Chapter 22

ZINC, CADMIUM, AND MERCURY

22-1 Introduction

The position of Zn, Cd, and Hg in the periodic table is discussed in Section 2-5, and some properties are given in Table 8-2. Mercury shows such unique behavior that it cannot be considered as homologous to Zn and Cd.

Although these elements characteristically form +2 cations, they do not have much in common with the Be, Mg, and Ca to Ra group except for some resemblances between Zn, Be, and Mg. Thus BeO, $Be(OH)_2$, and BeS have the same structures as ZnO, $Zn(OH)_2$, and ZnS, and there is some similarity in the solution and complex chemistry of Zn^{2+} and Mg^{2+}. The main cause of the differences between the Group IIA(2) and the Group IIB(12) ions arises because of the high polarizability of the filled *d* shell of the Group IIB(12) ions compared with the nonpolarizable, noble gas-like electron configurations of the Group IIA(2) ions.

22-2 Occurrence, Isolation, and Properties of the Elements

The elements have relatively low abundance in nature (of the order 10^{-6} of the earth's crust for Zn and Cd), but have long been known because they are easily obtained from their ores.

Zinc occurs widely, but the main source is *sphalerite,* (ZnFe)S, which commonly occurs with galena (PbS); cadmium minerals are scarce but, as a result of its similarity to Zn, Cd occurs by isomorphous replacement in almost all Zn ores. Methods of isolation involve flotation and roasting, which yield the oxides; the ZnO and PbO are then reduced with carbon. Cadmium is invariably a by/product and is usually separated from Zn by distillation or by precipitation from sulfate solutions by Zn dust.

$$Zn + Cd^{2+} = Zn^{2+} + Cd \quad E^\circ = +0.36\ V \qquad (22\text{-}2.1)$$

The only important ore of mercury is *cinnabar* (HgS); this ore is roasted to give the oxide which, in turn, decomposes at about 500 °C, the mercury vaporizing.

Zinc and cadmium are white, lustrous, but tarnishable metals. Their structures deviate only slightly from perfect hcp. Mercury is a shiny liquid at ordinary temperatures. All of these elements are remarkably volatile for heavy metals, mercury uniquely so. Mercury gives a monatomic vapor and has an appreciable vapor pressure (1.3×10^{-3} mm) at 20 °C. It is also surprisingly soluble in both polar and nonpolar liquids; a saturated solution in water at 25 °C has 6×10^{-8} g of Hg per gram of H_2O. Because of its high volatility and moderate toxicity, mercury should always be kept in stoppered containers and handled in well-ventilated areas. 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+}.

Both Zn and Cd are very electropositive and react readily with nonoxidizing acids, releasing H_2 and giving the divalent ions; Hg is inert to nonoxidizing acids. Zinc also dissolves in strong bases because of its ability to form zincate ions (see Reaction 22-2.2), commonly written ZnO_2^{2-}.

$$Zn + 2\,OH^- \longrightarrow ZnO_2^{2-} + H_2 \qquad (22\text{-}2.2)$$

Cadmium does not dissolve in bases.

Both Zn and Cd react readily when heated in O_2, to give the oxides. Although Hg and O_2 are unstable with respect to HgO at 25 °C, their rate of combination is exceedingly slow; the reaction proceeds at a useful rate at 300–350 °C, but above about 400 °C the ΔG becomes positive and HgO decomposes rapidly into the elements.

$$HgO(s) = Hg(\ell) + \tfrac{1}{2}\,O_2 \quad \Delta H_{diss} = 90.4 \text{ kJ mol}^{-1} \qquad (22\text{-}2.3)$$

This ability of Hg to absorb O_2 from the air and regenerate it as O_2 was of considerable importance in the earliest studies of the element oxygen by A. L. Lavoisier and J. Priestley.

All three elements react with halogens and with nonmetals such as S, Se, and P.

The elements Zn and Cd form many alloys. Some, such as brass, which is a copper–zinc alloy, are 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_2Na. Some of the transition metals do not form amalgams, and iron is commonly used for containers of Hg. Sodium amalgams and amalgamated Zn are frequently used as reducing agents for aqueous solutions.

22-3 The Univalent State

The elements Zn, Cd, and Hg form the ions M_2^{2+}. The Zn_2^{2+} and Cd_2^{2+} ions are unstable, especially Zn_2^{2+}, and are known only in melts or solids. Thus addition of Zn to fused $ZnCl_2$ gives a yellow solution and, on cooling, a yellow glass that contains Zn_2^{2+}.

The ions have a metal–metal bond ($^+M—M^+$); Raman spectra allow the estimation of force constants, and they show that the order of bond strength is $Zn_2^{2+} < Cd_2^{2+} < Hg_2^{2+}$.

The mercury(I) ion (Hg_2^{2+}) is formed on reduction of mercury(II) salts in aqueous solution. X-ray diffraction studies on many compounds such as Hg_2Cl_2, Hg_2SO_4, and $Hg_2(NO_3)_2 \cdot 2H_2O$ show that the Hg—Hg distances range from 2.50 to 2.70 Å, depending on the associated anions. The shortest distances are found with the least covalently bound anions (e.g., NO_3^-).

Hg^I–Hg^{II} Equilibria

An understanding of the thermodynamics of these equilibria is essential to an understanding of the chemistry of the mercury(I) state. The important values are the potentials.

$$Hg_2^{2+} + 2\,e^- = 2\,Hg \qquad E^\circ = 0.789\ V \qquad (22\text{-}3.1)$$

$$2\,Hg^{2+} + 2\,e^- = Hg_2^{2+} \qquad E^\circ = 0.920\ V \qquad (22\text{-}3.2)$$

$$Hg^{2+} + 2\,e^- = Hg \qquad E^\circ = 0.854\ V \qquad (22\text{-}3.3)$$

For the disproportionation equilibrium

$$Hg_2^{2+} = Hg + Hg^{2+} \qquad E^\circ = -0.131\ V \qquad (22\text{-}3.4)$$

from which it follows that

$$K = \frac{[Hg^{2+}]}{[Hg_2^{2+}]} = 6.0 \times 10^{-3} \qquad (22\text{-}3.5)$$

The implication of the standard potentials is clearly that only oxidizing agents with potentials in the range –0.79 to –0.85 V can oxidize mercury to Hg^I, but not to Hg^{II}. Since no common oxidizing agent meets this requirement, it is found that when mercury is treated with an excess of oxidizing agent it is entirely converted into Hg^{II}. However, when mercury is in at least 50% excess, only Hg^I is obtained since, according to Reaction 22-3.4, Hg readily reduces Hg^{2+} to Hg_2^{2+}.

The equilibrium constant for Reaction 22-3.4 shows that Hg_2^{2+} is stable with respect to disproportionation, but by only a small margin. Thus any reagents that reduce the activity (by precipitation or complexation) of Hg^{2+}, to a significantly greater extent than they lower the activity of Hg_2^{2+}, will cause *disproportionation* of Hg_2^{2+}. There are many such reagents, so that the number of stable Hg^I compounds is quite restricted.

Thus, when OH^- is added to a solution of Hg_2^{2+}, a dark precipitate consisting of Hg and HgO is formed; evidently mercury(I) hydroxide, if it could be isolated, would be a stronger base than HgO. Similarly, addition of sulfide ions to a solution of Hg_2^{2+} gives a mixture of Hg and the extremely insoluble HgS. Mercury(I) cyanide does not exist because $Hg(CN)_2$, although soluble, is so slightly dissociated. The reactions in these cited cases are

$$Hg_2^{2+} + 2\,OH^- \longrightarrow Hg + HgO(s) + H_2O \qquad (22\text{-}3.6)$$

$$Hg_2^{2+} + S^{2-} \longrightarrow Hg + HgS(s) \qquad (22\text{-}3.7)$$

$$Hg_2^{2+} + 2CN^- \longrightarrow Hg + Hg(CN)_2(aq) \qquad (22\text{-}3.8)$$

Dimercury(I) Compounds

As we indicated previously, no hydroxide, oxide, or sulfide can be obtained by addition of the appropriate anion to aqueous Hg_2^{2+}, nor have these compounds been otherwise made.

Among the best known dimercury(I) compounds are the *halides*. The fluoride is unstable toward water, being hydrolyzed to hydrofluoric acid and hydroxide (which immediately disproportionates as shown previously). The other halides are insoluble, which thus precludes the possibilities of hydrolysis or disproportionation to give Hg^{II} halide complexes. Mercury(I) nitrate and perchlorate are soluble in water, but Hg_2SO_4 is sparingly soluble.

22-4 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; oxide smokes can be obtained by combustion of the alkyls. 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, depending on its thermal history. These 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" ions and solid zincates such as $NaZn(OH)_3$ and $Na_2[Zn(OH)_4]$ can be crystallized from concentrated solutions. 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 ammine complexes, for example, $[Zn(NH_3)_4]^{2+}$. The complete set of formation constants for the cadmium system was presented in Section 6-4.

Sulfides

The *sulfides* are obtained by direct interaction or by precipitation by H_2S from aqueous solutions, acidic for CdS and neutral or basic for ZnS. The sulfides, as well as the selenides and tellurides, all have the wurtzite or zinc blende structures shown in Chapter 4.

Halides

The fluorides are essentially ionic, high melting solids, whereas the other *halides* are more covalent in nature. The fluorides are sparingly soluble in water, a reflection of the high lattice energies of the ZnF_2 (rutile) and CdF_2 (fluorite) structures. The other halides are much more soluble, not only in water but in alcohols, ketones, and similar donor solvents. Aqueous solutions of cadmium halides contain all the species Cd^{2+}, CdX^+, CdX_2, and CdX_3^- in equilibrium.

Oxo Salts and Aqua Ions

Salts of oxo acids such as the nitrate, sulfate, sulfite, perchlorate, and acetate are soluble in water. The Zn^{2+} and Cd^{2+} ions are rather similar to Mg^{2+}, and many of their salts are isomorphous with magnesium salts, for example, $Zn(Mg)SO_4 \cdot 7H_2O$. The aqua ions are acidic, and 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, for example,

$$Zn^{2+}(aq) + H_2O \rightleftharpoons ZnOH^+(aq) + H^+ \tag{22-4.1}$$

For more concentrated cadmium solutions, the principal species is Cd_2OH^{3+}.

$$2\ Cd^{2+}(aq) + H_2O \rightleftharpoons Cd_2OH^{3+}(aq) + H^+ \tag{22-4.2}$$

In the presence of complexing anions (e.g., halide), species such as $Cd(OH)Cl$ or $CdNO_3^+$ may be obtained.

Complexes

All of the halide ions except F^- form complex halogeno anions when present in excess, but for Zn^{2+} and Cd^{2+} the formation constants are many orders of magnitude smaller than those for Hg^{2+}. The same applies to complex cations with NH_3 and amines, many of which can be isolated as crystalline salts.

Zinc dithiocarbamates (Section 14-6) are industrially important as accelerators in the vulcanization of rubber by sulfur. Zinc complexes are also of great importance biologically (Section 31-9). Zinc compounds, especially $ZnCO_3$ and ZnO, are used in ointments, since zinc apparently promotes healing processes.

By contrast, 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).

22-5 Divalent Mercury Compounds

Binary Compounds

Red HgO is formed on gentle pyrolysis of mercury(I) or mercury(II) nitrate, by direct interaction at 300–350 °C, or as red crystals by heating of an alkaline solution of K_2HgI_4. Addition of OH^- to aqueous Hg^{2+} gives a yellow precipitate of HgO; the yellow form differs from the red only in particle size.

No hydroxide has been obtained, but the oxide is soluble in water (10^{-3}–10^{-4} mol L^{-1}), 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:

$$K = \frac{[Hg^{2+}][OH^-]^2}{[Hg(OH)_2]} = 1.8 \times 10^{-22} \tag{22-5.1}$$

and is somewhat amphoteric, though more basic than acidic.

Mercury(II) sulfide (HgS) is precipitated from aqueous solutions as a black, highly insoluble compound. The solubility product is 10^{-54}, but the sulfide is somewhat more soluble than this figure would imply because of hydrolysis of Hg^{2+} and S^{2-} ions. The black sulfide is unstable with respect to a red form identical with the mineral cinnabar and changes into it when heated or digested with alkali polysulfides or mercury(I) chloride.

Mercury(II) fluoride is essentially ionic and crystallizes in the fluorite structure; it is almost completely decomposed even by cold water, as would be expected for an ionic compound that is the salt of a weak acid and an extremely weak base.

In sharp contrast to the fluoride, the other halides show marked covalent character. *Mercury(II) chloride* crystallizes in an essentially molecular lattice. Relative to ionic HgF_2, the other halides have very low melting and boiling points, for example, $HgCl_2$, mp 280 °C. They also show marked solubility in many organic solvents. In aqueous solution they exist almost exclusively (~99%) as HgX_2 molecules, but some hydrolysis occurs, the principal equilibrium being, for example,

$$HgCl_2 + H_2O \rightleftharpoons Hg(OH)Cl + H^+ + Cl^- \qquad (22\text{-}5.2)$$

Mercury(II) Oxo Salts

Among the mercury(II) salts that are essentially ionic and, hence, highly dissociated in aqueous solution are the nitrate, sulfate, and perchlorate. Because of the great weakness of mercury(II) hydroxide, aqueous solutions of these salts tend to hydrolyze extensively and must be acidified to be stable.

In aqueous solutions of $Hg(NO_3)_2$ the main species are $Hg(NO_3)_2$, $HgNO_3^+$, and Hg^{2+}, but at high concentrations of NO_3^- the complex anions $[Hg(NO_3)_{3,4}]^{-,2-}$ are formed.

Mercury(II) carboxylates, especially the acetate and the trifluoroacetate, are of considerable importance because of their utility in attacking unsaturated hydrocarbons (Section 29-6). These compounds are made by dissolving HgO in the hot acid and crystallizing. The trifluoroacetate is also soluble in benzene, acetone, and THF, which increases its utility, while the acetate is soluble in water and alcohols.

Mercury(II) ions catalyze a number of reactions of complex compounds such as the aquation of $[Cr(NH_3)_5X]^{2+}$. Bridged transition states, for example,

$$[(H_2O)_5CrCl]^{2+} + Hg^{2+} = [(H_2O)_5Cr\text{—}Cl\text{—}Hg]^{4+} \qquad (22\text{-}5.3)$$

are believed to be involved.

The silver ion is similarly able to accelerate the rates of substitution of halo and other ligands. In both cases, the catalysis arises because Hg^{2+} or Ag^+ is able to enhance the breaking of the bond to the leaving group in what would otherwise be a slow, dissociative (D or I_d in the terminology of Section 6-5) mechanism.

Mercury(II) Complexes

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

In addition to halide or pseudohalide complex ions, such as $[HgCl_4]^{2-}$ or $[Hg(CN)_4]^{2-}$, there are cationic species, such as $[Hg(NH_3)_4]^{2+}$ and $[Hg(en)_3]^{2+}$.

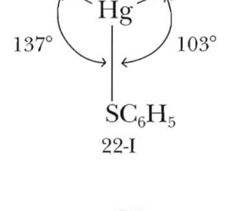
There are also a number of novel compounds in which —Hg— or —HgX is bound to a transition metal. Some of these compounds may be obtained by reaction of $HgCl_2$ with carbonylate anions (Section 28-9), for example,

$$2\ Na^+Co(CO)_4^- + HgCl_2 = 2\ NaCl + (CO)_4Co\text{—}Hg\text{—}Co(CO)_4 \qquad (22\text{-}5.4)$$

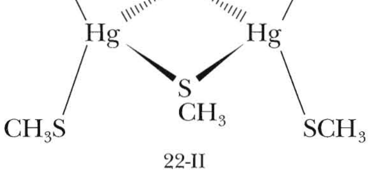
Mercury(II) also forms many compounds with PR_3 ligands. The compounds $HgX_2(PR_3)$ and $HgX_2(PR_3)_2$ are examples, and are either dimeric or polymeric with halide bridges.

With thiols, one obtains the well-known neutral thiolates, $Hg(SR)_2$, and thiolate anions such as $[Hg(SC_6H_5)_3]^-$ and $[Hg_2(SCH_3)_6]^{2-}$. In fact, the name "mercaptans" for thiols (RSH) originated from the high affinity of mercury for sulfur. The neutral thiolates are most commonly linear [e.g., $Hg(SCH_3)_2$ and $Hg(SC_2H_5)_2$], although there are often secondary bonding interactions in the solid state between sulfur and mercury. That is, a third or fourth thiolate ligand is found near enough to a given mercury atom to be considered to be within the van der Waals distance but not so close as to be regarded as covalently bonded. The 1:1 mercury(II) thiolates such as $[Hg(S\text{-}i\text{-}Pr)Cl]_n$ are chain polymers with thiolate bridges, as is the neutral 2:1 compound $[Hg(S\text{-}t\text{-}Bu)_2]_n$.

Anionic trithiolates, $[Hg(SR)_3]^-$, and tetrathiolates, $[Hg(SR)_4]^{2-}$, are also known. Some examples are $[Hg(SC_6H_5)_3]^-$, Structure 22-I, and $[Hg_2(SCH_3)_6]^{2-}$, Structure 22-II. Of the four-coordinate thiolates, only three have mononuclear, distorted tetrahedral geometries. One example is $[Hg(p\text{-}SC_6H_4Cl)_4]^{2-}$. The rest are at least dimeric, and sometimes polymeric, with sulfur atom bridges.



22-I



22-II

STUDY GUIDE

Study Questions

A. Review

1. Give the electronic structures of Zn, Cd, and Hg, and explain their position in the periodic table.
2. What are the electron configurations of the 2+ cations of Zn, Cd, and Hg?
3. Write balanced equations for the action on Zn of (a) 3 *M* HCl and (b) 3 *M* KOH.
4. Describe the interaction of Hg and O_2 and the properties of HgO.
5. What are the electron configurations of the 1+ cations?
6. What factors alter the ease of disproportionation of Hg^{I}?
7. Why do the hydroxide, oxide, or sulfide of Hg^{I} not exist?
8. Draw the structures of rutile, fluorite, and zinc blende.
9. What is the nature of $HgCl_2$ in solution and in the solid state?

B. Additional Exercises

1. Suggest the reason, in thermodynamic terms, why the sign of ΔG for the following reaction changes (from – to +) at about 400 °C

$$Hg(\ell) + \tfrac{1}{2} O_2(g) \longrightarrow HgO(s)$$

2. Why is it that when Hg is oxidized with an excess of oxidant only Hg^{II} is formed, yet when an excess of Hg is present during the oxidation, only Hg^{I} is formed?
3. By what methods can it be proved that the mercurous (mercury(I)) ion is the dimer Hg_2^{2+} in solution?
4. The zinc and cadmium dithiocarbamates are dimeric $[M(S_2CNR_2)_2]_2$. Draw a plausible structure.
5. Write balanced equations for
   (a) The disproportionation of mercury(I) hydroxide.
   (b) The hydrolysis of Hg^{II} fluoride.
   (c) The hydrolysis of zinc nitrate.
   (d) Thermal decomposition of mercury(II) oxide.
6. Calculate ΔG° for Reaction 22-3.4.

C. Questions from the Literature of Inorganic Chemistry

1. Based on the information concerning mercury(II) thiolate complexes presented by T. V. O'Halloran et al. (J. G. Wright, M. J. Natan, F. M. MacDonnell, D. M. Ralston, and T. V. O'Halloran, "Mercury(II)-Thiolate Chemistry and the Mechanism of Heavy Metal Biosensor MerR," in *Progress in Inorganic Chemistry,* Vol. 38, Wiley-Interscience, New York, 1990, 323, summarize the structural facts for the various Hg^{II}-thiolate complexes.
2. Two types of chloromercurate anions were found in the compounds reported by T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, and A. R. Siedle, "Crystal and Molecular Structure of an Unusual Salt formed from the Radical Cation of Tetrathiofulvalene (TTF) and the Trichloromercurate Anion ($HgCl_3^-$), (TTF)($HgCl_3$)," *Inorg. Chem.*, **1980,** *19,* 3604–3608.
   (a) What are the coordination geometries at Hg^{II} in the two types of halo-bridged ions reported in this article?

(b) What two types of chlorine atoms are there in these two ions, based on the Hg—Cl bond lengths?

(c) What are the relative numbers of terminal and bridging chlorine atoms in each ion reported here?

(d) If $Hg_2Cl_6^{2-}$ is described as an edge-sharing bitetrahedron, how might the sharing between adjacent units in polymeric $(HgCl_3^-)_n$ be described?

SUPPLEMENTARY READING

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