# CH105(I) – Topic 1: Trends in the properties of elements

P.S.: The students are requested to familiarise themselves with the periodic table by considering s, p, d & f blocks and their general inter relations and inter connectivity! There is no need to remember all the elements.

**Q01.** *Explain the van der Waals radius & van der Waals forces!*

The Van der Waal's radius of an element is half the distance between the two atoms of that element which are interacting through Van der Waal's forces without making any formal bond.

Three types of Van der Waals forces which operate between the atoms (or even molecules) are: (a) dipole – dipole interactions; (b) dipole – induced dipole interactions; (c) London dispersion forces.

The London forces arise because of a transitory and ever – changing deviation from spherical symmetry of an atom because of the uncertainity principle forbids the accurate placement of the nucleus in the surrounding electronic configuration. The very small transient dipoles of the atoms interact to give cohesion.

**Q02.** *Calculate Z\* for an electron in 4s orbital of Sc.*

$21 – [0.35 + (0.85 \times 9) + 10] = +3.0$

**Q03.** *What happens to the size when an atom A is ionized to $A^+ / A^-$ ion & why?*

$A \rightarrow A^+$ : Decreases. Explain as how this acts through $Z_{eff}$. Take an example of Na (190 pm) $\rightarrow$ $Na^+$ (~100 pm). In this example do not forget explaining the change in the 'n' value. Going from $3s^1$ to $2s^2p^6$, so there is a huge change due to 'n' change, but not in every case. If no change in 'n', the decrease in the $Z_{eff}$ is less.

$A \rightarrow A^-$: Increases. Explain using the arguments of added new electron without addition of any proton to the nucleus. Connect this $Z_{eff}$, it will be reverse to the cationic case.

**Q04.** *The difference between the second ionization potential to the first ionization potential is 700 kJ/mol in magnesium while it is ~4000 kJ/mol in case of sodium. Explain.*

Write the corresponding e-configurations and explain using the $Z_{eff}$.

Na: $2s^22p^63s^1$;          $Na^+$: $2s^2p^6$;          $Na^{2+}$: $2s^22p^5$

Mg: $3s^23p^64s^2$;          $Mg^+$: $3s^23p^64s^1$;          $Mg^{2+}$: $3s^23p^6$

Please calculate the $Z_{eff}$ as given in the lecture slides and use it for your discussions.

**Q05.** *Compare atoms Si & Sn using HSAB and comment!*

Si and Pb are in the same group and the size increases considerably (~25%) (from 118 pm to 158 pm) and hence Sn is more softer as compared to that Si. Hence, chemically Si is hard and Sn is soft.

**Q06.** *Compare atom Na with its ion $Na^+$ & I with its ion $I^-$ using HSAB and comment!*

Na with its ion $Na^+$: The size of the $Na^+$ (~100 pm) is almost half of that of the atom Na (190 pm) and hence is $Na^+$ is much harder as compared to Na. In both the cases the student should explain using effective nuclear charge concept.

I with its ion $I^-$: Exactly reverse argument is true for this case. Please explain. {I is ~130 pm & $I^-$ is ~210pm}.

***Q07.*** *Identify the oxidation state of the central atom in the following:* $NH_3$, $N_2H_4$, $NH_2OH$, $NO$, $HNO_2$, $NO_2$, $HNO_3$, $N_2O_3$, $N_2O_4$ *and* $N_2O_5$.

P.S.: Please take 'O' as more electronegative element than 'N' and 'H' as less electronegative element than 'N'. Using this clue, the student can easily workout.

***Q08.*** *While the oxidation of Li to* $Li^+$ *is more favourable, reduction of* $Ag^+$ *to Ag is more favourable. Explain.*

Please explain using the redox potentials: ($Ag^+$/Ag is +0.22 V & $Li^+$/Li is -3.0 V)

$$\Delta G^o = - nFE^o$$

**Q01**. Why are the metals Al and Ti are not produced by pyrometallurgical extraction of $Al_2O_3$ and $TiO_2$? What will be a better method to produce such metals?

Carbon can reduce any metal oxide provided that the temperature is sufficiently high. The plot of C (C→CO) in Ellingham Diagram will intersect all the metal - metal oxide curves because of the reverse slope of the C line. However, the use of C (coke) becomes impracticable for the metal oxides towards the bottom of the Ellingham Diagram, e.g., CaO, $Al_2O_3$.

$Al_2O_3$ and $TiO_2$ have rather large negative heats of formation. Therefore, their heats of decomposition (i.e., Dissociation Energies) are correspondingly high. For $\Delta G^o$ to be negative, it requires that $T\Delta S^o$ term to be very large, which means the temperature must be very high. In effect these substances are thermally very stable and resist decomposition.

$Al_2O_3$ $\Delta H_f$ = -1676 KJ/mol; this energy is sufficient enough to melt the reaction products.

For example, $Fe_2O_3 + 2\ Al$ → $Al_2O_3 + 2\ Fe$ (liquid)

(a) This is called Thermit process which is used for welding iron and steel.
(b) Thermit bombs used by the military as incendiary devices because of the intense heat of the reaction.

**Q02**. Using Elligham diagram for oxides, determine whether the Al can be used to reduce MgO? If so at what conditions?
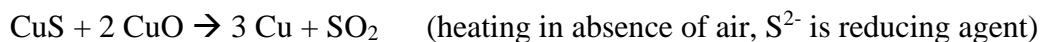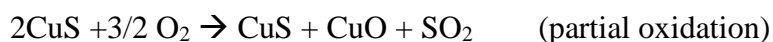
Yes. Above 1750 °C, where the Al curve intercepts the MgO curve.

**Q03**. Ellingham diagram predicts a negative $\Delta G°$ value for the reduction of $Cr_2O_3$ with Al at room temperature. In fact the reduction is carried out at a much higher temperature. Suggest an explanation.

**4/3 Al + 2/3 Cr₂O₃ → 4/3 Cr + 2/3 Al₂O₃   ΔH = -86 Kcal/mol**
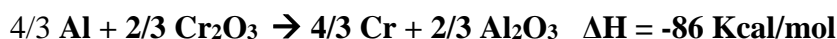
Every process needs activation energy, which is fairly high in this case. This reaction is often initiated with a pellet of Mg powder and $BaO_2$. Once initiated, the whole mass gets reduced instantaneously.

**Q04**. What is the reducing species in the self reduction of CuS ore?

$2CuS + 3/2\ O_2$ → $CuS + CuO + SO_2$      (partial oxidation)

$CuS + 2\ CuO$ → $3\ Cu + SO_2$     (heating in absence of air, $S^{2-}$ is reducing agent)

**Q05**. Can the carbon be used for the reduction of the metal sulphide ores and why?

No. The formation of $CS_2$ from C has no downward slope and hence will not intercept any of the metal-metal sulphide curves. This is due to the absence of CS formation, unlike the formation of CO.

**Q06**. Sodium metal is produced commercially by the electrolysis of a mixture of 40% NaCl and 60% of $CaCl_2$. What is the role of $CaCl_2$ in this process? Will Ca be produced along with Na.

Down's Cell: Sodium is produced commercially by the electrolysis of a Eutectic mixture of 40% NaCl and 60% $CaCl_2$, which has a m.p. of around 580 °C. Metallic sodium and calcium are liberated at the cylindrical steel cathode and rise through a cooled collecting pipe which allows the calcium to solidify and fall back into the melt.

**Q07**. Why is that $Sn^{4+}$ is more exclusively hydrolyzed in aqueous solution than $Pb^{4+}$?

The hydrolysis of these generally leads to $MO_2(H_2O)_2$, where M = Sn, Pb. $Pb^{2+}$ is more stable when compared to the corresponding 4+ ion because of the inert pair effect. Hence hydrolysis observed in case of lead is less exclusive as compared to that observed for tin. Explain the inert pair effect using the filling of d and f orbitals, effective nuclear charge, etc.

**Q01**. Crystalline AgO is diamagnetic. Explain.

Half of the silver atoms in AgO are linearly coordinated to two nearest neighbour oxygen atoms and half are coordinated to four nearest neighbour oxygen atoms in a square planar configuration.

i.e., the silver ions exist in a mixture of oxidation states, viz., $Ag^+$ and $Ag^{3+}$.

$Ag^+$, linear coordination, sp hybridization, $d^{10}$.

$Ag^{3+}$, square-planar coordination, $dsp^2$ hybridization, $d^8$

**Q02**. Work out the hybridization and geometry for the following complexes using the valence bond approach.

(a) $Ni(CO)_4$;  (b) $[Ni(CN)_4]^{2-}$;  (c) $[CoCl_4]^{2-}$;  (d) $OsO_4$;  (e) $VOCl_3$;

(f) $[Pt(NH_3)_4]^{2+}$;  (g) $[Ag(NH_3)_2]^+$;  (h) $[Pt(PPh_3)_4]$;  (i) $(Cr_2O_7)^{2-}$

| | | | | |
|---|---|---|---|---|
| $Ni(CO)_4$ | Ni(0) | $d^{10}$ | $sp^3$ | Td |
| $[Ni(CN)_4]^{2-}$ | Ni(II) | $d^8$ | $dsp^2$ | sq.planar |
| $(CoCl_4)^{2-}$ | Co(II) | $d^7$ | $sp^3$ | Td |
| $OsO_4$ | Os(VIII) | $d^0$ | $d^3s$ | Td |
| $VOCl_3$ | V(V) | $d^0$ | $d^3s$ | Td |
| $[Pt(NH_3)_4]^{2+}$ | Pt(II) | $d^8$ | $dsp^2$ | sq.planar |
| $[Ag(NH_3)_2]^+$ | Ag(I) | $d^{10}$ | sp | linear |
| $[Pt(PPh_3)_4]$ | Pt(0) | $d^{10}$ | $sp^3$ | Td |
| $(Cr_2O_7)^{2-}$ | Cr(VI) | $d^0$ | $d^3s$ | Td |

Q03.  When high pressure is applied, what type of electronic configuration is favoured for a $d^5$ transition metal complex?

Low spin; because it leads to low electron density between the metal and the ligand (i.e., along the bond axis).

Q04.  Provide reasons for the fact that a number of tetrahedral Co(II) complexes are stable, where as the corresponding Ni(II) complexes are not.

The CFSE of $d^7$ tetrahedral complex is greater than that of $d^8$ tetrahedral complex.

Similarly, the CFSE of $d^8$ octahedral complex is greater than that of the $d^7$ octahedral complex.

Q05.  Using the crystal field stabilization energy as criterion, indicate whether you expect the following spinels to be normal or inverse:  $Fe_3O_4$; $Co_3O_4$.

Spinel by definition, the 3+ ion has to go to the $O_h$ site leaving the 2+ ion in $T_d$.

$Fe_3O_4$ is composed of Fe(II) Td and Fe(III) Oh ions with d6 and d5 configurations respectively.  Since d5 has no CFSE, it is more advantageous to put it in a Td environment than in Oh.  In other words, by placing d6 ions in Oh environment there is more gain in more CFSE than keeping this in Td environment.  Here the $Fe_3O_4$ structure is inverse spinel.

$Co_3O_4$ has a similar structure with d7 and d6 configurations for 2+ and 3+ ions respectively. Co(III) d6 ion is low spin because (a) high charge (even with weak ligands like oxo) and (b) maximum gain in CFSE. So the $Co_3O_4$ structure is normal spinel.

Q06. By showing the details, determine the CFSE for the following complexes: (a) $[FeCl_4]^{2-}$; (b) $W(CO)_6$.

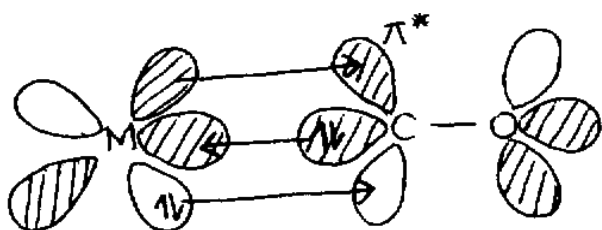(a) $e^3t_2^3$                     (b) $t_{2g}^6e_g^0$

Q07. Explain what is meant by the term "synergic bonding"?

In the synergic bonding the $\sigma$-donation of charge from the ligand to the metal is reinforced by $\pi$- back-donation from the metal to the ligand.

In a valence bond model it may be represented by $M^-CO^+$ and $M=C=O$.

The filled CO to empty M $\sigma$-donation. Filled M d-orbital to empty $\pi^*$ - back-donation.



Q08. The $Cr^{2+}$ ion in $CrF_2$ is surrounded by six fluoride ions. Of these, four are at a distance of ~2.00 Å, while the other two are at a distance of 2.43 Å from the metal ion center. Explain this observation.

$CrF_2$: $Cr^{2+}$ is surrounded by 6 fluoride ions in an $O_h$ environment.

$Cr^{2+}$ is $d^4$ high spin; $t_{2g}^3e_g^1$.

The unsymmetrical distribution of electrons in $e_g$ leads to Jahn-Teller Distortion. This observation suggests that the $e_g$ electrons in $d_{z2}$ orbital and $d_{x2-y2}$ is empty.

Q01. What are the permitted values of $m_l$ for f orbitals?

**What are the permitted values of $m_l$ for f orbitals?**

An atomic orbital is described in terms of three integral quantum numbers.

Principal quantum number n = 1,2, etc.

Orbital quantum number l has allowed values of (n-1) 0, 1, 2, etc.

The value l determines the shape of the atomic orbital and the orbital angular momentum of the electron.

The magnetic quantum number, $m_l$, gives information about the directionality of an atomic orbital and has integral values between +l and -l.

For any system containing more than one electron, the energy of an electron with principal quantum number n depends on the value of l.

The energy and the orbital angular momentum of a multi-electron species are determined by a new quantum number L which is related to the values of l for the individual electrons.

Since the orbital angular momentum has magnitude = $\sqrt{l(l + 1)}$(h/2π) and (2l + 1) spatial orientations with respect to the z-axis (i.e. the number of ml values), individual summation of individual l values is necessary.

$M_L = \sum ml$

Just as ml may have 2l+1 values so $M_l$ may have 2L+1 values

L = $(l_1+l_2)$... $(l_1-l_2)$ and intermediate values differing by one

L = 0 1 2 3 4 ...

    S P D F G ...

Orbital magnetic moment = $\sqrt{L(L + 1)}$(h/2π)

For f-orbital, the value of l = 3.

s = l = 0

p = l = 1

d = l = 2

f = l = 3

possible ml values = 2l+1 so ml =

| ml | ml | ml | ml | ml | ml | ml |
|----|----|----|---|----|----|----|
| +3 | +2 | +1 | 0 | -1 | -2 | -3 |

**Q02**. The following complexes have the indicated effective magnetic moments. Describe the structure and bonding of the complexes on the basis of the $\mu_{eff}$ values (in B.M.).

(b) K2NiF6 (0.0); (b) Ni(NH3)2Cl2 (3.3); (c) Ni(PEt3)2Cl2 (0.0); (d) Ni(Ph3AsO)2Cl2 (3.95)

The following complexes have the indicated effective magnetic moments. Describe the structure and bonding of the complexes on the basis of the $\mu_{eff}$ values.

K$_2$NiF$_6$ 0.0; Ni(NH$_3$)$_2$Cl$_2$ 3.3; Ni(PEt$_3$)Cl$_2$ 0.0; Ni(Ph$_3$AsO)$_2$Cl$_2$ 3.95

(a) K$_2$NiF$_6$

NiF$_6^{2-}$ ≡ Ni$^{4+}$ ≡ d$^6$
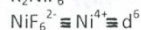
Very high charge; Hence high $\Delta_0$ and pairing tendency (c.f. Co$^{3+}$)

(CFSE depends on the charge on the metal)

d$^6$ ≡ t$_{2g}^6$e$_g^0$ ≡ no unpaired electrons.

The complex is hence diamagnetic.

(b) Ni(NH$_3$)$_2$Cl$_2$

NH$_3$ is a strong field ligand. Hence, no tetrahedral structure.
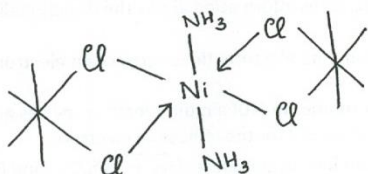
For square planar $\mu$ = 0: So, no square planar.

For O$_h$

Ground State: t$_{2g}^6$e$_g^2$ no orbital contribution.

Excited State: t$_{2g}^5$e$_g^3$ Orbital contribution possible.

So, the structure is



(c) Ni(PEt$_3$)Cl$_2$ ; phosphine is a strong field ligand.

$\mu$ = 0 and hence Square Planar.

(d) Ni(Ph$_3$AsO)$_2$Cl$_2$ ;

Both arsine oxide (this is a neutral oxygen donor) and chloride are weak field ligands. Hence tetrahedral geometry is preferred. In addition, the presence of bulky ligands also stabilizes low coordination numbers (i.e. Td). Since $\mu$ = 3.95 B.M., which is much higher than the spin only value, this is a <u>tetrahedral case with orbital contribution in ground state.</u>

**Q03**. Identify the transition metal configurations both in the octahedral and tetrahedral environments which are expected to have orbital contribution to the magnetic moment.

Name the transition metal configurations (both in octahedral and tetrahedral environments) which are expected to have orbital contribution to the magnetic moment.

Orbital contribution is possible for configurations with asymmetrically filled t$_{2g}$ (of O$_h$) and t$_2$ (of Td), because of the possibility of rotation of the electronic charge around the molecules.

For 'l$_s$ or l' due to the different symmetric of d$_{z2}$ and d$_{x2-y2}$, such a rotation is not possible.

The possible configurations for O$_h$ are;

t$_{2g}^1$e$_g^0$: t$_{2g}^2$e$_g^0$: t$_{2g}^4$e$_g^2$: t$_{2g}^5$e$_g^2$. (high spin).

Similarly work out low spin.

Do a similar exercise for tetrahedral case. {P.S.: Take all the T$_d$ ones are as high spin}

Q04. Which one would you expect to have greater magnetic moment: $CoCl_4^{2-}$ or $CoI_4^{2-}$? Why?

**Which one would you expect to have greater magnetic moment: $CoCl_4^{2-}$ or $CoI_4^{2-}$? Why?**
Both are tetrahedral.
$Co^{2+}$; $d^7$ ; $e^4t_2^3$
There is no orbital contribution in ground state. Orbital contribution in the excited state is possible because of the following configuration: $\underline{e^3t_2^4}$.
Mixing of the ground state and the excited state is more facile with the weaker of the two ligands, viz I⁻. So, $CoI_4^{2-}$ has a higher magnetic moment.

Q05. Calculate $\mu_{eff}$ for $Dy_2(SO_4)_3.8H_2O$.

$Dy^{3+} = f^9$

| 3 | 2 | 1 | 0 | -1 | -2 | 3 |
|---|---|---|---|----|----|---|
| ⇅ | ⇅ | ↑ | ↑ | ↑  | ↑  | ↑ |

L = 6+4+1-1-2-3 = 5   S = 5/2   Since more than half-field J = L+S = 5+5/2
$\mu = g\sqrt{J(J+1)}$
g = 3/2 + S(S+1) – L(L+1)/2J(J+1)
Substitute and work out. The answer is:
μ = 10.63 B.M.

Q06. Calculate $\mu_{eff}$ for $Gd^{3+}$.

**Calculate $\mu_{eff}$ for $Gd^{3+}$.**
$Gd^{3+} \equiv f^7 \equiv$
L=0 (hence no orbital contribution and spin-only formula is sufficient)
S = 7/2
$\mu_s = \sqrt{4S(S+1)}$ or $\sqrt{n(n+2)}$
= 7.9 B.M.

What are storage and transport proteins? Draw the structure of porphin.
Porphyrins are substituted porphine derivatives.
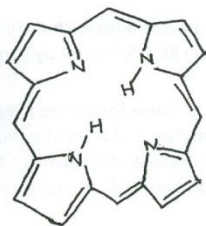
**Why is CN⁻ toxic ion to humans?**
CN⁻ binds with Fe(II) much strongly and the reaction becomes irreversible. Also the function of cytochrome is inhibited.

**What is the role of globular protein in oxygen transport?**
The globular protein generates a hydrophobic pocket and prevents $Fe(II)-O_2$ complex from solvation and also stops formation of $Fe-O_2-Fe$ etc.

**What is the "Cooperative effect"?**
Co-ordination of one $O_2$ leads to conformational changes in the protein chain leading to facilitated co-ordination of $O_2$ by other 3 sub-units.

**Why are all the oxygen carriers that contain iron and porphyrins found inside the cells?**
The inside cell environment is reducing and sustains Fe(II) whereas outside the cell the $O_2$ concentration is high thus increasing the probability of the oxidation of Fe(II) ions.

**Why is the size of high spin Fe(II) larger than low spin Fe(II)?**
High spin Fe(II) has $e_g^2$ wheras low spin Fe(II) has $e_g 0$. That id when the eg is empty, all the six ligands can approach the metal ion much more closely, thus leading to a reduction in the effective ionic radius. When the configuration is h.s. $e_g^2$, the approach of all the six ligands is hindered because of the repulsion vetween the ligand and metal $e_g$ electrons, thus leading to an enhancement of the metal ionic radius.

**What prevents synthetic iron porphyrins from functioning as $O_2$ carriers?**
Synthetic Fe-porphyrins easily form dimmers.

$O_2$ is a σ donor and a π acceptor. CO is also an example of this type of ligand. Can you use these facts to propose a mechanism for CO poisoning.

Since $O_2$ and CO are similar electronically as well as sterically, they can both bind to the same sites in metalloproteins such as haemoglobin. In fact haemoglobin and myoglobin ( and model porphyrin complexes) have a higher affinity for CO than $O_2$. Therefore, if CO is present, it can bind to and block the oxygen transport sites of haemoglobin thus preventing oxygen from being distributed to various tissues.

While the cis-platin is potent anticancer agent, its trans-isomer is not. Why?

The cis-platin forms an adduct with DNA that is stable and prevents the copying, while the trans- does not.

Are you convinced with the statement that the coordination complexes are capable of acting as drugs for various health disorders. How & Why?

The literature shows plethora of coordination complexes developed to suit as drugs for a variety of health disorders, such as, anti bacterial, anti viral, anti-diabetic, anti cancer, anti parasitic, anti HIV, and so on and so forth. All this is possible since the diversity in the generation of coordination complexes arises from change of metal ion & its oxidation state; change of the ligand and its bonding strength; ligand exchange reactivity variations; outer & inner sphere interactions with the biological molecules or systems, etc.