Chromium Chemistry

Cr : \(1s^22s^22p^63s^23p^64s^13d^5\)

Elemental Chromium

- Chief ore is chromite (FeCr$_2$O$_4$), which has a spinel structure consisting of Fe(II) [$T_d$] and Cr(III) [$O_h$].

- Pure Cr is a white, hard, lustrous, and brittle metal.

- First discovered in 1797 in the mineral crocoite (lead chromate) which is famous for its deep yellow color and is used extensively in paints.

- *The name chromium is derived from the Greek word "chrōma", meaning color, because many of its compounds are intensely colored.*

- Extremely resistant to corrosive reagents, which accounts for its extensive use as an electroplated protective coating.

- Readily dissolves in mineral acids HCl & H$_2$SO$_4$ but not oxidizing acids e.g HNO$_3$.
Chromium Oxidation States

- Oxidation states range from +2 to +6
- The highest oxidation state Cr(VI) exists only in oxo forms (strongly oxidizing)
- In today's lab we will see +6, +3, and +2

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>+6</th>
<th>+3</th>
<th>+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions</td>
<td>CrO$_4^{2-}$/Cr$_2$O$_7^{2-}$</td>
<td>Cr(III) $(aq)$</td>
<td>Cr(II) $(aq)$</td>
</tr>
<tr>
<td>Color</td>
<td>orange/red-orange</td>
<td>green</td>
<td>blue-violet</td>
</tr>
<tr>
<td>Configuration</td>
<td>$3d^0$</td>
<td>$3d^3$</td>
<td>$3d^4$</td>
</tr>
<tr>
<td>Magnetism</td>
<td>diamagnetic</td>
<td>paramagnetic</td>
<td>paramagnetic</td>
</tr>
</tbody>
</table>
• This low valent oxidation state of Cr can be stabilized by a highly electron withdrawing ligand-set by back-donation into a ligand $\pi^*$-orbital.

\[
\begin{align*}
\text{Metal } d_{x^2-y^2} & \overset{\sigma \text{ bond}}{\longleftrightarrow} \text{carbonyl} \\
\text{Metal } d_{yz} & \overset{\pi\text{-back-donation}}{\longrightarrow} \text{carbonyl}
\end{align*}
\]

Cr(0), $d^6$, 18e⁻ → (±)-Acorenone B
The most stable and generally most important oxidation states of chromium are Cr(II) and Cr(III).

Cr(III) is typically green, and Cr(II) is usually blue-violet. Cr³⁺ ion has the configuration 3d³, and Cr²⁺ ion has the configuration 3d⁴, so both species are expected to be paramagnetic in an O₉ₐ environment.

[Cr²⁺(OH₂)₆]²⁺ is prepared by the dissolution of elemental Cr in mineral acid resulting in a bright blue solution.

Alternatively, [Cr²⁺(OH₂)₆]²⁺ can be prepared by the reduction of Cr(III) by electrochemical or chemical (Zn/Hg) methods in the absence of O₂.

Even in the absence of O₂ [Cr²⁺(OH₂)₆]²⁺ will oxidize with concurrent H₂ evolution, i.e. H⁺ reduction.

\[
\begin{align*}
2H^+ + 2 e^- & \rightarrow H_2 & E^o = 0.000 \text{ V} \\
2Cr^{3+} + 2e^- & \rightarrow 2Cr^{2+} & E^o = -0.410 \text{ V} \\
2 \text{Cr}^{2+} + 2H^+ & \rightarrow H_2 + 2\text{Cr}^{3+} & E_{\text{cell}} = +0.410 \text{ V}
\end{align*}
\]
• $O_h$ Cr(II) complexes can exist in either high- or low-spin configurations depending upon the $O_h$ ligand-set involved.

High Spin ($m = 5$)

Low Spin ($m = 3$)

*distorted $O_h$ owing to the Jahn-Teller effect*

*regular $O_h$*
Potassium Dichromate - Cr(VI)

- Potassium dichromate, $K_2Cr_2O_7$, is the starting material for today's synthesis.
- In basic solution, chromium(VI) exists as the orange-colored tetrahedral $CrO_4^{2-}$ ion.
- In acid solution, this can become $HCrO_4^-$ but dimerization to red-orange $Cr_2O_7^{2-}$ predominates:

$$H_2CrO_4 + H_2O \rightleftharpoons HCrO_4^- + H_3O^+ \quad K_1 = 4.1$$

$$HCrO_4^- + H_2O \rightleftharpoons CrO_4^{2-} + H_3O^+ \quad K_2 = 1.3 \times 10^{-6}$$

$$2 \ CrO_4^{2-} + 2 \ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad K = 6.3 \times 10^{-3}$$

- The configuration of Cr in both chromate and dichromate ions is $d^0 \ [Cr(VI)]$. The intense colors of $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ are the result of ligand-to-metal ($O \rightarrow Cr$) charge transfer (LMCT) bands.

- Chromic acid in aqueous sulfuric acid and acetone is known as the Jones reagent, which will oxidize $1^0$ and $2^0$ alcohols to carboxylic acids and ketones respectively, while rarely affecting unsaturated bonds.
The dichromate ion has two tetrahedrally coordinated Cr atoms linked by an oxygen bridge:
Redox Synthesis

• In this synthesis we will reduce Cr(VI) to Cr(III) and then to Cr(II).

  • *Dichromate is a strong oxidizing agent:*

    \[
    \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \quad E^o = +1.33 \text{ V}
    \]

• Cr(III) is a weak oxidizing agent, which requires a strong reducing agent to produce Cr(II):

  \[
  \text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+} \quad E^o = -0.41 \text{ V}
  \]

• In this synthesis, zinc metal serves as the strong reducing agent:

  \[
  \text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad E^o = -0.76 \text{ V}
  \]
Overall Redox Reaction Uncertain

• From the electrode potentials, it might be assumed that the reduction of Cr(VI) to Cr(II) is accomplished by Zn as the reducing agent, in which case the balanced equation would be

\[
\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 4 \text{Zn} \rightarrow 2 \text{Cr}^{2+} + 4 \text{Zn}^{2+} + 7 \text{H}_2\text{O}
\]

• But in this preparation, Zn and H\(^+\) from the acid are also reacting to produce H\(_2\)(\(g\)), which itself can act as a reducing agent for converting Cr(VI) to Cr(III).

• If so, the reduction of Cr(III) to Cr(II) would then be effected by Zn as the reducing agent in a second step. Thus, the production of Cr\(^{2+}\) is a mixture of reduction by H\(_2\) and reduction by Zn.

• Regardless of the exact stoichiometry, the limiting reagent is Cr\(_2\)O\(_7\)\(^{2-}\), from which twice as many moles of Cr\(^{2+}\) is produced.
Reaction Summary

- Color of the original Cr(VI) dichromate solution changes from red/orange to green Cr(III) and then to blue Cr(II).

- When the solution is blue, conversion to Cr\(^{2+}\) is complete.

- At this point, using the pressure from the evolving H\(_2\)(g), the solution is pumped into a solution of sodium acetate, where the complex forms and is precipitated as a brick-red Cr(II) solid:

\[
2 \text{Cr}^{2+} + 4 \text{CH}_3\text{CO}_2^- + 2 \text{H}_2\text{O} \rightarrow \text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2
\]
• When wet, the \( \text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2 \) complex is subject to oxidation to \( \text{Cr(III)} \) from oxygen:

\[
\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \quad E^0 = +1.23 \text{ V}
\]

\[
4\text{Cr}^{3+} + 4\text{e}^- \rightarrow 4\text{Cr}^{2+} \quad E^0 = -0.41 \text{ V}
\]

\[
4\text{Cr}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 2\text{H}_2\text{O} \quad E_{\text{cell}} = +1.64 \text{ V}
\]

Avoid sucking air through the wet product during the cold water and alcohol washes.

• After the final ether wash, allow air to pass through the product on the filter for about 30 sec., then collect it on a large piece of dry filter paper or a porcelain plate to allow the residual ether to evaporate.
Chromium(II) Acetate

- Chromium(II) acetate dihydrate, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, was discovered in 1844.
- It has long been regarded as unusual for a Cr(II) compound because it is brick-red and diamagnetic.
- It is the longest-known example of a family of compounds that have the general formula $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$, which have the following structure:
Each Cr(II) ion has 4 \( d \) electrons but the complex is found to be diamagnetic which is explained by the formation of a quadruple bond between the two metal ions. The Cr-Cr bond distance in a range of these quadruply bonded species has been found to vary between 1.95-2.55 \( \text{Å} \).