**Ch 23 Transition Metal Chemistry Notes- PART -1**

**Electron Configurations of Atoms and Ions.** Recall that the transition metals have atoms or ions with *incompletely filled d subshells* - hence called d block elements.

For 'd' block elements, the general configuration for most elements is ns², (n-1)dₓ electrons; what is x? For 4th period elements, you can note what x is from the table below.

**Electron Configurations of Atoms and Ions**

<table>
<thead>
<tr>
<th></th>
<th>Atom</th>
<th>+2 ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>4s²3d¹</td>
<td>3d⁴</td>
</tr>
<tr>
<td>Ti</td>
<td>4s²3d²</td>
<td>3d⁵</td>
</tr>
<tr>
<td>V</td>
<td>4s²3d³</td>
<td>3d⁶</td>
</tr>
<tr>
<td>Cr</td>
<td>4s¹3d⁶</td>
<td>3d⁷</td>
</tr>
<tr>
<td>Mn</td>
<td>4s²3d⁶</td>
<td>3d⁷</td>
</tr>
<tr>
<td>Fe</td>
<td>4s²3d⁶</td>
<td>3d⁷</td>
</tr>
<tr>
<td>Co</td>
<td>4s²3d⁷</td>
<td>3d⁷</td>
</tr>
<tr>
<td>Ni</td>
<td>4s²3d⁸</td>
<td>3d⁸</td>
</tr>
<tr>
<td>Cu</td>
<td>4s¹3d¹⁰</td>
<td>3d⁹</td>
</tr>
</tbody>
</table>

The configurations of chromium [Ar]4s¹3d⁵ and copper [Ar]4s¹3d¹⁰ are exceptions to the order of filling. The basis for these exceptions is that the energies of a 3d orbital and a 4s orbital are almost the same for these elements. For chromium, the 4s and 3d orbitals are almost identical in energy, and so the electrons enter all six of the available orbitals singly in accordance with Hund's rule. In the case of copper, the exception shows the importance of extra stability associated with a completely filled 3d subshell.

To understand the electron configurations of the ions shown in the above table, it helps to recall that electrons are removed from the outermost 4s orbital before they are taken out of the 3d.

**Properties of Transition Elements.** For the representative elements, properties such as the atomic radius, ionization energy, and electronegativity vary markedly from element to element as the atomic number increases across any period. In contrast, the chemical and physical properties of the transition metal elements vary only slightly as we read across a period.

1. **General Physical Properties.** Transition metals have relatively high densities, high melting and boiling points, and high heats of fusion and vaporization.

2. **Atomic Radius**

   a) **Across a Period:** Recall that the atomic radii of representative (A group) elements decrease markedly as we read across a period of elements due to increased nuclear charge. (remember when electrons are added to outer orbitals, so they poorly shield the increasing nuclear charge; the greater the charge, the smaller the atom).

   In contrast, in the transition series, the decrease in atomic radii is not steady, because the electrons are being added to an inner d subshell, so they shield the outer electrons very efficiently, and so,
the outer s electrons are not pulled closer resulting in a very small decrease or relatively constant size as the shielding of nuclear charge increases.

b) across a group: this trend is also different from what is observed with “A” group elements. From Period 4 to 5, size increases as expected, but between Period 5 and 6 the size is virtually the same. The increase in nuclear charge due to the 14 additional protons resulting from the 14 lanthanide elements appearing between 4d and 5d series is responsible for this shrinkage – this is called lanthanide contraction.

3. Ionization Energy. The first ionization energies of the first transition metal series are remarkably similar, increasing very gradually from left to right. There is a slight increase over the first five elements then the ionization energy barely changes from iron to copper.

4. Variable Oxidation States. The variability of oxidation states for transition metal ions results from the fact that the 4s and 3d subshells are similar in energy. Therefore, an atom can form ions of roughly the same stability by losing different numbers of electrons.

The highest oxidation state of elements in groups 3B through 7B = the group number and this happens when they combine with O or F. For example, the ox. number of Mn in MnO$_4^-$ is +7.

Elements in groups 8B exhibit fewer ox. states, and the highest state is never = group number

For elements in groups 1B and 2B, the common state is +2.

5. Metallic behavior: Transition metals in their lower ox. state behave more like metals- have more ionic bonding character- form more basic oxides.

Example: TiCl$_2$ is an ionic solid, where is TiCl$_4$ is a molecular liquid.

6. Color and magnetism:

Electrons in a partially filled d sublevel of transition metal ions can absorb visible light and move to higher energy orbitals and hence their compounds have striking colors. Exceptions are compounds of Sc$^{3+}$, Ti$^{4+}$, (which have empty d orbitals) and Zn$^{2+}$ (which has filled d orbitals).

Transition metal compounds that have unpaired electrons are paramagnetic (attracted by magnetic field) and those with all paired electrons are diamagnetic (not attracted and is slightly repelled)

Exercise:

1. Write the electron configurations and orbital box diagrams of:
   a. a Mn atom
   b. a Mn$^{2+}$ ion
   c. a Mn$^{3+}$ ion
2. Which atom in each pair has the larger atomic radius?
   a) V, Fe    b) V, Nb

3. Which has the higher ionization energy?
   - Ti
   - Fe

4. Highest possible oxidation state of vanadium is ______.

5. No. of unpaired electrons present in Fe atom = ______ and hence it is _____ magnetic. No. of unpaired electrons present in Fe$^{3+}$ ion ______ and hence it is _____ magnetic.

**COORDINATION COMPOUNDS**

**Terminology.** A complex ion consists of a central metal cation (Lewis acid) to which several anions or molecules (Lewis bases) are bonded. The complex ion may be positively or negatively charged.

The metal cation is called the central atom, and the attached anions and molecules are called ligands. The free ligands each have at least one unshared pair of electrons which can be donated to the electron-deficient metal ions.

The donor atom is the atom in the ligand that is directly bonded to the metal. Some typical ligands are Cl$^-$, CN$^-$, NH$_3$, H$_2$O, and H$_2$NCH$_2$CH$_2$NH$_2$.

A coordination compound is an electrically neutral species.

a) It may contain one complex ion and one counter ion as shown in the examples below:

[Ag(NH$_3$)$_2$]Cl and K$_3$[Fe(CN)$_6$]

The complex ion is shown enclosed in brackets. In the silver compound, Cl$^-$ is a free (meaning uncomplexed) chloride ion, and in the iron compound each K$^+$ is a free potassium ion. K$^+$ and Cl$^-$ ions in the above formulas are examples of counter ions. They serve to balance or neutralize the charge of the complex ion.

b) A coordination compound may also be made up of 2 complex ions as shown below:

[Ag(NH$_3$)$_2$]$^+$ combined with [Fe(CN)$_6$]$^{3-}$ giving the compound [Ag(NH$_3$)$_2$]$_3$[Fe(CN)$_6$]

The above 2 types of coordination compounds behave like strong electrolyte in water- the complex ion and the counter ions separate, but the complex ion behaves like a polyatomic ion. Thus 1 mole of K$_3$[Fe(CN)$_6$] yields 3 moles of K$^+$ ions and 1 mole of [Fe(CN)$_6$]$^{3-}$ ions.

c) A third type of coordination compound may be a compound in which a central metal atom or ion is attached to a group of ionic or neutral ligands with no counter ions as shown below:

Pt (NH$_3$)$_2$Cl$_2$ -- Cisplatin, an anticancer drug

Fe(CO)$_5$ - a highly toxic, volatile liquid.
d) **Oxidation Number.** Each complex ion carries a net charge that is the sum of the charges on the central atom (or ion) and on each of the ligands. In \([\text{Fe(CN)}_6]^{3-}\), for example, each cyanide ion (CN\(^-\)) contributes a \(-1\) charge, and the iron ion a \(+3\) charge. The charge of the complex ion then is; \((+3) + 6(-1) = -3\). The *oxidation number* of iron is \(+3\) which is the same as its ionic charge.

e) The **coordination number** is defined as the number of donor atoms surrounding the central metal atom. Thus the coordination number of Pt\(^{2+}\) in \([\text{Pt(NH}_3)_4]^{2+}\) is 4, and that of Co\(^{2+}\) in \([\text{Co(NH}_3)_6]^{2+}\) is 6.

Some ligands contain more than one donor atom. Ligands that coordinate through two bonds are called **bidentate ligands**. Those with more than two donor atoms are referred as **polydentate ligands**. Ethylenediamine (en) and oxalate ion (ox) are bidentate ligands:

- Ethylenediamine (en): \(\text{H}_2\text{N}−\text{CH}_2−\text{CH}_2−\text{NH}_2\)
- Oxalate ion (ox): \(\text{C}−\text{O}\) \(\text{C}\) \(\text{O}−\text{O}−\)

Bidentate and polydentate ligands are often called **chelating ligands** (pronounced key-lateing). The name derives from the Greek word *chele* meaning "claw." Chelate complexes are extra stable because two bonds must be broken to separate a metal from a ligand. EDTA\(^{4-}\) is an excellent chelating ligand because it has six donor atoms. Its structure is shown below:
c. Both these ligands are _______ (mono, di, poly ?) dentates.

d. What is the charge on the complex ion?

e. What is the oxidation number (O.N.) of the central atom?

f. What is the coordination number of the central atom?

g. 4.0 moles of the compound when dissolved in water will yield ____ moles of total ions.

h) When aqueous silver nitrate is added to the aqueous solution of this compound, what visible change will you observe? ________________________________

2. What is the charge on the complex ion in K₂[PtCl₄]?

3. What is the coordination number of Hg in [Hg(en)₂]²⁻?

4. What is the oxidation number of Fe in [Fe(CN)₆]⁴⁻?

5. What is the coordination number and oxidation number of the central atom in K[Cr(NH₃)₃Cl₃]?
   
   coordination number = [ ]
   oxidation number = [ ]