ZINC, CADMIUM, AND MERCURY

- Now that we went through the main group elements,
- We have reached the part of the periodic system where we look at some transition metal elements,
- Or also called d-block elements.
- They are located in between the main block elements and their occurrence is due to the filling of the \((n-1)d\) orbitals.
- The group IIB elements Zn, Cd, Hg are also called the transition elements.
ZINC, CADMIUM, AND MERCURY

- Their characteristic is that either the neutral atom
- Or one of its ions has an incomplete set of d-electrons.
- The elements Zn, Cd, and Hg have unique properties.
- They resemble alkaline earth metals,
- No Oxidation state higher then +2
- Difference Polarizable nd\(^{10}\) shell instead of noble gas shell.
ZINC, CADMIUM, AND MERCURY

Physico-chemical properties of the elements are:

<table>
<thead>
<tr>
<th>Element</th>
<th>El. configuration</th>
<th>Mp (°C)</th>
<th>Ionic Radius (Å)</th>
<th>$E^\circ$ (V)</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>[Ar] 3d\textsuperscript{10}4s\textsuperscript{2}</td>
<td>420</td>
<td>0.88</td>
<td>-0.76</td>
<td>2632</td>
</tr>
<tr>
<td>Cd</td>
<td>[Kr] 4d\textsuperscript{10}5s\textsuperscript{2}</td>
<td>320</td>
<td>0.92</td>
<td>-0.40</td>
<td>2492</td>
</tr>
<tr>
<td>Hg</td>
<td>[Xe]4f\textsuperscript{14}5d\textsuperscript{10}6s\textsuperscript{2}</td>
<td>-39</td>
<td>1.16</td>
<td>+0.85</td>
<td>2805</td>
</tr>
</tbody>
</table>
ZINC, CADMIUM, AND MERCURY

- As can be seen from the table before, Hg
- Has very special properties as compared with the other elements
- Hg can not be considered as a homologue to Zn and Cd
ZINC, CADMIUM, AND MERCURY

- Apart from the resemblance that they also just form $+2$ ions
- They do not have much in common with the alkaline earth metals.
- $\text{BeO, Be(OH)}_2, \text{ and BeS} \rightarrow \text{ZnO, Zn(OH)}_2 \text{ and ZnS}$
- $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$ share some common properties in their solution and complex chemistry.
ZINC, CADMIUM, AND MERCURY

- Occurrence, Isolation, and Properties of the Elements

- Low occurrence in earth crust $10^{-6}$ for Zn, Cd.

- Have been known long time, easily prepared from ores

- Zinc occurs widely, *sphalerite, (ZnFe)S, occurs with PbS*

- *Cd occurs rare, but is found in Zn ores.*
ZINC, CADMIUM, AND MERCURY

- Occurrence, Isolation, and Properties of the Elements
- Methods of isolation involve
  - Flotation
  - Roasting
  - Yields metal oxides
  - ZnO and PbO → reduced with carbon to the metals.
- Cadmium is invariably a by/product and is usually separated from Zn by distillation
ZINC, CADMIUM, AND MERCURY

- Occurrence, Isolation, and Properties of the Elements

- precipitation from sulfate solutions by Zn dust.

- \[ \text{Zn} + \text{Cd}^{2+} = \text{Zn}^{2+} + \text{Cd} \quad E^O = +0.36 \, \text{V} \]
ZINC, CADMIUM, AND MERCURY

- Occurrence, Isolation, and Properties of the Elements

- The only mercury ore is cinnabar HgS.
- It is roasted to give the oxide
- The Oxide is thermically decomposed at 500 degC and Hg vaporizes.
- Zinc and cadmium are white, tarnishable metals
- Hg is a shiny liquid at ordinary temperature.
ZINC, CADMIUM, AND MERCURY

- All elements are volatile for heavy metals.

- Mercury gives a monatomic vapor
- vapor pressure \((1.3 \times 10^{-3} \text{ mm})\) at \(20 \text{ °C}\)
- Soluble in polar and apolar liquids
- Solubility of \(6 \times 10^{-8} \text{ g of Hg per gram of H}_2\text{O}\).
- high volatility and moderate toxicity should be handled in well-ventilated areas
ZINC, CADMIUM, AND MERCURY

- It becomes extremely hazardous in the biosphere because there are bacteria that convert it to the exceedingly toxic CH₃Hg⁺ ion

- Mercury is readily lost from aqueous solutions of mercuric salts owing to reduction by traces of reducing materials and by disproportionation of Hg²⁺
Both Zn and Cd are very electropositive and react readily with nonoxidizing acids releasing H₂ and giving the divalent ions; Hg is inert to nonoxidizing acids; Zn also dissolves in strong bases under formation of zincate ions:

\[
\text{Zn} + 2 \text{OH}^- \rightarrow \text{ZnO}_2^{2-} + \text{H}_2
\]
ZINC, CADMIUM, AND MERCURY

• Cadmium does not dissolve in bases.
• Both Zn and Cd react readily when heated in O₂, to give the oxides (roasting).
• Although Hg and O₂ are unstable with respect to HgO at 25 °C reaction rate is veeeerever slow.
• the reaction proceeds at a useful rate at 300-350 DC, but above about 400 °C the ΔG becomes positive and HgO decomposes rapidly into the elements.

• HgO(s) = Hg(l) + ½ O₂  \[ ΔH_{diss} = 90.4 \text{ kJ mol}^{-1} \]
ZINC, CADMIUM, AND MERCURY

- Hg ability to absorb O₂ from the air and regenerate it as O₂ was of importance in the early days in the study of the element Oxygen.

- All three elements react with halogens and with nonmetals such as S, Se, and P.
- The elements Zn and Cd form many alloys.
- E.g. brass, which is a copper-zinc alloy, which is of technical importance.
- Mercury combines with many other metals, sometimes with difficulty but sometimes, as with Na or K, very vigorously, giving amalgams.
Many amalgams are of continuously variable compositions, while others are compounds, such as Hg$_2$Na. Some of the transition metals do not form amalgams. Fe is commonly used for containers of Hg. Na amalgams and amalgamated Zn are frequently used as reducing agents for aqueous solutions.
ZINC, CADMIUM, AND MERCURY

- The Univalent State
- Zn, Cd, and Hg form the ions $M^{2+}$. 
- Zn$^{2+}$ and Cd$^{2+}$ ions are unstable 
- Found only in melts or solids. 
- If one adds Zn to fused ZnCl₂, this gives a yellow solution. 
- Upon cooling it gives a yellow glass, containing Zn$^{2+}$. 
- The ions have a metal-metal bond ($^+M-M^+$); 
- the order of bond strength is: $Zn^{2+} < Cd^{2+} < Hg^{2+}$. 
The mercury(I) ion (Hg$^{2+}_2$) is formed on reduction of Hg(II) salts in aqueous solution.
The Hg-Hg distances range from 2.50 to 2.70 Å.
Found by X-ray diffraction of Hg$_2$Cl$_2$, Hg$_2$SO$_4$, and Hg$_2$(NO$_3$)$_2$·2H$_2$O.
Distance is depending on the ion.
Shortest distance is found with the least covalently bound anion (here NO$_3^-$).
ZINC, CADMIUM, AND MERCURY

- Hg$^I$-Hg$^{II}$ Equilibria
- Understanding the thermodynamics of the equilibria is essential to understand the chemistry of the Hg$^I$ state.
- The important parameters are the potentials:
  - Hg$^{2+}$ + 2 e$^-$ = 2 Hg \hspace{1cm} E^o = 0.789 V
  - 2 Hg$^{2+}$ + 2 e$^-$ = Hg$_2^{2+}$ \hspace{1cm} E^o = 0.920 V
  - Hg$^{2+}$ + 2 e$^-$ = Hg \hspace{1cm} E^o = 0.854 V
ZINC, CADMIUM, AND MERCURY

- For the disproportionation equilibrium:

\[
\text{Hg}_2^{2+} = \text{Hg} + \text{Hg}^{2+} \quad E^\circ = -0.131 \text{ V}
\]

- From which it follows that:

\[
K = \frac{[\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]} = 6.0 \times 10^{-3}
\]
ZINC, CADMIUM, AND MERCURY

- The implication of the standard potentials is
- oxidizing agents with potentials -0.79 to -0.85 V
- can oxidize mercury to Hg¹, but not to Hg²⁺.
- No common oxidizing agent meets this requirement
- Hg treated with an excess of oxidizing agent is entirely converted into Hg²⁺
- Hg in at least 50% excess → only Hg¹ is obtained
- Because Hg readily reduces Hg²⁺ to Hg₂²⁺.
ZINC, CADMIUM, AND MERCURY

\[
\begin{align*}
\text{Hg}_2^{2+} + 2 \text{OH}^- & \rightarrow \text{Hg} + \text{HgO(s)} + \text{H}_2\text{O} \\
\text{Hg}_2^{2+} + \text{S}^{2-} & \rightarrow \text{Hg} + \text{HgS(s)} \\
\text{Hg}_2^{2+} + 2\text{CN}^- & \rightarrow \text{Hg} + \text{Hg(CN)}_2(\text{aq})
\end{align*}
\]
ZINC, CADMIUM, AND MERCURY

- Dimercury(I) Compounds

- no hydroxide, oxide, or sulfide can be obtained
- addition of the appropriate anion to aqueous Hg_{2}^{2+}
- best known dimercury(I) compounds are the halides
- Fluoride is unstable toward water
- hydrolyzes to hydrofluoric acid and hydroxide
- which immediately disproportionates

\[ \text{Hg}_{2}^{2+} + 2 \text{OH}^- \rightarrow \text{Hg} + \text{HgO}(s) + \text{H}_2\text{O} \]
Other halides are insoluble.

This prevents the possibilities of hydrolysis or disproportionation to give Hg^{II} halide complexes.

Mercury(I) nitrate and perchlorate are soluble in water.

Hg_{2}SO_{4} is sparingly soluble.
ZINC, CADMIUM, AND MERCURY

• Divalent Zinc and Cadmium Compounds
• Binary Compounds
  Oxides
  The oxides (ZnO and CdO) are formed on burning the metals in air or by pyrolysis of the carbonates or nitrates
  The cadmium oxide smokes are exceedingly toxic
  Zinc oxide is normally white but turns yellow on heating
  Cadmium oxide varies in color from greenish yellow through brown to nearly black → parameter thermal history
The colors are the result of various kinds of lattice defects.

Both oxides sublime at very high temperatures.

The hydroxides are precipitated from solutions of salts by addition of bases.

The compound Zn (OH)$_2$ readily dissolves in an excess of alkali bases to give "zincate".

NaZn(OH)$_s$ and Na$_2^[Zn(OH)$_4$]$ ions and solid zincates can be crystallised from concentrated solutions.
ZINC, CADMIUM, AND MERCURY

- Cadmium hydroxide, Cd(OH)$_2$, is insoluble in bases.
- Both Zn and Cd hydroxide readily dissolve in an excess of strong ammonia to form the amine complexes
  - $[\text{Zn(NH}_3\text{)}_4]^2+$.  

- Sulfides
  - The sulfides are obtained by direct interaction or by precipitation by $\text{H}_2\text{S}$ from aqueous solutions
  - Acidic solution for CdS and neutral or basic solution for ZnS
ZINC, CADMIUM, AND MERCURY

- Halides
- The fluorides are essentially ionic
- high melting solids
- the other halides are more covalent in nature
- The fluorides are sparingly soluble in water
- Due to the high lattice energies of the ZnF₂ and CdF₂
- other halides are much more soluble
- in water, in alcohols, ketones, and similar donor solvents (org. solvents).
ZINC, CADMIUM, AND MERCURY

- Aqueous solutions of cadmium halides contain
  - \( \text{Cd}^{2+}, \text{CdX}^+, \text{CdX}^2, \text{and CdX}^3 \) in equilibrium

- Oxo Salts and Aqua Ions
- Salts of oxo acids
- nitrate, sulfate, sulfite, perchlorate, and acetate are soluble in water
- The \( \text{Zn}^{2+} \) and \( \text{Cd}^{2+} \) ions are rather similar to \( \text{Mg}^{2+} \),
- Many salts are isomorphous with magnesium salts,
- \( \text{Zn(Mg)SO}_4 \times 7\text{H}_2\text{O} \).
ZINC, CADMIUM, AND MERCURY

- The aqua ions are acidic
- Aquous solutions of salts are hydrolyzed
- In perchlorate solution the only species for Zn, Cd, and Hg below 0.1 M are the MOH⁺ ions,

\[ \text{Zn}^{2+}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+(aq) + \text{H}^+ \]

- For more concentrated cadmium solutions, the principal species is Cd(OH)³⁺

\[ 2 \text{Cd}^{2+}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{Cd}_2\text{OH}^3+(aq) + \text{H}^+ \]
ZINC, CADMIUM, AND MERCURY

- In the presence of complexing anions (e.g., halide), species such as Cd(OH)Cl or CdNO; may be obtained.

- **Complexes**
  - All of the halide ions except F-form complex halogeno anions
  - when present in excess,
  - For Zn$^{2+}$ and Cd$^{2+}$ the formation constants are many orders of magnitude smaller than those for Hg$^{2+}$.
  - Same for complex cations with NH$_s$ and amines,
  - can be isolated as crystalline salts.
  - Zinc dithiocarbamates are industrially important as accelerators in the vulcanization of rubber by sulfur.
  - Zinc complexes are also of great importance biologically
  - Zinc compounds, especially ZnCO$_s$ and ZnO, are used in ointments, since zinc apparently promotes healing processes.
ZINC, CADMIUM, AND MERCURY

- Cadmium compounds are extremely poisonous,
- possibly because of the substitution of Cd for Zn in an enzyme system,
- and consequently they constitute a serious environmental hazard (e.g., in the neighborhood of Zn smelters).
- Divalent Mercury Compounds
- Binary Compounds
  - Red HgO is formed on gentle pyrolysis of mercury(I) or mercury(II) nitrate, at 300-350 °C,
  - or as red crystals by heating of an alkaline solution of K₂HgI₄.
  - Addition of OH⁻ to aqueous Hg²⁺ gives a yellow precipitate of HgO
  - the yellow form differs from the red only in particle size.
ZINC, CADMIUM, AND MERCURY

No hydroxide has been obtained, 
The oxide is soluble in water. 
The exact solubility depending on particle size, 
to give a solution of what is commonly assumed to be 
the hydroxide, although there is no proof for such a 
species. This "hydroxide" is an extremely weak base:

- and is somewhat amphoteric, though more basic than 
  acidic.
- Mercury(II) sulfide (HgS) is precipitated from aqueous 
  solutions as a black, highly insoluble compound
ZINC, CADMIUM, AND MERCURY

- Mercury(II) fluoride is essentially ionic and crystallizes completely decomposed even by cold water.
- Expected for an ionic compound that is the salt of a weak acid and an extremely weak base.
- The other halides show marked covalent character.
- Mercury(II) chloride crystallizes in an essentially molecular lattice.
- Relative to ionic HgF₂, the other halides have very low melting and boiling points.
- HgCl₂ mp 280°C.
**ZINC, CADMIUM, AND MERCURY**

- In aqueous solution they exist almost exclusively (~99%) as HgX₂ molecules

\[ \text{HgCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Hg(OH)}\text{Cl} + \text{H}^+ + \text{Cl}^- \]

- **Mercury(II) Oxo Salts**
- Mercury(II) salts are essentially ionic,
- highly dissociated in aqueous solution are the nitrate, sulfate, and perchlorate
- mercury(II) hydroxide tend to hydrolyze extensively and must be acidified to be stable.
ZINC, CADMIUM, AND MERCURY

- Mercury(II) Complexes
- The Hg$^{2+}$ ion forms many strong complexes.
- Coordination numbers and stereochemical arrangements are
  - two-coordinate (*linear*)
  - *four coordinate* (*tetrahedral*).
- Octahedral coordination is less common
- Few three and five-coordinate complexes are known
- There appears to be considerable covalent character in the mercury-ligand bonds, especially in the two-coordinate compounds.