

have still higher value of  $\mu$  in the range of  $4.7 - 5.2$  B.M. The increase in the value of  $\mu$  due to the orbital contribution. Similar is the case with tetrahedral and octahedral complexes of  $\text{Ni}^{+2}$  ( $d^8$  system). VBT cannot explain the increase in the value of  $\mu$ .

(6) VBT cannot interpret the spectra (colour) of the complexes.

(7) This theory does not predict or explain the magnetic behaviours of complexes. The theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. For example it was assumed for long that all square planar complexes of  $\text{Ni}^{+2}$  ( $d^8$  system) formed by  $dsp^2$  hybridisation were diamagnetic ( $n = 0$ ), while all tetrahedral complexes of  $\text{Ni}^{+2}$  formed by  $sp^3$  hybridisation were paramagnetic due to the presence of two unpaired electrons ( $n = 2$ ). X-ray study of 4-coordinate  $\text{Ni}^{+2}$  complexes has shown that one and the same complex can be obtained in both a *paramagnetic form* (having blue colour) and a *diamagnetic form* (having yellow colour). VBT has no explanation for it. VBT cannot explain the temperature dependent paramagnetism of the complexes.

(8) VBT cannot give any explanation for the order of reactivities of the inner-orbital inert complexes of  $d^3$ ,  $d^4$ ,  $d^5$  and  $d^6$  ions and of the observed differences in the energies of activation in a series of similar complexes.

(9) The magnetic moment values of the complexes of certain ions (e.g.,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.) are much higher than those expected by spin-only formula. VBT can not explain the enhanced values of magnetic moment.

### Crystal Field Theory (CFT)

This theory advanced by Brethe and Van Vleck was originally applied mainly to ionic crystals and is, therefore, called Crystal Field Theory (CFT). It was not until 1952 that Orgel popularised its use for inorganic chemists.

#### Important features of CFT

- The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.
- The ionic ligands (e.g.,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CN}^-$  etc.) are regarded as negative point charges (also called point charges) and the neutral ligands (e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc.) are regarded as point dipoles or simply dipoles, i.e., according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.
- The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e., it does not consider any orbital overlap.
- According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively-charged (i.e., cation) and negatively-charged (i.e., anions or dipole molecules which act as ligands) species. Complexes are thus presumed to form when centrally situated cations electrically attract ligands which may be either anions or dipole molecules. The attraction between the cations and the ligands is because the cations are positively charged and the anions are negatively charged and the dipole molecules, as well, can offer their negatively incremented ends for such electrostatic attractions.

#### Grouping of five $d$ -orbitals into $t_{2g}$ and $e_g$ sets of orbitals

On the basis of the orientation of the lobes of the five- $d$ -orbitals with respect to coordinates these have been grouped into the following two sets.

1.  $e_g$  set of orbitals:  $d_z^2$  and  $d_{x^2-y^2}$  orbitals. This set consists of the orbitals which have their lobes along the axes and hence are called *axial orbitals*. Quite obviously these are  $d_z^2$  and  $d_{x^2-y^2}$  orbitals. Group theory calls these  $e_g$  orbitals in which  $e$  refers to doubly degenerate set.

2.  $t_{2g}$  set of orbitals:  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals. This set includes the orbitals whose lobes lie between the axes and are called *non-axial orbitals*. Group theory calls these  $t_{2g}$  orbitals wherein  $t$  refers to triply degenerate set.

### CFT as applied to octahedral complexes: Crystal field splitting of *d*-orbitals in octahedral complexes

In case of free metal ion all the five *d*-orbitals are degenerate, i.e., these have the same energy. Now let us consider an octahedral complex,  $[ML_6]^{n+}$  in which the central metal cation,  $M^{n+}$  is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in Fig. 5.18. The three axes, viz.  $x$ -,  $y$ -, and  $z$ -axes which point along the corners have also been shown.

Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation,  $M^{n+}$  from both the ends of the axes. In this process the electrons in *d*-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. (Remember CFT regards the ionic ligands as negative point charges and neutral ligands as dipoles). This repulsion will raise the energy of all the five *d*-orbitals. If all the ligands approaching the central cation are at an equal distance from each of the *d*-orbitals (i.e., the ligand field is spherically symmetrical), the energy of each of five *d*-orbitals will raise by the same amount, i.e., all the *d*-orbitals will still remain degenerate, although they will have now higher energy than before. This is only a *hypothetical situation*. Since the lobes of the two  $e_g$  orbitals (i.e.,  $d_z^2$  and  $d_{x^2-y^2}$  orbitals) lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in three  $t_{2g}$  orbitals (i.e.,  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals) whose lobes are directed in space between the path of the approaching ligands i.e., the energy of  $e_g$  orbitals is increased while that of  $t_{2g}$  is decreased (Remember : greater is the repulsion, greater the increase in energy). Thus we find that under the influence of approaching ligands, the five *d*-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels viz.,  $t_{2g}$  level which is triply degenerate and is of lower energy, and  $e_g$  level which is doubly degenerate and is of higher energy (see Fig. 5.19). In other words the degeneracy of the five *d*-orbitals is removed under the influence of the ligands. The separation of five *d*-orbitals of the metal ion into two sets having different energies is called *crystal field splitting* or *energy level splitting*. This concept of crystal field splitting makes the basis of CFT.

The energy gap between  $t_{2g}$  and  $e_g$  sets is denoted by  $\Delta_0$  or  $10Dq$  where 0 in  $\Delta_0$  indicates an octahedral arrangement of the ligands round the central metal cation. This energy difference arises because of the difference in electrostatic field exerted by the ligands on  $t_{2g}$  and  $e_g$  sets of orbitals of the central metal cation.  $\Delta_0$  or  $10Dq$  is called *crystal field splitting energy*. With the help of simple geometry it can be shown that the energy of  $t_{2g}$  orbitals is  $0.4 \Delta_0$  ( $= 4Dq$ ) less than that of hypothetical degenerate *d*-orbitals (No splitting state shown by dotted line in Fig. 5.19) and, hence, that of  $e_g$  orbitals is  $0.6\Delta_0$  ( $= 6Dq$ ) above that of the hypothetical degenerate *d*-orbitals. Thus, we find that  $t_{2g}$  set loses an energy equal to  $0.4 \Delta_0$  ( $= 4Dq$ ) while  $e_g$  set gains an energy equal to  $0.6 \Delta_0$  ( $= 6Dq$ ). In Fig. 5.19 the loss and gain in energies of  $t_{2g}$  and  $e_g$

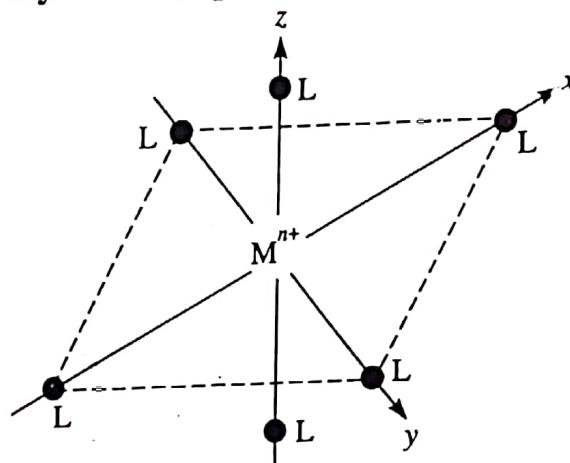
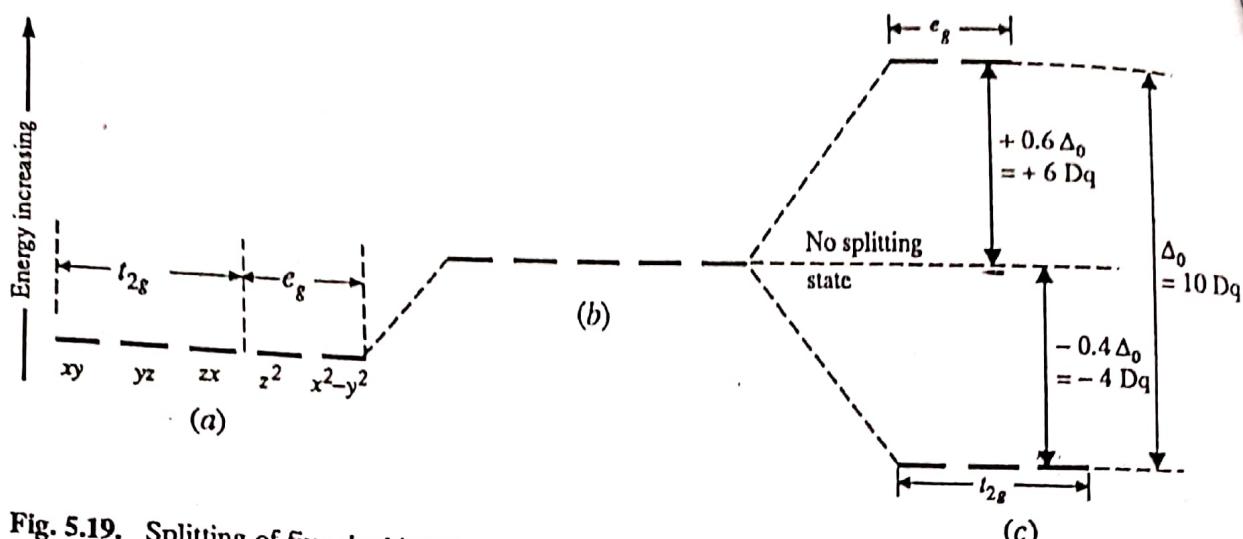


Fig. 5.18. Position of the central metal cation,  $M^{n+}$  and six ligands, L's in an octahedral complex,  $[ML_6]^{n+}$ .

orbitals is shown by negative (-) and positive (+) signs respectively.  $\Delta_0$  is generally measured in  $\text{cm}^{-1}$ .



**Fig. 5.19.** Splitting of five  $d$ -orbitals in an octahedral complex. (a) Five degenerate  $d$ -orbitals on the central metal cation which are free from any ligand field. (b) Hypothetical degenerate  $d$ -orbitals at a higher energy level (c) Splitting of  $d$ -orbitals into  $t_{2g}$  and  $e_g$  orbitals under the influence of six ligands in octahedral complex.

### Distribution of $d^x$ electrons ( $x = 1) of the central metal cation in $t_{2g}$ and $e_g$ orbitals in high spin and low spin octahedral complexes$

The distribution of  $d^x$  electrons of the central metal cation in  $t_{2g}$  and  $e_g$  orbitals in an octahedral complex depends on whether the six ligands are weak(er) or strong(er). Thus we have the following two cases:

**1. When the ligands are weak(er).** We have seen that under the influence of weak(er) ligands the energy difference,  $\Delta_0$  between  $t_{2g}$  and  $e_g$  sets is relatively small and hence all the five  $d$ -orbitals of these two sets may be supposed to be degenerate, i.e., in presence of weak(er) ligands all the  $d$ -orbitals have the same energy and consequently the distribution of  $d$ -electrons in  $t_{2g}$  and  $e_g$  sets takes place according to Hund's rule which states that electrons will pair up only when each of the five  $d$ -orbitals is at least singly filled. Thus in weak(er) field the first three electrons enter  $t_{2g}$  level, 4th and 5th electrons (two electrons) go to  $e_g$  set, 6th, 7th and 8th electrons (three electrons) occupy  $t_{2g}$  set and 9th and 10th electrons (last two electrons) go to  $e_g$  set. (See Table 5.6). The octahedral complexes containing weak(er) ligands are called weak-field or low-field complexes.

**2. When the ligands are strong(er).** In octahedral complexes containing strong(er) ligands, the distribution of  $d$ -electrons in  $t_{2g}$  and  $e_g$  orbitals does not obey Hund's rule. Thus in strong(er) field the first six electrons go to  $t_{2g}$  orbitals and the remaining four electrons enter  $e_g$  orbitals (Table 5.7). The octahedral complexes having strong(er) ligands are called strong-field or high-field complexes.

The following points may be noted from tables 5.6 and 5.7.

(i) Whether the ligand field is strong(er) or weak(er), for  $d^1$ ,  $d^2$  and  $d^3$  configurations, the electrons go to the lower energy  $t_{2g}$ -level (more stable), for  $d^8$ ,  $d^9$  and  $d^{10}$  configurations, the first six electrons go to the  $t_{2g}$ -level and the remaining two (in case of  $d^8$  ion), three (in case of  $d^9$  ion) and four (in case of  $d^{10}$  ion) electrons occupy the  $e_g$ -level. Thus, the distribution of electrons of  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  and  $d^{10}$  configurations in  $t_{2g}$  and  $e_g$  levels for both strong(er) and weak(er) octahedral ligand field is the same.

(ii) For each of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  configurations there is a difference in the arrangement of electrons in weak(er) and strong(er) ligand fields.

**Table 5.6.** Distribution of  $d^x$  electrons ( $x = 1$  to  $10$ ) in  $t_{2g}$  and  $e_g$  sets of orbitals in weak(er) field (high spin or spin free) octahedral complexes. ( $n$  = No. of unpaired electrons,  $S$  = Resultant spin =  $n/2$ ,  $p + q = x = 1, 2, \dots, 8, 9$  or  $10$ ). Here  $\Delta_0 < P$ .

$d^x$ ions	Distribution of $d^x$ electrons in $t_{2g}$ and $e_g$ orbitals		$t_{2g}^p e_g^q$ configuration	$n$	$S = n/2$
$d^1$	$t_{2g}$ (Lower energy) $\uparrow \quad \quad \quad =$	$e_g$ (Higher energy) $\quad \quad \quad -$	$t_{2g}^1 e_g^0$	1	$1/2$
$d^2$	$\uparrow \uparrow \quad \quad$	$\quad \quad \quad -$	$t_{2g}^2 e_g^0$	2	1
$d^3$	$\uparrow \uparrow \uparrow$	$\quad \quad \quad -$	$t_{2g}^3 e_g^0$	3	$3/2$
$d^4$	$\uparrow \uparrow \uparrow \uparrow$	$\uparrow \quad -$	$t_{2g}^3 e_g^1$	4	2
$d^5$	$\uparrow \uparrow \uparrow \uparrow$	$\uparrow \uparrow$	$t_{2g}^3 e_g^2$	5	$5/2$
$d^6$	$\uparrow \downarrow \uparrow \uparrow$	$\uparrow \uparrow$	$t_{2g}^4 e_g^2$	4	2
$d^7$	$\uparrow \downarrow \uparrow \downarrow \uparrow$	$\uparrow \uparrow$	$t_{2g}^5 e_g^2$	3	$3/2$
$d^8$	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	$t_{2g}^6 e_g^2$	2	1
$d^9$	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	$t_{2g}^6 e_g^3$	1	$1/2$
$d^{10}$	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	$t_{2g}^6 e_g^4$	0	0

**Table 5.7.** Distribution of  $d^x$  electrons ( $x = 1$  to  $10$ ) in  $t_{2g}$  and  $e_g$  orbitals in strong(er) field (low spin or spin paired) octahedral complexes ( $n$  = No. of unpaired electrons,  $S$  = Resultant spin =  $n/2$ ,  $p + q = x = 1, 2, \dots, 8, 9$  or  $10$ ). Here  $\Delta_0 > P$ .

$d^x$ ions	Distribution of $d^x$ electrons in $t_{2g}$ and $e_g$ orbitals		$t_{2g}^p e_g^q$ configuration	$n$	$S = n/2$
$d^1$	$t_{2g}$ (Lower energy) $\uparrow \quad \quad \quad -$	$e_g$ (Higher energy) $\quad \quad \quad -$	$t_{2g}^1 e_g^0$	1	$1/2$
$d^2$	$\uparrow \quad \uparrow \quad -$	$\quad \quad \quad -$	$t_{2g}^2 e_g^0$	2	1
$d^3$	$\uparrow \quad \uparrow \quad \uparrow$	$\quad \quad \quad -$	$t_{2g}^3 e_g^0$	3	$3/2$
$d^4$	$\uparrow \downarrow \quad \uparrow \quad \uparrow$	$\quad \quad \quad -$	$t_{2g}^4 e_g^0$	2	1
$d^5$	$\uparrow \downarrow \quad \uparrow \quad \uparrow$	$\quad \quad \quad -$	$t_{2g}^5 e_g^0$	1	$1/2$
$d^6$	$\uparrow \downarrow \quad \uparrow \quad \uparrow \quad \downarrow$	$\quad \quad \quad -$	$t_{2g}^6 e_g^0$	0	0
$d^7$	$\uparrow \downarrow \quad \uparrow \quad \uparrow \quad \downarrow$	$\quad \quad \quad -$	$t_{2g}^6 e_g^1$	1	$1/2$
$d^8$	$\uparrow \downarrow \quad \uparrow \quad \uparrow \quad \downarrow$	$\uparrow \quad \uparrow$	$t_{2g}^6 e_g^2$	2	1
$d^9$	$\uparrow \downarrow \quad \uparrow \quad \uparrow \quad \downarrow$	$\uparrow \downarrow \quad \uparrow$	$t_{2g}^6 e_g^3$	1	$1/2$
$d^{10}$	$\uparrow \downarrow \quad \uparrow \quad \uparrow \quad \downarrow$	$\uparrow \downarrow \quad \uparrow \downarrow$	$t_{2g}^6 e_g^4$	0	0

(iii) *Number of unpaired electrons (n)* : *High-spin and low-spin complexes.* Weak-field complexes of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  ions have greater number of unpaired electrons ( $n$ ) than those of (same ions) strong-field complexes and are thus with a higher value of resultant spin ( $S$ ). It is for this reason that the weak-field and strong-field complexes are also called *spin-free* or *high-spin* (abbreviated as HS) and *spin-paired* or *low-spin* (LS) complexes respectively. Recall that VBT has called these complexes as *ionic (Pauling)* or *outer-orbital (Huggin)* and *covalent (Pauling)* or *inner-orbital (Huggin)* complexes respectively.

The number of unpaired electrons (*i.e.*, the value of the resultant spin,  $S$ ) in the cases namely  $d^1$  to  $d^3$  and  $d^8$  to  $d^{10}$  is the same in both the fields, and it is due to this reason that for these configurations the question of the formation of HS- and LS-complexes does not arise. The question does arise for the system  $d^4$  to  $d^7$ .

The paramagnetism of HS-complexes is larger than that of LS-complexes, since, as is evident from Tables 5.6 and 5.7. HS-complexes have more unpaired electrons (*i.e.*, larger value of  $S$ ) than the LS-complexes (*i.e.*, smaller value of  $S$ ).

### Solved examples

**Example 1.** Give the number of unpaired electrons for the following complex ions (a)  $[VF_6]^{3-}$ , (b)  $[Fe(CN)_6]^{4-}$  (c)  $[Fe(CN)_6]^{3-}$  (d)  $[RhCl_6]^{3-}$ .

**Solution.** (a) In  $[VF_6]^{3-}$  vanadium is present as  $V^{3+}$  ion which is a  $3d^2$  system. Thus, in this case the question of the formation of HS- or LS- complex does not arise and the distribution of two  $3d$  electrons in  $t_{2g}^-$  and  $e_g$ -sets is as  $V^{3+}(3d^2) \rightarrow t_{2g}^2 e_g^0$ , which gives the number of unpaired electrons,  $n$ , equal to two, *i.e.*,  $n = 2$ .

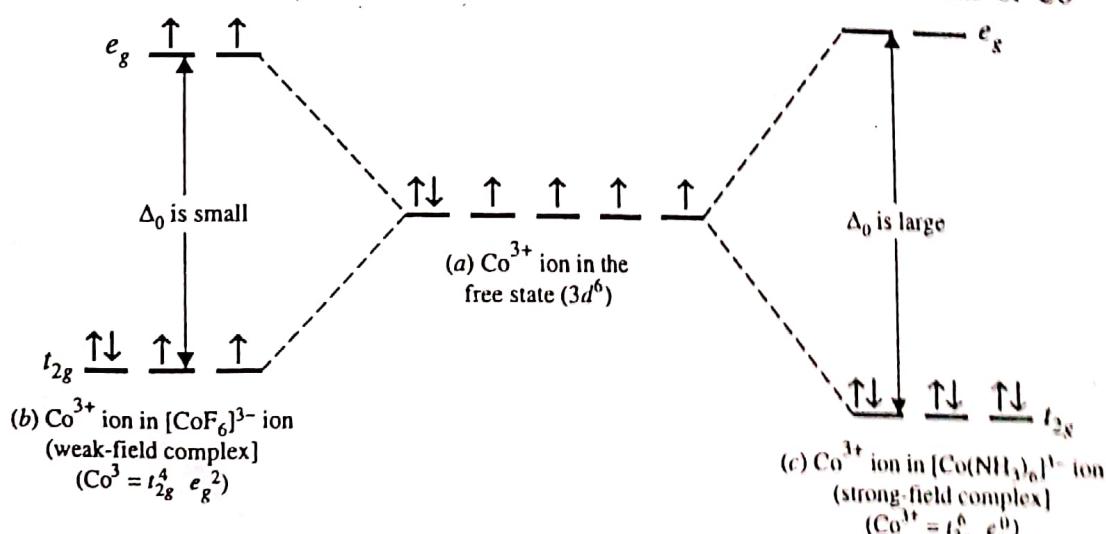
(b) In  $[Fe(CN)_6]^{4-}$  ion, Fe is present as  $Fe^{2+}$  with  $3d^6$  configuration. Since  $CN^-$  ion is a strong ligand,  $[Fe(CN)_6]^{4-}$  ion is a LS-complex and hence the distribution of six  $3d$ -electrons in  $t_{2g}$  and  $e_g$  sets is as  $Fe^{2+}(3d^6) \rightarrow t_{2g}^6 e_g^0$ , giving  $n = 0$ .

(c) in this case  $Fe^{3+}(3d^5) \rightarrow t_{2g}^5 e_g^0$ , giving  $n = 1$ .

(d)  $Cl^-$  ion is a weak ligand. Thus  $[RhCl_6]^{3-}$  is a HS-complex and consequently  $Rh^{3+}(4d^6) \rightarrow t_{2g}^4 e_g^2$ , giving  $n = 4$ .

**Example 2.** Show, with a labelled diagram, the distribution of six  $d$ -electrons in  $Co^{3+}$  ion in  $t_{2g}$  and  $e_g$  orbitals of the complex ion pair viz.  $[CoF_6]^{3-}$  and  $[Co(NH_3)_6]^{3+}$ .

**Solution.** We know from the spectro-chemical series, that  $6F^-$  ions are weaker ligands while  $6NH_3$  molecules are stronger ligands. Thus the distribution of  $d^6$  electrons of  $Co^{3+}$  ion



**Fig. 5.20.** Distribution of  $d^6$  electrons of  $Co^{3+}$  ion in the weak-field complex,  $[CoF_6]^{3-}$  and strong field complex,  $[Co(NH_3)_6]^{3+}$ .

in  $t_{2g}$  and  $e_g$  orbitals in  $[\text{CoF}_6]^{3-}$  is  $t_{2g}^4 e_g^2$  and in  $[\text{Co}(\text{NH}_3)_6]^{+3}$  ion is  $t_{2g}^6 e_g^0$ . Both these distribution have been shown in Fig. 5.20.

### Factors influencing the magnitude of $\Delta_0$

A mass of experimental data show that the magnitude of  $\Delta_0$  depends on the following factors:

#### A. Nature of the metal cation

The influence of this factor can be studied under the following four heading:

**1. Different charges on the cation of the same metal.** The cations from atoms of the same transition series and having the same oxidation state have almost the same value of  $\Delta_0$  but the cation with a higher oxidation state has a larger value of  $\Delta_0$  than that with lower oxidation state, e.g.,

- (a)  $\Delta_0$  for  $[\text{Fe}^{2+}(\text{H}_2\text{O})_6]^{2+} = 10,400 \text{ cm}^{-1}$  .....  $3d^6$   
 $\Delta_0$  for  $[\text{Fe}^{3+}(\text{H}_2\text{O})_6]^{3+} = 13,700 \text{ cm}^{-1}$  .....  $3d^5$
- (b)  $\Delta_0$  for  $[\text{Co}^{2+}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1}$  .....  $3d^7$   
 $\Delta_0$  for  $[\text{Co}^{3+}(\text{H}_2\text{O})_6]^{3+} = 18,200 \text{ cm}^{-1}$  .....  $3d^6$

This effect is probably due to the fact that the central ion with higher oxidation state (i.e., with higher charge) will polarise the ligands more effectively and thus the ligands would approach such a cation more closely than they can do the cation of lower oxidation state, resulting in larger splitting.

**2. Different charges on the cation of different metals.** Two different cations having the same number of  $d$ -electrons and the same geometry of the complex but with different charge can also be compared. The cation with a higher oxidation state has a larger value of  $\Delta_0$  than that with a lower oxidation state. For example, the behaviours towards the same ligand of V(II) and Cr(III), which are both  $d^3$  ions can be compared. It is observed that the value of  $\Delta_0$  in  $[\text{V}^{2+}(\text{H}_2\text{O})_6]^{2+}$  is less than that in  $[\text{Cr}^{3+}(\text{H}_2\text{O})_6]^{3+}$  as is shown below:

$$\Delta_0 \text{ for } [\text{V}^{2+}(\text{H}_2\text{O})_6]^{2+} = 12,400 \text{ cm}^{-1} \quad \dots \quad 3d^3 \\ \text{and } \Delta_0 \text{ for } [\text{Cr}^{3+}(\text{H}_2\text{O})_6]^{3+} = 17,400 \text{ cm}^{-1} \quad \dots \quad 3d^3$$

This fact can be explained in terms of the charge on the cation. The  $\text{Cr}^{3+}$  ion, which has greater positive charge than  $\text{V}^{2+}$  ion, exerts a greater attraction for water molecules (ligands) than does the  $\text{V}^{2+}$  ion. Hence the water molecules approach the  $\text{Cr}^{3+}$  ion more closely than they approach the  $\text{V}^{2+}$  ion and so exert a stronger crystal field effect on the  $d$ -electrons of  $\text{Cr}^{3+}$  ion.

**3. Same charges on the cation but the number of  $d$ -electrons is different.** In case of complexes having the cations with the same charges but with different number of  $d$ -electrons in the central metal cation the magnitude of  $\Delta_0$  decreases with the increase of the number of  $d$ -electrons, e.g.,

$$\Delta_0 \text{ for } [\text{Co}^{2+}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1} \quad \dots \quad 3d^7 \\ \Delta_0 \text{ for } [\text{Ni}^{2+}(\text{H}_2\text{O})_6]^{2+} = 8,500 \text{ cm}^{-1} \quad \dots \quad 3d^8$$

From the combination of 1, 2 and 3 mentioned above it can be concluded that :

(a) For the complexes having the same geometry and the same ligands but having different number of  $d$ -electrons, the magnitude of  $\Delta_0$  decreases with the increase of the number of  $d$ -electrons in the central metal cation (No. of  $d$ -electrons  $\propto \frac{1}{\Delta_0}$ )

(b) In case of complexes having the same number of  $d$ -electrons the magnitude of  $\Delta_0$  increases with the increase of the charges (i.e., oxidation state) on the central metal cation (oxidation state  $\propto \Delta_0$ ).

4. Quantum number ( $n$ ) of the  $d$ -orbitals of the central metal ion.  $\Delta_0$  increases about 30% to 50% from  $3d^n$  to  $4d^n$  and by about the same amount again from  $4d^n$  to  $5d^n$  complexes, e.g.,

$$\Delta_0 \text{ for } [\text{Co}^{3+}(\text{NH}_3)_6]^{3+} = 23,000 \text{ cm}^{-1} \dots \quad 3d^6$$

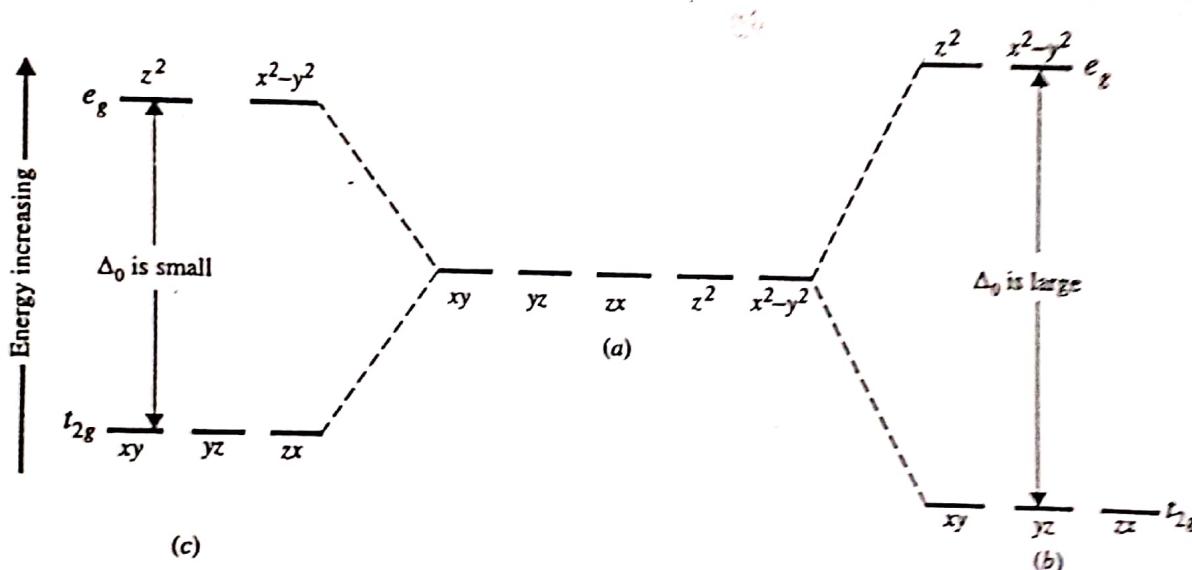
$$\Delta_0 \text{ for } [\text{Rh}^{3+}(\text{NH}_3)_6]^{3+} = 34,000 \text{ cm}^{-1} \dots \quad 4d^6$$

$$\Delta_0 \text{ for } [\text{Ir}^{3+}(\text{NH}_3)_6]^{3+} = 41,000 \text{ cm}^{-1} \dots \quad 5d^6$$

Presumably the  $5d$  and  $4d$  valence orbitals of the central ion are better than the  $3d$ -orbitals in  $\sigma$ -bonding with the ligands.

### B. Strong(er) and weak(er) ligands and spectrochemical series

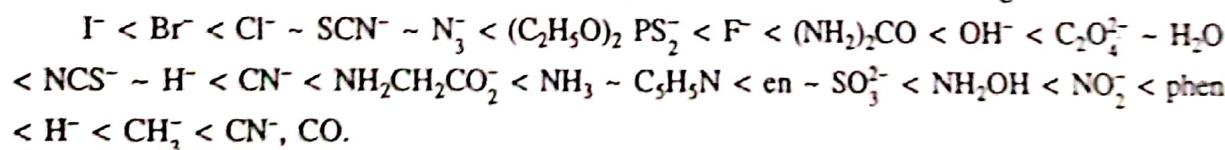
The magnitude of  $\Delta_0$  varies from strong(er) to weak(er) ligands. Strong(er) ligands are those which exert a strong(er) field on the central metal ion and hence have higher splitting power while the weak(er) ligands are those which have a weak(er) field on the central metal cation and consequently relatively lower splitting power. Thus strong(er) ligands (e.g.  $\text{CN}^-$ ) give larger value of  $\Delta_0$  and weak(er) ligands (e.g.  $\text{F}^-$ ) yield a smaller value of  $\Delta_0$  (See Fig. 5.21).



**Fig. 5.21.** Splitting of five  $d$ -orbitals in presence of strong(er) and weak(er) ligands in an octahedral complex.  
 (a) Five  $d$ -orbitals in the free metal ion  
 (b) Splitting of  $d$ -orbitals in presence of strong(er) ligands  
 (c) Splitting of  $d$ -orbitals in presence of weak(er) ligands.

Fig. 5.21 shows that not only  $\Delta_0$ , which represents the energy difference between the  $t_{2g}$  and  $e_g$ -sets of orbitals, is smaller in the weak(er) field complex than in the strong(er) field, but also that both the  $t_{2g}$  and  $e_g$ -levels of the weak(er) field are correspondingly closer to the level of the degenerate five  $d$ -orbitals of the free isolated metallic ion than are those, respectively, of the strong(er) field.

The common ligands can be arranged in the order of their increasing splitting power to cause  $d$ -orbitals splitting. This series is called *spectrochemical series* and is given below:



This series shows that the value of  $\Delta_0$  in the series also increases from left to right.

The order of field strength of the common ligands shown above is, in fact, independent of the nature of the central metal ion and the geometry of the complex.

The increase in the value of  $\Delta_0$  on proceeding from left to right in the spectrochemical

series is quite evident from the values of  $\Delta_0$  for some octahedral complexes given in Table 5.8 which clearly shows that since on proceeding from  $6\text{Br}^- \rightarrow 3 \text{ en}$ , the field strength of the ligands increases, the value of  $\Delta_0$  also correspondingly increases.

**Table 5.8.**  $\Delta_0$  values (i.e., energy difference between  $t_{2g}$  and  $e_g$  levels) in  $\text{cm}^{-1}$  for some octahedral complexes.

Ligands →	6 Br <sup>-</sup>	<	6 Cl <sup>-</sup>	<	6 H <sub>2</sub> O	<	6 NH <sub>3</sub>	<	3 en
Metal ion	Field strength increasing →								
Ni (II)	7,000 $\text{cm}^{-1}$	<	7,200 $\text{cm}^{-1}$	<	8500 $\text{cm}^{-1}$	<	10,800 $\text{cm}^{-1}$	<	11,500 $\text{cm}^{-1}$
Cr (III)	—		13,800		< 17,400		< 21,600		< 21,900
Co (III)	—		—		18,200		< 23,000		< 23,200
Rh (III)	19,000	<	20,300		< 27,000		< 34,100		< 34,600
	$\Delta_0$ values (in $\text{cm}^{-1}$ ) also increasing →								

### Mean pairing energy (P)

Mean pairing energy (P) is the energy which is required to pair two electrons against electron-electron repulsion in the same orbital. P is the pairing energy for one electron pair. P is generally expressed in  $\text{cm}^{-1}$ . Pairing energy depends on the principal energy level (*n*) of *d*-electrons.

### Calculation of total pairing energy of $d^x$ ion

If *m* is the total number of paired-electrons in  $t_{2g}$  and  $e_g$  orbitals in  $d^x$  ion and P is the pairing energy for one electron, then

$$\text{Total pairing energy for } m \text{ electron pairs} = mP \text{ cm}^{-1}.$$

### Solved examples

**Example 1.** Calculate the total pairing energy of  $d^7$  ion in high spin as well as in low spin octahedral complexes.

**Solution.** We know that the configuration of  $d^7$  ion in high spin state is  $t_{2g}^5 e_g^2$  which shows that  $m = 2 + 0 = 2$ .

$$\therefore \text{Total pairing energy for 2 paired electrons} = 2 \times P = 2P$$

The configuration of  $d^7$  ion in low spin state is  $t_{2g}^6 e_g^1$  which gives  $m = 3 + 0 = 3$ .

$$\therefore \text{Total pairing energy for 3 paired electrons} = 3 \times P = 3P$$

**Example 2.** Calculate the total pairing energy for  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion in high spin and low spin state. Given that mean pairing energy =  $23,500 \text{ cm}^{-1}$ .

**Solution.** In  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion, Cr is present as  $\text{Cr}^{2+}$  which is a  $d^4$  ion. Thus the configuration of  $d^4$  ion in high spin state is  $t_{2g}^3 e_g^1$  which gives  $m = 0$  and hence :

$$\text{Total pairing energy of } [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \text{ ion in high spin state} = 0 \times P = 0$$

The configuration of  $d^4$  ion in low spin state is  $t_{2g}^4 e_g^0$  which gives  $m = 1$  and hence :

Total pairing energy of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion in low spin state

$$= 1 \times P = 1 \times 23,500 \text{ cm}^{-1} = 23,500 \text{ cm}^{-1}$$

**Example 3.** Which complex of the following pairs has the larger value of  $\Delta_0$

(i)  $[\text{Co}^{3+}(\text{CN}_6)^{3-}]$  and  $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+}$

(ii)  $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}^{3+}\text{F}_6]^{3-}$

(iii)  $[Co^{3+}(H_2O)_6]^{3+}$  and  $[Rh^{3+}(H_2O)_6]^{3+}$

(iv)  $[Co^{2+}(H_2O)_6]^{2+}$  and  $[Co^{3+}(H_2O)_6]^{3+}$ ?

**Solution.** (i) Since  $CN^-$  is stronger than  $NH_3$  (i.e.,  $CN^-$  ion has greater field strength than  $NH_3$ ),  $\Delta_0$  for  $[Co(CN)_6]^{3-}$  is greater than  $\Delta_0$  for  $[Co(NH_3)_6]^{3-}$ .

(ii)  $[Co(NH_3)_6]^{3+}$  ion has greater value of  $\Delta_0$  than that for  $[CoF_6]^{3-}$ .

(iii) Rh is a member of 4d-series while Co is a member of 3d-series. Thus principal quantum number,  $n$ , for Rh is greater than that of Co and consequently  $\Delta_0$  for  $[Rh(H_2O_6)]^{3+}$  is greater.

(iv) The charge on Co in  $[Co(H_2O)_6]^{3+}$  is higher than that on Co in  $[Co(H_2O)_6]^{2+}$ . Thus,  $\Delta_0$  for  $[Co(H_2O)_6]^{3+}$  is higher.

### How to predict the spin state of a given octahedral complex ion

By comparing the values of  $\Delta_0$  and P of a given metallic ion, the spin state of the octahedral complex ion formed by that metallic ion can be predicted.  $\Delta_0$  tends to force as many electrons to occupy  $t_{2g}$  orbitals while P tends to prevent the electrons to pair in  $t_{2g}$  orbitals. This discussion shows that:

(i) When  $\Delta_0 > P$ , the electrons tend to pair and hence low spin (strong-field or spin paired) octahedral complex ions are obtained.

(ii) When  $\Delta_0 < P$ , the electrons tend to remain unpaired and hence high spin (weak-field or spin free) octahedral complex ions are obtained.

Examples of some HS- and LS-octahedral complexes are given in Table 5.9. In this table the value of P (in  $cm^{-1}$ ) of the central metal ion of the corresponding complex determined from spectroscopic data and that of  $\Delta_0$  (in  $cm^{-1}$ ) for the complexes are also listed. From this table it may be seen that the spin-state of the complexes predicted by CFT is the same as that observed experimentally. In every case where  $\Delta_0 < P$ , HS-complex is formed and in case where  $\Delta_0 > P$ , LS-complex is formed.

Table 5.9. Examples of some LS-and HS-octahedral complexes.

$d^x$ configuration	Examples of complexes	Value of P ( $cm^{-1}$ )	Value of $\Delta_0$ ( $cm^{-1}$ )	spin-state		Relative magnitudes of $\Delta_0$ and P
				Predicted by CFT	Observed experimentally	
$d^4$	$[Cr(H_2O)_6]^{2+}$	23,500	13,900	HS	HS	$\Delta_0 < P$
	$[Mn(H_2O)_6]^{3+}$	28,800	21,000	HS	HS	$\Delta_0 < P$
	$[Mn(CN)_6]^{3-}$	28,800	38,500	LS	LS	$\Delta_0 > P$
$d^5$	$Mn(H_2O)_6]^{2+}$	25,500	7,800	HS	HS	$\Delta_0 < P$
	$[Fe(H_2O)_6]^{3+}$	30,000	13,700	HS	HS	$\Delta_0 < P$
$d^6$	$[Fe(H_2O)_6]^{2+}$	17,600	10,400	HS	HS	$\Delta_0 < P$
	$[Fe(CN)_6]^{4-}$	17,600	33,000	LS	LS	$\Delta_0 > P$
	$[Co(NH_3)_6]^{3+}$	21,000	23,000	LS	LS	$\Delta_0 > P$
	$[CoF_6]^{3-}$	21,000	13,000	HS	HS	$\Delta_0 < P$
$d^7$	$[Co(H_2O)_6]^{2+}$	22,500	9,300	HS	HS	$\Delta_0 < P$

### Solved examples

**Example 1.** For  $Mn^{3+}$  ion, the electron pairing energy, P is about  $28,000\text{ cm}^{-1}$ .  $\Delta_0$  values for the complexes  $[Mn(H_2O)_6]^{3+}$  and  $[Mn(CN)_6]^{3-}$  are  $21,000\text{ cm}^{-1}$  and  $38,500\text{ cm}^{-1}$  respectively. Do these complexes have high-spin or low-spin configurations? Also write down the configurations corresponding to these states.

**Solution.** For  $[Mn(H_2O)_6]^{3+}$  ion, since  $P > \Delta_0$  ( $P = 28,000\text{ cm}^{-1}$ ,  $\Delta_0 = 21,000\text{ cm}^{-1}$ ), this

ion is a high spin complex and the configuration of  $d^4$  ion. ( $Mn^{3+}$  ion is a  $d^4$  system) is therefore,  $t_{2g}^3 e_g^1$ .

For  $[Mn(CN)_6]^{3-}$  ion, since  $P < \Delta_0$  ( $P = 28,000 \text{ cm}^{-1}$ ,  $\Delta_0 = 38,500 \text{ cm}^{-1}$ ), this ion is a low spin complex and the configuration of  $d^4$  ion ( $Mn^{3+}$  ion is a  $d^4$  system) is  $t_{2g}^4 e_g^0$ .

**Example 2.** For  $[Cr(H_2O)_6]^{2+}$  ion, the mean pairing energy ( $P$ ) is  $23,500 \text{ cm}^{-1}$  and the magnitude of  $\Delta_0$  is  $13,900 \text{ cm}^{-1}$ . State whether the given ion is stable in low spin state or in high spin state.

**Solution.** We know that when  $\Delta_0 < P$ , high spin state is more stable. Here since  $\Delta_0 (= 13,900 \text{ cm}^{-1}) < P (= 23,500 \text{ cm}^{-1})$ , high spin state is more stable.

### Crystal field stabilisation energies of $d^x$ configuration ( $x = 0$ to 10) of the central metal ion in octahedral complex

We have seen that according to CFT, under the influence of the six ligands approaching towards the central metal ion during the formation of an octahedral complex, the  $d$ -orbitals of the central metal ion are split into two sets of orbitals viz. lower energy triplet (or trio)  $t_{2g}$  and higher energy doublet (or pair),  $e_g$  sets.  $t_{2g}$  set of orbitals is triply degenerate while  $e_g$  set is doubly degenerate. The energy gap between these two sets is equal to  $\Delta_0$  (or  $10Dq$ ). The energy of  $t_{2g}$  set is lowered by  $2/5 \Delta_0$  ( $= 0.4 \Delta_0$ ) or  $4Dq$  while that of  $e_g$  set is raised by  $3/5 \Delta_0$  ( $= 0.6 \Delta_0$ ) or  $6Dq$  relative to the energy of hypothetical degenerate  $d$ -orbitals. Thus, each electron occupying  $t_{2g}$  orbitals decreases the energy of  $d$ -orbitals by  $-0.4 \Delta_0$  ( $= -4Dq$ ) while that going into  $e_g$  orbitals increases its energy by  $+0.6 \Delta_0$  ( $= +6Dq$ ). – and + signs indicate respectively the decrease and increase in the energy of  $d$ -orbitals caused by their splitting under the influence of six ligands. Now let us consider a  $d^x$  ion containing  $t_{2g}^p e_g^q$  configuration in which  $p$  is the number of electrons in  $t_{2g}$  set,  $q$  is the number of electrons in  $e_g$  set and  $x = p + q$ . Quite obviously :

*Change in energy (in terms of  $\Delta_0$ ) for  $t_{2g}^p e_g^q$  configuration*

$$\begin{aligned} &= \text{Loss in energy due to } p \text{ electrons in } t_{2g} \text{ set} \\ &\quad + \text{gain in energy due to } q \text{ electrons in } e_g \text{ set.} \\ &= -0.4 \Delta_0 \times p + 0.6 \Delta_0 \times q \\ &= [-0.4p + 0.6q] \Delta_0 \end{aligned} \quad \dots(i)$$

Now, since  $\Delta_0 = 10Dq$ , the above expression can also be written as :

*Change in energy (in terms of  $Dq$ ) for  $t_{2g}^p e_g^q$  configuration*

$$\begin{aligned} &= [-0.4p + 0.6q] \times 10 Dq \\ &= [-4p + 6q] Dq \end{aligned} \quad \dots(ii)$$

Thus equations (i) and (ii) give the energies of  $d^x$  ion containing  $t_{2g}^p e_g^q$  configuration. The change in energy for  $d^x$  ion containing  $t_{2g}^p e_g^q$  configuration calculated as above is called *crystal field stabilisation energy* (CFSE) of  $d^x$  ion, since it stabilises  $d$ -orbitals by lowering their energy which results from their splitting into  $t_{2g}$  and  $e_g$  orbitals.

In the derivation of equation (i) and (ii) we have not considered the pairing energy,  $P$ , of  $d^x$  ion which is the energy required to pair two electrons against electron-electron repulsion in the same orbital. If the pairing energy of the ion is also involved in the  $t_{2g}^p e_g^q$  configuration of a given  $d^x$  ion, then CFSE of the ion is given by the expression:

$$\text{CFSE} = [-0.4p + 0.6q] \Delta_0 + mP \quad \dots(iii)$$

$$= [-4p + 6q] Dq + mP \quad (\because \Delta_0 = 10 Dq) \quad \dots(iv)$$

Here  $m$  is the total number of paired electrons in  $t_{2g}$  and  $e_g$  sets of orbitals. Equations (iii) and (iv) have been used to calculate the CFSE values (in terms of  $\Delta_0$  and  $Dq$  respectively).

for  $d^0$  to  $d^{10}$  ions of HS and LS octahedral complexes. These values, as calculated from the above equations, are listed in Tables 5.10 and 5.11 respectively.

**Table 5.10.** CFSE values (in the units of  $\Delta_0$  and  $Dq$ ) for  $d^x$  configuration ( $x = 0$  to 10) of the central metal ion in weak field (spin free or high spin) octahedral complexes.  $m$  = Total number of paired electrons in  $t_{2g}$  and  $e_g$  orbitals,  $P$  = Mean pairing energy,  $p + q = x = 0, 1, 2, \dots, 8, 0$  or 10.

$d^x$ configuration	Distribution of $d^x$ electrons in $t_{2g}$ and $e_g$ orbitals		$t_{2g}^p e_g^q$ configuration	$m$	CFSE = $[-0.4p + 0.6q] \Delta_0 + mP$ = $[-0.4p + 0.6q] \times 10Dq + mP$ = $[-4p + 6q] Dq + mP$
$d^0$	$t_{2g}$ — — —	$e_g$ — —	$t_{2g}^0 e_g^0$	0	$0.0 \Delta_0$ (0.0 $Dq$ )
$d^1$	$t_{2g}$ ↑ — —	$e_g$ — —	$t_{2g}^1 e_g^0$	0	$-0.4 \Delta_0$ (-4 $Dq$ )
$d^2$	$t_{2g}$ ↑ ↑ —	$e_g$ — —	$t_{2g}^2 e_g^0$	0	$-0.8 \Delta_0$ (-8 $Dq$ )
$d^3$	$t_{2g}$ ↑ ↑ ↑	$e_g$ — —	$t_{2g}^3 e_g^0$	0	$-1.2 \Delta_0$ (-12 $Dq$ )
$d^4$	$t_{2g}$ ↑ ↑ ↑	$e_g$ ↑ —	$t_{2g}^3 e_g^1$	0	$-0.6 \Delta_0$ (-6 $Dq$ )
$d^5$	$t_{2g}$ ↑ ↑ ↑	$e_g$ ↑ ↑	$t_{2g}^3 e_g^2$	0	$-0.0 \Delta_0$ (0.0 $Dq$ )
$d^6$	$t_{2g}$ ↑↓ ↑ ↑	$e_g$ ↑ ↑	$t_{2g}^4 e_g^2$	1	$-0.4 \Delta_0$ (-4 $Dq$ ) + $P$
$d^7$	$t_{2g}$ ↑↓ ↑↓ ↑	$e_g$ ↑ ↑	$t_{2g}^5 e_g^2$	2	$-0.8 \Delta_0$ (-8 $Dq$ ) + 2 $P$
$d^8$	$t_{2g}$ ↑↓ ↑↓ ↑↓	$e_g$ ↑ ↑	$t_{2g}^6 e_g^2$	3	$-1.2 \Delta_0$ (-12 $Dq$ ) + 3 $P$
$d^9$	$t_{2g}$ ↑↓ ↑↓ ↑↓	$e_g$ ↑↓ ↑	$t_{2g}^6 e_g^3$	4	$-0.6 \Delta_0$ (-6 $Dq$ ) + 4 $P$
$d^{10}$	$t_{2g}$ ↑↓ ↑↓ ↑↓	$e_g$ ↑↓ ↑↓	$t_{2g}^6 e_g^4$	5	$0.0 \Delta_0$ (0.0 $Dq$ ) + 5 $P$

**Table 5.11.** CFSE values (in the units of  $\Delta_0$  and  $Dq$ ) for  $d^x$  configuration ( $x = 0$  to 10) of the central metal ion in strong field (spin paired or low spin) octahedral complexes.  $m$  = total number of paired electrons in  $t_{2g}$  and  $e_g$  orbitals,  $P$  = mean pairing energy,  $p + q = x = 0, 1, 2, \dots, 8, 9$  or 10.

$d^x$ configuration	Distribution of $d^x$ electrons in $t_{2g}$ and $e_g$ orbitals		$t_{2g}^p e_g^q$ configuration	$m$	CFSE = $[-0.4p + 0.6q] \Delta_0 + mP$ = $[0.4p + 0.6q] \times 10Dq + mP$ = $[-4p + 6q] Dq + mP$
$d^0$	$t_{2g}$ — — —	$e_g$ — —	$t_{2g}^0 e_g^0$	0	$0.0 \Delta_0$ (0.0 $Dq$ )
$d^1$	$t_{2g}$ ↑ — —	$e_g$ — —	$t_{2g}^1 e_g^0$	0	$-0.4 \Delta_0$ (-4 $Dq$ )
$d^2$	$t_{2g}$ ↑ ↑ —	$e_g$ — —	$t_{2g}^2 e_g^0$	0	$-0.8 \Delta_0$ (-8 $Dq$ )
$d^3$	$t_{2g}$ ↑ ↑ ↑	$e_g$ — —	$t_{2g}^3 e_g^0$	0	$-1.2 \Delta_0$ (-12 $Dq$ )
$d^4$	$t_{2g}$ ↑ ↑ ↑	$e_g$ ↑ —	$t_{2g}^4 e_g^0$	1	$-1.6 \Delta_0$ (-16 $Dq$ ) + $P$

(Contd.)

$d^2$	$\uparrow\downarrow \uparrow\downarrow \uparrow$	$---$	$t_{2g}^5 e_g^0$	2	$-2.0 \Delta_0 (-20 Dq) + 2P$
$d^3$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$---$	$t_{2g}^6 e_g^0$	3	$-2.4 \Delta_0 (-24 Dq) + 3P$
$d^4$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\quad$	$t_{2g}^6 e_g^1$	3	$-1.8 \Delta_0 (-18 Dq) + 3P$
$d^5$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\uparrow$	$t_{2g}^6 e_g^2$	3	$-1.2 \Delta_0 (-12 Dq) + 3P$
$d^6$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow\uparrow$	$t_{2g}^6 e_g^3$	4	$-0.6 \Delta_0 (-6 Dq) + 4P$
$d^{10}$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	$t_{2g}^6 e_g^4$	5	$0.0 \Delta_0 (0.0 Dq) + 5P$

**Example.** For the  $[Cr(H_2O)_6]^{2+}$  ion, the mean pairing energy,  $P$ , is found to be  $23,500 \text{ cm}^{-1}$ . The magnitude of  $\Delta_0$  is  $13,900 \text{ cm}^{-1}$ . Calculate the CFSE for this complex ion corresponding to high spin and low spin state.

**Solution.** Quite evidently in the given complex ion Cr is present as  $Cr^{2+}$  ion which is a  $d^4$  ion.

For  $d^4$  ion in high spin state, ( $m = 0$ )

$$\begin{aligned} \text{CFSE} &= -0.6 \Delta_0 + mP \\ &= -0.6 \times (13,900 \text{ cm}^{-1}) + 0 \times P = -8,340 \text{ cm}^{-1} \end{aligned}$$

For  $d^4$  ion in low spin state,

$$\begin{aligned} \text{CFSE} &= -1.6 \Delta_0 + 1 \times P \\ &= -1.6 \times (13,900 \text{ cm}^{-1}) + 1 \times (23,500 \text{ cm}^{-1}) \\ &= +1,260 \text{ cm}^{-1} \end{aligned}$$

### CFT as applied to tetrahedral complexes : Crystal field splitting of $d$ -orbitals in tetrahedral complexes

In case of a free metal ion ( $M^{n+}$ ) all the  $d$ -orbitals are degenerate, i.e., these have the same energy. Now let us consider a tetrahedral complex ion,  $[ML_4]^{n+}$  in which the central metal ion ( $M^{n+}$ ) is surrounded tetrahedrally by four ligands. A tetrahedron may be supposed to have been formed from a cube. The centre of the cube is the central of the tetrahedron at which is placed the central metal ion ( $M^{n+}$ ). Four alternate corners of the cube are the four corners of the tetrahedron at which the four ligands, L, (which have been shown by black circles) are placed (see Fig. 5.22). It may be seen from the figure that the four ligands are lying between the three axes viz, x, y and z axes which pass through the centres of the six faces of the cube and thus go through the centre of the cube. Now since the lobes of  $t_2$  orbitals ( $d_{xy}, d_{yz}$  and  $d_{zx}$ ) are lying between the axes, i.e., are lying directly in the path of the ligands, these orbitals will experience greater force of repulsion from the ligands than those of  $e$  orbitals ( $d_z^2$  and  $d_{x^2-y^2}$ ) whose lobes are lying along the axes, i.e., are lying in space between the ligands. Thus the  $d$  orbitals will be increased while that of  $e$  orbitals will be decreased. Consequently the  $d$  orbitals are again split into two sets as shown in Fig. 5.23 from which it may be

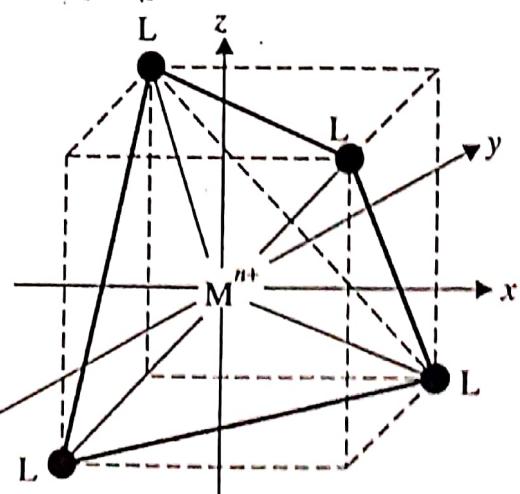


Fig. 5.22. Tetrahedral arrangement of four ligands (L) around the metal ion ( $M^{n+}$ ) in tetrahedral complex ion,  $[ML_4]^{n+}$ .

seen that the order of energy of  $t_2$  and  $e$  sets is the reverse of that seen for  $t_{2g}$  and  $e_g$  sets in octahedral complexes.

The energy difference between  $t_2$  and  $e$  sets for tetrahedral complex is represented as  $\Delta t$ . It has been shown that  $\Delta t < \Delta_0$ , the cause of which is that  $t_2$ -orbitals, although now closest to the ligands, do not point directly at the ligands, i.e., in an octahedral complex there is a ligand along each axis and in a tetrahedral complex no ligand lies directly along any axis. For this reason and also because there are only four ligands in the tetrahedral complex, while in an octahedral complex there are six ligands, the tetrahedral orbital splitting,  $\Delta t$  is less than  $\Delta_0$ , for the same metal and ligands and the same internuclear distances. It has also been shown that  $\Delta t = 0.45 \Delta_0$ . Thus the energy level of the  $t_2$  set is raised by  $0.4 \Delta t = 0.18 \Delta_0$  while that of  $e$  set is lowered by  $0.6 \Delta t = 0.27 \Delta_0$ . The relation namely  $\Delta t = 0.45 \Delta_0$  also shows that, other things being equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex.

In case of tetrahedral complex, since  $\Delta t$  is generally less than  $P$  ( $\Delta t < P$ ), the electrons tend to remain unpaired and hence *only high spin tetrahedral complexes are known, i.e., low spin tetrahedral complexes are not known*.

Since  $\Delta t < \Delta_0$ , crystal field splitting of  $d$ -orbitals favours the formation of octahedral complexes.

**Note.** The subscript  $g$  is not used for the splitting of  $d$ -orbitals in tetrahedral complexes because a tetrahedron has no centre of symmetry. The symbol  $g$  is used for the ligand fields which have centre of symmetry.

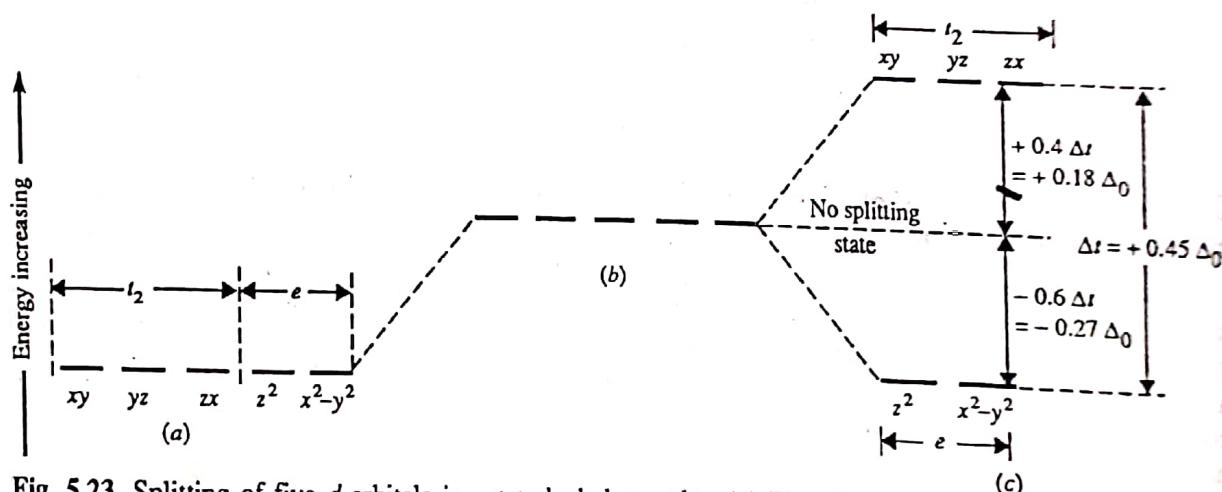


Fig. 5.23. Splitting of five  $d$ -orbitals in a tetrahedral complex (a) Five degenerate  $d$ -orbitals on the central metal cation which are free from any ligand field (b) Hypothetical degenerate  $d$ -orbitals at a higher energy level (c) Splitting of  $d$ -orbitals into  $e$  and  $t_2$  orbitals under the influence of four ligands in tetrahedral complex.

### Distribution of $d^x$ electrons ( $x = 1$ to $10$ ) of the central metal ion in $e$ and $t_2$ orbitals in high spin tetrahedral complexes

We have said above that only high spin tetrahedral complexes are known. In case of these complexes, the distribution of  $d^x$  electrons in  $e$  and  $t_2$  orbitals takes place according to Hund's rule, i.e., the electrons will pair up only when each of the five  $d$ -orbitals is at least singly-filled. The pairing of electrons will start from  $e$  orbitals, since these orbitals have less energy than  $t_2$  orbitals. The distribution of  $d^x$  electrons in high spin tetrahedral complexes has been shown in Table 5.12.

**Table 5.12.** Distribution of  $d^x$  electrons ( $x = 1$  to 10) in  $e$  and  $t_2$  orbitals in high spin tetrahedral complexes ( $n$  = Number of unpaired electrons,  $p + q = x = 1, 2, \dots, 8, 9$  or 10). Here  $\Delta t < P$ .

$d^x$ ions	Distribution of $d^x$ electrons in $e$ and $t_2$ orbitals		$e^p t_2^q$ configuration	$n$	$CFSE = -0.27 \Delta_0 \times p + 0.18 \Delta_0 \times q$ $= [-0.27 \times p + 0.18 \times q] \Delta_0$
	$e$ (Lower energy)	$t_2$ (Higher energy)			
$d^1$	$\uparrow$ —	— — —	$e^1 t_2^0$	1	$[-0.27 \times 1 + 0.18 \times 0] \Delta_0 = -0.27 \Delta_0$
$d^2$	$\uparrow \uparrow$	— — —	$e^2 t_2^0$	2	$[-0.27 \times 2 + 0] \Delta_0 = -0.54 \Delta_0$
$d^3$	$\uparrow \uparrow$	$\uparrow$ — —	$e^2 t_2^1$	3	$[-0.27 \times 2 + 0.18 \times 1] \Delta_0 = -0.36 \Delta_0$
$d^4$	$\uparrow \uparrow$	$\uparrow \uparrow$ —	$e^2 t_2^2$	4	$[-0.27 \times 2 + 0.18 \times 2] \Delta_0 = -0.18 \Delta_0$
$d^5$	$\uparrow \uparrow$	$\uparrow \uparrow \uparrow$	$e^2 t_2^3$	5	$[-0.27 \times 2 + 0.18 \times 3] \Delta_0 = 0.0 \Delta_0$
$d^6$	$\uparrow \downarrow \uparrow$	$\uparrow \uparrow \uparrow$	$e^3 t_2^3$	4	$[-0.27 \times 3 + 0.18 \times 3] \Delta_0 = -0.27 \Delta_0$
$d^7$	$\uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow \uparrow$	$e^4 t_2^3$	3	$[-0.27 \times 4 + 0.18 \times 3] \Delta_0 = -0.54 \Delta_0$
$d^8$	$\uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	$e^4 t_2^4$	2	$[-0.27 \times 4 + 0.18 \times 4] \Delta_0 = -0.36 \Delta_0$
$d^9$	$\uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \uparrow$	$e^4 t_2^5$	1	$[-0.27 \times 4 + 0.18 \times 5] \Delta_0 = -0.18 \Delta_0$
$d^{10}$	$\uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	$e^4 t_2^6$	0	$[0.27 \times 4 + 0.18 \times 6] \Delta_0 = 0.0 \Delta_0$

Crystals field stabilisation energies of  $d^x$  configuration ( $x = 1$  to 10) of the central metal ion in high spin tetrahedral complexes

We have seen that according to CFT, under the influence of four ligands approaching towards the central metal ion during the formation of a high spin tetrahedral complex, the  $d$ -orbitals of the central metal ion are split into lower energy doublet  $e$  orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals) and higher energy triplet  $t_2$  orbitals ( $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals). The energy gap between  $e$  and  $t_2$  orbitals is denoted by  $\Delta t$  which is equal to  $0.45 \Delta_0$ . The energy of  $e$  orbitals is lowered by  $0.6 \Delta t = 0.6 \times 0.45 \Delta_0 = 0.27 \Delta_0$  and that of  $t_2$  orbitals is raised by  $0.4 \Delta t = 0.4 \times 0.45 \Delta_0 = 0.18 \Delta_0$  relative to the energy of no splitting state. Thus each electron occupying  $e$  orbitals decreases the energy of  $d$ -orbitals by  $-0.6 \Delta t = -0.27 \Delta_0$  while that going to  $t_2$  orbitals increases its energy by  $+0.4 \Delta t = +0.18 \Delta_0$ . – and + signs indicate respectively the decrease and increase in the energy of  $d$ -orbitals caused by their splitting under the influence of four ligands. Now let us consider a  $d^x$  ion containing  $e^p t_2^q$  configuration in which  $p$  is the number of electrons in  $e$  set of orbitals and  $q$  is the number of electrons in  $t_2$  set of orbitals and  $x = p + q$ . Obviously:

CFSE for  $e^p t_2^q$  configuration = Loss in energy due to  $p$  electrons in  $e$  set of orbitals + gain in energy due to  $q$  electrons in  $t_2$  set of orbitals.

or

$$\begin{aligned} CFSE &= -0.27 \Delta_0 \times p + 0.18 \Delta_0 \times q \\ &= [-0.27 \times p + 0.18 \times q] \Delta_0 \end{aligned}$$

### 3.12: Optical Properties of Coordination Compounds (Color)

Last updated: May 4, 2021

[PDF](#) [Downloads](#) [Submit Adoption Report](#) [Peer Review](#) [Donate](#)

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow (Figure 3.12.1).

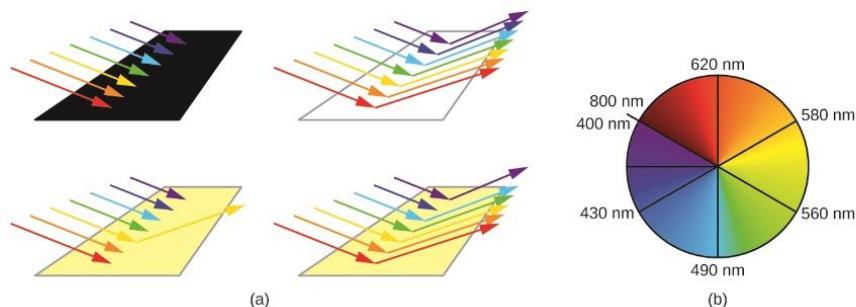


Figure 3.12.1: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (CC BY 4.0; OpenStax)

The blue color of the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 3.12.2). If white light (ordinary sunlight, for example) passes through  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  solution, some wavelengths in the light are absorbed by the solution. The  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through a  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  solution.

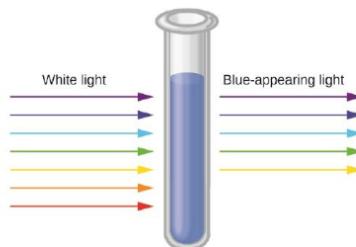


Figure 3.12.2: A solution of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue. (CC BY 4.0; OpenStax)

Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the complementary color wheel.



Figure 3.12.3: The partially filled d orbitals of the stable ions  $\text{Cr}^{3+}(\text{aq})$ ,  $\text{Fe}^{3+}(\text{aq})$ , and  $\text{Co}^{2+}(\text{aq})$  (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a **d-d transition** (Figure 3.12.4). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of  $\Delta_0$ .

Activ

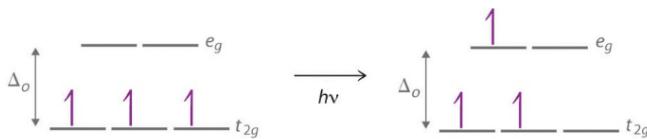


Figure 3.12.4: In a d-d transition of an octahedral complex, an electron in one of the  $t_{2g}$  orbitals of an octahedral complex such as the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion absorbs a photon of light with energy equal to  $\Delta_o$ , which causes the electron to move to an empty or singly occupied  $e_g$  orbital.

#### Example 3.12.1: Colors of Complexes

The octahedral complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has a single  $d$  electron. To excite this electron from the ground state  $t_{2g}$  orbital to the  $e_g$  orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to  $\Delta_o$  and occurs at 499 nm. Calculate the value of  $\Delta_o$  in Joules and predict what color the solution will appear.

#### Solution

We can convert wavelength to frequency:

$$\nu = \frac{c}{\lambda}$$

$$= \frac{3.00 \times 10^8 \text{ m/s}}{(499 \text{ nm}) \times \left( \frac{1 \text{ m}}{10^9 \text{ nm}} \right)}$$

$$= 6.01 \times 10^{14} \text{ s}^{-1} = 6.01 \times 10^{14} \text{ Hz}$$

And then using Planck's equation that related the frequency of light to energy

$$E = h\nu$$

so

$$E = (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) \times (6.01 \times 10^{14} \text{ Hz})$$

$$= 3.99 \times 10^{-19} \text{ J}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Note: This is the energy for one transition (i.e., in one complex). If you want to calculate the energy in J/mol, then you have to multiply this by Avogadro's number ( $N_A$ ).

#### Exercise 3.12.1

A complex that appears green, absorbs photons of what wavelengths?

**Answer**

#### Color Depends on Oxidation State

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 3.12.4, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.



Watch this [video](#) of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

#### Color Depends on Ligand Field

The specific ligands coordinated to the metal center also influence the color of coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of  $\Delta_o$ , which depends on the structure of the complex. For example, the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  has strong-field ligands and a relatively large  $\Delta_o$ . Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color. For example, the iron(II) complex  $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$  appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 3.12.5). In contrast, the low-spin iron(II) complex  $\text{K}_4[\text{Fe}(\text{CN})_6]$  appears pale yellow because it absorbs higher-energy violet photons.

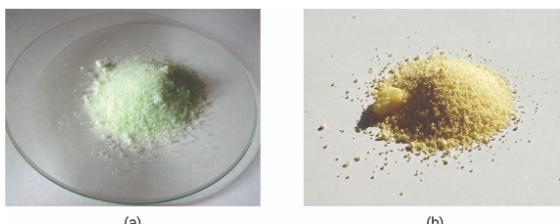


Figure 3.12.5: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d<sup>6</sup> iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum. (CC BY 4.0; OpenStax)

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large  $\Delta_{\text{oct}}$ ). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

*Strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom and transition metal coordination compounds with these ligands are typically yellow, orange, or red because they absorb higher-energy violet or blue light. Coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.*

### Example 3.12.2: Matching Colors to Ligand Fields

Identify the color (either blue, green, yellow, or orange) for the following complex ions formed with  $\text{Co}^{3+}$ :

- a.  $[\text{Co}(\text{CN})_6]^{3-}$
- b.  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- c.  $[\text{CoF}_6]^{4-}$
- d.  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

#### Solution

Each of these complex ions has the same metal with the same oxidation state, so the ligand field is the relevant factors. Each of the complex ions also has an octahedral ligand field, so we only need to compare the strength of the ligands in determining  $\Delta_o$ , which is determined by the spectrochemical series.

The ligands for each complex ions are: (a)  $\text{CN}^-$ , (b)  $\text{NH}_3$ , (c)  $\text{F}^-$  and (d)  $\text{H}_2\text{O}$ , which are ranked in increasing  $\Delta_o$  magnitude:

$$\text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- \quad (3.12.1)$$

The relationship between the  $\Delta_o$  and the energy of the photons are absorbed in the d-d transition of  $\text{Co}^{3+}$  is given by equating Planck's equation to the crystal field splitting parameter:

$$E = h\nu = \frac{hc}{\lambda} = \Delta_o \quad (3.12.2)$$

Now, we need to get a relative correlation between observed color (to the eye) and the wavelength of the light that is absorbed. From the complementary color wheel in Figure 3.12.1 we get the following relationships (arranged from highest energy absorbed to lowest):

- 400-nm Violet light absorbed → Green-yellow observed
- 430-nm Blue light absorbed → Orange observed
- 450-nm Blue light absorbed → Yellow observed
- 490-nm Blue-green light absorbed → Red observed
- 570-nm Yellow-green light absorbed → Violet observed
- 580-nm Yellow light absorbed → Dark blue observed
- 600-nm Orange light absorbed → Blue observed
- 650-nm Red light absorbed → Green observed

Of the four possible colors given in the problem (blue, green, yellow, and orange), the corresponding colors that are absorbed are (600 nm, 650 nm, 450 nm, and 430, respectively). From Equation 3.12.2, the smaller  $\lambda$  of absorbed light corresponds to the higher energy photons, so we would correlate the four wavelengths of absorbing photons in terms of increasing energy to observed color:

$$\underbrace{650 \text{ nm}}_{\text{green}} < \underbrace{600 \text{ nm}}_{\text{blue}} < \underbrace{450 \text{ nm}}_{\text{yellow}} < \underbrace{430 \text{ nm}}_{\text{orange}} \quad (3.12.3)$$

Now, just correlate the ranking in Equation 3.12.3 to the ranking in Equation 3.12.1:

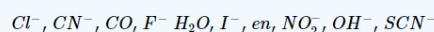
$$\underbrace{\text{F}^-}_{\text{green}} < \underbrace{\text{H}_2\text{O}}_{\text{blue}} < \underbrace{\text{NH}_3}_{\text{yellow}} < \underbrace{\text{CN}^-}_{\text{orange}}$$

and more specifically in terms of the original question

$$\underbrace{[\text{CoF}_6]^{4-}}_{\text{green}} < \underbrace{[\text{Co}(\text{H}_2\text{O})_6]^{3+}}_{\text{blue}} < \underbrace{[\text{Co}(\text{NH}_3)_6]^{3+}}_{\text{yellow}} < \underbrace{[\text{Co}(\text{CN})_6]^{3-}}_{\text{orange}}$$

### Exercise 3.12.1

If a complex ion  $[\text{M}(\text{NH}_3)_6]^{2+}$  is red in solution, which of the following ligands, after a ligand exchange reaction to substitute for the ammine ligands, may shift the solution to be orange? More than one answer is possible.



### Answer

A coordination compound of the  $\text{Cu}^+$  ion has a  $d^{10}$  configuration, and all the  $e_g$  orbitals are filled. To excite an electron to a higher level, such as the  $4p$  orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing  $[\text{Cu}(\text{CN})_2]^-$ , for example, is colorless. On the other hand, octahedral  $\text{Cu}^{2+}$  complexes have a vacancy in the  $e_g$  orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and  $\text{Cu}^{2+}$  complexes are almost always colored—blue, blue-green violet, or yellow (Figure 3.12.6). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

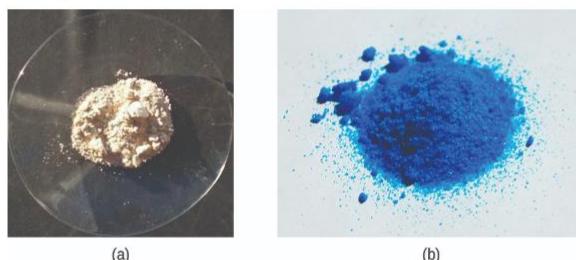


Figure 3.12.6: (a) Copper(I) complexes with  $d^{10}$  configurations such as  $\text{CuI}$  tend to be colorless, whereas (b)  $d^9$  copper(II) complexes such as  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  are brightly colored. (CC BY 4.0; OpenStax)

### Gems

A ruby is a pink to blood-red colored gemstone that consist of trace amounts of chromium in the mineral corundum  $\text{Al}_2\text{O}_3$ . In contrast, emeralds are colored green by trace amounts of chromium within a  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  matrix. We can now understand why emeralds and rubies have such different colors, even though both contain  $\text{Cr}^{3+}$  in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different ( $\text{Al}_2\text{O}_3$  in rubies and  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes  $\Delta_o$  relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large  $[\text{Si}_6\text{O}_{18}]^{12-}$  silicate rings; this results in decreased d orbital–ligand interactions and a smaller  $\Delta_o$ . Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of  $\text{Cr}^{3+}$  impurities in octahedral sites in an otherwise colorless metal oxide lattice.

The absorbance spectrum of a ruby is shown Figure 3.12.7; *left*. The number and positions of the peaks in the spectrum is determined by the electronic structure of the compound, which in this case depends upon the identity of the metal and the identities, number, and geometry of the surrounding ions. Crystal field theory may be used to predict the electronic structure and thus the absorbance spectrum. If white light is shown on the gem, the absorbance spectrum indicates which wavelengths of light are removed. In this case, there are strong bands centered at 414 and 561 nm. These wavelengths correspond with blue and yellow-green light, respectively. For the most part, these colors are not present in the light reaching ones eyes. An alternative way to express this concept is to recognize that the spectrum of light reaching the eye is the product of the spectrum of the incident light (white light) and the **transmittance spectrum**. For this ruby, the transmittance spectrum has a peak at 481 nm and a broad plateau past 620 nm. (Note that there is significant attenuation of the light across the entire spectrum.) Thus only light with wavelengths near 481 nm (cyan) and greater than 620 nm (red) reach the eye.

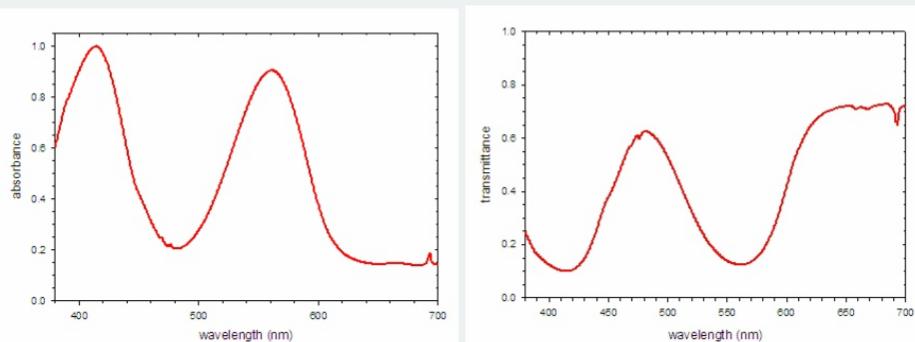
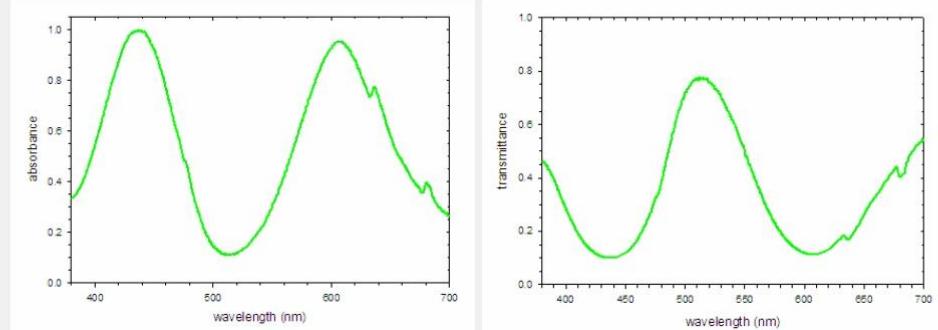


Figure 3.12.7: (left) Absorbance spectrum of a ruby from Chanthaburi, Thailand. (right) corresponding Transmittance spectrum of a ruby from Chanthaburi, Thailand. Data obtained from the [Caltech Mineral Spectroscopy Server](#)

A similar analysis of the spectrum of an emerald is possible. The absorbance spectrum (Figure 3.12.8; *left*) shows strong bands at 438 and 606 nm, which remove blue and orange light, respectively. The light that is not absorbed is shown by the transmittance spectrum, which indicates the dominant band of light reaching the eye is centered at 512 nm (green light) with smaller contributions from the far blue and red portions of the spectrum. This combination of wavelengths produces a deep green color.



(left) Absorbance spectrum of an emerald from Malyshevo, Ural, Russia. (right) Corresponding transmittance spectrum of the emerald from Malyshevo, Ural, Russia.  
Data obtained from the [Caltech Mineral Spectroscopy Server](#)

## Summary

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

## Magnetic Properties of Coordination Complexes

**Diamagnetic Compounds:** Those, which tend to move out of a magnetic field.

Example: N<sub>2</sub>

**Paramagnetic Compounds:** Those, which tend to move into a magnetic field.

Example: O<sub>2</sub>

The extent of paramagnetism is measured in terms of the **magnetic moment**,  $\mu$ . The larger the magnitude of  $\mu$ , greater the paramagnetism of the compound.

Magnetic moment has contributions from spin and orbital angular momentum. A non-spherical environment may lead to quenching of the contribution from orbital angular momentum.

However, the spin-only magnetic moment survives in all cases and is related to the total number of unpaired electrons.

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} = 2\sqrt{S(S+1)} = \sqrt{n(n+2)} \text{ BM}$$

## Magnetic Properties of Coordination Complexes

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)} = \sqrt{n(n+2)} \text{ BM}$$

Ion	# of unpaired electrons (n)	S	Predicted $\mu_{\text{eff}}$ values
$\text{Ti}^{3+}$	1	$\frac{1}{2}$	$\sqrt{3} = 1.73$
$\text{V}^{3+}$	2	1	$\sqrt{8} = 2.83$
$\text{Cr}^{3+}$	3	$\frac{3}{2}$	$\sqrt{15} = 3.87$
$\text{Mn}^{3+}$	4	2	$\sqrt{24} = 4.90$
$\text{Fe}^{3+}$	5	$\frac{5}{2}$	$\sqrt{35} = 5.92$

If there is a possibility for contribution from the orbital angular momentum,

$$\mu = \sqrt{L(L+1) + 4S(S+1)}$$

For a given value of the orbital quantum number  $l$ , the magnetic quantum number  $m$  can have any values from  $-l$  to  $+l$  and  $L = \text{sum of } m$

For  $d$  orbital electrons,  $m = 2, 1, 0, -1, -2$

If there is only one electron in the  $d$  orbitals,  $L = 2$

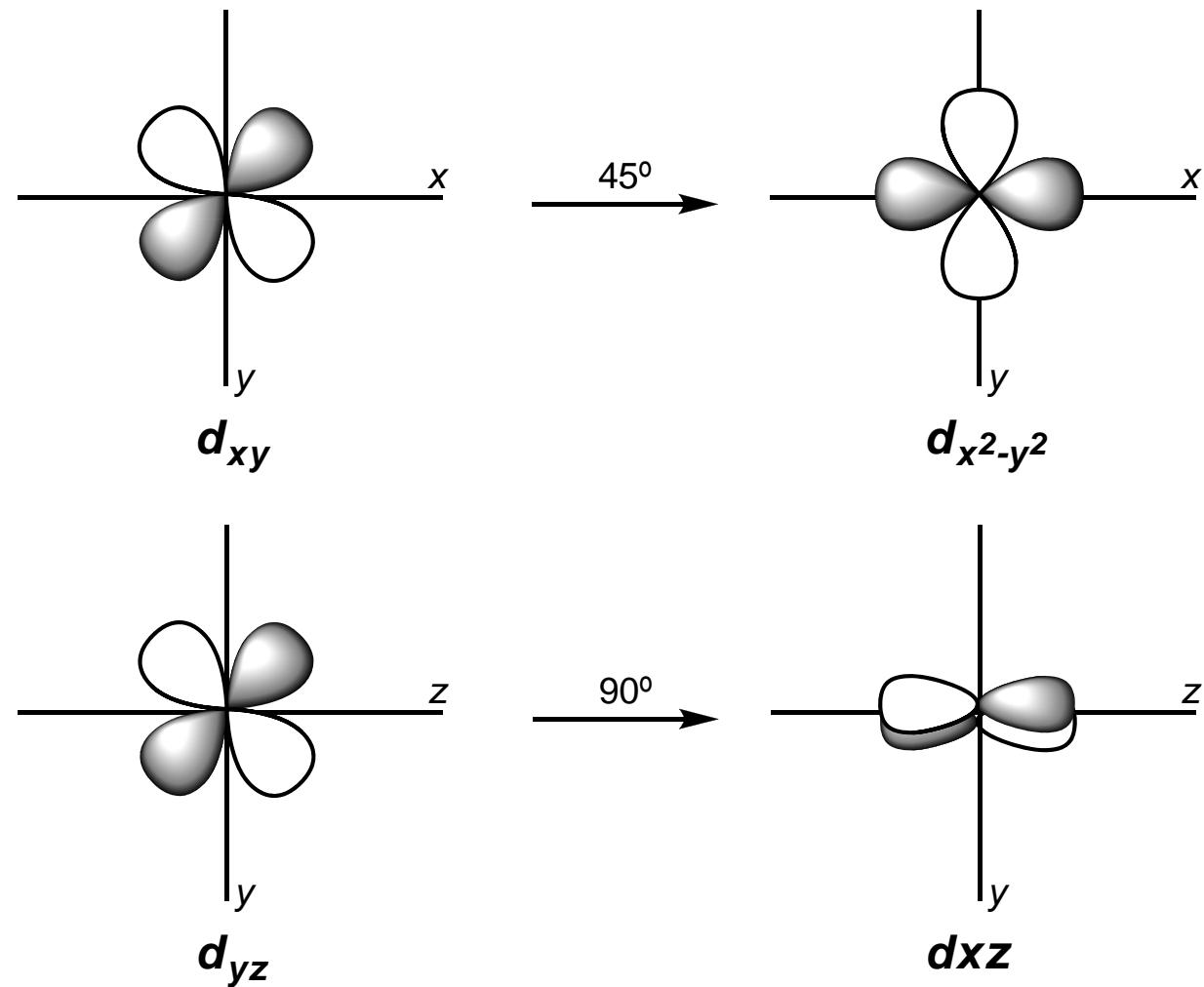
## Magnetic Properties of Coordination Complexes

config $3d^n, n =$	$\mu_{s+o}$ $= [L(L+1) + 4S(S+1)]^{1/2}$ B.M.	$\mu_s$ $= [4S(S+1)]^{1/2}$ B.M.	$\mu_{eff}$ obs at 300 K
1	3.00	1.73	1.7 – 1.8
2	4.47	2.83	2.8 – 2.9
3	5.20	3.87	3.7 – 3.9
4	5.48	4.90	4.8 – 5.0
5	5.92	5.92	5.8 – 6.0
6	5.48	4.90	5.1 – 5.7
7	5.20	3.87	4.3 – 5.2
8	4.47	2.83	2.9 – 3.9
9	3.00	1.73	1.7 – 2.2
10	0.00	0.00	0

$K_3[Fe(CN)_6]$  has a magnetic moment of 2.3 B.M., which is a  $d^5$  low-spin complex with one unpaired electron.

$[Fe(H_2O)_6]^{3+}$  ions are high-spin with 5 unpaired electrons. It has a magnetic moment of 6 B.M.

## Magnetic Properties of Coordination Complexes



For an octahedral complex, orbital contributions are possible only when the  $t_{2g}$  orbitals are differentially occupied and for a tetrahedral complex the  $t_2$  orbitals have to be differentially occupied.

## Magnetic Properties of Coordination Complexes

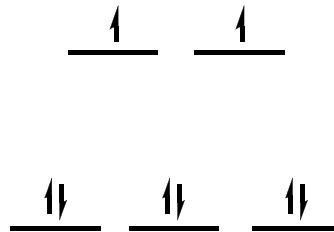
Consider a Ni(II) complex, electronic configuration is  $d^8$

For a free metal ion,



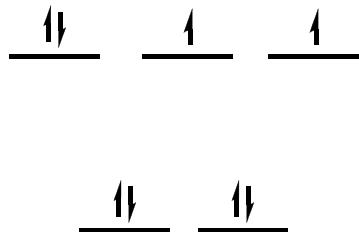
$$S = 1, L = 3 \text{ and } \mu = \sqrt{L(L+1) + 4S(S+1)} = 4.47 \text{ B.M.}$$

For an octahedral complex,



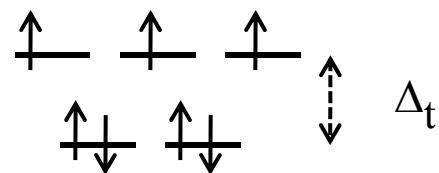
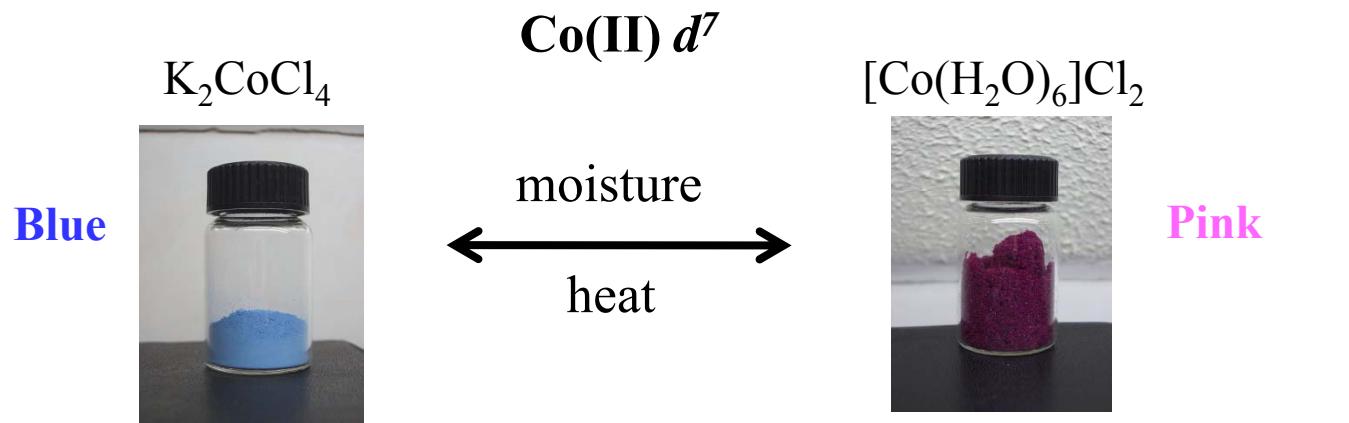
Orbital contribution is zero and magnetic moment is close to the spin only value

For a tetrahedral complex,

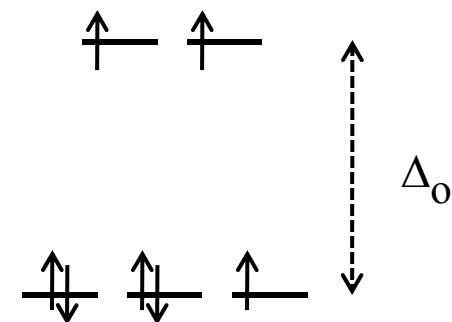


Magnetic moment is higher than the spin only value as there is positive orbital contribution

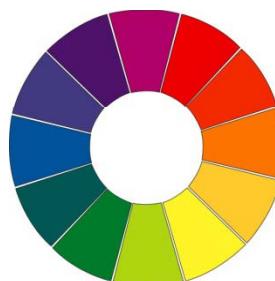
## Magnetic Properties of Coordination Complexes



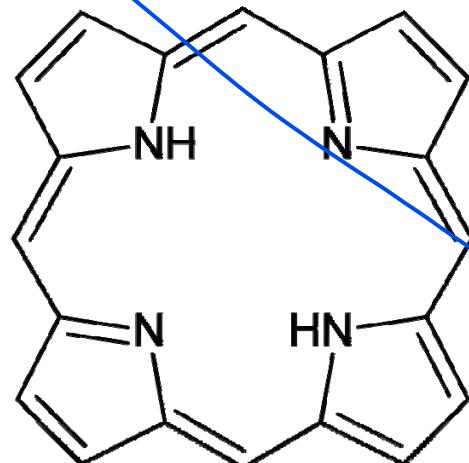
No orbital contribution  
Magnetic moment  $\mu = 3.73 \text{ BM}$



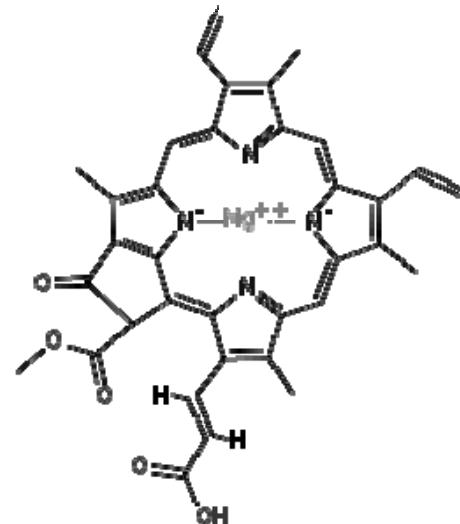
Orbital contribution  
Magnetic moment  $\mu = 4.2 \text{ B.M.}$   
higher than spin-only value



## Coordination Complexes in Biological Systems

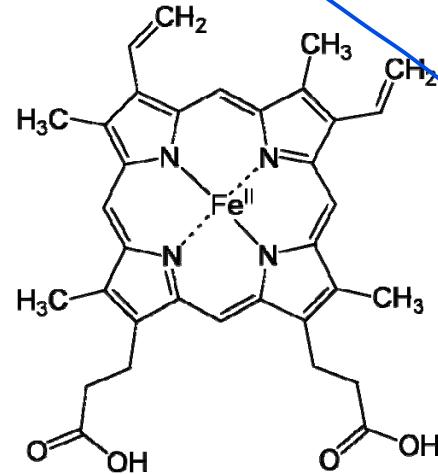


Porphine

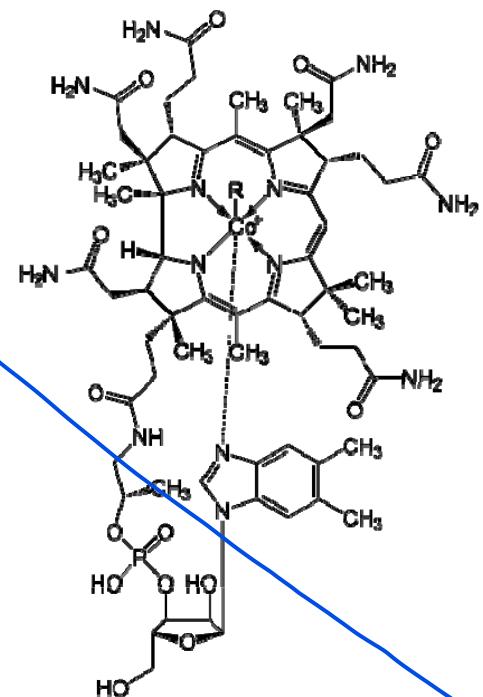


Chlorophyll *c*2

Porphyrins are heterocyclic macrocycles composed of four modified interconnected pyrrole subunits. They form coordination complexes with metal ions and are found in biological systems.



Heme B



Cobalamin

# Hemoglobin and Myoglobin

## Hemoglobin (Hb)

- MW= 64,500 g
- $\alpha_2\beta_2$
- $\alpha= 141$  residues
- $\beta= 146$  residues
- active site: Fe(por)
- function: cooperatively binds and transports O<sub>2</sub>

## Myoglobin (Mb)

- MW= 17,800 g
- $\alpha$
- $\alpha= 161$  residues
- active site: Fe(por)
- function: binds and transports O<sub>2</sub>

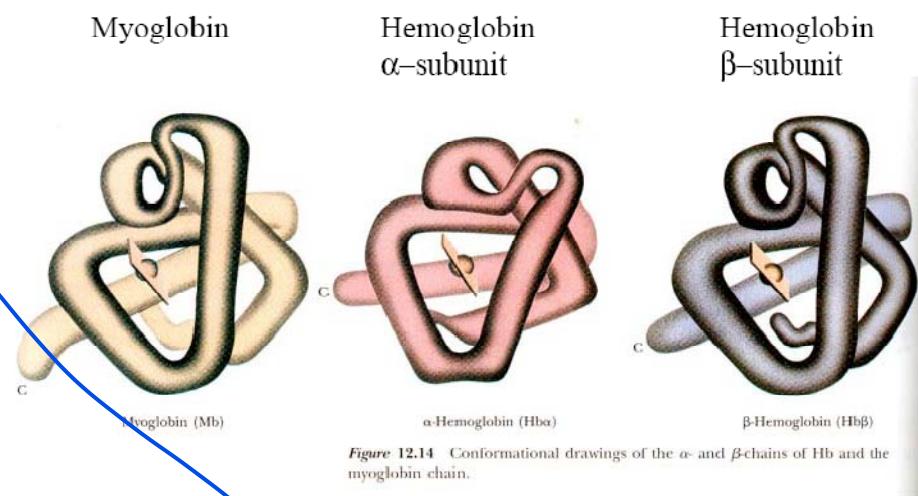
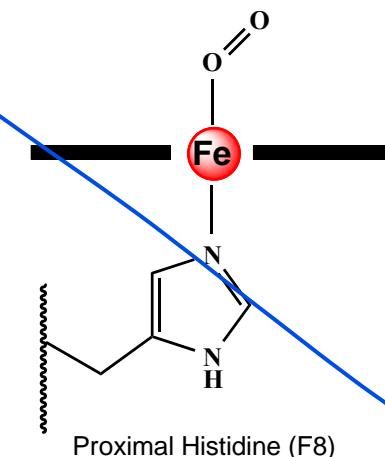
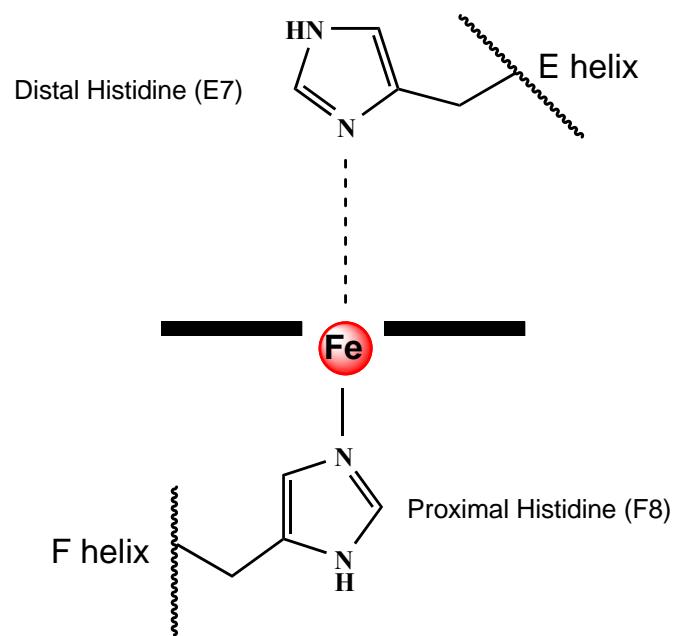
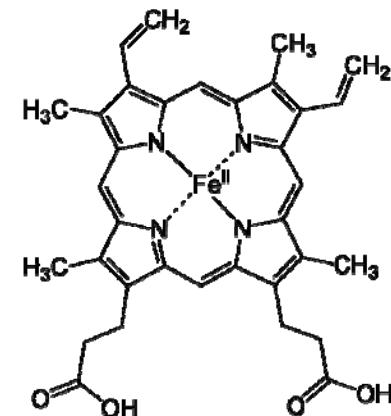
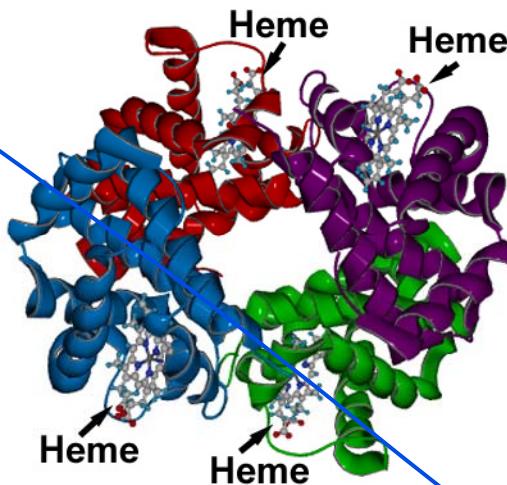


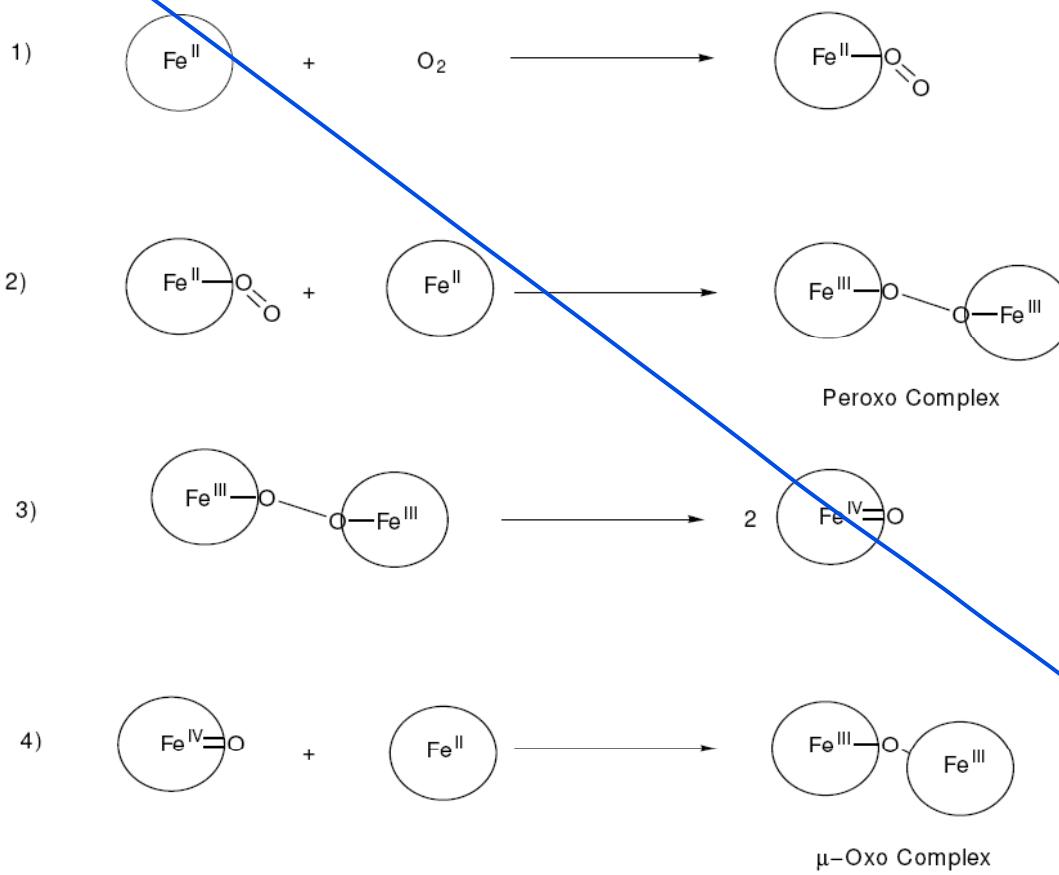
Figure 12.14 Conformational drawings of the  $\alpha$ - and  $\beta$ -chains of Hb and the myoglobin chain.

Notice that the hemoglobin is essentially a tetramer of myoglobin. (There are four myoglobin like units in hemoglobin.)

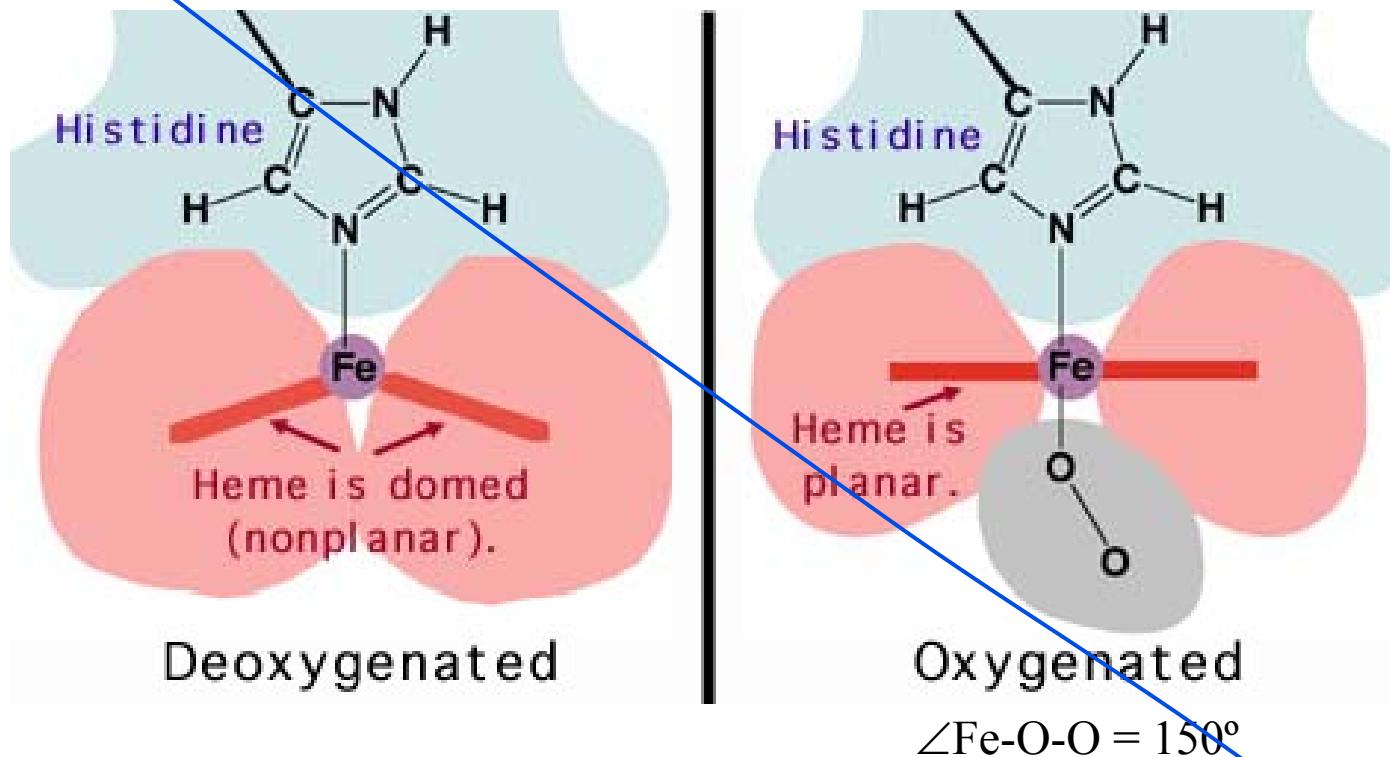
## Oxygenated and Deoxygenated Forms



## The Role of the Protein



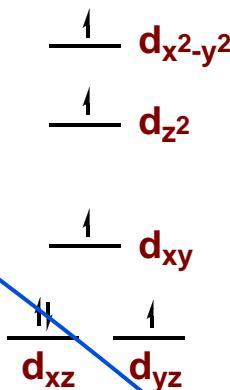
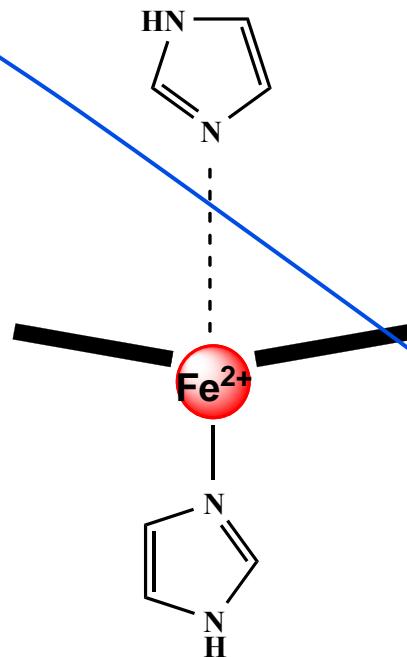
## Hemoglobin and Myoglobin



Raman Spectra gives  $\nu_{o-o}$  at  $1105\text{ cm}^{-1}$ . indicating that the complex should be in a superoxide state

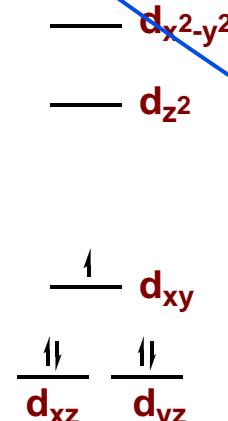
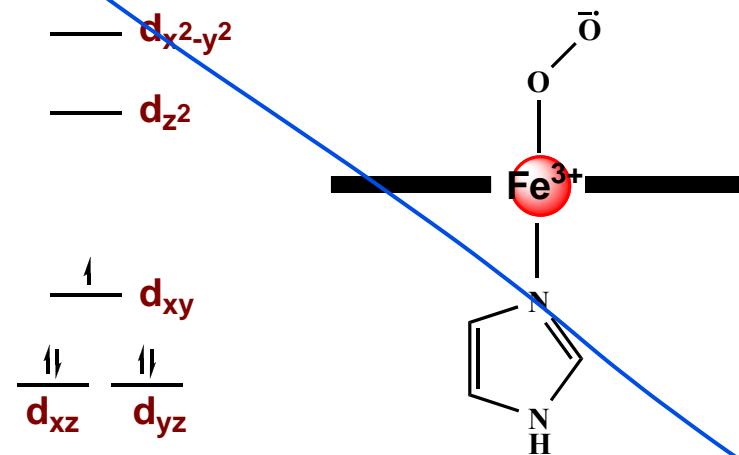
	$O_2$	$O_2^-$	$O_2^{2-}$
$\nu_{o-o}\text{ (cm}^{-1}\text{)}$	1560	1100	850-740

## Coordination Environment of Fe



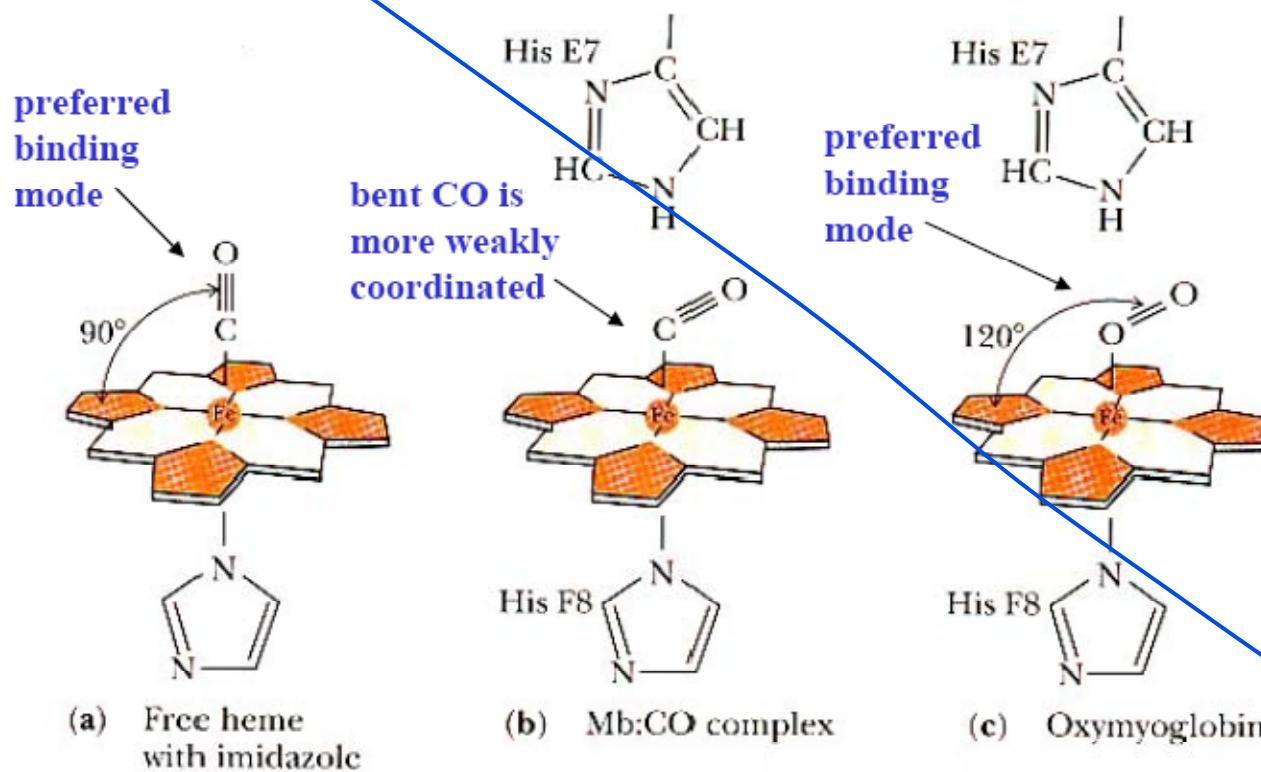
Total unpaired electrons = 4,  $S = 2$   
Deoxygenated form is high-spin and paramagnetic

Total unpaired electrons = 1,  $S = 1/2$   
Oxygenated form is low-spin  
The magnetic moment of  $\text{Fe}^{3+}$  and the superoxide radical involves in anti-ferromagnetic coupling and the oxygenated complex is not paramagnetic



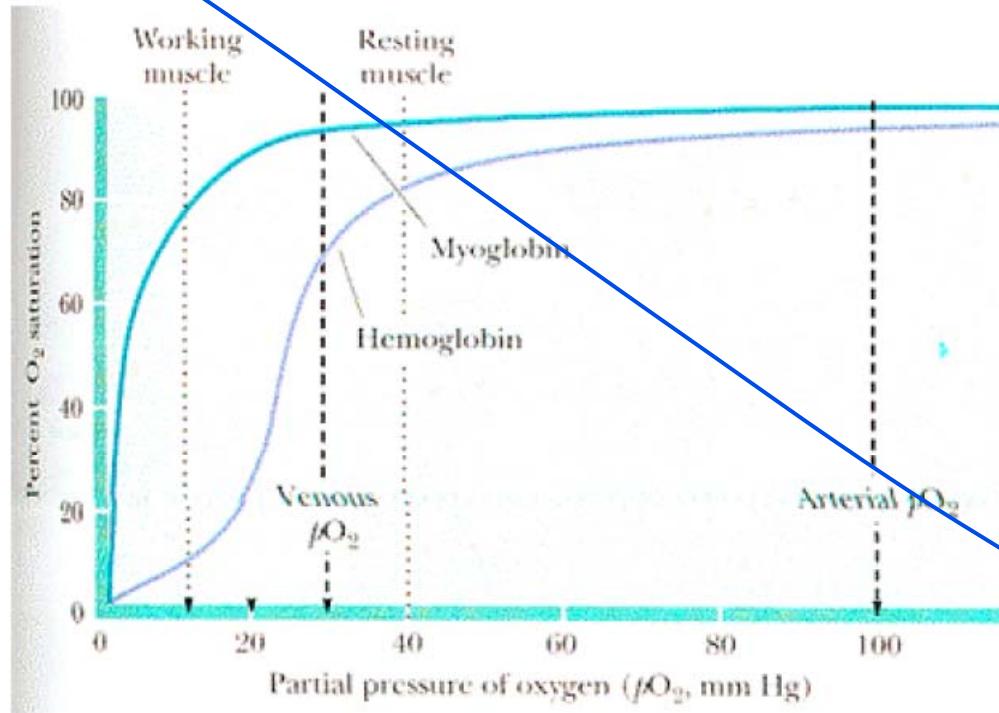
# Hemoglobin and Myoglobin

## Role of the distal base



# Hemoglobin and Myoglobin

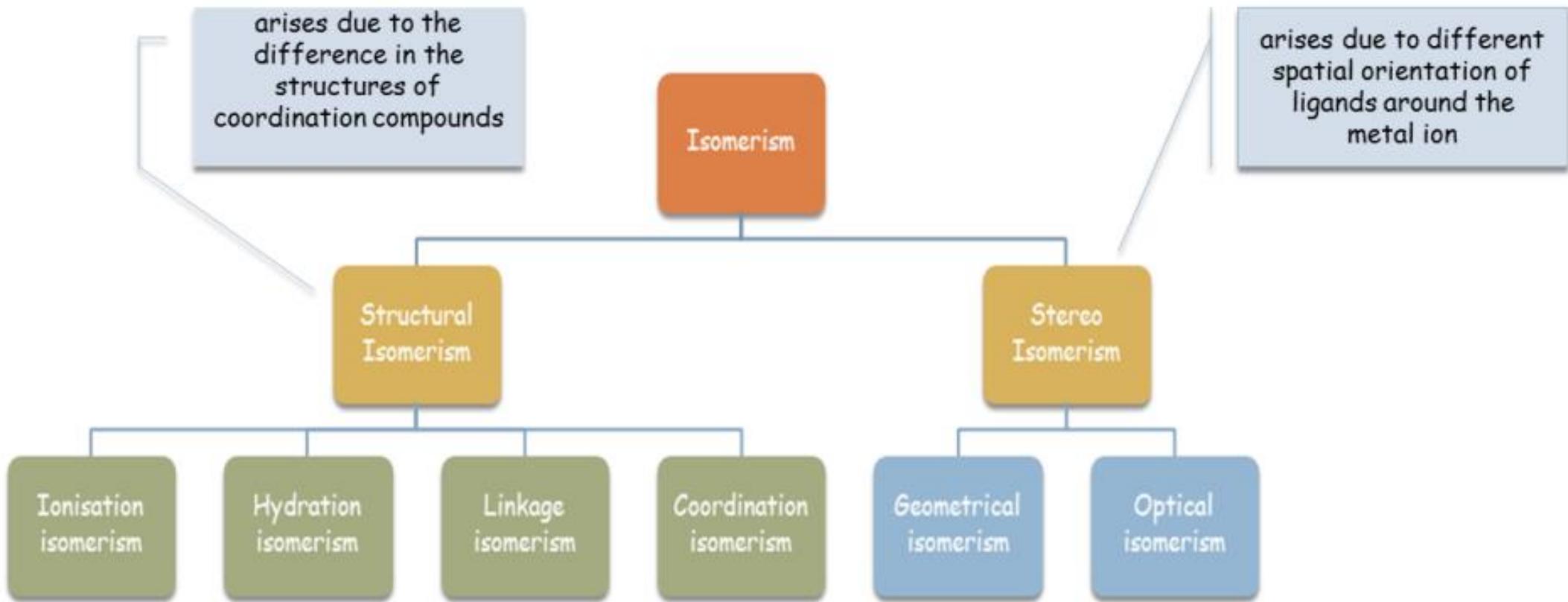
Cooperative Binding Curve for Hb





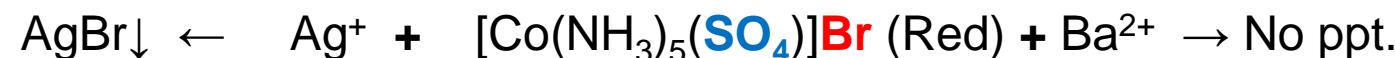
# Isomerism in Coordination Compound

Compounds that have the same chemical formula but different structural arrangements are called isomers. Due to their complicated formulae of many coordination compounds, the variety of bond types and the number of shapes possible, many different types of isomerism occur.



## **Ionization Isomerism:**

- This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it. (i.e. exchange of ligated anion with a counterion).
- e.g.  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$
- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is red-violet. An aqueous solution gives a white precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  solution, thus confirming the presence of free  $\text{SO}_4^{2-}$  ions.
- In contrast  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$  is red. A solution of this complex does not give a positive sulphate test with  $\text{BaCl}_2$ . It does give a cream-coloured precipitate of  $\text{AgBr}$  with  $\text{AgNO}_3$ , thus confirming the presence of free  $\text{Br}^-$  ions.



- other examples are  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$   
 $[\text{Co}(\text{en})_2\text{Cl}.\text{SCN}]\text{NO}_2$  and  $[\text{Co}(\text{en})_2\text{Cl}.\text{NO}_2]$  SCN and  $[\text{Co}(\text{en})_2\text{NO}_2.\text{SCN}]\text{Cl}$

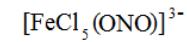
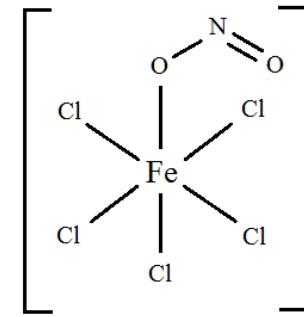
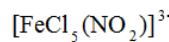
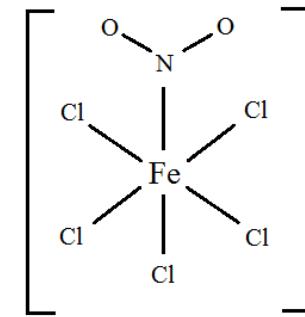
## Hydrate isomerism

- There is a replacement of co-ordinated group by water of hydration.
- They differ in chemical and physical properties
- Coordination number remains same.
- Differ in coordinated water molecules
- e.g. Three isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are known. From conductivity measurements and quantitative precipitation of the ionized chlorine, they have been given the following formulae:
  - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  : violet (three ionic chlorines)
  - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  : green (two ionic chlorines)
  - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$  : dark green (one ionic chlorine)

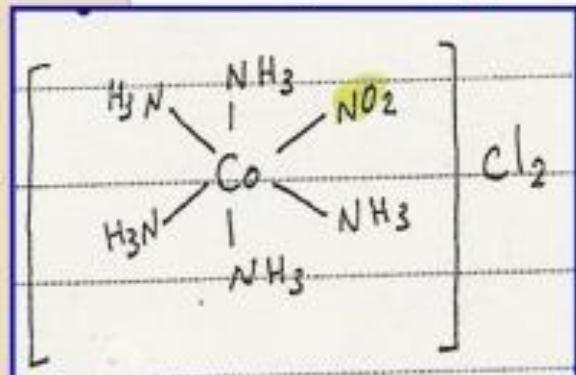
## Linkage Isomerism:

- Certain ligands contain more than one atom which could donate an electron pair. In the  $\text{NO}_2^-$  ion, either N or O atoms could act as the electron pair donor.
- Thus there is the possibility of isomerism.
- Two different complexes  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  have been prepared, each containing the  $\text{NO}_2^-$  group in the complex ion.

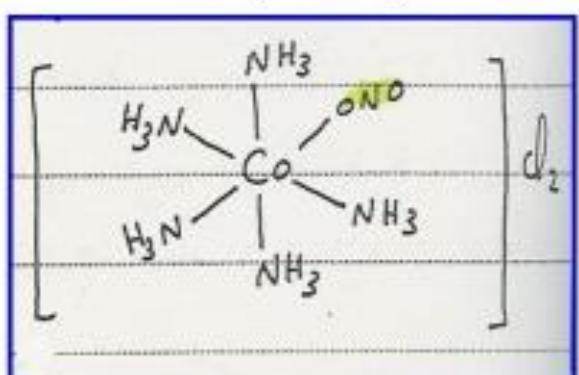
### LINKAGE ISOMERS



**There is this kind of isomerism when the coordination group contains the two atoms or more can be consistent with the central atom, such as for example a group (nitrite) can be linked through the nitrogen atom, known as nitro or linked through an oxygen atom known as (nitrito) such as :**



**nitropentaammine Cobalt (III) Chloride  
(yellow)**

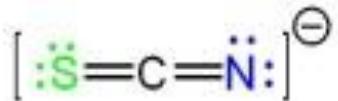


**nitritopentaammine Cobalt (III) Chloride  
(read)**

### Linkage isomers

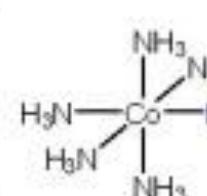
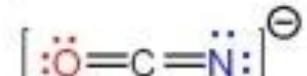
- Occur when a ligand has two alternative donor atoms.
- Example 1:

Thiocyanate ion



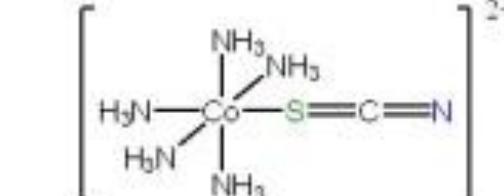
Thiocyanato  $\text{NCS}^-$  →  
Isothiocyanato  $\text{SCN}^-$  →  
cyanato  $\text{NCO}^-$  →  
isocyanato  $\text{OCN}^-$  →

cyanate ion



Pentaammineisothiocyanatocobalt(III)

and



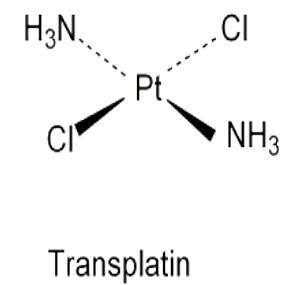
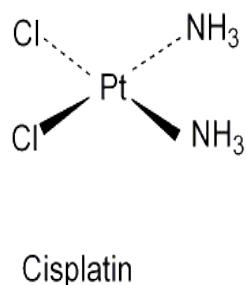
pentaamminethiocyanatocobalt(III)

## Coordination isomerism

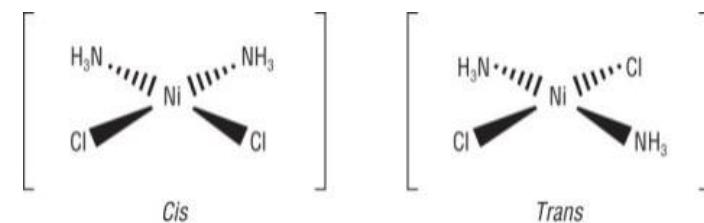
- When both the positive and negative ions are complex ions, isomerism may be caused by the interchange of ligands between the complex anion and the complex cation.
- Ligands are distributed differently between two metal centres.
- e.g.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$  octahedral  
 $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$  square planar  
 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{PtCl}(\text{NH}_3)_3][\text{PtCl}_3(\text{NH}_3)]$

## Geometric isomerism:

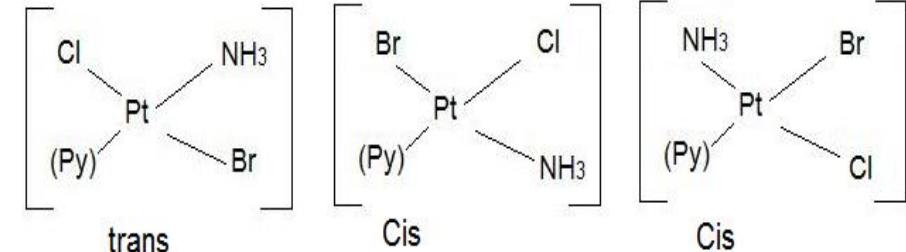
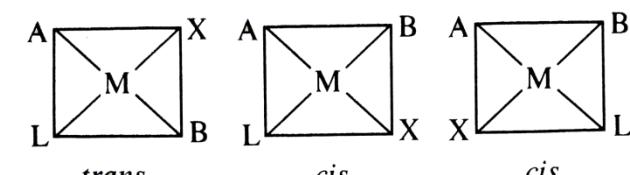
- In **disubstituted complexes**, the substituted groups may be adjacent or opposite to each other. This gives rise to geometric isomerism. Thus square planar complexes such as  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$  can be prepared in two forms, cis and trans. When the chlorine atoms are adjacent to each other it is called cis form. While when two chlorine atoms are opposite it is called transform.
- This type of isomerism takes place mainly in **heteroleptic complexes** because of the different possible geometric arrangements of ligands around the central metal atom.
- This type of isomerism is mainly found in coordination compounds with coordination **numbers 4 and 6**.
- In a square planar complex (i.e. coordination compounds with coordination number 4 which have  $[\text{MX}_2\text{L}_2]$  type formula (X and L are unidentate ligands), the two ligands X may be present adjacent to each other in a cis isomer, or opposite to each other to form a trans isomer.
- Square planar complex with **MABXL** type formula (where A, B, X, L are unidentate ligands) show three isomers-two cis and one trans.
- Cis trans isomerism is not possible for a tetrahedral geometry.



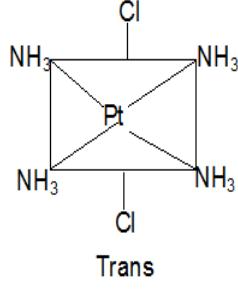
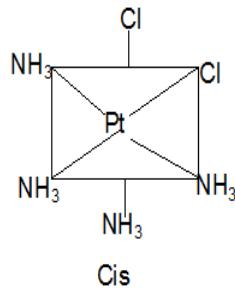
**$[\text{MX}_2\text{L}_2]$**



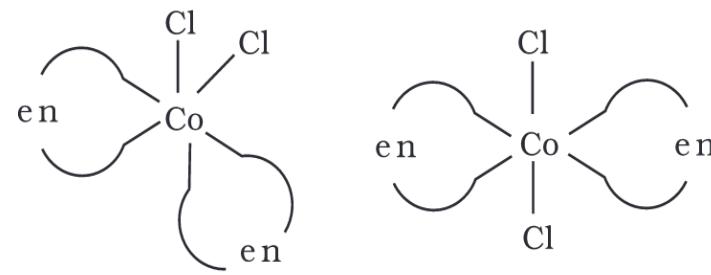
**$[\text{MX}_2\text{L}_2]$**



- But octahedral complexes do show cis trans isomerism. In complexes with formula  $[MX_2L_4]$  type, two ligands X may be oriented cis or trans to each other.
- This type of isomerism is also observed when bidentate ligands L–L [e.g.,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (en)] are present in complexes with  $[MX_2(L-L)_2]$  type formula
- There is another type of geometrical isomerism which occurs in octahedral coordination entities with  $[\text{Ma}_3\text{b}_3]$  type formula. Examples is  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ .
- If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer.
- When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer
- **Facial Isomers:** A set of three ligands (similar) arranged on an octahedron in all *cis* – fashion.
- **Meridional Isomers:** A set of three similar ligands arranged on an octahedron with one pair *trans*

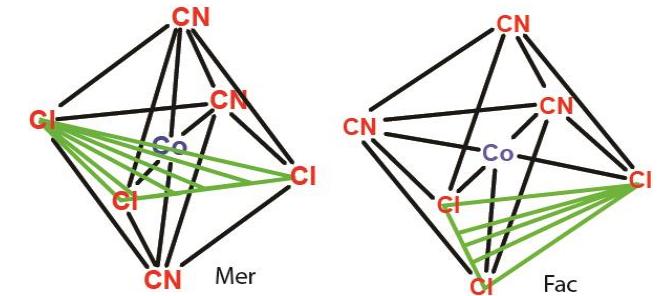


$[\text{MX}_2\text{L}_4]$



Geometrical isomers (*cis* and *trans*) of  $[\text{CoCl}_2(\text{en})_2]$

$[\text{MX}_2(L-L)_2]$



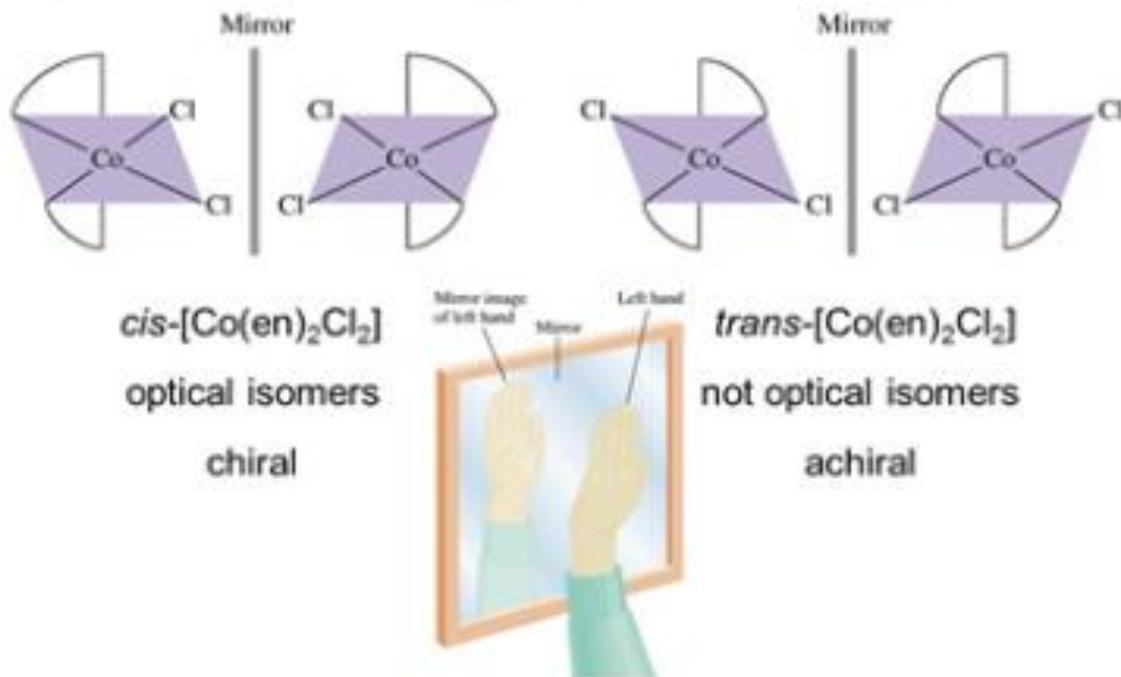
$[\text{Ma}_3\text{b}_3]$

## Optical Isomerism

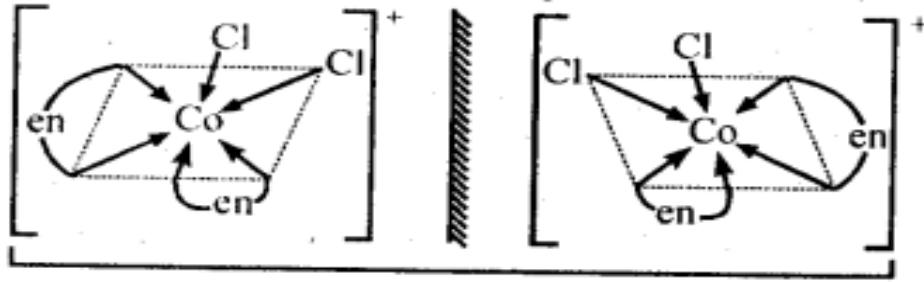
- The complexes which are non-superimposable on their mirror images are optically active.
- Optically active complexes are asymmetric in nature i.e. not divisible into two identical halves.
  - Levorotatory (l) – the compound which rotates plane polarised light to left hand side.
  - Dextrorotatory (d) – the compound which rotates plane polarised light to right hand side
  - d and l isomers of a compound are called enantiomers
- Octahedral complexes with coordination number 6 involving 2 or 3 bidentate ligands show optical isomerism.

### Structure of Coordination Compounds

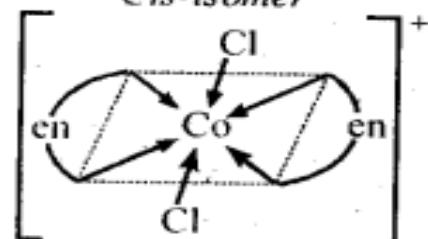
**Optical isomers** are nonsuperimposable mirror images.



(i)  $[\text{CoCl}_2(\text{en})_2]^+$  has 2 geometrical isomers.  
Further cis-form shows optical isomerism.

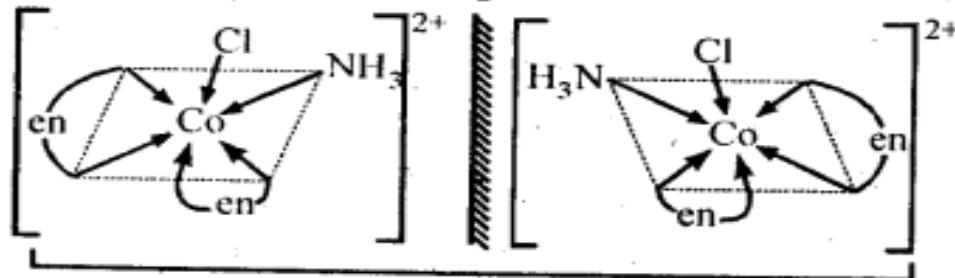


*Cis-isomer*

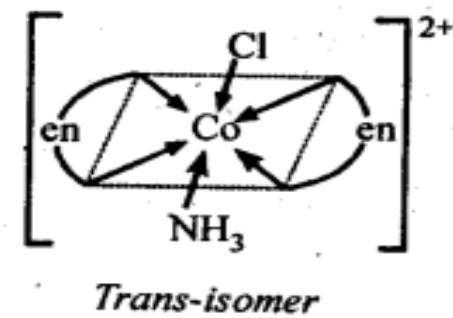


*Trans-isomer*

(ii)  $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$

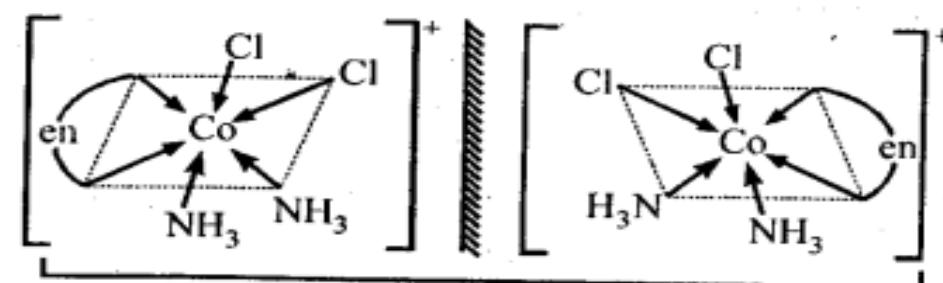


*Cis-isomer*

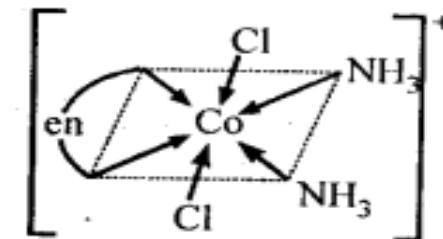


*Trans-isomer*

(iii)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$



*Cis-isomer*



*Trans-isomer*

# **Periodic table**

## **Effective nuclear charge (Slater's rule-formula)**

## **Families or Groups**

1A

2A

1

2

3

4

6

**Period**

## Lanthanide Series

## Actinide Series

## Transition Metal Family



## Effective Nuclear Charge ( $Z_{\text{eff}}$ )

- In a many-electron atom, each electron is attracted to the positively charged nucleus and repelled by the other negatively charged electrons.
- $Z_{\text{eff}}$  takes both of these factors into account and represents an estimate of the net electric field experienced by an electron.
- $Z_{\text{eff}} = Z - S$
- $Z$  = number of protons in the nucleus.
- $S$  = screening constant; the number of core electrons that screen the outer electrons from the positive charge in the nucleus.

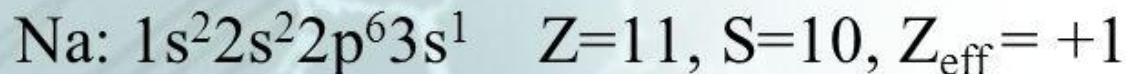
# Effective Nuclear Charge

---

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

where  $Z$  is the atomic number and  $S$  is a screening constant, usually close to the number of inner electrons

Example:



\*This is an approximation – there are better methods beyond the scope of this course – this calculation is close enough for us!

# Periodic Trends and Effective Nuclear Charge ( $Z_{\text{eff}}$ )

Examples: Which element has the *larger*  $Z_{\text{eff}}$  value?

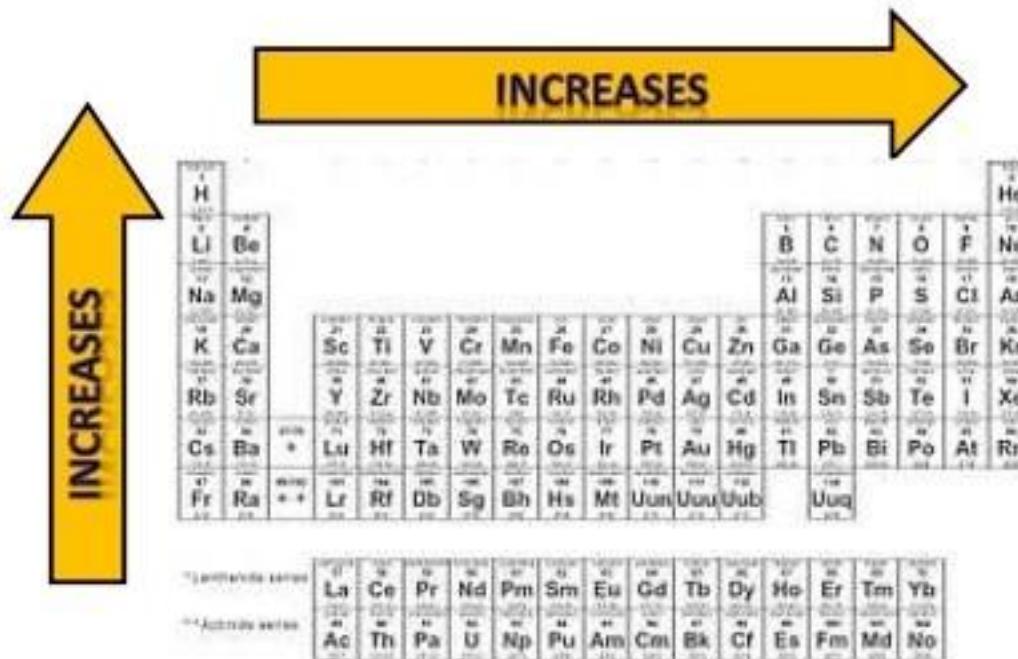
a) Li or K

b) C or O

c) C or P

d) C or Se

e) Li or Br



## SLATER'S RULES

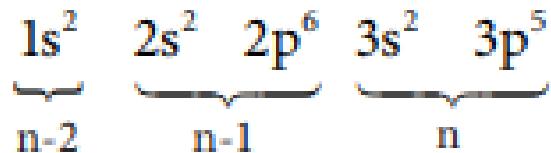
*Shielding and effective nuclear charge  $Z^*$ :*

$$Z^* = Z - S \text{ (a measure of the nuclear attraction for an electron)}$$

To determine  $S$  (Slater's rules):

1. Write electronic structure in groups as follows:  
(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) etc.
2. Electrons in higher groups (to the right) do not shield those in lower groups
3. For *ns* or *np* valence electrons:  
**other** electrons in the same  $n$  group: 0.35; except for 1s where 0.30  
is used.  
electrons in the  $n-1$  group: 0.85  
electrons in the  $n-2, n-3, \dots$  groups: 1.00
4. For *nd* and *nf* valence electrons:  
**other** electrons in the same *nd* or *nf* group: 0.35  
electrons in groups to the left: 1.00

**S is the sum of all contributions**



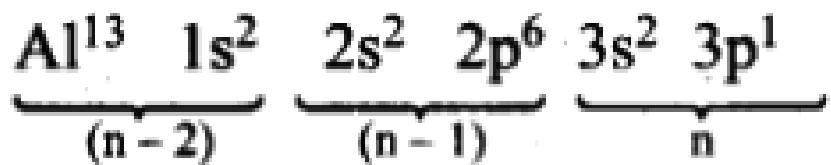
Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n - 1)	8	0.85	6.8
(n - 2)	2	1	2
S =			10.9

$$\therefore \text{Effective nuclear charge} = Z - S$$

$$= 17 - 10.9$$

$$(Z_{\text{eff}})_{\text{cl}} = 6.1$$

$(Z_{\text{eff}})_{\text{cl}} > (Z_{\text{eff}})_{\text{Al}}$  and. Hence  $r_{\text{cl}} < r_{\text{Al}}$ .



Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	2	0.35	0.70
(n - 1)	8	0.85	6.80
(n - 2)	2	1	2.00
			9.50

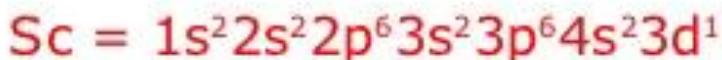
$$(Z_{\text{eff}})_{\text{Al}} = 13 - 9.5 = 3.5$$

# ELECTRON SHIELDING

- 1) Write out the electronic configuration of the element in the following order of groupings: (1s) (2s, 2p) (3s, 3p) (3d) (4s 4p) (4d) (4f) (5s 5p), etc.
  - 2) Electrons in any group to the right of the (*ns*, *np*) group contribute nothing to the shielding constant
  - 3) All of the other electrons in the (*ns*, *np*) group shield the valence electron to an extent of 0.35 each
  - 4) All electrons in the (*n* - 1) shell shield to an extent of 0.85 each
  - 5) All electrons (*n* - 2) or lower shield completely; i.e., their contribution is 1.00.
- When the electron being shielding is in an (*nd*) or (*nf*) group, rules 2 and 3 are the same but rules 4 and 5 become:**
- 6) All electrons in groups lying to the left of the (*nd*) or (*nf*) group contribute 1.00

## Example #2:

Consider the  $Z_{\text{eff}}$  for the valence electron of scandium:



Rule 1: (1s<sup>2</sup>) (2s<sup>2</sup>2p<sup>6</sup>) (3s<sup>2</sup>3p<sup>6</sup>) (3d<sup>1</sup>)(4s<sup>2</sup>)

Rule 2: does not apply

Rule 3: the other 4s electron = **1 x 0.35**

Rule 4: (3s<sup>2</sup>3p<sup>6</sup>)(3d<sup>1</sup>) = **9 x 0.85**

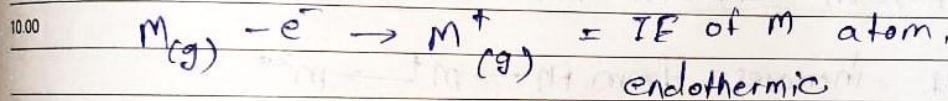
Rule 5: (1s<sup>2</sup>) (2s<sup>2</sup>2p<sup>6</sup>) = **10 x 1.00**

$$\begin{aligned}S &= (1 \times 0.35) + (9 \times 0.85) + \\&(10 \times 1.00) \\&= 18.00\end{aligned}$$

$$\begin{aligned}Z_{\text{eff}} &= Z - S \\&= 21.00 - 18.00 \\&= 3.00\end{aligned}$$

$$\therefore Z_{\text{eff}} = 3.00$$

Def<sup>n</sup>: Amount of energy required to remove an  $e^-$  from valence shell of the isolated gaseous atom of th element, to convert the atom into gaseous cation.



Units :-

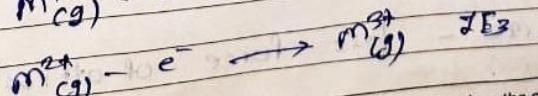
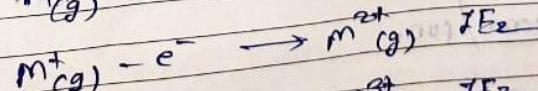
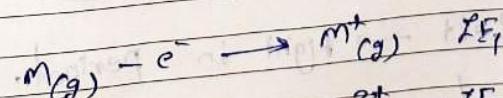
1)  $eV/atom$        $1eV/atom = 96,4705 \text{ kJ/mole}$   
 1Kcal/mole  
 1eJ/mole

Successive ionization energies; 2nd, 3rd etc

$\Delta E_1$  - energy required to remove one  $e^-$

$\Delta E_2$  - " " "  $e^-$  from  $M^+(g)$  ion

$\Delta E_3$  - " " "  $e^-$  from  $M^{2+}(g)$  ion



$\Delta E_1 < \Delta E_2 < \Delta E_3$  The time to repair the roof is when the sun is shining." - John F. Kennedy

Explanation for IE, < IE<sub>2</sub> < IE<sub>3</sub>

1) based on the size of atom/cation

8.00

Size  $\downarrow$  from which  $e^-$  is being removed.

9.00

2) base on effective nuclear charge ( $Z_{eff}$ ).

10.00

$Z_{eff}$  increases from  $m \rightarrow m^+ \rightarrow m^{2+}$

11.00

Lmp<sup>t</sup> Note.  $\cancel{IE_2 \neq 2IE_1}$

12.00

1.00 factors affecting IE.

1) Nuclear charge,

↑ in nuclear charge ↑ is IE

3.00 e.g. IE for  $Li^+$  ( $1s^2$ ) = 7298.1 kJ/mole

$He$  ( $1s^2$ ) = 2372.3 kJ/mol

SUN WK 48 (329 - 036)	element	Nuclear charge	No. of $e^-$
25	$Li^{3+}$	3	2
	$He$	2	2

IE ↑ from Left  $\rightarrow$  Right in period.

(2) Size of atom / ion.

Greater size - less force of attraction - less IE.

NOV 2018

26

$$M > M^+ > M^{2+} \therefore IE_1 < IE_2 < IE_3$$

8.00 down gr.  $\Delta E \downarrow$

9.00 (a) Principal quantum no.

10.00 (b) e.g. Mg ( $1s^2, 2s^2 p^6 3s^2$ )

$$\Delta E_1 = 737.7, \Delta E_2 = 1450.7 \quad \Delta E_3 = 7732.8 \text{ kJ/mole}$$

$$(b) Be (1s<sup>2</sup>, 2s<sup>2</sup>) \quad BC (1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>1</sup>) \\ \Delta E_3 = 14848.7 \text{ kJ/mole.} \quad 3659.8 \text{ kJ/mole.}$$

(c) as we pass from noble gas (zero qr.) to alkali, (IA) qr. of next period,  $\Delta E \downarrow$  as value of  $n$  increases.

(d) Shielding effect  
as  $z \uparrow, \Delta E \downarrow$

as move from zero qr. to IA qr.  $z \uparrow \therefore \Delta E \downarrow$

np orbitals in noble gases not effectively shielded by remaining 5 e<sup>-</sup> in p orbital while ns e<sup>-</sup> in IA qr. effectively shielded by (n-1)<sup>th</sup> shell.

(e) Energy of the orbital from which e<sup>-</sup> is to be removed:

order of energy ns < np < nd < nf  $\therefore$  ease with which e<sup>-</sup> removed is also ns < np < nd < nf  $\therefore$  ZE order ns > np > nd > nf

removing from s<sup>1</sup> earliest than s<sup>1</sup> of same shell.

### (6) Half filled and completely filled orbitals

8.00 half filled  $ns^1$ ,  $np^3$ ,  $nd^5$  and fully filled  $ns^2$ ,  $np^6$ ,  $nd^{10}$  are more stable  $\therefore IE \uparrow$

9.00 order of stability.  $o^5 < p^3 < d^{10} < p^6$

10.00  $\because IE$  of N, P & As greater than O, S, Se

11.00 IE of noble gases is highest ( $ns^2 np^6$ )

12.00 Variation of IE in main gr. elements.

13.00 ~~(a) variation in period~~

2.00 from L  $\rightarrow$  R, nuclear charge  $\uparrow$  by 1 at each next element.  
-  $\uparrow$  force of attraction -  $\uparrow$  in IE

3.00 In 2<sup>nd</sup> period, expected order is.

4.00  $Li < Be < B < C < N < O < F < Ne$

5.00 but:  $Li < B < Be < C < O < N < F < Ne$

6.00  $B: 2s^2 2p^1$        $N: 2s^2 2p^3$   
 $Be: 2s^2$        $O: 2s^2 2p^4$

7.00 Same trend in 3<sup>rd</sup> period also.

In each period, alkali metal have lowest IE & noble gases have highest. ~~for~~ since  $ns^2 np^6$ .

8.00

(b) Variation in gr. :-

9.00 down the gr. IE ↓ because,

10.00 (i) down the gr. size of atom & nuclear charge ↑

↑ in size of atom ↓ IE

11.00 ↑ in nuclear charge ↑ IE

12.00 but ↑ in size dominates. ∴ IE ↓

1.00 (ii) down the gr., no. of intervening e<sup>-</sup>s ↑ ∴ & ↑  
∴ IE ↓.

2.00

Variation in Gr IIA

3.00

Gr. IIA has lowest IE in PT.

4.00 IE for M<sup>+</sup> is low but IE for M<sup>2+</sup> very high.

5.00 Gr. IIA

tend to form M<sup>2+</sup> than M<sup>+</sup>

6.00

M<sup>3+</sup> not possible. ∵ stable ns<sup>2</sup> np<sup>6</sup> conf.

7.00

Gr. VIIA - halogens

IE ↑ down the gr.

halogens have highest I.E. In period after noble gases

F does not form M<sup>+</sup> but forms X<sup>-</sup> & X<sup>3-</sup>.

3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30

## Atomic & Ionic radii

WK 45 (311 - 054)

NOV 2018

Size of atom / ion is represented by mag. of radius of atom (atomic radius) or ion (ionic radius).

Radius of atom / ion is defined as distance bet. nucleus of atom/ion and e<sup>-</sup> cloud of outer-most shell.

If atom / ion is assumed to be sphere, it is radius of sphere,

Absolute size of atom/ an ion can not be defined due to following reasons :

(i) exact position of e<sup>-</sup> can not be defined ~~exactly~~ with certainty. wave mechanical picture - at one time e<sup>-</sup> may be close to N at other time far away from N.

(ii) Probability of finding the e<sup>-</sup> round the nucleus in an atom is influenced by the presence of other atoms in its environment. Size of atom changes with change of atoms surrounding it.

(iii) thus internuclear distances - used to calculate atomic & ionic radii. (covalent radius, van der Waals radius, ionic rad.)

## **Atomic radius**

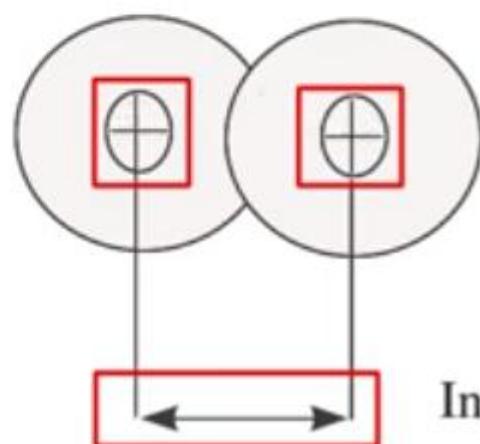
---

1. Atomic radius of an element cannot be determined because atoms never exist in their free state and position of their outermost  $e^-$  is uncertain.
2. Atomic radius is determined in bonded state

## *Type of Radius*

### 1. Covalent Radius ( $r_c$ )

- a. Such type of radius is determined if a single covalent bond is present between two similar atoms.



$$r_c = \frac{d_{a-a}}{2}$$

Internuclear distance( $d_{a-a}$ )

~~Def<sup>n</sup> of Covalent radius of A in A<sub>2</sub> molecule  
(homonuclear diatomic)~~

defined as half of the distance bet. nuclei of two A atoms (bond distance/internuclear distance/bond length)

$$r_A = \frac{d_{A-A}}{2}$$

$$\text{e.g. } H_2 = \frac{0.74 \text{ \AA}}{2} = 0.37 \text{ \AA}$$

$$Cl_2 = \frac{1.98 \text{ \AA}}{2} = 0.99 \text{ \AA}$$

$$Br_2 = \frac{2.28 \text{ \AA}}{2} = 1.14 \text{ \AA}$$

~~Heteronuclear diatomic (AB)~~

(1) If electro-negative diff. ( $\chi_A - \chi_B$ ) is very small,

then

$$d_{A-B} = r_A + r_B$$

e.g.  $d_{A-B}$  &  $r_A$  is known  $r_B$  can be calculated.

e.g. Covalent radius of C is  $0.77 \text{ \AA}$  & C-H internuclear distance is  $1.14 \text{ \AA}$ . find covalent radius of H-atom.

$$1.14 \text{ \AA} = 0.77 + r_H \quad \therefore r_H = 0.37 \text{ \AA}$$

<sup>25 26 27 28 29 30</sup>  
(ii) If diff. in electronegativities is large.

$$d_{A-B} < r_A + r_B \text{ e.g. HF, HCl, HBr, HI etc}$$

Shortening of bond length is because of ionic character in A-B bond. If A is more electro-negative than B, e<sup>-</sup> pair is shifted towards A atom. - Accumulation of charges on A(-ve) & B(+ve) - results in shortening of bond.

$$d_{A-B} = r_A + r_B - 0.09(x_A - x_B) \text{ Å}^{\circ}$$

$$\text{where, } r_A \text{ & } r_B \text{ in } \text{Å}^{\circ} \quad r_A = \frac{d_{A-A}}{2} \quad r_B = \frac{d_{B-B}}{2}$$

$$d_{A-B} = r_A + r_B - 9(x_A - x_B) \text{ pm}$$

$$\text{e.g. } d_{H-F} = r_H + r_F - 0.09(x_F - x_H)$$

$$= 0.37 + 0.72 - 0.09(4 - 2.1).$$

$$= 0.919 \text{ Å}^{\circ}$$

$$\text{Experimental} = 0.92 \text{ Å}^{\circ}$$

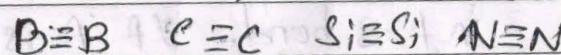
NOV 2010

Double bond & triple covalent radii

8.00 if atoms are bonded by double/triple bond,



9.00 double bond covalent radii ( $\text{\AA}^\circ$ )      0.76    0.67    0.60    0.55



10.00 Triple bond      "      "      "      0.68    0.60    1.07    0.85

11.00

Relation bet. single bond / double bond / triple bond radii of an atom.

12.00

Covalent radius of a given element decreases with  $\uparrow$  in multiplicity or bond order, of the bonds bet. atoms.

2.00

single bond covalent radius  $>$  double b. covalent R  $>$  triple bond, C.R.

3.00

Because of overlap of  $\pi$ -orbitals along with s orbitals atoms become closer.

bond distance      Covalent R

11	SUN WK 46 (315 - 050)	e.g.	C-C	$1.54 \text{ \AA}^\circ$	$1.54/2 = 0.77 \text{ \AA}^\circ$
			C=C	$1.34 \text{ \AA}^\circ$	$1.34/2 = 0.67 \text{ \AA}^\circ$
			C≡C	$1.20 \text{ \AA}^\circ$	$1.20/2 = 0.60 \text{ \AA}^\circ$

18 19 20 21 22 23  
25 26 27 28 29 30

## Atomic Radice

A size of atom in free state - called atomic radius.

Always found to be same with co-valent radius.

Factors affecting the magnitude of covalent radii of elements

### (1) Effective nuclear charge ( $Z_{eff}$ )

With ↑ in  $Z_{eff}$  ↑  $e^-$  in outermost shell, attraction b/w nucleus & outermost  $e^-$  increases.  $\rightarrow e^-$  cloud moves closer to N - covalent radius of atom ↓  
Observed in variation of (decrease) in covalent radii across the period.

### (2) No. of shells/ principal quantum no.

(n) represents total no. of shells present in element.

as 'n' ↑, outermost shell  $e^-$  gets farther & farther away from nucleus & hence co-valent radius ↑.

down Group → ↑  
across period → ↘

### (3) Multiplicity of bonds b/w atoms:

Multiplicity ↑, covalent radius ↓

13

NOV 2018

## Variation of covalent radii in Main Group elements

8.0 fa

## Variation in period

Ne<sub>10</sub> is expected to be smaller than F but it is larger.

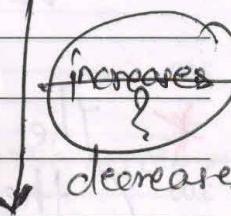
Because forces holding atoms in noble gases (i.e. interatomic forces) are only van-der Waal's forces, which are weak forces, radii of the atoms of noble gases are van der Waal's radii, which are larger than co-valent radii of atoms of halogen.

### (B) Variation in Group

covalent radii

↑ on moving down the group.

		IA	Covalent radii ( $\text{\AA}$ )	No. of shells	$Z_{\text{eff.}}$ felt by ns <sup>1</sup>
Li	1.23	1	1.23	1	1
Na	1.54	2	1.54	2	1
K	2.03	3	2.03	3	1
Rb	2.16	4	2.16	4	1
Cs	2.35	5	2.35	5	1
				6.	decreases



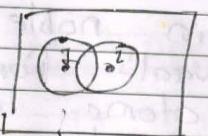
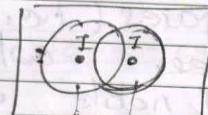
from Li → Cs, no. of shells / principal quantum no. increases and ' $Z_{\text{eff.}}$  felt by ns<sup>1</sup>' decreases. which tends to increase covalent radii.

NOV 2018

## Def<sup>n</sup> of vander Waals radius

	1	2	3	4
5	7	8	9	10
12	13	14	15	16
19	20	21	22	23
26	27	28	29	30

8.00



AK      B      BC  
        |  
        DF      FE

AB : covalent radius - internuclear distance =  $2.66 \text{ \AA}$

11.00

$$\text{FCI}! \quad \frac{\text{AB}}{2} = \frac{2.66}{2} = 1.33 \text{ \AA} = \text{covalent radius.}$$

12.00

BC : van der Waals inter-nuclear distance =  $4.30 \text{ \AA}$

$$\text{DB} = \frac{4.30}{2} \text{ \AA} = 2.15 \text{ \AA} = \text{van der Waals radius}$$

of iodine

3.00

The distance bet. nuclei of two adjacent  $I_2$  atoms  
(these atoms belong to two adjacent  $I_2$  molecules)  
is called van der Waals internuclear distance and  
half of this distance is called van der Waals  
radius of iodine atom.

4.00

5.00

6.00

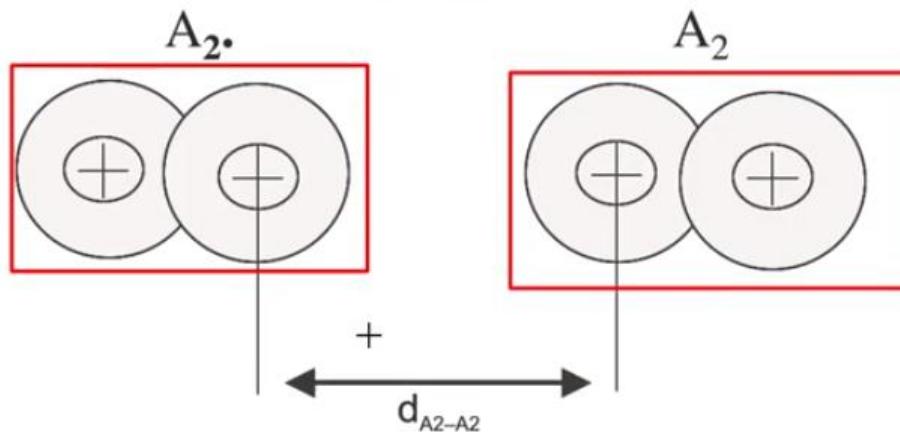
van der Waals radii of an element is larger than,  
its covalent radius.

7.00

Comparison of the radii of noble gas atoms  
with those of halogen atoms

noble gas > halogens because of weak forces.

3. **van der Waal's radius ( $r_v$ ):** Such type of radius is determined if molecules are bonded with van der Waal's force of attraction.



$$r_v = \frac{d_{A2 - A2}}{2}$$

$$r_v > r_m > r_c$$

**Note:** Noble gases are monoatomic molecules bonded with van der Waal's force of attraction hence, for noble gases, van der Waal's radius is considered.

1	12	13	14	15	16
8	19	20	21	22	23
25	26	27	28	29	30

## Ionic radius

WK 46 (320-045)

NOV 2018

16

Defn: if it is radius of an ion (cation/anion) in an ionic crystal. It may be defined as distance bet, nucleus of the ion and point upto which the nucleus exerts its attractive force on the  $e^-$  cloud of the ion.

### Additive property of ionic radii

if ions are assumed to be spheres.

$$d(C^+ - A^-) = r(C^+) + r(A^-)$$

$d(C^+ - A^-)$  - internuclear distance.

$r(C^+), r(A^-)$  - radii of  $C^+$  &  $A^-$  resp.

e.g. Ionic radius of  $\text{Na}^+$  ion is  $0.95 \text{ \AA}$  and inter-nuclear distance bet.  $\text{Na}^+$  &  $\text{Cl}^-$  ion pair in  $\text{NaCl}$  ionic crystal is equal to  $2.76 \text{ \AA}$ . find ionic radius of  $\text{Cl}^-$  ion

$$d(\text{Na}^+ - \text{Cl}^-) = r(\text{Na}^+) + r(\text{Cl}^-)$$

$$2.76 = 0.95 + r(\text{Cl}^-)$$

$$r(\text{Cl}^-) = 2.76 - 0.95 = 1.81 \text{ \AA}$$

### Comparison of bal. radii of $Z^+, Z^0, Z^-$ and conclusions drawn from it

$$Z^+ = 58, Z^0 = 54, Z^- = 57 \quad Z^0 = 53 + 1 = 54$$

$$Z^0 = 53$$

$$Z^+ = 53 - 1 = 52$$

NOV 2018

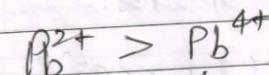
No. of e<sup>-</sup>s decrease as  $I^- > I^0 > I^+$

26 27 28 29 30

radii also in same order  $I^- > I^0 > I^+$

~~Conclusions~~

① Radii of various species having same nuclear charge diff but diff. O.S. ↓ with ↑ in o. oxidation number of the species.



$$(1.20 \text{ \AA}) \quad (0.84 \text{ \AA})$$

$$m^- < m^0 < m^{3-}$$

② Anion is larger in size than parent atom,

③ Cation is smaller " " " "

18

SUN  
WK 47  
(2018-2019)

Variation of ionic radii of isoelectronic ions

Isoelectronic means - same no. of e<sup>-</sup>s of same electronic configuration

size ↓ with ↑ in nuclear charge

20	21	22	23
27	28	29	30

## Isoelectronic ions

	No. of e <sup>-</sup> electronic conf.	Nuclear charge, (+z)	Size of ions (A°)
C <sup>4-</sup>	10 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	+6	2.60
N <sup>3-</sup>	10 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	+7	1.71
O <sup>2-</sup>	10	+8	1.42
F <sup>-</sup>	10	+9	1.36
Na <sup>+</sup>	10	+11	0.95
Mg <sup>2+</sup>	10	+12	0.65
Al <sup>3+</sup>	10	+13	0.50
Si <sup>4+</sup>	10	+14	0.41
P <sup>5+</sup>	10	+15	0.34
S <sup>6+</sup>	10	+16	0.29
Cl <sup>7+</sup>	10	+17	0.26

Period 1

Li

Period 2

Na

Period 3

K

Period 4

Rb

Period 5

Cs

Period 6

Fr

## Variation of ionic radii in main group elements

(a) Variation in a period.

$L \rightarrow R$  decrease.

(b) Variation in group.

down the gr. increases.

Na <sup>+</sup>	0.95	Li <sup>+</sup>	0.65
Li <sup>+</sup>	0.65	Na <sup>+</sup>	0.95
K <sup>+</sup>		K <sup>+</sup>	1.33
Rb <sup>+</sup>	1.48	Cs <sup>+</sup>	1.69
			— 0.15

Increase in ionic radius from  $Li^+ \rightarrow Na^+$

$\frac{Na^+ \rightarrow K^+}{Rb^+ \rightarrow Cs^+}$  is large but from  $Li^+ \rightarrow Pb^+$

$\frac{Rb^+ \rightarrow Cs^+}{Cs^+}$  is not. Their behaviour is

Because of presence of ten elements of 1st transition series ( $Sc_{21}$  to  $Zn_{30}$ ) bet.  $K^+$  &  $Rb^+$ , their

Increasing nuclear charge tends to cause the contraction of size of the atoms and ions which follow them.

9.00

Variation of atomic & ionic radii of elements in diff.-gr.s.

11.00 Gr. I A (alkali metals)

↑ down the gr. because of ↑ in no. of shells.

12.00

Strong tendency to lose  $e^-$  & form  $M^+$  cations.

1.00

Size of cations ↑ down gr.  $\& M^+ \subset M$

2.00

Gr. II A (alkaline earth metals)

At & ionic size ↑ down the gr.

Incase  $ns^2 e^-$  to form  $M^{2+}$  cations.

4.00

Size of cation also ↑ down the gr.  $M^{2+} \subset M$ .

5.00 Gr. III A

↑ down the gr. as expected due to ↑ in no. of shells.  
But from Al  $\rightarrow$  Ga.

$$1.43\text{ Å} \rightarrow 1.35\text{ Å}$$

7.00

Al  $4s^2$  4p $_1$

Ga  $3d^{10} 4s^2$  4p $_1$  resp.

Period 2

Li Be

B C N O F Ne

Period 3

Na Mg

Al Si P S Cl Ar

Period 4

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn

Ga Ge As Se Br Kr

↑ 3d orbitals are large in size, which screen nucleus poorly  $\therefore Z_{eff}$  in Ga becomes more than Al

$\checkmark$  C.  $\text{Ca} < \text{Al}$ .  $\text{Zn}$  &  $\text{Ti}$  show expected increasing trend in at. radii.  $\text{M}^{3+}$  &  $\text{M}^{2+}$  cations also  $\uparrow$  down gr.

### Gr. IV A

$\uparrow$  down gr.

$\text{M}^{4+}$  &  $\text{M}^{2+}$  also  $\uparrow$  down gr.

### Gr. VA

(electron shells) AT  $\downarrow$

$\uparrow$  down gr. to second rp att. no.  $\uparrow$

$\text{M}^{3+}$  &  $\text{M}^{5+}$   $\uparrow$  down gr. not of probab. profile

$\text{M}^{3+} > \text{M} > \text{M}^{5+}$  rp no.  $\uparrow$  erosion to 2s2

### Gr. VI A

(electron shells) AT  $\downarrow$

$\uparrow$  down gr.

$\text{M}^{2-} > \text{M} > \text{M}^{6+}$

### Gr. VII A - (halogens)

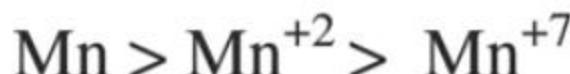
$\uparrow$  down gr. 2s2 becomes 2p  $\uparrow$  rp att. no.  $\uparrow$

$X^- > X$ .

Noble gas atoms. :- atoms linked by vander waals forces not covalent bonds :-  $\uparrow$  do vander waals radii  $\uparrow$  down gr.

4. **Ionic radius (radius of ions):**

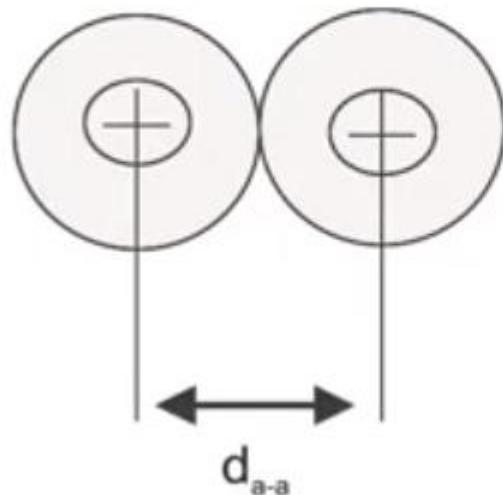
- a. A cation is always smaller than its parent atom because it has greater  $Z_{\text{eff}}$  than its parent atom. As positive oxidation state increases, radius decreases.



- b. An anion is always larger than its parent atom because the anion has lower  $Z_{\text{eff}}$  than its parent atom. As negative oxidation state increases, radius increases.



**2. Metallic radius ( $r_m$ ):** Such type of radius is determined if atoms are bonded with metallic bond.



+

$$r_m = \frac{d_{a-a}}{2}$$

29

WK 48 (333 - 032)

NOV 2018

## Electron affinity. (EA)

5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	28	29	30		

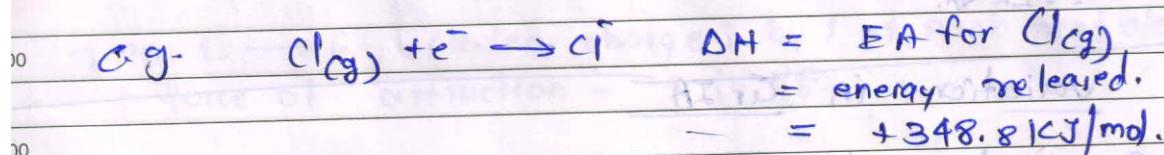
Defn:-

defined as amt. of energy released when an  $e^-$  is added to the valence-shell of an isolated gaseous atom of that element, to convert atom into, gaseous uni-negative ion (anion).



- it is a measure of an atom to change into an anion.

- Greater the amt. of energy released, greater is EA.
- EA of atom gives measure of the tightness with which additional  $e^-$  is held by that atom.



### Relation bet. EA of $X(g)$ and IE of $X^-(g)$ ion:-

- EA of  $X(g)$  atom = +IE of  $X^-(g)$  ion

$\therefore$  reactions are opp., mag. of EA & IE are same but opp. sign.

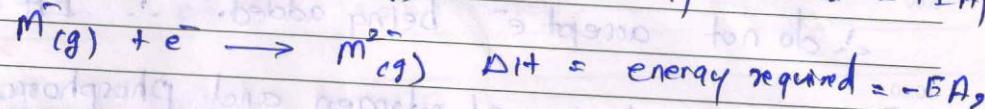
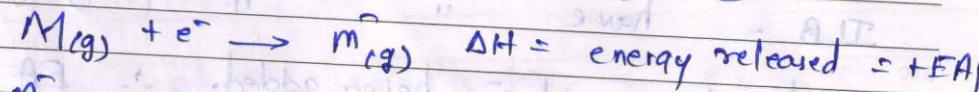
24 25 26 27 28 29 30

## Second IEA

NOV 2018

JU

Am. of energy required to add an  $e^-$  to uni-negative gaseous ion of that element (i.e.  $M^{(g)} \text{ ion}$ ).



$\cancel{EA}_1 \leftarrow \text{exothermic}$

$\cancel{EA}_2 \leftarrow \text{endothermic}$

EA<sub>2</sub> represents energy required why?

Since  $e^-$  is being added against electrostatic repulsion existing bet. +ve charge on  $e^-$  being added & -ve charge on  $M^{(g)}$  ion.

Factors affecting in EA.

1) Size of atom.

Smaller the size of atom greater is its EA.

2) Nuclear charge,

Greater the magnitude of nuclear charge (along period) stronger the attraction bet. of nucleus for  $e^-$  to be added. EA also increases.

17	18	19	20	21	22	23
24	25	26	27	28	29	30

(a) EA for elements of IIA & IIB

- 8.00 IIA - have completely filled ns orbital ( $ns^2$ )
- 9.00 IIB - have " "  $(n-1)d$  orbital ( $n-1)d^{10}$ .  
 $\therefore$  do not accept  $e^-$  being added.  $\therefore EA = 0$ .

(b) BA values of nitrogen and phosphorus

- N & P have half-filled np-orbital - very stable - less tendency to accept  $e^-$  - very low EA.

(c) EA values of noble gases -

- $Ne^2$  (He) or  $ns^2 2p^6$  conf. - very stable - less tendency to accept  $e^-$  - EA very low or zero.

Variation of EA in main group elements.

2

SUN  
WK 45  
(36-029)

(a) Variation in period

from L  $\rightarrow$  R, size decreases - nuclear charge  $\uparrow$  - bet.  $e^-$  being added & nucleus. EA  $\uparrow$

Alkali metals - lowest EA. nonmetals - highest EA - on gaining  $e^-$  attain stable configuration -  $(ns^2 np^6)$

5	16	17	18	19	20
2	23	24	25	26	27
9	30				

DEC 2018

(b) Variation in a group.  
down the gr. at. size ↑ & nuclear charge also ↑.

↑ in at-size ↗ EA

↑ in nuclear charge ↗ EA

but ↑ in at-size dominates.

∴ EA ↓ down the gr.

EA for H > Li > Na > K > Rb > Cs.

S > Se > Te > Po.

EA OCS & FCl

O -  $2s^2 2p^4$  F  $2s^2 2p^5$

S -  $3s^2 3p^4$  Cl  $3s^2 3p^5$

DEC 2018

10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30

## Variation of EA. in diff. groups

8.00 IA Gr

As atomic radii ↑ doo th gr. EA ↓.

9.00

IIA & IIB - page 123? already discussed.

10.00

### IIIA & IVA

12.00

do not show expected trend of ↓ in EA, No satisfactory explanation available.

1.00

### VIA

2.00

do not show regular trend. EA of N & P are very low. - reason already discussed.

3.00

### VIIA

4.00

decrease gradually from S → Po. EA of atom lower than S-atom, although expected to be higher.

5.00

### VIIIA (Halogens)

6.00

Atomic radii of halogens smallest in each period. - man tendency to gain an e<sup>-</sup> to form X<sup>(g)</sup>. ∵ highest EA. - moreover after gaining acquire stable noble gas conf. ns<sup>2</sup>, np<sup>6</sup>.

7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

DEC 2018

EA ↓ gradually from  $\text{Cl} \rightarrow \text{I}$  ( $\text{Cl} > \text{Br} > \text{I}$ ).

8.00 EA for F lower than Cl ( $\text{F} < \text{Cl}$ ).

9.00 Noble gases :- discussed.

10.00 Condition for the formation of an ionic compound by the combination of a metal with a non-metal :-

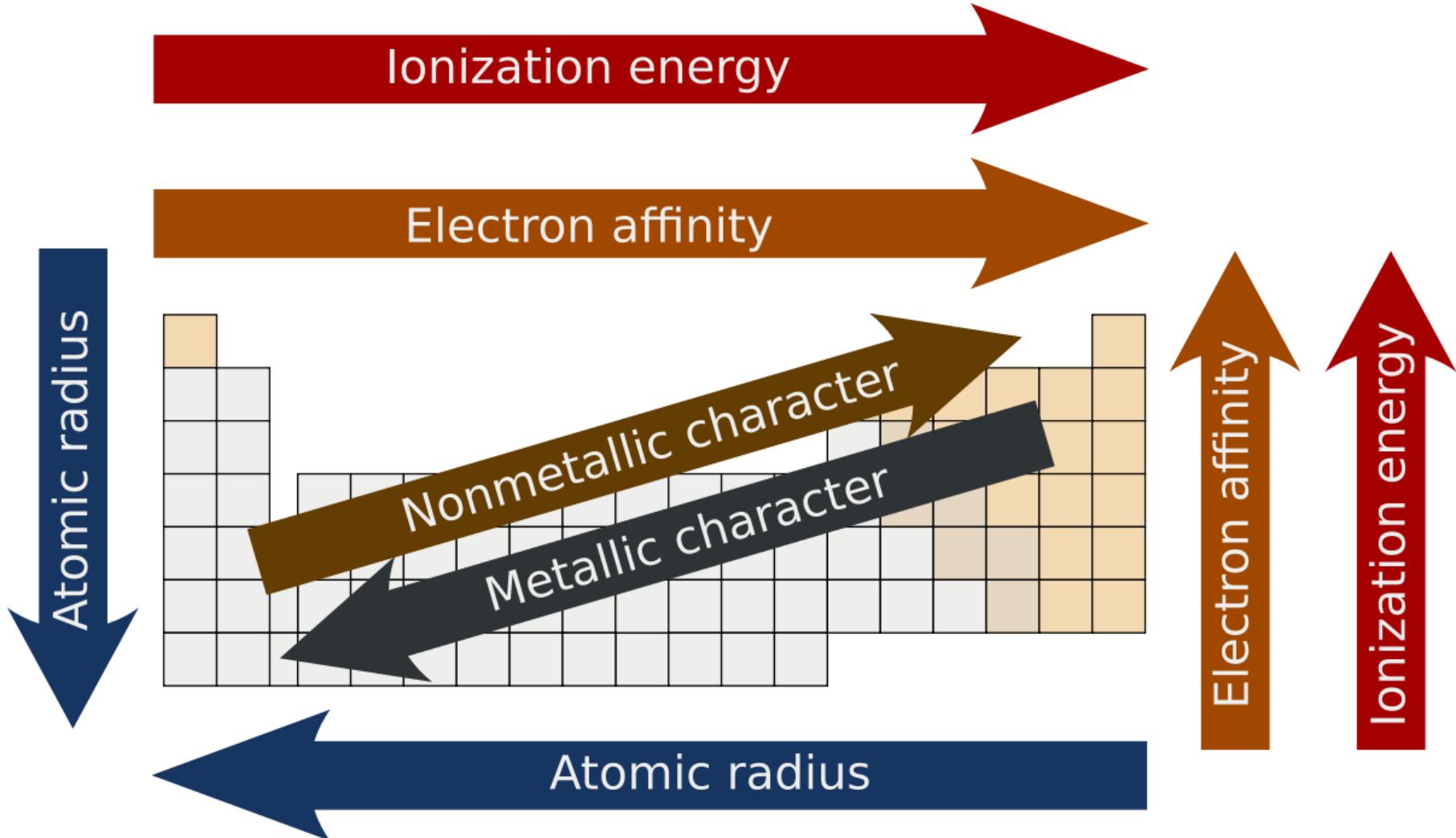
11.00 A combined appl'n of IE & EA

12.00 IIA & VIIA groups have tendency to lose e<sup>-</sup> and form cations. VIA & VIIA groups have tendency to accept e<sup>-</sup> & for an anion.

13.00 Cations and anions - combine - due to electrostatic force of attraction - forming ionic crystals.

14.00 low IE - forms cationic part of hig EA. forms anionic part. Combination of metal & a non-metal gives ionic compound.

15.00



13

THU  
WK 50 (347 - 018)  
DEC 2018

## Electronegativity (EN)

M	T	W	T	F	S	S
31					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30

### ① Pauling's approach (1932)

Defined as relative tendency (or power of ability) to attract the shared  $e^-$  pair towards itself.

Pauling eqn

$$(x_A - x_B) = 0.182 [E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}]^{1/2}$$

$E_{A-A}$ ,  $E_{B-B}$ ,  $E_{A-B}$  are dissociation energies in kcal/kJ.

He assumed arbitrary value of EN for H atom equal to 2.2. and determined the values for other elements with help of eqn. (Draw back: dissociation energies are less not known accurately for many elements)

$L \rightarrow R$  ↑ for noble gases zero.  
down gr. ↓

### ② Allred and Rochow's scale (1958)

$$(x_A)_{AR.} = \frac{0.859 \times Z_{eff}}{r^2} + 0.744$$

$L \rightarrow R$  ↑ noble gas - non-zero  
down gr. ↓

### ③ - Mulliken's approach

According to Mulliken, the average of EA & IE of an atom is the measure of its electronegativity.

$$\sigma_A = 0.874 \left[ \frac{(IE)_A + (EA)_A}{2} \right] + 0.17$$

## Factors affecting magnitude of electronegativity.



(1)

Size of the atom  
smaller the size, greater is tendency to attract shared  $e^-$  pair towards itself - greater is electronegativity.



(2)

O.S. of an element:-

size of atom  $\downarrow$  with  $\uparrow$  in O.S. e.g.  $Fe > Fe^{2+} > Fe^{3+}$ .

$\therefore$  smaller the higher the O.S. - smaller the size - higher EN.

$$Fe (1.80) < Fe^{2+} (1.83) < Fe^{3+} (1.96)$$

$$F^- (0.8), F (4.0)$$

anion is larger in size than parent atom & anion has less tendency to attract shared  $e^-$  pair towards itself. and hence has lower value of electronegativity.



(3)

Effective nuclear charge ( $Z_{eff}$ )

According to Allred Rochow's def<sup>n</sup> EN &  $Z_{eff}$ .

$\uparrow Z_{eff}$   $\uparrow$  in EN.

Variat<sup>n</sup> along gr. & period.

(4)

Electroitive character of elements :-

8.00 Electroitive character is opp. of its electro-ve character  
 i.e. elements which are highly electro-ve are  
 9.00 weakly electro-ve. In other words, elements which  
 are highly electro+ve have low values of EN.  
 10.00 (alkali metals)

11.00 Similarly elements - weak electroitive character (non-metallic  
 character) - high value of EN (e.g. halogens)

12.00

1.00 (5) Ionisation energy & electron affinity.

2.00 According to Mulliken's def<sup>n</sup>, avg. IE and EA of  
 an atom is measure of electro-negativity.

3.00

higher value of IE & EA - higher is EN.

16 SUN  
WK 51  
(350-015)

VII A (halogens) have highest IE, EA -

∴ highest EN.

IA (alkali metals) - have lowest IE, EA - lowest EN.

→ (6)

### Type of hybridization undergone by central atom.

$\text{CH}_4$   $\text{sp}^3$  s-character = ~~25%~~ 25%.

$\text{H}_2\text{C=CH}_2$   $\text{sp}^2$  " 33%.

$\text{C}_2\text{H}_2$   $\text{AC} \equiv \text{CH}$   $\text{sp}$  " 50%.

p in s-character in hybrid orbital p in EN.

s-orbital - more close to nucleus. (s.t.)

## Variation of EN in a group of s & p block

down the gr. EN ↓. based on following:

- 1) Smaller the size higher is electronegativity,
- 2)  $Z_{eff}$  :- Increase in size - increase in  $Z$  -  $\downarrow$  in  $Z_{eff}$ . -  $\downarrow$  EN.
- 3) Electro+ve character! -  $\uparrow$  down gr. - EN ↓
- 4) IE & EA ↓ down gr. - EN ↓

18

TUE

WK 51 (352 - 013)

DEC 2018

Gr I A

Variation in diff. groups

31	1	2
3	4	5
10	11	12
13	14	15
16	17	18
19	20	21
22	23	
24	25	26
27	28	29
30		

3.00

have highest at. size → lowest tendency to attract e<sup>-</sup> —  
lowest EN in resp. period.

9.00

Cs of all in PT.

10.00

∴ I A combine with halogens to form ionic compounds.

12.00

→ Gr II A ↓ down gr.  
Ca (1.2) exception

1.00

→ Gr III A 2 — more EA than Gr. II A. not in v.  
trend ↓ gr. not expected.

3.00

→ Gr IV A C 2.5 irregular trend due to filling of  
Si 1.8. d-orbitals in Ge and Sn and  
d & f orbitals in Pb.

4.00

Ge 2.0 2, 8, 3s<sup>2</sup> 3p<sup>6</sup>, 3d<sup>10</sup>, 4s<sup>2</sup> 4p<sup>2</sup>

5.00

Sn 1.9 2, 8, 18, 4s<sup>2</sup>, 4p<sup>6</sup> 5d<sup>10</sup>, 5s<sup>2</sup> 5p<sup>2</sup>

6.00

Pb 2.3 2, 8, 18, 32, 5s<sup>2</sup> 5p<sup>6</sup>, 6d<sup>10</sup> 6f<sup>14</sup>, 5s<sup>2</sup> 5p<sup>6</sup> 6d<sup>10</sup>,

6s<sup>2</sup> p<sup>2</sup>

7.00

→ Gr VA VI A expected trend.

O = 3.5 2nd most en element

8.00

→ Gr VII A halogen — least size — highest EN —  
F = 4.0 — max. EN —

9.00

→ Noble gases! — EN = 0.

Variation of EN in a period  $\rightarrow \uparrow$  in EN along period - due to,

1)  $Z_{\text{eff}}$   $\rightarrow Z_{\text{eff}} \uparrow$ , EN  $\uparrow$

2) Electroneg/ -ve character.  
 $L \rightarrow R$  electroneg character  $\downarrow$

3) Atomic size  
 $L \rightarrow R$ , Atomic size  $\downarrow$   $\rightarrow$  EN  $\uparrow$

4) JE & EA : both  $\uparrow$   $\therefore$  EN  $\uparrow$

Conclusions

PA - lower, halogen - higher, noble gases - zero.

F - highest (4.0)

Cs - lowest

	1	2	3	4
5	6	7	8	9
12	13	14	15	16
19	20	21	22	23
26	27	28		

## Polarization of ions and Fajan's rules

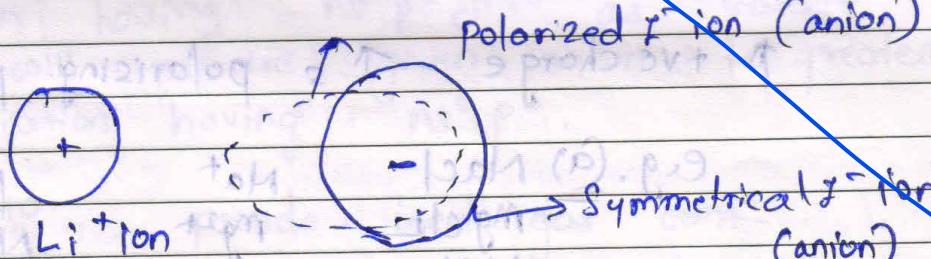
WK 01 (003 - 362)

3

JAN 2018

- 8.00 In formation of ionic molecule, when two oppositely charged ions (cation & anion) come closer to each other, cation attracts  $e^-$  charge cloud of the outermost shell of the anion towards itself and hence symmetrical shape of the anion gets deformed (distorted/polarized).
- 9.00 Def<sup>n</sup> the phenomenon in which the symmetrical shape of the anion gets deformed by the approach of the cation closer to it is called polarization (or distortion or deformation) of the anion.

Polarisation of  $I^-$  ion by  $Li^+$  ion in  $LiI$  ionic molecules



## ~~Polarising power / polarising ability.~~

- \* "the ability of a cation to polarise an anion is called its polarising power / polarising ability."
- Cations also get polarized - e<sup>-</sup> cloud remains strongly bound to nucleus → hence not attracted towards anion
- ✓ i.e., cation is not polarized to an appreciable extent by the anion.

→ **Polarisability:** - the tendency of an anion to get polarized by a cation is called its polarisability.



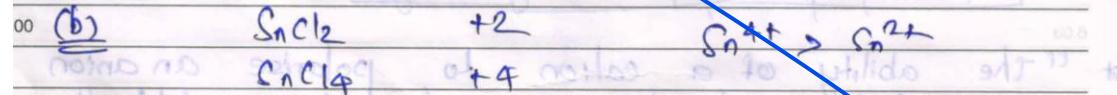
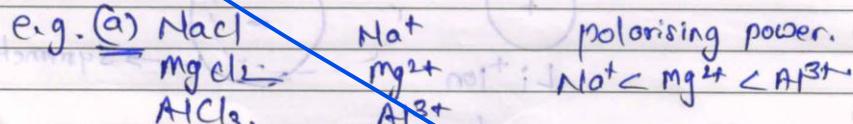
## Factors affecting magnitude of polarising power

### of a cation

#### 1) Magnitude of positive charge on the cation

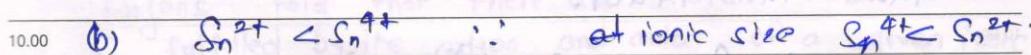
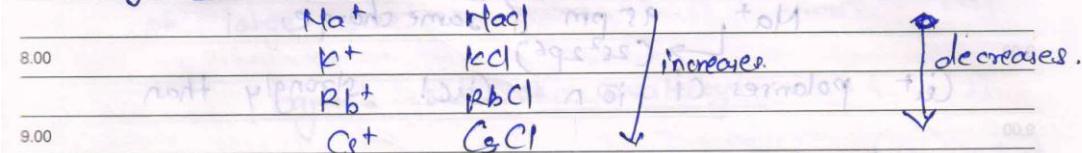
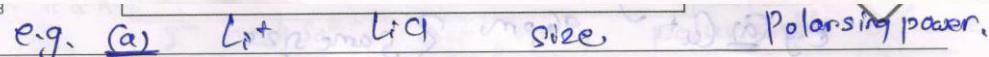
higher the +ve charge on the cation, - more strongly it attracts outermost e<sup>-</sup> cloud of anion towards itself. polarizes a given anion; more strongly.

↑ +ve charge ↑ s polarising power of cation.



#### (2) Size of the cation

Polarising power  $\propto \frac{1}{\text{size}}$



< polarising power

(P.P.) cation  $\propto \frac{\text{Positive charge on cation}}{\text{radius of cation}}$



00 (B)

### Electronic configuration of the cation

- 2.00 if +ve charge is same and size same  
then cation having  $ns^2 p^6 d^{1-10}$  as valence  
3.00 shell conf. will polarise given anion to greater extent than cation having  $ns^2 p^6$ .
- 4.00  $ns^2 p^6 d^{1-10}$  pseudo-inert gas conf.
- 5.00  $ns^2 p^6$  " " " "

- 6.00 i. cation containing  $18 e^-$  in valence shell has greater polarising power than cation containing  $8 e^-$ .  
Reason :  $d$  e's shield nucleus poorly as compared to  $s$  &  $p$ -electrons

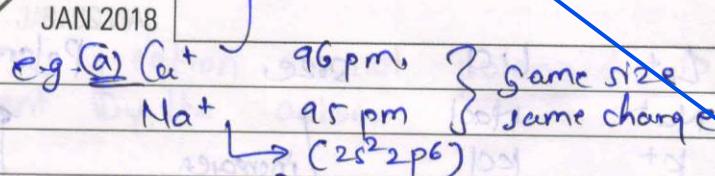
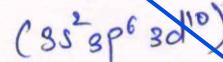
6

SAT

WK 01 (006-359)

JAN 2018

M	T	W	T	F	S	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30	31				



$Cu^+$  polarises  $Cl^-$  ion in  $CaCl_2$  strongly than

$Na^+$  in  $NaCl$ .

(b)  $Hg^{2+} (2, 8, 18, 3s^2 3p^6 d^0) (102 pm)$  p.p. ( $Hg^{2+}$ )  $>$   $Ca^{2+}$

$Ca^{2+} (2, 8, 3s^2 3p^6 d^0) (100 pm)$  (99)

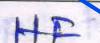
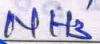
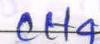
## Factors Affecting polarisability of an anion

①

Magnitude of -ve charge on the anion

Higher -ve charge - higher polarisability.

e.g. (a)



Polarisability

$\text{C}^4- > \text{N}^3- > \text{O}^{2-} > \text{F}^-$

by  $\text{H}^+$

7

SUN  
WK 02  
(007 - 358)

(2)

Size of the anion :-

$\uparrow$  in size  $\uparrow$  polarisability.

e.g. (b) hydrides of halogens



$\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

26 27 28

(b)  $\text{I}^-$  and  $\text{Se}^{2-}$  are easily polarisable because of large size.

## Fajans' rules of covalency

1924, Fajans told that there are certain conditions which, if fulfilled by the cation and anion of a given ionic molecule, make the ionic bond partially covalent (polar covalent) or purely covalent. These are called Fajans' rules given below:

1) Cation should have high +ve charge on it.

higher +ve charge - higher polarising power - greater magnitude of covalent character.

2) The cation should be small in size.

Smaller the size - greater is polarising power - greater amt. of covalent character.

3) Cation should have  $ns^2 np^6$  configuration.

e.g.  $CaCl_2$  - covalent character

$NaCl$  - ionic "

4) Anion should have high -ve charge.

5) Anion should be large in size.

## Summary of Fajan's rules

format<sup>n</sup> of covalent bond in an ionic molecule,  
is favored when cation has high +ve charge,  
small size &  $n^2 p^6 d^{10}$  conf. while the  
anion has high -ve charge & large size,

# **Coordination numbers and geometries with examples**

Coordination number	Name	Geometry	Hybridization	Polyhedron	Example
2	Linear	— M —	sp		AuCl(PPh <sub>3</sub> )
3	Trigonal planar	— M — \ /	sp <sup>2</sup>	△	Pt(PPh <sub>3</sub> ) <sub>3</sub>
4	Square planar	× × M ×	dsp <sup>2</sup> or sp <sup>2</sup> d	□	RhCl(PPh <sub>3</sub> ) <sub>3</sub>
4	Tetrahedral	M   \ / \ /	sp <sup>3</sup>	△△	Ni(CO) <sub>4</sub>
5	Trigonal bipyramidal	— M —	sp <sup>3</sup> d	○○○○○	Fe(CO) <sub>5</sub>
5	Square pyramidal	M   \ / \ / \ /	sp <sup>2</sup> d <sup>2</sup>	○○○○○	[VOCl <sub>4</sub> ] <sup>2-</sup>
6	Octahedral	M   \ / \ / \ / \ /	sp <sup>3</sup> d <sup>2</sup>	○○○○○○	Mo(CO) <sub>6</sub>
6	Trigonal prismatic	M   \ / \ / \ / \ / \ /	d <sup>2</sup> sp <sup>3</sup>	○○○○○○○○	W(CH <sub>3</sub> ) <sub>6</sub>

- Propose a formula for a plausible mineral containing each of the following ions.

a) zirconium(IV)

**Answer a:**  $\text{ZrO}_2$

b) cadmium(II)

**Answer b:**  $\text{CdS}$

c) tungsten(VI)

**Answer c:**  $\text{WO}_3$

d) zinc(II)

**Answer d:**  $\text{ZnS}$

e) copper(I)

**Answer e:**  $\text{Cu}_2\text{S}$



An ambidentate ligand



## HSAB Principle

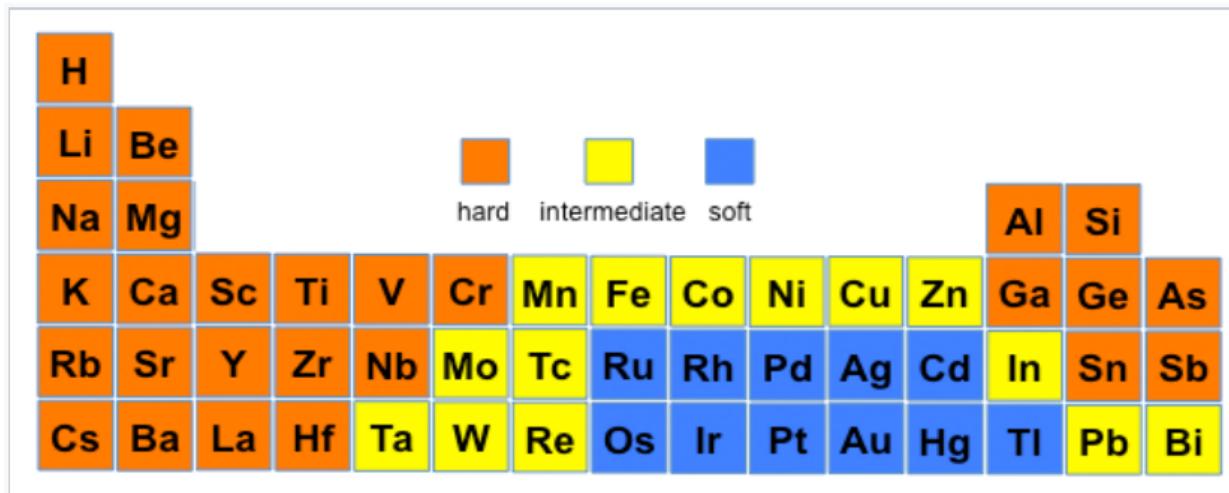
*According to HSAB concept, hard acids prefer binding to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes.*

- The **large electronegativity differences** between hard acids and hard bases give rise to strong ionic interactions.
- The **electronegativities** of soft acids and soft bases are **almost same** and hence have less ionic interactions. i.e. the interactions between them are more covalent.
- The interactions between hard acid - soft base or soft acid - hard base are **mostly polar covalent** and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

## Drawback of HSAB principle

- 1) The Pearson's HSAB theory is in **direct contradiction with Fajan's rules**.  
For example, the later predict the nature of Beryllium salts to be more covalent. But according to HSAB principle, the  $\text{Be}^{2+}$  ion is hard acid and is expected to show charge controlled bonding that results in more ionic nature for beryllium compounds. But this is not true.
- 2) Since hydrogen ion,  $\text{H}^+$  is a hard acid and hydride ion,  $\text{H}^-$  is a soft base, **according to HSAB principle** the interactions between them must be polar covalent and  **$\text{H}_2$  must be unstable**. Indeed  **$\text{H}_2$  is a stable molecule** with pure covalent nature.

## Hard-soft trends for acids



(A) Acids –

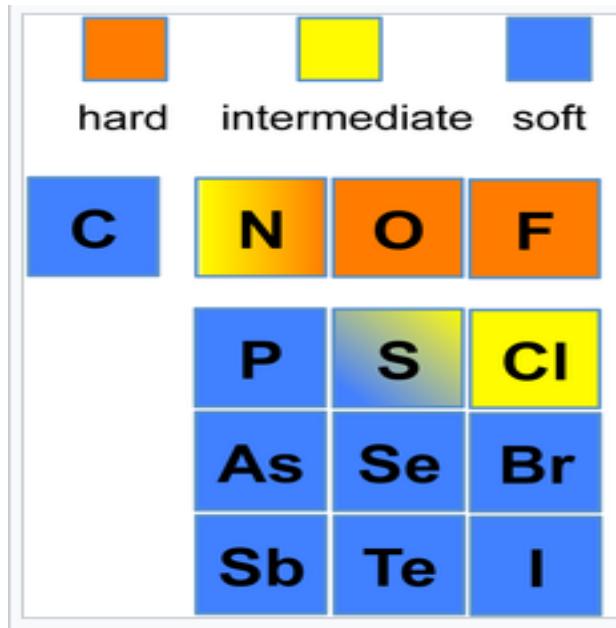
Hard	Borderline	Soft
$\text{H}^+$ , $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$	$\text{Fe}^{2+}$ $\text{Co}^{2+}$ $\text{Ni}^{2+}$	$\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Au}^+$ , $\text{Tl}^+$
$\text{Be}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$	$\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$	$\text{Hg}^+$ , $\text{Pd}^{2+}$ , $\text{Cd}^{2+}$ ,
$\text{Cr}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$	$\text{SO}_2$ , $\text{BBr}_3$	$\text{Pt}^{2+}$ , $\text{Hg}^{2+}$ , $\text{BH}_3$ , $\text{Br}_2$
$\text{SO}_3$ , $\text{BF}_3$ , $\text{BCl}_3$		$\text{Br}^+$ ,
$\text{HX}$ (H-bonding)		$\text{M}^0$ (metal atoms) and bulk metals

## Acids

### Features :

<b>Hard Acceptor atoms are marked by:</b>	<b>Soft Acceptor atoms are marked by:</b>
1) Small size	1) Large size
2) High positive oxidation state. 3) Absence of any outer electrons Which are easily excited to higher States.	2) Zero or low positive oxidation state 3) Presence of several excitable valence shell electrons.
4) Absence of d-electrons.	4) With nearly full d-electrons.
5) Usually light metal ions.	5) Mostly heavy metal ions.
6) Known as Lewis acids which Are not easily polarizable Prefer to coordinate with hard	6) Known as Lewis acids and are easily polarizable. Prefer to coordinate with soft bases.

## Hard-soft trends for bases



(B) Bases :

Hard	Borderline	Soft
$\text{F}^-$ , $\text{OH}^-$ , $\text{H}_2\text{O}$ , $\text{NH}_3$	$\text{NO}_2^-$ , $\text{SO}_3^-$ , $\text{Br}^-$	$\text{H}^-$ , $\text{R}^-$ , $\text{CN}^-$ , $\text{CO}^-$ , $\text{I}^-$
$\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{O}^{2-}$ ,	$\text{N}_3^-$ , $\text{N}_2$ , $\text{C}_6\text{H}_5\text{N}$ ,	$\text{SCN}^-$ , $\text{R}_3\text{P}$ , $\text{C}_6\text{H}_6$ ,
$\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$ , $\text{ClO}_4^-$ , $(\text{Cl}^-)$	$\text{SCN}^-$	$\text{R}_2\text{S}$ .

## Bases

### Features :

Hard	Soft
1) High electronegativity.	1) Low electronegativity
2) Low polarisability.	2) High Polarisability.
3) Presence of filled orbitals ; empty orbitals may exist at high energy level.	3) Partially filled orbitals, empty orbitals are low- lying.
4) These are anions or neutral molecule known as Lewis bases or ligands, prefer to co-ordinate with hard acids.	4) these are anions or neutral molecules called similarly as Lewis bases or ligands, prefer to bind with soft acids.

## Suggest which of the following ions is harder.

- a) zinc(II) or mercury(II)
- b) potassium(I) or copper(I)
- c) iron(II) or iron(III)

## Suggest which of the following bases is softer.

- a)  $\text{Me}_3\text{P}$  or  $\text{Me}_3\text{N}$
- b) chloride or iodide
- c) amide ( $\text{NH}_2^-$ ) or azide ( $\text{N}_3^-$ )

### Answer a:

$\text{Zn}^{(\text{II})}$ , because it is smaller and less polarizable.

### Answer b:

$\text{K}^+$ , because it is less electronegative.

### Answer c:

$\text{Fe}^{(\text{III})}$ , because of the higher charge.

### Answer a:

$\text{Me}_3\text{P}$ , because phosphorus is larger and more polarizable than nitrogen.

### Answer b:

Iodide, which is larger and more polarizable than chloride.

### Answer c:

Azide, which has a more polarizable, delocalized pi bonding system.