5   HF has the highest bond dissociation enthalpy amongst all the halogen acids. The hydration enthalpy of the fluoride ion is also highest. However, the former outweighs making HF the weakest of the halogen acids.

6   $HOCl < HOClO < HOClO_2 < HOClO_3$

7   (i)   T   (ii)   F   (iii)   T

    (iv)   F   (v)   F

Terminal Questions

1   i)   Fluorine   ii)   Fluorine   iii) I^-

    iv)   Chlorine   v) Br^- and I^-

2   i)   Atomic number should be 85.

    ii) At_2.

    iii)   Melting and boiling point should be higher than those of iodine.

    iv)   Solid.

    v)   At–At bond energy should be less than that of I–I bond.

    vi)   Strength of aqueous hydroastatic acid should be highest according to known trend HF < HCl < HBr < HI.

3   The highest oxidising power, high lattice energy of fluorides and high enthalpy of hydration of fluoride ion, lower F–F bond dissociation energy and a high fluorine element covalent bond energy are the factors contributing to this unique ability of fluorine to combine with other elements in their higher oxidation states. Chlorine, however, is a close second in this respect.

4   i)   Hypochlorous acid :   +1

    ii)   Chlorous acid :   +3

    iii)   Hypobromous acid :   +1

    iv)   Bromic acid :   +5

    v)   Periodic acid :   +7

    vi)   Perchloric acid :   +7

5   Fluorine has the smallest size of all the halogens. In the F–F bond, there is considerable repulsion in the nonbonding electrons which weakens the F–F bond. Therefore, the bond dissociation energy of F_2 is less than that of the Cl_2.

6   The salts of hypohalous acids undergo hydrolysis in water as shown below :

$$NaOX + H_2O \rightleftharpoons Na^+ + OH^- + HOX$$
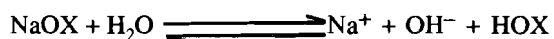
The hypohalous acids are fairly weak acids and remain largely undissociated in solution. As the solution contains OH^-, it becomes alkaline in nature.

UNIT 11 ELEMENTS OF GROUP 18

Structure

11.1 INTRODUCTION

In the preceding unit, you have learnt about the chemistry of a group of highly reactive elements, viz., the halogens. This unit deals with the chemistry of a group of elements which were considered to be rather inert till recently. These elements are helium, neon, argon, krypton, xenon and radon. These elements constitute Group 18 of the modern periodic table. If you compare Mendeleev's periodic table of 1871 with the modern periodic table, you will see that it is remarkably similar in its coverage to the modern periodic table, with the exception that the Group 18 is missing. Elements of Group 18 were not known at that time and have been discovered only about a hundred years back. Since these elements have very low reactivity, they were called inert. However, the term inert is no longer applicable to the group as a whole, as the heavier elements of this group form compounds and, thus, are not inert. These elements have also been called the rare gases, but as argon forms nearly 1% of the atomsphere, and the gases can be readily isolated by the fractional distillation of liquid air at low temperatures, this name is also not very appropriate. They are now called the noble gases by analogy with the noble metals, like gold and platinum which are not very reactive. The unique chemical inertness of the noble gases is well reflected in the history of their discovery which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative elements, fluorine and oxygen. In this unit you will study the discovery, isolation, uses, general characteristics and the compounds of noble gases.

Objectives

After studying this unit, you should be able to :

● describe the discovery of noble gases,

● discuss their electronic configuration and position in the periodic table,

● enumerate the properties of the noble gases and their uses, and

● describe the important compounds of the noble gases, particularly xenon, especially the bonding in these compounds.

11.2 DISCOVERY OF NOBLE GASES

The story of the discovery and investigation of the noble gases is one of the most brilliant and interesting chapters in the history of science. Their discovery can be traced back to 1785, when Henry Cavendish investigated the composition of air. He mixed excess oxygen with air and then passed electric sparks through the mixture. The oxides of nitrogen, thus formed, were removed by dissolving in alkali solution and the excess of oxygen was removed with potassium sulphite. The residual gas, which was always left behind, was neither nitrogen nor oxygen. It did not form more than 1/120th part of the original volume of air. Time was not

yet ripe for the discovery of noble gases. What Cavendish had actually isolated was, of course, a mixture of the noble gases, but he could not characterise them. It would be interesting for you to know that his figures about the volume of residual gas are remarkably close to the proportion of the noble gases in the atmosphere as we now know it. It was almost a century after the investigation of the composition of air by Cavendish that advances in spectroscopy, periodic classification and the study of radioactive elements made possible the discovery of all six noble gases.

Of all the noble gases, first came the **discovery of helium**, which is unique in being the first element to be discovered extra-terrestrially before being found on the earth. In 1868 the French astronomer Pierre Janssen came to India to study the total eclipse of the sun. Using a spectroscope he observed a new yellow line close to the sodium D lines in the spectrum of the sun's chromosphere. This led two Englishmen, chemist E. Frankland and astronomer Sir J. Norman Lockyer to suggest the existence of a new element, which, appropriately, they named helium, from the Greek word helios meaning the sun. The terrestrial existence of helium was established by Sir William Ramsay in 1895. He showed that a gas present in trace amounts in the uranium mineral, cleveite, has a spectrum identical with that of helium. Five years later, he and Travers isolated helium from air. Cady and McFarland discovered helium in natural gas in 1905 when they were asked to analyse a sample of natural gas that would not burn.

Most developments in noble gas chemistry date from Lord Rayleigh's observations in 1894. In order to test Prout's hypothesis, that the atomic weights of all elements are multiples of that of hydrogen, Rayleigh made accurate measurements of the densities of common gases and found, to his surprise that the density of nitrogen obtained from air by the removal of O_2, CO_2 and H_2O was consistently about 0.5% higher than that of nitrogen obtained chemically from ammonia. He observed that a litre of nitrogen obtained from air weighed 1.2572 grams while a litre of nitrogen obtained from ammonia weighed only 1.2506 grams under the same conditions. This small difference of 0.0066 gram in a gram and a quarter made Rayleigh to suspect an undiscovered element in the atmosphere. This reflects not only the extraordinary experimental skill of Lord Rayleigh but also his scientific and objective method of thinking and working which led to the discovery of á whole new group of elements.

Ramsay treated atmospheric nitrogen repeatedly with heated magnesium and found that a small amount of a much denser gas was left behind which would not combine with any other element. Lord Rayleigh and Sir W. Ramsay found that the residual gas showed spectral lines which were not observed earlier in the spectrum of any other element. In 1894, they announced the isolation of the noble gas which they named **argon**, from the Greek word argos meaning idle or lazy, because of its inert nature. They also realised that argon could not be put with any of the other elements in the groups already identified in the periodic table.

In 1898, Sir William Ramsay and his assistant Morris W. Travers isolated **neon** (from the Greek word meaning new) by the fractional distillation of impure liquid oxygen. Shortly thereafter, they showed that the less volatile fractions of liquid air contain two other new elements, **krypton** (from the Greek word meaning hidden) and **xenon** (from the Greek word meaning stranger).

Element 86, the last member of the group is a short lived radioactive element. It was isolated and studied in 1902 by Rutherford and Soddy and has been named as **radon** as it is formed by radioactive decay of radium.

11.2.1 Position of Noble Gases in the Periodic Table

Due to their almost inert chemical nature, the noble gases occupy a peculiar position in chemistry. Mendeleev had not left any vacant spaces for the noble gases in his periodic table although he had left such spaces for several other elements which were not known at that time. The reason was that he could not imagine the existence of a whole group of elements devoid of all chemical reactivity under ordinary conditions. Therefore, the discovery of the noble gases at the outset seemed to upset Mendeleev's scheme of classification of elements.

After studying the chemical nature of the noble gases, Ramsay introduced a new group in Mendeleev's periodic table to accommodate these elements. He placed this group after the halogens and before the alkali metals in the periodic table. As you have studied in Unit 1, in the long form of the periodic table, the noble gases occupy the last column of the table. The inclusion of the noble gases has actually improved the periodic table because it provides a

bridge between the strongly electronegative halogens and the strongly electropositive alkali metals.

As you have studied in Unit 7 of the course, initially the group consisting of noble gases used to be termed as the Group zero or the Group VIII A. But according to the latest IUPAC convention, number 18 has been assigned to this group. However, the position of the group in the periodic table remains unchanged, that is, after the halogens at the end of each period.

In the next section, you will study the occurrence, isolation and uses of noble gases. Before that you may like to try the following SAQ.

SAQ 1

a) What were the reasons for late discovery of noble gases?

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b) What made Lord Rayleigh suspect that there may be an additional element in air?

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11.3 OCCURRENCE, ISOLATION AND USES OF NOBLE GASES

The noble gases constitute about 1.18% by volume of the dry air at sea level. Of all the noble gases, argon is the most abundant constituting 0.93% by volume of the dry air. As shown in Table 11.1, He, Ne Ar and Rn are also found occluded, though in very minute quantities, in igneous rocks. Certain natural spring waters contain small amounts of dissolved He, Ne and Ar. Large reserves of helium have been recently discovered in hot water springs of Bakreswar and Tantloi in West Bengal. The gas coming out of these springs contains about 1.8% of helium. Natural gas in certain parts of the world, particularly in U.S.A., contains as high as 7% of helium.

Composition of dry air		
Gas	% by volume	B.P.(K)
N_2	78.03	77.2
O_2	20.99	90.1
Ar	0.93	87.2
CO_2	0.033	194.7
Ne	0.0018	27.2
H_2	0.0010	20.2
He	0.0005	4.2
Kr	0.0001	119.6
Xe	0.000008	165.1

The principal source of Ne, Ar, Kr and Xe is air. Due to the difference in their boiling points (Table 11.1), these gases are separated by fractional distillation of liquid air. Although the concentration of helium in the air is five times that of Kr and sixty times that of Xe, recovery of He from this source is uneconomical. The main source of helium is natural gas, which consists predominantly of hydrocarbons and nitrogen. These are liquefied by cooling under pressure. The residual helium is purified by passing it over activated charcoal cooled with liquid air. The charcoal absorbs traces of heavier noble gases, leaving pure helium. Radon is obtained by allowing radium or any of its salts to decay for some weeks in a sealed vessel.

Superconductivity is a phenomenon in which the material offers no resistance to the flow of electricity. It would, therefore, allow transmission of electrical energy with practically no loss.

Helium, being very light and non-inflammable is used to lift weather balloons and to inflate the tyres of large aircrafts, thereby increasing their payload. A mixture of 80% He and 20% O_2 is used in place of air for breathing by deep-sea divers. Because He is much less soluble in blood than N_2, it does not cause sickness by bubbling out when the pressure is released as the diver comes to the surface. Boiling point of helium is the lowest of any known substance. Hence, it is extensively used in cryoscopy as a cryogen. You must have heard of **superconductivity** which is expected to bring revolutionary changes in our life. So far, helium provides the only practical means of studying and utilising such low temperature phenomena as superconductivity, though intensive research is going on and claims have been made of achieving superconductivity in some materials at 125 K. Again, heat generated in the high temperature reactor (HTR) must be extracted by means of a suitable coolant. Helium serves as an excellent coolant in these reactors. It is also used as a flow gas in gas liquid chromatography and in microanalysis.

Helium and argon are used to provide an inert atmosphere in some chemical reactions, in welding operations of Mg, Al, Ti and stainless steel and in zone-refining of silicon and germanium. Argon is extensively used in place of nitrogen in incandescent electric bulbs and radio tubes to prevent the oxidation and evaporation of the metal filament. Neon, argon, krypton and xenon are used in discharge tubes—the so called neon lights for advertising, the colour produced depending upon the particular mixture of gases used. Radon finds a limited use in cancer treatment.

11.4 GENERAL CHARACTERISTICS

All the noble gas elements are colourless, odourless and tasteless monoatomic gases. Indeed, they are the only elements that exist as uncombined gaseous atoms at room temperature and one atmosphere pressure. Each atom, behaves as if it is effectively isolated. Some properties of noble gases are summarised in Table 11.1

Table 11.1 : Some properties of the noble gases

Property	Helium He	Neon Ne	Argon Ar	Krypton Kr	Xenon Xe	Radon Rn
Atomic number	2	10	18	36	54	86
Electronic configuration	$1s^2$	$[He]2s^2 2p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic weight	4.0026	20.183	39.948	83.80	131.30	(222)
van der Waals radius (pm)	-	131	174	189	210	215
Boiling point (K)	4.2	27.2	87.2	119.6	165.1	211
Melting point (K)	1 at 26 atm	24	84	116	161	202
Density of liquid at b.p. $(10^3 \times kg\,m^{-3})$	0.126	1.20	1.40	2.6	3.06	4.4
Ionisation energy (kJ mol^{-1})	2372	2081	1520	1350	1170	1037
Electron affinity (kJ mol^{-1})	54	99	-			
Abundance in dry air (ppm by volume)	5.2	18.2	93.40	1.14	0.087	0
Abundance in igneous rocks (ppm by weight)	3×10^{-3}	7×10^{-5}	4×10^{-2}			1.7×10^{-10}

You can see from the Table that all the noble gases have eight electrons in their valence shell except helium which has only two electrons. Till 1962, the noble gases were considered to be inert as their compounds were not known. Lewis and Kossel in formulating their **electronic theory of Valence** in 1916 stipulated that a grouping of eight electrons or an **octet** in the valence shell represents a very stable configuration. Hence, they proposed the octet rule. According to this, the reactions of elements can be explained in terms of their tendency to achieve stable electronic configuration of the nearest noble gas, ns^2np^6, by gaining, losing or sharing of electrons.

As all the noble gases have the stable $1s^2$ or ns^2np^6 configuration, they have the highest ionisation energies compared to other elements in their periods. This reflects their reluctance for chemical reactivity. Analogously, the electron affinity of these elements is either zero or has a small positive value. Therefore, they are unable to accept electrons to form anions. As we go down the group, the ionisation energy of the noble gases decreases. Thus, there is an increase in chemical reactivity of the noble gases as we go down the group from helium to radon.

Since, there are no usual electron pair interactions between the noble gas atoms, the only interactions are weak van der Waals forces. Therefore, they have very low melting and boiling points in comparison with those of other elements of comparable atomic or molecular weights. In fact, melting and boiling points of helium are the lowest of any known substance. The van der Waals attraction between the molecules/atoms increases with the increase in the number of electrons per molecule or atom. Heavy molecules containing more electrons attract one another more strongly than the lighter molecules. Thus, the van

der Waals forces between the noble gas atoms increase as we move down the group from helium to xenon. Consequently, melting and boiling points increase with the increase in atomic number.

Helium has two isotopes, ^3He and ^4He. The latter constitutes almost 100% of atmospheric helium. While ^3He behaves normally, ^4He has strange properties. When cooled below 2.2 K at one atmosphere pressure, ordinary liquid ^4He, called helium–I, changes to an abnormal form called helium-II. The temperature at which this transition of He–I to He–II takes place is known as Lambda point. Below this temperature, its thermal conductivity increases a million fold and the viscosity becomes effectively zero, hence it is described as a superfluid.

All the noble gases, especially helium, have tremendous ability to diffuse through almost all types of glass, rubber, PVC, etc.

SAQ 2

You have read above that boiling point is related to the binding forces in atoms/molecules. In noble gases, the atoms are held by van der Waals forces. Can you now explain in the space given below as to,

a) What is the relationship between the boiling point and van der Waals forces?

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b) Why there is a steady increase in boiling points from He to Rn?

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11.5 COMPOUNDS OF NOBLE GASES

Xenon difluoride, XeF_2, can now be made by a simple reaction of xenon and fluorine gases in a pyrex bulb in sunlight. But still the compounds of the noble gases were unknown until 1962. Is it not surprising that a compound which can be prepared so easily eluded the world of science for so long? One reason for this is that most of the reactions were carried out on argon, which was the most readily available, and the results of experiments on argon, were thought to apply to all noble gases. Moissan, in 1896, found that argon would not react with fluorine under any conditions. Secondly, attempts at reacting xenon with fluorine using electric discharge methods did not meet with success, although Pauling had predicted that some noble gas fluorides should be stable. Chemists were discouraged by these failures and also by the preconceived notion that the noble gases must be inert because of their stable configuration.

The first breakthrough in the noble gas compounds was achieved in 1960 by an English chemist Neil Bartlett. He was trying to make the newly discovered compound PtF_6, instead he obtained a deep red compound containing oxygen. The X–ray diffraction picture of the red solid showed it to be the first known salt of dioxygenyl cation, i.e., $[O_2]^+[PtF_6]^-$. This showed that PtF_6 oxidises the oxygen molecule. Bartlett realised that xenon should form an analogous compound because the ionisation energy of xenon, 1170 kJ mol^{-1}, is slightly lower than that of the oxygen molecule, 1180 kJ mol^{-1}. When he brought xenon and PtF_6 together, he obtained an orange yellow solid, xenon hexafluoroplatinate, $[Xe]^+[PtF_6]^-$. This opened the field for the study of the chemistry of noble gases.
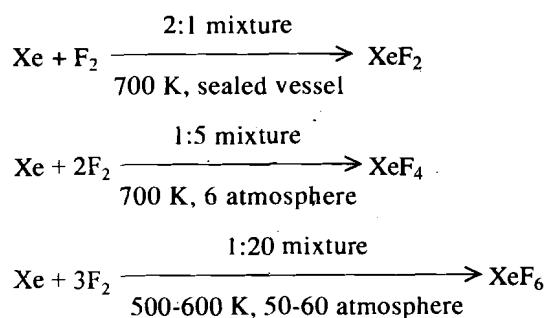
True chemical bonding in the noble gases seems to be restricted to krypton, xenon and radon with fluorine or oxygen as ligands. None, however, combines with oxygen directly. The

oxides are made from the fluorides when they react with water. Krypton chemistry is limited to the difluoride, KrF_2, which is stable only below 353 K, and one or two complexes with fluorine bridges between krypton and another element. Radon is known to form atleast one fluoride, but its formula has not yet been established because of the vigorous disintegration of the nucleus. Thus, the noble gas chemistry is effectively limited to the compounds of xenon.

11.5.1 Compounds of Xenon

The chemistry of xenon is the most extensive in this group and the known oxidation states of Xe range from +2 to +8. Structural details of some of the more important compounds of Xe are listed in Table 11.2.

Xenon reacts directly with fluorine on heating the gases in a nickel vessel. The products depend upon the amount of fluorine present and the reaction conditions :
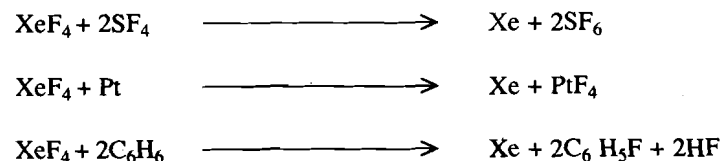
$$Xe + F_2 \xrightarrow[\text{700 K, sealed vessel}]{\text{2:1 mixture}} XeF_2$$

$$Xe + 2F_2 \xrightarrow[\text{700 K, 6 atmosphere}]{\text{1:5 mixture}} XeF_4$$

$$Xe + 3F_2 \xrightarrow[\text{500-600 K, 50-60 atmosphere}]{\text{1:20 mixture}} XeF_6$$

The compounds XeF_2, XeF_4 and XeF_6 are white solids which can be sublimed at room temperature. The lower fluorides react with fluorine on heating under pressure forming higher fluorides. The fluorides are extremely strong oxidising and fluorinating agents. They react quantitatively with hydrogen.

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \longrightarrow 4HF + Xe$$

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$
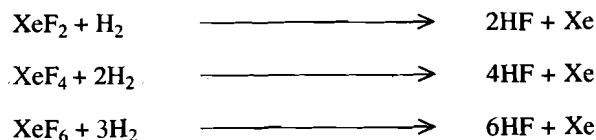
They oxidise chlorides to chlorine, iodides to iodine, cerium (III) to cerium (IV), Ag(I) to Ag(II), Cr(III) to Cr(VI) and Br(V) to Br(VII) :

$$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$$

$$XeF_4 + 4KI \longrightarrow Xe + 4KF + 2I_2$$

$$XeF_2 + BrO_3^- + H_2O \longrightarrow Xe + BrO_4^- + 2HF$$
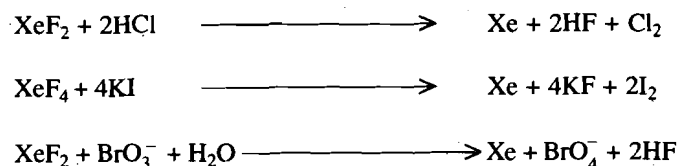
They fluorinate many compounds as well as elements :

$$XeF_4 + 2SF_4 \longrightarrow Xe + 2SF_6$$

$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$

$$XeF_4 + 2C_6H_6 \longrightarrow Xe + 2C_6H_5F + 2HF$$

The fluorides differ in their reactivity with water. XeF_2 dissolves unchanged in water or acidic solutions, but on standing, decomposition occurs slowly. Decomposition is more rapid with alkali ·
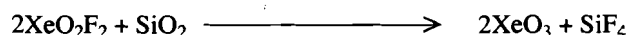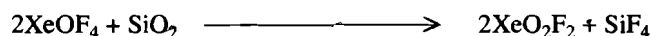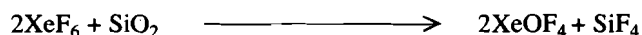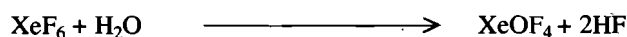
$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$
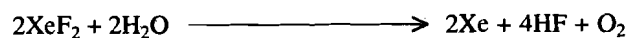
Reaction of XeF_4 with water is violent since xenon trioxide, XeO_3, formed is highly explosive :

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12\,HF + \frac{3}{2}O_2$$

53
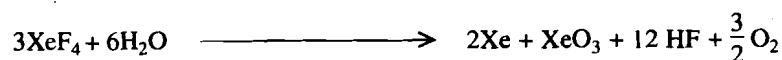
XeF_6 also reacts violently with water and hydrolysis by atmospheric moisture gives the highly explosive solid XeO_3 :

$$2XeF_6 + 6H_2O \longrightarrow 2XeO_3 + 12HF$$

With small quantities of water, partial hydrolysis occurs giving a colourless liquid xenon oxofluoride, $XeOF_4$. The same product is formed when XeF_6 reacts with silica or glass. Because of the stepwise reaction which finally produces the dangerous XeO_3, XeF_6 cannot be handled in glass or quartz apparatus.

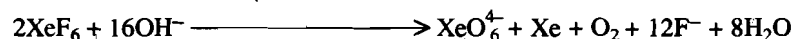$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

XeO_3 does not ionise in aqueous solution, but in alkaline solution above pH 10.5, it forms the xenate ion $HXeO_4^-$:

$$XeO_3 + NaOH \longrightarrow Na^+ HXeO_4^-$$
$$\text{sodium xenate}$$
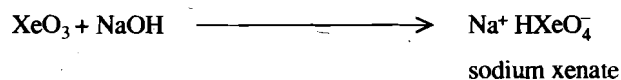
Xenates slowly disproportionate in alkaline solution to form perxenates and Xe gas :

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$
$$\text{Perxenate ion}$$

Alkaline hydrolysis of XeF_6 also forms perxenates :

$$2XeF_6 + 16OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 12F^- + 8H_2O$$

Perxenates are extremely powerful oxidising agents, and can oxidise HCl to Cl_2, H_2O to O_2 and Mn(II) to Mn(VII). With concentrated H_2SO_4, they give xenon tetroxide XeO_4, which is volatile and explosive :
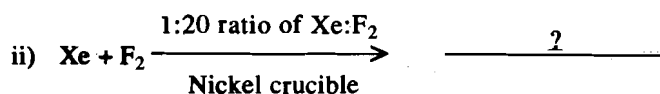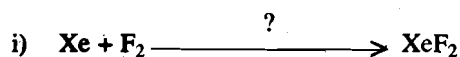
$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$
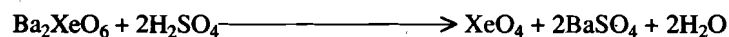
XeF_2 acts as a fluoride donor and reacts with pentafluorides such as, PF_5, AsF_5, SbF_5, NbF_5, TaF_5, RuF_5, RhF_5, IrF_5 and PtF_5 to form salts of the types $[XeF]^+[MF_6]^-$, $[XeF]^+[M_2F_{11}]^-$ and $[Xe_2F_3]^+[MF_6]^-$. XeF_4 is much less reactive in this respect and reacts only with the strongest F^- acceptors such as SbF_5 and BiF_5. But XeF_6 combines with pentafluorides to yield 1 : 1 complexes such as, $[XeF_5]^+[AsF_6]^-$ and $[XeF_5]^+[PtF_6]^-$.

Before proceeding to clathrates of noble gases, try the following SAQ related to xenon compounds.

SAQ 3

Complete the following reactions by writing the reaction conditions/products in the blank spaces given for each reaction.

i) $Xe + F_2 \xrightarrow{\quad ? \quad} XeF_2$

ii) $Xe + F_2 \xrightarrow[\text{Nickel crucible}]{1:20 \text{ ratio of } Xe:F_2} \underline{\quad ? \quad}$

iii) $XeF_2 + H_2O \longrightarrow Xe + \underline{\quad ? \quad} + \underline{\quad ? \quad}$

11.5.2 Clathrates of Noble Gases

Crystalline clathrates or inclusion complexes of noble gases have long been known. In these complexes the noble gas atoms are trapped in cavities in the crystal lattice of certain other compounds such as quinol or water. The formation of clathrates seems to depend on relative

molecular dimensions rather than on any particular chemical affinity. The atoms or molecules of any substance, which are of a suitable size to fit in the cavities in the host lattice, can form clathrates. Thus, O_2, SO_2, H_2S and MeOH are examples of other substances which form clathrates with quinol.

When quinol is crystallised from its aqueous solution in the presence of heavier noble gases like Ar, Kr or Xe under a pressure of 10-40 atmosphere, crystals of clathrates of the composition G.3Quinol are obtained. The crystals are quite stable and can persist for several years. However, when heated or dissolved in water, the gas escapes leaving behind quinol. Similarly, when water is allowed to freeze in the presence of Ar, Kr or Xe under pressure, atoms of noble gas get trapped in the crystal lattice of ice giving clathrates corresponding to the composition, $8G.46H_2O$. These clathrates are also known as the noble gas hydrates. You can see the hydrates may not be stoichiometric since the degree to which the cavities are filled depends on the partial pressure of the guest material.

The hydrates increase in thermal stability down the group as the noble gases become more polarisable. With xenon, at a partial pressure of one atmosphere, the hydrate is stable upto 275 K. Because of their very low polarisability, small size and low boiling points, no hydrates of helium and neon have been prepared. Clathrates provide a means of storing noble gases and of handling the various radioactive isotopes of Kr and Xe which are produced in nuclear reactors.

SAQ 4

Explain briefly :

i) Why no compounds of He and Ne are known ?

....
....
....
....

ii) Why noble gas compounds are formed only with O_2 and F_2?

....
....

iii) Why does the tendency to form clathrates increase down the group ?

....
....
....
....
....
....
....

11.5.3 Structure and Bonding in Xenon Compounds

You would recall that prior to 1962, it was widely believed that the noble gases are chemically inert because of the stability of their electronic configurations. However, the discovery that their compounds could be prepared, made it necessary that some description be given of the nature of bonding in the compounds they form. The nature of the bonds and the orbitals used for bonding in the compounds of noble gases is of great interest. It has been the subject of considerable controversy as will be evident from the discussion of bonding in some individual xenon compounds.

Xenon Difluoride

It is a linear molecule. Bonding in XeF_2 may be explained with the help of Valence Bond Theory (cf. Unit 4, Block 1, Atoms & Molecules course). An electron from the $5p$ level of Xe is promoted to the $5d$ level, followed by sp^3d hybridisation.
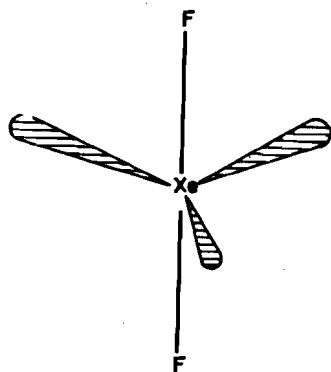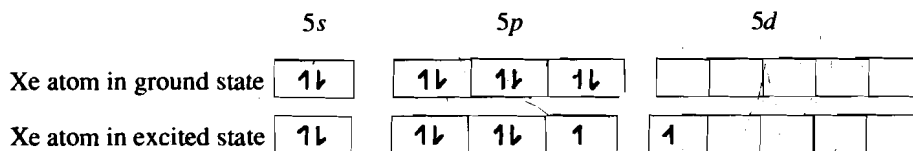
|	5s	5p	5d
Xe atom in ground state	⇅	⇅ ⇅ ⇅	☐ ☐ ☐ ☐ ☐
Xe atom in excited state	⇅	⇅ ⇅ ↑	↑ ☐ ☐ ☐ ☐

sp^3d–hybridisation

The two unpaired electrons in axial orbitals form bonds with two fluorine atoms and three lone pairs occupy the equatorial positions of the trigonal bipyramid giving rise to a linear molecule as shown in Fig. 11.1.

The objection to this model is that the $5d$ orbital of Xe appears to be too large and too high in energy to participate in hybridisation. However, it has been suggested that the highly electronegative atoms like fluorine cause a large contraction in the size of the d orbitals enabling them to participate in bonding.

Fig. 11.1: Structure of XeF_2

Molecular orbital approach involving three-centre four electron bonds has been found more acceptable. The outer electronic configuration of the atoms involved in bonding are:

	5s	$5p_x$	$5p_y$	$5p_z$		2s		$2p_x$	$2p_y$	$2p_z$
Xe	⇅	⇅	⇅	⇅	; F	⇅		⇅	⇅	↑
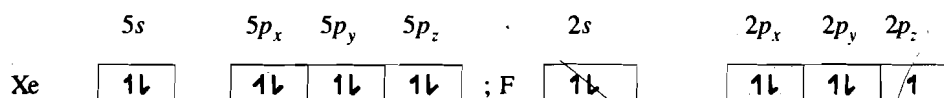
It is assumed that the $5p_z$ orbital of xenon and the $2p_z$ orbital of the two fluorine atoms are involved in bonding. These three atomic orbitals combine to give three molecular orbitals, one bonding, one nonbonding and one antibonding which can be represented as shown in Fig. 11.2.
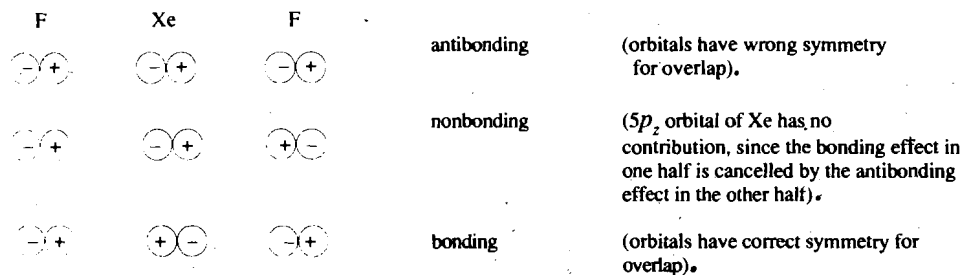

F	Xe	F		
			antibonding	(orbitals have wrong symmetry for overlap).
			nonbonding	($5p_z$ orbital of Xe has no contribution, since the bonding effect in one half is cancelled by the antibonding effect in the other half).
			bonding	(orbitals have correct symmetry for overlap).

Fig. 11.2 : Molecular orbital representation of the 3– centre 4– electron bond in XeF_2. .

The three original atomic orbitals contained four electrons. These occupy the molecular orbitals of lowest energy as shown in Fig. 11.3.
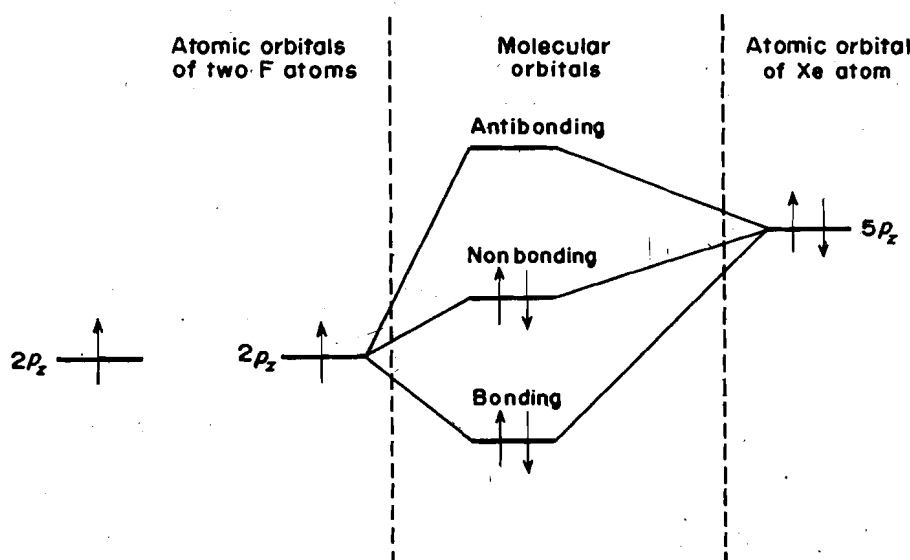

Fig . 11.3 : Molecular orbital energy level diagram for XeF_2 molecule.

A linear arrangement of the atoms gives the best overlap of orbitals, in accordance with the observed structure. The situation is similar to that in the boron hydrides, where there are three-centre B–H–B bonds (refer Unit 6), except that in XeF_2 there are four electrons involved compared with two electrons in the boranes.
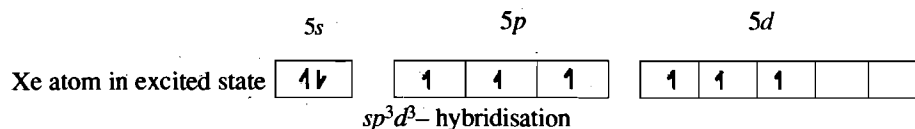
Xenon Tetrafluoride

The structure of XeF_4 is square planar (Fig. 11.4). The Valence Bond Theory explains this by promoting two electrons resulting in sp^3d^2 hybridisation. Two of the positions on the octahedron are occupied by two lone pairs. This gives rise to a square planar structure.

Fig 11.4 : Structure of XeF_4

	$5s$	$5p$			$5d$		
Xe atom in excited state	⬆⬇	⬆⬇	⬆	⬆	⬆	⬆	

$$sp^3d^2 \text{– hybridisation}$$
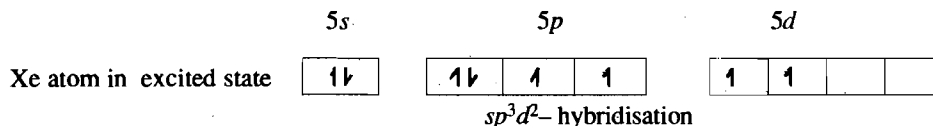
The alternative explanation is that in XeF_4, the Xe atom binds to four F atoms by using two of its p orbitals to form two three-centre molecular orbitals at right angle to each other, thus giving a square planar shape.

Xenon Hexafluoride

According to Valence Bond approach, 3 electrons are promoted and the hybridisation is sp^3d^3 which predicts a pentagonal bipyramidal or capped octahetral structure as shown in Fig.11.5.

Fig. 11.5 : Structure of XeF_6

	$5s$	$5p$			$5d$		
Xe atom in excited state	⬆⬇	⬆	⬆	⬆	⬆	⬆	⬆

$$sp^3d^3 \text{– hybridisation}$$

According to M.O. theory, the structure of XeF_6 can be explained by considering three three-centre molecular orbitals mutually at right angles and giving a regular octahedral shape. Thus, M.O. theory fails here to predict the correct structure. A more detailed discussion regarding this can be found in higher courses in the subject.

11.5.4 Molecular Shapes of Noble Gas Compounds and Valence Shell Electron Pair Repulsion (VSEPR) Theory

Thus, we have seen above that neither the Valence Bond approach nor the Molecular Orbital theory is able to explain the bonding in all the noble gas compounds. The approach which has given the most rational explanation about the stereochemistry of noble gas compounds and provided the most readily visualised description of their shapes is the Valence Shell Electron Pair Repulsion Theory (VSEPR) of Gillispie and Nyholm. You may have come across this in Unit 3 of **Atoms and Molecules** course. To recollect, this theory assumes that stereochemistry is determined by the repulsions between valence shell electron pairs, both bonding and nonbonding, and that the latter exert the stronger effect. Thus in XeF_2, the valence shell of Xe atom has ten electrons, eight from the Xe atom and one each from the two F atoms. These are distributed in five pairs, two bonding and three nonbonding, which are directed to the corners of a trigonal bipyramid. Because of their greater mutual repulsion, the three nonbonding pairs are situated in the equatorial plane at 120° to each other, leaving the two bonding pairs perpendicular to the plane and so producing a linear F–Xe–F molecule.

Fig. 11.6 : Structure of XeO_3

In the same way, XeF_4 with six electron pairs is considered as pseudo-octahedral with its two nonbonding pairs opposite to each other leaving the four F bonds in a plane around Xe.

More distinctively, the seven electron pairs around Xe in XeF_6 suggest the possibility of a non-regular octahedral geometry and imply a distorted structure based on either monocapped octahedral or a pentagonal pyramidal arrangement of electron pairs, with the Xe–F bonds bending away from the protruding nonbonding pair.

It will be interesting to devise similar rationalisations for the xenon oxides. Three electron pairs of the Xe atom can be used to complete the octet of three oxygen atoms, leaving one lone pair on xenon. This gives a trigonal pyramidal shape to XeO_3 molecule (Fig. 11.6). Similarly in xenon tetroxide, four electron pairs from xenon can coordinate with each of the four oxygens forming a tetrahedral molecule (Fig. 11.7). Such coordination, however, leaves a rather high positive charge on the central atom. The tetrahedral silicate, phosphate and sulphate ions, which are isoelectronic with XeO_4, are stabilised by $p\pi–d\pi$ back bonding in which lone-pair electrons on oxygen spend some time in d orbitals on the central atom. This helps to even out the charge distribution. But $5d$ orbitals of xenon are ill-matched with $2p$ orbitals of oxygen, thus weak Xe–O bond is consistent with rather little $p\pi–d\pi$ bonding and considerable polar character. Structural details of some xenon compounds based on VSEPR theory are given in Table 11.2. Although chemists were taken by surprise by the noble gas compounds, but as you can see, these were soon found to be readily accommodated by current bonding theories.
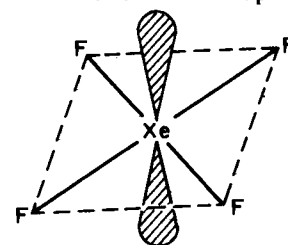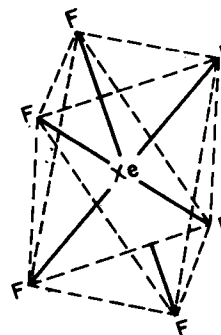

Fig. 11.7 : Structure of XeO_4

Table 11.2: Structures of some important xenon compounds
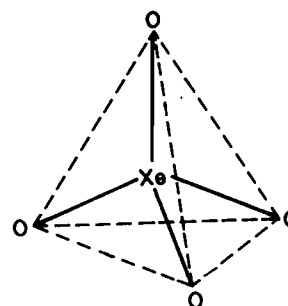
Compound	Oxidation State of Xe	No. of electron pairs around Xe			Structure	Remarks
		Bond pairs	Lone pairs	Total		
XeF_2	+II	2	3	5	Linear	Lone pairs occupy equatorial positions of trigonal bipyramid
XeF_4	+IV	4	2	6	Square planar	One lone pair above and the other below the plane of molecule
XeF_6	+VI	6	1	7	Distorted octahedral	Lone pair either at the centre of a face or at the midpoint of an edge
XeO_3	+VI	6	1	7	Trigonal pyramidal	Bond pairs are in three double bonds, lone pair protruding from the apex of the pyramid
XeO_4	+VIII	8	—	8	Tetrahedral	Bond pairs are in four double bonds
XeO_2F_2	+VI	6	1	7	see-saw	Four bond pairs in two Xe=O bonds, two bond pairs in two Xe–F bonds, lone pair occupying one equatorial site
$XeOF_4$	+VI	6	1	7	Square pyramidal	Two bond pairs in Xe=O bond, four bond pairs in four Xe–F bonds, lone pair protruding from the base
$XeOF_2$	+IV	4	2	6	'T' shaped	Two bond pairs in Xe=O bond, two bond pairs in two Xe–F bonds, lone pairs occupying two equatorial sites of trigonal bipyramid.

SAQ 5

Given below in Column I are the few expected compounds of noble gases. Write down in Column II the shapes of these compounds on the basis of VSEPR theory.

Column I	Column II
(i) XeF_4	(i) ....
(ii) $XeOF_4$	(ii) ....
(iii) XeO_4	(iii) ....
(iv) XeF_6	(iv) ....

11.6 SUMMARY

Let us now recall what you have learnt in this unit :

● The atmosphere surrounding the earth is a mixture of gases consisting of nitrogen (78%), oxygen (21%), noble gases (1%), some other gases like CO_2 and air pollutants.

● Noble gases were discovered in the order : helium in 1868, then neon, argon, krypton and xenon in the 1890s and finally radon in 1902.

● The characteristic stable electronic configuration of noble gases is $1s^2$ or ns^2np^6. They have the highest ionisation energies and the lowest electron affinity, melting and boiling points and heat of vaporisation in their periods.

● Noble gases have various applications like as coolants and for providing inert atmosphere. Their chemistry is limited due to the exceptional stability of their closed valence shells. Only xenon reacts directly with fluorine forming fluorides. Oxides may be prepared by the reaction of water with fluorides.

● The shapes of xenon compounds can usually be explained with the help of Valence Shell Electron Pair Repulsion Theory.

11.7 TERMINAL QUESTIONS

1 How did the terrestrial helium originate?

2 What are the factors which led Bartlett to think that Xe can be oxidised by PtF_6.

3 Would you expect nitrogen to form a compound of the type N_2^+ $[PtF_6]$? Give reason for your answer. (Ionisation energy of N_2 is 1403 kJ mol^{-1})

4 Would you expect radon to form more stable compounds than xenon? If so why ?

5 Work out the oxidation states of xenon in XeF_2, XeF_4 and XeF_6.

11.8 ANSWERS

Self-assessment Questions

1 a) Chemical inertness of lighter noble gases, i.e., He, Ne and Ar, and rare abundance of comparatively reactive noble gases, i.e, Kr, Xe and Rn were the reasons for the late discovery of noble gases.

   b) Lord Raleigh found that the density of nitrogen isolated from air was consistently about 0.5% higher than that of the nitrogen obtained chemically from ammonia. This observation made Lord Raleigh suspect that there may be an additional gaseous element in air.

2 a) Boiling point is directly proportional to the van der Waals forces between the atoms/molecules. More is the force of attraction, higher is the temperature required to overcome these binding forces and higher will be the boiling point.

   b) As we move down the group from He to Rn, the van der Waals force of attraction between the noble gas atoms increases giving rise to a steady increase in boiling points.

3 i) 2 : 1 ratio of Xe : F_2, nickel crucible

   ii) XeF_6

   iii) $2HF + 1/2O_2$

4 i) Valence shells of He and Ne are completely filled, so they have no tendency to lose, gain or share electrons. Because of these reasons, compounds of He and Ne are not known.

   ii) Because the noble gases have extremely low reactivity, they need the strongest oxidising agents to form compounds.

   iii) In clathrates, the noble gases are held by weak van der Waals forces which increase with the increase in the polarisability of the noble gas down the group. Therefore, the tendency to form clathrates increases down the group.

5 i) Square planar

   ii) Square pyramidal

iii) Tetrahedral

iv) Distorted octahedral

Terminal Questions

1   Terrestrial helium originated from the decay of radioactive elements in rocks.

2   The very fact that the first ionisation energy of xenon is slightly less than that of oxygen, led Bartlett to think that like oxygen, xenon can also be oxidised by PtF_6.

3   Oxygen and xenon which have ionisation energies, 1180 kJ mol^{-1} and 1170 KJ mol^{-1}, respectively, can be oxidised by PtF_6 while nitrogen having comparatively much higher ionisation energy, 1403 kJ mol^{-1} cannot be oxidised, so a compound of the type $[N_2]^+ [PtF_6]^-$ cannot be formed.

4   On the basis of comparatively high polarisability and low ionisation energy, radon is expected to form more stable compounds. But because of very short half-life, its compounds are highly unstable.

5   Oxidation state of xenon in XeF_2 is + 2.

Oxidation state of xenon in XeF_4 is + 4.

Oxidation state of xenon in XeF_6 is + 6.

FURTHER READING

1   A New Concise Inorganic Chemistry, J.D. Lee, ELBS, London, 3rd ed., 1977.

2   Chemistry : Facts, Patterns and Principles, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3   Comprehensive Inorganic Chemistry, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3th ed., 1986.

4   Principles of Inorganic Chemistry, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.