ZINC, CADMIUM, AND MERCURY

Kapitel 22

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

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- 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.

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Physico-chemical properties of the elements are:

Element	**El. configuration**	**Mp (°C)**	**Ionic Radius (Å)**	**E° (V)**	**ΔH (kJ/mol)**
Zn	[Ar] $3d^{10}4s^2$	420	0.88	-0.76	2632
Cd	[Kr] $4d^{10}5s^2$	320	0.92	-0.40	2492
Hg	[Xe]$4f^{14}5d^{10}6s^2$	-39	1.16	+0.85	2805

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- 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

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- Apart from the resemblance that they also just form +2 ions
- They do not have much in common with the alkaline earth metals.
- BeO, $Be(OH)_2$, and BeS → ZnO, $Zn(OH)_2$ and ZnS

- Zn^{2+} and Mg^{2+} share some common properties in their solution and complex chemistry.

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- **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.*

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- **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

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- **Occurrence, Isolation, and Properties of the Elements**

- precipitation from sulfate solutions by Zn dust.

- $\mathrm{Zn} + \mathrm{Cd}^{2+} = \mathrm{Zn}^{2+} + \mathrm{Cd} \quad E^{O} = +0.36\ V$

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- **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.

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- All elements are volatile for heavy metals.

- Mercury gives a monatomic vapor
- vapor pressure (1.3×10^{-3} mm) at 20 °C
- Soluble in polar and apolar liquids
- Solubility of 6×10^{-8} g of Hg per gram of H_2O.
- high volatility and moderate toxicity should be handled in well-ventilated areas

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- It becomes extremely hazardous in the biosphere because there are bacteria that convert it to the exceedingly toxic CH^3Hg+ ion

- Mercury is readily lost from aqueous solutions of mercuric salts owing to reduction by traces of reducing materials and by disproportionation of $Hg^{2+}\ {}_2$

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- 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:

$$Zn + 2\,OH^- \longrightarrow ZnO_2^{2-} + H_2$$

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- Cadmium does not dissolve in bases.
- Both Zn and Cd react readily when heated in O2, to give the oxides (roasting).
- Although Hg and O_2 are unstable with respect to HgO at 25 °C *reaction rate is veeeeery 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 *ΔHdiss = 90.4 kJ mol-*^{1}

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- 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*.

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- Many amalgams are of continuously variable compositions, while others are compounds, such as Hg2Na
- 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

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- **The Univalent State**
- Zn, Cd, and Hg form the ions $M^{2+}{}_2$.
- $Zn^{2+}{}_2$ and $Cd^{2+}{}_2$ ions are unstable
- Found only in melts or solids.
- If one adds Zn to fused $ZnCl_2$, this gives a yellow solution.
- Upon cooling it gives a yellow glass, containing $Zn^{2+}{}_2$
- The ions have a metal-metal bond ($^+M-M^+$);
- the order of bond strength is : $Zn^{2+}{}_2 < Cd^{2+}{}_2 < Hg^{2+}{}_2$.

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- 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_2Cl_2, Hg_2SO_4 , and $Hg_2(NO_3).2H_2O$
- Distance is depending on the ion.
- Shortest distance is found with the least covalently bound anion (here NO_3^-)

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- **Hg^{I}-Hg^{II} Equilibria**
- Understanding the thermodynamics of the equilibria is essential to understand the chemistry of the Hg^{I} state.
- The important parameter s are the potentials:
- $Hg^{2+} + 2\,e^{-} = 2\,Hg \qquad E^{o} = 0.789\ V$
- $2\,Hg^{2+} + 2\,e^{-} = Hg_2^{2+} \qquad E^{o} = 0.920\ V$
- $Hg^{2+} + 2\,e^{-} = Hg \qquad E^{o} = 0.854\ V$

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- For the disproportionation equilibrium:

$$\mathrm{Hg}_2^{2+} = \mathrm{Hg} + \mathrm{Hg}^{2+} \qquad E^\circ = -0.131\ \mathrm{V}$$

- From which it follows that:

$$K = \frac{[\mathrm{Hg}^{2+}]}{[\mathrm{Hg}_2^{2+}]} = 6.0 \times 10^{-3}$$

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- The implication of the standard potentials is
- oxidizing agents with potentials -0.79 to -0.85 V
- can oxidize mercury to Hg^{I}, but not to Hg^{II} .
- No common oxidizing agent meets this requirement
- Hg treated with an excess of oxidizing agent is entirely converted into Hg^{II}
- Hg in at least 50% excess → only Hg^{I} is obtained
- Because Hg readily reduces Hg^{2+} to Hg_2^{2+}.

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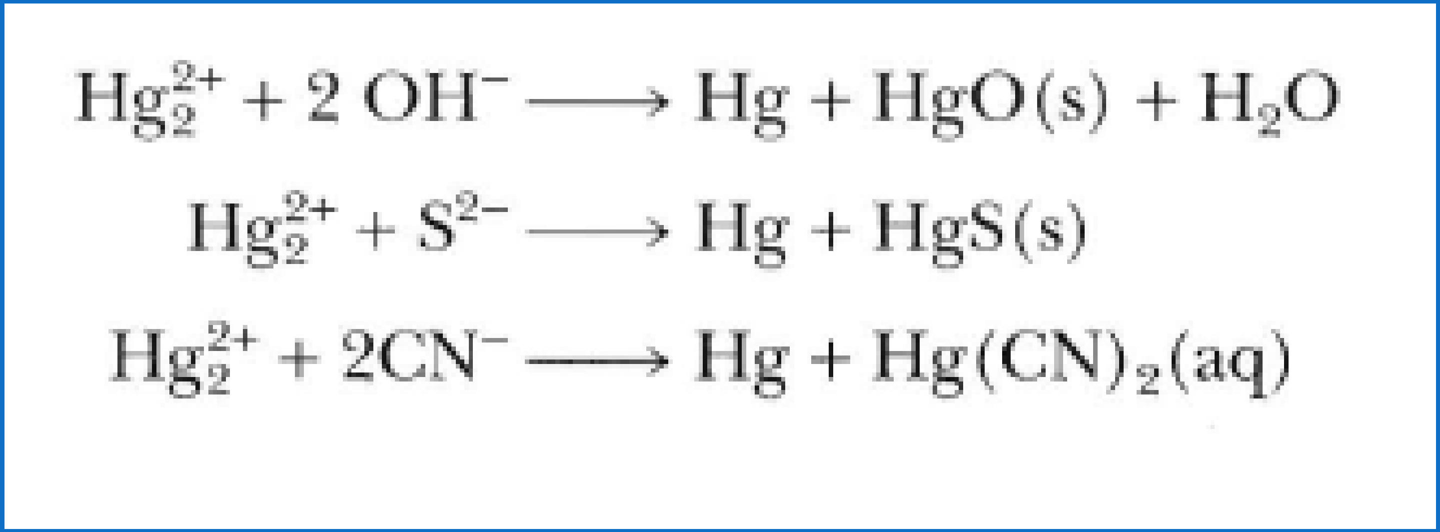

$$Hg_2^{2+} + 2\,OH^- \longrightarrow Hg + HgO(s) + H_2O$$

$$Hg_2^{2+} + S^{2-} \longrightarrow Hg + HgS(s)$$

$$Hg_2^{2+} + 2CN^- \longrightarrow Hg + Hg(CN)_2(aq)$$

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- Dimercury(l) 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

$$Hg_2^{2+} + 2\,OH^- \longrightarrow Hg + HgO(s) + H_2O$$

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- Other halides are insoluble
- prevents the possibilities of hydrolysis or disproportionation to give Hg^{II} halide complexes
- Mercury(I) nitrate and perchlorate are soluble in water
- Hg_2SO_4 is sparingly soluble

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- **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

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- 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

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- 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
- $[Zn(NH_3)4]^{2+}$.

- Sulfides
- The sulfides are obtained by direct interaction or by precipitation by $H\ _2S$ from aqueous solutions
- Acidic solution for CdS and neutral or basic solution for ZnS

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- 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 ZnF_2 and CdF_2
- other halides are much more soluble
- in water, in alcohols, ketones, and similar donor solvents (org. solvents).

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- Aqueous solutions of cadmium halides contain
- $Cd^{2}+$, $CdX+$, CdX^{2}, 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 Zn^{2+} and Cd^{2+} ions are rather similar to Mg^{2+},
- Many salts are isomorphous with magnesium salts,
- $Zn(Mg)SO4$ x $7H2O$.

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

$$Zn^{2+}(aq) + H_2O \rightleftharpoons ZnOH^+(aq) + H^+$$

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

$$2\,Cd^{2+}(aq) + H_2O \rightleftharpoons Cd_2OH^{3+}(aq) + H^+$$

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- 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.
-

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- 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 solutionof K^2HgI^4.

Addition of OH- to aqueous Hg^2+g ives a yellow precipitate of HgO

the yellow form differs from the red only in particle size.

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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(ll) sulfide (HgS) is precipitated from aqueous solutions as a black, highly insoluble compound

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- Mercury(Il) 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(Il) chloride crystallizes in an essentially molecular lattice
- Relative to ionic HgF_2, the other halides have very low melting and boiling points.
- $HgCl_2$ mp 280°C .

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

$$HgCl_2 + H_2O \rightleftharpoons Hg(OH)Cl + H^+ + Cl^-$$

- **Mercury(lI) 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.

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- **Mercury(lI) 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