

The Basis of the Periodic Table

INTRODUCTION AND HISTORICAL PERSPECTIVES

As more and more elements were discovered, chemists tried to generalise their physical and chemical properties.

Newland (1865) and later Lothar Meyer (1869) (mainly on the basis of the study of physical properties of elements) could show a recurrence of elements having similar properties in a **periodic** fashion, if the elements were arranged in the increasing order of atomic weights. In 1869 itself, D. I. Mendeleev independently constructed a periodic table of elements after carefully analysing both physical as well as chemical (e.g. valency) properties. The basis of the periodic table was the **periodic law**: **The properties of elements, as well as the formulae and properties of their compounds, depend in a periodic manner on the atomic weight of the elements.**

Mendeleev's Periodic Table

Mendeleev's periodic table as of 1869 was organised into seven horizontal rows called **periods** and eight vertical columns called **groups** (Table 1). The group numbers were meant to be indicative of the valency of the elements in their compounds. With the discovery of inert gases one more group, the **zero** group was added. (**Think it over**: Why the name **zero** group and not the ninth group?)

Table 1: **A part of Mendeleev's periodic table as of 1869**

	Gp 1	Gp 2	Gp 3	Gp 4	Gp 5	Gp 6	Gp 7	Gp 8
Row 1	H							
Row 2	Li	Be	B	C	N	O	F	
Row 3	Na	Mg	Al	Si	P	S	Cl	
Row 4	K	Ca						Ti V Cr Mn Fe Co Ni
Row 5	Cu	Zn			As	Se	Br	

Usefulness of Mendeleev's periodic table

1. Mendeleev predicted new elements and their properties wherever he had left spaces. This led to the discovery of new elements and Mendeleev's predictions met with outstanding success.
2. In many cases elements did not fit comfortably in the slots provided for them in accordance with their atomic weights. In case of chromium (Cr), indium (In), platinum (Pt) and gold (Au) Mendeleev pre-determined the atomic masses with greater accuracy and the new values justified their positions inside groups in his modified periodic table.

The Basis of the Periodic Table

Drawbacks of Mendeleev's periodic table

1. In some cases, however, the discrepancies in the atomic weight-based arrangements were real. Thus, on the basis of periodicity of properties Te (127.6) should come before I (126.9), Ar (39.95) should come before K (39.1) and Co

(58.93) should come before Ni (58.71).

2. Mendeleev's table had no separate place for isotopes though the table was based on atomic weights.

3. Similar elements were kept separately in different groups e.g. Cu and Fe.

4. H, a non-metal was kept along with metals such as Li, Na and K.

5. There was no proper place for lanthanides and actinides.

The Modern Periodic Law and its Significance

Regarding the last two drawbacks one must concede that even today hydrogen, the lanthanides and the actinides are not placed in any group of the periodic table but are placed separately.

However, the first of the three problems were sorted out after [Moseley's](#) X-ray experiments in 1914, where he developed a technique for determining atomic numbers. It was found that the atomic number had a better correlation with properties than atomic weights.

The modern periodic law states that:

The physical and chemical properties of the elements are a periodic function of their atomic numbers.

How do we explain the periodic variation in properties? As the **atomic number increases** so does the **number of electrons** which keep filling up the subshells in accordance with the **Aufbau principle**. Hence, elements having the same number of electrons in the outermost *s*, *p*, *d* and *f* subshells of their atoms, keep recurring with periodic regularity.

Table 2 shows this periodicity.

When elements $Z = 1$ to $Z = 109$ are arranged in sequence, they conveniently split up **into different blocks according to the subshells** filling up

seven <i>s</i> blocks accounting for	$7 \times 2 = 14$ elements
five <i>p</i> blocks accounting for	$5 \times 6 = 30$ elements
*three <i>d</i> blocks accounting for	$(3 \times 10) + 7 = 37$ elements
two <i>f</i> blocks accounting for	$2 \times 14 = 28$ elements
	Total: 109 elements

* Note: the fourth *d* block contains only 7 elements

Table 2

Period No.: value of 'n' for outer most shell	Subshell filling up	Electronic configuration depicting the subshells being filled in the given period		Number of elements	Atomic No. (Z)		Type of element
		from	to		from	to	
1	1s	1s ¹	1s ²	2	1	2	s block
Second (L) shell starts filling							
2	2s	2s ¹	2s ²	2	3	4	s block
	2p	2s ² 2p ¹	2s ² 2p ⁶	6	5	10	p block
Third (M) shell starts filling							
3	3s	3s ¹	3s ²	2	11	12	s block
	3p	3s ² 3p ¹	3s ² 3p ⁶	6	13	18	p block
Fourth (N) shell starts filling							
4	4s	4s ¹	4s ²	2	19	20	s block
	3d	3d ¹ 4s ²	3d ¹⁰ 4s ²	10	21	30	d block
	4p	3d ¹⁰ 4s ² 4p ¹	3d ¹⁰ 4s ² 4p ⁶	6	31	36	p block
Fifth (O) shell starts filling							
5	5s	5s ¹	5s ²	2	37	38	s block
	4d	4d ¹ 5s ²	4d ¹⁰ 5s ²	10	39	48	d block
	5p	4d ¹⁰ 5s ² 5p ¹	4d ¹⁰ 5s ² 5p ⁶	6	49	54	p block
Sixth (P) shell starts filling							
6	4s	6s ¹	6s ²	2	55	56	s block
	4f	4f ² 6s ²	4f ¹⁴ 6s ²	14	58	71*	f block
	5d	5d ¹ 6s ² 4f ¹⁴ 5d ² 6s ²	4f ¹⁴ 5d ¹⁰ 6s ²	10	57* 72	80	d block
	6p	4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶	6	81	86	p block
Seventh (Q) shell starts filling							
7	7s	7s ¹	7s ²	2	87	88	s block
	5f	5f ² 7s ²	5f ¹⁴ 6d ¹ 7s ²	14	90	103*	f block
	6d	6d ¹ 7s ² 5f ¹⁴ 6d ² 7s ²	5f ¹⁴ 6d ⁷ 7s ²	5	89* 104	109	d block

Some Important Points

1. There are seven periods in all.
2. The number of elements in each of these periods keep on increasing progressively: two in the first period, eight each in the second and third periods, eighteen each in the fourth and fifth periods and thirty-two in the sixth period.

Reason: Higher periods contain elements corresponding to filling of higher shells, which have a progressively greater number of subshells. Thus, the number of **blocks** of elements in higher shells is higher.

The first period has only *s* block i.e. 2 elements.

The second and third periods have only *s* and *p* blocks i.e. 2 + 6 = 8 elements

The fourth and fifth periods have *s*, *p*, and *d* block i.e. 2 + 6 + 10 = 18 elements

The sixth period has *s*, *p*, *d* and *f* block $\Rightarrow 2 + 6 + 10 + 14 = 32$ elements.

3. The seventh period is incomplete and contains only 23 elements. As the atomic number increases, atoms become less stable due to radioactivity. Stable elements beyond 109 are not known.

4. The maximum number of electrons in any atom in

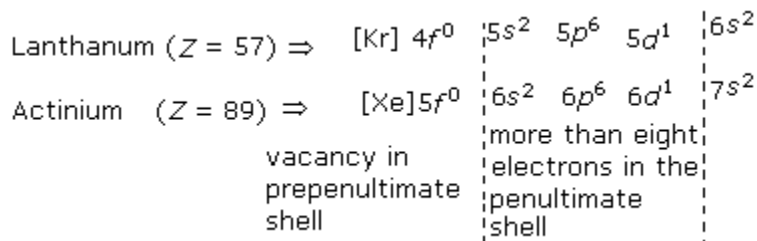
- a) its **outermost shell** is **two** in the **first** period and **eight** in other periods.
- b) its **penultimate shell** is **two** in the **second** period, **eight** in the **third** and **fourth** periods and **eighteen** in the **fifth** and **sixth** periods.
- c) its **pre-penultimate shell** is **two** in the **third** period, **eight** in the **fourth** period, **eighteen** in **fifth** period and **thirty-two** in the **sixth** and **seven** periods.

5. In no case can we have

- a) **more than two electrons in the outermost shell** till its penultimate shell is filled to its maximum capacity.
- b) **more than eight electrons in the penultimate shell** till its pre-penultimate shell is filled to its capacity.

Both these observations are related to the $(n + l)$ rule of the Aufbau principle.

6. There are two notable exceptions to the above generalisation in the form of $Z = 57$ and $Z = 89$.



Reason: This is because, in violation of the $(n + l)$ rule, the $(n - 1)$ d subshell has started filling before $(n - 2)$ f . The situation gets back to the $(n + l)$ order from $Z = 58$ and $Z = 90$, respectively.

In this process, elements 57 and 89 have taken up position in the d block, where otherwise elements 71 and 103 **should have been**. All these atomic numbers have been marked with an asterisk (*) in Table 2.

7. It has been observed that the properties of elements depend
- a) primarily on the outer shell (also known as the valence shell) configuration
- b) secondarily on the penultimate shell configuration and
- c) only tertiarily on the pre-penultimate shell configuration.

The following are apparent in Table 2:

1. Elements where the **outermost shell** is filling up belong to the **s and p block**, to constitute **eight** main groups.
2. Elements where the **penultimate shell** is filling up belongs to the **d block** to constitute **ten** side groups.
3. Elements where the **pre-penultimate shell** is filling up belongs to the **f block**, to constitute a separate series of **fourteen** elements in each.

The Modern Periodic Table

Some significant features of the modern periodic table are shown in table 3

Table 3

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

5. The ***d* block elements**, differing in the number of electrons in the **penultimate (*n* - 1) shells**, show enough similarities to merit the general classification as

transition elements. However, they show enough variation (different oxidation states) to merit their placement in the periodic table, (Groups IB to VIIIB). Group IB metals, **Cu, Ag and Au** are known as **coinage metals**.

Note that though **Zn, Cd and Hg** are *d* block elements, they **are not called transition metals** since they do not show most properties characteristic of transition elements. The properties of transition elements are characteristic of **partially filled *d* subshells**. These elements **as such, or in their stable compounds**, have completely filled *d* subshells.

But, why do we have two alternative conditions for inclusion in the list of transition metals, viz.

a) either the neutral atom, or

b) in the ion formed in its stable compounds, they should have **incomplete *d* subshells**?

The reason is that the neutral atom of Cu has a d^{10} (filled *d* sub shell) configuration but a d^9 configuration in its stable cation Cu^{+} .

The stable cation Sc^{3+} of scandium has a d^0 (empty *d* subshell) configuration though the corresponding neutral atom has a d^1 configuration.

Both Cu and Sc have properties characteristic of transition elements and deserve inclusion in this list. Hence **both** the alternatives have to be included as conditions.

Note that both M as well as M^{2+} corresponding to Zn, Cd and Hg have d^{10} configuration, thus justifying their exclusion.

6. The maximum variation of properties within the period are shown by **s and p block** elements (where the outermost or n^{th} shell fills up).

They are, therefore, called **main group elements** (IA to VIIA and VIII) or **representative elements**.

Elements with the outershell configuration ns^1 and ns^2 with the exception of hydrogen and helium, are called **alkali metals** and **alkaline earth metals**, respectively. Those with the outermost shell configuration $ns^2 np^4$ and $ns^2 np^5$ are called **chalcogens** and **halogens**, respectively.

7. According to the 1984 recommendation of the IUPAC (International Union of Pure and Applied Chemistry), the groups are numbered as s block element Groups 1 and 2 (with the exception of H and He, as explained earlier); *d* block elements, Groups 3 to 12; *p* block elements, Groups 13 to 18.

METALS AND NON-METALS

All *s*, *d* and *f* block elements (barring H and He) are metals.

The elements to the left of the diagonal 'staircase' cutting the *p* block are **metals**. The elements on its right are **non-metals** and those on either sides of the line are mostly **metalloids**.

Metals and non-metals, along with **acids and bases** are significant categories for chemical **classification of substances**.

Oxides of metals are usually bases which form salts with acids. **Oxides of non-metals** are usually acids which form salts with bases and **oxides of metalloids** are usually amphoteric and form salts with both acids and bases.

FAMILIARITY WITH THE PERIODIC TABLE

The following assignments are designed to make you familiar with the various aspects of the periodic table.

It is essential that the first 36 elements of the periodic table, along with their respective periods and groups, be memorised.

Periodicity of Properties and Variations in Electronic Configuration

In the previous sections we have seen how the organisation of the periodic table reflects the systematic variation of electronic configuration with increase in atomic number. We have also seen how the periodic table reflects the systematic variation of properties of elements with increase in atomic number. We have implied that the two variations are related to one another as a fact, which the periodic table (based on atomic numbers) exploits to our advantage. In this section, we will investigate the question of why such a correlation exists.

THE DIRECT CORRELATION

The value of n for the outermost shell and hence, the number of available orbitals in the n th shell

The number of electrons in the n th shell (valence shell)

The number of electrons in any incomplete $(n - 1)$ th shell

The fact that a filled subshell (particularly, a completed octet) leads to the stabilisation of an atomic species

We can predict/explain the valency and possible number of bonds that can be formed for any element. The electronic configuration directly gives us all this information.

VALENCY AND THE NUMBER OF BONDS

The above discussion, however, should not make you think that the number and nature of bonds are unrelated to each other. What we should stress upon is that it is possible to determine the allowed number of bonds (of any nature) for an element directly from the electronic configuration of its atoms.

We begin by first listing the different ways in which an atom may form bonds without detailed discussions.

1. **Ionic bond**: The atoms gain or lose electrons to form stable positively or negatively charged ions which then hold on to each other by electrostatic attraction. The charge on the stable ions is then referred to as valency, primary valency, electrovalency or oxidation state. For example, in CaCl_2 the valency or oxidation state of Ca is $2+$ and that of Cl is $1-$.
2. **Covalent bond**: Two atoms share a pair of electrons equally by the overlap of singly occupied (half-filled) orbitals belonging to each of them. The number of half-filled orbitals that an atom may have determines its valency or covalency. Note that, this may not be the maximum number of covalent bonds an atom may form (e.g. N has a covalency of 3 as in NH_3 or N_2 but it can form four bonds as in NH_4^+).
3. **Polar covalent bond**: This is a special type of covalent bond involving unequal sharing of a pair of electrons. This is somewhere between a covalent bond and an ionic bond. If polar covalent bonds are taken to their ionic extreme, we can imagine ions of the atoms, whose charges also correspond to their valency or oxidation state.

4. **Coordinate covalent bond**: This is another special type of covalent bond where two atoms share a pair of electrons by the overlap of orbitals, but one of the atoms contribute a 'filled' orbital and the other a vacant orbital.

The maximum number of covalent bonds of all types as in (2), (3) and (4) taken together that an atom may form is referred to as the coordinate ion number (sometimes also called secondary valency).

Without going into whether and when an atom actually forms a particular type of bond we may look into three possible types of numbers

- i) oxidation state - a number with a '+' or '-' sign
- ii) covalency - a number
- iii) coordination number - also a number

Note that the term valency is related to all these three different quantities. Simply using the word valency (unless in a given situation it can mean only one thing) may give rise to a lot of confusion and hence, should be avoided.

PERIODICITY OF OXIDATION STATE

1. *Maximum and minimum possible oxidation states*

a) For representative elements, the maximum possible oxidation state is given by $x+$ and the minimum possible oxidation state is given by $(8 - x)-$, where x is the total number of valence shell (nth shell) electrons. (The number 8 arises due to the stability of the octet.)

For example, if $n = 5$ then the maximum value is $5+$ and the minimum value is $3-$.

For N ($1s^2 2s^2 2p^3$) we have $5+$ in N_2O_5 and $3-$ in NH_3 . Usually, if $x > 3$ we do not observe the minimum value for energetic reasons.

- b) For transition elements, the maximum number is given by the sum of the number of nth shell electrons and that of $(n - 1)$ th shell d electrons. Thus, for Cr ($[Ar] 3d^5 4s1$), the maximum oxidation state is $6+$ as in $K_2Cr_2O_7$ or CrO_3 . For Mn ($[Ar] 3d^5 4s^2$), it is $7+$ as in $KMnO_4$.
- c) An oxidation state of $8+$ is rare and greater than $8+$ has not been observed. Transition elements do not show negative oxidation states.

Periodic behavior: Along any period from left to right, the maximum possible oxidation state increases and the minimum possible oxidation state decreases (the latter is not true for transition elements). Within a group, both of these remain the same and correspond to the group number in the old system. The only exceptions are for the group zero elements, which may show a maximum oxidation state of $8+$ (usually $6+$ is the actually observed maximum, as in XeF_6).

2. Variable oxidation states

a) For representative elements with $x \geq 2$ we have a fixed oxidation state of $x+$. If $x > 2$, then they may show variable oxidation states of $x+$, $(x - 2)+$, $(x - 4)+$, $(x - 6)+$ and $(x - 8)+$.

Thus, Br ($[\text{Ar}] 3d^{10} 4s^2 4p^5$) may have oxidation states of $7+$, $5+$, $3+$, $1+$ and $1-$

(note $(x - 8)+$ for Br is $1-$) and of course '0' corresponding to the elemental state.

S ($[\text{Ne}] 3s^2 3p^4$) may have oxidation states of $6+$, $4+$, $2+$, 0 and $2-$. The connection of the possible values with electronic configuration (value of x) requires no further elaboration. They are the same for a particular group.

However, the lower oxidation states {e.g. $(x - 2)+$ } become more common and more stable as we go down the group. We require more energy reaching higher oxidation states, which is compensated for by the greater number of bonds formed. As we go down the group the atomic size increases and weaker bonds are formed. In the absence of adequate stabilisation due to extra bond formation, the lower oxidation state is favoured. Thus, CCl_2 is unstable, SnCl_4 is more stable than SnCl_2 but PbCl_2 is more stable than PbCl_4 . This is also known as the inert pair effect.

The reason for this variation in units of two will be made clear while discussing covalency.

Note: In some cases, specially C and N, where an atom may form bonds simultaneously with different elements we may observe all oxidation states e.g. for N are, NH_3 ($3-$), N_2H_4 ($2-$), N_2H_2 ($1-$), N_2 (0), N_2O ($1+$), NO ($2+$), N_2O_3 ($3+$), NO_2 ($4+$), N_2O_5 ($5+$).

Actually in most of these cases, the term oxidation number instead of oxidation state should be used since the values are actually average values corresponding to more than one nitrogen atom, each in a different oxidation state. Further, NO and NO_2 being odd electron molecules are indeed special.

b) For transition elements we may observe any value of oxidation state from zero to the maximum possible depending on how many of the $(n - 1)d$ electrons are participating. The electrovalency is however, usually $2+$ or $3+$. Group IB $[(n - 1)d^{10} ns^1]$ has a tendency of showing an electrovalence of $1+$ as in CuCl or AgNO_3 , etc.

Group IIB $[(n - 1)d^{10} ns^2]$ does not show a variable oxidation state - but then they are not considered as transition elements. They show a fixed oxidation state of $2+$.

PERIODICITY OF COVALENCY

Whereas, the oxidation state depends only on x i.e. the number of electrons in the n th shell (plus the number of d electrons in the $(n - 1)$ th shell for transition elements), the maximum covalency also depends on the number of available orbitals. This is because covalency is equal to the number of half-filled orbitals. Filled or unfilled orbitals cannot participate in covalent bonding (they may, of course, participate in co-ordinate

covalent bonding). Thus, both the value of x and the number of available orbitals together define maximum covalency. The situation will become clearer through the following examples.

$\boxed{\uparrow\downarrow}$
 $\text{He } 1s$ cannot form any covalent bonds

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow}$
 $\text{Be } 1s \ 2s$ also cannot form any covalent bonds as such. However, it has vacant 2p orbitals in its valence shell and hence, its valence shell may expand in order to be able to form two bonds by an initial excitation of the atom from its ground state as follows:

Be (excited state)

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{\uparrow} \quad \boxed{} \quad \boxed{}$
 $1s \ 2s \ 2p$

Similarly, carbon may form two bonds as follows:

${}_6\text{C}$

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{} \quad \boxed{}$
 $1s \ 2s \ 2p$

or four bonds as follows:

C (excited state)

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{}$
 $1s \ 2s \ 2p$

Nitrogen can only form three bonds (though it may show a maximum oxidation state of 5+)

${}_7\text{N}$

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{}$
 $1s \ 2s \ 2p$

But, phosphorus may form either three bonds

${}_{15}\text{P}$

$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow}$
 $[\text{Ne}] \ 3s \ 3p$

or five bonds (valence shell expansion)

P(excited state)

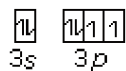
$\boxed{} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{} \quad \boxed{} \quad \boxed{}$
 $[\text{Ne}] \ 3s \ 3p \ 3d$

Sulphur can form 2, 4 or 6 bonds as follows:

S (different states)

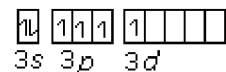
two bonds

[Ne]



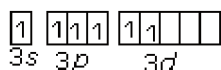
four bonds

[Ne]



six bonds

[Ne]



Note: It should be clear from the above examples why for representative elements, the oxidation states varied in units of 2 i.e. x, (x - 2), (x - 4), etc. It is the same also with covalency.

Periodic behaviour: The periodic behaviour of covalency is tricky. It depends on three factors

Value of x - property of the group

Number of available orbitals - property of the period

Inert pair effect - as highlighted while discussing oxidation states, also a property of the period

We may summarise the situation as follows:

The number of available orbitals for any element in the

First period is $1^2 = 1$

Second period is $2^2 = 4$

Third period is $3^2 = 9$

Since the maximum number of electrons in the nth shell is 8 we may say that the maximum covalency in the first and second periods are 1 and 4, respectively. From the third period onwards the maximum possible value may be 8 (maximum number of valence electrons) though this number is never actually achieved by any representative element.

Hence, in the second period the maximum covalency will first increase and then decrease as we go from the left to the right.

Li (1), Be (2), B (3), C (4), N (3), O (2), F (1), Ne (0).

and from the third period onwards, the maximum covalency will increase from left to right.

Na (1), Mg (2), Al (3), Si (4), P (5), S (6), Cl (7), Ar (8).

Argon, however, does not show 8 covalent bonds though Xe can show upto 6.

For transition elements which are there from the fourth period onwards, orbitals do not pose any restriction as vacant 4d orbitals are available in addition to the vacancy in 3d. The number of electrons also may go up to 11 (as in Cu). Thus, the periodic behaviour for covalency will be the same as observed for the oxidation states.

- 1) In a group (of representative elements) as we go down the maximum covalency remains the same throughout for Groups IA to IVA e.g. BF_3 , AlCl_3 , GaCl_3 , etc.
- 2) For Groups VA to zero, the maximum covalency increases as we go from the second period to the third period e.g. F_2 , SF_4 , SF_6 , NCl_3 , PCl_5 etc.
- 3) For Groups IIIA to zero, the lower value of covalency becomes more stable as we go down a group e.g. Al^+ is never observed but Tl^+ is observed in aqueous solutions.

PERIODICITY OF CO-ORDINATION NUMBER

The maximum value of the co-ordination number depends only on the number of available orbitals (irrespective of the number of valence shell electrons) and is, therefore, a characteristic of a particular period. Thus, the maximum co ordination number for the second period elements is 4.

For example, we may have $[\text{Be}(\text{OH})_4]^{2-}$, BF_4^- , CF_4 , NH_4^+ , etc.

Note: We may theoretically think about H_4O_2^+ but it will not be stable. However, we do have H_3O^+ .

For representative elements in the third period onwards, the most preferred coordination number is 6. This is also the most common co-ordination number for transition elements though co-ordination numbers of 2, 4, 8 are also observed. We will take this up in detail when we study d block elements.

The following exercises are designed to develop in you the skills required to use the rules regarding group and periodic behaviour of oxidation states, covalency and coordination numbers.

The Indirect Consequences of the Electronic Configurations

We have earlier discussed in detail, what the electronic configuration of an atom informs us directly about. You will observe that, we have mainly talked about the **number** and not the **nature** of the bonds.

Atoms rarely occur free in nature (except for noble gases). They occur in a bonded state as **elements** and **compounds** (substances). The properties of these substances, in turn, depend on the nature of the bonding between the atoms. Since the electronic configuration does correlate with the properties of elements (and their compounds), it must, therefore, also be telling us **indirectly** about the **nature** of bonds that an atom may form. If we want to use the periodic table to understand chemistry, we must follow the clues.

Bonding involves electrons holding more than one nuclei together through electrostatic attraction. The attraction between the electrons and the nucleus in the free atoms and their relative strengths should, therefore, determine the nature of bonding between the two atoms.

In the remaining part of this section, we will try to assess the effective electrostatic attraction of the electrons by the nucleus in an atom on the basis of its electronic configuration. In that process we will try to identify the factors, which set a general trend of periodic variations and those, which give rise to apparent anomalies.

General Trend in Electrostatic Attraction Between Valence Shell Electrons and the Nucleus

The greater the attraction experienced by the outer shell electrons, the smaller is the size of the atom. It is, therefore, more difficult to remove electrons from the atom but easier to add electrons to the atom. Electrostatic attraction depends on two things, the charge on the nucleus and the distance of the valence electrons from the nucleus i.e. the value of the principle quantum number n of the valence electrons. If n remains the same and Z increases, naturally the **attraction will increase**. This is the general trend that is **observed across a period from left to right**.

If both n and Z increase, there are two factors to be considered.

1. Since inner shell electrons shield the valence shell electrons from the nucleus, the effective nuclear charge (Z_{eff}) experienced by the valence electrons is considerably less than the actual Z .
2. With increasing n , the distance increases and attraction varies in an **inverse square manner**. Thus, **down a group from top to bottom the general trend observed is a decrease in attraction**.

ANOMALIES IN THE GENERAL TRENDS

I. Inner Shell Shielding

The shielding offered by the inner shell electrons, partially reduce the effective nuclear charge. Thus though for H, the nuclear charge is 1, for Li ($Z = 3$, $1s^2 2s^1$), due to shielding by the two $1s$ electrons, the $2s$ electron experiences an effective nuclear charge of 1.26 units.

The ability of an electron to shield is dependent on the subshell (the value of l), to which it belongs. Larger the value of l , greater is the number of nodes at the nucleus and lower is the electron density near the nucleus, lower is the ability to shield the outer shell electrons. Hence screening effectivity decreases in the order $s > p > d > f$.

1. Anomaly observed due to inefficient shielding of d electrons

This is most strongly observed in Group VIIA, which comes immediately after the d

block in each period, from the fourth period onwards. Consider Al ($Z = 13$, $[\text{Ne}] 3s^2 3p^1$); the inefficient shielding due to $3d$ and $4d$ electrons leads to the anomalous attraction felt by the np electron, $\text{In} > \text{Ga} > \text{Al}$. This is also observed in the case of Tl, but there the effect of $4f$ electrons play a stronger role.

This is also reflected in the attraction experienced by the $4s^1$ electrons in $\text{K}([\text{Ar}] 4s^1)$ and $\text{Cu}([\text{Ar}] 3d^{10} 4s^1)$.

2. Anomaly due to f subshell electrons, the lanthanide contraction In the lanthanide series, the $4f$ subshell gets filled up and the $6s$ electrons experience progressively higher degrees of attraction as we go from Ce ($Z = 58$) to Lu ($Z = 71$). Naturally, therefore, Lu is much smaller than Ce in size. This phenomenon, which is observed due to inefficient shielding by $4f$ electrons is known as **lanthanide contraction**. The effect manifests itself in terms of **higher attraction** in the sixth period elements, than in the fifth period elements of the corresponding groups from Group IVB onwards.

Thus, for example, in terms of attraction, $\text{Hf} (Z = 72, [\text{Xe}] 4f^{14} 5d^2 6s^2) > \text{Zr} (Z = 40, [\text{Kr}] 4d^2 5s^2)$, $\text{Au} (Z = 79, [\text{Xe}] 4f^{14} 5d^{10} 6s^1) > \text{Ag} (Z = 47, [\text{Kr}] 4d^{10} 5s^1)$. In fact $\text{Au} > \text{Cu} (Z = 29, [\text{Ar}] 3d^{10} 4s^1)$.

This effect is also observed in Groups IA and IIA, between the sixth and the seventh periods. Thus, for example in terms of attraction experienced by valence shell

electrons of $\text{Fr} (Z = 87, [\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6 7s^1)$ is greater than that experienced by $\text{Cs} (Z = 55, [\text{Xe}] 6s^1)$.

II. Filled and Half-filled Subshells

Why is the electronic configuration of $\text{Cu} (Z = 29, [\text{Ar}] 3d^{10} 4s^1)$ and **not** $[\text{Ar}] 3d^9 4s^2$?

Why is that of $\text{Cr} (Z = 24)$, $[\text{Ar}] 3d^5 4s^1$? Why is the inert gas configuration considered to be extra stable?

We have already seen that the half-filled or fully filled subshells, lend extra stability to the atom or ion concerned. Since subshells keep getting half-filled and fully filled, with periodic regularity as we go from left to right across a period, this leads to a **periodic anomaly**.

The net result is that the atoms or ions, which have a half-filled or a fully filled subshell have much less attraction for incoming electrons compared to one which has one electron less. Thus, for example in $\text{N} (Z = 7)$, $[\text{He}] 2s^2 2p^3$, half-filled $2p$ subshell, is far more reluctant to accept a fresh electron than $\text{C} (Z = 6)$, $[\text{He}] 2s^2 2p^2$, one electron required to half-fill the $2p$ subshell). This is exactly the opposite of what the general trend predicts. Similarly N is far more reluctant to lose an electron than $\text{O} (Z = 8)$, $[\text{He}] 2s^2 2p^4$ (one more electron than required to have a half-filled $2p$ subshell), also in opposition to the general trend.

Exercise 1

Explain why

a) Beryllium is more reluctant to gain an electron than lithium, as well as more reluctant to lose an electron as boron.

b) Argon is more reluctant to gain an electron than chlorine as well as more reluctant to lose an electron as potassium.

(**Note:** In each of the above cases, part of the observations is in keeping with the general trend.)

III. Electron-Electron Repulsion and Size of the Atom

While explaining the general trend of reduction in the ease of adding electrons to the atom as we go down a group, we have only considered the factors of electrostatic attraction of electrons by the nucleus and the repulsion by inner shell electrons leading to shielding. There is another effect due to repulsion by electrons of the same shell, a factor particularly important when the size of the atom proportional to r^2 is very small. Thus F, which is much smaller than Cl, is less inclined to add an electron than Cl. When the size of the atom increases, the general trend prevails.

Exercise 2

Which has a greater tendency to add an electron: O or S, S or Se, N or P? Explain.

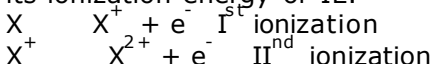
Ionization Energy

PERIODICITY OF PROPERTIES OF THE FREE ATOM

In the previous section, we have developed theories to explain qualitative facts. While this approach is used in chemical logic, in the ultimate analysis, chemistry as an experimental science must deal with **numbers** or **experimental data**. This section incorporates rigorous definitions of some quantitative atomic properties and the periodic correlation of their values.

IONIZATION ENERGY

The energy required to remove the least bound (outermost) electron from an isolated atom (also ion or molecule) of an element (also compound) in its gaseous state is called its ionization energy or IE.



Strictly speaking it is the change in internal energy at 0 K when a cation as above is generated. Normally, the values reported in SI units are the enthalpy change in the

process at one atmosphere and 25° C (H_{298}^0) in kJ mol^{-1} . But, they are very often also reported in eV or electron volts because of the method of experimental determination. The experimental determination may be carried out electrically, spectroscopically or thermochemically. In the electrical method we measure the potential across which a projectile electron (not the electron to be removed) has to be accelerated in order that it may dislodge the most loosely bound electron from an **isolated gaseous atom** (or molecule as the case may be). The potential called the ionization potential (IP) is also called the ionization energy. It is equal to the kinetic energy of the accelerated electron and is expressed in electron volts per atom (or molecule).

Conversion factor $1 \text{ eV} = 1.6 \times 10^{-19} \text{ volt coulombs} = 1.6 \times 10^{-19} \text{ J}$

J. For one mole it is $1.6 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J mol}^{-1} = 96.5 \text{ kJ mol}^{-1}$.

The table 5 gives the ionization energies of some elements. The anomalies are highlighted.

Table 5 Ionisation energies of some elements
(The number in brackets are values in eV. The other values are in kJ mol^{-1})

Group Period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0	VIII B			IB	IIB
Period 1	H (13.6) 1318							He (24.59) 2379					
Period 2	Li (5.39) 526	Be (9.32) 905	B (8.30) 807	C (11.26) 1093	N (14.53) 1407	O (13.61) 1320	F (17.42) 1687	Ne (21.56) 2087					
Period 3	Na (5.14) 502	Mg (7.65) 744	Al (5.99) 584	Si (8.15) 793	P (10.49) 1018	S (10.36) 1006	Cl (12.97) 1257	Ar (15.76) 1527					
Period 4	K (4.34) 425	Ca (6.11) 596	Ga (6.00) 585	Ge (7.90) 768	As (9.81) 953	Se (9.75) 947	Br (11.81) 1146	Kr (14.00) 1357	Fe (7.87) 766	Co (7.86) 764	Ni (7.64) 743	Cu (7.73) 752	Zn (9.39) 913
Period 5	Rb (4.18) 409	Sr (5.70) 556	In (5.79) 565	Sn (7.34) 715	Sb (8.64) 840	Te (9.01) 876	I (10.45) 1015	Xe (12.13) 1177				Ag (7.58) 737	Cd (8.99) 874
Period 6	Cs (3.89) 382	Ba (5.21) 509	Tl (6.11) 596	Pb (7.42) 722	Bi (7.29) 710	Po (8.42) 818	At -	Rn (10.75) 1043				Au (9.23) 896	Hg (10.49) 1013
Period 7	Fr (3.98) 390	Ra (5.28) 516											

The following solved examples are designed to give you the opportunity to test your understanding.

Exercise 1

- How does the ionization energy vary generally within a group? In which groups do you observe anomalies? Explain your observations.
- How does ionization energy generally vary within a period? Which groups provide exceptions? Explain your observations.

Anomalies in Group IIIA, the first group after the transition elements: The effect of poor shielding of d electrons is felt most in this period. Thus, ionization energy of Ga \approx Al. Also, the effect of poor shielding of f electrons is felt between In and Tl. The ionization energy of Tl is greater than In. Similarly, the effect of poor shielding of f electron is felt between the second and third transition series e.g. Ag < Au.

- From left to right it generally increases.

Groups IIIA and VIA provide exceptions since they have lower ionization energies than their previous groups. This is because Group IIA and VA elements have filled ns sub shell and half-filled np subshell respectively accounting for extra stability and higher than expected ionization energy. Group IIIA and VIA elements, on the other hand, gain the extra stability on losing an electron leading to unexpectedly low ionization energy. Hence, the anomalies.

The figure below highlights all these general trends for the first three periods in a graphical fashion.

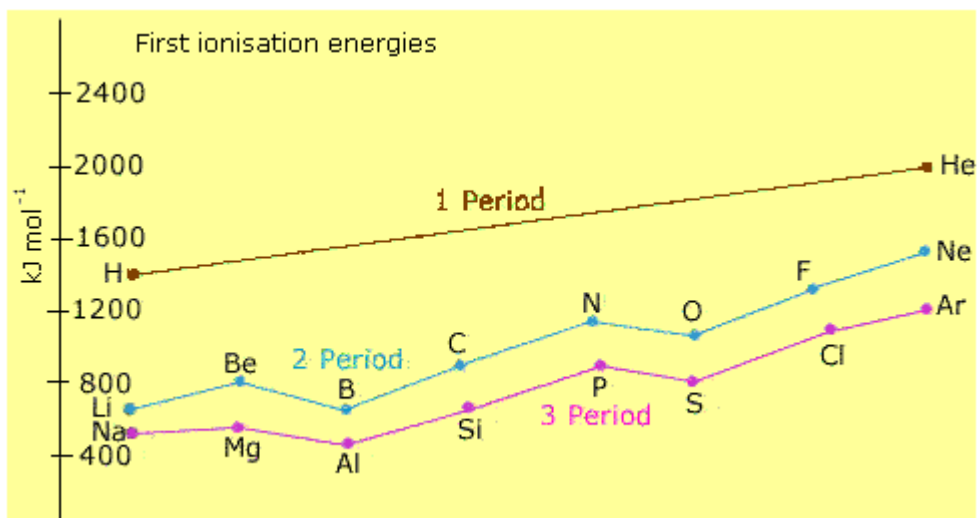


Fig. 1

Table 6 shows the first ten ionization energies (wherever applicable) in MJ mol^{-1} of elements $Z = 1$ to $Z = 14$. Observe the "staircases". The values to the right of each vertical line represent the energy required for removing an electron from a noble gas core and hence, you can observe the sudden 'jumps'.

Table 6: Higher ionization energies (MJ mol^{-1} where $1 \text{ MJ} = 10^6 \text{ J}$)

Z	Element	I	II	III	IV	V	VI	VII	VIII	IX	X
1	H	1.318									
2	He	2.379	5.257								
3	Li	0.526	7.305	11.822							
4	Be	0.906	1.763	14.855	21.013						
5	B	0.807	2.433	3.666	25.033	32.834					
6	C	1.093	2.359	4.627	6.229	37.838	47.285				
7	N	1.407	2.862	4.585	7.482	9.452	53.274	64.368			
8	O	1.320	3.395	5.307	7.476	10.996	13.333	71.343	84.086		
9	F	1.687	3.381	6.057	8.414	11.029	15.171	17.874	92.047	106.443	
10	Ne	2.087	3.959	6.128	9.376	12.184	15.245	20.006	23.076	115.389	131.442
11	Na	6.302	4.569	6.919	9.550	13.356	16.616	20.121	25.497	28.941	141.373
12	Mg	0.744	1.457	7.739	10.547	13.636	18.001	21.710	25.663	31.650	35.469
13	Al	0.584	1.823	2.751	11.584	14.837	18.384	23.302	27.466	31.905	38.464
14	Si	0.793	1.583	3.238	4.362	16.098	19.791	23.793	29.259	33.884	38.740

Observe also the arrows. The values below these arrows are lower than the values above them. This is in opposition to the general trend. Can you find an explanation for these?

Observe also a much sharper decrease in the values when you come down a column as you cross the horizontal lines of the "staircase". Can you guess why such large discrepancies are there?

Exercise 2

Explain the following observations from Table 6

a) The values of successive ionization energies of elements Li to F show the apparently erratic trend as follows:

First ionization energy: $\text{Li} < \text{Be} > \text{B} < \text{C} < \text{N} > \text{O} < \text{F}$

Second ionization energy: $\text{Li} >> \text{Be} < \text{B} > \text{C} < \text{N} < \text{O} > \text{F}$

Third ionization energy: $\text{Li} < \text{Be} \gg \text{B} < \text{C} > \text{N} < \text{O} < \text{F}$

The anomalous variation in the trend along the period seem to occur between different sets of elements for different extents of ionization. Can you explain these trends?

b) For any element $1^{\text{st}} \text{ IE} < 2^{\text{nd}} \text{ IE} < 3^{\text{rd}} \text{ IE}$, etc.

c) Second ionization energy of Li is greater than the third ionization energy of F.
(Remember that the first ionization energy of F is far greater than that of Li !)

Table. 7

Configuration Species undergoing	$1s^1$	$1s^2$	$[\text{He}] 2s^1$	$[\text{He}] 2s^2$	$[\text{He}] 2s^2 2p^1$	$[\text{He}] 2s^2 2p^2$	$[\text{He}] 2s^2 2p^3$	$[\text{He}] 2s^2 2p^4$	$[\text{He}] 2s^2 2p^5$	$[\text{He}] 2s^2 2p^6$
1st ionisation	H	He	Li	Be	B	C	N	O	F	
2nd ionisation		Li^+	Be^+	B^+	C^+	N^+	O^+	F^+		
3rd ionisation	Li^{2+}	Be^{2+}	B^{2+}	C^{2+}	N^{2+}	O^{2+}	F^{2+}			
Column number	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	

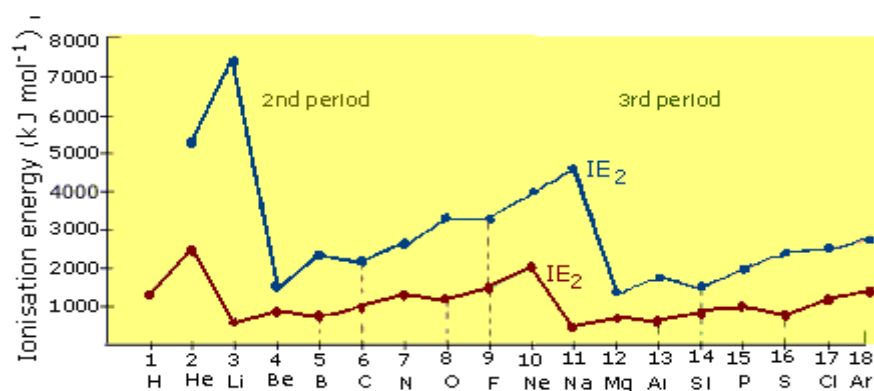


Fig. 2 First and Second ionization energies

The basic features in Table 7 are highlighted diagrammatically in the figure showing the variations in the first (IE_1) and second (IE_2) ionisation energies. Please note that the anomalously low values in IE_1 are for elements 5, 8, 13 and 16. The corresponding elements having anomalous values of IE_2 are shifted by one unit i.e. 6, 9, 14 and 17.

The process of ionisation involves absorption of energy. How then do we talk about **stable** cations?

Another way to look at it is, though it requires much more energy to produce a Mg^{2+} ion than a Mg^+ ion, why do we have MgCl_2 and not MgCl as the stable compound?

This can be explained as below.

Cations are always less stable than the neutral atoms. They however, may

subsequently gain extra stabilization due to release of energy by interaction with their surroundings as follows:

a) attraction by anions in the crystal lattice

b) solvation by solvent molecules in solution

Both these factors increase with increasing charge of the cation. Ultimately, questions such as

a) Will a stable cation be formed?

b) What will be the charge of the stable cation (1+, 2+, 3+, etc.)?

are decided by considering the energy absorbed due to ionisation and energy released due to stabilization by surroundings. The extra energy required to convert Mg^+ to Mg^{2+} is more than compensated for by extra attraction due to the double charge. We know, however, that the third ionisation energy of Mg is much greater than the second ionisation energy of Mg. The additional attraction of Mg^{3+} does not compensate for this.

Thus, we do not have MgCl_3 .

Note: Ionisation, i.e. conversions of an isolated gaseous atom to its gaseous ion, is only **one step** in a series of steps involved in the conversion of an atom under standard conditions to its ion in a crystal or in a solution. Commenting on anything with regard to the stability of any ion (i.e. cation, anion) without considering the energetics of all the processes involved is dangerous. We will study about such considerations when we study the Born-Haber cycle in the chapter on **energetics**.

We have, however, provided a simple answer, without going into the details of the Born-Haber cycle.

Electron Affinity

The electron affinity (EA) of an atom is the change in internal energy at 0 K that takes place when one mole of gaseous atoms and one mole of electrons combine to form one mole of gaseous negative ions. The enthalpy difference at 25°C (H_{298}°) is related to this change in internal energy i.e. E_0 as follows:

We normally deal with the heat that is liberated at 25°C and we use ΔH_{298}° values. Note that whereas ionisation energy deals with the **heat absorbed**, electron affinity deals with the **heat liberated**. If on adding an electron, heat is actually absorbed, then, the value of electron affinity is negative. See the cases of Be, N and Ne in Table 8, which gives certain electron affinity values. The anomalies to the general trend are highlighted.

Table 8 : Electron affinities of some elements (kJ mol^{-1})

Group No Period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0	VIIIB	IB	IIB		
Period 1	H 73							He -52					
Period 2	Li 60	Be <zero	B 27	C 122	N -7	O 141	F 328	Ne -50					
Period 3	Na 53	Mg -14	Al 43	Si 134	P 72	S 200	Cl 349						
Period 4	K 48	Ca 4	Ga 29	Ge 116	As 78	Se 195	Br 325		Fe 16	Co 64	Ni 111	Cu 118	Zn <zero
Period 5	Rb 47	Sr <zero	In 29	Sn 116	Sb 103	Te 190	C 295				Pd 52	Ag 126	Cd <zero
Period 6	Cs 46	Ba <zero	Tl 19	Pb 35	Bi 91	Po 183	At 270				Pt 214	Au 223	Hg <zero

The group and period variations in the electron affinity values of elements of the first two periods is also shown graphically, highlighting the anomalies, in figure 3.

Exercise

Identify and explain the anomalies in the electron affinity values in Table 8.

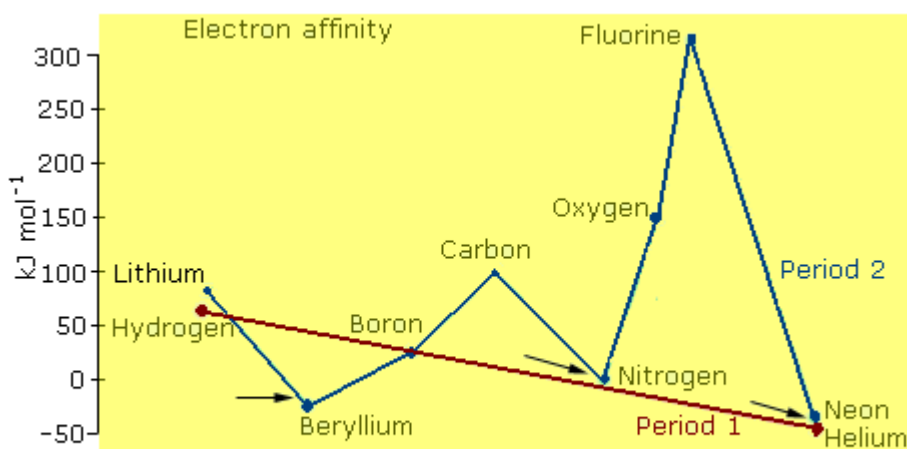


Fig. 3

Electron affinities of the elements of the first two periods

Energy is absorbed when a cation is formed due to ionisation. Why then is energy released in most cases when an anion is formed from its atoms?

This can be explained as follows:

Energy is normally released when an electron is added to an atom, which does not have a stable valence shell configuration. All noble gases have a negative electron affinity (energy is absorbed). Elements of groups IIA and VA having ns^2 or np^3 configurations also have either very **low electron affinity** or **negative electron affinity**. This is because they have stable valence shell configurations.

Herein lies the answer, if the extra electron can be added to the valence shell, it experiences a net attraction due to the effective nuclear charge which is shared by all the valence shell electrons. They experience the same amount of shielding due to the inner shell electrons.

Thus, energy is released unless:

1. the inter-electronic repulsion with the valence shell electrons is too large, or
2. the electron has to be added to the $(n + 1)$ shell, implying a greater shielding by the inner shell electrons.

The second electron affinity is however, always negative (as for all atoms the electron has to be brought near a negative ion, causing mutual repulsions).

The Size of the Atom and the State of Bonding

Given the modern concept of the atom, which implies that the electrons have small but finite probabilities, even at indefinitely large distances, it becomes problematic to define what we mean by the size of an atom.

However, size has always been considered an important periodic property. In fact, the periodicity in atomic volumes, calculated by Lothar Meyer, was a key factor correlating atomic weights with atomic properties.

Lothar Meyer calculated the atomic volume of elements using the following formula:

$$\text{atomic volume} = \frac{\text{density}}{\text{atomic weight}}$$

He showed that their values increased and decreased with a regular periodicity, if plotted against their atomic weights.

Since density is largely determined by other factors, such as the nature of bonding in the molecules of elements, the physical state of the element, the nature of crystal packing, etc., this cannot be the best method of assessing atomic volumes.

COVALENT, METALLIC, IONIC AND VAN DER WAALS RADII OF ATOMS

It is possible to experimentally determine the distance between two nuclei. A more useful concept of atomic or ionic size stems from the understanding that the inter-nuclear distance between two atoms is the sum of their radii. However, there is need for caution. Consider the data given in Table 9

(1 pm = 10^{-12} m = 10^{-2} Å).

Note that Bohr's radius for H is 52.9 pm, and is much larger than 37 pm as shown in the Table. Which is the correct value? Why do NaH and NaCl show discrepancies between the observed and calculated values of d ? Things begin to fall into place if we take the nature of bonding into consideration. NaH and NaCl are ionic and HCl is covalent. We consider the following values for obtaining proper inter-nuclear distances:

Ionic radius of Na^+ = 97 pm	Calculating for NaCl and NaOH
Ionic radius of H^- = 154 pm	
Ionic radius of Cl^- = 181 pm	
Covalent radius of Cl = 99 pm	Calculating for HCl
Covalent radius of H = 37 pm	

It is quite clear from the above example that we have to specify the two types of radii.

1. The metallic or covalent radii, when two atoms share electrons.
2. Ionic or van der Waals radii, when two ions (or even neutral species e.g. solid inert gases) come as close as possible to each other, but do not share electrons.

Table 10 shows the periodic correlation for the different types of radii r_{met} , r_{cov} , r_{ionic} (which may be r_+ or r_-) and $r_{\text{van der Waals}}$. The figure 4(a) gives you an idea of the relative magnitudes of r_{cov} and r_- of Cl. Figure 4(b) compares r_{met} and r_+ of Na with $r_{\text{van der Waals}}$ of Na (estimated indirectly).

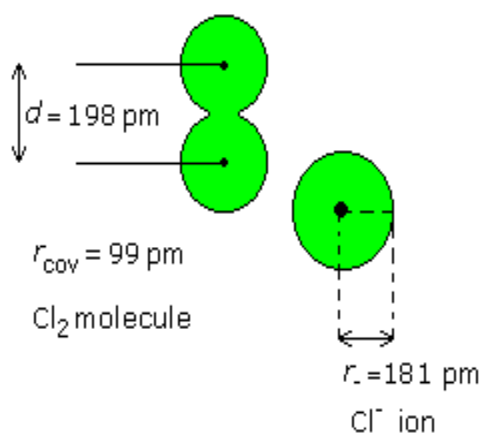


Fig. 4(a)
Comparison of r_{cov}
and r_- of chlorine

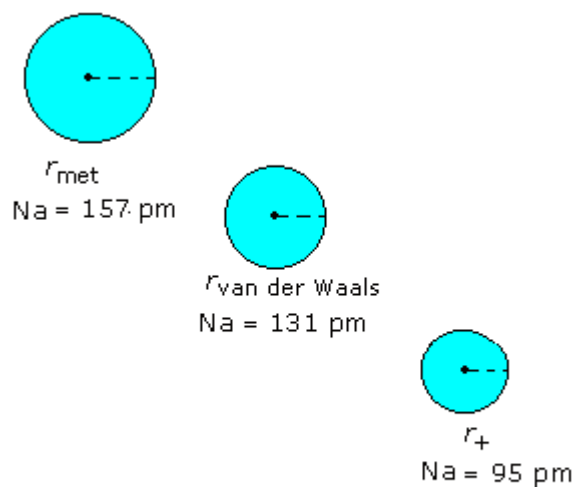


Fig. 4(b)
Comparison of r_{met} and r_+ of
Na with $r_{\text{van der Waals}}$ of Na

Figure 4a :

Figure 4b :

Figure 5 shows you the comparative sizes of some main group elements as per their covalent radii or metallic radii. Note that among the inert gases, only Kr and Xe have covalent radii since they can form covalent compounds. Being radioactive the physical and chemical properties of Rn are less studied.

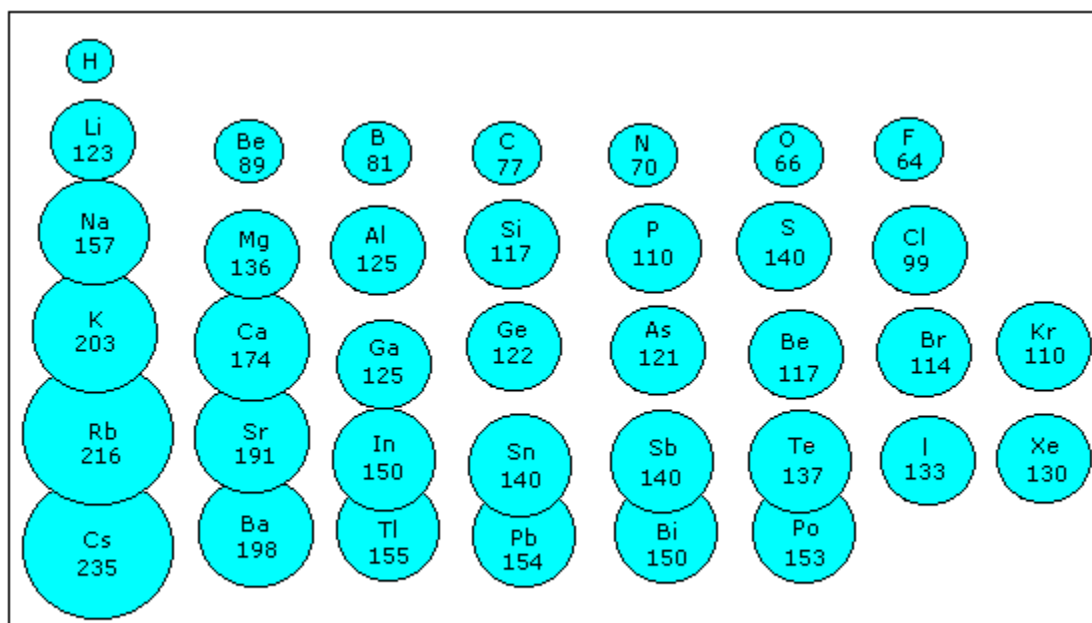


Fig. 5

Metallic or covalent radii of atoms of metals and non metals in pm.

Some important observations are given below

1. All types of radii increase down the group e.g.

a) $H < Li < Na$, $Be < Mg$, etc.: **covalent or metallic radii**

b) $He < Ne < Ar$: **van der Waals radii**

c) $Li^+ < Na^+$, $N^{3-} < P^{3-}$: **ionic radii**

Reason: The size increases with an increase in the number of shells.

2. The covalent or metallic radii decrease from left to right in a period.

For example, $Li > Be > B > C$, etc.

Reason: For the same shell, the size decreases with an increase in the atomic number.

3. The radius of the inert gas at the end of any period shows a sudden increase.

For example, $N > O > F << Ne$, $P > S > Cl << Ar$, etc.

Reason: This is because for the noble gases we have only van der Waals radius (they do not form bonds) while for the other elements we consider their covalent or metallic radii. In the case of Kr and Xe, where the covalent radii are known (Figure 5), they show the expected periodic trend.

4. Cationic radii are always less, whereas the anionic radii are always greater than the corresponding covalent or metallic radii.

For example, $r_+(Na^+) < r_{met}(Na)$, $r_-(H^-) > r_{cov}(H)$, etc.

Reason: In **cations**, the number of electrons are less than that in the atoms. There is less electron-electron repulsion in cations.

In **anions**, it is the other way round. So, there is greater electron-electron repulsion.

5. Ionic radii (cationic or anionic, whichever is applicable) show a continuous decrease from somewhere near the **middle of a period and includes van der Waals radius of the inert gas** at the end of the period, and ends somewhere near the **middle** of the next period.

For example: $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Ne} > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Si}^{4+}$.

Reason: All of these are isoelectronic and have the same number of electrons. However, the nuclear charge continuously increases, thus, causing a continuous decrease in size.

6. The ionic radii (van der Waals radii for noble gases) of ions having the same charge increases with the atomic number (increasing number of shells). For ions that are isoelectronic with different noble gases, anions have larger radii and cations have smaller radii than van der Waals radius of the corresponding noble gas. The size of the anion increases with the increasing charge, whereas that of the cation decreases with the increasing charge.

The situation will become clear if you look at figure 6. The line joining La^{3+} ($Z = 57$) to Lu^{3+} ($Z = 71$) deserves a special mention for the sharp decrease observed. This is because of the lanthanide contraction (poor shielding by f electrons).

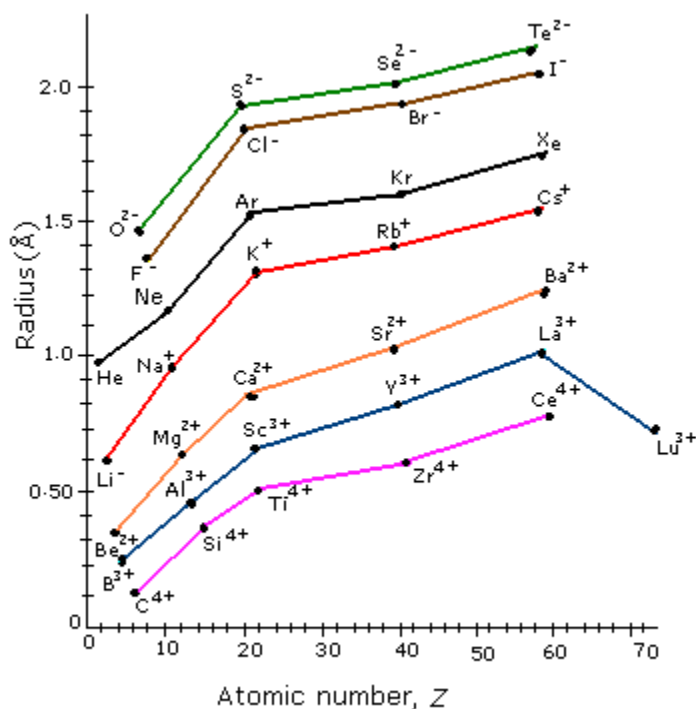


Fig. 6

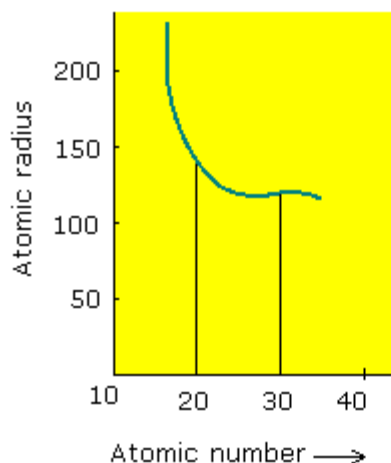


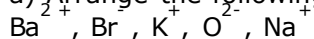
Fig. 7

Variation of covalent/metallic radius for the fourth period with atomic number $Z = 21$ to $Z = 30$, corresponding to d block elements.

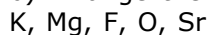
The variation of atomic sizes (metallic radii) of transition metals as shown in figure 12 also deserve special mention. The outer shell electronic configuration of these elements is identical and therefore, does not show too much variation with an increasing atomic number. However, as a result of the relatively poor shielding due to d electrons, we can observe the initial sharp decrease in size.

Exercise 1

a) Arrange the following in the order of increasing radii:

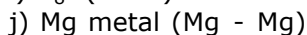
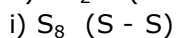
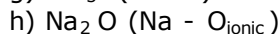
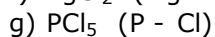
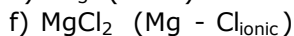
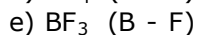
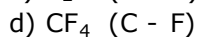
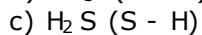
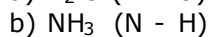
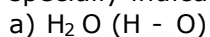


b) Arrange the following in the order of increasing covalent or metallic radii:



Exercise 2

Predict the approximate internuclear distances between the atoms specified in each of the following species. Use the values given in table 9. The ionic compounds are specially indicated.



Electronegativity - The Link between the Properties of the Free Atom and Properties of Substances

Electronegativity is perhaps the single most important chemical concept, which, along with the concept of resonance has had a far reaching impact on the development of chemical logic. It is an **average quantitative expression** of the **qualitative nature** of an atom participating in bond formation.

Electronegativity is defined as a measure of the ability of **a bonded atom in a molecule** to pull electrons towards itself.

Note: Electron affinity is different from electronegativity since, it deals with the energy released when an electron is added to a neutral atom in the gaseous state.

Though it is a powerful concept there are two problems.

1. There is no direct method of experimentally measuring electronegativity.
2. The scales designed to quantify electronegativity provide an average value and does not take care of the variations in the chemical environment of an atom.

We will address the second problem at a later stage. Before that we may take a look at the various semi empirical methods developed to provide a numerical scale of electronegativity.

ELECTRONEGATIVITY SCALES

1. **The Mulliken Scale** (1934): Atoms which have higher values of both electron affinity as well as ionisation energy will have higher electronegativity. This is quite obvious. But, what if between two atoms one has a higher electron affinity and the other a higher ionisation energy? Since the electron pulling ability of two bonded atoms will depend on both, their ionisation energy as well as the electron affinity, Mulliken proposed an absolute scale based on the average value of ionisation energy and electron affinity.

$$\text{Electronegativity} = \frac{IE + EA}{540}$$

where, IE and EA are in kcal mol^{-1} .

An analogy: Imagine two atoms engaged in a tug-of-war match with the shared pair of electrons instead of the rope. The winner will be the one who can pull harder (electron affinity) and also provide greater resistance to the pull of the other (ionisation energy).

2. **The Allred Rochow scale:** If r is the covalent radius of an atom and Z' is the effective nuclear charge experienced by the bonded electrons, then the Allred Rochow scale electronegativity value is given by

$$\text{Electronegativity} = 0.359 \frac{Z'}{r^2} + 0.744$$

Since the surface area of the electron cloud of an atom or ion of radius r is proportional to

r^2 ($4\pi r^2$ to be precise), $\frac{Z'}{r^2}$ corresponds to $\frac{\text{charge}}{\text{surface area}}$ or the surface density of the charge. This captures the essential physical and chemical features of an atom.

3. The Pauling scale: When two different atoms form a bond, the bond develops an ionic character. The percentage ionic character is dependent on the difference in electronegativity between the two atoms. Pauling used this fact to develop his scale of electronegativity by putting forward the following arguments:

1. When two atoms of element A form a single bond to give A_2 , it releases energy D_{A-A} equal to the bond energy of A_2 .
2. When two atoms each of elements A and B form a single bond A - B, it should release an energy $D_{A-B}(\text{cov})$ equal to the **theoretical covalent bond energy** of A - B, which should be equal to the mean of D_{A-A} and D_{B-B} . The actual bond energy of AB equal to $D_{A-B}(\text{actual})$ will be greater than $D_{A-B}(\text{cov})$ because of the ionic character of the A - B bond.

In fact, Pauling stressed that

$$\Delta = D_{A-B}(\text{actual}) - D_{A-B}(\text{cov})$$

will depend on the percentage ionic character of the bond.

Pauling calculated $D_{A-B}(\text{cov})$ values using the geometric mean

$$D_{A-B}(\text{cov}) = \sqrt{D_{A-A} \times D_{B-B}}$$

He proposed the difference in electronegativity between A and B (ΔEN_{A-B}) to be related as

or

This led to a **relative electronegativity scale**. The absolute values were obtained assuming electronegativity of F to be equal to 4 (3.98 to be exact) as reference. Table 11 give the values of electronegativities of some elements in the Pauling's scale.

Table 11: Electronegativities of some elements (Pauling's scale) based on their most common oxidation states

Group No. Period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0	VIB	VIIIB	IB	IIB	
1	H 2.1												
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0						
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0						
4	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8		Cr 1.7	Fe 1.0 Co 1.9 Ni 1.9	Cu 1.90	Zn 1.6	
5	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 3.1	Mo 2.2	Rh 2.3	Pd 2.2	Ag 1.93	Cd 1.7
6	Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0			W 2.4		Pt 2.3	Au 2.54	Hg 2.0

Figure 8 shows the periodic variation of electronegativities of the first three periods in a graphical fashion. This should be compared with the figure showing the periodic behaviour of ionisation energies and electron affinity. Note that along the

period, the electronegativity values increase monotonically and not in the zigzag fashion as in the other cases.

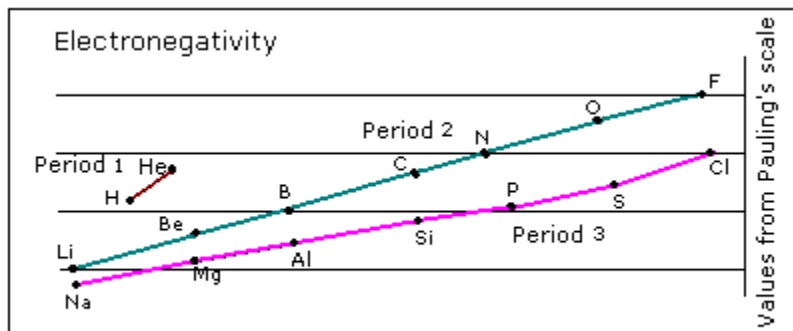


Fig. 8

The only anomalies you can observe in table 11. (**highlighted**) are when you move down some of the groups. These are naturally due to the effect of the poor shielding by *d* and *f* electrons.

The electronegativity values of noble gases have been the source of some confusion. For a long time noble gases were called inert gases, as they were not known to form compounds. (The first noble gas compound was synthesised by Bartlett in 1962, XePtF₆). Since electronegativity has no meaning in the absence of bonding, some sources had assigned **0 (zero)** as the electronegativity of noble gases. This has been proved **incorrect**. Xenon forms many compounds and has been assigned the value of 3.1, as shown in table 11.

SAME ELEMENT WITH DIFFERENT ELECTRONEGATIVITY VALUES

1. In the absence of any direct method of measuring electronegativity values, different sources quote slightly different values. We have tried to provide you with simplified rounded-off values.
2. These values are average values corresponding to the most common oxidation states of the elements concerned. The effective electronegativity values increase with increasing oxidation states. Chemically, this is reflected in terms of a greater non-metallic character of the element, and consequently a greater acidic character of its oxide.
Thus, while CO is a neutral oxide, CO₂ is an acidic oxide. Similarly Cr₂O₃ is a basic oxide soluble in acids, whereas CrO₃ is acidic and dissolves in NaOH to form a salt Na₂CrO₄.
3. The effective electronegativity also depends on another factor called hybridisation. The carbon atom in methane (CH₄) is *sp*³ hybridised, whereas that in acetylene (H - C ≡ C - H) is *sp* hybridised. The carbon atom in acetylene is more electronegative than that in methane. In fact, the *sp*³ hybridised nitrogen in ammonia (NH₃) is more electronegative than carbon in methane, but less than carbon in acetylene. Chemically, this reflects in the order of acidities of the three hydrides i.e.
CH₄ < NH₃ < C₂H₂

These factors have to be considered when we use electronegativity values for

understanding chemical properties.

PERIODIC BEHAVIOUR OF ELECTRONEGATIVITY VALUES

Salient Features

1. Electronegativity increases from left to right along a period and decreases from top to bottom down a group.
2. Elements with low electronegativity (electropositive elements) are metals, whereas elements with high electronegativity are non-metals. Metalloids are elements with intermediate electronegativities. We may thus state that the **metallic character decreases from left to right and increases from top to bottom in a periodic table**.
3. If we first move to the right and then down the periodic table, we have a diagonal movement. For electronegativity values, this means first an increase and then a decrease. For metallic character, this means first a decrease and then an increase. It is no wonder that electronegativity values tend to remain the same as we move diagonally. Compare for example, the value of Li and Mg, Be and Al, B and Si or P, C and S, N and Cl.

Chemical Consequences

1. One of the consequences of the similarity of electronegativities of diagonally placed elements is the occurrence of a diagonal relationship (as against group or period relationship) between these elements, resulting in similarities in their chemical properties. The pairs Li and Mg, Be and Al as also B and Si show a diagonal relationship.
2. A second consequence of the diagonal arrangement of elements having similar electronegativities is that the line dividing metals and non-metals moves diagonally from top left to bottom right across the *p*-block of the periodic table.
3. A third consequence of the nature of variation of electronegativity values is that the most electropositive metals are placed at the bottom left corner of the periodic table. Similarly, the most electronegative non-metals are placed at the top right corner. Thus, the highest metallic character is in Cs and the highest non-metallic character is in F.

Exercise 1

a) Which of the following has a higher electronegativity?

- i) $Z = 16$ or $Z = 20$
- ii) $Z = 14$ or $Z = 15$
- iii) $Z = 3$ or $Z = 11$
- iv) $Z = 4$ or $Z = 9$
- v) $Z = 8$ or $Z = 13$
- vi) $Z = 19$ or $Z = 29$

b) Which of the following has a higher electronegativity?

Note that it will be difficult to answer questions in this set as you have to know the actual values. Whereas, you need not **remember** all electronegativity values, the order of electronegativities in this set will be useful.

- i) Be or Al
- ii) B or Si
- ii) C or S
- iii) O or Cl
- iv) Na or Ca

METALS AND NON-METALS

Metallic and Non-metallic Characteristics and their Relation with Electronegativity

From our discussions in the previous sections you may tend to think that one can classify elements as metals or non-metals strictly on the basis of their electronegativities. This, however, is not correct. Just on the basis of the electronegativity value, we cannot say whether an element is a metal or a non-metal.

The following example will make this clear to you.

Gold has an electronegativity of 2.54, and has all the basic characteristics of metals. It has a metallic lustre, it is malleable and ductile, and it is a good conductor of heat and electricity just like any other metal.

Contrast this with the properties of the following elements having much lower electronegativities, boron (2.0) and hydrogen (2.1). Boron is a non-metallic metalloid. It is hard, brittle and non-conducting. Hydrogen is a non-metallic gas. Before we look into the correlation between electronegativity and metallic (or non-metallic) character, let us look into the various atomic properties, which are the characteristics of metals and non-metals.

a) Factors responsible for metallic and non-metallic properties.

- Metal atoms tend to lose a small number (1 or 2 or occasionally 3) of electrons to form cations. This is the reason why *s*, *d* and *f* block elements, which have one or two electrons in their valence shells are metals.
- Metals are characterised by low ionisation energies, high electron affinities and the large size of atoms. With hydrogen and helium (both *s* block elements), the above values are just the opposite and hence, they are not metals.
- Not just the first ionisation energy but the sum of successive ionisation energies required to form a cation with a stable electronic configuration has to be small for a metal. This goes to explain why electronegativity values cannot be always used to judge the metallic and non-metallic character. Electronegativity values usually take into account an average of the first ionisation energy and electron affinity.

Let us take the original example of Au and B.

Ionisation energy to form Au^+ ($[\text{Xe}] 4f^{14} 5d^{10} 6s^0$) = 896 kJ mol^{-1}

Ionisation energy of B^{3+} ($[\text{He}] 2s^0$) is

$$IE_1 + IE_2 + IE_3 = 807 + 2433 + 3666 = 6906 \text{ kJ mol}^{-1}$$

Thus, though Au has a higher ionisation energy value than B, Au requires less energy to form Au^+ and hence, is a metal. In fact, Au also forms Au^{2+} and the IE_2 and IE_3 values for Au are also much lower than the corresponding values for B.

b) The role of electronegativity

A general correlation exists.

- Along the period from left to right, the
 - electron energy increases
 - electron affinity increases
 - size decreases
 - metallic character decreases
 - electronegativity increases
- From top to bottom, as we move down the group, the
 - ionisation energy decreases
 - electron affinity decreases
 - size increases
 - metallic character increases
 - electronegativity decreases

It should, thus be clear that though electronegativity values cannot be used to make a distinction between metals and non-metals, they can be and are used for grading within each category. We can therefore say which of two metals is more metallic or which of two non-metals is more non-metallic.

c) **Electronegativity and reactivity of metals and non-metals**

What is the chemical meaning of a 'more metallic' metal or a 'more non-metallic' non-metal? The answer is **reactivity** and herein lies the utility of electronegativity as a chemical indicator.

The less electronegative (or more electropositive) a metal, the more reactive it is.
The more electronegative a non-metal, the more reactive it is.

Examples

1. If you look at the chemical activity series, you will find that the most active metals are the alkali metals at the top of the series and the most reactive non-metals are the halogens at the bottom of the series. Transition metals (e.g. Au with high electronegativity) are well below hydrogen.

2. Lithium is least reactive to water. The vigorousness with which water reacts with alkali metals increase down the group. Alkaline earth metals are less reactive than alkali metals.

3. F is more reactive than O, and among the halogens, the reactivity decreases from top to bottom, just as predicted by their **electronegativities and nature of oxides**.

As mentioned earlier, another indicator of the metallic and non-metallic character related to the electronegativities of elements is the strength and nature of their oxides.

Metals form basic oxides, whose strength increases as the electronegativity of the metal decreases.

Non-metals form acidic oxides, whose strength increases with an increase in the electronegativity.

Exercise 1

From each of the following pairs of elements, choose the ones which are more metallic (for metals) and more non-metallic (for non-metals)

- a) Li, Be
- b) Br, I
- c) B, C
- d) Mg, Al
- e) C, O
- f) O, S
- g) Si, P
- h) S, Ge
- i) Po, Pb
- j) Sb, Se

Exercise 2

Arrange the following oxides from the strongest basic oxides to the strongest acidic oxides:

K_2O , BeO , MgO , CO_2 , Al_2O_3 , SO_3 , P_4O_{10} , Cl_2O_7 .

When an atom enters into bonding, it tends to attain a stable electronic configuration. How it does so may be correlated with the electronegativity of the atom.

ELECTROPOSITIVE ELEMENTS

Most electropositive elements (Fig. 9(a)) tend to form cations by losing valence shell electrons and attaining their preceding noble gas electronic configuration. This however, is not always true. Transition elements tend to form cations having d orbital electrons in addition to the preceding noble gas octets. Inner transition elements also have f electrons. Thus, K ($Z = 19$ [Ar] $4s^1$) goes to K^+ (electronic configuration of Ar), Mg ($Z = 12$ [Ne] $3s^2$) goes to Mg^{2+} (electronic configuration of Ne) etc. However, Fe ($Z = 26$ [Ar] $3d^6 4s^2$) may go to Fe^{2+} ([Ar] $3d^6$) or Fe^{3+} ([Ar] $3d^5$). Cu ($Z = 29$, [Ar] $3d^{10} 4s^1$) may go to Cu^+ ([Ar] $3d^{10}$) or Cu^{2+} ([Ar] $3d^9$). Even Ga ($Z = 31$ [Ar] $3d^{10} 4s^2 4p^1$), which is a representative element, goes to Ga^{3+} ([Ar] $3d^{10}$).

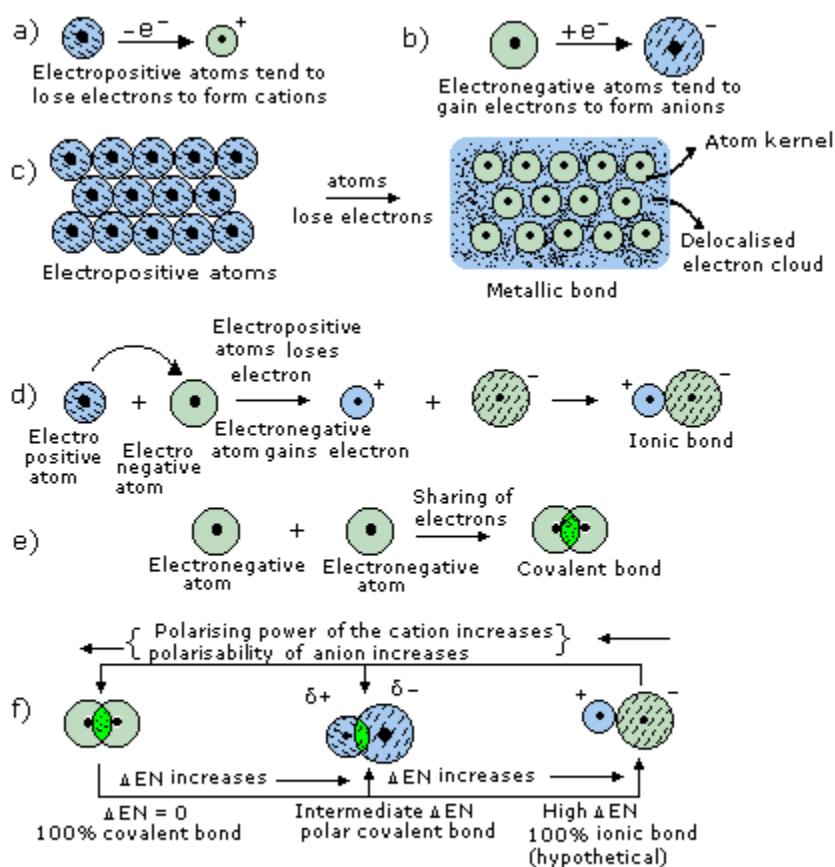


Fig. 9

Different types of bonding and electronegativity (EN)

Which are the groups in each period where the elements tend to form cations with the non-noble gas configuration?

Solution: Transition and inner transition elements.

ELECTRONEGATIVE ELEMENTS

On the other hand, all **electronegative elements** (Fig. 9(b)) tend to form anions by accepting electrons in order to attain their corresponding **subsequent** noble gas configuration. Thus, F ($Z = 9$, [He] $2s^2 2p^5$) goes to F^- (Ne configuration), P ($Z = 15$, [Ne] $3s^2 3p^3$) and S ($Z = 16$, [Ne] $3s^2 3p^4$) goes to P^{3-} and S^{2-} respectively with Ar configuration.

Note: Exceptions to the trends described above may be observed with most elements other than the most electropositive (Group I A and B, Group II A and B) and the most electronegative (O and F) elements. Thus, Cr in group VIB ($Z = 24$, $[\text{Ar}] 3d^5 4s^1$) may formally lose all six electrons to attain Ar configuration corresponding to an oxidation state of 6+, and in $\text{K}_2\text{Cr}_2\text{O}_7$ or Cl in group VIIA ($Z = 17$, $[\text{Ne}] 3s^2 3p^5$) may formally lose all seven electrons to attain Ne configuration corresponding to the oxidation state 7+.

NATURE OF BONDS

Bonding Involving Electropositive Elements - the Metallic Bond

Electropositive elements are all metals. They all tend to lose electrons of their outermost shell rather easily. At the same time, they are reluctant to accept electrons. When such atoms come together, they tend to form a collection of **kernels** (atoms minus valence electrons) with a sea of valence electrons filling up the intervening space (just as the sugar syrup in a can of tinned fruit), and providing the bonding or cementing force. This form of bonding is called metallic bonding. Metallic bonds are non-directional in nature (Fig.9(c))

Note: Metallic bonding may be observed both when all the atoms are identical (pure metals) or some are different (alloys). When all atoms are identical and their electronegativities become higher, a covalent character develops. When the atoms are different and the electronegativity of one of them increases, the metallic bond gives way to an ionic character.

Bonding between the Electropositive and Electronegative Elements - the Ionic Bond

The electropositive atoms lose electrons and form **stable cations**, **the electronegative atoms gain electrons** to form **stable anions**. The cations and anions attract each other electrostatically and constitute the electrovalent or ionic bond. The ionic bond is also non-directional in nature (Fig. 9(d)).

Bonding between Electronegative elements - the Covalent Bond

Electronegative elements do not lose electrons. They therefore tend to complete their octets by sharing electrons. Since covalent bonds involve the overlap of orbitals between two or sometimes three (three centre bonds) atoms, they are directed bonds (Fig. 9(e)). In the case of covalent bonds, the shared pair of electrons are considered localised between the bonding atoms. In ionic bonds, the electrons are localised on specific ions.

Q. What happens in the case of metallic bonds?

Ans. Delocalised bonding is present in the case of metallic bond.

The case of carbon monoxide deserves a special mention. The difference in electronegativity suggests a value greater than 18%, but the actual value is less than 3%. The reason for this will be explained in the chapter on bonding, but this also goes to show that electronegativity being an average quantity fails to take care of specific bonding environments.

Can there be a 100% ionic bond?

Take the case of CsF, the bond between the most electropositive and the most electronegative element. Calculate the percent ionic character using the Hannay Smith equation. Use the electronegativity values given in table 11.

In CsF, $\Delta\text{EN} = (4 - 0.7) = 3.3$

Percent ionic character = $16(3.3) + 3.5(3.3)^2 = 90.9$

It works out to be around 95%, using the other equation.

Note: The experimentally determined value is approximately 72%, as shown in figure 10.

Exercise 1

Classify the following bonds as ionic, covalent or metallic. Use the electronegativity values from table 11.

- a) K - I
- b) Cr - S
- c) Fe - Fe
- d) P - Br
- e) C - C
- f) Al - Ni

In case the electronegativity values are not provided you have to use the concept of metals (electropositive) and non-metals (electronegative).

Usually

metal + non-metal = ionic,

metal + metal = metallic and

non-metal + non-metal = covalent.

Exercise 2

Using electronegativity values wherever applicable from Table 1, arrange the bonds in the following sets in the order of increasing ionic character.

- a) N - H, N - C, N - O, N - F.
- b) Xe - F bond in XeF_2 , XeF_4 and XeF_6 .

Electronegativity, Charge Density and Polarization of Ion

CORRELATING ELECTRONEGATIVITY, POLARISING POWER AND POLARISABILITY

Electronegativity is a concept used mostly in connection with covalent bonds, the concepts dealt within this section are associated with ionic or electrovalent bonds, where instead of sharing a pair of electrons, the two atoms lose and gain electrons to form cations and anions respectively.

Cations have less electrons than protons, and their electron cloud remains under the tight control of the nucleus, and maintains their spherical geometry. On the other hand, anions have more electrons than protons. Their electron clouds are thus less under the control of their nucleus, and are more malleable or polarisable.

In an electrovalent compound, the cation is surrounded by anions and vice versa. When a cation is placed near an anion, the electron cloud of the anion is distorted. The centre of charge of the electron is displaced from the nucleus of the anion towards the nucleus of the cation. This is known as **polarisation**.

Since the cation **induces** polarisation, it is associated with a **polarising power**, which increases with an increased charge size ratio. On the other hand, the anion gets polarised and is associated with a polarisability which increases both, the increased charge as well as the increased size.

Note that the polarisation of ions is related to their charge density which we have seen is one of basis (Allred Rochow scale) for assigning electronegativity. Naturally,

the periodic variation of polarisation characteristics will correspond to that shown by the electronegativity values. Let us compare these trends.

Table Atomic and ionic radii

Period		Period 1		Period 2								Period 3							
Type of radius	Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar
r_{met} or r_{cov} (pm)		37	-	123	89	81	77	70	66	64	-	157	136	125	117	110	104	99	-
$r_{\text{vander Waals'}}$ (pm)		-	He ⁰ 93	-	-	-	-	-	-	-	Ne ⁰ 112	-	-	-	-	-	-	-	Ar ⁰ 154
r_{ionic}	r_+ (pm)	-	-	Li ⁺ 60	Be ²⁺ 31	-	-	-	-	-	F ⁻ 136	Na ⁺ 97	Mg ²⁺ 66	Al ³⁺ 51	Si ⁴⁺ 41	-	-	-	-
	r_- (pm)	H ⁻ 154	-	-	-	-	-	N ³⁻ 171	O ²⁻ 140	F ⁻ 136	-	-	-	-	-	P ³⁻ 212	S ²⁻ 184	Cl ⁻ 181	-

Trends within Periods and Groups

An examination of table above that shows the charges and sizes of ions will reveal the following:

1. The cationic charge increases from left to right in a period (only electropositive representative elements are considered). The size however, decreases along the period and increases down the group.

The polarising power of a cation thus increases along the period and decreases down the group.

Note that the **electronegativity values also vary identically**.

2. The anionic charge decreases from left to right in a period (only electronegative representative elements considered). The size, however, decreases along the period and increases down the group. **The polarisability of anions thus decreases along the period and increases down the group**, this is exactly the opposite trend viz-a-viz the polarising power of cations, as well as viz-a-viz the electronegativity values of the atom concerned.

3. **Diagonal trends:** In the periodic table, the polarising power of cations increases from left to right and decreases from top to bottom. Thus, as we go from left to right we come across cations having a similar polarising power. Similarly, the polarisability of anions decreases from left to right and increases from top to bottom. Thus, along the top-left to the bottom-right diagonal we observe a similarity in the polarisability of anions. This **correlates with electronegativity to explain the diagonal relationship**.

One important factor affecting the polarising power of cations is related to its electronic configuration. A noble gas configuration, which is usual for most cations, can shield the nuclear charge to the maximum extent. Cations of transition elements such as Cu⁺, Ag⁺ and even those of representative elements such as Pb²⁺, etc. have a non noble gas configuration and thus, a higher charge density. These cations have higher polarising powers.

Exercise 1

a) In each of the following pairs, which one has a higher polarising power?
Be²⁺ or Mg²⁺, Na⁺ or Mg²⁺, K⁺ or Cu⁺

b) Identify the pairs that have a similar polarising power from the following set:
 Li^+ , Na^+ , Be^{2+} , Mg^{2+} , B^{3+} , Al^{3+} , C^{4+} , Si^{4+} .
 Do you observe any correlation? Explain.

c) In each of the following pairs, which one has a higher polarisability?
 O^{2-} or F^- , N^{3-} or P^{3-} , Cl^- or Br^-

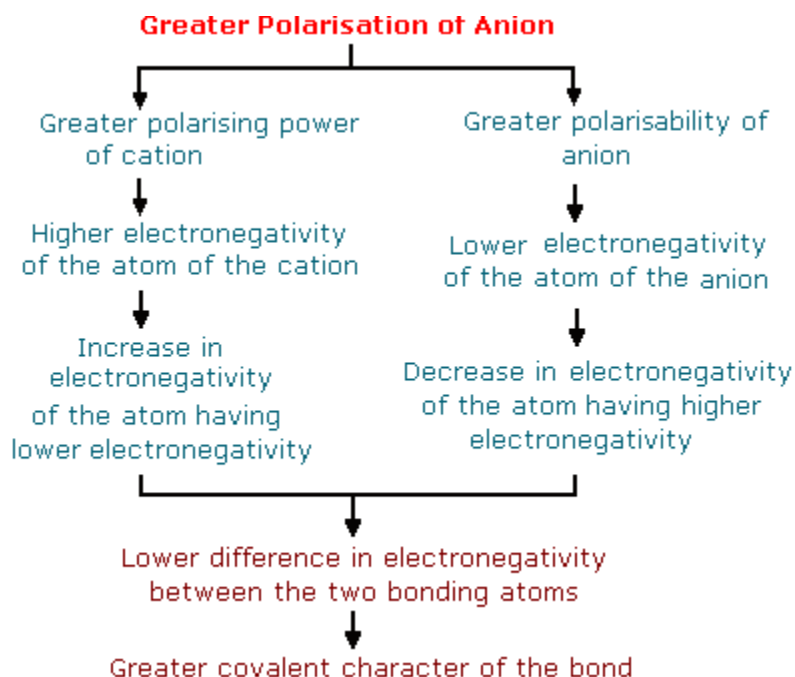
POLARISATION OF IONS

The Covalent Character of Ionic Bonds

We have seen how electronegativities and their differences help us in understanding qualitatively how the covalent bonds develop an ionic character.

If we want to qualitatively understand the development of the covalent character of ionic bonds, we can use the model given below. The polarization of the anionic charge cloud towards the cation implies a partial sharing of electrons between the ions.

The following model correlates perfectly with the difference in the electronegativity picture as shown.



Fajan's rules

The polarisation model of the evaluation of the covalent bonds forms the basis for a simple set of rules called Fajan's rules.

Covalency is favoured by the following:

- Small cation (high polarising power)
- Large anion (high polarisability)
- Large charge on either (or both) ions (increased polarisation) and
- Cations with non inert gas configuration (less shielding or higher effective nuclear charge and hence, higher polarising power)

Exercise 2

Arrange the following ionic bonds in the increasing order of the covalent character within each set.

- a) LiCl, NaCl, RbF
- b) The M - Cl bonds in CaCl_2 , SrCl_2 and ZnCl_2
- c) Pb - Cl bond in PbCl_2 and PbCl_4

Using the Periodic Table

In this section, we will take some examples where you can see how you can apply what you have learnt in this chapter to generalise the periodic behaviour of properties of elements and their compounds - specially where more than one factor is involved. This is not an exhaustive treatise and the examples are chosen only to give you an idea of how to approach a chemical question. A more comprehensive treatment will be taken up in the next chapter on bonding.

PROPERTIES OF ELEMENTS

1. Density of Metals

Density primarily depends on the ratio of size (metallic radius) and mass (mass number) of atoms. The effects can be best understood in the group behaviour of densities of alkali metals, where the nature of metallic bonding and the crystal structure factors do not complicate the issue.

The densities of alkali metals (in g cm^{-3}) are Li (0.53), Na (0.97), K (0.86), Rb (1.53) and Cs (1.90). The mass number of Na (23) is more than three times that of Li (7), hence, the sudden increase in density. The mass number of K (39) shows a comparatively smaller increase, and the increase in atomic size dominates this results in a decrease in density. The mass numbers of Rb (86) and Cs (133) are once again much larger, resulting in the increase in density. The contraction of metallic radii because of poor shielding by the inner shell *d* and *f* electrons also is a factor in support.

As more and more electrons participate in metallic bonding, the bonding becomes stronger and the metallic radii tend to decrease. Metals become denser and harder. Alkaline earth metals involve two electrons per atom (as against only one by alkali metals) in metallic bonding. Transition elements involve inner shell *d* electrons in metallic bonding - they are also much denser and harder.

2. Reducing Power of Metals and Oxidising Power of Non-metals

Metals tend to form cations by losing electrons and non-metals tend to form anions by gaining electrons. In the process, metals reduce (give electrons to) other substances and non-metals oxidise (take away electrons from) other substances. The reducing and oxidising powers of metals and non-metals correlate directly with their reactivities, and depend on the electropositivity of metals and electronegativity of non-metals.

It should be noted here that the process of oxidation and reduction does not depend on a single factor such as ionisation energy or electron affinity, but on several other factors such as bond energy, hydration energy, etc. A detailed analysis will be done in the chapter of energetics under the Born Haber cycle.

3. Thermal and Electrical Conductivity

For electrical conduction, we must have relatively free charge carriers, which must be charged particles. Thermal conductivity will also increase if mobile particles (not

necessarily charged) are present as carriers of kinetic energy. In metals, we have free electrons, which can serve both the purposes. Hence, metals are good conductors of heat and electricity.

It also makes sense that metals, which have lower ionisation energy and are more loosely packed (less dense) are better conductors.

With the development of the **covalent character** in bonding (electronegativities of atoms increasing), the atoms will tend to share electron and localise them. Thus, metals with higher electronegativities will have lower conductivities. Conductivity of Mg is less than that of Na.

In alloys, we have atoms of **different** electronegativities resulting in the development of the **ionic character** of metallic bonds. This also tends to localise the electrons and reduce the conductivity. Alloys have lower conductivities than pure metals. Thus, steel has a lower conductivity than iron.

PROPERTIES OF IONS

1. Solvation Energy

One of the important properties of ions is their solvation energy (the energy released when an isolated gaseous ion is added to a large amount of a solvent). This is highly dependent on the charge density (and hence, on the electronegativity of the concerned element). Small ions with a large charge have very high charge density and have very high solvation energies. Since the elements of group IIA have a higher charge than that of elements of group IA, they have higher solvation energies. Also, elements of the second period are much smaller in size than those belonging to those of the third period. They show disproportionately larger solvation energies compared to other ions corresponding to their groups. Thus, Li^+ and F^- have much larger solvation energies as compared to Na^+ and Cl^- respectively. This affects many properties such as the solubility of ionic solids, as we will see later.

2. Stability

Ions with lower charge densities are stable. Thus, the stability of halides in a gaseous solution varies as $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. The acid strength of their hydroxides depends on their stabilities. Thus, the order of acid strength of hydrides is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$, similarly, for chalcogen hydrides the acid strength varies as $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$.

3. Magnetic Properties and Colour

Ions with unpaired electrons are paramagnetic (attracted in the magnetic field) and are coloured. Ions of representative elements have a noble gas configuration and are without any unpaired electrons. Ions of transition elements with an incomplete (partially filled) *d* subshell have unpaired electrons and have both colour and magnetic moment. The value of magnetic moment depends on the number of unpaired electrons.

$$[\mu = \sqrt{n(n+2)} \text{ Bohr magneton}]$$

Thus, Fe^{3+} has a higher magnetic moment than Fe^{2+} . Cu^+ is colourless while Cu^{2+} has colour.

Write down the electronic configuration of these ions and confirm the observation.

4. Ability to Form Complexes

A high charge density on the cation leads to the increased ability to form complexes. Thus, transition elements form better complexes than the representative elements.

PROPERTIES OF IONIC COMPLEXES

The lattice energy, solvation or hydration energies and melting points of ionic solids are strongly dependent on the size and charge densities of the cations and anions.

1. Lattice Energy

The smaller the size of cations and anions and the higher their charge, the higher is their lattice energy (the energy evolved when one mole of the ionic solid is formed from their isolated gaseous ions). Thus, lattice energies are in the order $\text{LiF} > \text{LiCl} > \text{LiBr}$ or $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl}$ or $\text{MgCl}_2 > \text{NaCl}$, etc. (Increase in anion or cation size decreases the lattice energy since increase in inter ionic distance reduces electrostatic attraction between ions. Increase in the charge on either ion increases electrostatic attraction between ions.)

2. Melting Point

When melting implies ions dissociates, the melting point follows lattice energy. However, if there is a greater covalent character (see Fajan's rules), then the solid does not melt to give only ions, but a large part melts into unionised molecules. In extreme case is H_2O , it does not melt into H^+ and OH^- but into H_2O molecules. In such cases, the development of the covalent character leads to the lowering of the melting point. Compare the following melting points ($^\circ\text{C}$), with the order of their lattice energies.

LiF (870) $>$ LiCl (610) $>$ LiBr (550)

But, LiCl (610) $<$ NaCl (800) $>$ KCl (857) $>$ RbCl (775).

(LiCl has a high covalent character due to the small size of Li^+)

And MgCl_2 (712) $<$ NaCl (801)

(MgCl_2 has high covalent character due to a higher charge on Mg^{2+} compared to Na^+)

The factor of high charge on the cation explains why SnCl_4 is a liquid, whereas SnCl_2 is a solid at room temperature (SnCl_4 has a greater covalent character).

3. Hydration Energy and Stability

The hydration energy for an ionic compound is the sum of the hydration energies of their cations and anions as explained earlier. The solubility in water depends on the net effect of their lattice energies and hydration energies. A high lattice energy leads to a decrease in solubility, whereas high hydration energy results in its increase.

An interesting situation develops when one of the ions (usually the anion) is polyatomic, such as CO_3^{2-} , SO_4^{2-} . The lattice energy is a sum of r_+ and r_- , and if r_- is very large it does not decrease significantly down a group (as in the case of BeCO_3 , MgCO_3 , CaCO_3 , SrCO_3 , BaCO_3). The hydration energy, however, is the sum of hydration energies of cations and anions, and the hydration energy of cations decreases sharply down the group because of the increasing size. The net result is that solubilities of carbonates and sulphates of group IIA metals decrease down the group.

Another interesting situation develops when the ionic compound has significant covalent character and prefers to dissolve in units of molecules and not in units of ions. Such compounds have reduced solubilities in polar solvents such as water but higher solubilities in non-polar organic solvents such as acetone. LiI is almost insoluble in water but highly soluble in acetone (small cation, large anion, high covalent character). But, KI behaves just the other way.

4. Stabilities of Salts of Oxyacids

Salts of oxyacids such as carbonates, sulphates, nitrates, etc. are formed by the combination of corresponding acidic and basic oxides. On heating, they usually decompose back into the respective oxides.

Thus, CaCO_3 breaks into CaO and CO_2 , $\text{Fe}(\text{OH})_3$ breaks into Fe_2O_3 and H_2O , $\text{Mg}(\text{NO}_3)_2$

breaks into MgO and N_2O_5 , the latter further breaking into NO_2 and O_2 . The stronger the basic oxide (oxide of more electropositive metal) and the acidic oxide (oxide of more electronegative non-metal), the more stable the salt, i.e. the more difficult it is to bring the acidic and basic oxides apart.

The electronegativity of group IIA metals is $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$. The strength of their oxides as bases vary, as $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$.

The stabilities of their carbonates are $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$.

Similarly, SO_3 is a stronger acidic oxide than SO_2 , since S(VI) is more electronegative than S(IV) as in SO_2 . Thus, CaSO_3 is less stable than CaSO_4 .

PROPERTIES OF COVALENT COMPOUNDS

Many of the properties of covalent compounds involve bonding issues which involve factors such as size, availability of vacant orbitals, number of non-bonding (lone pair) electrons, etc. We can properly discuss them only after we have studied bonding. However, here we will discuss the bond lengths and stabilities of hydrides.

1. Bond length of hydrides

The covalent bond length depends on the sum of the covalent radii. Thus, the bond length of hydrides in a group increases with an increase in size of the non-metal. Within a period, not only does the size decrease with an increase in electronegativity, the ionic character of the hydrides also increases as we go from left to right. The increased ionic character leads to decreased bond lengths. Thus, the order of bond lengths in the following sets follows the given order.

$\text{C} - \text{H} < \text{Si} - \text{H} < \text{Ge} - \text{H}$ (covalent radius of non-metals increases)

or $\text{C} - \text{H} < \text{N} - \text{H} < \text{O} - \text{H} < \text{F} - \text{H}$ (increasing ionic character)

2. Bond Energies of Hydrides

The bond energies of larger bonds are lower (unless other factors such as multiple bonding, lone pair repulsion, etc. intervene). In the case of hydrides, where no complications exist, the bond energies are thus, exactly in reverse order of magnitude with respect to their bond lengths as discussed above.

Exercise 1

Explain the relative orders of magnitude for lattice energy, melting point and solubility values in the following table, mentioning the factors to be considered.

Compound	Lattice energy I (kJ mol^{-1})	Melting point ($^{\circ}\text{C}$)	Solubility (moles/litre)
LiF	1039	870	5×10^{-3}
NaF	920	992	1×10^{-1}
KF	816	857	1.1
RbF	780	775	1.25

Exercise 2

Which of the following ions will have colour?

Fe^{3+} , Co^{2+} , Cu^+ , Al^{3+} , Ni^{2+} , Zn^{2+} , Ti^{4+} , V^{3+} , Sc^{3+} , Ag^+

Also arrange them in order of increasing paramagnetism.

COMPLEXES

Werner's Approach

Double salts and complex salts:

When ferrous sulphate and ammonium sulphate are allowed to crystallise together from the same solution, crystals of ferrous ammonium sulphate

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt) are obtained. However a solution of Mohr's salt exhibits all the reactions of constituent ions i.e. NH_4^+ , Fe^{2+} and SO_4^{2-} . Such a compound, which loses its identity upon dissolution, is known as a **double salt**.

Similarly, on crystallising $\text{K}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ from the same solution we get potash alum $(\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O})$. Again, when dissolved in water, it shows reactions of all constituent ions i.e. K^+ , Al^{3+} and SO_4^{2-} .

These and many other compounds that exist only in crystalline form, but lose their identity in solution are called double salts.

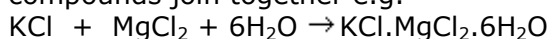
On the other hand when KCN solution is added to $\text{Fe}(\text{CN})_2$ it also forms an additional compound with stoichiometric composition $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$. However, this compound, unlike double salts, retains its identity in solution and does not show reactions of either Fe^{2+} or CN^- but shows reactions of a new ion FeCN_6^{4-} ferrocyanide. Such addition compounds, which have distinct entity in crystalline state as well as in a solution, are called **complex compounds** or **coordination compounds**. The formation of a new complex ion gives a new set of physical and chemical characteristic to the substance.

There are a large number of examples of formation of such complex compounds. In fact, the chemistry of metal ions, particularly *d* block metal ions, in solution is essentially the study of their complexes. Thus Cu^{2+} exists as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and Fe^{2+} exists as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution. When NH_3 is added to a solution of Cu^{2+} ions, it displaces some water molecules to form deep blue colored complex ion $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$, known as cuprammonium ion.

It is obvious from the above example, that metal ions in aqueous solution and H_2O can bond with each other. A pair of electrons on the oxygen atom of H_2O , forms a coordinate covalent bond with Cu^{2+} or Fe^{2+} , through their vacant orbitals. A similar process occurs when H_2O combines with NH_3 or Fe^{2+} , combines with CN^- . Therefore, it is essentially a Lewis acid - Lewis base reaction that is taking place resulting in formation of a coordinate covalent bond. For this reason, these complex compounds are more commonly referred to as coordination compounds and the metal ion together with the ligands is called **coordination sphere**.

A coordination compound therefore may be defined as a compound that results from the combination of apparently saturated molecules of different species, retaining their identity in the solid as well as dissolved state.

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together e.g.



carnallite



tetramminecopper(II) sulphate monohydrate

Addition compounds are of two types,

- (a) those which lose their identity in solution (double salt)
- (b) those which retain their identity in solution (complexes).

Werner's work - Discovery of complexes

In the year 1798, Tassaert, while working on cobalt chloride, found that its solution in ammonia on exposure to air, formed orange-yellow crystals of the composition $\text{CoCl}_3 \cdot 6\text{NH}_3$. Later on, Werner in 1893 studied the complexes and was able to explain the nature of bonding in these complexes. According to Werner, the formation of a complex is reflected in one or more of the following properties:

- (i) A sudden change in the solubility of the substance.
- (ii) A decrease in the electrical conductivity of the solution.
- (iii) A change in the colour of the substance.
- (iv) A change in the colligative properties of the solution.
- (v) A change in the magnetic moment of the substance.

According to the Werner theory of formation of complexes, metals have two different kinds of valencies:

1. Primary valency:

- iii) It is essentially ionic and non-directional and leads to formation of simple compounds.
- iv) The complex exists usually as a positive ion. The primary valency is the number of charges on the complex ion.
- v) In compounds, this charge is equal to the number of charges from negative ions.
- vi) Primary valencies apply to both simple salts and complexes.

2. Secondary valency:

- v) Every metal or metal ion has secondary valencies, which unite simple molecules to form complexes.
- vi) The number of secondary valencies is fixed for a metal ion, which is called its **coordination number**.
- vii) These secondary valencies are directed in space and so a complex ion has a shape just like any other covalent molecule.
- viii) In the modern concept, the primary valency depends on a number of ionisable electrons whereas secondary valencies equal the number of pairs of electrons that a metal or metal ion can accommodate from electron donor groups called **ligands**.

Due to the spatial arrangement of secondary valencies, complexes can exhibit isomerism like organic compounds. In fact, Werner prepared and isolated many such isomeric complexes.

Effective Atomic Number (EAN): In 1923 Sidgwick introduced the concept of effective atomic number. The coordination number of the central metal in a complex is the number of ligands bonded to it. Each ligand donates a pair of electrons to the metal ion for sharing. Sidgwick gave his effective atomic numbers rule and suggested that electron pairs from ligands were added until the central metal was surrounded by the same number of electrons as the next noble gas. For example EAN of $[\text{Fe}(\text{CN})_6]^{4-}$ can be determined as:

$_{26}\text{Fe}$ has 26 electrons, but it has 24 electrons when it forms Fe^{2+} . When it combines with 6CN^- , each CN^- gives a pair of electrons i.e. a total of $2 \times 6 = 12$ electrons. The total number of electrons in the orbit of the central metal ion in the formation of complex $[\text{Fe}(\text{CN})_6]^{4-}$ becomes $24 + 12 = 36$, which is the atomic number of the inert gas Kr and also the effective atomic number of iron in the complex.

The rule is violated in $\text{K}_3\text{Fe}(\text{CN})_6$, which has an EAN of 35 and many other complexes.

According to the modern concept, the central metal ion has vacancies in its orbitals. Depending on these vacancies, a metal or metal ion can accept a definite number of pairs of electrons, which is its coordination number.

Groups, molecules or ions, which can offer a pair of electrons for sharing with central metal ions, are called ligands. These ligands may be negatively charged, neutral or even positively charged so long as they provide a pair of electrons for sharing. The combination between a metal ion and a ligand is essentially a Lewis acid-base reaction.

General Characteristic Properties of Complexes

Some general characteristic properties of *d* block complexes, which have helped a lot in the understanding of bonding in these complexes, are discussed here in brief.

1. Colour or visible spectra of complexes of *d* block elements

Normally, the colour of a substance is because of the absorption of a certain wavelength in the visible spectrum. Many complexes of *d* block elements are coloured. The colour of these is the result of electronic transition between the two closely spaced *d* orbital energy levels, which is the outcome of crystal field splitting. As an example, let us consider the spectra of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. Ti^{3+} has $[\text{Ar}]3d^1$ configuration. In the presence of ligand H_2O molecules, crystal field splitting takes place and the lone 'd' electron occupies one of the lower energy *d* orbitals of the octahedral complex. The electron can jump from lower energy *d* orbital to a higher energy *d* orbital by absorbing visible light. The wavelength

(λ) of light absorbed is related to crystal field splitting (Δ)

$$\lambda = \frac{hc}{\Delta}$$

The complex absorbs at 500 nm and appears red purple in colour.

Replacing the H_2O ligands by a still weaker field ligand like F^- gives smaller crystal field splitting and colour of $[\text{TiF}_6]^{3-}$ shifts to violet blue (absorption at 590 nm).

With increase in the number of *d*-electrons, the absorption spectrum gets complicated, as there are several absorptions.

2. Magnetic properties of *d*-block elements

Magnetic properties in a substance generally arise due to the presence of unpaired

electrons in pairs. The metal or metal ion involved in the complex may have a certain number of unpaired electrons in isolated state but when it forms a complex, the ligands cause crystal field splitting of otherwise degenerate d -orbitals. Depending on the order of ligand in the spectrochemical series, the splitting may be small or large and cause, in some cases, to redistribute the electrons in these d -orbitals, thus affecting the number of unpaired electrons in the complex.

The number of unpaired electrons in the complex can be found from the observed magnetic moment of the complex from the following formula:

$$\mu_s \text{ (magnetic moment)} = \sqrt{n(n+2)}, \text{ where } n = \text{number of unpaired electrons.}$$

After determining the number of unpaired electrons, either the valence bond theory or crystal field theory can be applied to work out the oxidation state of metal, shape of the complex and whether it is inner orbital or outer orbital complex (in case of octahedral complexes).

For example, while discussing octahedral complexes of Co^{3+} in valence bond/crystal field theory, we had seen that its complex with strong field ligand like CN^- has all the electrons in d -orbitals in pairs and forms a low spin, inner orbital complex. Hence, magnetic moment of $[\text{Co}(\text{CN})_6]^{3-}$ is zero and it is diamagnetic. But in case of weak field ligand like F^- , the complex formed in high spin, outer orbital complex having 4 unpaired electrons. Its magnetic moment should be

$$\mu_s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 \text{ BM, the value which agrees with experimental data.}$$

The complex is, therefore, paramagnetic.

Similarly, in four coordinate complex of Ni^{2+} ion, when it is combining with CN^- ion, a strong field ligand, all the p electrons in the d orbitals of Ni^{2+} ion pair up to vacate one d orbital and hence the hybridisation in $[\text{Ni}(\text{CN})_4]^{2-}$ is dsp^2 , giving it a square planar shape and diamagnetic properties.

In case Ni^{2+} is combining with a comparatively weak field ligand like NH_3 to form $[\text{Ni}(\text{NH}_3)_4]^{2+}$, the distribution of d orbital electrons remains unaltered and the complex is formed by sp^3 hybridisation and is tetrahedral. The complex, therefore, has two unpaired electrons and is paramagnetic.

On the other hand, when Ni atom combines with CO, a very strong field ligand, all the $3d^8, 4s^2$ electrons pair up to occupy all the $3d$ orbitals, giving it a configuration of $3d^{10}$. The complex, therefore, has sp^3 hybridisation, tetrahedral shape and is diamagnetic.

In addition to the magnetic moment of unpaired electrons, orbital angular momentum and spin orbit coupling also affect the magnetic moment of the complexes, but the effect is not significant for 1st row of d block elements.

The Formation of Complexes and the Valence Bond Approach

The nature of bonding in complexes has been explained on the basis of following theories.

1. Valence Bond Theory
2. Crystal Field Theory and
3. Molecular Orbital Theory

Of these, we shall confine ourselves to the first two only.

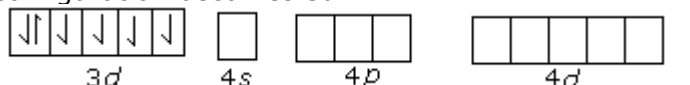
The properties of complexes that have led us to a better understanding of the bonding in complexes are as follows.

1. Magnetic properties of complexes
2. Colour of complexes and
3. Isomerism in complexes

Valence Bond Theory of Formation of Complexes:

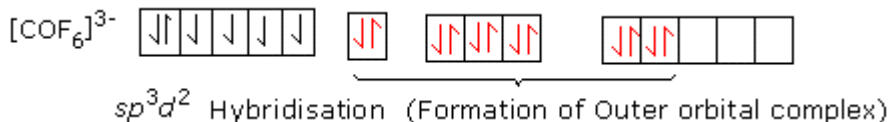
According to this theory developed by Pauling, the ligand must have a pair of electrons, which is coordinated to an empty orbital of suitable energy of the metal. The theory focuses on the atomic orbitals or hybrid orbitals of metal involved in bonding and helps in predicting the shape and stability of complexes. To simplify the tenets of the theory, formation of complex can be broken up into a series of hypothetical steps. Let us take the example of Cobalt.

Its outer electronic configuration is $3d^7 4s^2$. When it forms Co^{3+} ion, the electronic configuration becomes $3d^6$.



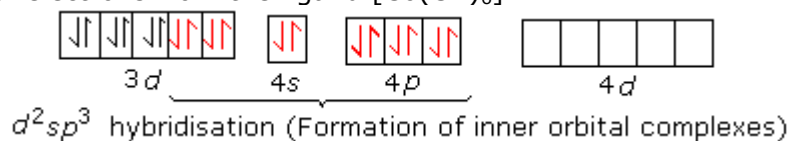
Electronic Configuration of Co^{3+}

If these ions form an octahedral complex with six ligands, then six empty orbitals are required on the metal ions to accommodate coordinated pairs of ligands. The empty $4s$, three $4p$ and two $4d$ orbitals hybridise to give a set of six equivalent sp^3d^2 hybrid orbitals and electron pairs donated by the ligands are accommodated in these hybrid orbitals. The diagram below shows the ions with electron pairs from the ligands.



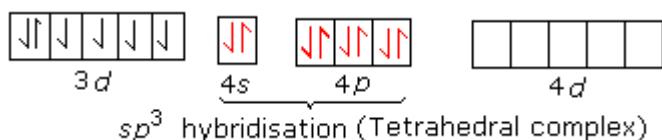
When Co^{3+} forms a complex with F^- , $[\text{CoF}_6]^{3-}$ it involves the outer $4d$ orbitals of Co^{3+} in bonding. Such complexes are called **outer orbital complexes**. The energy of these hybrid orbitals is high because of the involvement of $4d$ orbitals and therefore the complexes will be reactive or less stable. In this case the $3d$ orbitals have the maximum number of unpaired electrons (to be precise 4) for a d^6 arrangement and hence the complexes are called **high spin** or **spin free** complexes.

An alternative process for the formation of octahedral complex may be that first the electrons in the $3d$ level of metal ion pair up to occupy only three $3d$ orbitals leaving two $3d$ orbitals vacant. In such case d^2sp^3 hybridisation may occur involving two $3d$, one $4s$ and three $4p$ orbitals of the metal ion which can then accommodate six pairs of electrons from the ligand $[\text{Co}(\text{CN})_6]^{3-}$.

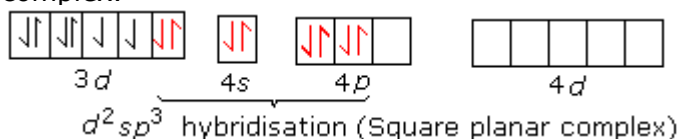


When Co^{3+} forms a complex with CN^- , it involves the inner $3d$ orbitals (which are of lower energy) in hybridisation and hence the complexes are **inner orbital** complexes. These complexes are more stable than outer orbital complexes. Since the unpaired electrons of metals ions have been paired up these are also called **low spin** complexes. In this case there is no unpaired electron and hence the complexes will be diamagnetic.

If the metal ion i.e. Co^{3+} were to form a four coordinate complex, then also two different arrangements are possible. In one case the vacant $4s$ and three $4p$ orbitals undergo sp^3 hybridisation to accommodate four pairs of electrons from the ligands to give a tetrahedral complex.



Alternatively, by pairing some electrons in the $3d$ orbital, one $3d$ orbital is vacated and dsp^2 hybridisation may occur, involving $3d$, $4s$ and two $4p$ orbitals, to accommodate four pairs of electrons from the ligands to give a square planar complex.



The valence bond theory cannot explain the colour and spectra of various complexes.

Crystal Field Theory:

According to this theory proposed by Hans Bethe and Vleck, the attraction between central metal ion and ligands which results in complex formation is purely electrostatic. The bonding may be due to ion-ion interactions (of course of opposite charge) or ion-dipole interactions resulting in sigma (σ) overlap, π overlap or $d\pi - p\pi$ overlap (also known as back bonding).

The salient features of the crystal field theory are as follows:

- (i) The central metal in the complex is considered as a positive ion of charge equal to its oxidation state.
- (ii) Ligands are treated as point charges.
- (iii) There is no interaction between metal orbitals and ligand orbitals.
- (iv) In an isolated atom or metal ion all the d orbitals have same energy but during the formation of complexes, the ligands may destroy the degeneracy of these orbitals. In most complexes of transition metals, either six or four ligands surround the metal producing a field which is not spherically symmetrical and causes the splitting of energy levels of d orbitals.

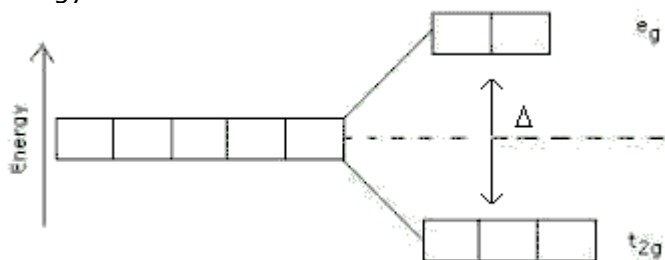
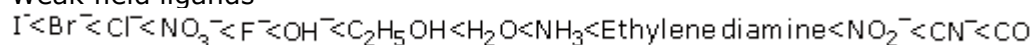


Fig: Splitting of energy of d orbitals in an octahedral field

(v) The splitting of energy levels is dependent on (a) the nature of ligands and (b) the charge on the metal ion.

(vi) Ligands, which cause small crystal field splitting, are called **weak field** ligands, while those which cause large crystal field splitting are called **strong field** ligands. The common ligands arranged in increasing order of crystal field splitting constitute the **spectrochemical series**.

Weak field ligands



Strong Field ligands

Crystal field theory is successful in explaining electronic spectra of complexes and the colour of complexes (because of $d \rightarrow d$ transition as the energy required for these is small). It can now be explained that when Co^{3+} forms complex with CN^- , a strong field

ligand, splitting of energy levels of d orbitals result in the six d electrons occupying the lower t_{2g} orbitals, thus forming a low spin inner orbital complex.

The theory fails to explain the formation of complexes by metals in zero oxidation state, as there is no electrostatic attraction. To explain it, the role of covalency is considered and the theory is called the **ligand field theory**.