

PERIODIC PROPERTIES

PREFACE

The periodic table provides a systematic framework for organizing the large available information on the chemical behaviour of the elements into simple logical patterns. The elements are arranged in rows and columns. Using the position of an element in the periodic table, it is possible to predict its chemical behaviour.

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1. EARLY CLASSIFICATION ATTEMPTS

1.1 OBERENER'S TRIADS

In 1829, Oberener made an important first step towards a systematic classification by arranging elements into groups of three (triads). He observed that atomic mass of the middle element is arithmetic mean of upper and lower elements.

$$\frac{39 + 7}{2} = 23 \quad \left| \begin{array}{c} \text{Li}^7 \\ \text{Na}^{23} \\ \text{K}^{39} \end{array} \right| \left| \begin{array}{c} \text{Cl} \\ \text{Br} \\ \text{I} \end{array} \right| \left| \begin{array}{c} \text{Ca} \\ \text{Sr} \\ \text{Ba} \end{array} \right|$$

Other triads:

1.	P ³¹	As ⁷⁵	Sb ¹²⁰
2.	Cl ^{35.5}	Br ⁸⁰	I ¹²⁷
3.	Ca ⁴⁰	Sr ⁸⁸	Ba ¹³⁷
4.	Fe ^{55.85}	Ni ^{58.71}	Co ^{58.93}

1.2 NEWLAND'S LAW OF OCTAVES

Newland arranged the elements in increasing order of atomic weight in a series and observed that first element has similar properties as 8th element in that series. This is known as Newland law of octaves.

Li	Be	B	C	N	O	F
Na	Mg					

Li & Na have similar properties.

1.3 MENDELEEV'S PERIODIC TABLE

Mendeleev's Periodic Law – According to Mendeleev, the physical and chemical properties of the elements are periodic function of their atomic masses. On the basis of this law he arranged all the elements in order of increasing atomic mass and he found that after certain regular intervals repetition in properties occur.

(A) Merits of Mendeleev's table:

- (i) First of all systematic classification of elements by forming table.
- (ii) Correction of Atomic Masses of the elements.
- (iii) He left a certain gap in the periodic table for the undiscovered elements and he predicted the properties of that element correctly.

Eka Aluminium – Now a days Gallium

Eka Silicon – Now a days Germanium

(B) Demerits of Mendeleev's table:

- (i) Anomalous position of Hydrogen atom. He failed to justify the position of H-atom because some of the properties of H-atom were similar to alkali metals and some of the properties were similar to halogen atom.
- (ii) Cause of periodicity – He failed to explain why the repetition in properties occur after certain regular intervals.
- (iii) He failed to accommodate Lanthanides & Actinides in the main body of periodic table.

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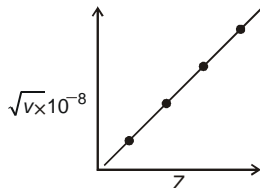
- (iv) Some pairs do not obey the rule of increasing atomic masses. ^{40}Ar was placed before ^{39}K .
(v) He failed to justify the position of isotopes that were placed together but have different atomic masses.

2 MODERN PERIODIC LAW AND MODERN PERIODIC TABLE

Mosley proved that the square root of frequency (ν) of the X-rays which are obtained from a metal on showering high velocity electrons is proportional to the nuclear charge of the atom. This can be represented by the following expression.

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

Where Z is nuclear charge on the atom; a & b are constants. The nuclear charge on an atom is equal to the atomic number.



2.1 MODERN PERIODIC LAW

The modern periodic law states *“The physical and chemical properties of the elements are periodic functions of their atomic numbers”*.

The horizontal rows in the periodic table are called **periods** and elements having similar outer electronic configuration in their atoms are grouped in vertical columns called **groups or families**. According to IUPAC recommendation, the groups are numbered from 1 to 18.

The elements have been divided into three categories—metals, non-metals and metalloids. A metal is a good conductor of heat and electricity while a non-metal is usually a poor conductor of heat and electricity. A metalloid has properties that are intermediate between those of metals & non-metals. Of the total elements discovered till date, majority of them are metals, only seventeen elements are non-metals and eight elements are metalloids. From left to right across any period, the physical and chemical properties of the elements change gradually from metallic to non-metallic.

The group 1 (Earlier IA) elements (Li, Na, K, Rb, Cs and Fr) are called **alkali metals** and the group 2 (Earlier II A) elements (Be, Mg, Ca, Sr, Ba and Ra) are called **alkaline earth metals**. Elements in group 17 (Earlier VII A) elements (F, Cl, Br, I and At) are known as **halogens** and elements in group 18 (Earlier VIII A) elements (He, Ne, Ar, Kr, Xe and Rn) are called **noble gases or rare gases**.

According to the type of subshell being filled, the elements can be divided into the given categories—**the representative elements, the noble gases, the transition elements, the lanthanides and the actinides**. The representative elements (also called main group elements) are the elements in I A through VII A, all of which have incompletely filled s or p subshells of the highest principal quantum number. The noble gases (group VIII A) have a completely filled p subshell, except for helium, which have completely filled s subshell. The transition metals are the elements in groups I B and III B through VIII B, which have incompletely filled d subshells or readily produce cations with incompletely filled d subshells. The group II B elements (Zn, Cd and Hg) are neither representative elements nor transition metals. There is no special name for this group of metals. The lanthanides and actinides are sometimes called f-block or inner transition elements because they have incompletely filled f subshells.

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All the elements of the periodic table are classified into four blocks namely s-block, p-block, d-block and f-block, depending on the type of subshell being filled with last electron. In helium, although the s-orbital is filled but it is kept in the p-block because it has completely filled valence shell like that of noble gases. Hydrogen has single s-electron. It can gain an electron to achieve a noble gas arrangement and thus can behave similar to group 17 (halogens) elements but it is positioned in IA group (group 1) since it has one valence electron like that of alkali metals (group IA).

Important features of the modern periodic table:

- (a) It consists of eighteen groups. Each group consists of a number of elements having the same electronic configuration of outermost shell.
- (b) The elements of 18th group are called inert gases or noble gases.
- (c) The elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 are called transition elements.
- (d) Two series, each of 14 elements, are placed at the bottom of the periodic table, known as Lanthanides and Actinides.
- (e) Distribution of element in different periods are as below:

1 st period	2
2 nd and 3 rd period	8
4 th and 5 th period	18
6 th period	32
7 th period	incomplete

2.2 The s-BLOCK ELEMENTS

s-block comprises of elements of group 1 (alkali metals) and group 2 (alkaline earth metals). Alkali metals have electron configuration ns^1 while alkaline earth metal have ns^2 configuration. All the members of IA and IIA group are very reactive and readily lose the outer most electrons to form +1 and +2 ions respectively. On moving from top to bottom, the metallic character and reactivity increases.

2.3 The p-BLOCK ELEMENTS

The p-block comprises of elements of group 13 to 18. Their valence electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. Each period ends with a noble gas having ns^2np^6 configuration. The ns^2np^6 configuration is very stable as the addition or removal of electrons is very difficult, thus elements with such configuration are also called inert gases. Preceding the group 18, halogens (group 17) and chalcogens (group 16) are present. The elements of group 17 and 16 readily add 1 and 2 electrons respectively to form anions having stable noble gas electronic configuration. The p-block elements are mostly non-metals and non-metallic character increases when we move from left to right across a period and it decreases when we go down the group.

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s-block												p-block																									
1	IA	2	IIA	d-block												13	IIIA	14	IVA	15	VA	16	VIA	17	VIIA	18	VIIIA										
1	1 H 1s ¹	2	4 Be 2s ²													5	13 B 2s ² 2p ¹	6	14 C 2s ² 2p ²	7	15 N 2s ² 2p ³	8	16 O 2s ² 2p ⁴	9	17 F 2s ² 2p ⁵	10	18 Ne 2s ² 2p ⁶										
2	3 Li 2s ¹	4	20 Ca 4s ²	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
3	11 Na 3s ¹	12	21 Sc 4s ² 3d ¹	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
4	19 K 4s ¹	20	21 Sc 4s ² 3d ¹	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
5	37 Rb	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
6	55 Cs	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89		
7	87 Fr	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121		

f-block

Lanthanides

Actinides

*58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
*90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

2.4 The d-BLOCK ELEMENTS or TRANSITION METALS

The d-block is constituted by elements of group 3 to 12. These elements are all metals and are characterized by the filling of inner d orbitals. Their valence electronic configuration is $(n-1)d^{1-10}ns^{1-2}$. Zn, Cd and Hg are not considered as true transition elements because they have filled d subshells [electron configuration $(n-1)d^{10}ns^2$]. The elements of d-block possess intermediate properties. They are less reactive than s-block but more reactive than p-block elements. They possess the characteristic features of forming coloured ions, showing variable valencies and forming coordination (complex) compounds.

2.5 The f-BLOCK ELEMENTS or INNER TRANSITION METALS

These are placed at the bottom of the periodic table having valence electronic configuration as $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. In this block, the electrons are filled in the f orbital. There are two series of elements, namely lanthanides (from $_{58}\text{Ce}$ through $_{71}\text{Lu}$) and actinides (from $_{90}\text{Th}$ through $_{103}\text{Lr}$). The elements after uranium in actinides series are called trans-uranium elements. They all are metals and possess characteristics like formation of coloured ions, exhibiting variable valencies etc.

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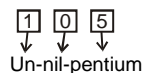
2.6 NOMENCLATURE OF THE ELEMENTS (IUPAC)

Nomenclature of the elements with atomic number Greater than 100:

The IUPAC names are derived by using roots for three digits in the atomic number of the element

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	hept	oct	enn

After writing roots of three digits is added “- ium” at last.



If same alphabet repeated for three times then one alphabet may be omitted. e.g. 190 Unennnilium is written as Unennilium.

Atomic Number	Roots of 3 digits	Name	Symbol
105	Un nil pent	Unnilpentium	Unp
108	Un nil oct	Unniloctium	Uno
118	Un un oct	Ununoctium	Uuo
140	Un quad nil	Unquadnilium	Uqn
144	Un quad quad	Unquadquadium	Uqq

2.7 PREDICTION OF PERIOD, GROUP AND BLOCK OF A GIVEN ELEMENT

- (i) Period of an element corresponds to the principal quantum number of the valence shell.
- (ii) Block of an element corresponds to the type of subshell which receives the last electron (Except La, Ce, Ac etc.)
- (iii) The group is predicted from the number of electrons in valence shell or penultimate shell.

For *s*-block, Group no. = No. of electrons in valence *s* subshell.

For *p*-block, Group no. = 10 + No. of electrons in valence *p* subshell.

For *d*-block, Group no. = No. of e^- in $(n - 1)d$ subshell + No. of e^- in valence shell

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3. PERIODIC PROPERTIES:

The properties of elements, that are periodic function of their atomic number and show a general gradation while moving in group or in period, are called periodic properties.

3.1 THE SCREENING EFFECT OR SHIELDING EFFECT

Between the outer most valence electrons and the nucleus of an atom, there exists finite number of shells containing electrons. Due to the presence of these intervening electrons, the valence electrons are unable to experience the attractive pull of the actual number of protons in the nucleus. These intervening electrons act as shield between the valence electrons and protons in the nucleus. Thus, the presence of intervening (shielding) electrons reduces the electrostatic attraction between the protons in the nucleus and the valence electrons because intervening electrons repel the valence electrons. The concept of effective nuclear charge allows us to account for the effects of shielding on periodic properties.

For example, let us consider a helium atom, which has ground state electron configuration as $1s^2$. Helium has two protons in the nucleus which gives it a charge of +2 but the full attractive force of this charge on the two 1s electrons is partially nullified by electron–electron repulsion. Consequently, the 1s electrons shield each other from the nucleus.

To illustrate shielding effect, let us remove both the electrons from a helium atom, one by one. It would take 2370 kJ of energy to remove the first electron from 1 mole of He atoms and 5250 kJ of energy to remove the remaining electron from 1 mole of He^+ ions. The removal of second electron takes much more energy than the removal of first electron because in He^+ ion, only one electron is present and there would be no shielding and the electron experiences the full effect of +2 nuclear charge.

For atoms with three or more electrons, the electrons in a given shell are shielded by electrons in the same shell and electrons in the inner shells but not by electrons in outer shells. For example, in lithium atom (electron configuration $1s^2 2s^1$), the 2s electron is shielded by the two 1s electrons but 1s electrons are not shielded by 2s electron. In addition, the electrons of the inner shell shield the electrons of outer shell, more effectively than the electrons of the same inner shell.

Slater's Rule: There are some simple rules for estimating the degree to which electrons in the various types of orbitals shield other electrons from the nucleus.

1. After writing the full electron configuration, rearrange it in the following groupings and order. Group ns and np orbitals together while all other type of orbitals are grouped separately. For example, (1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d, 4f), (5s, 5p), (5d, 5f), (6s, 6p), etc
2. Electrons to the right of the group of electrons in question contribute nothing to the shielding of that group of electrons.
3. All other electrons in the same group as the electron in question shield that electron to an extent of 0.35 unit of nuclear charge each.

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4. If the electron in question is an s or p electron: (a) All electrons with principal quantum number one less than the electron in question shield it to an extent of 0.85 unit of nuclear charge each (b) All electrons with principal quantum number two or more less than the electron in question shield it completely i.e. to an extent of 1 unit.
5. If the electron in question is a d or f electron: All electrons to the left of the group of the electron in question shield the 'd' or 'f' electron completely (to an extent of 1 unit). This is due to poor penetration effect of 'd' or 'f' electron.
6. Sum the shielding constants from steps 2–5 and subtract them from the actual nuclear charge (Z) of the atom in question to obtain the Z_{eff} felt by the electron in question.

It must be clear that the magnitude of screening constant increases in a period as well as in a group as the atomic number increases.

3.2 EFFECTIVE NUCLEAR CHARGE

The effective nuclear charge (Z_{eff}) is the charge felt by the valence electron. Z_{eff} is given by $Z_{\text{eff}} = Z - \sigma$

Here, Z is the actual nuclear charge (atomic number of the element) and σ is the shielding (screening) constant. The shielding constant is greater than zero but smaller than Z and depends on the number of intervening electrons and their type of subshell.

- (i) In a multi electronic atom, the internal electrons decrease the nuclear attraction on the electrons of the outermost orbit.
- (ii) Therefore, only a part of the nuclear charge is effective on the electrons of the outermost orbit. Thus, the inner electrons shield the nucleus and thereby decrease the effect of nuclear charge towards the electrons of the outermost orbit.
- (iii) Thus the part of the nuclear charge works against outer electrons, is known as effective nuclear charge.

$$Z_{\text{eff}} = Z - \sigma; \quad Z_{\text{eff}} = \text{Effective nuclear charge}$$

$$\sigma = \text{Shielding constant} \quad \text{and} \quad Z = \text{Actual nuclear charge}$$

Some Important Facts:

- (a) Development of positive charge increases Z_{eff} and development of negative charge decrease Z_{eff} and Vice Versa.
- (b) Z_{eff} increase along the period as well as in a group also.
- (c) For n^{th} shell, order of Screening effect on any outer electron is $s > p > d > f$.

3.3 PENETRATING POWER

Penetrating power is the measure of closeness of the electron cloud with the nucleus. More the penetrating power of electron more is its closeness with nucleus.

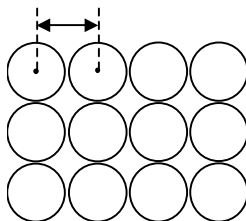
- (i) For same value of principal quantum number, more the value of l more is average distance of electron from nucleus and lesser is penetrating power.
 $ns > np > nd > nf$
- (ii) For same value of azimuthal quantum number l , more the value of n more is average distance of electron from nucleus and lesser is penetrating power.
 $2p > 3p > 4p > 5p$

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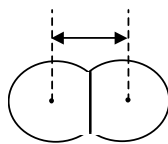
3.4 ATOMIC RADIUS

Electron clouds do not have sharp edges but when atoms are packed together in solids, their centers are found at definite distances from one another.

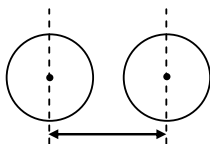
For atoms, which link together, to form an extensive three-dimensional network, atomic radius is one-half the distance between the nuclei in two neighbouring atoms. This is called metallic or crystal radius.



For elements that exist as simple diatomic molecules, the atomic radius is one-half the distance between the nuclei of the two atoms in a particular molecule. This is called covalent radius.



In case of mono atomic gases (like noble gases), the atomic radius is one-half of the distance between the nuclei of two atoms at some distance. This is called Van der Waals radius.



$$\text{Thus, } R_{\text{covalent}} < R_{\text{metallic}} < R_{\text{Van der Waals}}$$

Variation of Atomic Radius

Let us see the variation of atomic radius in a period. For example, consider the second period elements from Li to F. On moving from left to right, we can see that the number of electrons in the inner shell ($1s^2$) remains constant while the nuclear charge increases. The electrons that are added to counter balance the increasing nuclear charge are ineffective in shielding one another (each added electron screens nuclear charge by 0.35 units only). Consequently, the effective nuclear charge increases steadily while the principal quantum number remains constant ($n = 2$). For example, the outer 2s electron in lithium is shielded from the nucleus (which has 3 protons) by the two 1s electrons. Each 1s electron shields the 2s electron by 0.85 units, so net shielding by two 1s electrons is $1.7(\sigma)$. Thus, the effective nuclear charge of Li is 1.3. The electron configuration of Be is $1s^2 2s^2$. One 2s electron shields other 2s electron by 0.35 unit while each 1s electron shields 2s electron by 0.85. So, the Z_{eff} for Be would be $4 - [(2 \times 0.85) + 0.35] = 1.95$. Similarly, the Z_{eff} for B would be $5 - [(2 \times 0.85) + (2 \times 0.35)] = 2.6$. Thus, it is evident that the effective nuclear charge increases, so

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progressively the outermost electrons are held more strongly by the nucleus and thus the atomic radius decreases steadily from Li to F.

Now, let us observe the trend of atomic radius in a group. For the alkali metals in group 1 (IA) elements (Li, Na, K, Rb, Cs & Fr), the outermost electron resides in the ns orbital. In moving from Li to Na, the increase in Z_{eff} is very less (Z_{eff} for Li is 1.3 while for Na is 2.5) but orbital size increases with the increasing principal quantum number n, which supersedes the effect of increasing Z_{eff} . Therefore, the sizes of the metal atoms increase from Li to Na and so on. Thus, atomic radius increases on moving from top to bottom in a group.

In transition elements, the increase in atomic radius is much less as can be seen by comparing the values for the representative and transition elements.

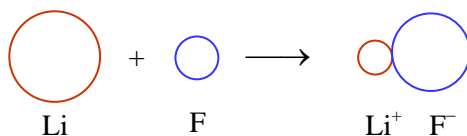
This can be explained on the basis of the fact that, between 3d and 4d transition series, 18 electrons are added of which 10 are poorly shielding d-orbital electrons. Hence the effect of the increase of a new quantum shell is not fully reflected in the increase in the atomic radius. 32 electrons are added between the 4d and 5d elements, of which 10 are the poor shielding d-electrons and 14 are the extremely poor shielding f-electrons. Hence, the size may become either same or decrease for the elements immediately following the 4f-elements.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1.62	1.45	1.34	1.29	–	1.24	1.25	1.28	1.34	1.41
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

3.5 IONIC RADIUS

Ionic radius is the radius of a cation or an anion. When a neutral atom is converted to an ion, there would be change in size, as the Z_{eff} will change but the number of protons in nucleus remains same.

If the atom forms an anion, its size (or radius) increases, since the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electron cloud. On the other hand, if one or more electrons are removed from an atom, it reduces the electron–electron repulsion but the nuclear charge remains the same, so the electron cloud shrinks and the cation is smaller than the atom. When a lithium atom reacts with a fluorine atom to form a LiF unit, the changes in size are very peculiar. Out of Li and F, Li is bigger in size. When lithium changes to Li^+ , its size decreases and when F changes to F^- , its size increases. In LiF, Li^+ is smaller than F^- (Note that Li^+ is smaller than F atom and F^- is smaller than Li atom).



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The variation of ionic radii in a period and a group is same as that of atomic radii. Thus, ionic radius decreases in a period from left to right while it increases in a group from top to bottom.

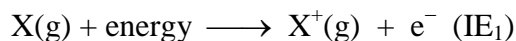
For ions derived from elements in different groups, a size comparison is meaningful only if the ions are isoelectronic. If we examine isoelectronic ions, the cations are smaller than anions. Let us compare the radius of Na^+ ion and F^- ion. Both ions have same number of electrons (10), but Na ($Z = 11$) has more protons than F ($Z = 9$). Thus, Z_{eff} of Na^+ is more than that of F^- , so Na^+ ion is smaller in size than F^- ion. Similarly, for the three isoelectronic ions of third period, Al^{3+} , Mg^{2+} and Na^+ , they all have the same number of electrons (10) but their numbers of protons are 13, 12 and 11 respectively. Thus, the electron cloud in Al^{3+} is pulled inward more than that in Mg^{2+} and Mg^{2+} would be smaller than Na^+ . Thus in general in an isoelectronic cation series, the radii of tripositive ions are smaller than those of dipositive ions, which in turn are smaller than unipositive ions. Similarly, in isoelectronic anions series, the radius increases as we go from uni-negative ion to di-negative ion and so on.

3.6 IONIZATION ENERGY

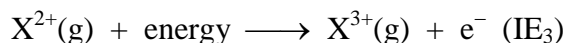
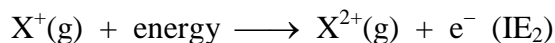
The stability of the outermost electrons is reflected directly in the atom's ionization energies.

Ionization energy is the minimum energy (in kJ/mole) required to remove the most loosely bound electron from an isolated gaseous atom in its ground state. Alternatively, ***ionization energy is the amount of energy in kilojoules needed to knock out one mole of electrons from one mole of isolated gaseous atoms.*** In this definition, gaseous atoms are specifically used because an atom in the gas phase is virtually uninfluenced by its neighbors and so there are no intermolecular forces to take into account while measuring ionization energy.

The magnitude of ionization energy is a measure of how “tightly” the electron is held in the atom. The higher the ionization energy, the more difficult it is to remove the electron. ***For a multi-electron atom, the amount of energy required to remove the first electron from the atom in its ground state is called the first ionization energy (IE_1).***



The second ionization energy (IE_2) and the third ionization energy (IE_3) are shown in the following equations:



The pattern continues for the removal of subsequent electrons. Theoretically, an atom can have as many ionization energy values as the number of electrons present in that atom.

When any electron is removed from a neutral atom, the repulsion among the remaining electrons decreases. Since the nuclear charge remains constant, more energy is needed to remove another electron from the positively charged ion. Thus, ionization energy increases in the order $\text{IE}_1 < \text{IE}_2 < \text{IE}_3 < \dots$

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Ionization is always an endothermic process, thus ionization energies are all positive quantities. The first ionization energy of the elements in a period increases with some irregularities. This trend is due to increase in Z_{eff} from left to right. A larger Z_{eff} means a more tightly held outer electron and hence a higher first ionization energy. In a period, highest ionization energy is of noble gases. The high ionization energies of the noble gases stems from the fact that they have stable ground state electron configurations (ns^2np^6). Among noble gases, He($1s^2$) has the highest ionization energy. In a period, lowest ionization energy is of alkali metals.

Alkali metals have one valence electron, which is effectively shielded by the completely filled inner shells. Consequently, it is easy to remove an electron to form a unipositive ion having stable noble gas configuration.

In the second period from Li to Ne, the first ionization energy increases from Li to Be, then decreases at B, then increases till N, then again decreases at O and then increases till Ne.

Let us look at the first ionization energies of Be & B. The electron configurations of the two elements are $1s^22s^2$ and $1s^22s^22p^1$. Although the Z_{eff} of B is more than Be, yet ionization energy of B is less than Be. It is because when an electron is taken out from B atom, it results in the formation of a stable configuration ($1s^22s^2$) for B^+ while same process when done with Be results in configuration ($1s^22s^1$) for Be^+ . If stable configuration is obtained for an ion, by removing an electron from an atom, less energy is required to remove the electron. Conversely, large amount of energy is needed to remove electron from a stable configuration of $1s^22s^2$ in Be than in B ($1s^22s^22p^1$).

In case of N and O, N has stable half-filled configuration ($1s^22s^22p^3$) while oxygen's electron configuration is $1s^22s^22p^4$. Thus, it is evident that knocking an electron out from N would require greater energy than required for oxygen.

The group IIA elements have higher first ionization energies than the group IA elements. The alkaline earth metals have two valence electrons. Because these two s electrons do not shield each other well, the Z_{eff} for an alkaline earth metal atom is larger than that for the preceding alkali metal. But second ionization energy is higher for alkali metals than for alkaline earth metals because after removing one electron, alkali metal atoms have acquired stable noble gas configurations & thus the removal of second electron becomes more difficult.

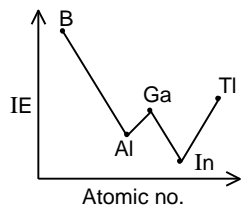
Metals have relatively low ionization energies compared to non-metals. The ionization energies of the metalloids generally fall between those of metals and non-metals. This difference in ionization energies of metal & non-metals suggest why metals always form cations and non-metal form anions in ionic compound.

For a given group, the ionization energy decreases as we move down the group. Elements in the same group have similar outer electronic configurations. However, as the principal quantum number (n) increases, the average distance of a valence electron from the nucleus also increases. A greater separation between the electron and the nucleus means a weaker attraction, so it becomes increasingly easier to remove the first electron as we go from element to element down a group. Thus, the metallic character of the elements within a group increases from top to bottom.

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The general trend in ionization energies is not seen in case of III A group (values are in kJ/mole)

B	Al	Ga	In	Tl
801	577	579	558	589

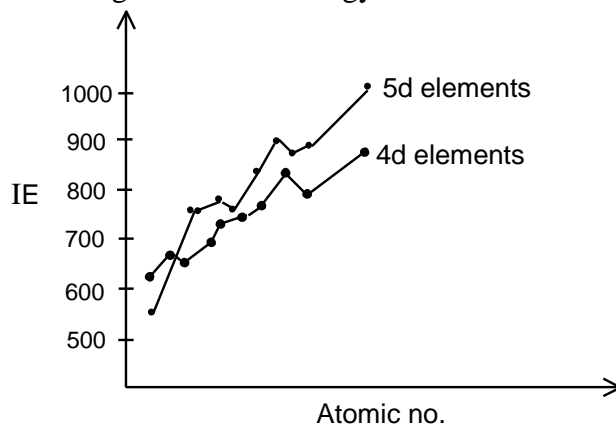


and transition elements (values are in kJ/mole).

3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. E	631	656	650	652	717	762	758	736	745	906
4d series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
I. E	616	674	664	685	703	711	720	804	731	876
5d series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
I. E	541	760	760	770	759	840	900	870	889	1007

From 3d \rightarrow 4d series general trend is observed but not from 4d \rightarrow 5d series because of incorporation of the 14 lanthanides elements between La and Hf. Third period of transition elements have the highest ionization energy. This reflects the fact that any increase in radius due to addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

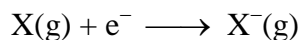
Hence, the radius of 4d and 5d elements more or less remains the same, due to which Z_{eff} increase to more extent, which result in high ionization energy of the 5d elements of transition series.



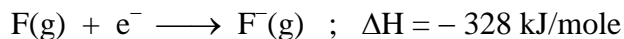
PERIODIC PROPERTIES

3.7 ELECTRON AFFINITY

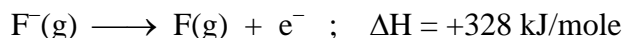
Electron affinity is the energy change that occurs when an electron is accepted by an isolated atom in the gaseous state to form an anion.



The sign of electron affinity is opposite to that used for ionization energy. A positive electron affinity signifies that energy is liberated when an electron is added to an atom. To clarify this apparent paradox, let us consider the process in which a gaseous fluorine atom accepts an electron.



The sign of the enthalpy change indicates that this is an exothermic process. However, the electron affinity of fluorine is assigned a value of +328 kJ/mole. Thus we can think of electron affinity as the energy that must be supplied to remove an electron from a negative ion. For the removal of an electron from a fluoride ion, we have

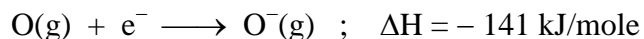


Do remember two unique features of electron affinity as

- (i) The electron affinity of an element is equal to the enthalpy change that accompanies the ionization process of its anion and
- (ii) a large positive electron affinity means that the negative ion is very stable (i.e. atom has a great tendency to accept an electron), just as a high ionization energy of an atom means that the atom is very stable.

In a period, the electron affinity increases on moving from left to right. Thus, the tendency to accept electrons increases in a period and the electron affinity values become more and more positive. The halogens have the highest electron affinity values in a given period. This is not surprising because after accepting an electron, each halogen atom assumes the stable electron configuration of the noble gas immediately to its right. The noble gases have no or very little tendency to accept electrons, thus all the noble gases have electron affinities less than zero. This means that the anions of noble gases (if formed) would be inherently unstable. The electron affinities of metals are generally lower than those of non-metals.

The second electron affinity values are always negative. For example, the electron affinity of oxygen has a positive value (141 kJ/mole), which means that the process



is exothermic. On the other hand, the electron affinity of the O^{-} ion is highly negative (−780 kJ/mole), which means the process

$O^{-}(g) + e^{-} \longrightarrow O^{2-}(g) ; \Delta H = 780 \text{ kJ/mole}$ is endothermic even though the O^{2-} ion has a stable noble gas configuration. This process is unfavorable in the gas phase because the resulting increase in

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electron–electron repulsion outweighs the stability gained by achieving a noble gas configuration. In solid phase, the process becomes favoured because O^{2-} ion is stabilized by the adjacent cations to form ionic lattice releasing lattice energy.

The trend of electron affinity in a group decreases. But the electron affinity values of the elements of II period are less than the elements of III period. For example, electron affinity values of F and Cl are 328 and 349 kJ/mole respectively. Addition of an electron to F atom is more difficult since the added electron experiences greater repulsions due to its small size (having high electron density). Thus the addition of electron is easy in Cl atom since it has less electron density than F atom. Similar is the trend observed for O & S and N & P.

3.8 ELECTRONEGATIVITY

Electronegativity is defined as the power of an atom in a molecule to attract electrons towards it.

It is evident from this fact that electronegativity is not a property of the isolated atom but rather a property of an atom in a molecule, in the environment and under the influence of surrounding atoms. One must also note that the “power to attract” is merely another way of describing the “reluctance to release” electrons from itself to a more electronegative element.

Let us have a covalent molecule X–Y and Y possesses more tendency to attract bonding electron pair towards itself than X possesses. Thus, Y is said to be more electronegative than X.



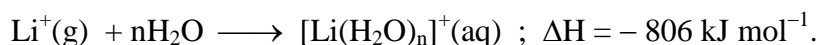
It is also observed that hybridization too affects electronegativity because of the lower energy and hence greater electron attracting power of s–orbital. For example, methane (CH_4) with sp^3 hybridization and 25% ‘s’ character is rather unreactive. In ($CH_2=CH_2$) ethylene, carbon is sp^2 hybridised and the hydrogen atom is more reactive reflecting increased electronegativity of carbon with 33% s–character. Finally acetylene has hydrogen which are highly acidic in which carbon is ‘sp’ hybridised.

Relating the various factors that guide the variation in electronegativity such as orbital energy, enthalpy of formation, covalent radii etc. In general, it can be said that in a period, on moving from left to right, the electronegativity increases. The halogens have the highest electronegativity among other elements of the period. The noble gases have zero value of electronegativity and alkali metals have lowest value among the elements in a period. The electronegativity of transition elements do not change much in a period. Fluorine is the most electronegative element in the periodic table and the second most electronegative element is oxygen. In a group, on moving from top to bottom, the electronegativity decreases.

Electronegativity is very similar to electron affinity with a difference that electrons are not taken completely by the element but they shift slightly towards the element, which thus acquires partial negative charge. Electronegativity is not defined for an isolated gaseous atom, but it is defined for a covalently bonded atom in a molecule.

3.9 HYDRATION AND HYDRATION ENERGY

Hydration energy is the enthalpy change that accompanies when one mole of the gaseous ion is dissolved in water. For example, reaction of the hydration of Li ion is shown as:



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Extent of hydration (means the number of water molecules surrounding a given ion) depends on the size and charge of the ion. If the size of the ion is small and its charge is greater, then there would be greater attraction for water molecules, hence greater the extent of hydration and greater the hydration energy. The total hydration energy of a salt (M^+X^-) is related to the size of ions as

$$\text{Total hydration energy} \propto \left(\frac{1}{r_{M^+}} \right) + \left(\frac{1}{r_{X^-}} \right)$$

The first term in this expression defines the hydration energy due to cation and second term defines the hydration energy due to anion.

Let us take Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ ions for comparison. The charge on all the ions is same (unipositive) but the size increases from Li^+ to Cs^+ . Thus, the positive charge density decreases from Li^+ to Cs^+ and hence Li^+ ion would attract H_2O molecules more strongly than Na^+ and so on. Therefore, hydration energy decreases from Li^+ ion to Cs^+ ion and the size of the hydrated ion also decreases from Li^+ to Cs^+ ion and thus the ionic mobility increases from Li^+ to Cs^+ ion.

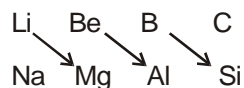
In a period, on moving from left to right the hydration energy increases. You can very well see this trend in the third period involving ions Na^+ , Mg^{2+} and Al^{3+} .

3.10 DIAGONAL RELATIONSHIPS

A diagonal relationship is a similarity in properties between diagonal neighbours in the main groups of the periodic table. Because these properties lie in a diagonal pattern, it is not surprising to find that the elements within a diagonal band show similar chemical properties. Diagonal relationship helps in making predictions about the properties of elements and their compounds.

Some elements of II period resemble much in properties with the element of III period of next group .

Diagonal relationship is exhibited by lithium & magnesium and beryllium & aluminium. For example, lithium and magnesium react directly with nitrogen to form nitrides. Beryllium and aluminum, both are amphoteric i.e. reacts with acids as well as bases.



Their similar properties are due to

- (a) Nearly similar size of atom and their ion.
- (b) Similar electropositive character
- (c) Similar charge to radius ratio.

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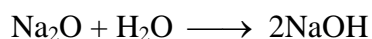
3.11 PROPERTIES OF OXIDES

Properties of the representative elements across a period can be compared by examining the properties of their oxides. Let us see the difference in the behaviour of the oxides of third period elements. Some elements in the third period (P, S and Cl) form several types of oxides but we will consider those oxides in which the elements have the highest oxidation number. The oxides of the elements of third period are Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} , SO_3 and Cl_2O_7 .

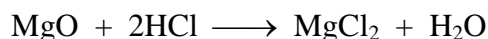
We know that oxygen has a tendency to form the oxide ion. This tendency is greatly favoured when oxygen combines with metals having low ionization energies (like I A and II A group elements plus aluminium). Thus, Na_2O , MgO and Al_2O_3 are ionic compounds having extensive three-dimensional structures in which each cation is surrounded by a specific number of anions and vice versa. As the ionization energies of the elements increase from left to right, so does the molecular structure of the oxides that are formed. Silicon is a metalloid whose oxide (SiO_2) has a giant three-dimensional network, although no ions are present. The oxides of phosphorous, sulfur & chlorine are molecular compounds composed of small discrete units.

Most oxides can be classified as acidic or basic depending on whether they produce acids or bases when dissolved in water or react as acids or bases in certain processes. Some oxides

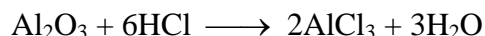
are amphoteric, which mean they display both acidic and basic properties. The first two oxides of the third period (Na_2O & MgO) are basic oxides. For example, Na_2O reacts with water to form the base (NaOH).



MgO is quite insoluble in H_2O but it reacts with acids showing its basic nature.



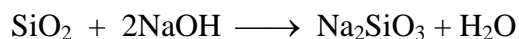
Al_2O_3 is even less soluble in H_2O than MgO , it also does not react with water but it shows basic properties by reacting with acids.



It also exhibits acidic properties by reacting with bases.



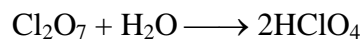
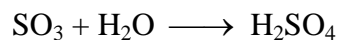
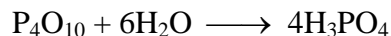
Thus, Al_2O_3 is classified as an amphoteric oxide because it has properties of both acids and bases. Other amphoteric oxides are ZnO , BeO , Bi_2O_3 etc. SiO_2 is insoluble and does not react with water. It has acidic properties as it reacts with very concentrated bases.



For this reason, concentrated aqueous, strong bases such as NaOH should not be stored in glasswares, which are made of SiO_2 .

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The remaining oxides are acidic. They react with water to form phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) and perchloric acid (HClO_4).



Thus the oxides of third period elements shows that as the metallic character of the elements decrease from left to right across the period, their oxides changes from basic to amphoteric to acidic. Metallic oxides are usually basic and most oxides of non-metals are acidic. The intermediate properties of the oxides are exhibited by elements which are placed between metals and non-metals. As the metallic character of the elements increases from top to bottom in a group of representative elements, the basic character of oxides also increases from top to bottom. Thus, Na_2O is less basic than K_2O , K_2O is less basic than Rb_2O and so on.

3.12 HYDRIDES

Hydrogen combines with a number of other elements (metals and non-metals) to form compounds called hydrides. The hydrides can be either ionic or covalent. The ionic hydrides are formed by the elements of I A & II A group while other elements mostly form covalent hydrides.

Covalent nature of hydrides increases across a period and decreases down the group, while, ionic nature of hydrides decreases across a period and increases down the group.

Ionic hydrides are better reducing agent than covalent hydrides and reducing nature of hydrides decreases across a period and increases down the group.