
	Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl
Atomic number	5	13	31	49	81
Atomic mass(g mol^{-1})	10.81	26.98	69.72	114.82	204.38
Electronic Configuration	[He]$2s^2 2p^1$	[Ne]$3s^2 3p^1$	[Ar]$3d^{10} 4s^2 4p^1$	[Kr]$4d^{10} 5s^2 5p^1$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius/pm[a]	(88)	143	135	167	170
Ionic radius M^{3+}/pm[b]	(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm	-	-	120	140	150
Ionization enthalpy (kJ mol^{-1}) $\Delta_i H_1$ $\Delta_i H_2$ $\Delta_i H_3$	801 2427 3659	577 1816 2744	579 1979 2962	558 1820 2704	589 1971 2877
Electronegativity[c]	2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K	2.35	2.70	5.90	7.31	11.85
Melting point / K	2453	933	303	430	576
Boiling point / K	3923	2740	2676	2353	1730
E^V/ V for (M^{3+}/M)	-	–1.66	–0.56	–0.34	+1.26
E^V / V for (M^+/M)	-	+0.55	-0.79(acid) –1.39(alkali)	–0.18	–0.34

[a]Metallic radius, [b] 6-coordination, [c] Pauling scale,

whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$





$AlCl_3$ achieves stability by forming a dimer

In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $[M(OH)_4]^-$ species; the hybridisation state of element M is *sp*^{3}. Aluminium chloride in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion.

Problem 11.1

Standard electrode potential values, E° for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution

Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make $Al^{3+}(aq)$ ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^{+} is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s) \qquad (E = \text{element})$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$

Sodium tetrahydroxoaluminate(III)

(iii) Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI_3).

$2E(s) + 3X_2(g) \rightarrow 2EX_3(s)$ (X = F, Cl, Br, I)

Problem 11.2

White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Solution

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

Problem 11.3

Boron is unable to form BF_6^{3-} ion. Explain.

Solution

Due to non-availability of *d* orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$F_3B + :NH_3 \rightarrow F_3B \leftarrow NH_3$

It is due to the absence of *d* orbitals that the maximum covalence of B is 4. Since the *d* orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (*e.g.,* $AlCl_3$) are dimerised through halogen bridging (*e.g.,* Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

GROUP 14 ELEMTS: THE CABON FAMILY

Carbon, silicon, germanium, tin led and flerovium are the member of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond: however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and Sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7% by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Flerovium is synthetically prepared radioactive element.

Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Symbol of Flerovium is Fl. It has atomic number 114, atomic mass 289 g mol^{-1} and electronic configuration [Rn] $5f^{14}6d^{10}7s^2\,7p^2$. It has been prepared only in small amount. Its half life is short and its chemistry has not been established yet. The important atomic and physical properties along with their electronic configuration of the elements of group 14 leaving flerovium are given in Table 11.3. Some of the atomic, physical and chemical properties are discussed below:

Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members.

Table 11.3 Atomic and Physical Properties of Group 14 Elements

Property		Element				
		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic Number		6	14	32	50	82
Atomic mass (g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		[He]$2s^2 2p^2$	[Ne]$3s^2 3p^2$	[Ar]$3d^{10} 4s^2 4p^2$	[Kr]$4d^{10} 5s^2\,5p^2$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionization enthalpy/ kJ mol^{-1}	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d]/g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ohm cm (293 K)		10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

[a]for M^{IV} oxidation state; [b]6–coordination; [c]Pauling scale; [d]293 K; [e]for diamond; for graphite, density is 2.22; [f]β-form (stable at room temperature)

Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general, the ionisation enthalpy decreases down the group.Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Physical Properties

All members of group14 are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

Chemical Properties

Oxidation states and trends *in chemical reactivity*

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge<Sn<Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent). Lead compounds in +2 state are stable and in +4 state are strong oxidising agents. In tetravalent state the number of electrons around the central atom in a molecule (*e.g.*, carbon in CCl_4) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them.

Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridization of central atom is sp^3d^2.

(i) *Reactivity towards oxygen*

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of the formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Problem 11.5

Select the member(s) of group 14 that(i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Solution

(i) carbon (ii) lead (iii) silicon and germanium

(ii) Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

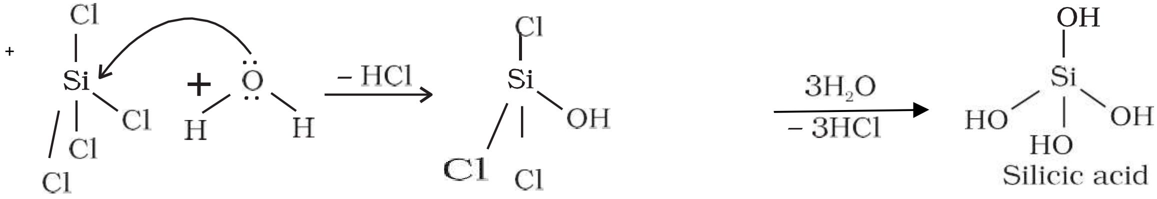
Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group.

Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2 , whereas PbX_2 is more than PbX_4 . Except CCl_4 , other tetrachlorides are easily hydrolysed by water because the central atom can accommodatethe lone pair of electrons from oxygen atom of water molecule in d orbital.

Hydrolysis can be understood by taking the example of $SiCl_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown below :



IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d* orbitals.

In carbon, only *s* and *p* orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of *d* orbitals. Carbon also has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, $C\equiv C$, C = O, C = S, and $C\equiv N$. Heavier elements do not form $p\pi - p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is $C >> Si > Ge \approx Sn$. Lead does not show catenation.

Due to property of catenation and $p\pi - p\pi$ bond formation, carbon is able to show allotropic forms.

Bond	Bond enthalpy / kJ mol $^{-1}$
C—C	348
Si —Si	297
Ge—Ge	260
Sn—Sn	240

Adapted from NCERT textbook of class XII 2006 edition reprinted edition pre rationalization

Group 15 Elements

Group 15 includes nitrogen, phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.

Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins in plants and animals. Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. CaX_2 (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6$. CaF_2) which are the main components of phosphate rocks. Phosphorus is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals.

The important atomic and physical properties of this group elements along with their electronic configurations are given in Table 7.1.

Table 7.1: Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass/g mol^{-1}		14.01	30.97	74.92	121.75	208.98
Electronic configuration		[He]$2s^22p^3$	[Ne]$3s^23p^3$	[Ar]$3d^{10}4s^24p^3$	[Kr]$4d^{10}5s^25p^3$	[Xe]$4f^{14}5d^{10}6s^26p^3$
Ionisation enthalpy	I	1402	1012	947	834	703
($\Delta_i H$/(kJ mol^{-1})	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm^a		70	110	121	141	148
Ionic radius/pm		171^b	212^b	222^b	76^c	103^c
Melting point/K		63*	317^d	1089^e	904	544
Boiling point/K		77.2*	554^d	888^f	1860	1837
Density/[g cm^{-3}(298 K)]		0.879^g	1.823	5.778^h	6.697	9.808

^{a} E^{III} single bond (E = element); ^{b} E^{3-}; ^{c} E^{3+}; ^{d} White phosphorus; ^{e} Grey α-form at 38.6 atm; ^{f} Sublimation temperature;
^{g} At 63 K; ^{h}Grey α-form; $_2$ Molecular N .*

Trends of some of the atomic, physical and chemical properties of the group are discussed below.

Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^3. The *s* orbital in these elements is completely filled and *p* orbitals are half-filled, making their electronic configuration extra stable.

Atomic and Ionic Radii

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

Ionisation Enthalpy

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p* orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$ (Table 7.1).

Electronegativity

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Physical Properties

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

Chemical Properties

Oxidation states and trends in chemical reactivity

The common oxidation states of these elements are –3, +3 and +5. The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. In fact, last member of the group, bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterized Bi (V) compound is BiF_5. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding. The heavier elements have vacant *d* orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^-.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d* orbitals. Nitrogen has unique ability to form **$p\pi$ -$p\pi$ multiple** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form $p\pi$ -$p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one *s* and two *p*) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state. However, the single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result, the catenation tendency is weaker in nitrogen.

Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form **$d\pi - p\pi$ bond** as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphorus and arsenic can form **$d\pi - d\pi$ bond** also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) *Reactivity towards hydrogen*: All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table7.2. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

Table 7.2: Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H$ /kJ mol^{-1}	–46.1	13.4	66.4	145.1	278
$\Delta_{diss}H$ (E–H)/kJ mol^{-1}	389	322	297	255	–

(ii) *Reactivity towards oxygen*: All these elements form two types of oxides: E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(iii) *Reactivity towards halogens*: These elements react to form two series of halides: EX_3 and EX_5. Nitrogen does not form pentahalide due to non-availability of the *d* orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) *Reactivity towards metals*: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Example 7.1

Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Solution

Nitrogen with n = 2, has *s* and *p* orbitals only. It does not have *d* orbitals to expand its covalence beyond four. That is why it does not form pentahalide.

Example 7.2

PH_3 has lower boiling point than NH_3. Why?

Solution

Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

Intext Questions

7.1 Why are pentahalides more covalent than trihalides ?

7.2 Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?

Group 16 Elements

Oxygen, Sulphur, selenium, tellurium and polonium constitute Group 16 of the periodic table. This is sometimes known as group of chalcogens. The name is derived from the Greek word for brass and points to the association of Sulphur and its congeners with copper.
Most copper minerals contain either oxygen or Sulphur and frequently the other members of group.

Occurrence

Oxygen is the most abundant of the elements on earth. Oxygen forms about 46.6%by mass earth's crust. Dry air contains 20.946% oxygen by volume. However, the abundance of Sulphur in the earth's crust I only 0.03-0.1%. Combined Sulphur exists primarily as sulphates such as gypsum $CaSO_4.2H_2O$, Epsom salt $MgSO_4.7H_2O$, barite $BaSO_4$ and sulphides such as galena PbS, zinc blende ZnS, copper pyrites $CuFeS_2$. Traces of Sulphur occur as hydrogen sulphide in volcanoes, Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain Sulphur Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals. The important atomic and physical properties of Group16 along with electronic configuration are given in Table 7.3. Some of the atomic, physical and chemical properties and their trends are discussed below.

Electronic Configuration

The elements of Group16 have six electrons in the outermost shell and have ns^2np^4 general electronic configuration.

Atomic and Ionic Radii

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.

Ionisation Enthalpy

Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group15 in the corresponding periods. This is due to the fact that Group 15 elements have extra stable half-filled *p* orbitals electronic configurations.

Electron Gain Enthalpy

Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.

Electronegativity

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Example 7.3

Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

Solution

Due to extra stable half-filled *p* orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

Physical Properties

Some of the physical properties of Group 16 elements are given in Table 7.3 Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8).

Chemical Properties

Oxidation states and trends in chemical reactivity

The elements of Group 16 exhibit a number of oxidation states (Table 7.3). The stability of -2 oxidation state decreases down the group. Polonium hardly shows –2 oxidation state. Since electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except in the case of OF_2 where its oxidation state is + 2.

Table 7.3: Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol^{-1}	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10} 4s^2 4p^4$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius/(pm)[a]	66	104	117	137	146
Ionic radius, E^{2-}/pm	140	184	198	221	230[b]
Electron gain enthalpy, $\Delta_{eg}H$/ kJ mol^{-1}	–141	–200	–195	–190	–174
Ionisation enthalpy ($\Delta_i H_1$) /kJ mol^{-1}	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Density /g cm^{-3} (298 K)	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	55	393[f]	490	725	520
Boiling point/K	90	718	958	1260	1235
Oxidation states*	–2,–1,1,2	–2,2,4,6	–2,2,4,6	–2,2,4,6	2,4

Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in +4 and +6 oxidation states is primarily covalent.

Anomalous behaviour of oxygen

The anomalous behaviour of oxygen, like other members of *p*-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.

The absence of *d* orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalence exceeds four.

(i) *Reactivity with hydrogen*: All the elements of Group 16 form hydrides of the type H_2E (E = O, S, Se, Te, Po). Some properties of hydrides are given in Table 7.4. Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H–E bond down the group. Owing to the decrease in enthalpy for the dissociation of H–E bond down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

(ii) *Reactivity with oxygen*: All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) *Reactivity towards the halogens*: Elements of Group 16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as *see-saw* geometry.

All elements except oxygen form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus, have tetrahedral structure. The well-known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

Table 7.4: Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p/K	273	188	208	222
b.p/K	373	213	232	269
H–E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H/\text{kJ mol}^{-1}$	–286	–20	73	100
$\Delta_{diss} H\ (H\text{–}E)/\text{kJ mol}^{-1}$	463	347	276	238
Dissociation Constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

[a] *Aqueous solution, 298 K*

Example 7.4

H_2S is less acidic than H_2Te. Why?

Solution

Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Intext Questions

7.3 List the important sources of sulphur.

7.4 Write the order of thermal stability of the hydrides of Group 16 elements.

7.5 Why is H_2O a liquid and H_2S a gas ?

Group 17 Elements

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the **halogens** (Greek *halo* means salt and *genes* means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. That much similarity is not found in the elements of other groups of the periodic table. Also, there is a regular gradation in their physical and chemical properties. Astatine is a radioactive element.

Occurrence

Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite $3Ca_3(PO_4)_2.CaF_2$ and small quantities are present in soil, river water plants and bones and teeth of animals. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass). The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $KCl.MgCl_2.6H_2O$. Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

The important atomic and physical properties of Group 17 elements along with their electronic configurations are given in Table 7.5.

Table 7.5: Atomic and Physical Properties of Halogens

Property	F	Cl	Br	I	At[a]
Atomic number	9	17	35	53	85
Atomic mass/g mol^{-1}	19.00	35.45	79.90	126.90	210
Electronic configuration	[He]$2s^2 2p^5$	[Ne]$3s^2 3p^5$	[Ar]$3d^{10}4s^2 4p^5$	[Kr]$4d^{10}5s^2 5p^5$	[Xe]$4f^{14}5d^{10}6s^2 6p^5$
Covalent radius/pm	64	99	114	133	–
Ionic radius X^-/pm	133	184	196	220	–
Ionisation enthalpy/kJ mol^{-1}	1680	1256	1142	1008	–
Electron gain enthalpy/kJ mol^{-1}	–333	–349	–325	–296	–
Electronegativity[b]	4	3.2	3.0	2.7	2.2
$\Delta_{Hyd} H(X^-)$/kJ mol^{-1}	515	381	347	305	–
	F_2	Cl_2	Br_2	I_2	–
Melting point/K	54.4	172.0	265.8	386.6	–
Boiling point/K	84.9	239.0	332.5	458.2	–
Density/g cm^{-3}	1.5 (85)[c]	1.66 (203)[c]	3.19(273)[c]	4.94(293)[d]	–
Distance X – X/pm	143	199	228	266	–
Bond dissociation enthalpy /(kJ mol^{-1})	158.8	242.6	192.8	151.1	–
E^{V}/V[e]	2.87	1.36	1.09	0.54	–

[a] Radioactive; [b] Pauling scale; [c] For the liquid at temperatures (K) given in the parentheses; [d] solid; [e] The half-cell reaction is $X_2(g) + 2e^- \rightarrow 2X^-(aq)$.

The trends of some of the atomic, physical and chemical properties are discussed below.

Electronic Configuration

All these elements have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. The atomic radius of fluorine like the other elements of second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

Ionisation Enthalpy

They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.

Electron Gain Enthalpy

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2*p* orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity

They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

Example 7.5

Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Solution

Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

Physical Properties

Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2 , greenish yellow, Br_2, red and I_2, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

One curious anomaly we notice from Table 7.5 is the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 whereas X-X bond dissociation enthalpies from chlorine onwards show the expected trend: Cl – Cl > Br – Br > I – I. A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

Example 7.6 Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Solution It is due to

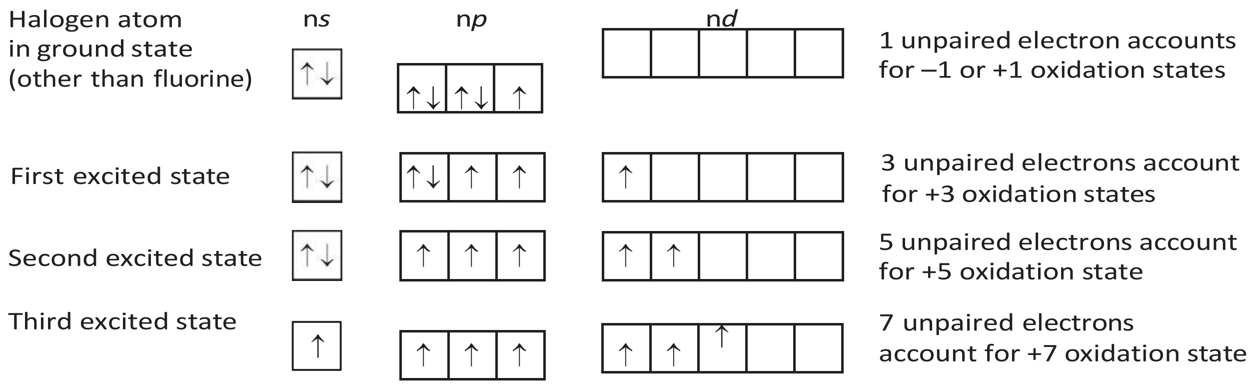
(i) low enthalpy of dissociation of F-F bond (Table 7.8).

(ii) high hydration enthalpy of F^- (Table 7.8).

Chemical Properties

Oxidation states and trends in chemical reactivity

All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:



The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids. The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no *d* orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \ (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \ (X = Br \text{ or } I)$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials (Table 7.5) which are dependent on the parameters indicated below:

$$1/2\ X_2\,(g) \xrightarrow{1/2\ \Delta_{diss}H^{V}} X\,(g) \xrightarrow{\Delta_{eg}H^{V}} X \xrightarrow{\Delta_{hyd}H^{V}} X^{-}\,(aq)$$

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is non-spontaneous. In fact, I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2\,(g) + 2H_2O(l) \rightarrow 4H^+\,(aq) + 4F^-\,(aq) + O_2\,(g)$$

$$X_2\,(g) + H_2O(l) \rightarrow HX\,(aq) + HOX\,(aq)$$

(where X = Cl or Br)

$$4I^-\,(aq) + 4H^+\,(aq) + O_2\,(g) \rightarrow 2I_2\,(s) + 2H_2O(l)$$

Anomalous behaviour of fluorine

Like other elements of *p*-block present in second period of the periodic table, fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected. The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non-availability of *d* orbitals in valence shell.

Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) *Reactivity towards hydrogen*: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are given in Table 7.6. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H–X) dissociation enthalpy in the order: H–F > H–Cl > H–Br > H–I.

Table 7.6: Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H – X)/pm	91.7	127.4	141.4	160.9
$\Delta_{diss}H^{V}$/kJ mol^{-1}	574	432	363	295
pK_a	3.2	–7.0	–9.5	–10.0

(ii) *Reactivity towards oxygen*: Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors leads to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.The iodine oxides, I_2O_4 , I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) *Reactivity towards metals*: Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

$$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$$

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is a monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

(iv) *Reactivity of halogens towards other halogens*: Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX' , XX'_3, XX'_5 and XX'_7 where X is a larger size halogen and X' is smaller size halogen.

Example 7.7 Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.

Solution Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d* orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

Intext Questions

7.6 Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.

7.7 Give two examples to show the anomalous behaviour of fluorine.

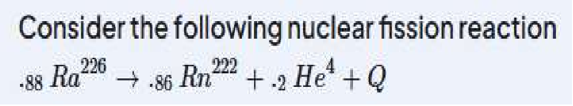
7.8 Sea is the greatest source of some halogens. Comment.

7.3 Group 18 Elements

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

Occurrence

All the noble gases except radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra.



Consider the following nuclear fission reaction

$${}_{\cdot 88}Ra^{226} \rightarrow {}_{\cdot 86}Rn^{222} + {}_{\cdot 2}He^{4} + Q$$

Example 7.8 Why are the elements of Group 18 known as noble gases?

Solution The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

The important atomic and physical properties of the Group 18 elements along with their electronic configurations are given in Table 7.7. The trends in some of the atomic, physical and chemical properties of the group are discussed her.

Table 7.7:Atomic and Physical Properties of Group 18 Elements

* *radioactive*

Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]\ 3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionisation enthalpy /$kJmol^{-1}$	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /$kJmol^{-1}$	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

Electronic Configuration

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$ (Table 7.7). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Ionisation Enthalpy

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.

Atomic Radii

Atomic radii increase down the group with increase in atomic number.

Electron Gain Enthalpy

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Physical Properties

All the noble gases are monoatomic. They are colourless, odourless and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Helium has the lowest boiling point (4.2 K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Noble gases have very low boiling points. Why?

Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

Chemical Properties

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6electronic configuration in their valence shell.

(ii)They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally, ever since their discovery, but all attempts to force them to react to form the compounds, were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound whichis formulated as $O\ ^{+}PtF\ ^{-}$. He, then realised that the first ionization enthalpy of molecular oxygen (1175 $kJmol^{-1}$) was almost identical with that of xenon (1170 $kJmol^{-1}$). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^{+}PtF_6^{-}$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesized.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.