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GENERAL CHARACTERISTICS OF THE P-BLOCK ELEMENTS

The p -block of the periodic table consists of the elements of groups 13, 14, 15, 16, 17 and 18. These elements are characterised by the filling up of electrons in the outermost p -orbitals of their atoms. Some of these elements and their compounds play an important role in our daily life. For example:

- Nitrogen is used in the manufacture of ammonia, nitric acid and fertilizers. Trinitrotoluene (TNT), nitroglycerine, etc., are compounds of nitrogen, which are used as explosives.
- Oxygen present in air is essential for life and combustion processes.
- Carbohydrates, proteins, vitamins, enzymes, etc., which contain chain of carbon atoms, are responsible for the growth and development of living organism.

The usual trends (vertical as well as horizontal) in various properties observed in the s -block are observed in this block, too. As we move from top to bottom through a vertical column (group) some similarities are observed in the properties. However, this vertical similarity is less marked in the p -block than that observed in the s -block, especially in groups 13 and 15; vertical similarity is increasingly shown by the later groups. As far as the horizontal trend is concerned, the properties vary in a regular fashion as we move from left to right across a row (period).

In this lesson we shall study some important physical properties w.r.t. the of electronic configuration of the atom. Finally, we shall relate the periodicity in atomic properties to the observed chemical behaviour of their compounds, with special reference to their oxides, hydrides and halides.



OBJECTIVES

After reading this lesson you will be able to:

- describe the general mode of occurrence of these elements in nature;
- recall the electronic configurations of the p-block elements;
- explain the variations in atomic and physical properties such as
 - (i) atomic and ionic sizes;
 - (ii) ionization enthalpy;
 - (iii) electronegativity;
 - (iv) electron-gain enthalpy;
 - (v) metallic and non-metallic behaviours along the period and in a group of the periodic table;
- correlate the properties of the elements and their compounds with their positions in the periodic table;
- explain the anomalous properties of the first element in each group of this block and
- explain inert pair effect.



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18.1 OCCURRENCE OF THE P-BLOCK ELEMENTS IN NATURE

The *p*-block elements do not follow any set pattern of mode of occurrence in nature. Some of them occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the forms. Noble gases occur in free state only. All other elements usually occur in the combined state. The distribution of these elements in nature is also far from any uniform pattern. Some of them are quite abundant, *e.g.*, oxygen, silicon, aluminium, nitrogen etc. On the other hand the heavier members in each group of the block are generally much less abundant. The important minerals associated with elements will be considered whenever it is necessary at the appropriate places in the text.

18.2 ELECTRONIC CONFIGURATION

Among the elements of *p*-block, the *p*-orbitals are successively filled in a systematic manner in each row. Corresponding to the filling up of $2p$, $3p$, $4p$, $5p$ and $6p$ orbitals five rows of *p*-block elements are there. The outer electronic configuration of the atoms of these elements is ns^2np^{1-6} .

18.3 ATOMIC SIZE

The atomic radius of the of *p*-block elements generally decreases on moving across a period from left to right in the periodic table. It is because the addition of electrons takes place in the same valence shell and are subjected to an increased pull of the nuclear charge at each step. The variation in atomic size along a period is shown in Table 18.1.

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Table 18.1 : Variation in Atomic Size in a row from boron to fluorine

Element	Boron	Carbon	Nitrogen	Oxygen	Fluorine
Outer electronic configuration	$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$
Nuclear charge	+5	+6	+7	+8	+9
Effective nuclear charge	+ 2.60	+ 3.25	+ 3.90	+ 4.55	+ 5.20
Atomic size (pm)	88	77	70	66	64

On moving down a group, the atomic radius of the elements increases as the atomic number increases. This is due to the increase in the number of shells as we move from one element to the next down the group. The increase in nuclear charge is more than compensated by the additional shell. The variation in atomic size on moving down a group is shown in Table 18.2.

Table 18.2 : Variation in atomic size down a group

Elements of Group 13	Outer electron configuration	Nuclear charge	Effective nuclear charge	Atomic size (pm)
Boron	$2s^2 2p^1$	+ 5	+ 2.60	88
Aluminium	$3s^2 3p^1$	+ 13	+ 11.60	118
Gallium	$4s^2 4p^1$	+ 31	+ 29.60	124
Indium	$5s^2 5p^1$	+ 49	+ 47.60	152
Thallium	$6s^2 6p^1$	+ 81	+ 79.60	178

18.4 IONIZATION ENTHALPY

It is the amount of energy required to remove the most loosely bound electron from the outermost shell of a neutral gaseous atom. It is measured in kJ mol^{-1} and is known as first ionization enthalpy.

The first ionization enthalpy of the *p*-block elements generally increases on moving from left to right along a period. It is because as we move from left to right along a period, the atomic size decreases. In a small atom, the electrons are held tightly. The larger the atom, the less strongly the electrons are held by the nucleus. The ionization enthalpy, therefore, increases with decrease in atomic size. However, there are certain exceptions, e.g., the first ionization enthalpy of a group 16 element

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is lower than that of a group 15 element. It is because in case of a group 15 element, the electron is to be removed from the half-filled p -orbitals. A comparison of first ionization energies of some elements is given in Table 18.3.

Table 18.3 : Comparison of first ionization enthalpies (kJ mol^{-1})

B	C	N	O	F	Ne
801	1086	1403	1310	1681	2080
Al	Si	P	S	Cl	Ar
577	796	1062	999	1255	1521

In general the first ionization enthalpy decreases in a regular way on descending a group. It is because on descending a group, the atomic size increases. As a result the electrons are less tightly held by the nucleus and therefore, first ionization enthalpy decreases.

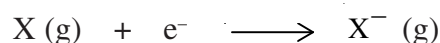


INTEXT QUESTIONS 18.1

- Which of the following atoms is expected to have smaller size?
(i) ${}_9\text{F}$ and ${}_{17}\text{Cl}$ (ii) ${}_6\text{C}$ and ${}_{14}\text{Si}$ (iii) ${}_5\text{B}$ and ${}_6\text{C}$ (iv) ${}_6\text{C}$ and ${}_7\text{N}$
- Which atom in the following pairs of atoms is expected to have higher ionization enthalpy?
(i) ${}_4\text{Be}$ and ${}_5\text{B}$ (ii) ${}_{16}\text{S}$ and ${}_{17}\text{Cl}$ (iii) ${}_2\text{He}$ and ${}_{10}\text{Ne}$ (iv) ${}_8\text{O}$ and ${}_{16}\text{S}$
- Arrange the following atoms in order of increasing ionization enthalpy: ${}_2\text{He}$, ${}_4\text{Be}$, ${}_7\text{N}$, ${}_{11}\text{Na}$.
- How does the ionization enthalpy vary in general in a group and in a period of the p -block elements?

18.5 ELECTRON GAIN ENTHALPY

When an electron is added to a neutral gaseous atom, heat energy is either released or absorbed. The amount of heat energy released or absorbed when an extra electron is added to a neutral gaseous atom is termed as electron gain enthalpy, i.e., energy change for the process :



Generally for most of the atoms, the electron gain enthalpy is negative, i.e., energy is released when an electron is added to a neutral gaseous atom. But for some atoms, the electron gain enthalpy is a positive quantity, i.e., energy is absorbed during the addition of an electron.

Electron affinity generally becomes more negative on moving from left to right along a period. It is because on moving across a period, the atomic size decreases. As a result the force of attraction exerted by the nucleus on the electron increases.

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Consequently the atom has a greater tendency to gain an electron. Hence, electron gain enthalpy becomes more negative.

On moving down a group, the electron gain enthalpy becomes less negative. This is due to the increase in atomic size and thus, less attraction for the electrons; the atom will have less tendency to gain an electron. Hence, electron gain enthalpy becomes less negative. But in the halogen group, the electron gain enthalpy of chlorine is more negative than that of fluorine. It is because the size of the F atom is very small which makes the addition of electron less favourable due to inter electronic repulsion. Similar situation exists for the first element of each group.

Table 18.4 : Electron gain enthalpies of some p-block elements in kJ mol^{-1}

B	C	N	O	F
- 0.30	- 1.25	+ 0.20	- 1.48	- 3.6
Al	Si	P	S	Cl
- 0.52	- 1.90	- 0.80	- 2.0	- 3.8

18.6 ELECTRONEGATIVITY

Electronegativity is defined as a measure of the ability of an atom to attract the shared electron pair in a covalent bond to itself.

Electronegativity increases along the period and decreases down the group.

Fluorine is the most electronegative of all the elements. The second most electronegative element is *oxygen* followed by *nitrogen* in the third position.

18.7 METALLIC AND NON-METALLIC BEHAVIOUR

The elements can be broadly classified into metals and non-metals. Metals are electropositive in character i.e., they readily form positive ions by the loss of electrons, whereas non-metals are electronegative in character i.e., they readily form negative ions by the gain of electrons. The metallic and non-metallic character of *p*-block elements varies as follows:

Along the period the metallic character decreases, whereas non-metallic character increases. It is because on moving across the period, the atomic size decreases due to the increased nuclear charge and hence, ionization energy increases.

On moving down the group the metallic character increases, whereas non-metallic character, decreases. It is because on moving down a group, the atomic size increases. As a result the ionization energy decreases and tendency to lose electrons increases. Therefore, metallic character increases and non-metallic character decreases.

18.8 ANOMALOUS BEHAVIOUR OF THE FIRST ELEMENT IN EACH GROUP OF THE *p*-BLOCK

The elements comprising *s*-block and *p*-block are called main groups or representative elements.

Since the atomic radii decrease across a period, the *p*-block atoms are smaller than their nearest *s* or *d* block atoms; thus F atom has the smallest radius. Associated with small atom the $2p$ orbitals are very compact and influence the bonds formed. Interelectronic repulsions are thus more significant in $2p$ than in np orbitals (where $n > 2$). This results in the N–N, O–O and F–F bonds being comparatively weaker than the P–P, S–S and Cl–Cl bonds, respectively.

The small size of the atoms of N, O and F results in their high electronegativity values. This is reflected in the formation of relatively strong hydrogen bonds in X – H...Y, where X and Y may be N, O or F.

Carbon, nitrogen and oxygen differ from other elements of their respective groups due to their unique ability to form $p\pi$ – $p\pi$ multiple bonds. For example C=C, C≡C, N=N, O=O, etc. The later members such as Si, P, S, etc., do not form $p\pi$ – $p\pi$ bonds because the atomic orbitals ($3p$) are too large to achieve effective overlapping.

The valence shell capacity of the *p*-block elements in the second period limits the coordination number to a maximum of 4. However, in compounds of the heavier members the higher coordination numbers are attainable. Thus BH_4^- and BF_4^- contrast with $[\text{AlF}_6]^{3-}$; CF_4 contrasts with $[\text{SiF}_6]^{2-}$ and NH_4^+ contrasts with $[\text{PCl}_6]^-$. In the heavier members of each group *d*-orbitals are available for bonding and their participation may be envisaged in the attainment of the higher coordination number.

18.9 INERT PAIR EFFECT

Among the elements of *p*-block, in groups 13, 14 and 15, there is a general trend that the higher oxidation states become less stable in going down the group. Thus although boron and aluminium are universally trivalent, gallium, indium and thallium exhibit +1 state as well. In fact +1 state of thallium is very stable. Similar situations are noticed in groups 14 and 15. Though carbon is universally tetravalent, it is possible to prepare divalent germanium, tin and lead compounds. The stable state of +3 in antimony and bismuth in group 15 is another example.

Outer electron configurations of group 13, 14 and 15 elements are ns^2np^1 , ns^2np^2 and ns^2np^3 , respectively. They are thus expected to show the higher oxidation state of +3, +4 and +5 respectively. But the preference of heavier elements of these



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groups to show +1, +2 and +3 states, respectively indicate that two electrons do not participate in bonding. The reluctance of s -electrons to take part in chemical bonding is known as *inert pair effect*.

The so called “inert pair effect” is therefore, ascribed to two factors.

1. The increase in the promotion energy from the ground state ($ns^2 np^1$) to the valence state ($ns^1 np^2$)
2. Poorer overlap of the orbitals of the large atoms and hence poorer bond energy.

The net result is the lesser stability of higher oxidation state with the increasing atomic number in these groups. Once the involved energies are taken into consideration, the so called “inert pair effect” term loses its significance.



INTEXT QUESTIONS 18.2

1. Why does fluorine have electron gain enthalpy lower than chlorine?
2. Which atom in the following pair of atoms has greater electron gain enthalpy?
(i) F, Cl (ii) Br, I (iii) I, Xe (iv) O, F (v) O, S
3. Give two reasons for the fact that the first element in each group of p -block exhibits unique behaviour.
4. Explain why oxygen exists as a gas whereas sulphur exists as a solid.
5. Mention two reasons which are responsible for the so called “inert pair effect”.
6. What is the consequence of “inert pair effect” on the oxidation states of Tl and Pb?

18.10 GENERAL TRENDS IN THE CHEMISTRY OF THE P-BLOCK ELEMENTS

The p -block elements except noble gases react with hydrogen, oxygen and halogens to form various hydrides, oxides and halides respectively. A more or less regular trend is observed in the properties of these compounds on moving down any particular group. The noble gases have almost zero electron affinity and have very high ionization enthalpies. Therefore, under normal conditions, the atoms of noble gases have little tendency to gain or lose electrons.

18.10.1 Hydrides

The hydrides of the *p*-block elements are listed in table 18.5. They are covalent molecules and their bond angles are consistent with VSEPR theory. The angles decrease from 109.5° in CH_4 to 107° in NH_3 and 104° in H_2O .

These hydrides are volatile in nature. Generally their acid strength increases from left to right and from top to bottom.

Table 18.5 : Hydrides of p-block elements

Group				
13	14	15	16	17
B_2H_6	CH_4	NH_3	H_2O	HF
$(\text{AlH}_3)_x$	SiH_4	PH_3	H_2S	HCl
Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr
InH_3	SnH_4	SbH_3	H_2Te	HI
TlH_3	PbH_4	BiH_3	H_2Po	–

18.10.2 Oxides

p-Block elements form a number of oxides on reacting with oxygen. The oxides E_2O_n ($n = 3, 5$ or 7) are the highest oxides formed by the elements in the groups 13, 15 or 17 respectively. The oxides EO_n ($n = 2, 3$ or 4) are formed by the elements in groups 14, 16 or 18 respectively. Thus, nitrogen forms NO , NO_2 , N_2O_3 , and N_2O_5 ; phosphorus forms P_4O_6 and P_4O_{10} , xenon forms XeO_3 and XeO_4 .

- In any particular group, the basic nature of the oxides (oxidation state of the element remaining same) increases with increase in atomic number.
- In a particular period the acidity increases with increase in the oxidation state of the element.

18.10.3 Halides

A review of the properties of halides of *p*-block elements reveals that most of them are covalent halides. In a group the covalent character of halides decreases down the group. Where an element exhibits more than one oxidation state, the covalent character of a halide increases with the increase in the oxidation state of the element forming halides. For example, whereas PbCl_2 is an ionic halide, PbCl_4 is covalent. Similarly the covalent character of halides of a particular element increases from fluoride to chloride to bromide.

Covalent halides are generally gases, liquids or solids with low melting points. These halides usually hydrolyse to give the oxoacid of the element. For example SiCl_4 reacts vigorously with water



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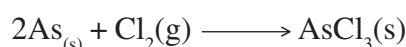
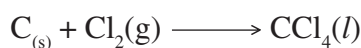
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In general the chlorides, bromides and iodides are found to be more stable with lower oxidation state of the element, whereas fluorides are formed in the higher oxidation states. The halides are usually formed by the direct union of the element with the halogen. For example



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INTEXT QUESTION 18.3

- Which of the following oxides is the most acidic?
(i) Al_2O_3 (ii) CO_2 (iii) SO_2
- Which of the following hydrides of main group elements is the most acidic?
(i) H_2Se (ii) H_2O (iii) HCl (iv) HI
- Arrange the following in the increasing order of covalent character.
 $\text{SiCl}_4, \text{CCl}_4, \text{SnCl}_4, \text{GeCl}_4$
- What happens when SiCl_4 reacts with water. Write complete chemical equation for the reaction.
- How do the bond angles vary among the following hydrides $\text{NH}_3, \text{PH}_3, \text{AsH}_3, \text{SbH}_3$
- Give equations for the formation of the following from the elements:
(i) Al_2O_3 (ii) SiCl_4 (iii) CCl_4
- Which is more covalent in each of the following pairs?
(i) AlCl_3 and BCl_3 (ii) PbCl_2 and PbCl_4



WHAT YOU HAVE LEARNT

- The elements of groups 13, 14, 15, 16, 17 and 18 constitute the *p*-block of the periodic table.
- Some of the elements of the *p*-block are widely and abundantly found in nature, viz., oxygen, silicon, aluminium, etc.
- Many physical and chemical properties of the *p*-block main group elements show periodic variation with atomic number.

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- The *ionization enthalpy* is the energy required to remove the outermost electron from a neutral gaseous atom.
- The *electron gain enthalpy* is the energy change when a neutral atom in a gaseous state accepts an electron.
- *Electronegativity* is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself.
- The top element in each group shows a unique behaviour.
- The reluctance of *s*-electrons to take part in bond formation is known as “inert pair effect”.
- *p*-Block elements form a number of oxides on reacting with oxygen.
- Most of the elements of the *p*-block form covalent halides.
- General characteristics of the *p*-block hydrides, halides and oxides.



TERMINAL EXERCISE

1. Which groups of the ‘periodic table’ constitute *p*-block?
2. How does the magnitude of ionization energy of an atom vary along the group in the periodic table?
3. How does electronegativity change along a row of elements in the periodic table?
4. Explain ‘Metallic character decreases along a period but increases on moving down a group’.
5. Discuss the trends in the chemistry of *p*-block elements with respect to:
 - (i) acidic and basic nature of the oxides;
 - (ii) ionic and covalent nature of the hydrides.
6. What is the cause of anomalous behaviour of the top element in each group of the *p*-block elements.
7. What is ‘inert pair effect’? Is there any inert pair present or is it a misnomer?
8. Comment on the nature (ionic/covalent) of the hydrides of the *p*-block elements
9. How does the covalent character of halides of an element change with oxidation state of the element?
10. Which is likely to form higher halides with an element exhibiting variable oxidation state, F_2 or Cl_2 ?

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ANSWERS TO INTEXT QUESTIONS



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18.1

- (i) ${}_9\text{F}$ (ii) ${}_6\text{C}$ (iii) ${}_6\text{C}$ (iv) ${}_7\text{N}$
- ${}_4\text{Be}$ (ii) ${}_{17}\text{Cl}$ (iii) ${}_2\text{He}$ (iv) ${}_8\text{O}$
- $\text{Na} < \text{Be} < \text{N} < \text{He}$
- In a group, it decreases down the group and it usually increases along a period.

18.2

- The unexpectedly low value of electron gain enthalpy for F as compared to that of Cl atom may be attributed to the extremely small size of F atom vis-a-vis Cl atom. The addition of an electron produces a negative ion which has a high electron density and leads to increased interelectronic repulsions.
- (i) Cl (ii) Br (iii) I (iv) F (v) S
- (i) Small size (ii) absence of *d*-orbitals
- Because oxygen can form multiple bonds ($\text{O} = \text{O}$).
- (i) Lower bond energy in the compounds of heavier atoms and (ii) the higher energy involved in promotion from the ground state (s^2p^1) to the valence state (s^1p^2).
- Lower oxidation states become more stable.
For Tl, +1 and for Pb, +2.

18.3

- SO_2
- HI
- $\text{SnCl}_4 < \text{GeCl}_4 < \text{SiCl}_4 < \text{CCl}_4$
- $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{HCl}$
- The bond angle decreases from 107° to almost 90° .
- (i) $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$
(ii) $\text{Si(s)} + 2\text{Cl}_2\text{(g)} \rightarrow \text{SiCl}_4\text{(l)}$
(iii) $\text{C(s)} + 2\text{Cl}_2\text{(g)} \rightarrow \text{CCl}_4\text{(l)}$
- (i) BCl_3 (ii) PbCl_4