

B. Sc. Part-III (Hons), Paper-6 (Inorganic Chemistry)
 Group-B, Unit: 2 Comparative Chemistry of Cr, Mo & W.
 (By Dr. Birendra Kumar, Maharaja College)

Group-6 (Chromium group) of Modern PT comprises of three metals: Chromium (Cr), Molybdenum (Mo) & Tungsten (W). They resemble each other due to the member of same group, but they do resemble each other due to difference in atomic weights and atomic sizes. Comparative Chemistry of these elements are as follows:

Property	Chromium (Cr)	Molybdenum (Mo)	Tungsten (W)
1. Outer electronic Conf.	$3d^5 4s^1$	$4d^5 5s^1$	$5d^5 6s^1$
2. Melting & Boiling points	It has high melting pt. (1875°C) & boiling pt. (2665°C)	It also has high melting pt. (2610°C) & boiling point (5560°C)	It has very high melting pt. (3410°C) & boiling pt. ()
3. Oxidation States	It shows Oxidation states +1 to +6. The most common O. states of Cr are +2, +3 & +6. O. states +1 & +5 are rare and unstable. Cr(II) is reducing and Cr(III) is most stable and important. Cr(VI) is strongly oxidising. O. state +1 occurs in dipyrrolyl, Carbonyl complexes.	It shows Oxidation states -2, 0 to +6. The most common oxidation state of Mo are +5 & +6. O. state +6 is stable and O. state +3 is strongly reducing.	It shows Oxidation states -2, 0 to +6. The most common Oxidation states are +5 & +6. O. state +6 is stable and O. state +3 is strongly reducing.
4. Reducing character	It is strong reducing agent.	It does not has such reducing character.	It does not has such reducing character.
5. Chemical reactivity	It is unreactive or passive at low temp. because it is protected by a surface coating of oxide. It does dissolve in HCl, H_2SO_4 & alkalis, but not in HNO_3 or aqua regia. It absorbs hydrogen gas.	It is relatively inert and is only slightly attacked by aqueous acids and alkalis. It reacts initially with HNO_3 but then become passive. It dissolves in HNO_3 & HF mixture. It does not absorb H_2 gas.	It is also relatively inert and is only slightly attacked by aqueous acids and alkalis. It dissolves in HNO_3 & HF mixture, and also in fused Na_2O_2/KNO_3 & NaOH. It does not absorb H_2 gas.
6. Formation of oxides	It forms Oxides in O. States +3, +4 & +6. Cr_2O_3 & $Cr(OH)_3$ are amphoteric but are more acidic than basic. It gives $[Cr(H_2O)_6]^{3+}$ with acids and Chromates with alkali. CrO_2 is a Corundum Structure.	It forms Oxides in O. States +4, +5 & +6. Mo_2O_3 & $Mo(OH)_3$ though amphoteric but are relatively more basic. It gives molybdate salts with alkalis.	It forms Oxides in O. States +4 & +6 only. WO_3 is amphoteric but relatively more basic. It gives tungstate salts with alkalis.

Property	Chromium(Cr)	Molybdenum(Mo)	Tungsten(W)
7. Formation of Halides	It forms stable trihalides in anhydrous as well as hydrated states. But it does not form hexa halides. All halides are covalent, volatiles can be easily hydrolysed. Cr(II) halide can be prepared but it readily oxidized in air (O ₂) to the Cr(III) halide. CrCl ₂ is the most important and strongest reducing agent that exist in water.	It forms trihalides. However, it form hexafluoride & hexachloride. The Mo(II) halides do not have simple formulae and do not exist as simple ions. MoBr ₂ is really [Mo ₆ Br ₂]Br ₄ ·2H ₂ O. It's anion has an octahedral cluster structure. MoCl ₂ is not reducing agent.	It does not form trihalides but it forms hexa-fluoride, hexachloride & hexabromide. The halides are all covalent, volatile and can be hydrolysed. WCl ₂ is reducing in solution. The W(II) halides do not have simple formulae and simple ion.
8. Formation of double salts	It forms a number of double salts. Chrome alum, [K ₂ SO ₄ ·Cr ₂ (SO ₄) ₃ ·24H ₂ O] is an important one.	It does not form double salts.	It does not form double salts.
9. Complex formation	It forms complexes in 0 state 0 to 6 with varying c. No. 4 to 8. The most stable & common 0 state is +3 in which an octahedral complex (t _{2g} ³ e _g ⁰) e.g. [Cr(NH ₃) ₆] ³⁺ , [Cr(acac) ₃] ³⁻ , K ₃ [Cr(CN) ₆] etc. These are kinetically inert and cationic. Cr(II) forms complexes with hydrazine & dipyrindyl, e.g. [Cr(N ₂ H ₄) ₂ Cl ₂] ²⁺ , [Cr(dipy) ₃] ²⁺ . It also form Cr(II) alkanoates, which is diamagnetic. [Cr(CN) ₆] ⁴⁻ is low spin complex of Cr(II). Many complex anions of the type [CrX ₆] ³⁻ in 0 state +3 are known (X = monodentate ligands). The most common one is M ₄ [Cr(NCS) ₄ (NH ₃) ₂]·H ₂ O, called Reinecke's salt. The only example of Cr(II) with a coordination no. other than 6 are salts such as [Cr(CO) ₂ diars ₂ ·X] ₂ X.	It forms complexes in different 0 states with varying c. No. 5 to 9, but it forms few cationic complexes in 0 state +3. In 0 state +6, most complexes are anionic with P or O as the ligand atoms. In 0 state +5, it forms M[MoF ₆] type of complexes, where M = Na, K, Rb or Cs. The most important complexes of Mo(II) are the octacyanides, [Mo(CN) ₈] ⁴⁻ , which are diamagnetic and square antiprism structure. It forms some cationic complexes in 0 state +3 in aqueous solution, e.g. [Mo(Phen) ₃]Cl ₃ & [Mo(dipy) ₃]X ₃ . It forms complexes of type [MoX ₆] with several halogens and pseudo halogens.	It forms complexes in different 0 states with c. No. 5 to 9, but it forms cationic complexes in 0 state +3. In 0 state +6, complexes are anionic with P or O as the ligand atoms. In 0 state +5, it forms M[W ₆ F ₆] type of complexes, where M = Na, K, Rb or Cs. It also forms alkoxides in 0 state +6, e.g. [WCl ₆ (OEt) ₂], which is blue and paramagnetic and [WCl ₆ (OEt) ₂], which is red and diamagnetic. It forms octacyanide complexes in 0 state +4, e.g. [W(CN) ₈] ⁴⁻ . It forms only mono nuclear cationic W(III) 7 coordinated complex, [W(dian)Br ₂] ⁺ . The only W(III) cationic complex is the ion [WCl ₆] ³⁺ . A well known pyridyl complex of W(IV) is [WCl ₄ Py ₂].