

B. Sc. Part-II (Hons), Paper-III B (Inorganic Chemistry)
 Group-B, Unit-2: Comparative Chemistry of Iron triad elements (Fe, Co & Ni)

[By Dr. Birendra Kumar, Maharaja College]

Iron triad comprises three elements: Iron (Fe), Cobalt (Co) and Nickel (Ni). They are ferromagnetic elements irrespective strong magnetic property. They show horizontal similarities, however, they show desimilarities also.

Property	Iron (Fe)	Cobalt (Co)	Nickel (Ni)
1. Electronic Configuration	[Ar] 3d ⁶ 4s ² It has d ⁶ system.	[Ar] 3d ⁷ 4s ² It has d ⁷ system.	[Ar] 3d ⁸ 4s ² It has d ⁸ system.
2. Oxidation States	This shows oxidation states: 0, +2, +3, +4, +6, but only 0, +2, +3 are common. 0 state +3 is most stable.	This shows only oxidation states: 0, +2, +3 & 4. The 0, +2 & +3 are more common. 0 state +2 is most stable. 0 state +3 is stable in aqueous solution.	This also shows oxidation states: 0, +2, +3 & +4, but only +2 state is stable and common.
3. Allotropy	This has four allotropic forms: α-Fe, β-Fe, γ-Fe & δ-Fe. α-Fe is stable below 770°C & is converted into β-Fe at 770°C without change in crystal structure. β-Fe is transformed in γ-Fe at 912°C and at 1394°C into δ-Fe (body centred cubic lattice structure).	This exists in two allotropic forms: α-Co & β-Co. α-Co has hexagonal lattice structure and stable at temp. below 417°C. α-Co is converted into β-Co at temp. above 417°C. β-Co has face centred cubic lattice structure.	This also exists in two allotropic forms. α-Ni & β-Ni. α-Ni has hexagonal lattice structure and stable at temp. below 250°C. β-Ni has face centred cubic lattice structure and stable above 250°C.
4. Colour of ions or compounds	Fe(II) & Fe(III) ions/compds. give different colours in solution. Fe(II) ion has pale green colour while Fe(III) ion has yellowish brown colour. Fe(III) ions are hydrolysed to give [Fe(OH)] ²⁺ $Fe^{3+} + H_2O \rightarrow [Fe(OH)]^{2+} + H^+$ Colour of hydrated salt are due to d-d transition, as the presence of H ₂ O molecule (ligand) causes splitting of d-orbitals moves to the high energy d-orbitals and the compound appears coloured. Some compds. of Fe, e.g. FeCl ₃ , Fe ₃ O ₄ , K ₄ [Fe(CN) ₆] possess deep colours due to charge transfer or non-stoichiometric defect.	Cobalt generally form compounds in oxidation states +2 & +3. Co ²⁺ does not oxidised into less stable Co ³⁺ . Co ²⁺ undergoes hydrated in aqueous solution to form [Co(H ₂ O) ₆] ²⁺ and possesses pink colour. On heating, Co ²⁺ compounds become anhydrous, so possess blue colour. Co ³⁺ ion reduces to Co ²⁺ in aqueous solution and possesses same colour as Co ²⁺ colour of hydrated ion due to d-d transition. CoS is coloured due to non-stoichiometric defect.	Nickel only form compounds in 0 state +2. Ni ²⁺ undergoes hydrated to form [Ni(H ₂ O) ₆] ²⁺ and possesses green colour. Hence, Ni ²⁺ compounds are either green or blue (deep) colour.
5. Magnetic property	Iron has strong ferromagnetic property. It is very readily attracted by magnet. This property lost on heating above 766°C.	Cobalt also possesses ferromagnetic property, but less extent than iron.	It's ferromagnetism property is relatively very lower than iron.

[Note: Magnetic property is due to its ionic lattice structure. When magnetic field is applied, all the unpaired electrons in the lattice orient in one direction giving rise to strong paramagnetism, i.e., ferromagnetism]

Property	Iron (Fe)	Cobalt (Co)	Nickel (Ni)
6. Complex formation	<p>Fe(II) forms a number of complex compounds in coordination no. 6 most of which are octahedral structure. Most common complex ion of Fe(II) is $[\text{Fe}(\text{CN})_6]^{4-}$, hexacyano-ferrate(II) ion and $[\text{Fe}(\text{CN})_5]^{3-}$ is most important complex compound. Its important useful complex compound is sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$.</p> <p>Fe(III) forms more complex compounds than Fe(II) in which coordination number of Fe is 6 and shape is octahedral. Fe(III) also form complex compounds in coordination no. 4. These complex compounds are tetrahedral in shape $[\text{FeCl}_4]^-$ is an important complex ion in this case. Fe³⁺ or Fe(III) has strong affinity to coordinate with oxygen atom of ligand. Its trioxalato complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is highly stable while $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is less stable. $[\text{FeCl}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are highly stable because of only one unpaired electron in it. Fe(III) forms both inner orbital and outer orbital complexes. The 0 state -2 occurs in carbonyl ion $[\text{Fe}(\text{CO})_4]^{2-}$ and 0 state 0 in carbonyls e.g. $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}_2(\text{CO})_9]$, $[\text{Fe}_3(\text{CO})_{12}]$ etc.</p>	<p>Co(II) forms some complex compounds in coordination no. 4 which are tetrahedral in shape, deep blue and paramagnetic, e.g. $[\text{CoCl}_4]^{2-}$, $[\text{CoBr}_4]^{2-}$. Co(II) generally forms complex compounds in C.No. 6, which is pale pink colour, less paramagnetic, octahedral and outer orbital type, e.g. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$.</p> <p>Co(III) forms a large number of complex compounds. These complex compounds have C.No. 6, octahedral, diamagnetic, yellow-orange colour and both inner & outer orbital type. Some of the important complex compounds of Co(III) are: $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ etc.</p> <p>Co forms tetrahedral complexes in 0 state -1, e.g. $[\text{Co}(\text{CO})_4]$, $[\text{Co}(\text{CO})_3\text{NO}]$ etc. Cobalt forms carbonyl complexes in 0 state 0, e.g. $[\text{Co}_2(\text{CO})_8]$, $[\text{Co}(\text{PMe}_3)_4]$, $\text{K}_4[\text{Co}(\text{CN})_6]$ etc.</p>	<p>Ni(0) also forms a large number of complex compounds like Fe & Co. It forms complex ions in its most stable oxidation state +2 which can be reduced to 0 state +1, but cannot be oxidised to 0 state +3. Some of the important complex compounds of Ni(II) in which C.No. of Ni is +6 are: $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$, $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$ etc. These complex compounds are octahedral and outer orbital type. Ni(II) forms complex compounds with X^-, CN^- in C.No. 4. Former complex compound is tetrahedral while latter is square planar. Tetrahedral complex compounds are paramagnetic while square planar complex compounds are diamagnetic. Octahedral and tetrahedral complex compounds are blue while square planar complex compounds are red or brown yellow. Nickel forms tetrahedral complex compounds in zero oxidation state, e.g. $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{PF}_3)_4]$, $\text{K}_4[\text{Ni}(\text{CN})_6]$ etc. Ni forms complex ion in 0 state -1 is $[\text{Ni}_2(\text{CO})_6]^{2-}$ and in 0 state +1 is $\text{K}_4[\text{Ni}(\text{CN})_6]$. Few Ni(III) complex compounds e.g. $[\text{Ni}(\text{PET}_3)_2\text{Br}_2]$, $[\text{Ni}(\text{en})_2\text{Cl}_2]\text{Cl}$ etc. also known.</p>
7. Reactivity	<p>Iron is most reactive. It easily reacts in moist air to form basic oxide (brown). Fe²⁺ or Fe(II) is reducing agent. Iron is strong electropositive (E° element than Cu, Ag etc, so displace them from salt solutions).</p>	<p>Reducing agent Cobalt is less reactive than Fe (iron). It is not attacked by dry or moist air at ordinary temp. It is slightly electropositive ($E^\circ = 0.28$ volt).</p>	<p>Nickel is least reactive in the triad. It is not attacked by dry or moist air at ordinary temp.</p>