

# CHAPTER-9

## NOBLE GASES

The group 18 (or Group 0) of the periodic table consists of six monoatomic gases, i.e., helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Except radon, all other gases are present in the atmosphere in very small quantities and hence they are known as rare gases of the atmosphere. These gases are also sometimes referred to as aerogens (present in the air).

All these gases do not show any chemical reactivity at ordinary temperatures and hence they were earlier called inert gases. However, later a number of compounds of these gases, particularly those of xenon and krypton, have been prepared. This suggests that these gases are not completely inert. Consequently, these gases are now called noble gases on analogy with noble metals like gold and platinum which show reluctance to react rather than complete inertness.

### Occurrence of Noble Gases

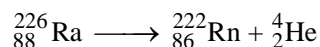
Except for radon, which is a radioactive element all other noble gases occur in the elemental state in the atmosphere. Their total percentage in dry air is about 1% by volume of which argon is the major component. Helium is the second most abundant element in the universe (23% as compared to 76% hydrogen) although its terrestrial abundance is very low. Helium is also present in the natural gas to an extent of 2–7%. In addition helium is also present in small quantities, in various radioactive minerals such as cleveite, monazite, pitchblende etc. Helium, neon and argon are also present in trace amounts in some spring waters: The relative abundance of different noble gases in the atmosphere are given below.

Element	Abundance in Air (%by volume)
Helium (He)	$5.24 \times 10^{-4}$
Neon (Ne)	$18.2 \times 10^{-4}$
Argon (Ar)	0.934
Krypton (Kr)	$1.14 \times 10^{-4}$
Xenon (Xe)	$8.7 \times 10^{-6}$
Radon (Rn)	Trace

**Helium :** The main commercial source of helium is natural gas, which mainly contains hydrocarbons (mostly methane along with small amounts of hydrocarbons up to six carbon atoms) along with varying amounts of carbon dioxide, nitrogen, hydrogen sulphide and helium (2–7%). The natural gas is compressed to about 100 atm and cooled to 73 K. Under these conditions, helium does not liquefy while other gases get liquefied. About pure helium is prepared by this method.

**Neon, argon, krypton and xenon are obtained by fractionation of liquid air :** Fractional distillation of liquid air gives O<sub>2</sub>, N<sub>2</sub> and the mixture of noble gases. The individual noble gases are then separated by adsorption over coconut charcoal which adsorbs different gases at different temperature.

Radon is obtained as the decay product of radium.



### 1. Uses of Helium

- (i) The chief use of helium is in filling of balloons which are employed for meteorological observations. Although lifting power of helium is 8% less than that of hydrogen, yet it is preferred because it is non-inflammable.
- (ii) Liquid helium (b.p. 4.2 K) is used as a cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems used for clinical diagnosis.
- (iii) An oxygen-helium mixture is used for artificial respiration in deep sea diving instead of air because nitrogen present in air dissolves in blood under high pressure when sea diver goes into deep sea. When he comes to the surface, nitrogen bubbles out of the blood due to sudden release of pressure, causing pains. This disease is called bends.
- (iv) Helium is less soluble in blood than nitrogen. Therefore, an oxygen-helium mixture is also used in the treatment of asthma.
- (v) Helium is also used for creating inert atmosphere during welding of Mg and Al which are easily oxidizable.
- (vi) Helium is chemically inactive and does not become radioactive. Hence it is used in gas cooled atomic reactors as a heat transfer agent.

### 2. Uses of Neon

- (i) Neon is mainly used in discharge tubes and fluorescent lamps for advertising purposes. Neon when used in a discharge tube produces an orange red glow which can be seen at long distances even in mists and fogs. However, when neon is mixed with other gases and used in discharge tubes, glows of different colours known as neon signs are produced. These are widely used for advertising purposes.
- (ii) Neon has a remarkable property of carrying extremely high currents even under high voltage. Therefore, neon is used in safety devices for protecting electrical instruments such as voltmeters, relays and rectifiers from high voltage.
- (iii) It is used in beacon light as a safety signal for air navigators since its light has fog penetration power.
- (iv) It is used for filling sodium vapour lamps.

### 3. Uses of Argon

- (i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes such as arc welding of metals and alloys. In the laboratory, it is used for handling substances which are air sensitive.
- (ii) It is used in filling incandescent and fluorescent lamps where its presence retards the sublimation of the filament and thus increases the life of the lamp.
- (iii) It is also used in 'neon signs' for obtaining lights of different colours.

#### 4. Uses of Krypton

- (i) Krypton and xenon are more efficient than argon in gas filled lamps because of their lower thermal conductivities but due to their scarcity and high cost they are used to a much smaller extent.
- (ii) A mixture of krypton and xenon has also been used in some tubes for high speed photography.

#### 5. Uses of Radon

- (i) Being radioactive, radon is used in radioactive research.
- (ii) It is used for normal treatment of cancer and other malignant growths.
- (iii) It is used in X-ray photography for the detection of flaws in metals and other solids.

#### Electronic Configuration

The general outer electronic configuration of noble gases is  $ns^2np^6$ . Helium, however, has  $1s^2$  configuration. In all these gases, all the orbitals, which are occupied by the electrons are completely filled. This imparts stability to the atoms of these gases. As a result of this stable arrangement of electrons, the atoms of these gases neither have any tendency to gain electrons nor to lose electrons. Consequently, these gases are almost chemically inert. The electronic configuration of noble gases is given in the following table.

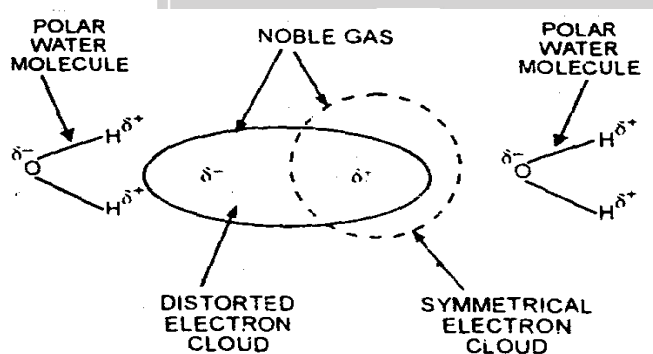
Name	Atomic Number	Electronic Configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$1s^2 2s^2 2p^6$
Argon (Ar)	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Krypton (Kr)	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
Xenon (Xe)	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Radon (Rn)	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Some important atomic and physical properties of noble gases are discussed below.

1. **Monoatomic nature :** All the noble gases are monoatomic, colourless and odourless gases. Their monoatomic nature is due to the stable outer electronic configuration ( $ns^2 np^6$ ) of their atoms. As a result, they do not enter into chemical combination even amongst themselves. Their monatomic nature is further supported by the following facts :
  - (i) The ratio of their specific or molar heats at constant pressure and constant volume, i.e.,  $C_p/C_v$  is 1.67.
  - (ii) 22.4 litres of each gas at NTP weighs equal to the atomic weight of the gas in grams.
2. **Atomic radii :** The atomic radii of noble gases are by far the largest in their respective periods. This is due to the reason that noble gases (because they do not form molecules) have only van der waals radii while others have covalent radii. Van der Waals radii, by definition, are larger than covalent radii. As we move down the group from He to Rn, the atomic radii further increase primarily due to the increase in the number of shells.
3. **Ionisation enthalpy:** The ionization enthalpies of noble gases are the highest in their respective periods due to their stable electronic configurations. However, as we move down the group from He to Rn, the ionization enthalpies decrease due to a corresponding increase in their atomic radii and shielding effect.

- Electron affinity:** The electron affinity of noble gases is zero. This is due to the reason that the atoms of these elements have all their subshells complete. As such there is no room for additional electron in the valence shell. In other words, noble gases have a little tendency to accept an additional electron and hence their electron affinity is zero.
- Melting and boiling points :** The melting and boiling points of noble gases are very low. This is due to the reason that the atoms of these elements are held together by weak van der Waals forces of attraction both in the liquid and in the solid states. Further, as we move down the group from He to Rn, the melting and boiling points of these elements show a regular increase due to a corresponding increase in the magnitude of their van der Waals forces of attraction as the size of the atom increases. Helium has the lowest boiling point of any known substance.
- Ease of liquefaction :** The ease of liquefaction of a gas depends upon the magnitude of the attractive forces present in its atoms or molecules. Since the atoms of noble gases are held together by weak van der Waals forces of attraction these gases cannot be easily liquefied. However, as the atomic size increases, the magnitude of their van der Waals forces of attraction increases and hence ease of liquefaction increases as we move down the group from He to Xe.
- Solubility in water :** These gases are slightly soluble in water. The solubility, in general, increases from He to Rn.

**Explanation:** Water is a polar molecule. Therefore, when it comes near a noble gas, it induces dipole in the noble gas by distorting or polarizing its otherwise symmetrical electron cloud as shown in following fig. The induced dipole thus set up in the noble gas then interacts with the dipole of polar water molecule. As a result of this dipole-induced dipole interaction, the noble gas dissolves in water. As the size of the noble gas increases, the extent of polarization increases. Consequently, the magnitude of the dipole-induced dipole interaction increases and hence the solubility of the noble gas in water increases from He to Rn.



**Fig. :** Polarisation of a noble gas by polar water molecule

- Enthalpy of fusion and enthalpy of vaporization.** The enthalpy of fusion and enthalpy of vaporization of noble gases are very low due to weak inter atomic forces of attraction in the liquified state. The values of these properties are found to increase from He to Rn due to an increase in the magnitude of the interatomic forces as the atomic size of the noble gas increases.
- Adsorption over charcoal.** Except He, all other noble gases are adsorbed by coconut charcoal at low temperature. The extent of adsorption increases as the atomic size of the noble gas increases.

## NOTE :

- Helium has the unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.
- Clathrates of Noble gases.** Noble gases form a number of compounds in which the gases are entrapped within cavities of crystal lattices of certain organic and inorganic compounds. Such compounds are called clathrates or cage compounds. These are also sometimes referred to as host-guest compounds. The organic or inorganic compound with cavities is called the host while the gas atoms entrapped in it are called the guest. Only Ar, Kr and Xe form clathrates since their sizes match the size of cavities present in most of the organic and inorganic compounds. As such He and Ne do not form clathrates since they are too small to be entrapped within the cavities of organic and inorganic compounds.
- Interstitial compounds.** These compounds are formed when small atoms occupy positions in the interstices of the metal lattice. Only He forms such compounds since the atomic size of He is the smallest amongst the noble gases and matches the size of the interstices available in the lattice of most of the heavy metals.

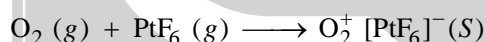
**Compounds of Xenon**

The noble gases are chemically inert due to the following reasons :

- The noble gases have completely filled  $ns^2 np^6$  electronic configuration in their valence shells.
- The noble gases have high ionization enthalpies.
- The electron affinities of noble gases are almost zero.

Therefore, noble gases neither have a tendency to lose nor to gain electrons and hence do not enter into chemical combination. Before 1962, it was thought that noble gases do not combine at all and hence no compounds of noble gases were possible.

However, in 1962, Neil Bartlett observed that platinum hexafluoride ( $\text{PtF}_6$ )—a powerful oxidising agent—reacts with dioxygen to yield an ionic solid dioxygenylhexafluoroplatinate (V),  $\text{O}_2^+ [\text{PtF}_6]^-$ .



In this reaction,  $\text{O}_2$  has been oxidised to  $\text{O}_2^+$  by  $\text{PtF}_6$ .

Since the first ionization energy of xenon ( $1170 \text{ kJ mol}^{-1}$ ), is fairly close to that of  $\text{O}_2$  molecule ( $1175 \text{ kJ mol}^{-1}$ ), Bartlett thought that  $\text{PtF}_6$  should also oxidise Xe to  $\text{Xe}^+$ . Thus, when Xe and  $\text{PtF}_6$  were mixed, a rapid reaction occurred and a red solid with the formula  $\text{Xe}^+ \text{PtF}_6^-$  was obtained.



This observation led to the conclusion that noble gases particularly Kr and Xe can form chemical compounds and hence they cannot be regarded as inert gases. They are more correctly called as noble gases or zero group gases. Some important stable compounds of xenon in different oxidation states are given in following table.

**Table: Some important stable compounds of xenon**

+2 oxidation state	+4 oxidation state	+6 oxidation state	+8 oxidation state
$\text{XeF}_2$ , Xenon difluoride	$\text{XeF}_4$ , Xenon tetrafluoride $\text{XeOF}_2$ , Xenon oxydifluoride	$\text{XeF}_6$ , Xenon hexafluoride $\text{XeOF}_4$ , Xenon oxytetrafluoride $\text{XeO}_2\text{F}_2$ , Xenon dioxydifluoride $\text{XeO}_3$ , Xenon trioxide	$\text{XeO}_4$ , Xenon tetroxide $\text{XeO}_3\text{F}_2$ , Xenon trioxydifluoride

## Structure of Xenon Compounds

Both VSEPR theory and concept of hybridization are applied to predict the molecular geometries of xenon compounds as discussed below.

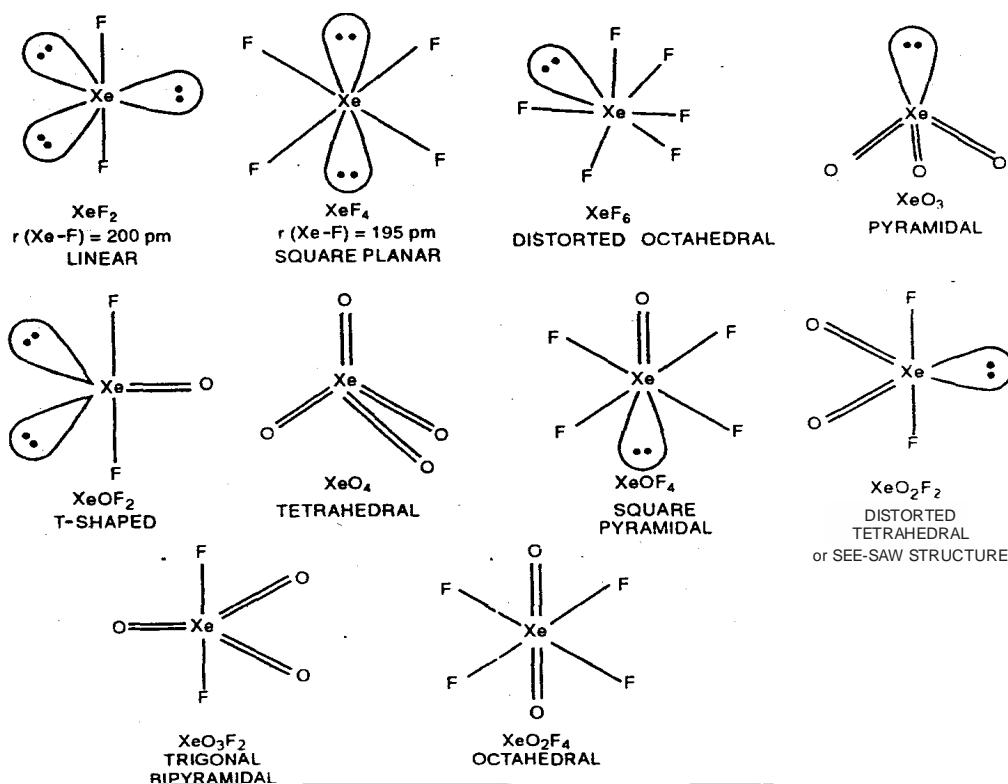
There are two, four and six Xe–F covalent bonds in  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  respectively. Depending on the number of Xe–F covalent bonds to be formed in each case, the requisite number of electrons of the  $5p$ -orbital of the valence shell of Xe get unpaired and promoted to the vacant  $5d$ -orbitals followed by hybridization. According to VSEPR theory, the shape of the molecule is predicted by the total number of electron pairs (lone pairs + bond pairs) in the valence shell of the central Xe atom as shown in following Table. Their structures are given in following figure.

**Table : Hybridisation and shapes of xenon fluorides**

Molecule	No. of bond pairs of electrons	No. of lone pairs of electrons	Total electrons pairs	Hybridisation	Shape
$\text{XeF}_2$	2	3	5	$sp^3d$	Linear
$\text{XeF}_4$	4	2	6	$sp^3d^2$	Square planar
$\text{XeF}_6$	6	1	7	$sp^3d^3$	Distorted octahedral

**Table : Hybridisation and shapes of some oxides and oxyfluorides**

Molecule	Hybridisation	Geometry	Shape
$\text{XeO}_3$	$sp^3$	Tetrahedral	Pyramidal
$\text{XeO}_4$	$sp^3$	Tetrahedral	tetrahedral
$\text{XeOF}_2$	$sp^3d$	Triogonal bipyramidal	T-shaped
$\text{XeOF}_4$	$sp^3d^2$	Square pyramidal	Square pyramidal
$\text{XeO}_2\text{F}_2$	$sp^3d$	Trigonal bipyramid	Distorted tetrahedral
$\text{XeO}_3\text{F}_2$	$sp^3d$	Trigonal bipyramid	Trigonal bipyramid
$\text{XeO}_2\text{F}_4$	$sp^3d^3$	Octahedral	Octahedral



**Figure :** Shapes of compounds of xenon

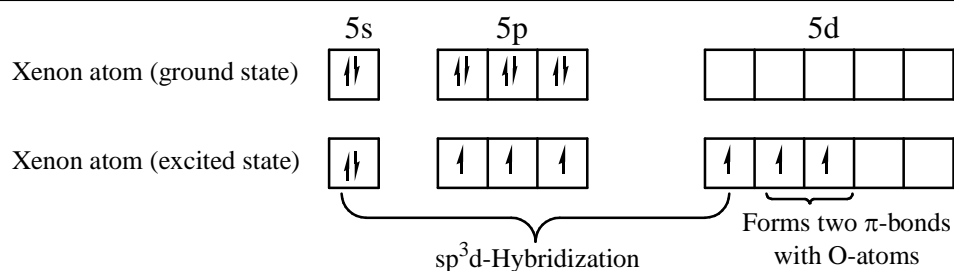
The geometry of  $\text{XeF}_6$  not yet been confirmed. It probably has a distorted octahedral structure in which all the six positions are occupied by fluorine atoms and the lone pair is present at the corner of one of the triangular faces (above figure).

The geometries and shapes of xenon oxides and oxyfluorides can be better explained on the basis of concept of hybridization (above table). Since in all these compounds, each oxygen atom forms a double bond with xenon, therefore, total number of half-filled orbitals needed for bond formation = no. of monovalent atoms + twice the number of oxygen atoms. The requisite number of half-filled orbitals are then obtained by promotion of  $5p$  and even  $5s$ -electrons. Now, in order to make  $\pi$ -bonds with the O atom,  $5d$ -orbitals equal to the number of O atoms are left out while the remaining orbitals are hybridized. The type of hybridization thus obtained determines the geometry of the molecule. As an illustration, consider the molecule of  $\text{XeO}_2\text{F}_2$ .

$$\text{Total number of half filled orbitals needed} = 2 \times 2 + 2 \times 1 = 6$$

Now promotion of three electrons, one from each of the three  $5p$ -orbitals to  $5d$ -subshell gives six half filled orbitals.

Two of the  $5d$ -orbitals are kept as such to form two  $\pi$ -bonds with oxygen atoms. The remaining five orbitals undergo



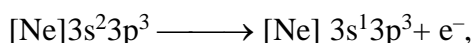
$sp^3d$ -hybridization to give five  $sp^3d$ -orbitals. Two of these five orbitals form two  $\sigma$ -bonds with F-atoms, another two form two  $\sigma$  bonds with O-atoms while the fifth one contains a lone pair of electrons. The two unhybridized half filled  $5d$ -orbitals overlap with half-filled  $p$ -orbitals of O-atoms to form two  $\pi$ -bonds. As a result, the molecule of  $\text{XeO}_2\text{F}_2$  has bipyramidal geometry with one of the equatorial positions occupied by a lone pair. Consequently, the molecule has trigonal bipyramidal shape. Similarly, the shapes of all the other oxides and oxyfluorides of xenon can be deduced.





## SOLVED PROBLEMS

1. Do you expect that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment for the process.



be larger than, smaller than, or the same as the 4th ionization energy ( $IE_4$ ) of phosphorus?

- (a) Smaller (b) Larger  
(b) The same (d) cannot be answered from the given information

**Soln.** Photoelectron spectroscopy refers to energy measurement of electrons emitted from solids, gases or liquids by the photoelectric effect, in order to determine the binding energies of electrons in a substance. The minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment is found to be smaller than 4<sup>th</sup> ionization energy ( $IE_4$ ) of phosphorus.

**Correct option is (a)**

2. Which of the following fluorides is not formed by xenon?

- (a)  $\text{XeF}_2$  (b)  $\text{XeF}_3$  (c)  $\text{XeF}_4$  (d)  $\text{XeF}_6$

**Soln.**  $\text{XeF}_3$  is a odd electron species, hence it is unstable so Xe does not formed  $\text{XeF}_3$  type fluorides.

**Correct option is (b)**

3. The most abundant noble gas in air is

- (a) neon (b) helium (c) xenon (d) argon

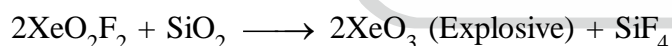
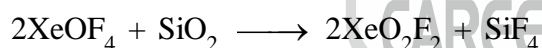
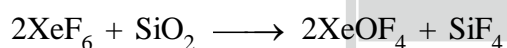
**Soln.** Argon (Ar) is the most abundant noble gas in the atmosphere there is so much Ar in the atmosphere because most of it was produced by a long-lived radioactive isotope of potassium in the earth's crust.

**Correct option is (d)**

4.  $\text{XeF}_6$  cannot be handled in a quartz vessel, because it reacts with  $\text{SiO}_2$  forming

- (a)  $\text{XeOF}_4$  (b)  $\text{XeF}_4$   
(c)  $\text{XeF}_2$  (d)  $\text{XeO}_4$

**Soln.** Xenon hexa fluorides is extremely reactive it cannot be stored in glass or quartz vessels because it reacts with silica of the glass and give the dangerously explosive xenontrioxide.



**Correct option is (a)**

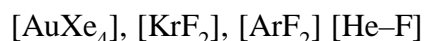
5. The first noble gas compound reported is:

- (a)  $\text{XeO}_3$  (b)  $\text{KrF}_2$  (c)  $\text{XeF}_6$  (d)  $\text{Xe}^+(\text{PtF}_6)^-$

**Soln.** The first compound of a noble gas  $\text{XePtF}_6(\text{s})$  was synthesized using a very strong oxidizing agent ( $\text{PtF}_6(\text{g})$ )

**Correct option is (d)**

6. Which ones of the following compounds do not exist?



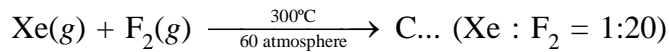
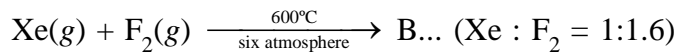
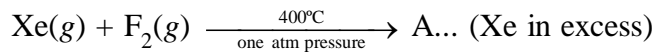
Choose the correct choice out of the following

- (a)  $[\text{AuXe}_4]$  and  $[\text{He-F}]$  (b)  $[\text{KrF}_2]$  and  $[\text{ArF}_2]$   
(c)  $[\text{Ar-F}_2]$ , and  $[\text{He-F}]$  (d)  $[\text{ArF}_2]$   $[\text{He-F}]$ ,  $[\text{AuXe}_4]$

**Soln.**  $[\text{Ar-F}_2]$  and  $[\text{He-F}]$  does not exist

**Correct option is (c)**

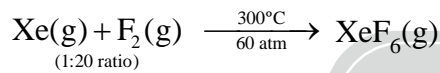
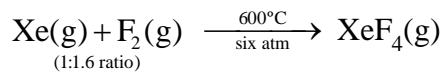
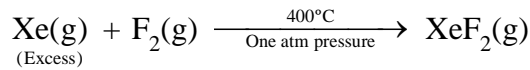
7. Given the following reaction conditions for the formations of the fluorides of Xe



A, B and C in these reactions respectively are

- (a)  $\text{XeF}_4$ ,  $\text{XeF}_2$ ,  $\text{XeF}_6$  (b)  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$   
 (c)  $\text{XeF}_6$ ,  $\text{XeF}_4$ ,  $\text{XeF}_2$  (d)  $\text{XeF}_2$ ,  $\text{XeF}_6$ ,  $\text{XeF}_4$

**Soln.**  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  are obtained by a direct reaction between Xe and  $\text{F}_2$ . The condition under which the reaction is carried out

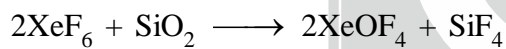


**Correct option is (b)**

8. When  $\text{XeF}_6$  reacts with silica or glass, it gives a colourless liquid of the following composition

- (a)  $\text{SiXeO}_2\text{F}_6$  (b)  $\text{XeO}_3$  (c)  $\text{XeO}_4\text{F}_2$  (d)  $\text{XeOF}_4$

**Soln.** By the action of  $\text{XeF}_6$  on silicon dioxide



**Correct option is (d)**

