Chromium, Molybdenum & Tungsten

• First row d electrons fall below valence shell, +6 oxidation state is now highly oxidising. Those of 5th & 6th period non-oxidising.
• First row +3 oxidation state most stable.
• Melting points: Cr/Mo lower than V/Nb, but W highest of all metals. Can be seen in energy of atomization.
• Electrical resistivity Cr lower than V, Much larger drop in resistivity is seen in 5th & 6th period.
• Chromium has an extensive aqueous chemistry in oxidation states II-VI.
• Coordination chemistry Cr very important in the development of Crystal Field Theory and Ligand Field Theory.

High Spin Cr(II) Jahn-Teller Distortions

\[
\text{Cr}^{2+} - \text{d}^4 \text{ electron configuration in octahedral crystal field predict a single } \varepsilon \text{ to } \varepsilon_T \text{ transition. Experiment shows two absorptions - a Jahn-Teller distortion of the O}_6 \text{ crystal field.}
\]

- Elongation of the "axial" fluorines will lower the energy of the \(d_{z^2}\) atomic orbital relative to the \(d_{x^2-y^2}\) atomic orbital.
- The complex undergoes a "tetragonal distortion breaking the degeneracy of the \(\varepsilon\) set as a result of their unequal filling. The electron goes to the orbital having the lowest ligand interaction (coulomb repulsion).
Halides or Cr, Mo & W

- **CrF₆** – 400°C, 200 atm F₂, disproportionates at lower pressure. 
  \[ \text{CrF}_6 \rightarrow \text{CrF}_3 + \text{F}_2 \]
- **MoF₆** – Highly oxidizing, volatile, octahedral molecule.
- **WF₆** – Not highly oxidizing, volatile, octahedral molecule.
- **MoF₅, WF₅** – Cyclic tetramers, octahedral M, bridging fluorine. 
  \[ \text{WF}_5 \rightarrow \text{WF}_4 + \text{WF}_6 \]
- **CrCl₃, MoCl₃** – have layer structures, Cr(III) occupying 2/3 of octahedral sites of alternate layers, 1/3 empty giving a cleavage plane resulting in mica-like flake cleavage. Mo(III) isostructural.
- **WCl₃** – A cluster compound based on \( M_6X_{12}^{n+} \) (see Group 5 Nb, Ta) with 6 additional Cl atoms at each metal apex.
- **WBr₃** – Cluster Compound based on \( M_6X_8 \); \([W_6Br_8]^{6+}(Br_4^{2-})(Br^-)\).

Metal – Metal Bonding

\[ \text{Cr} + \text{dilute HCl} \quad \rightarrow \text{Cr}^{2+} \quad \text{octahedral high spin d}^4\text{ complexes} \quad \sim 4.9 \text{ BM, nearly all are “sky blue”} \]

\[ \text{Cr} + \text{dilute CH}_3\text{COOH} \quad \rightarrow \quad \text{Red or pink, nearly diamagnetic, anhydrous or hydrated species. Sulfates are violet colored.} \]

\[ \text{Mo(CO)}_6 + \text{dilute CH}_2\text{COOH} \quad \rightarrow \quad [\text{Mo}_2(\text{CH}_3\text{COO})_4] \quad \text{completely diamagnetic} \]

\[ \text{HCl conc.} \quad [\text{Mo}_2\text{Cl}_8]^{-4} \quad \text{Red, diamagnetic, Cl’s eclipsed} \]

\[ d_{\text{Cr-Cr}} = 183 \text{ pm} \]

\[ d_{\text{Mo-Mo}} = 224 \text{ pm} \]
Organometallic Compounds Cr, Mo, W

Dicyclopentadienylchromium, NVE = 16, paramagnetic, 2 unpaired electrons; Mo, W compounds polymerize above 10K. \([\text{MCp}_2\text{H}_2]\) \(M = \text{Cr}, \text{Mo}, \text{W}\) known.

Dibenzenechromium, NVE = 18, Mo & W derivatives known.

\(\text{M(CO)}_3(\text{CH}_3\text{CN})_3\) or \(\text{M(CO)}_6\) reflux hexaalkylborazine chromium tricarbonyls have also been prepared.