CADMIUM COMPOUNDS

1. Introduction

Naturally occurring cadmium compounds are limited to the rare minerals, greenockite [1317-58-4], CdS, and otavite (1), an oxycarbonate, but neither is an economically important source of cadmium metal or its compounds. Instead, cadmium compounds are more usually derived from metallic cadmium [7440-43-9] which is produced as a by-product of lead–zinc smelting or electrolysis (see CADMIUM AND CADMIUM ALLOYS). Typically, this cadmium metal is burnt as a vapor, to produce the brown-black cadmium oxide [1306-19-0], CdO, which then acts as a convenient starting material for most of the economically important compounds.

2. Properties

Cadmium is a member of Group 12 (Zn, Cd, Hg) of the Periodic Table, having a filled d shell of electrons $4d^{10}5s^2$ which dictates the usual valence state of $+2$. In rare instances the $+1$ oxidation state may be produced in the form of dimeric Cd_2^{2+} species [59458-73-0], eg, as dark red melts of Cd^0 dissolved in molten cadmium halides or as diamagnetic yellow solids such as $(Cd_2)^{2+}$ $(AlCl^-{}_4)_2$ [79110-87-5] (2). The $Cd^{2+}{}_2$ species is unstable in water or other donor solvents, immediately disproportionating to Cd^{2+} and Cd. In general, cadmium compounds exhibit properties similar to the corresponding zinc compounds. Compounds and properties are listed in Table 1. Cadmium(II) [22537-48-0] tends to favor tetrahedral coordination in its compounds, particularly in solution as complexes, eg, tetraamminecadmium(II) [18373-05-2], $Cd(NH_3)^{2+}{}_4$. However, solid-state cadmium-containing oxide or halide materials frequently exhibit octahedral coordination at the Cd^{2+} ion, eg, the rock-salt structure found for CdO.

Table 1. **Physical and Chemical Properties of Selected Cadmium Compounds**[a]

Compound	CAS Registry Number	$\Delta H^\circ_{f,298}$, kJ/mol[b]	$\Delta G^\circ_{f,298}$, kJ/mol[b]	S°_{298}, J/mol·K[b]	Density, g/mL	C°_p J/mol·K[b]	Mp, °C	ΔH_{fus}, kJ/mol[b]	Aqueous solubility, g/100 g H_2O[c]	Crystal[d] structure	Unit cell dimensions, nm
cadmium anti-monide CdSb	[12050-27-0]	−14.4	−13.0	92.9	6.92		452	32.05		ortho–rhomb	$a = 0.6471$ $b = 0.8253$ $c = 8.526$
cadmium bromide $CdBr_2$	[7789-42-6]	−316	−296	137.2	5.192	76.7	568	20.92	95_{18}	hex	$a = 0.395$ $c = 1.867$
cadmium carbo-nate $CdCO_3$	[513-78-0]	−751	−669	92.5	4.26		332 dec				2.8×10^{-6}
	rhomb				$a = 0.61306$						
cadmium chloride $CdCl_2$	[10108-64-2]	−391	−344	115.3	4.05	74.7	568	22.176	128.6_{30}	hex	$a = 0.3854$ $c = 1.746$
cadmium fluoride CdF_2	[7790-79-6]	−700	−648	77.4	6.39		1048	22.594	3.45_{25}	cubic	$a = 0.53880$
cadmium hydroxide $Cd(OH)_2$	[21041-95-2]	−561 hex	−474	96.2 $a = 0.3475$	4.79		150 dec				2.6×10^{-4}
										$c = 0.467$	
cadmium iodide CdI_2, α-form	[7790-80-9]	−203	−201	161.1	5.67	80.0	387	33.472	86_{25}	hex (hex)[e]	$a = 0.424$ $c = 0.684$ ($c = 1.367$)[e]
cadmium nitrate $Cd(NO_3)_2$	[10325-94-7]	−456	−255	197.9			350		109_0	cubic	$a = 0.756$
cadmium nitrate tetrahydrate $Cd(NO_3)_2 \cdot 4H_2O$	[10022-68-1]	−1649			2.455		59.4	32.636	215_0	ortho–rhomb	$a = 0.583$ $b = 2.575$ $c = 1.099$
cadmium oxide CdO	[1306-19-0]	−258	−228	54.8	8.2	43.4	1540 sub	243.509 sub			9.6×10^{-4}

	cubic				$a = 0.46953$						
cadmium selenide CdSe, α-form	[1306-24-7]	−136	−100	96.2	5.81		1350 dissoc	305.307 dissoc		hex (cubic)e	$a = 0.4309$ $c = 0.7021$ ($a = 0.605$)e
cadmium *m*-silicate $CdSiO_3$	[13477-19-5]	−1189	−1105	97.5	4.928	88.6	1242			monoclinic	$a = 1.504$ $b = 0.710$ $c = 0.696$
cadmium sulfate $CdSO_4$	[10124-36-4]	−933	−823	123.0	4.691	99.6	1000	20.084	76.6_{20}	ortho–rhomb	$a = 0.4717$ $b = 0.6559$ $c = 0.4701$
cadmium sulfate hydrate $CdSO_4 \cdot H_2O$	[13477-20-8]	−1240	−1069	154.0	3.79	134.6	105 trans			monoclinic	$a = 7.607$ $b = 0.7541$ $c = 8.186$
cadmium sulfate hydrate $3CdSO_4 \cdot 8H_2O$	[7790-89-3]	−1729	−1465	229.6	3.09	213.3	80 trans		113_0	monoclinic	$a = 0.947$ $b = 1.184$ $c = 1.635$
cadmium sulfide CdS, α-form	[1306-23-6]	−162 hex	−156	64.9	4.82 (4.50)[e]		980 sub in N_2 $c = 0.6749$	201.669 subl			$1.3 \times 10^{-4}_{18}$ $a = 0.41348$
cadmium telluride CdTe	[1306-25-8]	−92	−92	100.4	6.20		1045			(cubic)e hex (cubic)e	($a = 0.5818$)e $a = 0.457$ $c = 0.747$ ($a = 0.6480$)e

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[a] Refs. 3–12.

[b] To convert J to cal, divide by 4.184.

[c] Subscript denotes temperature in °C.

[d] Ortho–rhomb is orthorhombic and hex is hexagonal.

[e] β-form.

3. Inorganic Compounds

3.1. Cadmium Arsenides, Antimonides, and Phosphides. Cadmium arsenide [12511-93-2], CdAs, cadmium diarsenide [12044-40-5], $CdAs_2$, and tricadmium diarsenide [12006-15-4], Cd_3As_2, are known. Cd_3As_2 is prepared as grey tetragonal crystals, $a = 0.8945$ nm, $c = 1.265$ nm; $d = 6.25$ g/mL; mp 721°C (4, 7); $\Delta H^{\circ}_{f,298} = -41.84$ kJ/mol (– kcal/mol) (3) by heating stoichiometric amounts of the elements to fusion in an argon atmosphere. It is an n-type semiconductor having high electron mobility ($10,000\ cm^2/V{\cdot}s$), electron concentration of $3 \times 10^{18}/cm^3$ and a band gap energy of 0.13 eV. It may also be prepared by wet chemical methods involving passage of arsine gas through a weakly ammoniacal solution of cadmium sulfate. The fine black precipitate liberates arsine when treated with acid and inflames upon treatment with oxidants. Thin films (qv) of Cd_3As_2 find application as ultrasonic multipliers, photodetectors, thermodetectors, and Hall generators (13). $CdAs_2$ is prepared by slow heating, to 700°C, of stoichiometric amounts of the elements in a sealed, evacuated, quartz ampul. The grey tetragonal crystals, $a = 0.465$ nm; $c = 0.793$ nm; $d = 5.80$ g/mL; mp 621°C; $\Delta H^{\circ}_{f,298} = -17.5$ kJ/mol (-4.18 kcal/mol) (3), decompose upon heating to give arsenic and Cd_3As_2. The additional, less well characterized phase, CdAs, has been prepared by decomposition of $CdAs_2$ at high pressure to give orthorhombic grey crystals, $a = 0.5993$ nm, $b = 0.7819$ nm, $c = 0.8011$ nm; $d = 6.63$ g/mL; which decomposes instead of melting (14).

Antimonides of formulas CdSb and Cd_3Sb_2 have been reported. Both are usually prepared by direct union of the elements, the former is a hole-type semiconductor (9), with properties shown in Table 1, and finds use as a thermoelectric generator. Reagent-grade material costs \$2.00/g in small lots. The band gap energy is 0.46 eV (2.70 μm) (15); ΔH_{vap} is 138 kJ/mol (33.0 kcal/mol). Dicadmium triantimonide [12014-29-8], Cd_2Sb_3, is a metastable, white crystalline compound of monoclinic symmetry: $a = 0.72$ nm, $b = 1.351$ nm, $c = 0.616$ nm, $\beta = 100°14'$; $d = 7.014$ g/mL; mp 423°C (7).

The phosphides tricadmium diphosphide [12014-28-7], Cd_3P_2, cadmium diphosphide [12133-44-7], CdP_2, and cadmium tetraphosphide [12050-26-9], CdP_4, may all be prepared by indirect fusion of the elements, usually by passing phosphorus vapors, in a nitrogen or hydrogen carrier gas, over heated cadmium. Cd_3P_2 forms grey metallic needles of tetragonal symmetry, $a = 0.894$ nm, $c = 1.228$ nm; $d = 5.95$ g/mL; mp 700°C (4,7). It may also be prepared by passage of phosphine gas through a solution of cadmium ion and, if a surfactant such as polyphosphate is present, may be maintained in solution as a size-quantized semiconductor colloid the color of which ranges from pale yellow to black, dependent on particle size (16). It is an n-type semiconductor with near metallic mobilities (15) and was the first $A_3(II)B_2$ (15) compound to show laser action (13). CdP_2 may be prepared by heating a mixture of ammonium phosphate, cadmium carbonate, and carbon black and has a structure consisting of P chains where each P atom is bonded to two other P atoms and two Cd atoms. CdP_4 has the Cd atoms in octahedral coordination sandwiched between layers of P atoms (17).

3.2. Cadmium Borates. Of general formula $n\mathrm{CdO} \cdot m\mathrm{B_2O_3}$, the cadmium borates are prepared from $CdO{-}B_2O_3$ melts (7) and are used as phosphors. Materials $n = 1$, $m = 3$ [20571-45-3]; $n = 2$, $m = 3$, and $n = 3$, $m = 1$, all show green cathodoluminescence. Mn-doped material with $n = 2$, $m = 1$ luminesces strongly orange in electromagnetic radiation. Cadmium borotungstate [1306-26-9], $2\text{CdO} \cdot \text{B}_2\text{O}_3 \cdot \text{WO}_3 \cdot 18\text{H}_2\text{O}$, solutions can have densities up to 3.28 g/mL and have utility as flotation (qv) media for mineral separations. Cadmium fluoroborate [14486-19-2], $\text{Cd(BF}_4)_2$, is very hygroscopic and is used to prepare electroplating baths for high strength steels where the normal cyanide baths cause problems of hydrogen embrittlement.

3.3. Cadmium Carbonate. Pure cadmium carbonate, as the hemihydrate, $\text{CdCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, is obtained only when ammonium carbonate is used to precipitate the white, prismatic crystals from cadmium ion solutions; alkali carbonates precipitate the oxycarbonate. The carbonate is also produced by heating an acidified solution of cadmium chloride and urea in a sealed tube at 200°C (7). Cadmium oxide also slowly absorbs carbon dioxide to form the normal carbonate. The decomposition$\text{CdCO}_3 \longrightarrow \text{CdO} + \text{CO}_2$ gives a CO_2 partial pressure of 101 kPa (1 atm) at 357°C. The carbonate eliminates CO_2 in acids and acts as a convenient source of other Cd compounds in this type of reaction. It is soluble, because of complex ion formation, in ammonium ion- or cyanide ion-containing solutions.

3.4. Cadmium Complexes. Aqueous cadmium ion complexes are listed in Table 2. Cadmium binds four or less anionic ligands in solution generally resulting in colorless complexes. Many organic ligands form complexes with cadmium ion, the more common being methylamine, thiourea, oxalic acid, tartaric acid, dimethylglyoxime, pyridine, acetic acid, ethylenediamine tetraacetic acid, thiols, and glycolic acid. Stability constants are provided in the literature (18).

Cadmium complexes are of importance to the electroplating industry because baths containing complexed cadmium have excellent covering power and yield dense, fine grains. The complexed cation permits high cathodic overvoltages and this changed deposition potential allows codeposition of other metals.

Table 2. **Thermodynamic and Stability Constant Data for Selected Aqueous Cadmium Complexes**[a,b]

Complex ion	CAS Registry Number	$\Delta H^\circ_{f,298}$ kJ/mol[c]	$\Delta G^\circ_{f,298}$ kJ/mol[c]	Stability constant
CdCl^+	[14457-58-0]	−240.5	−224.4	$\log K_1 = 1.32$
$\text{CdCl}^-{}_3$	[21439-35-0]	−561.0	−487.0	$\log K_3 = 0.09$
$\text{Cd(CN)}^{2-}{}_4$	[16041-14-8]	428.0	507.5	$\log K_4 = 3.58$
$\text{Cd(NH}_3)^{2+}{}_2$	[47942-20-1]	−266.1	−159.0	$\log K_2 = 2.24$
$\text{Cd(NH}_3)^{2+}{}_4$	[18373-05-2]	−450.2	−226.4	$\log K_4 = 1.18$
CdBr^+	[15691-37-9]	−200.8	−193.9	$\log \text{K}_1 = 1.97$
$\text{CdBr}^-{}_3$	[21439-36-1]		−407.5	$\log K_3 = 0.24$
CdI^+	[15691-38-0]	−141.0	−141.4	$\log K_1 = 2.08$
$\text{CdI}^-{}_3$	[15691-42-6]		−259.4	$\log \text{K}_3 = 2.09$
$\text{CdI}^{-2}{}_4$	[15975-72-1]	−341.8	−315.9	$\log K_4 = 1.59$
CdSCN^+	[18194-99-5]		7.5	$\log K_1 = 1.90$
$\text{Cd(SCN)}^{-2}{}_4$	[19438-35-8]			$\log K_4 = \text{ca } 0.1$
$\text{Cd(N}_3)^{-2}{}_4$	[16408-27-8]		1,295.0	$\log K_4 = 0.76$

[a] Standard state $M = 1$.

[b] Refs. 3 and 18.

[c] To convert kJ to kcal, divide by 4.184.

In commercial operation the cyanide-plating bath, containing the complex ion $Cd(CN)^{2-}{}_4$ and formed from CdO (24 g/L), Cd metal (25 g/L), and NaCN (105 g/L), is the bath of choice. The exception is for high strength steels, which suffer embrittlement as a result of hydrogen incorporation, or in areas where cyanide effluent control is particularly difficult. In such cases the fluoroborate bath is the usual alternative although other electrolytes such as sulfate, sulfamate, chloride, and pyrophosphate have been used.

3.5. Cadmium Halides.

Cadmium halides show a steadily increasing covalency of the metal–halide bond proceeding from fluoride through to iodide. Bond lengths increase through the series: F, 0.197 nm; Cl, 0.221 nm; Br, 0.237 nm; I, 0.255 nm. The fluoride is much less soluble in water than the others (see Table 1) and the Cl, Br, and I compounds dissolve to a significant extent in alcohols, ethers, acetone, and liquid ammonia. Boiling points and corresponding ΔH_{vap}'s are CdF_2, 1747°C, 234 kJ/mol (55.9 kcal/mol); $CdCl_2$, 960°C, 125 kJ/mol (29.9 kcal/mol); $CdBr_2$, 963°C, 113 kJ/mol (27.0 kcal/mol); and CdI_2, 787°C, 106 kJ/mol (25.3 kcal/mol).

Aqueous solutions have low conductivities resulting from extensive complex ion formation. The halides, along with the chalcogenides, are sometimes used in pyrotechnics to give blue flames and as catalysts for a number of organic reactions.

Cadmium Fluoride. Elemental fluorine reacts with cadmium metal as well as the oxide, sulfide, and chloride to give CdF_2 [7790-79-6]. Alternatively, treatment of $CdCO_3$ with 40% HF yields a solution of CdF_2, which may be evaporated to recover efflorescent crystals of the dihydrate. CdF_2 has been used in phosphors, glass manufacture, nuclear reactor controls, and electric brushes.

Cadmium Chloride. Data for anhydrous material are listed in Table 1 but cadmium chloride also exists as hydrates having 1, 2, 2.5, and 4 molecules of water per formula unit, all of which are efflorescent in dry air. The pentahydrate $2CdCl_2 \dot{} 5H_2O$ [7790-78-5] is the most normal commercial form of the chloride and exists as colorless crystals of $d = 3.33$ g/mL; $\Delta H_{f,298} = -1132$ kJ/mol (−270.6 kcal/mol) (3). It may be prepared by dissolving the metal, the carbonate, oxide, sulfide, or hydroxide in hydrochloric acid and evaporating the solution. Anhydrous material may be derived from this by heating in a stream of dry HCl. It has been used in photography, photocopying, dyeing, and calico printing (with thiosulfate), vacuum tube manufacture, cadmium pigment manufacture, galvanoplasty, lubricants, ice-nucleation agents, and in the manufacture of special mirrors.

Cadmium Bromide. The hydrated bromide is prepared by dissolution of cadmium carbonate, oxide, sulfide, or hydroxide in hydrobromic acid. The white crystalline material is cadmium bromide tetrahydrate [13464-92-1], $CdBr_2 \cdot 4H_2O$, $\Delta H_{f,298} = -1492.55$ kJ/mol (−356.73 kcal/mol) (3) which dehydrates to the monohydrate at 36°C and to the yellow, anhydrous material $CdBr_2$ at 200°C. The anhydrous material may be prepared directly from the elements at elevated temperature or from anhydrous cadmium acetate [543-90-8], $Cd(CH_3COO)_2$, mixed with glacial acetic acid and acetyl bromide. Uses include photography, process engraving, and lithography.

Cadmium Iodide. Two crystal morphologies exist for CdI_2 [7790-80-9], the white α-form (see Table 1) and the brown β-form. The latter crystallizes from fused-salt mixtures. The more common α-form has a saltlike layered crystal structure where individual layer sheets contact each other through van der Waals' interactions of the outer iodide ions (17). This structure dictates the highly lamellar and easily cleaved nature of CdI_2 crystals. CdI_2 is prepared either by direct combination of the elements in the absence of oxygen or by the dissolution of cadmium metal, the oxide, carbonate, hydroxide, or sulfide in hydroiodic acid. Precipitation of CdI_2 from a solution of the sulfate using KI also yields the hexagonal, lamellar, lustrous crystals of the α-form. The iodide is used in electro-deposition of Cd, as a nematocide, in phosphors, lubricants, photoconductors, in photography, process engraving, and lithography (qv).

3.6. Cadmium Hydroxide. $Cd(OH)_2$ [21041-95-2] is best prepared by addition of cadmium nitrate solution to a boiling solution of sodium or potassium hydroxide. The crystals adopt the layered structure of CdI_2: there is contact between hydroxide ions of adjacent layers. $Cd(OH)_2$ can be dehydrated to the oxide by gentle heating to 200°C; it absorbs CO_2 from the air forming the basic carbonate. It is soluble in dilute acids and solutions of ammonium ions, ferric chloride, alkali halides, cyanides, and thiocyanates forming complex ions.

$Cd(OH)_2$ is much more basic than $Zn(OH)_2$ and is soluble in 5 N NaOH at 1.3 g/L as the anionic complex tetrahydroxocadmate [26214-93-7], $Cd(OH)_4^{2-}$. Its most important utility is as the active anode in rechargeable Ni–Cd and Ag–Cd storage batteries. The chemical reaction responsible for the charge–discharge of the batteries is (19):

$$Cd(OH)_2 + 2\ Ni(OH)_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Cd + 2\ NiOOH + 2\ H_2O$$

These batteries accounted for 75% of 2001 U.S. annual consumption of cadmium and are used in heavy-duty, long-life applications such as rechargeable tools, appliances, instruments, and electronics (20). Several new applications could include use in electric and hybrid electric vehicles, remote area power storage systems, and solar cells (21).

3.7. Cadmium Nitrate. Anhydrous $Cd(NO_3)_2$ [10325-94-7] is obtained by action of nitric acid on the carbonate to give cadmium nitrate tetrahydrate [10022-68-1] by crystallization; this may then be dried by careful exposure to concentrated nitric acid at 20°C. The tetrahydrate, bp 132°C, is soluble in alcohols, acetone, and ethyl acetate and most polar organic solvents.

Cadmium nitrate is the preferred starting material for $Cd(OH)_2$ for use as the anode in alkaline batteries. The sintered anode matrix of such batteries is saturated with cadmium nitrate (480–500 g/L Cd) and cadmium hydroxide is formed therein by standardized electrolysis and drying (22). Other uses include photographic emulsions and as a colorant in glass and ceramics.

3.8. Cadmium Oxide. Cadmium vapor burns in air to produce the dark brown oxide CdO [1306-19-0] and the commercial process for its production is as follows. Pure Cd metal is melted and then vaporized whereupon air is blown through the hot vapor, oxidizing the cadmium and carrying the product to a baghouse. The resultant oxide (particle size controlled by the air–Cd ratio) is calcined at 550°C to ensure uniform properties. Other preparative approaches include calcination of the carbonate, nitrate, sulfate, or hydroxide in air;

oxidation of the sulfide by heating in air and by pyrolysis of cadmium formate [4464-23-7] or cadmium oxalate [814-88-0]. These last two methods give very finely divided material of high activity. Oxide smokes of extreme toxicity may be produced by spontaneous combustion of the cadmium alkyls, eg, $Cd(CH_3)_2$, in air. CdO has the rock-salt crystal structure with octahedral coordination at the Cd and O ions. Cadmium peroxide [12139-22-9], CdO_2, has been reported and is also cubic having $a = 0.5313$ nm and $d = 6.396$ g/mL.

CdO is soluble in dilute acids but not in water or alkalies and forms a variety of soluble complexes, the most important being with sodium cyanide in the bath used in electroplating. CdO is an n-type semiconductor of band gap energy 222 kJ/mol (53.1 kcal/mol). It may be reduced to the metal with hydrogen, carbon, or carbon monoxide at 600°C. It finds uses as a starting material for PVC heat stabilizers and other inorganic Cd compounds and as the cadmium source in cyanide plating baths. Ag–CdO contacts are used in electrical devices whereas high purity CdO is used as a second depolarizer, along with Ag_2O, in Ag–Zn storage batteries (23). CdO is also used in nitrile rubbers and plastics such as Teflon where it improves high temperature properties and heat resistance. Its use as a high temperature resistor material takes advantage of its low specific resistivity and low negative temperature coefficient of resistivity. Other uses include in phosphors, as a glass colorant, as a nematocide, as an ascaricide or anthelmintic in swine, and as a catalyst of a variety of organic chemical reactions.

3.9. Cadmium Phosphates. Cadmium phosphate [13477-17-3], $Cd_3(PO_4)_2$, is prepared by reaction of cadmium nitrate with potassium dihydrogen phosphate in the presence of sodium hydroxide to neutralize the KH_2PO_4 (7). This material is both a catalyst and a phosphor. Cadmium dihydrogen phosphate [17695-54-4], $Cd(H_2PO_4)_2$, is prepared by adding phosphoric acid to a slurry of cadmium carbonate in water and acts as a catalyst for the polymerization of gaseous olefins (24). Roasting the dihydrogen compound to 300°C leads to cadmium metaphosphate [14466-83-2], $Cd(PO_3)_2$, which finds utility as an exceptionally bright and stable phosphor.

3.10. Cadmium Selenide and Telluride. Both materials are n-type semiconductors having band gap energies of 1.74 eV (712 nm) for CdSe [1306-24-7] and 1.45 eV (855 nm) for CdTe [1306-25-8] (25). They are best prepared by direct reaction of the elements at elevated temperatures in evacuated, sealed quartz tubes. However, the materials may also be prepared by simple wet chemical techniques whereby a solution of cadmium ion is exposed to H_2Se or H_2Te gases in an inert atmosphere or to solutions of the alkali metal selenide or telluride. The heavy precipitates can vary in color from yellow-orange to deep red-black, depending on the particle size of the compound, and this is a manifestation of the size-quantization phenomenon (16) which is particularly well demonstrated by the cadmium chalcogenides. Colloidal suspensions of the semiconductors may be maintained by addition of a surfactant (polyphosphate or micelle-forming agent) to the precipitating solution and such solutions of nanoparticulates have been under intense investigation as nonlinear optical media (16) (see NONLINEAR OPTICAL MATERIALS).

CdSe forms solid solutions with CdS which are used as pigments ranging in color from orange to deep maroon and are called cadmium sulfoselenides. Other uses are in photocells, rectifiers, luminous paints, and as a ruby colorant for glass manufacture.

CdTe is used in infrared optics (26), phosphors, electroluminescent devices, photocells, and as a detector for nuclear radiation (27).

3.11. Cadmium Silicates. Cadmium orthosilicate [15857-59-2], Cd_2SiO_4, (mp 1246°C; $d = 5.83$ g/mL) and cadmium metasilicate [13477-19-5], $CdSiO_3$, are both prepared by direct reaction of CdO and SiO_2 at 390°C under 30.4 MPa (300 atm) or at 900°C and atmospheric pressure in steam. The materials are phosphors when activated with Mn(II) ion and are both fluorescent and phosphorescent.

3.12. Cadmium Sulfate. $CdSO_4 \cdot \frac{8}{3}H_2O$ [7790-84-3] is the normal form of cadmium sulfate and is prepared by crystallization of solutions made by dissolving cadmium metal, oxide, sulfide, hydroxide, or carbonate in sulfuric acid. Alternatively, the $\frac{8}{3}$ hydrate is precipitated from such solutions with alcohol. The monohydrate [13577-20-8] may be prepared by dehydrating this material by heating to 80°C. Anhydrous cadmium sulfate [10124-36-4] is prepared by oxidation of the sulfide or sulfite under carefully controlled oxidizing atmospheres at high temperature. An alternative method involves treatment of powdered cadmium nitrate, halides, oxide, or carbonate with dimethyl sulfate (7).

Cadmium sulfate solutions are used in the standard Weston cell and as electrolytes in electroplating as alternatives to cyanide baths. Other uses include phosphors and as a nematocide.

3.13. Cadmium Sulfide. CdS [1306-23-6] is dimorphic and exists in the sphalerite (cubic) and wurtzite (hexagonal) crystal structures (25). At very high pressures it may exist also as a rock-salt structure type. It is oxidized to the sulfate, basic sulfate, and eventually the oxide on heating in air to 700°C, especially in the presence of moisture (9).

CdS may be prepared ranging in color from white to deep orange-red depending on the preparative method and resultant particle size of the material. The smaller the particle size the lighter the coloration (16) and glass colored with cadmium sulfide is colorless when first cast from the melt where the particle size of the CdS is less than 2 nm. Upon annealing (striking) at 700°C, yellow-orange color develops as the particle size increases as a result of aggregation in the glass matrix. Direct reaction between H_2S and Cd vapor or between sulfur and cadmium metal or its oxide at high temperature produces CdS. However, a simple method involves treatment of an acidic or neutral cadmium ion solution with H_2S or Na_2S and collection of the dense yellow precipitate is straightforward. At room temperature this method gives yellow solids whereas from boiling solutions one obtains yellow solids at neutral pH but reddish solids at low pH. Acidified cadmium acetate solutions precipitate yellow CdS; ammoniacal solutions give a red modification.

CdS finds its main use as a pigment, particularly in the glass and plastics industry.

Increased concerns over the toxicity and environmental impact of cadmium materials and increased imports of Cd pigments from Europe contributed to the decrease in production in the latter 1980s and 1990s. Pure yellow cadmium sulfides are formulated with red cadmium selenides to form solid solutions called C.P. toners ranging from yellows and oranges (low selenium content) to reds and maroons (high selenide). Such pigments are manufactured on an industrial scale in three steps: (*1*) cadmium sticks are dissolved in sulfuric acid to give a sulfate solution; (*2*) sodium sulfide and selenide are mixed in the desired proportion and added to the cadmium sulfate solution; and (*3*) the precipitated pigment is filtered, washed, dried, and calcined at 700°C in an inert atmosphere to obtain a uniform product.

The cadmium lithopones, $ZnS{-}CdS/Se{-}BaSO_4$, are additional cadmium sulfide-based pigments prepared by adding barium sulfide to zinc–cadmium sulfate mixtures. Again the colors range from yellow to deep red-maroon depending on additive content. Cadmium pigments in general are very resistant to H_2S, SO_2, light, heat, and other atmospheric conditions and are dense, heavy colorants having good covering power and bright deep shades.

CdS colorants find use in plastics, paints, soaps, rubber, paper, glass, printing inks, ceramic glazes, textiles, and fireworks. Luminescent pigments based on CdS–ZnS are also produced.

Other uses of CdS take advantage of its semiconducting properties. It is an *n*-type semiconductor with a band gap (wurtzite phase) at 2.58 *e*V (480 nm). It is used as a thin-film cell to convert solar energy to electrical power, is a photoconductor, and is electroluminescent (25). These properties have found use in phosphors, photomultipliers, radiation detectors, thin-film transistors, diodes and rectifiers, electron-beam pumped lasers, and smoke detectors (19). CdS, when shock fractured by pressure release from the cubic phase, has been reported to be a high temperature superconductor having a critical temperature for conversion to the superconductive state in excess of 190 K (28). Finally the nonlinear optical properties of colloidal suspensions of CdS in glass or polymer matrices have been explored as possible light transistors for optical computing applications (16).

3.14. Cadmium Tungstate. Cadmium tungstate [7790-85-4], $CdWO_4$, forms white or yellow monoclinic crystals which are highly luminescent, $a = 0.5029$ nm, $b = 0.5859$ nm, $c = 0.5074$ nm; $d = 8.033$ g/mL. It is prepared by the action of tungstic acid on cadmium oxide in a little water (7) and finds use in x-ray screens, scintillation counters, phosphors, and as a catalyst in organic reactions (29).

4. Organic Compounds

Many organocadmium compounds are known but few have been of commercial importance. Wanklyn first isolated diethylcadmium in 1856. The properties of this and other dialkylcadmiums are listed in Table 3. In general, these materials are prepared by reaction of an anhydrous cadmium halide with a Grignard or alkyllithium reagent followed by distillation of the volatile material in an inert atmosphere or *in vacuo*. Only the liquid dimethyl compound is reasonably stable and then only when stored in a sealed tube. Dimethylcadmium is mildly pyrophoric in air and produces dense clouds of white, then brown, cadmium oxide smoke, which is highly toxic if breathed (30). When dropped into water, the liquid sinks in large droplets that decompose with a series of small explosive jerks and pops. For this reason, and particularly because of the low thermal stability, most dialkylcadmium materials are prepared and used *in situ* without separation, eg, in the conversion of acid chlorides to speciality ketones (qv):

$$2\ RCOCl + CdR'_2 \longrightarrow 2\ RCOR' + CdCl_2$$

Table 3. **Properties of Dialkyl Cadmium Compounds**

Compound	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C[a]	Density, g/mL
dimethylcadmium	[506-82-1]	$(CH_3)_2Cd$	−4.5	105.5 (101.3)	1.9846
diethylcadmium	[592-02-9]	$(C_2H_5)_2Cd$	−21	64(2.6)	1.6564
dipropylcadmium	[5905-48-6]	$(C_3H_7)_2Cd$	−83	84(2.8)	1.4184
dibutylcadmium	[3431-67-2]	$(C_4H_9)_2Cd$	−48	103.5 (1.6)	1.3054
diisobutylcadmium	[3431-67-2]	$(C_4H_9)_2Cd$	−37	90.5 (2.6)	1.2674
diisoamylcadmium	[35061-27-9]	$(C_5H_{11})_2Cd$	−115	121.5 (2.0)	1.2184

[a] Pressure of bp determination is given in kPa in parentheses. To convert kPa to mm Hg, multiply by 7.5.

Dimethylcadmium has a linear C−Cd−C core with a Cd−C bond length of 0.211 nm (17).

Many dialkyl and diaryl cadmium compounds have found use as polymerization catalysts. For example, the diethyl compound catalyzes polymerization of vinyl chloride, vinyl acetate, and methyl methacrylate (30), and when mixed with $TiCl_4$, can be used to produce polyethylene and crystalline polypropylene for filaments, textiles, glues, and coatings (30). With >50% $TiCl_4$, diethyl cadmium polymerizes dienes. Diethyl cadmium may be used as an intermediate ethylating agent in the production of tetraethyllead. The diaryl compounds such as diphenylcadmium [2674-04-6], $(C_6H_5)_2Cd$, (mp 174°C) are also polymerization catalysts. These compounds are also prepared using Grignard or aryllithium reagents in tetrahydrofuran (THF) solvent but may be prepared by direct metal substitution reactions such as:

$$(C_6H_5)_2Hg + Cd \longrightarrow (C_6H_5)_2Cd + Hg$$

Dimethylcadmium has found use as a volatile source of Cd for metal organic chemical vapor deposition (MOCVD) production of cadmium-containing semiconductor thin films (qv) such as CdS, $Cd_{1-x}Hg_xTe$, or $Cd_{1-x}Mn_xTe$, as multiple quantum well species (16).

Cadmium alkyl and aryl halides, RCdX, as well as cadmium allyls have been prepared by Grignard reactions but, as yet, have not realized any commercially important uses despite reactivity toward a number of organic and inorganic materials.

4.1. Cadmium Acetate. Cadmium acetate [543-90-8], $Cd(CH_3COO)_2 \cdot n\,H_2O$, can exist as the anhydrous salt ($n = 0$) mp 256°C, $d = 2.341$ g/mL or as one of a series of hydrates ($n = 1 - 3$). The anhydrous material may be prepared by treating cadmium nitrate with acetic anhydride or by very careful heating and drying the dihydrate at ~130°C. The cadmium acetate dihydrate [5743-04-4], $d = 2.01$ g/mL, is obtained by dissolving cadmium metal or its oxide, hydroxide, or carbonate in acetic acid and crystallizing. Cadmium acetate monohydrate [543-90-8] may be obtained from the dihydrate by careful drying. All acetates are very soluble in water and alcohols.

Cadmium acetate is a colorant for glass and textiles, a glaze for ceramics where it produces iridescent effects, a starting material for preparation of the cadmium halides, and is an alternative to the cyanide bath for cadmium electroplating.

4.2. Organocadmium Soaps.

Other salts of organic acids, apart from the acetate, have found wide usage as heat and light stabilizers for plastics, especially flexible PVC. During the molding process, unstabilized PVC begins to lose HCl at 95°C resulting in marked yellowing of the molded article. In addition, the free HCl acts as a catalyst for further degradation of the polymer and the unsaturated polymer chains left behind upon HCl elimination absorb more uv radiation which also breaks down the polymer chains leading to embrittlement. Cadmium salts of long-chain fatty acids such as laurate and stearate, cadmium soaps, are acid acceptors that react with HCl to give the weak organic acid and $CdCl_2$, and so their incorporation into the plastic article prevents early discoloration. However, cadmium chloride is a strong Lewis acid, capable of initiating polymer degradation itself. For this reason, barium compounds of the same fatty acids are used in conjunction with the cadmium stabilizers because there is a rapid exchange of chloride from cadmium to barium. A phosphite chelator is typically added to the mixture to produce an almost complete stabilizer package (19).

The solid soaps are prepared from cadmium chloride solution by precipitation with sodium salts of the fatty acids. Cadmium laurate [2605-44-9], $Cd(C_{12}H_{24}O_2)_2$, cadmium stearate [2223-93-0], $Cd(C_{18}H_{36}O_2)_2$, cadmium palmitate [6427-86-7], $Cd(C_{16}H_{32}O_2)_2$, and cadmium myristate [10196-67-5], $Cd(C_{14}H_{28}O_2)_2$, are of this type. Liquid stabilizers such as cadmium octoate [2191-10-8], $Cd(C_8H_{16}O_2)_2$, cadmium phenolate [18991-05-4], $Cd(C_6H_6O)_2$, cadmium decanoate [2847-16-7], $Cd(C_{10}H_{20}O_2)_2$, cadmium benzoate [3026-22-0], $Cd(C_7H_6O_2)_2$, and cadmium naphthenate are more versatile and economical in use and are prepared from CdO and the organic acid in an inert solvent. The water by-product is driven off as the reaction proceeds and the clear solution of cadmium soap in the organic solvent is used directly in plastics manufacture. FDA regulations have decreed that plastics that contact foodstuffs may not contain Cd–Ba stabilizers. Overall environmental concerns have led most plastics manufacturers to move away from heavy metal-based stabilizers, toward alternatives such as Ca–Zn, Ba–Zn or organotin materials (21,31). There has therefore been a decrease in consumption of Cd compounds in the stabilizer field that began in the late 1970s.

5. Economic Aspects

Compared with 2000, both production and consumption of cadmium in the U.S. declined during 2001. Domestic production of cadmium metal declined by 64% and production of cadmium compounds, including cadmium sulfide, declined by more than 93%. World consumption was 16,000 t in 2001, 17% less than in 2000 (21).

In 2000 the United States was the net exporter of cadmium sulfide, most of which was exported to the Philippines (59%), Germany (26%), and Saudi Arabia (10%) (21). Table 4 gives U.S. production of cadmium compounds.

One of the most promising applications is the use of cadmium telluride solar cells to convert sunlight into electricity and the use of NiCd batteries to store

Table 4. **U.S. Production of Cadmium Compounds, t, Cd content**[a]

Year	Cadmium sulfide[b]	Other cadmium compounds[c]
2000	42	417
2001	31	0

[a] Ref. 21.
[b] Includes cadmium lithopone and cadmium sulfoselenide.
[c] Includes oxide and plating salts (acetate, carbonate, nitrate, sulfate, etc.).

that energy (21). Critical to the cadmium market is the industry's ability to recycle cadmium products.

6. Analytical Methods

Because of the increasing emphasis on monitoring of environmental cadmium the determination of extremely low concentrations of cadmium ion has been developed. Table 5 lists the most prevalent analytical techniques and the detection limits. In general, for soluble cadmium species, atomic absorption is the method of choice for detection of very low concentrations. Mobile prompt gamma *in vivo* activation analysis has been developed for the nondestructive sampling of cadmium in biological samples (32).

At higher levels, cadmium may be estimated gravimetrically following precipitation with sulfide (34), β-naphthoquinoline (35), or after plating from a cyanide-containing solution onto a stationary platinum cathode. Volumetric procedures rely on preliminary precipitation of the sulfide that is purified and then dissolved in acid whereupon the liberated H_2S may be titrated with iodine. An alternative, should zinc be a likely contaminant, is to precipitate with diethyldithiocarbamate and then to redissolve in acid and titrate with sodium ethylenetriaminetetraacetate (EDTA) using Eriochrome Black T as indicator (36).

7. Health and Safety Factors

Cadmium, both as the free metal and in its compounds, is highly toxic and has been designated one of the 100 most hazardous substances under Section 110 of

Table 5. **Analytical Methods and Detection Limits for Cadmium Ion**[a]

Method	Detection limit, ppb
atomic absorption spectroscopy (graphite furnace)	0.008
polarography (square wave)	10
x-ray fluorescence (energy dispersive)	5000
neutron activation analysis	1
isotope dilution	10
inductively coupled plasma emission spectra	1

[a] Ref. 33.

the Superfund Amendments and Reauthorization Act of 1986 (37). Poisoning may occur either via inhalation or ingestion. Only about 6% of the estimated 40–50 μg/d of ingested cadmium is absorbed by the body, whereas 25–50% of the 2–10 μg/d of cadmium in inhaled dust is absorbed (33,38). Cadmium is present in cigarette smoke and as much as 0.1–0.2 micrograms per cigarette may be absorbed by the lungs (39).

Chemical pneumonitis or pulmonary edema may result from acute exposure to cadmium fumes, as oxide or chloride aerosols, at a dose of 5 mg/m^3 over an 8-h period. One mg/m^3 inhaled over the same time period gives rise to clinically evident symptoms in sensitive individuals. Deaths from acute cadmium poisoning have resulted from inhalation of cadmium oxide smokes and fumes, usually from welding operations on cadmium plated steels in poorly ventilated areas. Acute ingestion of cadmium concentrations above ~15 ppm (0.1–1.0 mg/(kg · d)) produce symptoms of nausea, vomiting, abdominal cramps, and headache (40). Possible sources of such poisoning have been traced to cadmium-plated cooking utensils, cadmium solders in water coolers, or from acid juices stored in ceramic pots glazed using cadmium-containing compounds. Table 6 lists exposure limits for cadmium and cadmium compounds as Cd.

Cadmium is efficiently scavenged by the body and biological half-times for cadmium excretion are on the order of 10–30 years. The kidneys and liver appear to be the organs of concentration for cadmium; kidney damage leading to proteinuria is probably the most common manifestation of chronic cadmium exposure. The combination of dietary deficiency and high cadmium exposure resulted in the most infamous example of suspected cadmium poisoning on record where a disease known as itai-itai afflicted elderly Japanese women from the Zinzu river basin after World War II. Whereas the role of cadmium in the disease is still controversial, it seems clear that the severe weakening of bone tissue associated with the disease was a result of demineralization induced by cadmium (33). Although there is some evidence that cadmium may be carcinogenic in animals under certain exposure conditions, the association between cadmium exposure and cancer in humans remains tenuous. The increased risk of prostatic cancer in workers exposed to cadmium dusts and fumes has been reported to be significant, but the number of cases reported so far is very small (33) and the conclusions have been questioned. More recent data have described a possible link

Table 6. **Exposure Limits for Cadmium and Cadmium Compounds as Cd**[a]

Exposure Limits	OSHA PEL	NIOSH Exposure Limit	ACGIH TLV
time-weighted average	0.005 mg/m^3	lowest feasible conc.	0.01 mg/m^3 0.002 mg/m^3 (respirable fraction)
short-term exposure limit			
ceiling limit			
biological limits (if available)	3 μg/g creatinine (urine) 5 μg/L (blood)		5 μg/g creatinine (urine) 5 μg/L (blood)

[a] Ref. 41.

between cadmium exposure and lung cancer in humans (40). In 1989 the EPA denied a petition requesting removal of CdS and CdSe from their list of toxic chemicals, citing available cancer data on CdS and other cadmium compounds (42). EPA maintains that cadmium is a probable human carcinogen (Group B1) but only by the inhalation route.

8. Environmental Concerns

Cadmium discharges to air and water are decreasing as primary zinc producers have largely converted to electrolytic processing and as more efficient pollution control technologies take effect (43). Most of the cadmium released to the environment is now in the form of solid wastes such as coal ash, sewage sludge (5– 20 ppm), flue dust, and fertilizers (2–20 ppm). Effluent limits of all sources have been strictly regulated in recent years and cadmium emissions are controlled by the best available technology including membrane filtration (see EXHAUST CONTROL, INDUSTRIAL). Recycling programs have been instituted by several battery manufacturers, eg, in France, Belgium, Japan, Sweden, and Korea (37), aimed at reducing cadmium pollution from spent Ni–Cd batteries. U.S. and Canadian collection and recycling programs for small rechargeable batteries are expected to expand. About 1,700 t of rechargeable batteries were recycled in 2000 (21).

9. Uses

The principal areas of cadmium usage in terms of U.S. consumption at the end of 2001 were batteries (75%); pigments (12%); coatings and plating (8%); plastic stabilizers (4%); nonferrous alloys and other uses (1%).

Cadmium hydroxide is the anode material of Ag–Cd and Ni–Cd rechargeable storage batteries (see BATTERIES, SECONDARY CELLS). Cadmium sulfide, selenide, and especially telluride find utility in solar cells (see SOLAR ENERGY). Cadmium sulfide, lithopone, and sulfoselenide are used as colorants (orange, yellow, red) for plastics, glass, glazes, rubber, and fireworks.

A cadmium sulfide interface layer can improve III-V semiconductor device performance (44).

In flexible PVC, cadmium salts of long-chain organic acids, such as stearate and laurate, are used in combination with similary Ba^{2+} salts as heat and light stabilizers (see HEAT STABILIZERS) but these uses are in decline since these compounds can now be replaced by less toxic compounds. Cadmium cyanide, acetate, fluoroborate, or sulfate is used as an electrolyte in coating a thin cadmium layer, ie, electroplating (qv), onto other metals thereby imparting enhanced corrosion protection. Cadmium protective overlayers are also deposited by mechanical plating or vapor deposition (see METALLIC COATINGS).

The cadmium chalcogenide semiconductors (qv) have found numerous applications ranging from rectifiers to photoconductive detectors in smoke alarms. Many Cd compounds, eg, sulfide, tungstate, selenide, telluride, and oxide, are used as phosphors in luminescent screens and scintillation counters.

Glass colored with cadmium sulfoselenides is used as a color filter in spectroscopy and has recently attracted attention as a third-order, nonlinear optical switching material (see NONLINEAR OPTICAL MATERIALS). Dialkylcadmium compounds are polymerization catalysts for production of poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVA), and poly(methyl methacrylate) (PMMA). Mixed with $TiCl_4$, they catalyze the polymerization of ethylene and propylene.

Dimethyl cadmium is toxic and can be replaced with a more stable cadmium oxide to form nanocrystals for use in electronics and optoelectronic devices (45). At the University of California, Berkeley, new forms of cadmium sulfide crystals have been developed for use in the manufacture of solar panels. The new crystals facilitate electron flow and could boost efficiency by more than 20% (46).

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