Where Z is the atomic number and 'S' is the screening constant which can be calculated usi ng Slater's rules as described below.

Step 1:

Write the electronic configuration of the atom and rearrange it by grouping ns and np orbitals together and others separately in the following form.

Step 2:

Identify the group in which the electron of interest is present. The electron present right to this group does not contribute to the shielding effect.

Each of the electrons within the identified group (denoted by 'n') shields to an extent of 0.35 unit of nuclear charge. However, it is 0.30 unit for 1s electron.

Step 3:

Shielding of inner shell electrons.

If the electron of interest belongs to either s or p orbital,

- i) each electron within the (n-1) group shields to an extent of 0.85 unit of nuclear charge, and
- ii) each electron within the (n-2) group (or) even lesser group (n-3, (n-4) etc... completely shields i.e. to an extent of 1.00 unit of nuclear charge.

If the electron of interest belongs to d or f orbital, then each of electron left of the group of electron of interest shields to an extent of 1.00 unit of nuclear charge.

Step 4:

Summation of the shielding effect of all the electrons gives the shielding constant 'S'

Example: Let us explain the calculation of effective nuclear charge on 4s electron and 3d electron in scandium. The electronic configuration of scandium is 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹. we can rearrange as below.

$$\underbrace{(1s)^2}_{\text{(n-3)}} \underbrace{(2s,2p)^8}_{\text{(n-2)}} \underbrace{(3s,3p)^8 (3d)^1}_{\text{(n-1)}} \underbrace{(4s)^2}_{\text{n}}$$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
(n)	1	0.35	0.35
(n-1)	9	0.85	7.65
(n-2) & others	10	1	10.00
S value			18.00

$$Z_{eff} = Z - S$$
 i.e.= 21-18 $\therefore Z_{eff} = 3$

Calculation of effective nuclear charge on 3d electron

$$\underbrace{(1s)^2}_{\text{(n-3)}} \underbrace{(2s,2p)^8}_{\text{(n-2)}} \underbrace{(3s,3p)^8}_{\text{(n-1)}} (3d)^1 \underbrace{(4s)^2}_{\text{n}}$$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
n	0	0.35	0
(n-1) & others	18	1	18
	S Value		

$$\therefore$$
 Z_{eff} = Z - S i.e. = 21 - 18 \therefore Z_{eff} = 3

Table 3.12 Shielding effect from inner shell electrons (Slater's rules)

Electron Group	Electron of interest either S or P	Electron of interest either d or f
n	0.35 (0.30 for (S electron)	0.35
(n-1)	0.85	1.00
(n-2) and others	1.00	1.00

Table 3.13 Atomic radius (covalent radius) of second period elements.

Elements	Effective nuclear charge	Covalent radius (pm)
Li ³	1.30	167
Be ⁴	1.95	112
C ⁶	2.60	87
N^7	3.25	67
O_8	3.25	56
F ⁹	4.55	48
Ne ¹⁰	5.85	38 [*]

* Van der waals radius

Evaluate Yourself

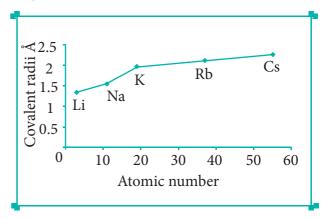


4. Using Slater's rule calculate the effective nuclear charge on a 3p electron in aluminium and chlorine. Explain how these results relate to the atomic radii of the two atoms.

Variation in Group

In the periodic table, the atomic radius of elements increases down the group. As we move down a group, new shells are opened to accommodate the newly added valence electrons. As a result, the distance between the centre of the nucleus and the outermost shell containing the valence electron increases. Hence, the atomic radius increases. The trend in the variation of the atomic radius of the alkali metals down the group os shown below.

Table 3.14 Variation of covalent radius of group 1 elements



Element	Outermost shell containing valence electron	Covalent radius (Å)
Li	L (n=2)	1.34
Na	M (n=3)	1.54
K	N (n=4)	1.96
Rb	O (n=5)	2.11
Cs	P(n=6)	2.25

Activity 3.1

Covalent radii (in Å) for some elements of different groups and periods are listed below. Plot these values against atomic number. From the plot, explain the variation along a period and a group.

2nd group elements: Be (0.89), Mg (1.36), Ca (1.74), Sr (1.91) Ba(1.98)

17th group elements: F (0.72), Cl (0.99), Br (1.14), I (1.33)

 3^{rd} Period elements : Na(1.57), Mg(1.36), Al (1.25), Si(1.17), P(1.10), S(1.04), Cl(0.99)

4th period elements: K(2.03),Ti(1.32),Ca(1.74),Sc(1.44),V(1.22),Cr(1.17),Mn(1.17),Fe(1.17), Co(1.16), Ni(1.15),Cu(1.17),Zn(1.25),Ga(1.25),Ge(1.22),As(1.21),Se(1.14),Br(1.14)

3.5.2 Ionic radius

It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the inter ionic distance between the nuclei of the cation and anion. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other therefore,

$$d = r_C^+ + r_A^-$$
 ----- (1)

Where d is the distance between the centre of the nucleus of cation C^+ and anion A^- and r_C^+ , r_A^- are the radius of the cation and anion respectively.

Pauling also assumed that the radius of the ion having noble gas electronic configuration (Na⁺ and Cl⁻ having 1s² 2s², 2p⁶ configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

i.e.
$$r_{C}^{+} \alpha \frac{1}{(Z_{eff})_{C+}}$$
 and
$$r_{A}^{-} \alpha \frac{1}{(Z_{eff})_{A^{-}}}$$
 (3)

Where Z_{eff} is the effective nuclear charge and Z_{eff} = Z - S

Dividing the equation 1 by 3

On solving equation (1) and (4) the values of $\rm r_{C^+}$ and $\rm r_{A^-}$ can be obtained

Let us explain this method by calculating the ionic radii of Na^+ and F^- in NaF crystal whose interionic distance is equal to 231 pm .

$$d = r_{Na^{+}} + r_{F^{-}} - - - (5)$$

i.e. $r_{Na^{+}} + r_{r^{-}} = 231 \text{ pm}$

We know that

$$\frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{\left(Z_{eff}\right)_{F^{-}}}{\left(Z_{eff}\right)_{Na^{+}}}$$

$$\left(Z_{eff}\right)_{F^{-}} = Z - S$$

$$= 9 - 4.15$$

$$= 4.85$$

$$\left(Z_{eff}\right)_{Na^{+}} = 11 - 4.15$$

$$= 6.85$$

$$\therefore \frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{4.85}{6.85}$$

$$= 0.71$$

$$\Rightarrow r_{Na^{+}} = 0.71 \times r_{F^{-}}$$
Substituting (3) in (1)
$$(1) \Rightarrow 0.71 r_{F^{-}} + r_{F^{-}} = 231 \text{ pm}$$

$$1.71 r_{F^{-}} = 231 \text{ pm}$$

$$r_{F^{-}} = \frac{231}{1.71} = 135.1 \text{ pm}$$

Substituting the value of r_{F^-} in equation (1)

$$r_{Na^{+}} + 135.1 = 231$$

 $r_{Na^{+}} = 95.9 \text{ pm}$

Evaluate Yourself



5. A student reported the ionic radii of isoelectronic species X³⁺, Y²⁺ and Z⁻ as 136 pm, 64 pm and 49 pm respectively. Is that order correct? Comment.

3.5.3 Ionisation energy

It is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state. It is expressed in kJ mol⁻¹ or in electron volts (eV).

$$M_{(g)} + IE_1 \rightarrow M^+_{(g)} + 1 e^{-1}$$

Where IE_1 represents the first ionisation energy.

Successive Ionisation energies

The minimum amount of energy required to remove an electron from a unipositive cation is called second ionisation energy. It is represented by the following equation.

$$M^{+}_{(g)} + IE_2 \rightarrow M^{2+}_{(g)} + 1 e^{-}$$

In this way we can define the successive ionisation energies such as third, fourth etc.

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order

$$IE_1 < IE_2 < IE_3 <$$

Periodic Trends in Ionisation Energy

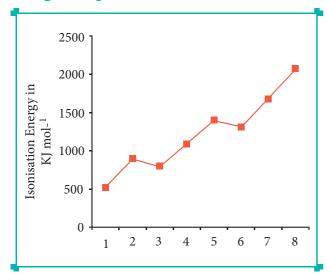
The ionisation energy usually increases along a period with few exceptions. As discussed earlier, when we move from left to right along a period, the valence electrons are added to the same shell, at the same time protons are added to the nucleus. This successive increase of nuclear charge increases the electrostatic attractive force on the valence electron and more energy is required to remove the valence electron resulting in high ionisation energy.

Let us consider the variation in ionisation energy of second period

elements. The plot of atomic number vs ionisation energy is given below.

In the following graph, there are two deviation in the trends of ionisiation energy. It is expected that boron has higher ionisation energy than beryllium since it has higher nuclear charge. However, the actual ionisation energies of beryllium and boron are 899 and 800 kJ mol⁻¹ respectively contrary to the expectation. It is due to the fact that beryllium with completely filled 2s orbital, is more stable than partially filled valence shell electronic configuration of boron. (2s² 2p¹)

Figure 3.2 Variation of Ionisation energy along the I period



The electronic configuration of beryllium (Z=4) in its ground state is $1s^2$, $2s^2$ and that of boran (Z = 5) $1s^2$ $2s^2$ $2p^1$

Similarly, nitrogen with 1s², 2s², 2p³ electronic configuration has higher ionisation energy (1402 kJ mol⁻¹) than oxygen (1314 kJ mol⁻¹). Since the half filled electronic configuration is more stable, it requires higher energy to remove an electron from 2p orbital of nitrogen. Whereas the removal one 2p electron from oxygen leads to a stable half filled

configuration. This makes comparatively easier to remove 2p electron from oxygen.

Periodic variation in group

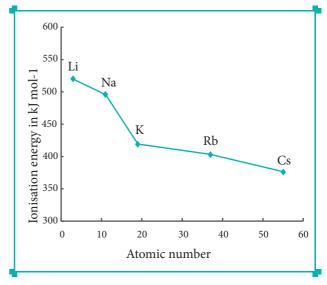
The ionisation energy decreases down a group. As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases. So, the nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

Ionisation energy and shielding effect

As we move down a group, the number of inner shell electron increases which in turn increases the repulsive force exerted by them on the valence electrons, i.e. the increased shielding effect caused by the inner electrons decreases the attractive force acting on the valence electron by the nucleus. Therefore the ionisation energy decreases.

Let us understand this trend by considering the ionisation energy of alkali metals.

Figure 3.3 Variation of Ionisation energy down the I Group.



Evaluate Yourself



6. The first ionisation energy (IE₁) and second ionisation energy (IE2) of elements X, Y and Z are given below.

Element	IE ₁ (kJ mol ⁻¹)	IE ₂ (kJ mol ⁻¹)
X	2370	5250
Y	522	7298
Z	1680	3381

Which one of the above elements is the most reactive metal, the least reactive metal and a noble gas?

3.5.4 Electron Affinity

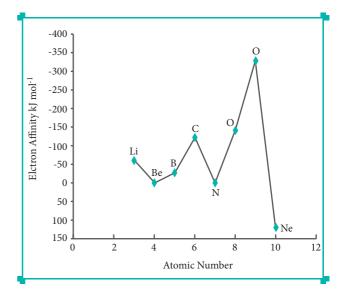
It is defined as the amount of energy released (required in the case noble gases) when an electron is added to the valence shell of an isolated neutral gaseous atom in its ground state to form its anion. It is expressed in kJ mol⁻¹

$$A + 1 e^{-} \rightarrow A^{-} + E_{A}$$

Variation of Electron Affinity in a period:

The variation of electron affinity is not as systematic as in the case of ionisation energy. As we move from alkali metals to halogens in a period, generally electron affinity increases, i.e. the amount of energy released will be more. This is due to an increase in the nuclear charge and decrease in size of the atoms. However, in case of elements such as beryllium (1s², 2s²), nitrogen (1s², 2s², 2p³) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

Figure 3.4 Variation of electron affinity (electron gain energy) along I period



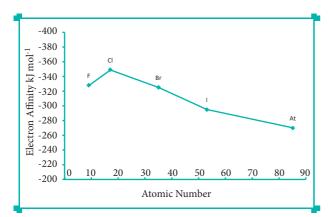
Noble gases have stable ns², np⁶ configuration, and the addition of further electron is unfavourable and requires energy. Halogens having the general electronic configuration of ns², np⁵ readily accept an electron to get the stable noble gas electronic configuration (ns², np⁶), and therefore in each period the halogen has high electron affinity. (high negative values)

Variation of Electron affinity in a group:

As we move down a group, affinity generally the electron decreases. It is due to increase in atomic size and the shielding effect of inner shell electrons. However, oxygen and fluorine have lower affinity than sulphur and chlorine respectively. The sizes of oxygen and fluorine atoms are comparatively small and they have high electron density. Moreover, the extra electron added to oxygen and fluorine has to be accommodated in the 2p orbital which is relatively compact compared to the 3p orbital of sulphur

and chlorine so, oxygen and fluorine have lower electron affinity than their respective group elements sulphur and chlorine.

Figure 3.5 Variation of Electron Affinity (electron gain energy) along I period



Evaluate Yourself



7. The electron gain enthalpy of chlorine is 348 kJ mol⁻¹. How much energy in kJ is released when 17.5 g of chlorine is completely converted into Cl⁻ ions in the gaseous state?

3.5.5 Electronegativity:

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

Electronegativity is not a measurable quantity. However, a number of scales are available to calculate its value. One such method was developed by Pauling, he assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.2 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression

$$(\chi_A - \chi_B) = 0.182 \sqrt{E_{AB} - (E_{AA}^* E_{BB})^{1/2}}$$

Where E_{AB} , E_{AA} and E_{BB} are the bond dissociation energies of AB, A_2 and B_2 molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound. The electronegativity values play an important role in predicting the nature of the bond.

Variation of Electronegativity in a period:

The electronegativity generally increases across a period from left to right. As discussed earlier, the atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electronegativity also increases in a period

Figure 3.6 Variation of Electronegativity along I period

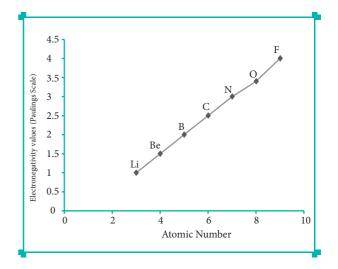
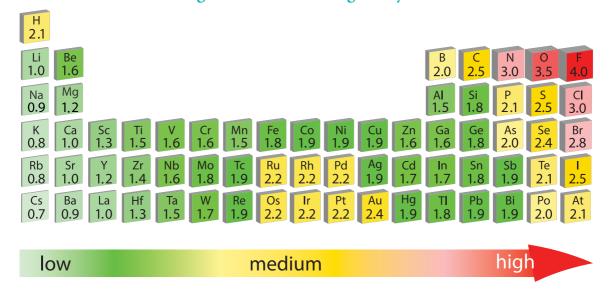


Table 3.15 Paulings scale of electronegativity valuee of elements

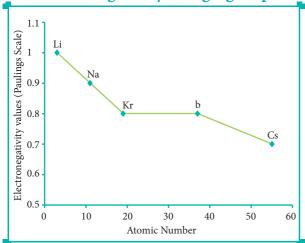


Variation of Electronegativity in a group:

The electronegativity generally decreases down a group. As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence, the electronegativity decreases.

Noble gases are assigned zero electronegativity. The electronegativity values of the elements of s-block show the expected decreasing order in a group. Except 13th and 14th group all other p-block elements follow the expected decreasing trend in electronegativity.

Figure 3.7 Variation of electronegativity along I group



3.6 Periodic Trends in Chemical Properties:

Sofar, we have studied the periodicity of the physical properties such as atomic radius, ionisation enthalpy, electron gain enthalpy and electronegativity. In addition, the chemical properties such as reactivity, valence, oxidation state etc... also show periodicity to certain extent.

In this section, we will discuss briefly about the periodicity in valence (oxidation state) and anomalous behaviour of second period elements (diagonal relationship).

Valence or Oxidation States

The valence of an atom is the combining capacity relative to hydrogen atom. It is usually equal to the total number of electrons in the valence shell or equal to eight minus the number of valence electrons. It is more convenient to use oxidation state in the place of valence.

Periodicity of Valence or Oxidation States

The valence of an atom primarily depends on the number of electrons in the

valence shell. As the number of valence electrons remains same for the elements in same group, the maximum valence also remains the same. However, in a period the number of valence electrons increases, hence the valence also increases.

Table 3.16 Variation of valence in groups

Alkali Metals (Group 1)				Group 15	
Element	No. of electrons in valence shell	Valence	Element	No. of electrons in valence shell	Valence
Li	1	1	N	5	3, 5
Na	1	1	Р	5	3, 5
K	1	1	As	5	3, 5
Rb	1	1	Sb	5	3, 5
Cs	1	1	Bi	5	3, 5
Fr	1	1			

Table 3.17 Variation of valence in period (1st period)

Element	Li	Ве	В	С	N	О	F	Ne
No. of electrons in valence shell	1	2	3	4	5	6	7	8
Valence (Combining capacity)	1	2	3	4	5, 3	6, 2	7, 1	8, 0

In addition to that some elements have variable valence. For example, most of the elements of group 15 which have 5 valence electrons show two valences 3 and 5. Similarly transition metals and inner transition metals also show variable oxidation states.

3.6.1 Anomalous properties of second period elements:

As we know, the elements of the same group show similar physical and chemical properties. However, the first element of each group differs from other members of the group in certain properties. For example, lithium and beryllium form more covalent compounds, unlike the alkali and alkali earth metals which predominantly form ionic compounds. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences. For example, boron forms BF_4^- and aluminium forms AlF_6^{3-}

Diagonal Relationship

On moving diagonally across the periodic table, the second and third period elements show certain similarities. Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.



The similarity in properties existing between the diagonally placed elements is called 'diagonal relationship'.

3.6.2 Periodic Trends and Chemical Reactivity:

chemical The physical and properties of elements depend on the valence shell electronic configuration as discussed earlier. The elements on the left side of the periodic table have less ionisation energy and readily loose their valence electrons. On the other hand, the elements on right side of the periodic table have high electron affinity and readily accept electrons. As a consequence of this, elements of these extreme ends show high reactivity when compared to the elements present in the middle. The noble gases having completely filled electronic configuration neither accept nor lose their electron readily and hence they are chemically inert in nature.

The ionisation energy is directly related to the metallic character and the elements located in the lower left portion of the periodic table have less ionisation energy and therefore show metallic

character. On the other hand the elements located in the top right portion have very high ionisation energy and are non-metallic in nature.

Let us analyse the nature of the compounds formed by elements from both sides of the periodic table. Consider the reaction of alkali metals and halogens with oxygen to give the corresponding oxides.

$$4 \text{ Na} + \text{O}_2 \rightarrow 2 \text{ Na}_2\text{O}$$

$$2 \text{ Cl}_2 + 7 \text{ O}_2 \rightarrow 2 \text{ Cl}_2 \text{O}_7$$

Since sodium oxide reacts with water to give strong base sodium hydroxide, it is a basic oxide. Conversely Cl_2O_7 gives strong acid called perchloric acid upon reaction with water So, it is an acidic oxide.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$Cl_2O_7 + H_2O \rightarrow 2 HClO_4$$

Thus, the elements from the two extreme ends of the periodic table behave differently as expected.

As we move down the group, the ionisation energy decreases and the electropositive character of elements increases. Hence, the hydroxides of these elements become more basic. For example, let us consider the nature of the second group hydroxides:

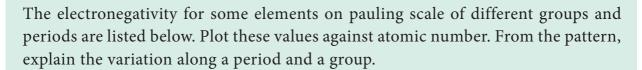
 $\mathrm{Be(OH)}_2$ amphoteric; $\mathrm{Mg(OH)}_2$ weakly basic; $\mathrm{Ba(OH)}_2$ strongly basic

Beryllium hydroxide reacts with both acid and base as it is amphoteric in nature.

$$Be(OH)_2 + HCl \rightarrow BeCl_2 + 2H_2O$$

$$Be(OH)_2 + 2 NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

Activity 3.2



2nd group elements: Be (1.6), Mg (1.2), Ca (1.0), Sr (1.0) Ba(0.9)

17th group elements : F (4.0), Cl (3.0), Br (2.8), I (2.5)

3rd Period elements: Na(0.9), Mg(1.2), Al (1.5), Si(1.8), P(2.1), S(2.5), Cl(3.0)

 4^{th} period elements: K(0.8), Ca(1.0), Sc(1.3), Ti(1.5), V(1.6), Cr(1.6), Mn(1.5), Fe(1.8), Co(1.9), Ni(1.9), Cu(1.9), Zn(1.6), Ga(1.6), Ge(1.8), As(2.0), Se(2.4), Br(2.8)



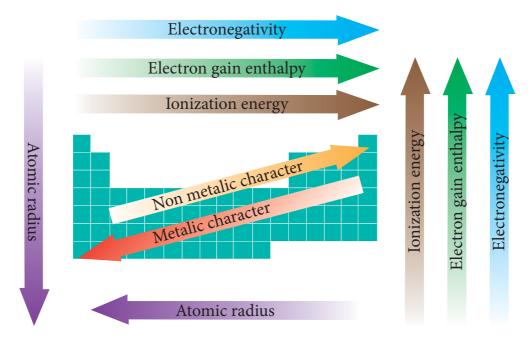
The periodic table was developed to systematically arrange the different elements. Lavoisier made the first attempt to arrange the known elements in a particular order based on properties. This followed by Johann Dobereiner, A. E. B. de Chancourtois and Newlands. First meaningful periodic table was constructed by Mendeleeve based on atomic mass. This was later modified based on the modern periodic law which states that the properties of elements are the periodic functions of their atomic numbers. The modern periodic table is made up of 18 groups and 7 periods.

The elements in the same groups have similar properties because their valence shell electronic configurations are similar. The properties of the elements of the same period differ because they have different valence shell electronic configurations. On the basis of electronic configuration the elements are also classified as s-block, p-block, d-block and f-block elements. The elements belonging to "s, p, d and f" blocks have unique characteristic

properties. In this table, more than 78% of all known elements are metals. They appear on the left side of the periodic table. Nonmetals are located at the top right hand side of the periodic table. Some elements show properties that are characteristic of both metals and non-metals and are called semimetals or metalloids.

The periodic properties such as atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy, electronegativity are possessing periodic trends. The variations of these properties are described in the following scheme.

The elements at the extreme left exhibit strong reducing property whereas the elements at extreme right strong oxidizing property. The reactivity of elements at the centre of the periodic table is low compared to elements at the extreme right and left. The similarity in chemical properties observed between the elements of second and third period which are diagonally related.



EVALUATION:

I. Choose the best Answer:

1.	What would be the	ould be the IUPAC name for an element with atomic number 222?			
	a) bibibiium	b) bididium	c) didibium	d)bibibium	
2.				1s ² , 2s ² , 2p ⁶ ,3s ² and 1s ² , t can be formed between	
	a) AB	b) AB ₂	c) A ₂ B	d) none of the above.	
3.	The group of elemen shell of atoms are ca		entiating electron en	ters the anti penultimate	
	a) p-block elements		b) d-block element	s	
	c) s-block elements		d) f-block elements	3	
4.	In which of the followariation of propert	-	•	does not agree with the e 1)	
	a) I < Br < Cl < F (ir	ncreasing electron ga	nin enthalpy)		
	b) Li < Na < K < Rb	(increasing metallic	radius)		
	c) $Al^{3+} < Mg^{2+} < Na^{-1}$	+ <f- (increasing="" ion<="" td=""><td>ic size)</td><td></td></f->	ic size)		
	d) B < C < O < N (in	ncreasing first ionisa	ation enthalpy)		
5.	Which of the follow	ring elements will ha	we the highest electr	onegativity?	

6. Various successive ionisation enthalpies (in kJ mol⁻¹) of an element are given below.

IE ₁	IE ₂	IE ₃	IE_4	${\rm IE}_5$
577.5	1,810	2,750	11,580	14,820

b) Nitrogen

The element is

a) Chlorine

- a) phosphorus
- b) Sodium
- c) Aluminium

c) Cesium

d) Silicon

d) Fluorine

7. In the third period the first ionization potential is of the order.

a) Na > Al > Mg > Si > P

b) Na < Al < Mg < Si < P

c) Mg > Na > Si > P > Al

d) Na < Al < Mg < Si < P

8. Identify the wrong statement.

a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius

b) Amongst isoelectric species greater the negative charge on the anion, larger is the ionic radius

c) Atomic radius of the elements increases as one moves down the first group of the periodic table

d) Atomic radius of the elements decreases as one moves across from left to right in the 2^{nd} period of the periodic table.

9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy

a) Al < O < C < Ca < F

b) Al < Ca < O < C < F

c) C < F < O < Al < Ca

d) Ca < Al < C < O < F

10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively is

a) I > Br > Cl > F

b) F > Cl > Br > I

c) Cl > F > Br > I

d) Br > I > Cl > F

11. Which one of the following is the least electronegative element?

a) Bromine

b) Chlorine

c) Iodine

d) Hydrogen

12. The element with positive electron gain enthalpy is

a) Hydrogen

b) Sodium

c) Argon

d) Fluorine

13. The correct order of decreasing electronegativity values among the elements X, Y, Z and A with atomic numbers 4, 8, 7 and 12 respectively

a) Y > Z > X > A

b) Z > A > Y > X

c) X > Y > Z > A

d) X > Y > A > Z

14. Assertion: Helium has the highest value of ionisation energy among all the elements known

Reason: Helium has the highest value of electron affinity among all the elements known

- a) Both assertion and reason are true and reason is correct explanation for the assertion
- b) Both assertion and reason are true but the reason is not the correct explanation for the assertion
- Assertion is true and the reason is false c)
- d) Both assertion and the reason are false
- The electronic configuration of the atom having maximum difference in first and second ionisation energies is

a)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^1$

b)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$

d)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^1$

- Which of the following is second most electronegative element? 16.
 - a) Chlorine
- b) Fluorine
- c) Oxygen
- d) Sulphur
- IE₁ and IE₂ of Mg are 179 and 348 kcal mol⁻¹ respectively. The energy required for the reaction Mg \rightarrow Mg²⁺ + 2 e⁻ is

In a given shell the order of screening effect is

a)
$$s > p > d > f$$
 b) $s > p > f > d$ c) $f > d > p > s$ d) $f > p > s > d$

b)
$$s > p > f > d$$

c)
$$f > d > p > s$$

d)
$$f > p > s > d$$

Which of the following orders of ionic radii is correct?

a)
$$H^- > H^+ > H$$

a)
$$H^- > H^+ > H$$
 b) $Na^+ > F^- > O^{2-}$ c) $F > O^{2-} > Na^+$ d) None of these

c)
$$F > O^{2-} > Na^+$$

- 20. The First ionisation potential of Na, Mg and Si are 496, 737 and 786 kJ mol⁻¹ respectively. The ionisation potential of Al will be closer to

Which one of the following is true about metallic character when we move from left 21. to right in a period and top to bottom in a group?

- a) Decreases in a period and increases along the group
- b) Increases in a period and decreases in a group
- c) Increases both in the period and the group
- d) Decreases both in the period and in the group
- 22. How does electron affinity change when we move from left to right in a period in the periodic table?
 - a) Generally increases

b) Generally decreases

c) Remains unchanged

- d) First increases and then decreases
- 23. Which of the following pairs of elements exhibit diagonal relationship?
 - a) Be and Mg
- b) Li and Mg
- c) Be and B
- d) Be and Al

II. Write brief answer to the following questions

- 24. Define modern periodic law.
- 25. What are isoelectronic ions? Give examples.
- 26. What is effective nuclear charge?
- 27. Is the definition given below for ionisation enthalpy is correct?
 - "Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"
- 28. Magnesium loses electrons successively to form Mg⁺, Mg²⁺ and Mg³⁺ ions. Which step will have the highest ionisation energy and why?
- 29. Define electronegativity.
- 30. How would you explain the fact that the second ionisation potential is always higher than first ionisation potential?
- 31. Energy of an electron in the ground state of the hydrogen atom is -2.8×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of kJ mol⁻¹.
- 32. The electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain
- 33. In what period and group will an element with Z = 118 will be present?
- 34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

35. Elements a, b, c and d have the following electronic configurations:

a:
$$1s^2$$
, $2s^2$, $2p^6$

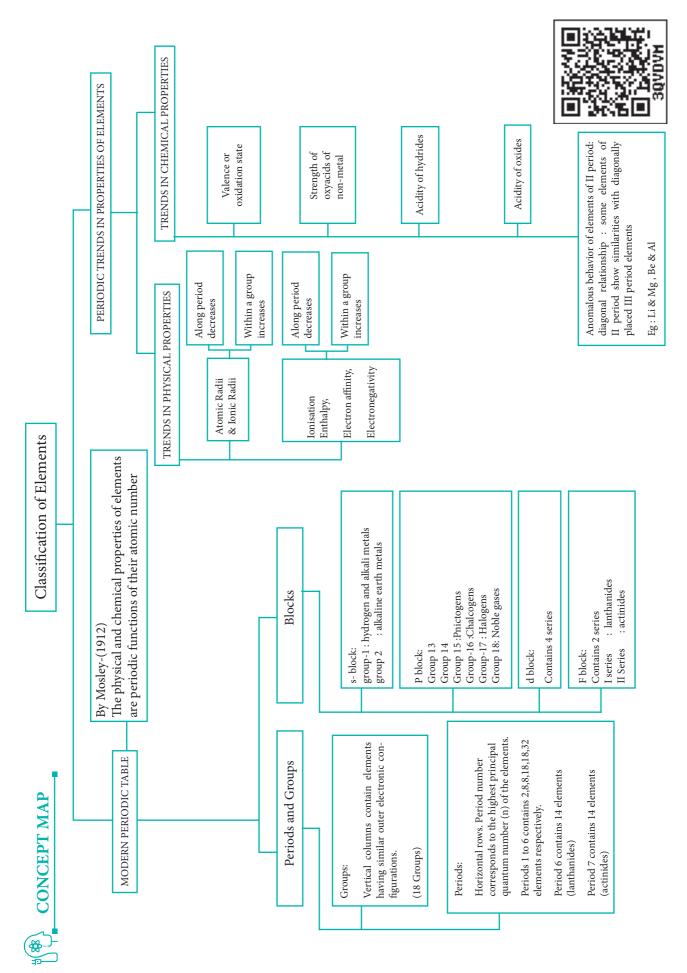
b:
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^1$

c:
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^6$

d:
$$1s^2$$
, $2s^2$, $2p^1$

Which elements among these will belong to the same group of periodic table

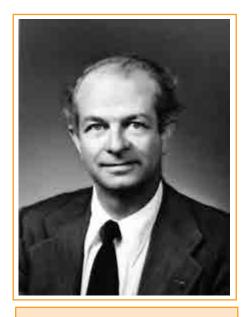
- 36. Give the general electronic configuration of lanthanides and actinides?
- 37. Why halogens act as oxidising agents?
- 38. Mention any two anomalous properties of second period elements.
- 39. Explain the pauling method for the determination of ionic radius.
- 40. Explain the periodic trend of ionisation potential.
- 41. Explain the diagonal relationship.
- 42. Why the first ionisation enthalpy of sodium is lower that that of magnesium while its second ionisation enthalpy is higher than that of magnesium?
- 43. By using paulings method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that $d_{K+-Cl_-} = 3.14$ A
- 44. Explain the following, give appropriate reasons.
 - (i) Ionisation potential of N is greater than that of O
 - (ii) First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.
 - (iii) The electron affinity values of Be, Mg and noble gases are zero and those of N (0.02 eV) and P (0.80 eV) are very low
 - (iv) The formation of $F^-(g)$ from F(g) is exothermic while that of $O^{2-}(g)$ from O(g) is endothermic.
- 45. What is screening effect? Briefly give the basis for pauling's scale of electronegativity.
- 46. State the trends in the variation of electronegativity in group and periods.





Chemical bonding





Linus Carl Pauling was an American chemist, biochemist, peace activist, author and educator. In addition to his contribution chemistry and also worked with many biologists.

He received the Nobel Prize in Chemistry in 1954 for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.

Learning Objectives (6)



After studying this unit students will be able to

- describe Kossel Lewis approach to chemical bonding
- explain the octet rule
- sketch the Lewis structures of simple molecules
- describe the formation of different types of bonds and bond parameters
- sketch the resonance structures for simple molecules
- apply the concept of electronegativity to explain the polarity of covalent bonds
- describe VSEPR theory and predict the shapes of simple molecules
- explain the valence bond approach for the formation of covalent bonds
- explain the different types of hybridisation involving s, p & d orbitals and sketch shapes of simple covalent molecules
- explain the molecular orbital theory, calculate the bond order and explain the magnetic properties of H₂, O₂, N₂ CO and NO
- describe metallic bonding briefly.

10.1 Introduction

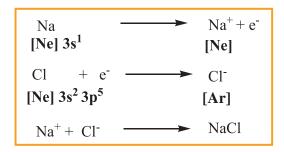
Diamond is very hard while its allotrope graphite is very soft. Gases like hydrogen and oxygen are diatomic while the inert gases are monoatomic. Carbon combines with chlorine to form carbon tetrachloride, which is a liquid and insoluble (immiscible) in water. Sodium combines with chlorine atom to form sodium chloride, a hard and brittle compound that readily dissolves in water. The possible reason for these observations lies in the type of interaction that exists between the atoms of these molecules and these interactions are responsible for holding the atoms/ions together. The interatomic attractive forces which hold the constituent atoms/ions together in a molecule are called chemical bonds.

Why do atoms combine only in certain combinations to form molecules? For example oxygen combines with hydrogen to give water (H₂O) and with carbon it gives carbon dioxide (CO₂). The structure of water is 'V' shaped while that of the carbon dioxide is linear. Such questions can be answered using the principles of chemical bonding. In this unit we will analyse the various theories and their principles, which were developed over the years to explain the nature of chemical bonding.

10.1.1 Kossel – Lewis approach to chemical bonding

A logical explanation for chemical bonding was provided by Kossel and Lewis in 1916. Their approach to chemical bonding is based on the inertness of the noble gases which have little or no tendency to combine with other atoms. They proposed that the noble gases are stable due to their completely filled outer shell electronic configuration. Elements other than noble gases, try to attain the completely filled electronic configurations by losing, gaining

or sharing one or more electrons from their outer shell. For example, sodium loses one electron to form Na⁺ ion and chlorine accepts that electron to give chloride ion (Cl⁻), enabling both atoms to attain the nearest noble gas configuration. The resultant ions, Na⁺ and Cl⁻ are held together by electrostatic attractive forces and the attractive force is called a chemical bond, more specifically an electrovalent bond.



G. N. Lewis proposed that the attainment of stable electronic configuration in molecules such as diatomic nitrogen, oxygen etc... is achieved by mutual sharing of the electrons. He introduced a simple scheme to represent the chemical bond and the electrons present in the outer shell of an atom, called Lewis dot structure. In this scheme, the valence electrons (outer shell electrons) of an element are represented as small dots around the symbol of the element. The first four valence electrons are denoted as single dots around the four sides of the atomic symbol and then the fifth onwards, the electrons are denoted as pairs. For example, the electronic configuration of nitrogen is 1s², 2s², 2p³. It has 5 electrons in its outer shell (valence shell). The Lewis structure of nitrogen is as follows.



Fig 10.1 Lewis Structure of Nitrogen atom

Similarly, Lewis dot structure of carbon, oxygen can be drawn as shown below.



Fig 10.2 Lewis Structures of C & O atoms

Only exception to this is helium which has only two electrons in its valence shell which is represented as a pair of dots (duet).



Fig 10.3 Lewis Structures of He atoms

Octet rule

The idea of Kossel – Lewis approach to chemical bond lead to the octet rule, which states that "the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valence shell)".

10.2 Types of chemical bonds

The chemical bonds can be classified based on the nature of the interaction between the bonded atoms. Two major types of chemical bonds are covalent bonds and ionic bonds. Generally metals reacts with non-metals to form ionic compounds, and the covalent bonds are present in the compounds formed by nonmetals.

10.2.1 Covalent bonds:

Do you know all elements (except noble gases) occurs either as compounds or as polyatomic molecules? Let us consider hydrogen gas in which two hydrogen atoms bind to give a dihydrogen molecule. Each hydrogen atom has one electron and it requires one more electron to attain the electronic configuration of the nearest noble gas helium. Lewis suggested that both hydrogen atoms will attain the stable

configuration by mutually sharing the electrons available with them. Similarly, in the case of oxygen molecule, both the oxygen atoms share two electron pairs between them and in nitrogen molecule three electron pairs are shared between two nitrogen atoms. This type of mutual sharing of one or more pairs of electrons between two combining atoms results in the formation of a chemical bond called a covalent bond. If two atoms share just one pair of electron a single covalent bond is formed as in the case of hydrogen molecule. If two or three electron pairs are shared between the two combining atoms, then the covalent bond is called a double bond or a triple bond, respectively.

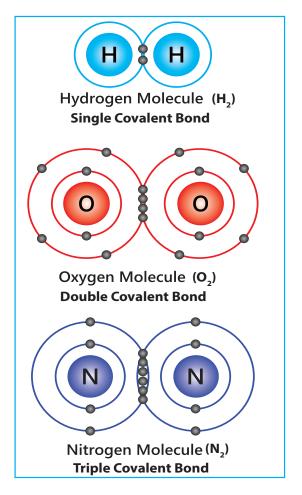


Fig 10. 4 Representation of Lewis Structures of covalent bonds

10.2.2 Representing a covalent bond - Lewis structure (Lewis dot structure)

Lewis structure (Lewis dot structure) is a pictorial representation of covalent bonding between the combining atoms. In this structure the shared valence electrons are represented as a pair of dots between the combining atoms and the unshared electrons of the atoms are represented as a pair of dots (lone pair) on the respective individual atoms.

The Lewis dot structure for a given compound can be written by following the steps given below. Let us understand these steps by writing the Lewis structure for water.

1. Draw the skeletal structure of the molecule. In general, the most electronegative atom is placed at the centre. Hydrogen and fluorine atoms should be placed at the terminal positions. For water, the skeletal structure is

2. Calculate the total number of valence electrons of all the atoms in the molecule. In case of polyatomic ions the charge on ion should also be considered during the calculation of the total number of valence electrons. In case of anions the number of negative charges should be added to the number of valence electrons. For positive ions the total number of positive charges should be subtracted from the total number of valence electrons.

In water, total number of valence electron = $[2 \times 1]$ (valence electron of

- hydrogen)] + $[1 \times 6$ (valence electrons of oxygen)] = 2 + 6 = 8.
- 3. Draw a single bond between the atoms in the skeletal structure of the molecule. Each bond will account for two valence electrons (a bond pair). For water, we can draw two bonds accounting for four valence electrons as follows.

$$H - O - H$$

4. Distribute the remaining valence electrons as pairs (lone pair), giving octet (only duet for hydrogen) to the atoms in the molecule. The distribution of lone pairs starts with the most electronegative atoms followed by other atoms.

In case of water, the remaining four electrons (two lone pairs) are placed on the most electronegative central oxygen, giving octet.

5. Verify weather all the atoms satisfy the octet rule (for hydrogen duet). If not, use the lone pairs of electrons to form additional bond to satisfy the octet rule.

In case of water, oxygen has octet and the hydrogens have duets, hence there is no need for shifting the lone pairs. The Lewis structure of water is as follows

Fig 10. 5 Lewis structure of water

Let us draw the Lewis structure for nitric acid.

1. Skeletal structure

Н	O	N	О
		O	

- 2. Total number of valence electrons in HNO₃
 - = $[1 \times 1(hydrogen)] + [1 \times 5(nitrogen)]$ + $[3 \times 6(oxygen)] = 1 + 5 + 18 = 24$
- 3. Draw single bonds between atoms. Four bonds can be drawn as shown in the figure for HNO₃ which account for eight electrons (4 bond pairs).

4. Distribute the remaining sixteen (24
 - 8= 16) electrons as eight lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens

(three each) to satisfy their octet and two pairs are distributed to the oxygen that is connected to hydrogen to satisfy its octet.

5. Verify weather all the atoms have octet configuration. In the above distribution, the nitrogen has one pair short for octet. Therefore, move one of the lone pair from the terminal oxygen to form another bond with nitrogen.

The Lewis structure of nitric acid is given as

Fig 10. 6 Lewis structure of Nitric acid

Table 10.1: The Lewis dot structures for some molecules

S. No	Molecule	Lewis Stru	ıcture
1.	Sulphur trioxide (SO ₃)	;;: ;;;—s=;;	; <u>Ö</u> : ;Ö: S ∷ Ö
2.	Ammonia (NH ₃)	H H—N—H	<u>н</u> н:n:н
3.	Methane	H H—C—H H	н:С:н н:С:н н
4.	Dinitrogen Pentoxide (N_2O_5)	:Ö: :Ö: 	:Ö: :Ö: :Ö: :Ö:





It is to be noted that nearly in all their compounds, certain elements form a fixed number of bonds. For example, Fluorine forms only one bond. Hydrogen, oxygen, nitrogen and carbon atoms form one, two, three and four bonds, respectively.

Evaluate Yourself

- 1) Draw the lewis structures for
 - Nitrous acid (HNO₂) i)
 - ii) Phosphoric acid
 - iii) Sulphur troxide (SO₂)

10.2.3 Formal charge:

Let us draw the Lewis structure for carbon dioxide.

1. Skeletal structure



Total number of valence electrons in CO,

=
$$[1 \times 4(carbon)] + [2 \times 6(oxygen)] =$$

4+ 12 = 16

Draw single bonds between atoms. Two bonds can be drawn as shown in the figure for CO₂ which accounts for four electrons (2 bond pairs).

Distribute the remaining electrons (16 - 4= 12) as six lone pairs starting from most electronegative atom, the oxygen. Six lone pairs are distributed to the two terminal oxygens (three each) to satisfy their octet.

Verify weather all the atoms have octet configuration. In the above distribution, the central carbon has two pair short

for octet. Therefore, to satisfy the octet rule two lone pairs from one oxygen or one pair from each oxygen can be moved to form multiple bonds, leading the formation of two possible structures for carbon dioxide as shown below

Fig 10.7 (a) two possible structures for carbon dioxide

Similarly, the Lewis structure for many molecules drawn using the above steps gives more than one acceptable structure. Let us consider the above mentioned two structures of carbon dioxide.

Which above forms one the represents the best distribution of electrons in the molecule. To find an answer, we need to know the formal charge of each atom in the Lewis structures. Formal charge of an atom in a molecule, is the electrical charge difference between the valence electron in an isolated atom and the number of electrons assigned to that atom in the Lewis structure.

Formal charge of an atom =
$$N_v - \left(N_l + \frac{N_b}{2}\right)$$

Where,

- Number of valence electron of atom N..in its isolated state.
- Number of electrons present as lone N_{i} pairs around the atom in the Lewis structure
- N_b Number of electrons present in bonds around the atom (bond pairs) in the

Lewis structure]

Now let us calculate the formal charge on all atoms in both structures,

For Structure 1,

Formal charge on carbon =
$$N_v - \left(N_l + \frac{N_b}{2}\right)$$

$$=4-\left(0+\frac{8}{2}\right)=0$$

Formal charge on oxygen = $6 - \left(4 + \frac{4}{2}\right)$

= 0 (for both oxygens)

For structure 2

Formal charge on carbon

$$= N_{v} - \left(N_{l} + \frac{N_{b}}{2} \right)$$
$$= 4 - \left(0 + \frac{8}{2} \right) = 0$$

Formal charge on singly bonded oxygen

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

Formal charge on triply bonded oxygen

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

$$0 0 0 0 +1 0 -1
0 = C = 0 :0 = C - 0 :$$
structure 1 structure 2

Fig 10. 7 (b) two possible structures for carbon dioxide (with formal charges)

After calculating the formal charges, the best representation of Lewis structure can be selected by using following guidelines.

1. A structure in which all formal charges are zero preferred over the one with charges.

- 2. A structure with small formal charges is preferred over the one with higher formal charges.
- 3. A structure in which negative formal charges are placed on the most electronegative atom is preferred.

In case of CO₂ structures, the structure one is preferred over the structure 2 as it has zero formal charges for all atoms.

10.2.4 Lewis structures for exceptions to octet rule

The octet rule is useful for writing Lewis structures for molecules with second period element as central atoms. In some molecules, the central atoms have less than eight electrons around them while some others have more than eight electrons. Exception to the octet rule can be categorized into following three types.

- 1. Molecules with electron deficient central atoms
- 2. Molecules containing odd electrons
- 3. Molecules with expanded valence shells

Molecules with electron deficient central atoms

Let us consider boron trifluoride, as an example. The central atom boron has three valence electron and each fluorine has seven valence electrons. The Lewis structure is

Fig 10. 8 (a) Lewis structure of BF₃

In the above structure, only six

electrons around boron atom. Moving a lone pair from one of the fluorine to form additional bond as shown below.

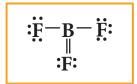


Fig 10. 8 (b) Lewis structure of BF₃

However, the above structure is unfavourable as the most electronegative atom fluorine shows positive formal charge and hence the structure with incomplete octet is the favourable one. Molecules such as BCl₃, BeCl₂, etc... also have incomplete octets.

Molecules containing odd electrons

Few molecules have a central atom with an odd number of valence electrons. For example, in nitrogen dioxide and nitric oxide all the atoms does not have octet configuration. The lewis structure of the above molecules are shown in the figure.

$$\ddot{N} = \ddot{N} = \ddot{N} - \ddot{N} = \dot{N} - \ddot{N}$$

Fig 10. 9 Lewis structures of Nitric oxide and Nitrogen dioxide (with formal charges)

Molecules with expanded valence shells

In molecules such as sulphur hexafluoride (SF₆), phosphorous pentachloride (PCl₅) the central atom has more than eight valence electrons around them. Here the central atom can accommodate additional electron pairs by using outer vacant d orbitals. In SF₆ the central atom sulphur is surrounded by six

bonding pair of electrons or twelve electrons.

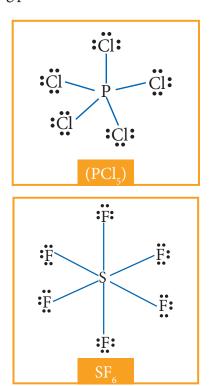


Fig 10. 10 Lewis structures for SF_6 and PCl_5

Evaluate Yourself

2) Calculate the formal charge on each atom of carbonyl chloride (COCl₂)

10.3 Ionic or electrovalent bond

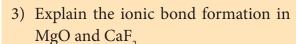
When the electronegativity difference between the two combining atoms is large, the least electronegative atom completely transfers one or more of its valence electrons to the other combining atom so that both atoms can attain the nearest inert gas electronic configuration. The complete transfer of electron leads to the formation of a cation and an anion. Both these ions are held together by the electrostatic attractive force which is known as ionic bond.

Let us consider the formation potassium chloride. The electronic configuration of potassium and chlorine are Potassium (K): [Ar] 4s1

Chlorine (Cl): [Ne]3s², 3p⁵

Potassium has one electron in its valence shell and chlorine has seven electron in its valence shell. By loosing one electron potassium attains the inert gas electronic configuration of argon and becomes a unipositive cation (K⁺) and chlorine accepts this electron to become uninegative chloride ion (Cl⁻) there by attaining the stable electronic configuration of argon. These two ions combine to form an ionic crystal in which they are held together by electrostatic attractive force. The energy required for the formation of one mole of K+ is 418.81 kJ (ionization energy) and the energy released during the formation of one mole of Cl- is -348.56 kJ (electron gain enthalpy). The sum of these two energies is positive (70.25 kJ) However, during the formation of one mole potassium chloride crystal from its constituent ions, 718 kJ energy is released. This favours the formation of KCl and its stabilises.

Evaluate Yourself



10.4 Coordinate covalent bond

In the formation of a covalent bond, both the combining atoms contribute one electron each and the these electrons are mutually shared among them. However, in certain bond formation, one of the combining atoms donates a pair of electrons i.e. two electrons which are necessary for the covalent bond formation, and these electrons are shared by both the combining atoms.

These type of bonds are called coordinate covalent bond or coordinate bond. The combining atom which donates the pair of electron is called a donor atom and the other atom an acceptor atom. This bond is denoted by an arrow starting from the donor atom pointing towards the acceptor atom. (Later in coordination compound, we will refer the donor atom as ligand and the acceptor atom as central-metal atom/ion.

For Example, in ferrocynide ion $[Fe(CN)_6]^{4-}$, each cyanide ion (CN^-) donates a pair of electrons to form a coordinate bond with iron (Fe^{2+}) and these electrons are shared by Fe^{2+} and CN^- .

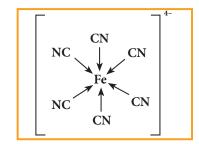


Fig 10. 11 Structure of Ferrocyanide ion

In certain cases, molecules having a lone pair of electrons such as ammonia donates its pair to an electron deficient molecules such as BF₃. to form a coordinate

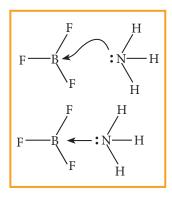


Fig 10. 12 Structure of $BF_3 \rightarrow NH_3$

10.5 Bond parameters

A covalent bond is characterised by parameters such as bond length, bond angle, bond order etc... A brief description of some of the bond parameters is given below.

10.5.1 Bond length

The distance between the nuclei of the two covalently bonded atoms is called bond length. Consider a covalent molecule A-B. The bond length is given by the sum of the radii of the bonded atoms $(r_A + r_B)$. The length of a bond can be determined by spectroscopic, x-ray diffraction and electron-diffraction techniques The bond length depends on the size of the atom and the number of bonds (multiplicity) between the combining atoms.

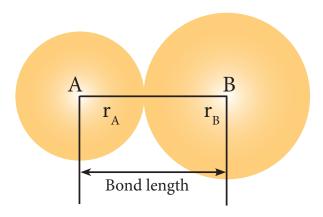


Fig 10. 13 Bond length of covalent molecule A-B

Greater the size of the atom, greater will be the bond length. For example, carbon-carbon single bond length (1.54 Å) is longer than the carbon-nitrogen single bond length (1.43 Å).

Increase in the number of bonds between the two atoms decreases the bond

length. For example, the carbon-carbon single bond is longer than the carbon-carbon double bond (1.33 Å) and the carbon-carbon triple bond (1.20 Å).

10.5.2 Bond order

The number of bonds formed between the two bonded atoms in a molecule is called the bond order. In Lewis theory, the bond order is equal to the number of shared pair of electrons between the two bonded atoms. For example in hydrogen molecules, there is only one shared pair of electrons and hence, the bond order is one. Similarly, in H₂O, HCl, Methane, etc the central atom forms single bonds with bond order of one.

Table 10.2 Bond order of some common bonds:

S. No.	Molecule	Bonded atoms	Bond order (No. of shared pair of electrons between bonded atoms)
1	H_{2}	Н-Н	1
2	O_2	O=O	2
3	N_2	N≡N	3
4	HCN	C≡N	3
5	НСНО	C=O	2
6	$\mathrm{CH}_{_4}$	С–Н	1
7	C_2H_4	C=C	2

10.5.3 Bond angle

Covalent bonds are directional in nature and are oriented in specific directions in space. This directional nature creates a fixed angle between two covalent bonds in a molecule and this angle is termed as bond angle. It is usually expressed in degrees. The bond angle can be determined by spectroscopic methods and it can give some idea about the shape of the molecule.

Table 10.3 Bond angles for some common molecules

S. No.	Molecule	Atoms defining the angle	Bond angle (°)
1	CH ₄	Н-С-Н	109° 28′
2	NH ₃	H-N-H	107° 18'
3	H ₂ O	Н-О-Н	104° 35′

10.5.4 Bond enthalpy

The bond enthalpy is defined as the minimum amount of energy required to break one mole of a particular bond in molecules in their gaseous state. The unit of bond enthalpy is kJ mol⁻¹. Larger the bond enthalpy, stronger will be the bond. The bond energy value depends on the size of the atoms and the number of bonds between the bonded atoms. Larger the size of the atom involved in the bond, lesser is the bond enthalpy.

In case of polyatomic molecules with, two or more same bond types, in the term average bond enthalpy is used. For such bonds, the arithmetic mean of the bond energy values of the same type of bonds is considered as average bond enthalpy. For example in water, there are two OH bonds present and the energy needed to break them are not same.

$$H_2O(g) \rightarrow H(g) + OH(g)$$
 $\Delta H_1 = 502 \text{ kJ mol}^{-1}$
 $OH(g) \rightarrow H(g) + O(g)$ $\Delta H_2 = 427 \text{ kJ mol}^{-1}$

The average bond enthalpy of OH bond in water = $\frac{502+427}{2}$ = 464.5 kJ mol⁻¹

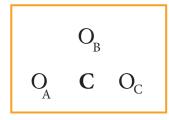
Table 10.4 Bond lengths and bond enthalpies of some common bonds:

S. No.	Bond type	Bond Enthalpy (kJ mol ⁻¹)	Bond Length (Å)
1	Н-Н	432	0.74
2	H-F	565	0.92
3	H-Cl	427	1.27
4	H-Br	363	1.41
5	H-I	295	1.61
6	С-Н	413	1.09
7	C-C	347	1.54
8	C-Si	301	1.86
9	C-N	305	1.47
10	C-O	358	1.43
11	C-P	264	1.87
12	C-S	259	1.81
13	C-F	453	1.33
14	C-Cl	339	1.77
15	C-Br	276	1.94
16	C-I	216	2.13

10.5.5 Resonance

When we write Lewis structures for a molecule, more than one valid Lewis structures are possible in certain cases. For example let us consider the Lewis structure of carbonate ion $[CO_3]^{2-}$.

The skeletal structure of carbonate ion (The oxygen atoms are denoted as O_A , $O_B & O_C$



Total number of valence electrons = [1 x 4(carbon)] + [3 x 6 (oxygen)] + [2 (charge)] = 24 electrons.

Distribution of these valence electrons gives us the following structure.

Complete the octet for carbon by moving a lone pair from one of the oxygens (O_A) and write the charge of the ion (2-) on the upper right side as shown in the figure.

$$\begin{bmatrix} \vdots \vdots \\ \vdots \\ \vdots \\ A = C - \vdots \end{bmatrix}^{2-}$$

Fig 10. 14 (a) Lewis Structure of CO₃²⁻

In this case, we can draw two additional Lewis structures by moving the lone pairs from the other two oxygens

 $(O_B \text{ and } O_C)$ thus creating three similar structures as shown below in which the relative position of the atoms are same. They only differ in the position of bonding and lone pair of electrons. Such structures are called resonance structures (canonical structures) and this phenomenon is called resonance.

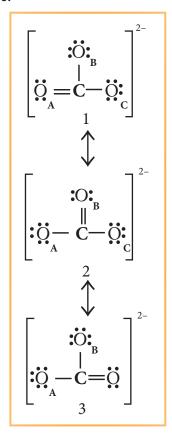


Fig 10. 14 (b) Resonance structures of CO₃²⁻

It is evident from the experimental results that all carbon-oxygen bonds in carbonate ion are equivalent. The actual structure of the molecules is said to be the resonance hybrid, an average of these three resonance forms. It is important to note that carbonate ion does not change from one structure to another and vice versa. It is not possible to picturise the resonance hybrid by drawing a single Lewis structure. However, the following structure gives a qualitative idea about the correct structure.

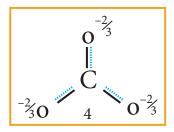


Fig 10. 14 (c) Resonance Hybrid structures of CO,2-

It is found that the energy of the resonance hybrid (structure 4) is lower than that of all possible canonical structures (Structure 1, 2 & 3). The difference in energy between structure 1 or 2 or 3, (most stable canonical structure) and structure 4 (resonance hybrid) is called resonance energy.

Evaluate Yourself



- 4) Write the resonance structures for
 - Ozone molecule ii) N₂O

10.5.6 Polarity of Bonds

Partial ionic character in covalent bond:

When a covalent bond is formed between two identical atoms (as in the case of H2, O2, Cl2 etc...) both atoms have equal tendency to attract the shared pair of electrons and hence the shared pair of electrons lies exactly in the middle of the nuclei of two atoms. However, in the case of covalent bond formed between atoms having different electronegativities, the atom with higher electronegativity will have greater tendency to attract the shared pair of electrons more towards itself than the other atom. As a result the cloud of shared electron pair gets distorted.

Let us consider the covalent bond between hydrogen and fluorine in hydrogen fluoride. The electronegativities of hydrogen and fluorine on Pauling's scale are 2.1 and 4 respectively. It means that fluorine attracts the shared pair of electrons approximately twice as much as the hydrogen which leads to partial negative charge on fluorine and partial positive charge on hydrogen. Hence, the H-F bond is said to be polar covalent bond.

Here, a very small, equal and opposite charges are separated by a small distance (91 pm) and is referred to as a dipole.

Dipole moment:

The polarity of a covalent bond can be measured in terms of dipole moment which is defined as

$$\mu = q \times 2d$$

Where μ is the dipole moment, q is the charge and 2d is the distance between the two charges. The dipole moment is a vector and the direction of the dipole moment vector points from the negative charge to positive charge.

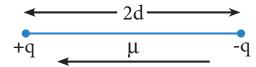


Fig 10. 15 Representation of Dipole

The unit for dipole moment is columb meter (C m). It is usually expressed in Debye unit (D). The conversion factor is 1 Debye = $3.336 \times 10^{-30} \text{ C m}$

Diatomic molecules such as H₂, O₂, F_2 etc... have zero dipole moment and are called non polar molecules and molecules such as HF, HCl, CO, NO etc... have non zero dipole moments and are called polar molecules.

Molecules having polar bonds will not necessarily have a dipole moment. For example, the linear form of carbon dioxide has zero dipole moment, even though it has two polar bonds. In CO₂, the dipole moments of two polar bonds (CO) are equal in magnitude but have opposite direction. Hence, the net dipole moment of the CO₂ is, $\mu = \mu_1 + \mu_2 = \mu_1 + (-\mu_1) = 0$

$$\frac{O = C = O}{\mu_1}$$
In this case $\mu = \overrightarrow{\mu_1} + \overrightarrow{\mu_2}$

$$= \overrightarrow{\mu_1} + \overrightarrow{(-\mu_1)} = 0$$

Incase of water net dipole moment is the vector sum of μ_1 + μ_2 as shown.

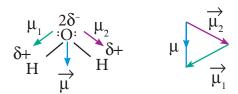


Fig 10. 16 Dipole moment in water

Dipole moment in water is found to be 1.85D

Table 10. 5 Dipole moments of common molecules

S. No.	Molecule	Dipole moment (in D)
1	HF	1.91
2	HCl	1.03
3	H_2O	1.85
4	NH ₃	1.47
5	CHCl ₃	1.04

The extent of ionic character in a covalent bond can be related to the electro negativity difference to the bonded atoms. In a typical polar molecule, $A^{\delta-}$ - $B^{\delta+}$, the electronegativity difference $(\chi_{\text{A}}\text{-}\ \chi_{\text{B}})$ can be used to predict the percentage of ionic character as follows.

If the electronegativity difference $(\chi_A - \chi_B)$, is

equal to 1.7, then the bond A-B has 50% ionic character

if it is greater than 1.7, then the bond A-B has more than 50% ionic character,

and if it is lesser than 1.7, then the bond A-B has less than 50% ionic character.

Evaluate Yourself



5) Of the two molecules OCS and CS₂ which one has higher dipole moment value? why?

Partial covalent character in ionic bonds:

Like the partial ionic character in covalent compounds, ionic compounds show partial covalent character. For example, the ionic compound, lithium chloride shows covalent character and is soluble in organic solvents such as ethanol.

The partial covalent character in ionic compounds can be explained on the basis of a phenomenon called polarisation. We know that in an ionic compound, there is an electrostatic attractive force between the cation and anion. The positively charged cation attracts the valence electrons of anion while repelling the nucleus. This causes a distortion in the electron cloud of the anion and its electron density drifts towards the cation, which results in some sharing of the valence electrons between these ions. Thus, a partial covalent character is developed between them. This phenomenon is called polarisation.

The ability of a cation to polarise an anion is called its polarising ability and the tendency of an anion to get polarised is called its polarisability. The extent of polarisation in an ionic compound is given by the Fajans rules

Fajans Rules

(i) To show greater covalent character, both the cation and anion should have high charge on them. Higher the positive charge on the cation, greater will be the attraction on the electron cloud of the anion. Similarly higher the magnitude of negative charge on the anion, greater is its polarisability. Hence, the increase in charge on cation or in anion increases the covalent character

Let us consider three ionic compounds aluminum chloride, magnesium chloride and sodium chloride. Since the charge of the cation increase in the order $Na^+ < Mg^{2+} < Al^{3+}$, the covalent character also follows the same order $NaCl < MgCl_2 < AlCl_3$.

(ii) The smaller cation and larger anion show greater covalent character due to the greater extent of polarisation.

Lithium chloride is more covalent than sodium chloride. The size of Li⁺ is smaller than Na⁺ and hence the polarising power of Li⁺ is more. Lithium iodide is more covalent than lithium chloride as the size of I⁻ is larger than the Cl⁻. Hence I⁻ will be more polarised than Cl⁻ by the cation, Li⁺.

(iii) Cations having ns² np⁶ nd¹⁰ configuration show greater polarising power than the cations with ns² np⁶ configuration. Hence, they show greater covalent character.

CuCl is more covalent than NaCl. Compared to Na $^+$ (1.13 Å) . Cu $^+$ (0.6 Å) is small and have $3s^2$ $3p^6$ $3d^{10}$ configuration.

Electronic configuration of Cu⁺ [Ar] 3s², 3p⁶, 3d¹⁰

Electronic Configuration of Na⁺ [He] 2s², 2p⁶

10.6 Valence Shell Electron Pair Repulsion (VSEPR) theory

Lewis concept of structure of molecules deals with the relative position of atoms in the molecules and sharing of electron pairs between them. However, we cannot predict the shape of the molecule using Lewis concept. Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules.

Important principles of VSEPR Theory are as follows:

- 1. The shape of the molecules depends on the number of valence shell electron pair around the central atom.
- 2. There are two types of electron pairs namely bond pairs and lone pairs. The bond pair of electrons are those shared between two atoms, while the lone pairs are the valence electron pairs that are not involved in bonding.
- 3. Each pair of valence electrons around the central atom repels each other and hence, they are located as far away as possible in three dimensional space to minimize the repulsion between them.

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4. The repulsive interaction between the different types of electron pairs is in the following order.

The lone pair of electrons are localised only on the central atom and interacts with only one nucleus whereas the bond pairs are shared between two atoms and they interact with two nuclei. Because of this the lone pairs occupy more space and have greater repulsive power than the bond pairs in a molecule.

The following Table illustrates the shapes of molecules predicted by VSEPR theory. Consider a molecule AB_x where A is the central atom and x represents the number of atoms of B covalently bonded to the central atom A. The lone pairs present in the atoms are denoted as L.

Table 10. 6 Shapes of molecules predicted by VSEPR theory.

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
2	AB_2	2	-	B A B	B A B	BeCl ₂ , HgCl ₂ , CO ₂ , CS ₂ , HCN, BeF ₂
3	AB_3	3	-	B A A B Trigonal planar	B B B Trigonal planar	BF ₃ , BCl ₃ , NO ₃ , BF ₃ , CO ₃ ²⁻
J	AB_2L	2	1	B Bent or V - Shape	B Bent or V - Shape	HCHO, SO ₂ , O ₃ , PbCl ₂ , SnBr ₂
4	$\mathrm{AB}_{_4}$	4	-	A B B B B Tetrahedral	B 109.5° B B Tetrahedral	CH ₄ , CCl ₄ , CCl ₂ F ₂ , SO ₄ ²⁻ ,ClO ₄ ⁻ , NH ₄ ⁺

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Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_3L	3	1	B B B pyramidal	B B pyramidal	NH ₃ , PF ₃ , ClO ₃ ⁻ , H ₃ O ⁺ ,
	AB_2L_2	2	2	B Bent (V Shaped)	Bent (V Shaped)	H ₂ O, OF ₂ , SCl ₂
5	$\mathrm{AB}_{_{5}}$	5	-	B B B B Trigonal bipyramidal	B B B B Trigonal bipyramidal	PCl ₅ , ASF ₅ , SOF ₄
	$\mathrm{AB}_4\mathrm{L}$	4	1	Seesaw	B B Seesaw	SF ₄ , XeO ₂ F ₂ , IF ₄ ⁺ , IO ₂ F ₂ ⁻
	AB_3L_2	3	2	B B T shaped	B———A: B B T Shaped	BrF ₃ , ClF ₃ ,

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Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_2L_3	2	3	B A B Linear	B A A B Linear	XeF ₂ , I ₃ , IF ₂
	AB_6	6	-	B B B B Octathedral	B B B	SF ₆ , IOF ₅ ,
6	$\mathrm{AB}_5\mathrm{L}$	5	1	B B B B Square pyramidal	B B Square pyramidal B	BrF₅, IF₅, TeF₅, XeOF₄,
	$\mathrm{AB_4L_2}$	4	2	B A B Square planar	B Square Planar B	XeF ₄ , ICl ₄
7	$\mathrm{AB}_{_{7}}$	7	-	B B B B B	B B B B pentagonal bi-pyramidal	IF_{7}

Evaluate Yourself

- 6) Arrange the following in the decreasing order of Bond angle
 - i) CH₄, H₂O, NH₃ ii) C₂H₂, BF₃, CCl₄

10.7 Valence Bond Theory

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. The wave mechanical treatment of VB theory is beyond the scope of this textbook. A simple qualitative treatment of VB theory for the formation of hydrogen molecule is discussed below.

Consider a situation wherein two hydrogen atoms (H_a and H_b) are separated by infinite distance. At this stage there is no interaction between these two atoms and the potential energy of this system is arbitrarily taken as zero. As these two atoms approach each other, in addition to the electrostatic attractive force between the nucleus and its own electron (purple arrows), the following new forces begins to operate.

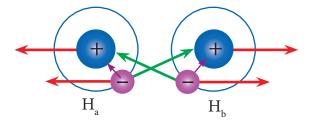


Fig 10. 17 (a) VB theory for the formation of hydrogen molecule

The new attractive forces (green arrows) arise between

- (i) nucleus of H_a and valence electron of H_b
- (ii) nucleus of H_b and the valence electron of H_a

The new repulsive forces (red arrows) arise between

- (i) the nucleus of H_a and H_b
- (ii) valence electrons of H_a and H_b.

The attractive forces tend to bring H_a and H_b together whereas the repulsive forces tends to push them apart. At the initial stage, as the two hydrogen atoms approach each other, the attractive forces are stronger than the repulsive forces and the potential energy decreases. A stage is reached where the net attractive forces are exactly balanced by repulsive forces and the potential energy of the system acquires a minimum energy.

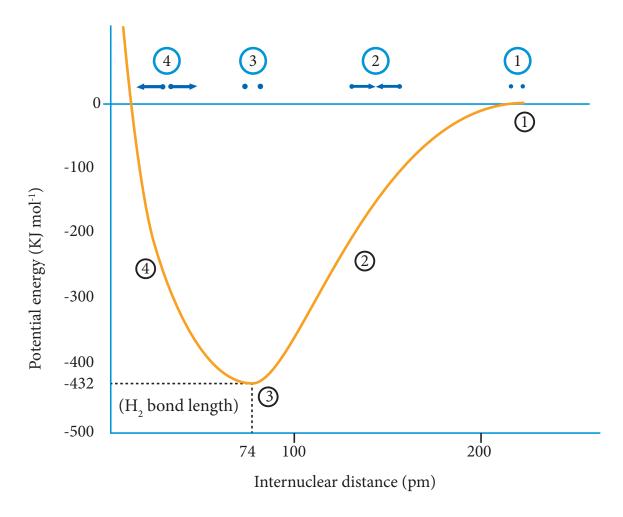


Fig 10. 17 (b) VB theory for the formation of hydrogen molecule

At this stage, there is a maximum overlap between the atomic orbitals of H_a and H_b , and the atoms H_a and H_b are now said to be bonded together by a covalent bond. The internuclear distance at this stage gives the H-H bond length and is equal to 74 pm. The liberated energy is 436 kJ mol⁻¹ and is known as bond energy. Since the energy is released during the bond formation, the resultant molecule is more stable. If the distance between the two atoms is decreased further, the repulsive forces dominate the attractive forces and the potential energy of the system sharply increases

10.7.1 Salient features of VB Theory:

- (i) When half filled orbitals of two atoms overlap, a covalent bond will be formed between them.
- (ii) The resultant overlapping orbital is occupied by the two electrons with opposite spins. For example, when H_2 is formed, the two 1s electrons of two hydrogen atoms get paired up and occupy the overlapped orbital.
- (iii) The strength of a covalent bond depends upon the extent of overlap of atomic orbitals. Greater the overlap, larger is the energy released and stronger will be the bond formed.

(iv) Each atomic orbital has a specific direction (except s-orbital which is spherical) and hence orbital overlap takes place in the direction that maximizes overlap

Let us explain the covalent bond formation in hydrogen, fluorine and hydrogen fluoride using VB theory.

10.8 Orbital Overlap

When atoms combines to form a covalent molecule, the atomic orbitals of the combining atoms overlap to form a covalent bond. The bond pair of electrons will occupy the overlapped region of the orbitals. Depending upon the nature of overlap we can classify the covalent bonding between the two atoms as sigma (σ) and pi (π) bonds.

10.8.1 Sigma and Pi bonds

When two atomic orbitals overlap linearly along the axis, the resultant bond is called a sigma (σ) bond. This overlap is also called 'head-on overlap' or 'axial overlap'. Overlap involves an s orbital (s-s and s-p overlaps) will always result in a sigma bond as the s orbital is spherical. Overlap between two p orbitals along the molecular axis will also result in sigma bond formation. When we consider x-axis as molecular axis, the p_x - p_x overlap will result in σ -bond.

When two atomic orbitals overlaps sideways, the resultant covalent bond is called a pi (π) bond. When we consider x-axis as molecular axis, the p_y - p_y and p_z - p_z overlaps will result in the formation of a π -bond.

Following examples will be useful to understand the overlap:

10.8.2 Formation of hydrogen (H₂) Molecule

Electronic configuration of hydrogen atom is 1s¹

During the formation of H_2 molecule, the 1s orbitals of two hydrogen atoms containing one unpaired electron with opposite spin overlap with each other along the internuclear axis. This overlap is called s-s overlap. Such axial overlap results in the formation of a σ -covalent bond.

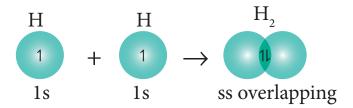


Fig 10. 18 Formation of hydrogen molecule

Formation of fluorine molecule (F₂):

Valence shell electronic configuration of fluorine atom : $2s^2 2p_x^2$, $2p_y^2$, $2p_z^1$

When the half filled p_z orbitals of two fluorine overlaps along the z-axis, a σ -covalent bond is formed between them.

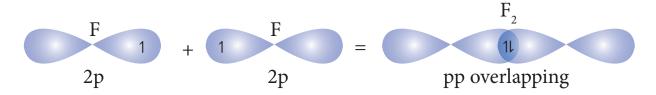


Fig 10. 19 Formation of F, Molecule

Formation of HF molecule:

Electronic configuration of hydrogen atom is 1s¹

Valence shell electronic configuration of fluorine atom : $2s^2 2p_x^2$, $2p_y^2$, $2p_z^1$

When half filled 1s orbital of hydrogen linearly overlaps with a half filled $2p_z$ orbital of fluorine, a σ -covalent bond is formed between hydrogen and fluorine.

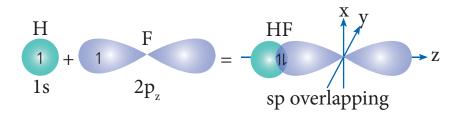


Fig 10.20 Formation of HF Molecule

Formation of oxygen molecule (O₂):

Valence shell electronic configuration of oxygen atom : $2s^2 2p_x^2$, $2p_y^1$, $2p_z^1$

			π bond	σ bond
Oxygen 1	11	11	1	1
	$2s^2$	$2p_x^2$	$2p_y^1$	$2p_z^1$
Oxygen 2	11	11	1	1
	$2s^2$	$2p_{x}^{2}$	$2p_y^1$	$2p_{z}^{1}$

When the half filled p_z orbitals of two oxygen overlaps along the z-axis (considering molecular axis as z axis), a σ -covalent bond is formed between them. Other two half filled p_y orbitals of two oxygen atoms overlap laterally (sideways) to form a π -covalent bond between

the oxygen atoms. Thus, in oxygen molecule, two oxygen atoms are connected by two covalent bonds (double bond). The other two pair of electrons present in the 2s and $2p_x$ orbital do not involve in bonding and remains as lone pairs on the respective oxygen.

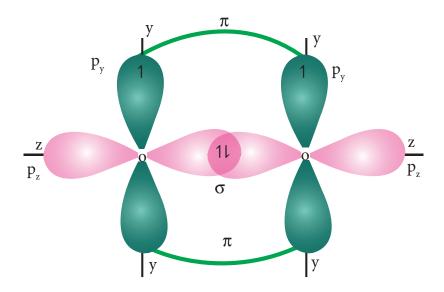


Fig 10. 21 Formation of π bond in O_2 Molecule



7) Bond angle in PH₄ is higher than in PH₃ why?

10.9 Hybridisation

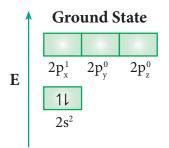
Bonding in simple molecules such as hydrogen and fluorine can easily be explained on the basis of overlap of the respective atomic orbitals of the combining atoms. But the observed properties of polyatomic molecules such as methane, ammonia, beryllium chloride etc... cannot be explained on the basis of simple overlap of atomic orbitals. For example, it was experimentally proved that methane has a tetrahedral structure and the four C-H bonds are equivalent. This fact cannot be explained on the basis of overlap of atomic orbitals of hydrogen (1s) and the atomic orbitals of carbon with different energies $(2s^2 2p_x^2 2p_y 2p_z)$.

In order to explain these observed facts, Linus Pauling proposed that the valence atomic orbitals in the molecules are different from those in isolated atom and he introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. The resultant orbitals are called hybridised orbitals and they posses maximum symmetry and definite orientation in space so as to minimize the force of repulsion between their electrons .

10.9.1 Types of hybridisation and geometry of molecules

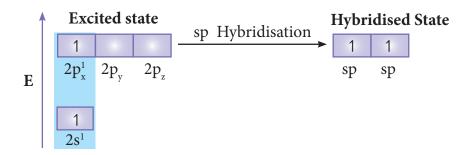
sp Hybridisation:

Let us consider the bond formation in beryllium chloride. The valence shell electronic configuration of beryllium in the ground state is shown in the figure.



In BeCl₂ both the Be-Cl bonds are equivalent and it was observed that the molecule is linear. VB theory explain this observed behaviour by sp hybridisation. One of the paired electrons in the 2s orbital gets excited to 2p orbital and the electronic configuration at the excited state is shown.

Now, the 2s and 2p orbitals hybridise and produce two equivalent sp hybridised orbitals which have 50 % s-character and 50 % p-character. These sp hybridised orbitals are oriented in opposite direction as shown in the figure.



Overlap with orbital of chlorine

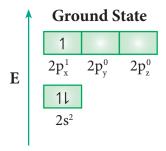
Each of the sp hybridized orbitals linearly overlap with p_z orbital of the chlorine to form a covalent bond between Be and Cl as shown in the Figure.



Fig 10.22 sp Hybridisation: BeCl₂

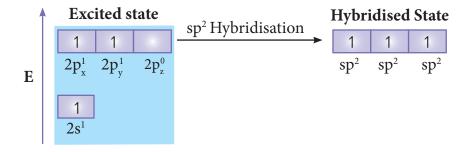
sp2 Hybridisation:

Consider boron trifluoride molecule. The valence shell electronic configuration of boron atom is $[He]2s^2 2p^1$.



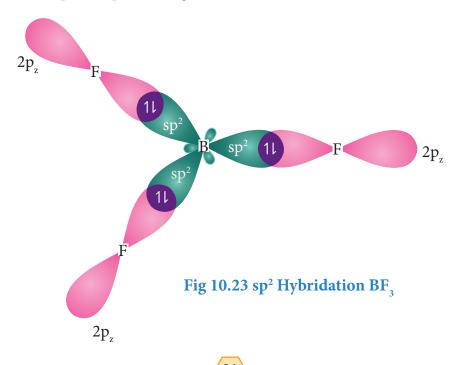
In the ground state boron has only one unpaired electron in the valence shell. In order to form three covalent bonds with fluorine atoms, three unpaired electrons are required. To achieve this, one of the paired electrons in the 2s orbital is promoted to the $2p_y$ orbital in the excite state.

In boron, the s orbital and two p orbitals (p_x and p_y) in the valence shell hybridses, to generate three equivalent sp^2 orbitals as shown in the Figure. These three orbitals lie in the same xy plane and the angle between any two orbitals is equal to 120^0



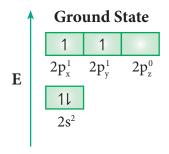
Overlap with 2pz orbitals of fluorine:

The three sp² hybridised orbitals of boron now overlap with the $2p_z$ orbitals of fluorine (3 atoms). This overlap takes place along the axis as shown below.



sp3 Hybridisation:

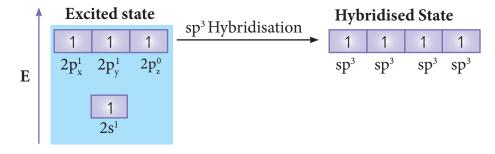
sp³ hybridisation can be explained by considering methane as an example. In methane molecule the central carbon atom bound to four hydrogen atoms. The ground state valence shell electronic configuration of carbon is $[He]2s^2 2p_x^1 2p_y^0 2p_z^0$.



In order to form four covalent bonds with the four hydrogen atoms, one of the paired electrons in the 2s orbital of carbon is promoted to its $2p_z$ orbital in the excite state. The one 2s orbital and the three 2p orbitals of carbon mixes to give four equivalent sp³ hybridised orbitals. The angle between any two sp³ hybridised orbitals is 109^0 28'

Overlap with 1s orbitals of hydrogen:

The 1s orbitals of the four hydrogen atoms overlap linearly with the four sp^3 hybridised orbitals of carbon to form four C-H σ -bonds in the methane molecule, as shown below.



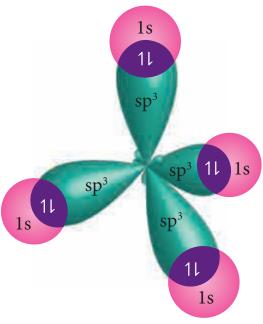
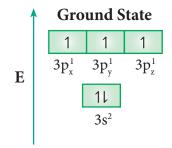


Fig 10.24 sp³ Hybridisation CH₄

sp³d Hybridisation:

In the molecules such as PCl_5 , the central atom phosphorus is covalently bound to five chlorine atoms. Here the atomic orbitals of phosphorous undergoes sp^3d hybridisation which involves its one 3s orbital, three 3p orbitals and one vacant 3d orbital (d_{z^2}) . The ground state electronic configuration of phosphorous is $[Ne]3s^2 3p_x^1 3p_y^1 3p_z^1$ as shown below.



One of the paired electrons in the 3s orbital of phosphorous is promoted to one of its vacant 3d orbital (d_{z^2}) in the excite state. One 3s orbital, three 3p orbitals and one $3d_{z^2}$ orbital of phosphorus atom mixes to give five equivalent sp³d hybridised orbitals. The orbital geometry of sp³d hybridised orbitals is trigonal bi-pyramidal as shown in the figure 10. x.

Overlap with 3p_x orbitals of chlorine:

The $3p_z$ orbitals of the five chlorine atoms linearly overlap along the axis with the five sp^3d hybridised orbitals of phosphorous to form the five P-Cl σ -bonds, as shown below.

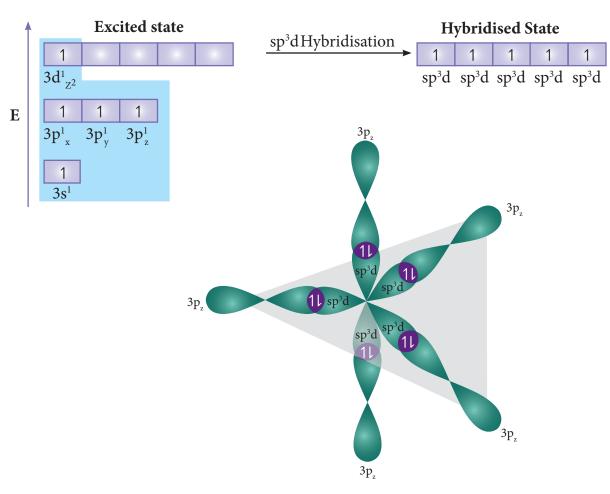
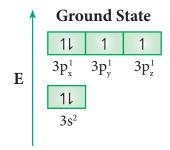


Fig 10.25 sp³d Hybridisation PCl₅

sp³d² Hybridisation:

In sulphur hexafluoride (SF₆) the central atom sulphur extend its octet to undergo sp^3d^2 hybridisation to generate six sp^3d^2 hybridised orbitals which accounts for six equivalent S-F bonds. The ground state electronic configuration of sulphur is [Ne]3s² 3p_x¹ 3p_y¹ 3p_z¹.



One electron each from 3s orbital and 3p orbital of sulphur is promoted to its two vacant 3d orbitals $(d_{z^2} \text{ and } d_{x^2-y^2})$ in the excite state. A total of six valence orbitals from sulphur (one 3s orbital, three 3p orbitals and two 3d orbitals) mixes to give six equivalent sp³d² hybridised orbitals. The orbital geometry is octahedral as shown in the figure.

Overlap with 2pz orbitals of fluorine:

The six sp^3d^2 hybridised orbitals of sulphur overlaps linearly with $2p_z$ orbitals of six fluorine atoms to form the six S-F bonds in the sulphur hexafluoride molecule.

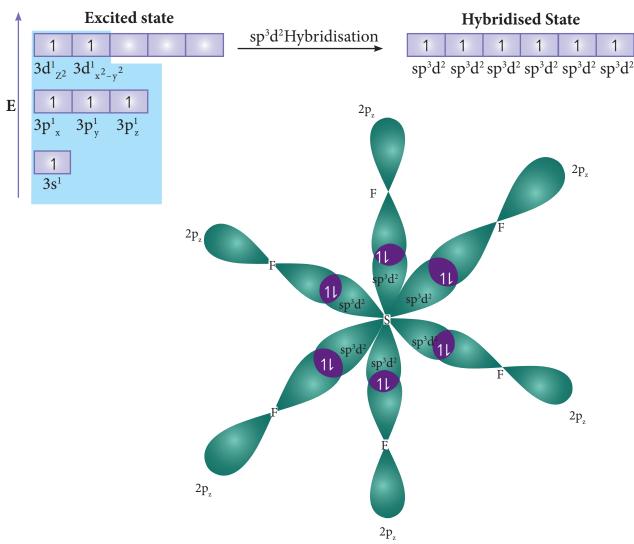


Fig 10.26 sp³d² Hybridisation: SF₆

In ethylene both the carbon atoms undergoes sp^2 hybridisation involving 2s, $2p_x$ and $2p_y$

orbitals, resulting in three equivalent sp2

hybridised orbitals lying in the xy plane

at an angle of 120° to each other. The

unhybridised 2p_z orbital lies perpendicular

One of the sp² hybridised orbitals of each

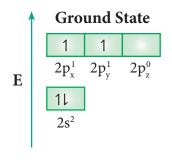
carbon lying on the molecular axis (x-axis) linearly overlaps with each other resulting in the formation a C-C sigma bond. Other two sp² hybridised orbitals of both carbons linearly overlap with the four 1s orbitals of four hydrogen atoms leading to the formation of two C-H sigma bonds on each

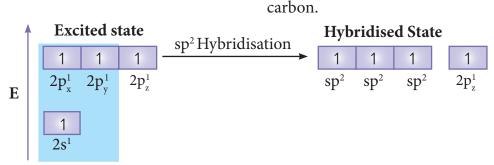
to the xy plane.

Formation of sigma bond:

Bonding in ethylene:

The bonding in ethylene can be explained using hybridisation concept. The molecular formula of ethylene is C_2H_4 . The valency of carbon is 4. The electronic configuration of valence shell of carbon in ground state is $[He]2s^2 2p_x^1 2p_y^1 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_z$ orbital in the excited state.





Formation of pi bond:

The unhybridised $2p_z$ orbital of both carbon atoms can overlap only sideways as they are not in the molecular axis. This lateral overlap results in the formation a pi bond between the two carbon atoms as shown in the figure.

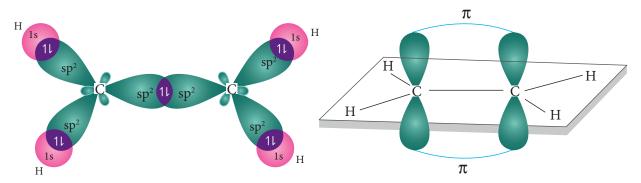


Fig 10.27 sp² Hybridisation : C_2H_4

Bonding in acetylene:

Similar to ethylene, the bonding in acetylene can also be explained using hybridisation concept. The molecular formula of acetylene is C_2H_2 . The electronic configuration of valence shell of carbon in ground state is $[He]2s^2 2p_x^1 2p_y^1 2p_z^0$. To satisfy the valency of carbon promote an electron from 2s orbital to $2p_x$ orbital in the excited state.

In acetylene molecule, both the carbon atoms are in sp hybridised state. The 2s and $2p_x$ orbitals, resulting in two equivalent sp hybridised orbitals lying in a straight line along the molecular axis (x-axis). The unhybridised $2p_y$ and $2p_z$ orbitals lie perpendicular to the molecular axis.

Formation of sigma bond:

One of the two sp hybridised orbitals of each carbon linearly overlaps with each other resulting in the formation a C-C sigma bond. The other sp hybridised orbital of both carbons linearly overlap with the two 1s orbitals of two hydrogen atoms leading to the formation of one C-H sigma bonds on each carbon.

Formation of pi bond:

The unhybridised $2p_y$ and $2p_z$ orbitals of each carbon overlap sideways. This lateral overlap results in the formation of two pi bonds (p_y - p_y and p_z - p_z) between the two carbon atoms as shown in the figure.

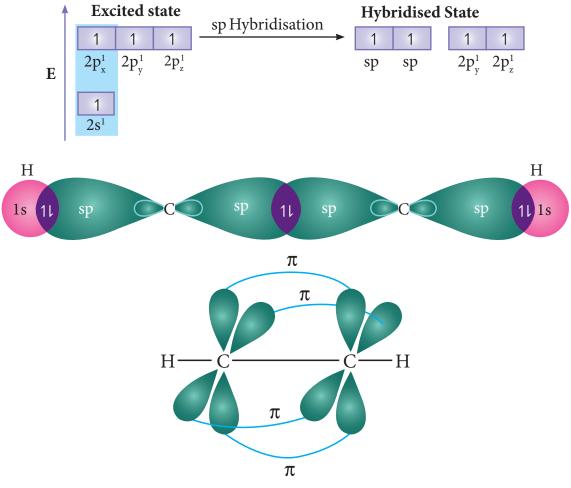


Fig 10.28 sp Hybridisation in acetylene

Evaluate Yourself



8) Explain the bond formation in SF₄ and CCl₄ using hybridisation concept.

Evaluate Yourself



9) The observed bond length of N_2^+ is larger than N, while the bond length in NO+ is less than in NO. Why?

10.10 Molecular orbital theory

Lewis concept and valence bond theory qualitatively explains the chemical bonding and molecular structure. Both approaches are inadequate to describe some of the observed properties of molecules. For example, these theories predict that oxygen is diamagnetic. However, it was observed that oxygen in liquid form was attracted towards the poles of strong magnet, indicating that oxygen is paramagnetic. As both these theories treated the bond formation in terms of electron pairs and hence they fail to explain the bonding nature of paramagnetic molecules. F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory which explains the magnetic behaviour of molecules.

The salient features of this theory are as follows.

- When atoms combines to molecules, their individual atomic orbitals lose their identity and forms new orbitals called molecular orbitals.
- The shapes of molecular orbitals depend upon the shapes of combining atomic orbitals.

- The number of molecular orbitals formed is the same as the number of combining atomic orbitals. Half the number of molecular orbitals formed will have lower energy than the corresponding atomic orbital, while the remaining molecular orbitals will have higher energy. The molecular orbital with lower energy is called bonding molecular orbital and the one with higher energy is called anti-bonding molecular orbital. The bonding molecular orbitals are represented as σ (Sigma), π (pi), δ (delta) and the corresponding antibonding orbitals are denoted as σ^* , π^* and δ^* .
- The electrons in a molecule are accommodated in the newly formed molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.
- Bond order gives the number of covalent bonds between the two combining atoms. The bond order of a molecule can be calculated using the following equation

Bond order =
$$\frac{N_b - N_a}{2}$$

Where, N_b = Total number of electrons present in the bonding molecular orbitals

 N_a = Total number of electrons present in the antibonding molecular orbitals and

A bond order of zero value indicates that the molecule doesn't exist.

10.10.1 Linear combination of atomic orbitals

The wave functions for the molecular orbitals can be obtained by solving Schrödinger wave equation for the molecule. Since solving the Schrödinger equation is too complex, approximation methods are used to obtain the wave function for molecular orbitals. The most common method is the linear combination of atomic orbitals (LCAO).

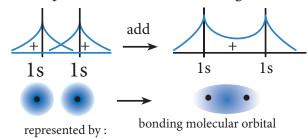
We know that the atomic orbitals are represented by the wave function Ψ . Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals. One is bonding molecular orbital($\psi_{bonding}$) and the other is antibonding molecular orbital($\psi_{antibonding}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

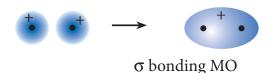
$$\psi_{bonding} = \psi_A + \psi_B$$

$$\psi_{antibonding} = \psi_A - \psi_B$$

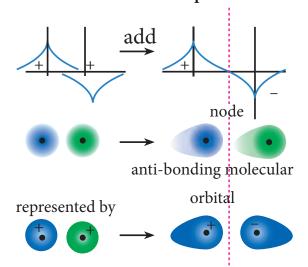
The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

Constructive interaction: The two 1s orbitals are in phase and have the same sign.





Destructive interaction The two 1s Orbitals are out phase



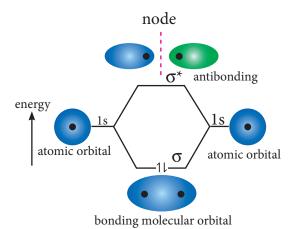
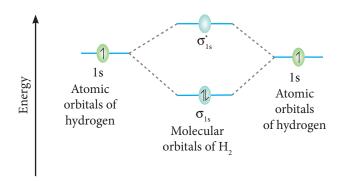


Fig 10.29 Linear Combination of atomic orbitals

10.10.2 Bonding in some Homonuclear di-atomic molecules:



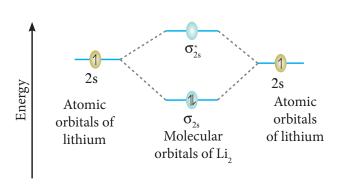
Molecular orbital diagram of hydrogen molecule (H₂)

Electronic configuration of H atom $1s^1$ Electronic configuration of H_2 molecule σ_{1s}^2

Bond order =
$$\frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.30 MO Diagram for H₂ molecule



Molecular orbital diagram of lithium molecule (Li₂)

Electronic configuration of Li atom 1s²

Electronic configuration of Li_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^{*2}$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.31 MO Diagram for Li₂ molecule

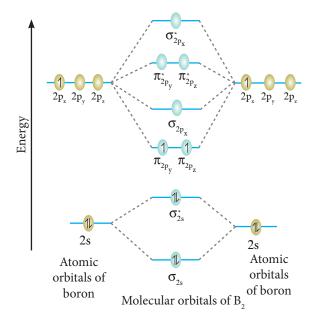


Fig 10.32 MO Diagram for B₂ molecule

Molecular orbital diagram of boron molecule (B₂)

Electronic configuration of B atom 1s² 2s² 2p¹

Electronic configuration of B_2 molecule $\sigma_{1s}^{\ 2}, \sigma_{1s}^{^{*2}}, \sigma_{2s}^{^{2}}, \sigma_{2s}^{^{*2}}, \pi_{2p_v}^{^{1}}, \pi_{2p_z}^{^{1}}$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{6 - 4}{2} = 1$$

Molecule has two unpaired electrons hence it is paramagnetic.

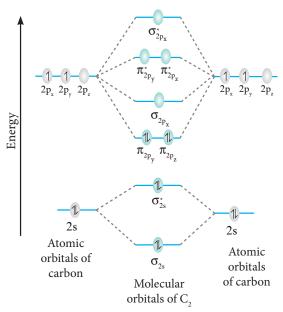


Fig 10.33 MO Diagram for C, molecule

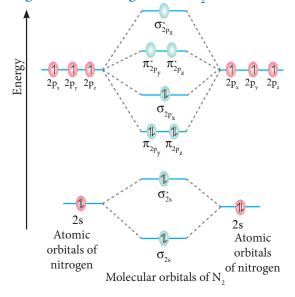


Fig 10.34 MO Diagram for N, molecule

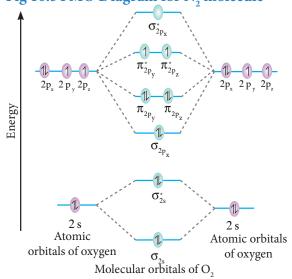


Fig 10.35 MO Diagram for O₂ molecule

Molecular orbital diagram of carbon molecule (C_2)

Electronic configuration of C atom $1s^2 2s^2 2p^2$

Electronic configuration of C_2 molecule $\sigma_1^2, \sigma_2^{*2}, \sigma_2^{*2}, \sigma_2^{*2}, \pi_2^2, \pi_2^2$

$$\sigma_{1s}^{2}, \sigma_{1s}^{2}, \sigma_{2s}^{2}, \sigma_{2s}^{2}, \pi_{2p_{y}}^{2}, \pi_{2p_{z}}^{2}$$
Bond order = $\frac{N_{b} - N_{a}}{2} = \frac{8 - 4}{2} = 2$

Molecule has no unpaired electrons hence it is diamagnetic.

Molecular orbital diagram of nitrogen molecule (N₂)

Electronic configuration of N atom $1s^2 2s^2 2p^3$

Electronic configuration of N_2 molecule $\sigma_{1s}^{\ 2}, \sigma_{1s}^{*2}, \sigma_{2s}^{2}, \sigma_{2s}^{*2}, \pi_{2p_v}^{2}, \pi_{2p_z}^{2}, \sigma_{2}^{2p_X}$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

Molecule has no unpaired electrons hence it is diamagnetic.

Molecular orbital diagram of oxygen molecule (O₂)

Electronic configuration of O atom $1s^2 2s^2 2p^4$

Electronic configuration of O_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^{*2}, \sigma_{2s}^{*2}, \sigma_{2p_x}^2 \pi^2_{2p_y}, \pi^2_{2p_z}, \pi^{*1}_{2p_y}, \pi^{*1}_{2p_z}$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

Molecule has two unpaired electrons hence it is paramagnetic.

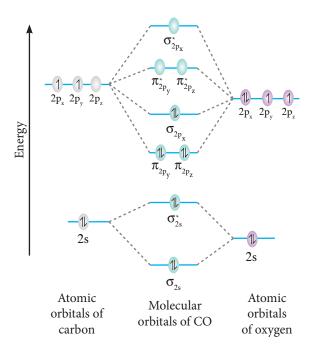


Fig 10.36 MO Diagram for CO molecule

σ_{2p_x} τ_{2p_y} σ_{2p_y} σ_{2p_y} σ_{2p_x} σ_{2p_x}

Fig 10.36 MO Diagram for NO molecule

Evaluate Yourself

10) Draw the MO diagram for acetylide ion C_2^{2-} and calculate its bond order.

Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom 1s² 2s² 2p²

Electronic configuration of O atom 1s² 2s² 2p⁴

Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^{*2}, \sigma_{2s}^{*2}, \pi_{2p_v}^2, \pi_{2p_z}^2, \sigma_{2p_x}^2$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

Molecule has no unpaired electrons hence it is diamagnetic.

Molecular orbital diagram of Nitric oxide molecule (NO)

Electronic configuration of N atom 1s² 2s² 2p³

Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^{*2}, \sigma_{2s}^{*2}, \pi_{2p_v}^2, \pi_{2p_z}^2, \sigma_{2p_z}^2, \pi_{2p_y}^*$

Bond order =
$$\frac{N_b - N_a}{2} = \frac{10 - 5}{2} = 2.5$$

Molecule has one unpaired electron hence it is paramagnetic.

Metallic bonding

Metals have some special properties of lustre, high density, high electrical and thermal conductivity, malleability and ductility, and high melting and boiling points. The forces that keep the atoms of the metal so closely in a metallic crystal constitute what is generally known as the metallic bond. The metallic bond is not just an electrovalent bond(ionic bond), as the latter is formed between atoms of different electro negativities. Similarly, the metallic bond is not a covalent bond, as the metal atoms do not have sufficient number of valence electrons for mutual sharing with 8 or 12 neighboring metal atoms in a crystal. So, we have to search for a new theory to explain metallic bond. The first successful theory is due to Drude and Lorentz, which regards metallic crystal as an assemblage of positive ions immersed in a gas of free electrons. The free electrons are due to ionization of the valence electrons of the atoms of the metal. As the valence electrons of the atoms are freely shared by all the ions in the crystal, the metallic bonding is also referred to as electronic bonding. As the free electrons repel each other, they are uniformly distributed around the metal ions. Many physical properties of the metals can be explained by this theory, nevertheless there are exceptions.

The electrostatic attraction between the metal ions and the free electrons yields a three-dimensional close packed crystal with a large number of nearest metal ions. So, metals have high density. As the close packed structure contains many slip planes along which movement can occur during mechanical loading, the metal acquires ductility. Pure metals can undergo 40 to 60% elongation prior to rupturing under mechanical loading. As each metal ion is surrounded by electron cloud in all directions, the metallic bonding has no directional properties.

As the electrons are free to move around the positive ions, the metals exhibit high electrical and thermal conductivity. The metallic luster is due to reflection of light by the electron cloud. As the metallic bond is strong enough, the metal atoms are reluctant to break apart into a liquid or gas, so the metals have high melting and boiling points.

The bonding in metal is better treated by Molecular orbital theory. As per this theory, the atomic orbitals of large number of atoms in a crystal overlap to form numerous antibonding bonding and molecular orbitals without any band gap. The bonding molecular orbitals are completely filled with an electron pair in each, and the antibonding molecular orbitals are empty. Absence of band gap accounts for high electrical conductivity of metals. High thermal conductivity is due to thermal excitation of many electrons from the valence band to the conductance band. With an increase in temperature, the electrical conductivity decreases due to vigorous thermal motion of lattice ions that disrupts the uniform lattice structure, that is required for free motion of electrons within the crystal. Most metals are black except copper, silver and gold. It is due to absorption of light of all wavelengths. Absorption of light of all wavelengths is due to absence of bandgap in metals.

SUMMARY



In molecules, atoms are held together by attractive forces, called chemical bonds. Kossel and Lewis are the first people to provide a logical explanation for chemical bonding. They proposed that atoms try to attain the nearest noble gas electronic configuration by losing, gaining or sharing one or more electrons during the bond formation. The noble gases contain eight electrons in their valance shell which is considered to be stable electronic configuration. The idea of Kossel - Lewis approach to chemical bond lead to the octet rule, which states that "the atoms transfer or share electrons so that all atoms involved in chemical bonding obtain 8 electrons in their outer shell (valance shell)".

There are different types of chemical bonds. In compounds such as sodium chloride, the sodium atom loses an electron which is accepted by the chlorine atom resulting in the formation of Na+ and Cl- ions. These two ions are held together by the electrostatic attractive forces. This type of chemical bond is known as ionic bonds or electrovalent bonds. In certain compounds, instead of the complete transfer of electrons, the electrons are shared by both the bonding atoms. The two combining atoms are held together by their mutual attraction towards the shared electrons. This type of bond is called covalent bonding. In addition, there also another bond type known as coordinate covalent bonds, where the shared electrons of a covalent bond are provided by only one of the combining atoms. Metallic bonding is another type of bonding which is observed in metals.

Lewis theory in combination with VSEPR theory will be useful in predicting the shape of molecules. According to this theory, the shape of the molecules depends on the number of valance shell electron pair (lone pairs and bond pairs) around the central atom. Each pair of valance electrons around the central atom repels each other and hence, they are located as far away as possible in three-dimensional space to minimise the repulsion between them.

Heitler and London gave a theoretical treatment to explain the formation of covalent bond in hydrogen molecule on the basis of wave mechanics of electrons. It was further developed by Pauling and Slater. According to this theory when half-filled orbitals of two atoms overlap, a covalent bond will be formed between them. Linus Pauling introduced the concept of hybridisation. Hybridisation is the process of mixing of atomic orbitals of the same atom with comparable energy to form equal number of new equivalent orbitals with same energy. There are different types of hybridization such as sp, sp2, sp3, sp3d2 etc..

F. Hund and Robert. S. Mulliken developed a bonding theory called molecular orbital theory. According to this theory, when atoms combines to form molecules, their individual atomic orbitals lose their identity and forms new orbitals called molecular orbitals. The filling of electrons in these orbitals follows Aufbau's principle, Pauli's exclusion principle and Hund's rule as in the case of filling of electrons in atomic orbitals.

Evaluation



- 1. In which of the following Compounds does the central atom obey the octet rule?
 - a) XeF₄
- b) AlCl₂
- c) SF₆
- d) SCl,
- 2. In the molecule $O_A = C = O_B$, the formal charge on O_A , C and O_B are respectively.
 - a) -1, 0, +1
- b) +1, 0,-1
- c) -2,0,+2
- d) 0,0,0
- 3. Which of the following is electron deficient?
 - a) PH₂
- b) (CH₂)₂
- c) BH₃
- d) NH₃
- 4. Which of the following molecule contain no π bond?
 - a) SO₂
- b) NO,
- c) CO₂
- d) H, O
- 5. The ratio of number of sigma (σ) and pi (π) bonds in 2- butynal is
 - a) 8/3
- b) 5/3
- c) 8/2
- d) 9/2
- 6. Which one of the following is the likely bond angles of sulphur tetrafluoride molecule?
 - a) 120°,80°
- b) 109°.28
- c) 90^{0}
- d) 89°,117°
- 7. **Assertion:** Oxygen molecule is paramagnetic.

- Reason: It has two unpaired electron in its bonding molecular orbital
- a) both assertion and reason are true and reason is the correct explanation of assertion
- b) both assertion and reason are true but reason is not the correct explanation of assertion
- c) assertion is true but reason is false
- d) Both assertion and reason are false
- 8. According to Valence bond theory, a bond between two atoms is formed when
 - a) fully filled atomic orbitals overlap
 - b) half filled atomic orbitals overlap
 - c) non- bonding atomic orbitals overlap
 - d) empty atomic orbitals overlap
- 9. In ClF₃,NF₃ and BF₃ molecules the chlorine, nitrogen and boron atoms are
 - a) sp³ hybridised
 - b) sp³,sp³ and sp² respectively
 - c) sp² hybridised
 - d) sp³d, sp³ and sp hybridised respectively
- 10. When one s and three p orbitals hybridise,
 - a) four equvivalent orbitals at 90° to each other will be formed
 - b) four equvivalent orbitals at 109°

28' to each other will be formed.

- four equivalent orbitals, that c) are lying the same plane will be formed
- none of these d)
- Which of these represents the correct order of their increasing bond order.
 - a) $C_2 < C_2^{2} < O_2^{2} < O_3$
 - b) $C_2^{2-} < C_2^{+} < O_2 < O_2^{2-}$
 - c) $O_2^{2-} < O_2 < C_2^{2-} < C_2^{+}$
 - d) $O_2^{2-} < C_2^{+} < O_2 < C_2^{2-}$
- Hybridisation of central atom in PCl₅ 12. involves the mixing of orbitals.
 - a) s, p_{x} , p_{y} , d_{x2} , d_{x2-y2}
 - b) s, p_x . p_y , p_{xy} . d_{x2-y2}
 - c) s, p_{y} , p_{y} , p_{z} , $d_{y_{2}-y_{2}}$
 - d)s, p_x , p_v , d_{xv} , d_{x2-v2}
- The correct order of O-O bond length 13. in hydrogen peroxide, ozone and oxygen is
 - a) $H_2O_2 > O_3 > O_3$
 - b) $O_2 > O_3 > H_2 O_3$
 - c) $O_2 > H_2 O_2 > O_3$
 - d) $O_3 > O_2 > H_2 O_3$
- Which one of the following is 14. diamagnetic.?
 - a) O₂
- b) O₂²-
- c) O_{2}^{+}
- d) None of these
- Bond order of a species is 2.5 and the 15. number of electons in its bonding molecular orbital is formd to be 8 The no. of electons in its antibonding

molecular orbital is

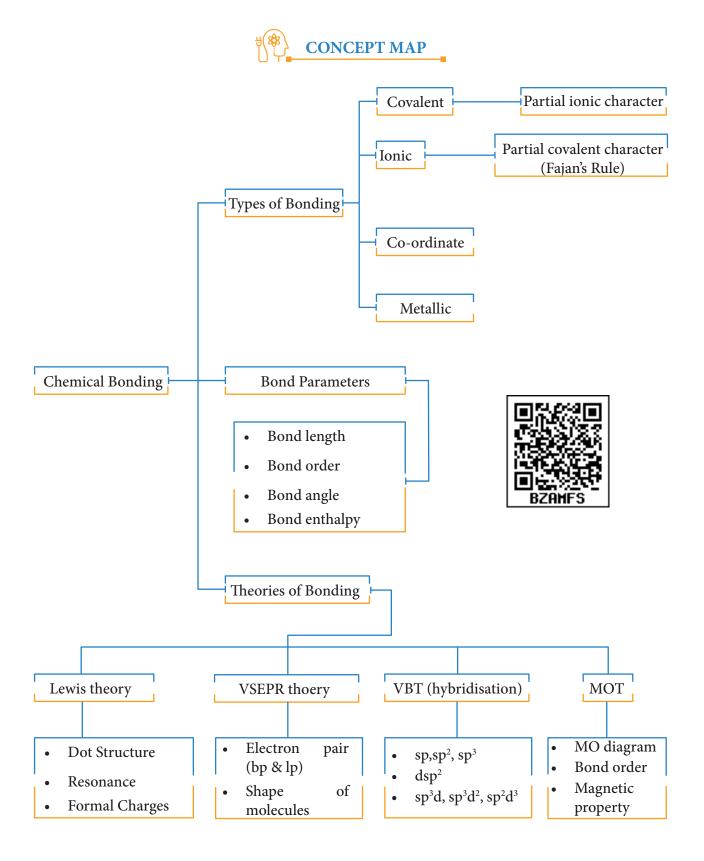
- a) three
- b) four
- c) Zero
- d) can not be calculated form the given unformation.
- Shape and hybridisation of IF₅ are
 - a) Trigonal bipyramidal, Sp³d²
 - b) Trigonal bipyramidal, Sp³d
 - c) Square pyramidal, Sp³d²
 - d) Octahedral, Sp³d²
- Pick out the incorrect statement from 17. the following
 - Sp³ hybrid orbitals are equivalent and are at an angle of 1090 28' with eachother
 - dsp2 hybrid orbitals are equivalent b) and bond angle between any two of them is 90°
 - All five sp³d hybrid orbitals are c) not equivalent out of these five sp3d hybrid orbitals, three are at an angle of 120°, remainir two are perpendicular to the plane containing the other three
 - none of these d)
- The 18. molecules having same hybridisation, shape and number of lone pairs of electons are
 - a) SeF_4 , XeO_2F_2 b) SF_4 , XeF_2
- - c) XeOF₄, TeF₄ d) SeCl₄, XeF₄
- In which of the following molecules / 19. ions BF₃, NO₂, H₂ O the central atom is sp² hybridised?
 - a) NH₂ and H₂O
 - b) NO,- and H,O

- c) BF₃ and NO₂-
- d) BF₃ and NH₂
- 20. Some of the following properties of two species, NO₃ and H₃O⁺ are described below. which one of them is correct?
 - a) dissimilar in hybridisation for the central atom with different structure.
 - b) isostructural with same hybridisation for the Central atom.
 - c) different hybridiration for the central atom with same structure
 - d) none of these
- 21. The types of hybridiration on the five carbon atom from right to left in the, 2,3 pentadiene.
 - a) sp³, sp², sp, sp², sp³
 - b) sp³, sp, sp, sp, sp³
 - c) sp², sp, sp², sp²
 - d) sp³, sp³, sp², sp³, sp³
- 22. Xe F₂ is isostructural with
 - a) SbCl₂
- b) BaCl₂
- c) TeF₂
- d) ICl₂
- 23. The percentage of s-character of the hybrid orbitals in methane, ethane, ethene and ethyne are respectively
 - a) 25, 25,33.3,50
 - b) 50,50,33.3,25
 - c) 50,25,33.3,50
 - d) 50,25,25,50
- 24. Of the following molecules, which have shape similar to carbondixide?

- a) SnCl₂
- b) NO₂
- c) C, H,
- d) All of these.
- 25. According to VSEPR theory, the repulsion between different parts of electrons obey the order.
 - a) l.p l.p > b.p-b.p > l.p-b.p
 - b) b.p-b.p> b.p-l.p> l.p-b.p
 - c) l.p-l.p > b.p-l.p > b.p-b.p
 - d) b.p-b.p>l.p-l.p>b.p-l.p
- 26. Shape of ClF₃ is
 - a) Planar triangular
 - b) Pyramidal
 - c) 'T' Shaped
 - d) none of these
- 27. Non- Zero dipole moment is shown by
 - a) CO_2
 - b) p-dichlorobenzene
 - c) carbontetrachloride
 - d) water.
- 28. Which of the following conditions is not correct for resonating structures?
 - a) the contributing structure must have the same number of unpaired electrons
 - b) the contributing structures should have similar energies
 - c) the resonance hybrid should have higher energy than any of the contributing structure.
 - d) none of these

- 29. Among the following, the compound that contains, ionic, covalent and Coordinate linkage is
 - a) NH₄Cl
- b) NH₂
- c) NaCl d) none of these
- 30. CaO and NaCl have the same crystal structure and approximately the same radii. It U is the lattice energy of NaCl, the approximate lattice energy of CaO
 - a) U
- b) 2U
- c) U/2
- d) 4U
- Define the following 31.
 - i) Bond order
 - ii) Hybridisation
 - iii) σ- bond
- 32. What is a pi bond?
- 33. In CH₄, NH₃ and H₂O, the central atom undergoes sp³ hybridisation - yet their bond angles are different. why?
- 34. Explain Sp² hybridisation in BF₃
- 35. Draw the M.O diagram for oxygen molecule calculate its bond order and show that O_2 is paramagnetic.
- 36. Draw MO diagram of CO and calculate its bond order.
- 37. What do you understand by Linear combination of atomic orbitals in MO theory.
- 38. Discuss the formation of N_2 molecule using MO Theory
- 39. What is dipolment?
- 40. Linear form of carbondioxide molecule has two polar bonds. yet the molecule has Zero dipolement why?
- 41. Draw the Lewis structures for the following species.

- i) NO_3^- ii) SO_4^{2-} iii) HNO_3 iv) O₂
- 42. Explain the bond formation in BeCl, and MgCl₂.
- 43. Which bond is stronger σ or π ? Why?
- 44. Define bond energy.
- 45. Hydrogen gas is diatomic where as inert gases are monoatomic - explain on the basis of MO theory.
- 46. What is Polar Covalent bond? explain with example.
- 47. Considering x- axis as molecular axis, which out of the following will form a sigma bond.
 - i) 1s and $2p_y$ ii) $2P_x$ and $2P_x$
- - iii) $2p_x$ and $2p_z$ iv) 1s and $2p_z$
- 48. Explain resonance with reference to carbonate ion?
- 49. Explain the bond formation in ethylene and acetylene.
- 50. What type of hybridisations are possible in the following geometeries?
 - a) octahedral
 - b) tetrahedral
 - c) square planer.
- 51. Explain VSEPR theory. Applying this theory to predict the shapes of IF₇, and SF_6
- 52. CO, and H₂O both are triatomic molecule but their dipole moment values are different. Why?
- 53. Which one of the following has highest bond order?
 - N_2 , N_2^+ or N_2^-
- 54. Explain the covalent character in ionic bond.
- 55. Describe fajan's rule.













The Nobel Prize chemistry 2005 was awarded jointly to Yves Chauvin, Robert H. Grubbs and Richard **R. Schrock** for the development of new chemicals based on Green chemistry.

In 1971 Yves Chauvin explainedthe types of metal compound that act as catalysts in the reactions. Richard Schrock was the first to produce efficient metal compound catalysts for metathesis in 1990. Two years later Robert Grubbs developed better catalysts, stable in air thatwas highlighted in many applications.

Learning Objectives (6)



After studying this unit, students will be able to

- Know the various concepts of environmental chemistry
- classify the various types of environmental pollutions.
- recognize the particulate pollutants and their effects.
- explain the cause and hazardous effects of acid rain, greenhouse effect, ozone depletion and global warming.
- know the reason for water pollution and recognize the prescribed standard for drinking water.
- highlight the strategies to control various types of pollution
- appreciate the meaning of green chemistry and comprehend the importance of green chemistry in day today life.

15. INTRODUCTION

We are very familiar with the word environment. It includes the air we breathe, the water that covers most of the earth's surface, the plants and animals around us and much more. These days, when we hear people talk about "the environment", they are often referring to the overall condition of our planet, or how healthy it is.

Environmental chemistry is a branch of chemistry which deals with the study of chemicals and chemical processes. occuring in the environment by direct human activities. It also deals with sources, causes and methods of controlling air, water and soil pollution.

15.1 Environmental Pollution

Any undesirable change in our environment that has harmful effects on plants, animals and human beings is called environmental pollution.

Environmental pollution is usually caused by the addition of waste products of human activity to the environment. The substances which cause pollution of environment are called pollutants. The pollutants may be solids, liquids or gaseous substances present in significant concentration in the environment. Our environment becomes polluted day by day, by the increased addition of industrial and domestic wastes to it. The air we breathe, the water we drink and the place where we live in, are highly contaminated.

The pollutants are classified as bio-degradable and non-biodegradable pollutants.

i. Bio-degradable pollutants:

The pollutants which can be easily decomposed by the natural biological processes are called bio-degradable pollutants. Examples:plant wastes, animal wastes etc.

ii. Non bio-degradable pollutants:

The pollutants which cannot be decomposed by the natural biological processes are called Non bio-degradable pollutants. Examples: metal wastes (mainly Hg and Pb), D.D.T, plastics, nuclear wastes etc., These pollutants are harmful to living organisms even in low concentration. As they are not degraded naturally, it is difficult to eliminate them from our environment.

15.2.Atmospheric Pollution

Earth's atmosphere is a layer of gases retained by the earth's gravity. It contains roughly 78% nitrogen, 21% oxygen, 0.93% argon, 0.04% carbon dioxide, trace amounts of other gases and little amount of water vapour. This mixture is commonly known as air.

Earth's atmosphere can be divided into different layers with characteristic altitude and temperature. The various regions of atmosphere are given in table 15.1.

Table 15.1 Regions of atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/ species present	
Troposphere	0-10 km	15° C to -56°C	N_2O_2 CO_2 H_2O (vap)	

Region	Altitude from earth's surface	Temperature range	Gases/ species present	
Stratosphere (ozonosphere)	10-50 km	-56°C to -2°C	N_2 O_2 O_3 O atoms	
Mesosphere	50-85 km	-2°C to- 92°C	N_2 O_2^+ N_Q^+	
Thermosphere	85- 500 km	-92°C to 1200°C	O ₂ + O+ NO+ e-	

Troposphere:

The lowest layer of the atmosphere is called the troposphere and it extends from 0 – 10 km from the earth surface. About 80% of the mass of the atmosphere is in this layer. This troposphere in further divided as follows.

i) Hydrosphere:

Hydrosphere includes all types of water sources like oceans, seas, rivers, lakes, streams, underground water, polar icecaps, clouds etc. It covers about 75% of the earth's surface. Hence the earth is called as a blue planet.

ii) Lithosphere:

Lithosphere the includes soil, rocks and mountains which are solid components of earth.

iii) Biosphere:

It includes the lithosphere hydrosphere and atmosphere intergrating

the living organism present in the lithosphere, hydrosphere and atmosphere.

The Bhopal Tragedy The world's worst chemical disaster happened in the Indian city of Bhopal in the early morning hours of December 3, 1984. An explosion at the Union Carbide pesticide plant released a cloud of toxic gas (methyl isocyanate) CH₂NCO into the air. Since the gas was twice as heavy as air, it did not drift away but formed a 'blanket' over the surrounding area. It attacked people's lungs and affected their breathing. Thousands of people died and the lives of many were ruined. The lungs, brain, eyes, muscles as well as gastrointestinal, neurological and immune systems of those who survived were severely affected.

15.3. Types of environmental pollution

Atmospheric pollution is generally studied as tropospheric pollution. Different types of atmospheric pollutions are

- (1) Air pollution (2) Water pollution
- (3) Soil pollution.

15.3.1 Air pollution

Any undesirable change in air which adversely affects living organisms is called air pollution. Air pollution is limited to troposphere and stratosphere. Air pollution is mainly due to the excessive discharge of undesirable foreign matter in to the atmospheric air.



Fig 15.1 Air Pollution

types of air pollutants

Air pollutants may exist in two major forms namely, gases and particulates.

15.3.1.1 Gaseous air pollutants

Oxides of sulphur, oxides of nitrogen, oxides of carbon, and hydrocarbons are the gaseous air pollutants.

a. Oxides of Sulphur

Sulphur dioxide and sulphur trioxide are produced by burning sulphur containing fossil fuels and roasting sulphide ores. Sulphur dioxide is a poisonous gas to both animals and plants. Sulphur dioxide causes eye irritation, coughing and respiratory diseases like asthma, bronchitis, etc.

Sulphur dioxide is oxidised into more harmful sulphur trioxide in the presence of particulate matter present in polluted air.

$$2SO_2 + O_2 \xrightarrow{\text{Particulate matter}} 2SO_3$$

 SO_3 combines with atmospheric water vapour to form H_2SO_4 , which comes

down in the form of acid rain.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Some harmful effects of acid rain will be discussed in section 15.3

b. Oxides of nitrogen

Oxides of nitrogen are produced during high temperature combustion processes, oxidation of nitrogen in air and from the combustion of fuels (coal, diesel, petrol etc.).

$$N_2 + O_2 \xrightarrow{>1210^{\circ}\text{C}} 2\text{NO}$$

$$2\text{NO} + O_2 \xrightarrow{1100^{\circ}\text{C}} 2\text{NO}_2$$

$$NO + O_3 \xrightarrow{} \text{NO}_2 + O_2$$

The oxides of nitrogen are converted into nitric acid which comes down in the form of acid rain. They also form reddish brown haze in heavy traffic. Nitrogen dioxide potentially damages plant leaves and retards photosynthesis. NO₂ is a respiratory irritant and it can cause asthma and lung injury. Nitrogen dioxide is also harmful to various textile fibres and metals.

c. Oxides of carbon

The major pollutants of oxides of carbon are carbon monoxide and carbon dioxide.

(i) Carbon Monoxide

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal are firewood. It is released into the air mainly by automobile exhaust. It binds with haemoglobin and

form carboxy haemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, Loss of consciousness, blurring of eye sight and cardiac arrest.

(ii) Carbon dioxide

Carbon dioxide is released into the atmosphere mainly by the process of respiration, burning of fossil fuels, forest fire, decomposition of limestone in cement industry etc.

Green plants can convert CO₂ gas in the atmosphere into carbohydrate and oxygen through a process called photosynthesis. The increased CO₂ level in the atmosphere is responsible for global warming. It causes headache and nausea.

(d) Hydrocarbon

The compounds composed of carbon and hydrogen only are called hydrocarbons. They are mainly produced naturally (marsh gas) and also by incomplete combustion of automobile fuel.

They are potential cancer causing (carcinogenic) agents. For example, polynuclear aromatic hydrocarbons (PAH) are carcinogenic, they cause irritation in eyes and mucous membranes.

15.3.1.2Greenhouse effect and Global warming:

In 1987, Jean Baptiste Fourier a French mathematician and scientist

coined the term"Greenhouse Effect" for trapping of heat in the atmosphere by certain gases.

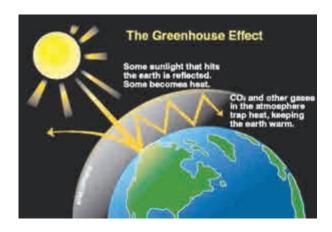


Fig 15.2 Greenhouse effect

The earth's atmosphere allows most of the visible light from the Sun to pass through and reach Earth's surface. As Earth's surface is heated by sunlight, it radiates part of this energy back toward space as longer wavelengths (IR).

Some of the heat is trapped by CH₄, CO₂, CFCs and water vapour present in the atmosphere. They absorb IR radiation and effectively block a large portion of earth's emitted radiation. The radiation thus absorbed is partly reemitted to earth's surface. Therefore, the earth's surface gets heated up by a phenomenon called greenhouse effect.

Thus Greenhouse effect may be defined as the heating up of the earth surface due to trapping of infrared radiations reflected by earth's surface by CO_2 layer in the atmosphere". The heating up of earth through the greenhouse effect is called global warming.

Without the heating caused by the

greenhouse effect, Earth's average surface temperature would be only about -18 °C (0 °F). Although the greenhouse effect is a naturally occurring phenomenon, it is intensified by the continuous emission of greenhouse gases into the atmosphere.

During the past 100 years, the amount of carbon dioxide in the atmosphere increased by roughly 30 percent and the amount of methane more than doubled. If these trends continue, the average global temperature will increase which can lead to melting of polar ice caps and flooding of low lying areas. This will increase incidence of infectious diseases like dengue, malaria etc.

15.3.1.3 Acid Rain

Rain water normally has a pH of 5.6 due to dissolution of atmospheric CO₂ into it. Oxides of sulphur and nitrogen in the atmosphere may be absorbed by droplets of water that make up clouds and get chemically converted into sulphuric acid and nitric acid respectively as a results of pH of rain water drops to the level 5.6, hence it is called acid rain.

Acid rain is a by-product of a variety of sulphur and nitrogen oxides in the atmosphere. Burning of fossil fuels (coal and oil) in power stations, furnaces and petrol, diesel in motor engines produce sulphur dioxide and nitrogen oxides. The main contributors of acid rain are SO₂ and NO₂. They are converted into sulphuric acid and nitric acid respectively by the reaction with oxygen and water.

$$2\mathrm{SO_2} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{H_2SO_4}$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

Harmful effects of acid rain:

Some harmful effects are discussed below.

(i) Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

- (ii) Acid rain affects plants and animal life in aquatic ecosystem.
- (iii) It is harmful for agriculture, trees and plants as it dissolves and removes the nutrients needed for their growth.
- (iv) It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water which have toxic effects.
- (v) It causes respiratory ailment in humans and animals.



FIG 15. 3. Effect Of Acid Rain On Tajmahal

15.3.2 Particulate matter (Particulate pollutants)

Particulate pollutants are small solid particles and liquid droplets suspended in air. Many of particulate pollutants are hazardous. Examples: dust, pollen, smoke, soot and liquid droplets (aerosols) etc,.

They are blown into the atmosphere by volcanic eruption, blowing of dust, incomplete combustion of fossil fuels induces soot. Combustion of high ash fossil fuels creates fly ash and finishing of metals throws metallic particles into the atmosphere.

15.3.2.1. Types of Particulates:

Particulate in the atmosphere may be of two types, viable or non-viable.

a. Viable particulates

The viable particulates are the small size living organisms such as bacteria, fungi, moulds, algae, etc. which are dispersed in air. Some of the fungi cause allergy in human beings and diseases in plants.

b. Non-viable particulates

The non- viable particulates are small solid particles and liquid droplets suspended in air. They help in the transportation of viable particles. There are four types of non-viable particulates in the atmosphere. They are classified according to their nature and size as follows

(i) Smoke

Smoke particulate consists of solid particles (or) mixture of solid and liquid particles formed by combustion of organic matter.

For example, cigarette smoke, oil smoke, smokes from burning of fossil fuel, garbage and dry leaves.

(ii) Dust:

Dust composed of fine solid particles produced during crushing and grinding of solid materials.

For example, sand from sand blasting, saw dust from wood works, cement dust from cement factories and fly ash from power generating units.

(iii) Mists

They are formed by particles of spray liquids and condensation of vapours in air.

For example, sulphuric acid mist, herbicides and insecticides sprays can form mists.

(iv) Fumes

Fumes are obtained by condensation of vapours released during sublimation, distillation, boiling and calcination and by several other chemical reactions.

For example, organic solvents, metals and metallic oxides form fume particles.

15.3.2.2. Health effects of particulate pollutants:

. Dust, mist, fumes, etc., are air borne

particles which are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to settle in the nasal passage whereas particles of about 10 micron enters the lungs easily and causes scaring or fibrosis of lung lining. They irritate the lungs and causes cancer and asthma. This disease is also called pneumoconiosis. Coal miners may suffer from black lung disease. Textile workers may suffer from white lung disease.

- ii. Lead particulates affect children's brain, interferes maturation of RBCs and even cause cancer.
- iii. Particulates in the atmosphere reduce visibility by scattering and absorption of sunlight. It is dangerous for aircraft and motor vehicles
- iv. Particulates provide nuclei for cloud formation and increase fog and rain.
- v. Particulates deposit on plant leaves and hinder the intake of CO₂ from the air and affect photosynthesis.

15.3.2.3. Techniques to reduce particulate pollutants

The particulates from air can be removed by using electrostatic precipitators, gravity settling chambers, and wet scrubbers or by cyclone collectors. These techniques are based on washing away or settling of the particulates.

15.3.3 Smog

Smog is a combination of smoke

and fog which forms droplets that remain suspended in the air.



Fig 15.4 classical smog

Smog is a chemical mixture of gases that forms a brownish yellow haze over urban cities. Smog mainly consists of ground level ozone, oxides of nitrogen, volatile organic compounds, SO₂, acidic aerosols and gases, and particulate matter.

There are two types of smog. One is Classical smog caused by coal smoke and fog, second one is photo chemical smog caused by photo chemical oxidants. They are discussed below in detail.

(i) Classical smog or London smog

Classical smog was first observed in London in December 1952 and hence it is also known as London smog. It consists of coal smoke and fog.

It occurs in cool humid climate. This atmospheric smog found in many large cities. The chemical composition is the mixture of SO₂, SO₃ and humidity. It generally occurs in the morning and becomes worse when the sun rises.

This is mainly due to the induced oxidation of SO₂ to SO₃, which reacts with

water yielding sulphuric acid aerosol.

Chemically it is reducing in nature because of high concentration of SO₂ and so it is also called as reducing smog.

Effects of classical smog:

- a. Smog is primarily responsible for acid rain.
- b. Smog results in poor visibility and it affects air and road transport.
- c. It also causes bronchial irritation.

Great London Smog

The great smog of London, or great smog of 1952, was a severe air-pollution event that affected the British capital of London in early December 1952. It lasted from Friday, 5 December to Tuesday, 9 December 1952 and then dispersed quickly when the weather changed. It caused major disruption by reducing visibility and even penetrating indoor areas. Government medical reports in the following weeks, however, estimated that until 8 December, 4,000 people had died as a direct result of the smog and 100,000 more were made ill by the smog's effects on the human respiratory tract.

ii)Photo chemical smog or Los Angel Smog

Photo Chemical smog was first observed in Los Angels in 1950. It occurs in warm, dry and sunny climate. This type of smog is formed by the combination of

smoke, dust and fog with air pollutants like oxides of nitrogen and hydrocarbons in the presence of sunlight.

It forms when the sun shines and becomes worse in the afternoon. Chemically it is oxidizing in nature because of high concentration of oxidizing agents NO₂ and O₃, so it is also called as oxidizing smog.

Photo chemical smog is formed through sequence of following reactions.

$$N_{2} + O_{2} \rightarrow 2NO$$

$$2NO + O_{2} \rightarrow 2NO_{2}$$

$$NO_{2} \xrightarrow{\text{sun light}} NO + (O)$$

$$(O) + O_{2} \rightarrow O_{3}$$

$$O_{3} + NO \rightarrow NO_{2} + O_{2}$$

$$NO_{2} \xrightarrow{\text{sun light}} NO + (O)$$

NO and O₃ are strong oxidizing agent and can react with unburnt hydrocarbons in polluted air to form formaldehyde, acrolein and peroxy acetyl nitrate (PAN).

Effects of photo chemical smog

The three main components of photo chemical smog are nitrogen oxide, ozone and oxidised hydro carbon like formaldehyde(HCHO), Acrolein (CH₂=CH-CHO), peroxy acetyl nitrate (PAN).

Photochemical smog causes irritation to eyes, skin and lungs, increase in chances of asthma.

High concentrations of ozone and NO can cause nose and throat irritation, chest pain, uncomfortable in breathing, etc.

PAN is toxic to plants, attacks younger leaves and cause bronzing and glazing of their surfaces

It causes corrosion of metals stones, building materials and painted surfaces.

Control of Photo chemical smog

The formation of photochemical smog can be suppressed by preventing the release of nitrogen oxides and hydrocarbons into the atmosphere from the motor vehicles by using catalytic convertors in engines. Plantation of certain trees like Pinus, Pyrus, Querus Vitus and juniparus can metabolise nitrogen oxide.

15.4. Stratospheric pollution

At high altitudes to the atmosphere consists of a layer of ozone (O_3) which acts as an umbrella or shield for harmful UV radiations. It protects us from harmful effect such as skin cancer. UV radiation can convert molecular oxygen into ozone as shown in the following reaction.

$$O_2(g) \xrightarrow{uv} O(g) + O(g)$$

$$O(g) + O_2(g) \xrightarrow{uv} O_3(g)$$

Ozone gas is thermodynamically unstable and readily decomposes to molecular oxygen.

15.4.1 Depletion of Ozone Layer (Ozone hole)

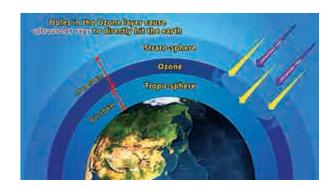


Fig 15.5 Ozone Depletion

In recent years, a gradual depletion of this protective ozone layer has been reported. Nitric oxide and CFC are found to be most responsible for depletion of ozone layer.

Generally substances that cause depletion of ozone or make it thinner are called Ozone Depletion Substances abbreviated as ODS. The loss of ozone molecules in the upper atmosphere is termed as depletion of stratospheric ozone.

Oxides of Nitrogen:

Nitrogen oxides introduced directly into the stratosphere by the supersonic jet aircraft engines in the form of exhaust gases.

These oxides are also released by combustion of fossil fuels and nitrogen fertilizers. Inert nitrous oxide in the stratosphere is photo chemically converted into more reactive nitric oxide. Oxides of nitrogen catalyse the decomposition of ozone and are themselves regenerated. Ozone gets depleted as shown below.

$$NO +O_3 \rightarrow NO_2 +O_2$$

$$O_2 \xrightarrow{hv} O + O$$

$$NO_2 +O \rightarrow NO +O_2$$

Thus NO is regenerated in the chain reaction.

Chloro Fluoro Carbons (CFC) Freons

The chloro fluoro derivatives of methane and ethane are referred by trade name Freons. These Chloro Fluoro Carbon compounds are stable, non-toxic, noncorrosive and non-inflammable, easily liquefiable and are used in refrigerators, air- conditioners and in the production of plastic foams. CFC's are the exhaust of supersonic air craft's and jumbo jets flying in the upper atmosphere. They slowly pass from troposphere to stratosphere. They stay for very longer period of 50 - 100 years. In the presence of uv radiation, CFC's break up into chlorine free radical

$$CF_{2} Cl_{2} \xrightarrow{hv} CF_{2} Cl + Cl$$

$$CFCl_{3} \xrightarrow{hv} CFCl_{2} + Cl$$

$$Cl + O_{3} \rightarrow ClO + O_{2}$$

$$ClO + O \rightarrow Cl + O_{2}$$

Chlorine radical is regenerated in the course of reaction. Due to this continuous attack of Cl° thinning of ozone layer takes place which leads to formation of ozone hole.

It is estimated that for every reactive chlorine atom generated in the stratosphere 1,00,000 molecules of ozone are depleted.

15.4.2 Environmental Impact of Ozone Depletion

The formation and destruction of ozone is a regular natural process, which never disturbs the equilibrium level of ozone

in the stratosphere. Any change in the equilibrium level of the ozone in the atmosphere will adversely affect life in the biosphere in the following ways.

Depletion of ozone layer will allow more UV rays to reach the earth surface and layer would cause skin cancer and also decrease the immunity level in human beings.

UV radiation affects plant proteins which leads to harmful mutation of cells.

UV radiation affects the growth of phytoplankton, as a result ocean food chain is disturbed and even damages the fish productivity.

15.5 Water Pollution

Water is essential for life. Without water life would have been impossible. The slogan, 'Save Water, Water will save you' tell us the importance of water. Such slogans tell us to save water. Apart from saving water, maintaining its quality is also equally important.



Fig 15.6 water pollution

Now a days water is getting polluted due to human activities and the availability of potable water in nature is becoming rare day by day. Water pollution is defined as "The addition of foreign substances or factors like heat which degrades the

quality of water, so that it becomes health hazard or unfit to use."

The water pollutants originate from both natural and human activities. The source of water pollution is classified as Point and Non-point source.

Easily identified source of place of pollution is called as point source. Example: municipal and industrial discharge pipes.

Non-point source cannot be identified easily, example: agricultural runoff, mining wastes, acid rain, and storm-water drainage and construction sediments.

Table 15.2: List of major water pollutants and their sources.

No	Pollutant	Sources	
1	Microorganisms	Domestic sewage, domestic waste water, dung heap	
2	Organic wastes	Domestic sewage, animal excreta, food processing factory	
		waste, detergents and decayed animals and plants,	
3	Plant nutrients	Chemical fertilisers	
4	Heavy metals	Heavy metal producing factories	
5	Sediments	Soil erosion by agriculture and strip-mining	
6	Pesticides	Chemicals used for killing insects, fungi and weeds	
7	Radioactive	Mining of uranium containing minerals	
	substances		
8	Heat	Water used for cooling in industries	

15.6 Causes of water pollution

(i) Microbiological (Pathogens)

Disease causing microorganisms like bacteria, viruses and protozoa are most serious water pollutants.

They come from domestic sewage and animal excreta. Fish and shellfish can become contaminated and people who eat them can become ill. Some serious diseases like polio and cholera are water borne diseases. Human excreta contain bacteria such as Escherichia coli and Streptococcus faecalis which cause gastrointestinal diseases

(ii) Organic wastes:

Organic matter such as leaves, grass, trash etc can also pollute water. Water pollution is caused by excessive phytoplankton growth within water.

Microorganisms present in water decompose these organic matter and consume dissolved oxygen in water.

Eutrophication:

Eutrophication is a process by which water bodies receive excess nutrients that stimulates excessive plant growth (algae, other plant weeds). This enhanced plant growth in water bodies is called as algae bloom.

The growth of algae in extreme abundance covers the water surface and reduces the oxygen concentration in water. Thus, bloom-infested water inhibits thegrowth of other living organisms in the water body. This process in which the nutrient rich water bodies support a dense plant population, kills animal life by depriving it of oxygen and results in loss of biodiversity is known as eutrophication.

Biochemical oxygen demand(BOD)

The total amount of oxygen in milligrams consumed by microorganisms in decomposing the waste in one litre of water at 20°C for a period of 5 days is called biochemical oxygen demand (BOD) and its value is expressed in ppm.

BOD is used as a measure of degree of water pollution. Clean water would have BOD value less than 5 ppm whereas

highly polluted water has BOD value of 17 ppm or more.

Chemical Oxygen Demand (COD)

BOD measurement takes 5 days so another parameter called the Chemical Oxygen Demand (COD) is measured.

Chemical oxygen demand (COD) is defined as the amount of oxygen required by the organic matter in a sample of water for its oxidation by a strong oxidising agent like K2Cr2O7 in acid medium for a period of 2 hrs.

(iii) Chemical wastes:

A whole variety of chemicals from industries, such as metals and solvents are poisonous to fish and other aquatic life.

Some toxic pesticides can accumulate in fish and shell fish and poison the people who eat them. Detergents and oils float and spoil the water bodies. Acids from mine drainage and salts from various sources can also contaminate water sources.

Harmful effects of chemical water pollutants:

- 1. Cadmium and mercury can cause kidney damage.
- 2. Lead poisoning can leads to the severe damage of kidneys, liver, brain etc. it also affects central nervous system
- 3. Polychlorinated biphenyls (PCBs) causes skin diseases and are carcinogenic in nature.

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15.7 Quality of drinking water:

Now a days most of us hesitate to use natural water directly for drinking, because biological, physical or chemical impurities from different sources mix with surface water or ground water.

Institutions like WHO (World Health Organisation) at world level and BIS (Bureau of Indian Standards) and ICMR (ICMR: Indian Council of Medical Research) at national level have prescribed standards for quality of drinking water. Standard characteristics prescribed for deciding the quality of drinking water by BIS, in 1991 are shown in Table.15.3

Table 15.3 Standard characteristics of drinking water

S.No	Characteristics	Desirable limit	
I	Physico-chemical Characteris	tics	
i)	рН	6.5 to 8.5	
ii)	Total Dissolved Solids (TDS)	500 ppm	
iii)	Total Hardness (as CaCO ₃)	300 ppm	
iv)	Nitrate	45 ppm	
v)	Chloride	250 ppm	
vi)	Sulphate	200 ppm	
vii)	Fluoride	1 ppm	
II	Biological Characteristics		
i)	Escherichia Coli (E.Coli)	Not at all	
ii)	Coliforms	Not to exceed 10 (In 100 ml water sample)	

Fluoride:

Fluoride ion deficiency in drinking water causes tooth decay. Water soluble fluorides are added to increase the fluoride ion concentration upto 1 ppm.

The Fluoride ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_3]$.

However, Fluoride ion concentration above 2 ppm causes brown mottling of teeth. Excess fluoride causes damage to bone and teeth.

Lead:

Drinking water containing lead contamination above 50ppb can cause damage to

liver, kidney and reproductive systems.

Sulphate:

Moderate level of sulphate is harmless. Excessive concentration (>500ppm) of sulphates in drinking water causes laxative effect.

Nitrate:

Use of drinking water having concentration of nitrate higher than 45 ppm may causes methemoglobinemia (blue baby syndrome) disease in children.

Total dissolved solids (TDS):

Most of the salts are soluble in water. It includes cations like calcium, magnesium, sodium, potassium, iron and anions like carbonate, bicarbonate, chloride, sulphate, phosphate and nitrate. Use of drinking water having total dissolved solids concentration higher than 500 ppm causes possibilities of irritation in stomach and intestine.

15.8 Soil Pollution



Fig 15.7 soil pollution

Soil is a thin layer of organic and inorganic material that covers the earth's rocky surface. Soil constitutes the upper crust of the earth, which supports land, plants and animals.

Soil pollution is defined as the buildup of persistent toxic compounds , radioactive materials, chemical salts and disease causing agents in soils which have harmful effects on plant growth and animal health.

Soil pollution affects the structure and fertility of soil, groundwater quality and food chain in biological ecosystem.

15.8.1 Sources of soil pollution

The major sources of which pollute the soil are discussed below

1) Artificial fertilizers:

Soil nutrients are useful for growth of plants. Plants obtains carbon, hydrogen and oxygen from air or water, whereas other essential nutrients like nitrogen, phosphorous, potassium, calcium, magnesium, sulphur are being absorbed from soil. To remove the deficiency of nutrients in soil, farmers add artificial fertilizers. Increased use of phosphate fertilizers or excess use of artificial fertilizers like NPK in soil, results in reduced yield in that soil.

2) Pesticides:

Pesticides are the chemicals that are used to kill or stop the growth of unwanted organisms. But these pesticides can affect the health of human beings. These are further classified as

a. Insecticides:

Insecticides like DDT ,BHC ,aldrin etc. can stay in soil for long period of time and are absorbed by soil. They contaminate root crops like carrot, raddish, etc.

b. Fungicide:

Organo mercury compounds are used as most common fungicide. They dissociate in soil to produce mercury which is highly toxic.

c. Herbicides:

Herbicides are the chemical compounds used to control unwanted plants. They are otherwise known as weed killers. Example sodium chlorate (NaClO₃) and sodium arsenite (Na₃ as O₃). Most of the herbicides are toxic to mammals.

3) Industrial wastes

Industrial activities have been the biggest contributor to the soil pollution especially the mining and manufacturing activities.

Large number of toxic wastes are released from industries. Industrial wastes include cyanides, chromates, acids, alkalis, and metals like mercury, copper, zinc, cadmium and lead etc. These industrial wastes in the soil surface lie for a long time and make it unsuitable for use.

15.9 Strategies to control environmental pollution

After studying air, water and soil pollution, as responsible individuals we must take responsibility to protect our environment. Think of steps which you would like to undertake for controlling environmental pollution not only in your locality but also in national and international level. We must realize about our environmental threat, focus strongly on this issues and be an eye opener to save our environment. We can think about following strategies to control environmental pollution.

- 1. Waste management: Environmental pollution can be controlled by proper disposal of wastes.
- 2. Recycling: a large amount of disposed waste material can be reused by recycling the waste, thus it reduces the land fill and converts waste into useful forms.
- 3. Substitution of less toxic solvents for highly toxic ones used in certain industrial processes.
- 4. Use of fuels with lower sulphur content (e.g., washed coal)
- 5. Growing more trees.
- 6. Control measures in vehicle emissions are adequate.

Efforts to control environmental pollution have resulted in development of science for synthesis of chemical favorable to environment and it is called green chemistry.

15.10 Green Chemistry

Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

For this, scientist are trying to develop methods to produce eco-friendly compounds. This can be best understood by considering the following example in which styrene is produced both by traditional and greener routes.

Traditional route

This method involves two steps. Carcinogenic benzene reacts with ethylene to form ethyl benzene. Then ethyl benzene on dehydrogenation using Fe₂O₃/ Al₂O₃ gives styrene.

Greener route

To avoid carcinogenic benzene, greener route is to start with cheaper and environmentally safer xylenes.

15.10.1. Green chemistry in day-to-day life

A few contribution of green chemistry in our day to day life is given below

(1) Dry cleaning of clothes

Solvents like tetrachloroethylene used in dry cleaning of clothes, pollute the ground water and are carcinogenic. In the place of tetrachloroethylene, liquefied CO₂ with suitable detergent, is an alternate solvent used. Liquified CO₂ is not harmful

to the ground water. Now a days H_2O_2 used for bleaching clothes in laundry, gives better results and utilizese less water.

(2) Bleaching of paper

Conventional method of bleaching was done with chlorine. Now a days H_2O_2 can be used for bleaching paper in presence of catalyst.

(3) Synthesis of chemicals

Acetaldehyde is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with 90% yield.

$$CH_2 = CH_2 + O \xrightarrow{\text{Catalyst}} CH_3 CHO$$

Ethylene Acetaldehyde

(4) Instead of petrol, methanol is used as a fuel in automobiles.

(5) Neem based pesticides have been synthesised, which are more safer than the chlorinated hydrocarbons.

Every individual has an important role for preventing pollution and improving our environment. We are responsible for environmental protection. Let us begin to save our environment and provide a clean earth for our future generations.

SUMMARY

Environmental chemistry plays a vital role in environment. Environmental chemistry means scientific study of chemical and bio chemical process occurring in environment. World

Environmental Day is celebrated on fifth of June of every year.

Environmental Pollution:

Environmental pollution is the effect of undesirable changes in the surrounding that haveharmful effects on living things.

Pollutants are generally classified as rapidly degradable (e.g. discarded vegetables), slowly degradable (e.g. Agriculture waste) and non-bio degradable pollutants (e.g. DDT, plastic materials).

Atmospheric pollution

Atmospheric pollutions include tropospheric and stratospheric pollution. Troposphere and stratosphere greatly affect the biosphere of the earth due to which the study of pollutions in these regions is most important.

Tropospheric pollution:

Troposphere is the lowest region of atmosphere in which man, animal and plants exist. Gaseous pollutants like SOx,NOx,CO,CO₂,O₃ hydrocarbons and particulate pollutants like dust, mist, fumes, smog cause pollutions in troposphere

Acid rain:

When the PH of rain water becomes lower than 5.6 it is called acid rain. Acid rain is a byproduct of various human activities that emit sulphuroxides and nitrogen oxides in atmosphere. It damages buildings, statues and other monuments..

The acid rain in water reservoir like rivers, ponds adversely affects microbes, aquatic plants and fishes.

Greenhouse effect:

The process of warming up of earth is known as greenhouse effect or global warming. CO_2 , CH_4 , O_3 , CFC, N_2 and water vapour present in atmosphere act as a greenhouse gases. Heat retaining capacity of greenhouse gases are called Global Warming Potential (GWP). The GWP based sequence of greenhouse gases is as $CFC>N_2O>CH_4>CO_2$.

Stratospheric pollution:

Stratosphere extends above troposphere up to 50Km above.

Depletion of ozone layer:

Ozone layer present in stratosphere protect the living species against harmful UV rays from space but Ozone Depletion Substance (ODS) used by humans deplete ozone layer. To create awareness in the Whole world, United Nations decided to celebrate 16th September of every year as "Ozone Layer Protection Day".

Water pollution

Water is the elixir of life, but it is polluted by point and nonpoint sources. Institutions like World Health Organization (WHO) and Bureau of Indian standards (BIS) and Indian Council of Medical Research (ICMR) have prescribed standards for quality of drinking water.

Soil pollution

Lithosphere with humus cover is known as soil. The topsoil provides water and all nutrients required by plants for their growth. Industrial waste, artificial fertilisers and pesticides result in soil pollution.

Waste management

The strategies for controlling environmental pollution are called can be waste management. Waste management involves reduction and proper disposal of waste. Wastes are produced in three forms, solid, liquid and gase. Solid waste can be disposed by segregation, dumping, incineration and composting.

Green chemistry

Efforts to control environmental pollution resulted in development of science for synthesis of chemicals favorable to environment which is called green chemistry. Green chemistry means science of environmentally favorable chemical synthesis.

Evaluation



- 1. The gaseous envelope around the earth is known as atmosphere. The region lying between an altitudes of 11-50 km is ______
 - a) Troposphere
- b) Mesosphere
- c) Thermosphere
- d) stratosphere
- 2. Which of the following is natural and human disturbance in ecology?

- a) Forest fire b) Floods
- c) Acid rain
- d) Green house effect
- 3. Bhopal Gas Tragedy is a case of
 - a) thermal pollution
 - b)air pollution
 - c) nuclear pollution
 - d) land pollution
- 4. Haemoglobin of the blood forms carboxy haemoglobin with
 - a) Carbon dioxide
 - b) Carbon tetra chloride
 - c) Carbon monoxide
 - d) Carbonic acid
- 5. Which sequence for green house gases is based on GWP?
 - a) $CFC > N_2O > CO_2 > CH_4$
 - b) CFC > CO₂ > N₂O > CH₄
 - c) CFC > N₂O > CH₄> CO₂
 - d) $CFC > CH_4 > N_2O > CO_2$
- 6. Photo chemical smog formed in congested metropolitan cities mainly consists of
 - a) Ozone, SO₂ and hydrocarbons
 - b) Ozone, PAN and NO,
 - c) PAN, smoke and SO,
 - d) Hydrocarbons, SO₂ and CO₂
- 7. The pH of normal rain water is
 - a) 6.5 b) 7.5
 - c) 5.6 d) 4.6

- 8. Ozone depletion will cause
 - a) forest fires
 - b) eutrophication
 - c) bio magnification
 - d) global warming
- 9. Identify the wrong statement in the following
 - a) The clean water would have a BOD value of more than 5 ppm
 - b) Greenhouse effect is also called as Global warming
 - c) Minute solid particles in air is known as particulate pollutants
 - d) Biosphere is the protective blanket of gases surrounding the earth
- 10. Living in the atmosphere of CO is dangerous because it
 - a) Combines with O_2 present inside to form CO_2
 - b) Reduces organic matter of tissues
 - c) Combines with haemoglobin and makes it incapable to absorb oxygen
 - d) Dries up the blood
- 11. Release of oxides of nitrogen and hydrocarbons into the atmosphere by motor vehicles is prevented by using
 - a) grit chamber
 - b) scrubbers
 - c) trickling filters
 - d) catalytic convertors

- 12. Biochemical oxygen Demand value less than 5 ppm indicates a water sample to be
 - a) highly polluted
 - b) poor in dissolved oxygen
 - c) rich in dissolved oxygen
 - d) low COD
- 13. Match the List I with List II and select the correct answer using the code given below the lists

	List I	List	II
A	Depletion of ozone layer	1	CO ₂
В	Acid rain	2	NO
С	Photochemical smog	3	SO ₂
D	Green house effect	4	CFC

Code:

	A	В	C	D
a	3	4	1	2
b	2	1	4	3
c	4	3	2	1
d	2	4	1	3

14.

	List I	List	II
A	Stone leprosy	1	CO
В	Biological magnification	2	Green house gases
С	Global warming	3	Acid rain
D	Combination with haemoglobin	4	DDT

Code:

	A	В	C	D
a	1	2	3	4
b	3	4	2	1
c	2	3	4	1
d	4	2	1	3

The questions gives below consists of an assertion the reason. Choose the correct option out of the choices given below each question

- i) Both (A) and R are correct and (R)is the correct explanation of (A)
- ii) Both (A) and R are correct and (R) is not the correct explanation of (A)
- iii) Both (A) and R are not correct
- iv) (A) is correct but(R) is not correct
- 15. Assertion (A): If BOD level of water in a reservoir is more than 5 ppm it is highly polluted

Reason(R): High biological oxygen demand means high activity of bacteria in water

- a) i
- b) ii
- c) iii
- d) iv
- 16. **Assertion** (A): Excessive use of chlorinated pesticide causes soil and water pollution.

Reason (R): Such pesticides are non-biodegradable.

- a) i b) ii
- c) iii d) iv

17. **Assertion (A):** Oxygen plays a key role in the troposphere

Reason (**R**): Troposphere is not responsible for all biological activities

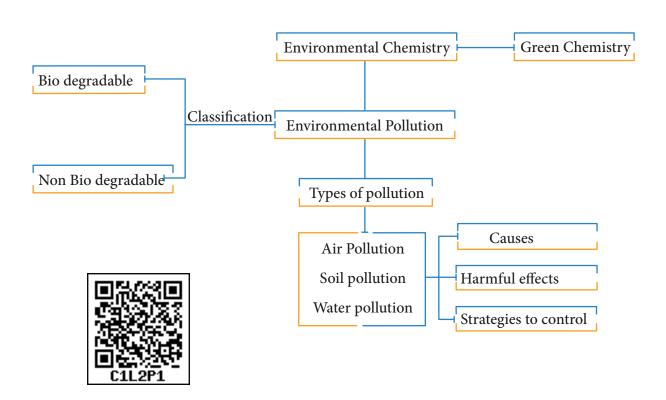
- a) i b) ii
- c) iii d) iv
- 18. Dissolved oxygen in water is responsible for aquatic life. What processes are responsible for the reduction in dissolved oxygen in water?
- 19. What would happen, if the greenhouse gases were totally missing in the earth's atmosphere?
- 20. Define smog.
- 21. Which is considered to be earth's protective umbrella? Why?
- 22. What are degradable and non-degradable pollutants?
- 23. From where does ozone come in the photo chemical smog?
- 24. A person was using water supplied by corporation. Due to shortage of water he started using underground water. He felt laxative effect. What could be the cause?
- 25. What is green chemistry?
- 26. Explain how does greenhouse effect cause global warming
- 27. Mention the standards prescribed by BIS for quality of drinking water
- 28. How does classical smog differ from photochemical smog?
- 29. What are particulate pollutants? Explain any three.

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- 30. Even though the use of pesticides increases the crop production, they adversely affect the living organisms. Explain the function and the adverse effects of the pesticides.
- 31. Ethane burns completely in air to give CO2, while in a limited supply of air gives CO. The same gases are found in automobile exhaust. Both CO and CO2 are atmospheric pollutants
 - i) What is the danger associated with these gases
 - ii) How do the pollutants affect the human body?

- 32. On the basis of chemical reactions involved, explain how do CFC's cause depletion of ozone layer in stratosphere?
- 33. How is acid rain formed? Explain its effect
- 34. Differentiate the following
 - (i) BOD and COD
 - (ii) Viable and non-viable particulate pollutants
- 35. Explain how oxygen deficiency is caused by carbon monoxide in our blood? Give its effect
- 36. What are the various methods you suggest to protect our environment from pollution?





PERIODIC CLASSIFICATION OF ELEMENTS

"An awareness of the periodic table is essential to anyone who wishes to disentangle the word and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements"

- Glenn T. Seaborg



Glenn T. Seaborg

Glenn Theodore Seaborg received Nobel Prize in 1951 in chemistry for the discoveries trans-uranium of elements. He was the co-discoverer of plutonium and other transuranium elements. He along with his colleagues has discovered over a hundred isotopes of other elements. He demonstrated that actinide elements are analogues to rare earth series of lanthanide elements.

Learning Objectives (©



After studying this unit, students will be able to

 recognise the development of the periodic table



- explain the work of Mosley's and modern periodic law
- outline the concept of grouping elements
- name the elements with atomic number greater than 100 using IUPAC nomenclature
- classify the elements into s, p, d and f blocks
- recognise the periodic trends and describe qualitatively the variation in periodic properties such as atomic radius, ionisation energy etc.
- explain the anomalies in the expected trend in the periodic properties
- calculate the effective nuclear charge using Slater's rule
- calculate the ionic radius using Pauling's method
- predict the probable position for a given element in the periodic table
- explain the anomalous properties of second period elements and the diagonal relationship

Introduction

There are millions of chemical compounds existing in nature with different compositions and properties, formed from less than 100 naturally occurring elements.

The discovery of elements is linked with human civilization. In stone age man has used some metals to suit his needs without knowing that they are elements. Soon he learnt to extract elements from ores and fashion them into his daily life. Over the years, more and more elements were discovered. In 1789, Lavoisier from France, published the first list of chemical elements containing 23 elements after several experimental investigations.

Antoine Lavoisier classified the substances into four groups of elements namely acid-making elements, gas-like elements, metallic elements and earthy elements

Table 3.1 Lavoisier table

acid-making elements	gas-like elements
sulphur	light
phosphorus	caloric (heat)
charcoal (carbon)	oxygen
	azote (nitrogen)
	hydrogen

metallic elements	earthy elements
cobalt, mercury, tin	lime (calcium
cobart, increary, tim	oxide)
copper, nickel, iron	magnesia (magne-
copper, meker, from	sium oxide)
gold, lead, silver, zinc	barytes (barium
gold, icad, silver, zinc	sulphate)
manganese, tungten	argilla (aluminium
manganese, tungten	oxide)
platina (platinum)	silex (silicon diox-
piacina (piacinani)	ide)

3.1 Classification of Elements

During the 19th century, scientists have isolated several elements and the list of known elements increased. Currently, we have 118 known elements. Out of 118 elements, 92 elements with atomic numbers 1 to 92 are found in nature. Scientists have found out there are some similarities in properties among certain elements. This observation has led to the idea of classification of elements based on their properties. In fact, classification will be beneficial for the effective utilization of these elements. Several attempts were made to classify the elements. However, classification based on the atomic weights led to the construction of a proper form of periodic table.

In 1817, J. W. Döbereiner classified some elements such as chlorine, bromine and iodine with similar chemical properties into the group of three elements called as triads. In triads, the atomic weight of the middle element nearly equal to the arithmetic mean of the atomic weights of the remaining two elements. However, only a limited number of elements can be grouped as triads.

Table 3.2 Döbereiner Triads

S. No.	Elements in the Triad	Atomic weight of middle element	Average atomic weight of the remaining elements
1	Li, Na, K	23	$\frac{-7+39}{2} = 23$
2	Cl, Br, I	80	$\frac{35.5 + 127}{2} = 81.25$
3	Ca, Sr, Ba	88	$\frac{40+137}{2} = 88.5$

This concept can not be extended to some triads which have nearly same atomic masses such as [Fe, Co, Ni], [Ru, Rh, Pd] and [Os, Ir, Pt].

In 1862, A. E. B. de Chancourtois reported a correlation between properties of the elements and their atomic weights. He said 'the properties of bodies are the properties of numbers'. He intended the term numbers to mean the value of atomic weights. He designed a helix by tracing at an angle 45° to the vertical axis of a cylinder with circumference of 16 units. He arranged the elements in the increasing atomic weights along the helix on the surface of this cylinder. One complete turn of a helix corresponds to an atomic weight increase of 16. Elements which lie on the 16 equidistant vertical lines drawn on the surface of cylinder shows similar properties. This was the first reasonable attempt towards the creation of periodic table. However, it did not attract much attention.

In 1864, J. Newland made an attempt to classify the elements and proposed the law of octaves. On arranging the elements in the increasing order of atomic weights, he observed that the properties of every eighth element are similar to the properties of the first element. This law holds good for lighter elements up to calcium.

Table 3.3 Newlands' Octaves

⁷ Li	⁹ Be	¹¹ B	¹² C	¹⁴ N	¹⁶ O	¹⁹ F
²³ Na	²⁴ Mg	²⁷ Al	²⁹ Si	³¹ P	³² S	^{35.5} Cl
³⁹ K	⁴⁰ Ca					

3.1.1 Mendeleev's Classification

In 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. He plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and observed a periodical pattern.

During same period Dmitri Mendeleev independently proposed that "the properties of the elements are the periodic functions of their atomic weights" and this is called periodic law. Mendeleev listed the 70 known elements at that time in several vertical columns in order of increasing atomic weights. Thus, Mendeleev constructed the first periodic table based on the periodic law.

Table 3.4 Mendeleev's periodic table

Series						Group	Group of Elements				
	0	1	II	III	IV	Λ	IN	VII		VIII	
-)	Hvdrogen									
1		H									
	'	1 0000		1	ı						
2	Heitum	Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine			
	Ge	Li	Be	В	O	Z		ц			
	4.0	7.03	9.1	11.0	12.0	14.04	16.00	19.0			
3	Neon	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine			
	Ne	Na	Mg	Al	Si	P	S	CI			
	19.9	23.5		27.0	28.04	31.0	32.06	35.45			
4	Argon	Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel
	Ar	K	Ca	Sc	ΙΪ	Λ	Cr	Mn	Fe	Co	(Ni (Cu
	38	39.1	40.1	44.1	48.1	51.4	51.99	55.0	55.9	59	59
2		Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine			
		Cu	Zn	Ga	Ge	As	Se	Br			
		63.6			72.3	75	79	79.95			
9	Krypton	Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	1	Ruthenium	Rhodium	Palladium
	Kr	Rb	Sr	Y	Zr	N _P	Mo		Ru	Rh	(Pd (Ag
	81.8	85.4	87.6	89.0	90.6	94.0			101.7		106.5
7		Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine			
		Ag	Cd	In	Sn	Sb	Te	I			
		1(112.4	114.0	119.0	120.0	127.6	126.9			
8	Xenon	Caesium	Barium	Lanthanum	Cerium	1	ı	1	1		
	Xe	S	Ba	La	Ce						
	128	132.9	137.4	139	140						
6	1	1	1	1	1	1	1	•	1		
10				Ytterbium		Tantalum	Tungsten		Osmium	Iridium	Platinum
	1	1	1	Yb	1	Ta	W	1	Os	Ir	(Pt (Au
						183			191	193	194.9
11			Gold	Mercury	Thallium	Lead	Bismuth	I	1		
			Au	$_{ m Hg}$	工	Pb	Bi				
			197.2	200.0	204.1	206.9	208				
12			Radium		Thorium		Uranium				
	,	,	Ra	,	£	,	11				
			224		232		239				
					-	Higher Saline Oxides					
	R	R_2O	R_2O_3		RO ₂	R_2O_5	RO ₃	R_2O_7		Od	
					Higher G	aseous Hydrog	en Compo			4	
					\mathbb{RH}_4	RH3	RH2	RH			

As shown in the periodic table, he left some blank spaces since there were no known elements with the appropriate properties at that time. He and others predicted the physical and chemical properties of the missing elements. Eventually these missing elements were discovered and found to have the predicted properties. For example, Gallium (Ga) of group III and germanium (Ge) of group IV were unknown at that time. But Mendeleev predicted their existence and properties. He referred the predicted elements as eka-aluminium and eka-silicon. After discovery of the actual elements, their properties were found to match closely to those predicted by Mendeleev (Table 3.4).

Table 3.5 Properties predicted for Eka-aluminium and Eka-silicon

S.No.	Property	Eka-aluminium (Predicted)	Gallium (Observed)	Eka-silicon (Predicted)	Germanium (Observed)
1.	Atomic weight	68	70	72	72.59
2.	Density (g/cm ³)	5.9	5.94	5.5	5.35
3.	Melting point	low	29.78°C	High	947°C
4.	Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
5.	Formula of chloride	ECl ₃	GaCl ₃	ECl ₄	GeCl ₄

3.1.2 Anomalies of Mendeleev's Periodic Table

Some elements with similar properties were placed in different groups and those with dissimilar properties were placed in same group.

Example: Tellurium (127.6) was placed in VI group but Iodine (127.0) was placed in VII group.

Similarly elements with higher atomic weights were placed before lower atomic weights based on their properties in contradiction to his periodic law. Example $^{59}\mathrm{Co}_{27}$ was placed before $^{58.7}\mathrm{Ni}_{28}$

3.2 Moseley's Work and Modern Periodic Law

In 1913, Henry Moseley studied the characteristic X-rays spectra of several elements by bombarding them with high energy electrons and observed a linear correlation between atomic number and the frequency of X-rays emitted which is given by the following expression.

$$\sqrt{\upsilon} = a(Z - b)$$

Where, v is the frequency of the X-rays emitted by the element with atomic number 'Z'; a and b are constants and have same values for all the elements.

The plot of $\sqrt{\nu}$ against Z gives a straight line. Using this relationship, we can determine the atomic number of an unknown (new) element from the frequency of X-ray emitted.

Based on his work, the modern periodic law was developed which states that, "the physical and chemical properties of the elements are periodic functions of their atomic numbers." Based on this law, the elements were arranged in order of their increasing atomic numbers. This mode of arrangement reveals an important truth that the elements with similar properties recur after regular intervals. The repetition of physical and chemical properties at regular intervals is called periodicity.

3.2.1 Modern Periodic Table

The physical and chemical properties of the elements are correlated to the arrangement of electrons in their outermost shell (valence shell). Different elements having similar outer shell electronic configuration possess similar properties. For example, elements having one electron in their valence shell s-orbital possess similar physical and chemical properties. These elements are grouped together in the modern periodic table as first group elements.

Table 3.6 Electronic configuration of alkali metals (ns¹)

Elements in Group 1	Atomic number		Valence shell configuration
Li	3	2, 1	2s ¹
Na	11	2, 8, 1	$3s^1$
K	19	2, 8, 8, 1	4s ¹
Rb	37	2,8,18,8,1	5s ¹
Cs	55	2, 8, 18, 18, 8, 1	6s ¹
Fr	87	2, 8, 18, 32, 18, 8, 1	7s ¹

Similarly, all the elements are arranged in the modern periodic table which contains 18 vertical columns and 7 horizontal rows. The vertical columns are called groups and the horizontal rows are called periods. Groups are numbered 1 to 18 in accordance with the IUPAC recommendation which replaces the old numbering scheme IA to VIIA, IB to VIIB and VIII.

Each period starts with the element having general outer electronic configuration ns¹ and ends with np⁶. Here 'n' corresponds to the period number (principal quantum number). The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the modern periodic table.

Evaluate Yourself



1. What is the basic difference in approach between Mendeleev's periodic table and modern periodic table ?

Table 3.7 Modern periodic table

Noble gases	0	2 He	$1s^2$	10	$\frac{\text{Ne}}{2s^22p^6}$	18	$\frac{\text{Ar}}{3s^2 3p^6}$	36	Kr	$4s^24p^6$	54	Xe	$5s^{2}5p^{6}$	98	$\frac{\mathrm{Rn}}{6s^26p^6}$	118	Og	
		17	VIIB	6	$\frac{\mathrm{F}}{2s^2 2p^5}$	17	$\frac{\text{Cl}}{3s^23p^5}$	35	Br	$4s^24p^5$			$5s^{2}5p^{5}$	85	$At \\ 6s^26p^5$	117	Ts	
Representative elements ——GROUP NUMBER		16	VIB	∞	O $2s^22p^4$	16	$\frac{S}{3s^23p^4}$	34	Se	$4s^24p^4$		Te		84	$\begin{array}{c} \text{Po} \\ 6s^26p^4 \end{array}$	116	Lv	
esentative GROUP		15	VB	7	$N \\ 2s^2 2p^3$	15	$\frac{P}{3s^23p^3}$	23	As	$4s^24p^3$	15	Sb	$5s^25p^3$	83	${\rm Bi} \\ 6s^26p^3$	115	Mc	
Represe ——GF		14	IV B	9	$\frac{\mathrm{C}}{2s^22p^2}$	14	$\frac{\mathrm{Si}}{3s^2 3p^2}$	32	Ge	$4s^24p^2$	95	Sn	$5s^{2}5p^{2}$	82	$_{6s^26p^2}^{\text{Pb}}$	114	Fl	
		13	III B	5	$\mathbf{B}_{2s^22p^1}$	13	$\begin{array}{c} \text{Al} \\ 3s^2 3p^1 \end{array}$	31	Ga	$4s^24p^1$	65	In	$5s^25p^1$	81	Γl $6s^26p^1$	113	NN	
						- 2	II B	30	Zn	$3d^{4}4s^{2}$	48	Cd	$4d^{10}5s^2$	80	$_{5d^{10}6s^2}^{\mathrm{Hg}}$	112	Cn	
						=	IB	67	Cu	$3d^{10}4s^{1}$	47	Ag	$4d^{10}5s^{1}$	62	$\mathop{\mathrm{Au}}_{5d^{10}6s^1}$	111	Rg	
						10		28	ïZ	$3d^{8}4s^{2}$	46	Pd	$4d^{10}$	78	Pt 5 <i>d</i> 6 <i>s</i> ¹	110	Ds	
				nts	Ж -	6	- VIII	27	္	$3d^{7}4s^{2}$	45	Rh	$4d^85s^1$	77	$\lim_{5d'6s^2}$	109	Mt	
				n eleme	NUMBER	×	, \	97	Fe	$3d^{6}4s^{2}$	44		$4d^{7}5s^{1}$	92	$\underset{5d^{6}s^{2}}{\operatorname{Os}}$	108	Hs	
	1	$\begin{array}{c} { m H} \\ { m Is}_{ m l} \end{array}$		d-Transition elements	GROUP]	7	VIIA	25	Mn	$3d^{5}4s^{2}$	43	Tc	$4d^{5}5s^{2}$	75	$\mathop{\rm Re}_{5d^5\!6s^2}$	107	Bh	
				d-T	5	9	>	24		$3d^{5}4s^{1}$		Mo		74	$\frac{W}{5d^46s^2}$	106	$_{\rm g}$	
						v	VA	23	>	$3d^{3}4s^{2}$	41	SP	$4d^{4}5s^{1}$	73	La* Hf Ta $5d^{4}6s^{2}$ $4f^{4}5d^{2}6s^{2}$ $5d^{3}6s^{2}$	105	Db	
						4	IVA	22	Ti	$3d^{2}4s^{2}$	40	Zr	$4d^{2}5s^{2}$	72	$^{\mathrm{Hf}}_{4f^{14}5d^{2}6s^{2}}$	104	Rf	
						- (r	IIIA	21	Sc	$3d^{1}4s^{2}$	39	Υ	$4d^{1}5s^{2}$	57	La^*	68	Ac*	6d ⁻ 7s ⁻
Representative elements	UP BER 🗌	2	IIA	4	$\frac{\mathrm{Be}}{2s^2}$	12	${ m Mg}_{3s^2}$	20	Ca	$4s^{2}$	38	Sr	$5s^{2}$	99	$\frac{\mathrm{Ba}}{6s^2}$	88	Ra	787
Repres elem	GROUP NUMBER	-	IA	3	Li 2s1	111	$\frac{Na}{3s^1}$	19	K	$4s^1$	37	Rb	$5s^1$	55	Cs 6s ¹	87	Fr	$7s^{1}$
		,	Ĺ		5		œ BE <i>K</i>	IW.	UN 4	D I	ΙΟΙ	∾ EK	d -		9			

f- Inner transition elements

					7
71	Lu	$4f^{14}5d^{1}6s^{2}$	103	Lr	25f146d17s
0/	Yb	$4f^{14}5d^{0}6s^{2}$	102	No	5f146d07s
69	Tm	$4f^{13}5d^{0}6s^{2}$	101	Md	5f136d07s
89	Er	$ 4f^{12}5d^{0}6s^{2}$	100	Fm	$ 5f^{12}6d^{0}7s^{2}$
29	Но	$ 4f^{11}5d^{0}6s^{2}$	66	Es	$5f^{11}6d^{0}7s^{2}$
99	Dy	$4f^{10}5d^{0}6s^{2}$	86	Cf	$5f^{10}6d^{0}7s^{2}$
65	Tb	$ 4f^{9}5d^{0}6s^{2}$	26	Bk	5f96d07s2
64	Cd	$4f^{7}5d^{1}6s^{2}$	96	Cm	$5f^{7}6d^{1}7s^{2}$
63	Eu	$4f^{7}5d^{0}6s^{2}$	95	Am	$5f^{7}6d^{0}7s^{2}$
62	Sm	$ 4f^{6}5d^{0}6s^{2}$	94	Pu	$ 5f^{6}6d^{0}7s^{2}$
61	Pm	$ 4f^{5}5d^{0}6s^{2}$	93	dN	$ 5f^{4}6d^{1}7s^{2}$
09	pN	$ 4f^{4}5d^{0}6s^{2}$	92	Ω	$ 5f^36d^47s^2$
59	Pr	$4f^{3}5d^{0}6s^{2}$	91	Pa	$ 5f^26d^47s^2$
58	Ce Pr	$4f^{2}5d^{0}6s^{2}$	06	Th	$5f^{0}6d^{2}7s^{2}$
	* anthanoids	s9 pc	÷	*Actinoids	"6d" 7s²

3.3 Nomenclature of Elements with Atomic Number Greater than 100

Usually, when a new element is discovered, the discoverer suggests a name following IUPAC guidelines which will be approved after a public opinion. In the meantime, the new element will be called by a temporary name coined using the following IUPAC rules, until the IUPAC recognises the new name.

1. The name was derived directly from the atomic number of the new element using the following numerical roots.

Table 3.8 Notation for IUPAC Nomenclature of elements

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	р	h	s	0	e

- 2. The numerical roots corresponding to the atomic number are put together and 'ium' is added as suffix
- 3. The final 'n' of 'enn' is omitted when it is written before 'nil' (enn + nil = enil) similarly the final 'i' of 'bi' and 'tri' is omitted when it written before 'ium' (bi + ium = bium; tri + ium = trium)
- 4. The symbol of the new element is derived from the first letter of the numerical roots.

The following table illustrates these facts.

Table 3.9 Name of elements with atomic number above 100

Atomic number	Temporary Name	Temporary Symbol	Name of the element	Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordiium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs

Atomic number	Temp. Name	Temp. Symbol	Name of the element	Symbol
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Roentgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Мс
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Evaluate Yourself



2. The element with atomic number 120 has not been discovered so far. What would be the IUPAC name and the symbol for this element? Predict the possible electronic configuration of this element.

3.4 Grouping of Elements based on Electronic Configurations

In the modern periodic table, the elements are organised in 7 periods and 18 groups based on the modern periodic law. The placement of element in the periodic table is closely related to its outer shell electronic configuration. Let us analyse the change in the electronic configuration of elements along the periods and down the groups.

3.4.1 Variation of Electronic Configuration along the periods

We have already learnt that each period starts with the element having general outer electronic configuration ns¹ and ends with ns², np⁶ where n is the period number. The first period starts with the filling of valence electrons in 1s orbital, which can accommodate only two electrons. Hence, the first period has two elements, namely hydrogen and helium. The second period starts with the filling of valence electrons in 2s orbital followed by three 2p orbitals with eight elements from lithium to neon. The third period starts with filling of valence electrons in the 3s orbital followed by 3p orbitals. The fourth period starts with filling of valence electrons from 4s orbital followed by 3d and 4p orbitals in accordance with Aufbau principle. Similarly, we can explain the electronic configuration of elements in the subsequent periods (Table 3.10).

Table 3.10 Electronic configuration of elements in a period

Period number	Filling of electrons in	orbitals	Number of elements	Outer shell Electronic con- figuration			
(n)	Starts from	Ends with	elements	First element	Last element		
1	1s —	1s	2	H – 1s ¹	He – 1s ²		
2	2s	→ 2p	8	Li – 2s ¹	Ar- 2s ² 2p ⁶		
3	3s	→ 3p	8	Na – 3s ¹	Ne – $3s^23p^6$		
4	4s 3d	→4p	18	K – 4s ¹	Kr- 4s ² 4p ⁶		
5	5s 4d	→ 5p	18	Rb – 5s ¹	$Xe - 5s^2 5p^6$		
6	6s 4f 3	→ 6p	32	Cs – 6s ¹	$Rn - 6s^26p^6$		
7	$7s \longrightarrow 5f \longrightarrow 6d$	→7p	32	Fr – 7s ¹	$Og - 7s^2 7p^6$		

In the fourth period the filling of 3d orbitals starts with scandium and ends with zinc. These 10 elements are called first transition series. Similarly 4d, 5d and 6d orbitals are filled in successive periods and the corresponding series of elements are called second, third and fourth transition series respectively.

In the sixth period the filling of valence electrons starts with 6s orbital followed by 4f, 5d and 6p orbitals. The filling up of 4f orbitals begins with Cerium (Z=58) and ends at Lutetium (Z=71). These 14 elements constitute the first inner-transition series called Lanthanides. Similarly, in the seventh period 5f orbitals are filled, and it's -14 elements constitute the second inner-transition series called Actinides. These two series are placed separately at the bottom of the modern periodic table.

3.4.2 Variation of Electronic Configuration in the Groups:

Elements of a group have similar electronic configuration in the outer shell. The general outer electronic configurations for the 18 groups are listed in the Table 3.11. The groups can be combined as s, p, d and f block elements on the basis of the orbital in which the last valence electron enters.

The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. The group 1 elements are called alkali metals while the group 2 elements are called alkaline earth metals. These are soft metals and possess low melting and boiling points with low ionisation enthalpies. They are highly reactive and form ionic compounds. They are highly electropositive in nature and most of the elements imparts colour to the flame. We will study the properties of these group elements in detail in subsequent chapters.

The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns², np¹-6. The elements of the group 16 and 17 are called chalcogens and halogens respectively. The elements of 18th group contain completely filled valence shell electronic configuration (ns², np6) and are called inert gases or nobles gases. The elements of p-block have high negative electron gain enthalpies. The ionisation energies are higher than that of s-block elements. They form mostly covalent compounds and shows more than one oxidation states in their compounds.

The elements of the groups 3 to 12 are called d-block elements or transition elements with general valence shell electronic configuration ns^{1-2} , $(n-1)d^{1-10}$. These elements also show more than one oxidation state and form ionic, covalent and co-ordination compounds. They can form interstitial compounds and alloys which can also act as catalysts. These elements have high melting points and are good conductors of heat and electricity.

The lanthanides $(4f^{1-14}, 5d^{0-1}, 6s^2)$ and the actinides $(5f^{0-14}, 6d^{0-2}, 7s^2)$ are called f-block elements. These elements are metallic in nature and have high melting points. Their compounds are mostly coloured. These elements also show variable oxidation states.

Table 3.11 General outer electronic configuration of elements in groups:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ns ¹	ns ²	$ns^2 (n-1)d^1$	$ns^2 (n-1)d^2$	$ns^2 (n-1)d^3$	ns ¹ (n-1)d ⁵	$ns^2 (n-1)d^5$	ns ² (n-1)d ⁶	$ns^2 (n-1)d^7$	$ns^2 (n-1)d^8$	$ns^1 \left(n\text{-}1 \right) d^{10}$	$ns^2 (n-1)d^{10}$	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	ns² np ⁶
	Block elements p-Block elements										ents						
f blo	ock	->	Lanthanides 4f ¹⁻¹⁴ 5d ⁰⁻¹ 6s ²														
elen	nents		Actinides 5f ⁰⁻¹⁴ 6d ⁰⁻² 7s ²														

Evaluate Yourself



3. Predict the position of the element in periodic table satisfying the electronic configuration $(n-1)d^2$, ns^2 where n=5

3.5 Periodic Trends in Properties

As discussed earlier, the electronic configuration of the elements shows a periodic variation with increase in atomic numbers. Similarly a periodic trend is observed in physical and chemical behaviour of elements. In this section, we will study the periodic trends in the following properties of elements.

- 1. Atomic radius
- 2. Ionic radius
- 3. Ionisation enthalpy (energy)
- 4. Electron gain enthalpy (electron affinity)
- 5. Electronegativity

3.5.1 Atomic radius

Atomic radius of an atom is defined as the distance between the centre of its nucleus and the outermost shell containing the valence electron.

It is not possible to measure the radius of an isolated atom directly. Except for noble gases, usually atomic radius is referred to as covalent radius or metallic radius depending upon the nature of bonding between the concerned atoms.

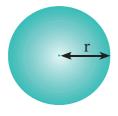


Figure 3.1 (a) Atomic radius

Covalent radius

It is one-half of the internuclear distance between two identical atoms linked together by a single covalent bond. Inter nuclear distance can be determined using x-ray diffraction studies.

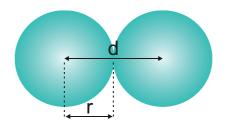


Figure 3.1 (b) Atomic and covalent radius

Example:

The experimental internuclear distance in Cl_2 molecule is 1.98 Å. The covalent radius of chlorine is calculated as below.

$$d_{Cl-Cl} = r_{Cl} + r_{Cl}$$

$$\Rightarrow d_{Cl-Cl} = 2r_{Cl}$$

$$\Rightarrow r_{Cl} = \frac{d_{Cl-Cl}}{2}$$

$$= \frac{1.98}{2} = 0.99\text{Å}$$

$$Cl \leftarrow covalent diameter$$

Figure 3.1 (c) Covalent radius of Cl

The covalent radius of chlorine =
$$\frac{198}{2}$$
 pm = 99 pm

The formation of covalent bond involves the overlapping of atomic orbitals and it reduces the expected internuclear distance. Therefore covalent radius is always shorter than the actual atomic radius.

The covalent radius of individual atom can also be calculated using the internuclear distance (d_{A-B}) between two different atoms A and B. The simplest method proposed by Schomaker and Stevenson is as follows.

$$d_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B)$$

where χ_A and χ_B are the electronegativities of A and B respectively in Pauling units. Here $\chi_A > \chi_B$ and radius is in Å.

Let us calculate the covalent radius of hydrogen using the experimental $d_{\text{H-Cl}}$ value is 1.28 Å and the covalent radius of chlorine is 0.99 Å. In pauling scale the electronegativity of chlorine and hydrogen are 3 and 2.1 respectively.

$$d_{H-Cl} = r_H + r_{Cl} - 0.09 (\chi_{Cl} - \chi_H)$$

$$1.28 = r_H + 0.09 - 0.09 (3 - 2.1)$$

$$1.28 = r_H + 0.09 - 0.09 (0.9)$$

$$1.28 = r_H + 0.09 - 0.081$$

$$1.28 = r_H + 0.909$$

$$\therefore r_H = 1.28 - 0.909 = 0.317 \text{ Å}$$

Metallic radius

It is defined as one-half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

For example, the distance between the adjacent copper atoms in solid copper is 2.56 Å and therefore the metallic radius of copper is

$$\frac{2.56}{2}$$
 = 1.28 Å

The metallic radius can be calculated using the unit cell length of the metallic crystal. You will study the detailed calculation procedure in XII standard solid state unit.

Periodic Trends in Atomic Radius

Variation in Periods

Atomic radius tends to decrease in a period. As we move from left to right along a period, the valence electrons are added to the same shell. The simultaneous addition of protons to the nucleus, increases the nuclear charge, as well as the electrostatic attractive force between the valence electrons and the nucleus. Therefore atomic radius decreases along a period.

Effective nuclear charge

In addition to the electrostatic forces of attraction between the nucleus and the electrons, there exists repulsive forces among the electrons. The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect.

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge. It is approximated by the below mentioned equation.

$$Z_{eff} = Z - S$$

Where Z is the atomic number and 'S' is the screening constant which can be calculated usi ng Slater's rules as described below.

Step 1:

Write the electronic configuration of the atom and rearrange it by grouping ns and np orbitals together and others separately in the following form.

Step 2:

Identify the group in which the electron of interest is present. The electron present right to this group does not contribute to the shielding effect.

Each of the electrons within the identified group (denoted by 'n') shields to an extent of 0.35 unit of nuclear charge. However, it is 0.30 unit for 1s electron.

Step 3:

Shielding of inner shell electrons.

If the electron of interest belongs to either s or p orbital,

- i) each electron within the (n-1) group shields to an extent of 0.85 unit of nuclear charge, and
- ii) each electron within the (n-2) group (or) even lesser group (n-3, (n-4) etc... completely shields i.e. to an extent of 1.00 unit of nuclear charge.

If the electron of interest belongs to d or f orbital, then each of electron left of the group of electron of interest shields to an extent of 1.00 unit of nuclear charge.

Step 4:

Summation of the shielding effect of all the electrons gives the shielding constant 'S'

Example: Let us explain the calculation of effective nuclear charge on 4s electron and 3d electron in scandium. The electronic configuration of scandium is 1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹. we can rearrange as below.

$$\underbrace{(1s)^2}_{\text{(n-3)}} \underbrace{(2s,2p)^8}_{\text{(n-2)}} \underbrace{(3s,3p)^8 (3d)^1}_{\text{(n-1)}} \underbrace{(4s)^2}_{\text{n}}$$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
(n)	1	0.35	0.35
(n-1)	9	0.85	7.65
(n-2) & others	10	1	10.00
	S value	18.00	

$$Z_{eff} = Z - S$$
 i.e. = 21 - 18 $\therefore Z_{eff} = 3$

Calculation of effective nuclear charge on 3d electron

$$\underbrace{(1s)^2}_{\text{(n-3)}} \underbrace{(2s,2p)^8}_{\text{(n-2)}} \underbrace{(3s,3p)^8}_{\text{(n-1)}} (3d)^1 \underbrace{(4s)^2}_{\text{n}}$$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value		
n	0	0.35	0		
(n-1) & others	18	1	18		
	18				

$$\therefore$$
 Z_{eff} = Z - S i.e. = 21 - 18 \therefore Z_{eff} = 3

Table 3.12 Shielding effect from inner shell electrons (Slater's rules)

Electron Group	Electron of interest either S or P	Electron of interest either d or f
n	0.35 (0.30 for (S electron)	0.35
(n-1)	0.85	1.00
(n-2) and others	1.00	1.00

Table 3.13 Atomic radius (covalent radius) of second period elements.

Elements	Effective nuclear charge	Covalent radius (pm)
Li ³	1.30	167
Be ⁴	1.95	112
C ⁶	2.60	87
N^7	3.25	67
O_8	3.25	56
F ⁹	4.55	48
Ne ¹⁰	5.85	38 [*]

* Van der waals radius

Evaluate Yourself

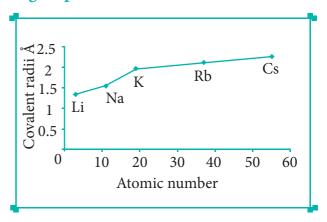


4. Using Slater's rule calculate the effective nuclear charge on a 3p electron in aluminium and chlorine. Explain how these results relate to the atomic radii of the two atoms.

Variation in Group

In the periodic table, the atomic radius of elements increases down the group. As we move down a group, new shells are opened to accommodate the newly added valence electrons. As a result, the distance between the centre of the nucleus and the outermost shell containing the valence electron increases. Hence, the atomic radius increases. The trend in the variation of the atomic radius of the alkali metals down the group os shown below.

Table 3.14 Variation of covalent radius of group 1 elements



Element	Outermost shell containing valence electron	Covalent radius (Å)
Li	L (n=2)	1.34
Na	M (n=3)	1.54
K	N (n=4)	1.96
Rb	O (n=5)	2.11
Cs	P(n=6)	2.25

Activity 3.1

Covalent radii (in Å) for some elements of different groups and periods are listed below. Plot these values against atomic number. From the plot, explain the variation along a period and a group.

2nd group elements: Be (0.89), Mg (1.36), Ca (1.74), Sr (1.91) Ba(1.98)

17th group elements: F (0.72), Cl (0.99), Br (1.14), I (1.33)

 3^{rd} Period elements : Na(1.57), Mg(1.36), Al (1.25), Si(1.17), P(1.10), S(1.04), Cl(0.99)

4th period elements: K(2.03),Ti(1.32),Ca(1.74),Sc(1.44),V(1.22),Cr(1.17),Mn(1.17),Fe(1.17), Co(1.16), Ni(1.15),Cu(1.17),Zn(1.25),Ga(1.25),Ge(1.22),As(1.21),Se(1.14),Br(1.14)

3.5.2 Ionic radius

It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the inter ionic distance between the nuclei of the cation and anion. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other therefore,

$$d = r_C^+ + r_A^-$$
 ----- (1)

Where d is the distance between the centre of the nucleus of cation C^+ and anion A^- and r_C^+ , r_A^- are the radius of the cation and anion respectively.

Pauling also assumed that the radius of the ion having noble gas electronic configuration (Na⁺ and Cl⁻ having 1s² 2s², 2p⁶ configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

i.e.
$$r_{C}^{+} \alpha \frac{1}{(Z_{eff})_{C+}}$$
 and
$$r_{A}^{-} \alpha \frac{1}{(Z_{eff})_{A^{-}}}$$
 (3)

Where Z_{eff} is the effective nuclear charge and Z_{eff} = Z - S

Dividing the equation 1 by 3

On solving equation (1) and (4) the values of $\rm r_{C^+}$ and $\rm r_{A^-}$ can be obtained

Let us explain this method by calculating the ionic radii of Na^+ and F^- in NaF crystal whose interionic distance is equal to 231 pm .

$$d = r_{Na^{+}} + r_{F^{-}} - - - (5)$$

i.e. $r_{Na^{+}} + r_{F^{-}} = 231 \text{ pm}$

We know that

$$\frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{\left(Z_{eff}\right)_{F^{-}}}{\left(Z_{eff}\right)_{Na^{+}}}$$

$$\left(Z_{eff}\right)_{F^{-}} = Z - S$$

$$= 9 - 4.15$$

$$= 4.85$$

$$\left(Z_{eff}\right)_{Na^{+}} = 11 - 4.15$$

$$= 6.85$$

$$\therefore \frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{4.85}{6.85}$$

$$= 0.71$$

$$\Rightarrow r_{Na^{+}} = 0.71 \times r_{F^{-}}$$
Substituting (3) in (1)
$$(1) \Rightarrow 0.71 \, r_{F^{-}} + r_{F^{-}} = 231 \, \text{pm}$$

$$1.71 \, r_{F^{-}} = 231 \, \text{pm}$$

$$r_{F^{-}} = \frac{231}{1.71} = 135.1 \, \text{pm}$$
Substituting the value of $r_{F^{-}}$ in equation (1)

Substituting the value of $r_{_{\!\Pi^{-}}}$ in equation (1)

$$r_{Na^{+}} + 135.1 = 231$$

 $r_{Na^{+}} = 95.9 \text{ pm}$

Evaluate Yourself



5. A student reported the ionic radii of isoelectronic species X³⁺, Y²⁺ and Z⁻ as 136 pm, 64 pm and 49 pm respectively. Is that order correct? Comment.

3.5.3 Ionisation energy

It is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state. It is expressed in kJ mol⁻¹ or in electron volts (eV).

$$M_{(g)} + IE_1 \rightarrow M^+_{(g)} + 1 e^{-1}$$

Where IE_1 represents the first ionisation energy.

Successive Ionisation energies

The minimum amount of energy required to remove an electron from a unipositive cation is called second ionisation energy. It is represented by the following equation.

$$M^{+}_{(g)} + IE_2 \rightarrow M^{2+}_{(g)} + 1 e^{-}$$

In this way we can define the successive ionisation energies such as third, fourth etc.

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order

$$IE_1 < IE_2 < IE_3 <$$

Periodic Trends in Ionisation Energy

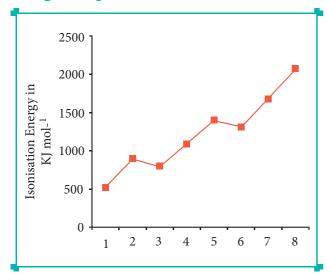
The ionisation energy usually increases along a period with few exceptions. As discussed earlier, when we move from left to right along a period, the valence electrons are added to the same shell, at the same time protons are added to the nucleus. This successive increase of nuclear charge increases the electrostatic attractive force on the valence electron and more energy is required to remove the valence electron resulting in high ionisation energy.

Let us consider the variation in ionisation energy of second period

elements. The plot of atomic number vs ionisation energy is given below.

In the following graph, there are two deviation in the trends of ionisiation energy. It is expected that boron has higher ionisation energy than beryllium since it has higher nuclear charge. However, the actual ionisation energies of beryllium and boron are 899 and 800 kJ mol⁻¹ respectively contrary to the expectation. It is due to the fact that beryllium with completely filled 2s orbital, is more stable than partially filled valence shell electronic configuration of boron. (2s² 2p¹)

Figure 3.2 Variation of Ionisation energy along the I period



The electronic configuration of beryllium (Z=4) in its ground state is $1s^2$, $2s^2$ and that of boran (Z = 5) $1s^2$ $2s^2$ $2p^1$

Similarly, nitrogen with 1s², 2s², 2p³ electronic configuration has higher ionisation energy (1402 kJ mol⁻¹) than oxygen (1314 kJ mol⁻¹). Since the half filled electronic configuration is more stable, it requires higher energy to remove an electron from 2p orbital of nitrogen. Whereas the removal one 2p electron from oxygen leads to a stable half filled

configuration. This makes comparatively easier to remove 2p electron from oxygen.

Periodic variation in group

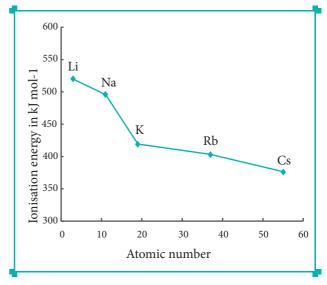
The ionisation energy decreases down a group. As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases. So, the nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

Ionisation energy and shielding effect

As we move down a group, the number of inner shell electron increases which in turn increases the repulsive force exerted by them on the valence electrons, i.e. the increased shielding effect caused by the inner electrons decreases the attractive force acting on the valence electron by the nucleus. Therefore the ionisation energy decreases.

Let us understand this trend by considering the ionisation energy of alkali metals.

Figure 3.3 Variation of Ionisation energy down the I Group.



Evaluate Yourself



6. The first ionisation energy (IE₁) and second ionisation energy (IE2) of elements X, Y and Z are given below.

Element	IE ₁ (kJ mol ⁻¹)	IE ₂ (kJ mol ⁻¹)
X	2370	5250
Y	522	7298
Z	1680	3381

Which one of the above elements is the most reactive metal, the least reactive metal and a noble gas?

3.5.4 Electron Affinity

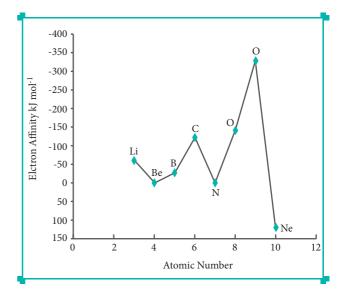
It is defined as the amount of energy released (required in the case noble gases) when an electron is added to the valence shell of an isolated neutral gaseous atom in its ground state to form its anion. It is expressed in kJ mol⁻¹

$$A + 1 e^{-} \rightarrow A^{-} + E_{A}$$

Variation of Electron Affinity in a period:

The variation of electron affinity is not as systematic as in the case of ionisation energy. As we move from alkali metals to halogens in a period, generally electron affinity increases, i.e. the amount of energy released will be more. This is due to an increase in the nuclear charge and decrease in size of the atoms. However, in case of elements such as beryllium (1s², 2s²), nitrogen (1s², 2s², 2p³) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

Figure 3.4 Variation of electron affinity (electron gain energy) along I period



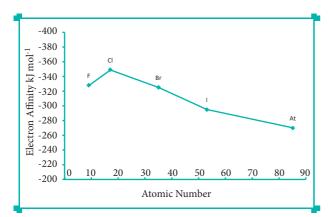
Noble gases have stable ns², np⁶ configuration, and the addition of further electron is unfavourable and requires energy. Halogens having the general electronic configuration of ns², np⁵ readily accept an electron to get the stable noble gas electronic configuration (ns², np⁶), and therefore in each period the halogen has high electron affinity. (high negative values)

Variation of Electron affinity in a group:

As we move down a group, affinity generally the electron decreases. It is due to increase in atomic size and the shielding effect of inner shell electrons. However, oxygen and fluorine have lower affinity than sulphur and chlorine respectively. The sizes of oxygen and fluorine atoms are comparatively small and they have high electron density. Moreover, the extra electron added to oxygen and fluorine has to be accommodated in the 2p orbital which is relatively compact compared to the 3p orbital of sulphur

and chlorine so, oxygen and fluorine have lower electron affinity than their respective group elements sulphur and chlorine.

Figure 3.5 Variation of Electron Affinity (electron gain energy) along I period



Evaluate Yourself



7. The electron gain enthalpy of chlorine is 348 kJ mol⁻¹. How much energy in kJ is released when 17.5 g of chlorine is completely converted into Cl⁻ ions in the gaseous state?

3.5.5 Electronegativity:

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

Electronegativity is not a measurable quantity. However, a number of scales are available to calculate its value. One such method was developed by Pauling, he assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.2 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression

$$(\chi_A - \chi_B) = 0.182 \sqrt{E_{AB} - (E_{AA}^* E_{BB})^{1/2}}$$

Where E_{AB} , E_{AA} and E_{BB} are the bond dissociation energies of AB, A_2 and B_2 molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound. The electronegativity values play an important role in predicting the nature of the bond.

Variation of Electronegativity in a period:

The electronegativity generally increases across a period from left to right. As discussed earlier, the atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electronegativity also increases in a period

Figure 3.6 Variation of Electronegativity along I period

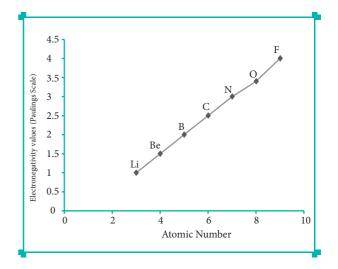
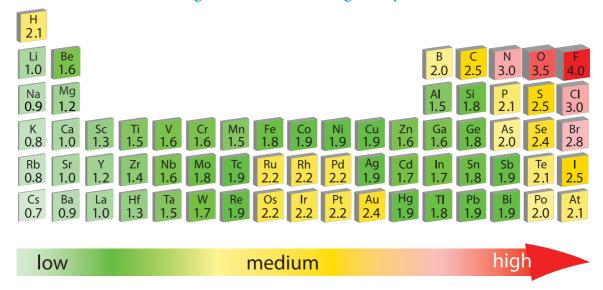


Table 3.15 Paulings scale of electronegativity valuee of elements

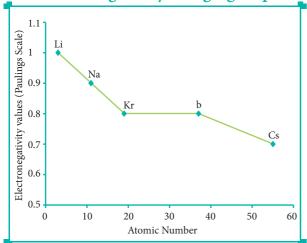


Variation of Electronegativity in a group:

The electronegativity generally decreases down a group. As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence, the electronegativity decreases.

Noble gases are assigned zero electronegativity. The electronegativity values of the elements of s-block show the expected decreasing order in a group. Except 13th and 14th group all other p-block elements follow the expected decreasing trend in electronegativity.

Figure 3.7 Variation of electronegativity along I group



3.6 Periodic Trends in Chemical Properties:

Sofar, we have studied the periodicity of the physical properties such as atomic radius, ionisation enthalpy, electron gain enthalpy and electronegativity. In addition, the chemical properties such as reactivity, valence, oxidation state etc... also show periodicity to certain extent.

In this section, we will discuss briefly about the periodicity in valence (oxidation state) and anomalous behaviour of second period elements (diagonal relationship).

Valence or Oxidation States

The valence of an atom is the combining capacity relative to hydrogen atom. It is usually equal to the total number of electrons in the valence shell or equal to eight minus the number of valence electrons. It is more convenient to use oxidation state in the place of valence.

Periodicity of Valence or Oxidation States

The valence of an atom primarily depends on the number of electrons in the

valence shell. As the number of valence electrons remains same for the elements in same group, the maximum valence also remains the same. However, in a period the number of valence electrons increases, hence the valence also increases.

Table 3.16 Variation of valence in groups

Alk	ali Metals (Grou	p 1)	Group 15			
Element	No. of electrons in valence shell	Valence	Element	No. of electrons in valence shell	Valence	
Li	1	1	N	5	3, 5	
Na	1	1	Р	5	3, 5	
K	1	1	As	5	3, 5	
Rb	1	1	Sb	5	3, 5	
Cs	1	1	Bi	5	3, 5	
Fr	1	1				

Table 3.17 Variation of valence in period (1st period)

Element	Li	Ве	В	С	N	О	F	Ne
No. of electrons in valence shell	1	2	3	4	5	6	7	8
Valence (Combining capacity)	1	2	3	4	5, 3	6, 2	7, 1	8, 0

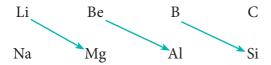
In addition to that some elements have variable valence. For example, most of the elements of group 15 which have 5 valence electrons show two valences 3 and 5. Similarly transition metals and inner transition metals also show variable oxidation states.

3.6.1 Anomalous properties of second period elements:

As we know, the elements of the same group show similar physical and chemical properties. However, the first element of each group differs from other members of the group in certain properties. For example, lithium and beryllium form more covalent compounds, unlike the alkali and alkali earth metals which predominantly form ionic compounds. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences. For example, boron forms BF_4^- and aluminium forms AlF_6^{3-}

Diagonal Relationship

On moving diagonally across the periodic table, the second and third period elements show certain similarities. Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.



The similarity in properties existing between the diagonally placed elements is called 'diagonal relationship'.

3.6.2 Periodic Trends and Chemical Reactivity:

chemical The physical and properties of elements depend on the valence shell electronic configuration as discussed earlier. The elements on the left side of the periodic table have less ionisation energy and readily loose their valence electrons. On the other hand, the elements on right side of the periodic table have high electron affinity and readily accept electrons. As a consequence of this, elements of these extreme ends show high reactivity when compared to the elements present in the middle. The noble gases having completely filled electronic configuration neither accept nor lose their electron readily and hence they are chemically inert in nature.

The ionisation energy is directly related to the metallic character and the elements located in the lower left portion of the periodic table have less ionisation energy and therefore show metallic

character. On the other hand the elements located in the top right portion have very high ionisation energy and are non-metallic in nature.

Let us analyse the nature of the compounds formed by elements from both sides of the periodic table. Consider the reaction of alkali metals and halogens with oxygen to give the corresponding oxides.

$$4 \text{ Na} + \text{O}_2 \rightarrow 2 \text{ Na}_2\text{O}$$

$$2 \text{ Cl}_2 + 7 \text{ O}_2 \rightarrow 2 \text{ Cl}_2 \text{O}_7$$

Since sodium oxide reacts with water to give strong base sodium hydroxide, it is a basic oxide. Conversely Cl_2O_7 gives strong acid called perchloric acid upon reaction with water So, it is an acidic oxide.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$Cl_2O_7 + H_2O \rightarrow 2 HClO_4$$

Thus, the elements from the two extreme ends of the periodic table behave differently as expected.

As we move down the group, the ionisation energy decreases and the electropositive character of elements increases. Hence, the hydroxides of these elements become more basic. For example, let us consider the nature of the second group hydroxides:

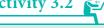
 $\mathrm{Be(OH)}_2$ amphoteric; $\mathrm{Mg(OH)}_2$ weakly basic; $\mathrm{Ba(OH)}_2$ strongly basic

Beryllium hydroxide reacts with both acid and base as it is amphoteric in nature.

$$Be(OH)_2 + HCl \rightarrow BeCl_2 + 2H_2O$$

$$Be(OH)_2 + 2 NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

Activity 3.2



The electronegativity for some elements on pauling scale of different groups and periods are listed below. Plot these values against atomic number. From the pattern, explain the variation along a period and a group.

2nd group elements: Be (1.6), Mg (1.2), Ca (1.0), Sr (1.0) Ba(0.9)

17th group elements : F (4.0), Cl (3.0), Br (2.8), I (2.5)

3rd Period elements: Na(0.9), Mg(1.2), Al (1.5), Si(1.8), P(2.1), S(2.5), Cl(3.0)

4th period elements: K(0.8), Ca(1.0), Sc(1.3), Ti(1.5), V(1.6), Cr(1.6), Mn(1.5), Fe(1.8), Co(1.9), Ni(1.9), Cu(1.9), Zn(1.6), Ga(1.6), Ge(1.8), As(2.0), Se(2.4), Br(2.8)



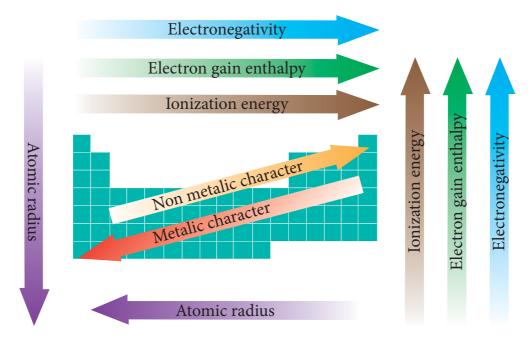
The periodic table was developed to systematically arrange the different elements. Lavoisier made the first attempt to arrange the known elements in a particular order based on properties. This followed by Johann Dobereiner, A. E. B. de Chancourtois and Newlands. First meaningful periodic table was constructed by Mendeleeve based on atomic mass. This was later modified based on the modern periodic law which states that the properties of elements are the periodic functions of their atomic numbers. The modern periodic table is made up of 18 groups and 7 periods.

The elements in the same groups have similar properties because their valence shell electronic configurations are similar. The properties of the elements of the same period differ because they have different valence shell electronic configurations. On the basis of electronic configuration the elements are also classified as s-block, p-block, d-block and f-block elements. The elements belonging to "s, p, d and f" blocks have unique characteristic

properties. In this table, more than 78% of all known elements are metals. They appear on the left side of the periodic table. Nonmetals are located at the top right hand side of the periodic table. Some elements show properties that are characteristic of both metals and non-metals and are called semimetals or metalloids.

The periodic properties such as atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy, electronegativity are possessing periodic trends. The variations of these properties are described in the following scheme.

The elements at the extreme left exhibit strong reducing property whereas the elements at extreme right strong oxidizing property. The reactivity of elements at the centre of the periodic table is low compared to elements at the extreme right and left. The similarity in chemical properties observed between the elements of second and third period which are diagonally related.



EVALUATION:

I. Choose the best Answer:

1.	What would be the IUPAC name for an element with atomic number 222?						
	a) bibibiium	b) bididium	c) didibium	d)bibibium			
2.		The electronic configuration of the elements A and B are $1s^2$, $2s^2$, $2p^6$, $3s^2$ and $1s^2$ $2s^2$, $2p^5$ respectively. The formula of the ionic compound that can be formed between these elements is					
	a) AB	b) AB ₂	c) A ₂ B	d) none of the above.			
3.	The group of elements in which the differentiating electron enters the anti penultimate shell of atoms are called						
	a) p-block elements		b) d-block element	s			
	c) s-block elements		d) f-block elements	3			
4.	In which of the following options the order of arrangement does not agree with the variation of property indicated against it? (NEET 2016 Phase 1)						
	a) I < Br < Cl < F (increasing electron gain enthalpy)						
	b) Li < Na < K < Rb (increasing metallic radius)						
	c) $Al^{3+} < Mg^{2+} < Na^{-1}$	$Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)					
	d) B < C < O < N (in	(increasing first ionisation enthalpy)					
5.	Which of the follow	ing elements will ha	ve the highest electr	onegativity?			

6. Various successive ionisation enthalpies (in kJ mol⁻¹) of an element are given below.

IE ₁	IE ₂	IE ₃	IE_4	${\rm IE}_5$
577.5	1,810	2,750	11,580	14,820

b) Nitrogen

The element is

a) Chlorine

- a) phosphorus
- b) Sodium
- c) Aluminium

c) Cesium

d) Silicon

d) Fluorine

7. In the third period the first ionization potential is of the order.

a) Na > Al > Mg > Si > P

b) Na < Al < Mg < Si < P

c) Mg > Na > Si > P > Al

d) Na < Al < Mg < Si < P

8. Identify the wrong statement.

a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius

b) Amongst isoelectric species greater the negative charge on the anion, larger is the ionic radius

c) Atomic radius of the elements increases as one moves down the first group of the periodic table

d) Atomic radius of the elements decreases as one moves across from left to right in the 2^{nd} period of the periodic table.

9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy

a) Al < O < C < Ca < F

b) Al < Ca < O < C < F

c) C < F < O < Al < Ca

d) Ca < Al < C < O < F

10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively is

a) I > Br > Cl > F

b) F > Cl > Br > I

c) Cl > F > Br > I

d) Br > I > Cl > F

11. Which one of the following is the least electronegative element?

a) Bromine

b) Chlorine

c) Iodine

d) Hydrogen

12. The element with positive electron gain enthalpy is

a) Hydrogen

b) Sodium

c) Argon

d) Fluorine

13. The correct order of decreasing electronegativity values among the elements X, Y, Z and A with atomic numbers 4, 8, 7 and 12 respectively

a) Y > Z > X > A

b) Z > A > Y > X

c) X > Y > Z > A

d) X > Y > A > Z

14. Assertion: Helium has the highest value of ionisation energy among all the elements known

Reason: Helium has the highest value of electron affinity among all the elements known

- a) Both assertion and reason are true and reason is correct explanation for the assertion
- b) Both assertion and reason are true but the reason is not the correct explanation for the assertion
- Assertion is true and the reason is false c)
- d) Both assertion and the reason are false
- The electronic configuration of the atom having maximum difference in first and second ionisation energies is

a)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^1$

b)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$

d)
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^1$

- Which of the following is second most electronegative element? 16.
 - a) Chlorine
- b) Fluorine
- c) Oxygen
- d) Sulphur
- IE₁ and IE₂ of Mg are 179 and 348 kcal mol⁻¹ respectively. The energy required for the reaction Mg \rightarrow Mg²⁺ + 2 e⁻ is

In a given shell the order of screening effect is

a)
$$s > p > d > f$$
 b) $s > p > f > d$ c) $f > d > p > s$ d) $f > p > s > d$

b)
$$s > p > f > d$$

c)
$$f > d > p > s$$

d)
$$f > p > s > d$$

Which of the following orders of ionic radii is correct?

a)
$$H^- > H^+ > H$$

a)
$$H^- > H^+ > H$$
 b) $Na^+ > F^- > O^{2-}$ c) $F > O^{2-} > Na^+$ d) None of these

c)
$$F > O^{2-} > Na^+$$

- 20. The First ionisation potential of Na, Mg and Si are 496, 737 and 786 kJ mol⁻¹ respectively. The ionisation potential of Al will be closer to

Which one of the following is true about metallic character when we move from left 21. to right in a period and top to bottom in a group?

- a) Decreases in a period and increases along the group
- b) Increases in a period and decreases in a group
- c) Increases both in the period and the group
- d) Decreases both in the period and in the group
- 22. How does electron affinity change when we move from left to right in a period in the periodic table?
 - a) Generally increases

b) Generally decreases

c) Remains unchanged

- d) First increases and then decreases
- 23. Which of the following pairs of elements exhibit diagonal relationship?
 - a) Be and Mg
- b) Li and Mg
- c) Be and B
- d) Be and Al

II. Write brief answer to the following questions

- 24. Define modern periodic law.
- 25. What are isoelectronic ions? Give examples.
- 26. What is effective nuclear charge?
- 27. Is the definition given below for ionisation enthalpy is correct?
 - "Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"
- 28. Magnesium loses electrons successively to form Mg⁺, Mg²⁺ and Mg³⁺ ions. Which step will have the highest ionisation energy and why?
- 29. Define electronegativity.
- 30. How would you explain the fact that the second ionisation potential is always higher than first ionisation potential?
- 31. Energy of an electron in the ground state of the hydrogen atom is -2.8×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of kJ mol⁻¹.
- 32. The electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain
- 33. In what period and group will an element with Z = 118 will be present?
- 34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

35. Elements a, b, c and d have the following electronic configurations:

a:
$$1s^2$$
, $2s^2$, $2p^6$

b:
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^1$

c:
$$1s^2$$
, $2s^2$, $2p^6$, $3s^2$, $3p^6$

d:
$$1s^2$$
, $2s^2$, $2p^1$

Which elements among these will belong to the same group of periodic table

- 36. Give the general electronic configuration of lanthanides and actinides?
- 37. Why halogens act as oxidising agents?
- 38. Mention any two anomalous properties of second period elements.
- 39. Explain the pauling method for the determination of ionic radius.
- 40. Explain the periodic trend of ionisation potential.
- 41. Explain the diagonal relationship.
- 42. Why the first ionisation enthalpy of sodium is lower that that of magnesium while its second ionisation enthalpy is higher than that of magnesium?
- 43. By using paulings method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that $d_{K+-Cl_-} = 3.14$ A
- 44. Explain the following, give appropriate reasons.
 - (i) Ionisation potential of N is greater than that of O
 - (ii) First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.
 - (iii) The electron affinity values of Be, Mg and noble gases are zero and those of N (0.02 eV) and P (0.80 eV) are very low
 - (iv) The formation of $F^-(g)$ from F(g) is exothermic while that of $O^{2-}(g)$ from O(g) is endothermic.
- 45. What is screening effect? Briefly give the basis for pauling's scale of electronegativity.
- 46. State the trends in the variation of electronegativity in group and periods.

