The Solubility of Some Sparingly Soluble Salts of Zinc and Cadmium in Water and in Aqueous Electrolyte Solutions

H. Lawrence Clever, M. Elizabeth Derrick[a], and Susan A. Johnson

Solubility Research and Information Project, Department of Chemistry, Emory University, Atlanta, GA 30322

Received February 12, 1991; revised manuscript received March 4, 1992

The literature on the solubility of the sparingly soluble inorganic salts of zinc and cadmium in water and in aqueous electrolyte solutions has been reviewed. The solubility data have been compiled and evaluated. Recommended or tentative values of the solubilities and the solubility products have been given when warranted. Auxiliary thermodynamic and crystallographic data useful in the interpretation of solubility data are given. For the many zinc and cadmium substances for which only limited solubility data are available, unevaluated values are given in an annotated bibliography with emphasis on solubility data published since 1950.

Key words: aqueous electrolyte solutions; cadmium salts; equilibrium constants; solubility products; zinc salts.

Contents

List of Tables

---

[a] Department of Chemistry, Valdosta State College, Valdosta, GA 31698.

Reprints available from ACS; see Reprints List at back of issue.

0047-2689/92/050941-64/$16.00

List of Figures

Nomenclature

A	Debye-Huckel constant
A_1, A_2, A_3	Parameters of regression equation for solubility and solubility product
B	Debye-Huckel constant
C_p°	Standard heat capacity at constant pressure
F	Faraday constant, 96,485.309 C mol^{-1}
G°	Standard Gibbs energy
H°	Standard enthalpy
I	Ionic strength, $(1/2)\Sigma c_i z_i^2$(molar scale)
K_H	Equilibrium constant, Henry's constant
K_n	Equilibrium constant, ligand metal formation constant ($ML_{n-1} + L = ML_n$)
K_{s0}, K_{s0}°	Equilibrium constant, solubility ion product constant (may be designated either concentration or molality scale) $ML(s) = M^{z+} + L^{z-}$; superscript indicates the thermodynamic (activity) constant
K_{snm}, K_{snm}°	Equilibrium constant, solubility product constant when a complex M_mL_n is formed in solution. When $m = 1$, the second subscript ($m = 1$) is omitted; the notation also applies when a protonated ligand reacts with elimination of a proton. The superscript indicates the thermodynamic (activity) constant.
K_{a1}, K_{a2}, K_{a3}	Equilibrium constants, weak acid dissociation constants
R	Gas constant
S°	Standard entropy
T	Thermodynamic temperature
Z	Molecules per unit cell
a, b, c	Unit cell dimensions
a	Activity
c_B	Amount-of-substance concentration of substance B (amount of B divided by volume of solution)
f	Fugacity
m_B	Molality of solute substance B (amount of B divided by the mass of solvent)
n	Amount of substance
p, p_B	Pressure, total pressure, partial pressure of substance B
x_B	Mole fraction of substance B; $n_B/\Sigma n_i$
$y, y_\pm$	Activity coefficient, mean ionic activity coefficient, concentration (molar) scale
x	Ion charge
β_n	Equilibrium constant, cumulative ligand metal formation contant ($M + nL = ML_n$) $\beta_n = \prod_{i=1}^{n} K_i$ (see K_n above)
ρ	Density
$\gamma, \gamma_\pm$	Activity coefficient, mean ionic activity coefficient, molal scale

1. Introduction

Heavy metal salts contribute to enviromental problems in ground, brackish, and sea water. A knowledge of solubility and related solution equilibria is needed by scientists who model the transport and transformation of inorganic pollutants in aqueous systems. This is the third paper in a series of compilations and critical evaluations of the solubilities, solubility products, and related aqueous solution equilibria of heavy metal salts, intended to meet this need. The earlier papers covered lead salts[1], and metallic mercury and mercury salts[2]. The present paper covers salts of zinc and cadmium. The introductory sections and the sections on weak acid dissociation constants in the first two papers should be consulted for general information that is not repeated here.

Although solubility data were located for a large number of zinc and cadmium substances, there appear to be fewer reliable data than were found for the lead and mercury salts. The available solubility data for zinc and cadmium sulfides, and most other metal sulfides, are of particularly doubtful value. Many papers contain sulfide solubility data of some empirical value, but none of the workers have rigorously characterized the solid; controlled oxygen and hydrogen sulfide activity (vapor pressure) in the gas phase; or followed the pH and the concentration of the minimum number of solution species to define thermodynamically the aqueous metal sulfide systems. Crerar and co-workers[3] outline the problem for the FeS + NaCl + H_2O system. Their approach, with modification for the individual sulfide, could profitably be applied to the study of other metal sulfide + electrolyte + water systems.

2. Scope and Approach

The present review includes the solubility of sparingly soluble salts of zinc and cadmium in water and in aqueous electrolyte solutions with special emphasis on data published since 1950. Pre-1950 data are also included, but the search of the older literature was not as thorough. By sparingly soluble we mean solubilities of about 0.1 mol L^{-1} or less. The very soluble chlorides, bromides, iodides, nitrates, perchlorates and other soluble salts are not included. Most of the data are for inorganic substances, but zinc and cadmium salts with a number of organic anions are included in the annotated bibliography.

The Solubility Series volumes on oxides and hydroxides (Vol. 23)[4], and sulfites, selenites, and tellurites (Vol. 26)[5] contain compilations and evaluations of the corresponding zinc and cadmium substances. Only summaries of these evaluations are given here.

Solubility data reported since 1950 were traced by a combined hand and computer search of Chemical Abstracts through December of 1989. Earlier solubility data were traced through Chemical Abstracts and standard compilations of solubility data, including Seidell and Linke[6], Stephen and Stephen[7], Sillen and Martell[8], Kirgintsev, Trushnikova and Lavent'eva[9] and Comey and Hahn[10].

The Crystal Data Determinative Tables[11] and papers found in Chemical Abstracts were the sources of crystallographic information and density values given for the solid substances in the sections on physical characteristics of the salts. The NBS Tables of Chemical Thermodynamic Properties[12], the Geological Survey Bulletin on Thermodynamic Properties of Minerals[13], the CODATA Key Values[390], and the IUPAC sponsored Standard Potentials in Aqueous Solution[14] were sources of evaluated auxiliary thermodynamic data.

3. Auxiliary Thermodynamic Data

Reliable standard potentials of zinc and cadmium and their aqueous solution species and solid salts, and dissociation constants of weak acids remain useful auxiliary data. A review of the chemical forms of zinc and cadmium in natural waters by Prokof'ev[388] contains a summary of the chemical forms of the ions in aqueous solution.

3.1. Standard Potential Values

Reviews in the Encyclopedia of Electrochemistry of the Elements[15a,b] summarize well the past experimental work on the standard potentials of $M^{2+}(aq) + 2e^- = M(s)$ where M is either Zn or Cd. Reviews in Standard Potentials in Aqueous Solution[14a,b] give the authors' best estimate of evaluated standard potential data and related thermodynamic data. For the most part the authors repeat values from the NBS Tables[12], but there are a few important differences.

Zinc. Brodd and Werth[14a] recommend a standard Gibbs energy of formation of the $Zn^{2+}(aq)$ ion of −147.16 kJ/mol, which is 0.1 kJ more negative than the NBS Table 298.15 K value. It was derived from their recommended $E°$ value of −0.7626 V. Their enthalpy of formation and entropy values for the aqueous zinc ion of −152.84 kJ/mol and −107.53 J/(K mol), repectively, differ even more from the NBS Table values. However, the recent CODATA[390] key values of −153.39 kJ/mol and −109.8 J/K mol agree better with NBS Table values. The CODATA values lead to a Gibbs energy of formation of −147.20 kJ/mol and an $E°$ of −0.7628 volts at one atm pressure. The Gibbs energy and $E°$ values are both more negative than either the NBS Table or Brodd and Werth values.

Other of the Brodd and Werth values that differ significantly are for $Zn(OH)_4^{2-}(aq)$, the Gibbs energy of formation differs in both sign and magnitude and is probably in error. The wurtzite and sphalerite forms of ZnS(s) differ by 0.02 to 0.01 kJ in enthalpy and Gibbs energy and the entropy by 0.2 J/K.

Table 1 lists some zinc and zinc species standard potentials recommended by Brodd and Werth of possible application to solubility problems. We have added $(dE°/dT)$ values calculated by the method of de Bethune and coworkers[16,17], using data from Brodd and Werth's Table for the Zn species and from the NBS Tables[12] for other species. The use of the Brodd and Werth $\Delta S°$ value changes the temperature coefficient for the Zn^{2+}/Zn standard potential from 0.119 to 0.096 mv/K.

Cadmium. Table 1 also contains standard potential data for cadmium and cadmium species recommended by Okinaka[14b]. We have confirmed the $(dE°/dT)$ values given by him from the data in the NBS Tables.

3.2. Weak Acid Dissociation Constants

The solubilities of salts of weak acids are pH dependent. To obtain a value of the solubility product of a salt of a weak acid from experimental data requires knowledge of the weak acid dissociation constant or constants. If a gas is evolved as well, as for example with carbonates (CO_2), sulfides (H_2S) or sulfites (SO_2), then Henry's constant for the gas needs to be known.

There is little new information in this area since we made recommendations in the mercury salt solubility paper[2]. The earlier recommendations stand with the exception of H_2S. The case of H_2S is still not settled, although a smaller magnitude second dissociation constant is recognized by most workers. A recent paper of Licht[18] gives aqueous solubilities, solubility products and standard potentials of the metal sulfides based on a Gibbs energy of formation of the aqueous sulfide ion of (111 ± 2) kJ/mol at 298.15 K. This value is based on the smaller second dissociation constant, a $pK_2 = (17.3 \pm 0.3)$ for H_2S. The results are given for over forty sulfides. The values for ZnS and CdS will be discussed later in the paper.

4. Solubility Data

This section contains solubility data on the sparingly soluble salts of zinc and cadmium in water and in aqueous electrolye solutions. Each sparingly soluble substance is identified by its formula, Chemical Abstracts Registry Number (when located) and formula weight. The 1985 atomic weights[19] were used. These are 65.39 ± 0.02 for zinc and 112.411 ± 0.008 for cadmium, based on terrestrial isotopic composition.

The physical characteristics of each sparing soluble salt are briefly described when crytallographic information is available. The primary source is the Crystal Data Determinative Tables[11]. The section is followed by a discussion of the available experimental solubility data. The experimental data are evaluated and recommended or tentative data are tabulated. When appropriate an equation for smoothed data is presented. The solubility product values are treated similarly. An unevaluated list of typical formation constants of ions formed in the saturated solution is often given.

The chemical substances in the following discussions are arranged according to the "Standard Order of Arrangement" described in the NBS Tables of Chemical Thermodynamic Properties[12]. The zinc and cadmium substances are discussed by anion.

TABLE 1. Some zinc and cadmium standard potentials at 298.15 K

Reaction	$E°$/V	$(\partial E°/\partial T)_p$ /mV K^{-1}
Zinc		
$Zn^{2+}(aq) + 2e^- = Zn(s)$	−0.7626	+0.096
$Zn(OH)_2(s) + 2e^- = Zn(s) + 2OH^-(aq)$	−1.246	−0.996
$Zn(OH)_4^{2-}(aq) + 2e^- = Zn(s) + 4OH^-(aq)$	−1.285	–
$ZnO(s) + H_2O + 2e^- = Zn(s) + 2OH^-(aq)$	−1.248	−1.162
$Zn(NH_3)_4^{2+}(aq) + 2e^- = Zn(s) + 4NH_3(aq)$	−1.04	0.286
$Zn(CN)_4^{2-}(aq) + 2e^- = Zn(s) + 4CN^-(aq)$	−1.34	0.318
$ZnCO_3(s) + 2e^- = Zn(s) + CO^{2-}{}_3(aq)$	−1.06	−1.184
$ZnS(s)$ (wurzite) $+ 2e^- = Zn(s) + S^{2-}(aq)$	−1.44	−0.836
$Zn(C_2O_4)_2^{2-}(aq) + 2e^- = Zn(s) + 2C_2O_4^{2-}(aq)$	−0.99	–
$Zn(C_4O_6H_4)_4^{6-}(aq) + 2e^- = Zn(s) + 4C_4O_6H_4^{2-}(aq)$	−1.15	–
Cadmium		
$Cd^{2+}(aq) + 2e^- = Cd(s)$	−0.4025	−0.030
$Cd^{2+} + Hg + 2e^- = Cd(Hg)$	−0.3515	−0.229
$Cd(OH)_2(aq) + 2e^- = Cd(s) + 2OH^-$	−0.824	−1.018
$Cd(OH)_4^{2-} + 2e^- = Cd(s) + 4OH^-(aq)$	−0.670	–
$CdO(s) + H_2O + 2e^- = Cd(s) + 2OH^-$	−0.783	−1.167
$Cd(NH_3)_4^{2+}(aq) + 2e^- = Cd(s) + 4NH_3(aq)$	−0.622	0.155
$Cd(CN)_4^{2-}(aq) + 2e^- = Cd(s) + 4CN^-(aq)$	−0.943	−0.127
$CdCO_3(s) + 2e^- = Cd(s) + CO_3{}^{2-}(aq)$	−0.734	−1.183
$CdS(s) + 2e^- = Cd(s) + S^{2-}(aq)$	−0.255	−0.821
$CdSe(s) + 2e^- = Cd(s) + Se^{2-}(aq)$	−1.32	–
$CdTe(s) + 2e^- = Cd(s) + Te^{2-}(aq)$	−1.62	–

Note 1. The $E°$ values are for a standard pressure of 1 atm (101325 Pa). For $Zn^{2+}(aq) + 2e^- = Zn(s)$ the CODATA[390] key values leads to $E° = -0.7628$ V at 1 atm and to -0.7627 V at 1 bar (100000 Pa). The temperature coefficient is 0.108 mv K^{-1}.

Note 2. For $Zn^{2+}(aq) + 2e^- = Zn(s)$ the second temperature derivative, $(\partial^2 E°/\partial T^2)_p = -0.86$ μV K^{-1}.

Note 3. The $Zn^{2+} + Hg + 2e^- = Zn(Hg)$ standard electrode potential appears to be identical to the Zn(s) electrode potential.

Note 4. Solid zinc hydroxide exists in γ, β, ε and precipitated forms, each with their own Gibbs energy of formation. The ε form is considered most stable. The $Zn(OH)_2(s)$ in the table above is not identified, but it appears to be the ε form.

Often the experimental solubility product constant, K_{s0}°, K_{s0}°, is compared with the constant calculated from Gibbs energy values from the NBS Tables[12]. Agreement between the experimental and calculated value should be looked upon with caution. We may be comparing the same data since the sources of the table values are usually not known.

The data for a number of salt + electrolyte + water systems are too numerous to be tabulated. For such systems a table presenting the references and range of experimental conditions used in the study is given as a guide to the literature. These tables, 1A–6A, are given following the solubility data containing tables. Table 2A (ZnS) and 3A (CdS) do contain solubility data values, but they are values based on older models no longer considred valid.

A summary table, Table 2, containing only recommended and tentative solubility values from this study follows for quick reference. The more detailed tables, 3 to 61, follow the discussions of each substance. Table 62 lists single system solubility and solubility product values reported for the most part since since 1954. These values are also tentative values.

4.1. Zinc and Cadmium

Zn [7440–66–6] Atomic weight 65.39
Cd [7440–43–9] Atomic weight 112.411

Physical characteristics: Both metals are hexagonal-zinc with $Z = 2$, $a = 2.6595 \times 10^{-10}$ m, $c = 4.9331 \times 10^{-10}$ m, and a calculated density of 7.140×10^3 kg m^{-3}; and cadmium with $Z = 2$, $a = 2.9736 \times 10^{-10}$ m, $c = 5.6058 \times 10^{-10}$ m, and a calculated density of 8.642×10^3 kg m^{-3}.

The measurement of the solubility of an unionized metal in water is a difficult experiment. The metal surface must be oxide- and carbonate-free. The water must be gas-free ultra-pure neutral water. One worker has suggested the experiment should be carried out in a container made of the metal under study to prevent changes in the water by leached impurities from glass or other

TABLE 2. Summary of recommended and tentative solubility data from the present study

Solid phase	T/K	Solubility or solubility product	Recommended, R, Tentative, T	Table
$Zn(OH)_2$	298.15	See equations and equilibrium constants in Sec. 4.2	T	
$Cd(OH)_2$	298.15	See equations and equilibrium constants in Sec. 4.2	T	
$ZnF_2{\cdot}4H_2O$	298.15	0.1552 mol kg^{-1}	T	3
$Zn(IO_3)_2{\cdot}2H_2O$	298.15	0.01549 mol L^{-1}	T	12
	293.15	K°_{s0} 3.5 × 10^{-6} $mol^3 L^{-3}$	T	13
	298.15	(4.1 ± 0.4) × 10^{-6} “	R	13
	303.15	5.2 × 10^{-6} “	T	“
	308.15	6.2 × 10^{-6} “	T	“
	313.15	7.4 × 10^{-6} “	T	“
	318.15	8.8 × 10^{-6} “	T	“
$Cd(IO_3)_2$	298.15	(1.97 ± 0.13) × 10^{-3} mol L^{-1}	T	14
	298.15	K°_{s0} 2.5 × 10^{-8} $mol^3 L^{-3}$	T	15
ZnS				
sphalerite	298.15	K°_{s0} 1.3 × 10^{-29} $mol^2 L^{-2}$	T	18
wurtzite	298.15	K°_{s0} 7.9 × 10^{-27} $mol^2 L^{-2}$	T	18
precipitated	298.15	K_{s0} 4.0 × 10^{-26} $mol^2 L^{-1}$	T	18
		See also equations, equilibrium constants and discusion in Sec. 4.5a.		
CdS	298.15	K°_{s0} 5.0 × 10^{-34} $mol^2 L^{-1}$	T	20
ZnSe	298.15	K°_{s0} 3.6 × 10^{-26} $mol^2 L^{-2}$	T	23
$ZnSeO_3{\cdot}H_2O$	298.15	K°_{s0} 1.59 × 10^{-7} $mol^2 L^{-2}$	T	24
$Zn_3(AsO_4)_2$	298.15	K°_{s0} 2.8 × 10^{-28} $mol^5 L^{-5}$	T	39
$Cd_3(AsO_4)_2$	298.15	K°_{s0} 2.2 × 10^{-33} $mol^5 L^{-5}$	T	41
$ZnCO_3$	298.15	1.98 × 10^{-3} mol L^{-1} at P_{co2} = 0.987 bar	T	42
	298.15	1.64 × 10^{-4} mol L^{-1} at P_{co2} = 0.00032 bar	T	42
	298.15	K°_{s0} 1.46 × 10^{-10} $mol^2 L^{-2}$	T	43
	323.15	9.02 × 10^{-11} “ “	“	“
	373.15	1.59 × 10^{-11} “ “	“	“
	423.15	1.5 × 10^{-12} “ “	“	“
	473.15	1.0 × 10^{-13} “ “	“	“
	523.15	6.2 × 10^{-15} “ “	“	“
	573.15	3.5 × 10^{-16} “ “	“	“
$CdCO_3$	298.15	K°_{s0} 1.0 × 10^{-12} $mol^2 L^{-2}$	T	46
a-$ZnC_2O_4{\cdot}2H_2O$	283.15	0.64 × 10^{-4} mol L^{-1}	T	47
	288.15	0.89 × 10^{-4} “ “	“	“
	293.15	1.23 × 10^{-4} “ “	“	“
	298.15	1.67 × 10^{-4} “ “	“	“
	298.15	K°_{s0} 1.38 × 10^{-9} $mol^2 L^{-2}$	T	48
$CdC_2O_4{\cdot}3H_2O$	298.15	(3.01 ± 0.10) × 10^{-4} mol L^{-1}	T	49
	298.15	K°_{s0} 1.42 × 10^{-8} $mol^2 L^{-1}$	T	50
$Zn_2[Fe(CN)_6]{\cdot}2H_2O$	298.15	(9.7 ± 1.7) × 10^{-6} mol L^{-1}	R	58
	298.15	K°_{s0} 1.9 × 10^{-16} $mol^3 L^{-3}$	R	59
$Cd_2[Fe(CN)_6]{\cdot}7H_2O$	298.15	(5.1 ± 1.7) × 10^{-6} mol L^{-1}	T	60
	298.15	K°_{s0} 3.6 × 10^{-18} $mol^3 L^{-3}$	T	61

container material. Pariaud and Archinard [20] equilibrated electroanalytically pure zinc with degassed triple distilled water for 32 days at 305 K. The dissolved atomic zinc was oxidized and determined colorimetrically. The zinc solubility is $(700 \pm 50) \times 10^{-6}$ g L^{-1} or $(1.07 \pm 0.08) \times 10^{-5}$ mol L^{-1}. The value is judged doubtful. It is of concern that the Zn solubility is nearly identical to the solubility of ZnO and $Zn(OH)_2$, which suggests the zinc surface may have been contaminated by oxide. If the value is in error it is probably too large. It would be difficult to maintain an absolute oxygen-free carbon dioxide-free system over a number of days. No other reports of the solubility of either zinc or cadmium metal were found.

4.2. Zinc and Cadmium Oxides and Hydroxides

There are extensive data on the solubility of the oxides and hydroxides of zinc and cadmium. These data have been surveyed in detail in a recent Solubility Series volume edited by Dirkse [4]. Only a brief summary of Dirkse's evaluation is given here.

ZnO [1314–13–2] Molecular weight 81.38
$Zn(OH)_2$ [20427–58–1] Molecular weight 99.40

Physical Characteristics: Zinc oxide is considered a stable material, but its rate of solution and some other physical properties appear to depend on its method of preparation. Zinc oxide (zincite) is hexagonal with $Z = 2$, $a = 3.24 \times 10^{-10}$ m, $c = 5.176 \times 10^{-10}$ m, and a density of 5.70×10^3 kg m^{-3}. At about 100 kbar a more dense cubic form exists. Zinc hydroxide is a substance whose purity and stability have often been called into question. Unless prepared by a most elaborate method the hydroxide is often contaminated with another anion or basic oxide. Conditions for the preparation of six forms of $Zn(OH)_2$ and x-ray patterns of each are reported by Feitknecht[21]. The ϵ-form is considered most stable. It is orthorhombic with $Z = 4$, $a = 5.170 \times 10^{-10}$ m, $b = 8.547 \times 10^{-10}$ m, $c = 4.93 \times 10^{-10}$ m, and a density of 3.03×10^3 kg m^{-3}. Other forms are described including a hexagonal form of density 4.253×10^3 kg m^{-3}.

The more reliable experimental values of the solubility of zinc oxide in water range between $(2\text{–}8) \times 10^{-5}$ mol L^{-1} at 298.15 K. The solubility values of zinc hydroxide show an even larger range. An order of magnitude for the solubility of $Zn(OH)_2$ in water is 1×10^{-5} mol L^{-1} at 298.15 K.

Gubeli and Ste-Marie[22] report cumulative formation constants (mol L^{-1}) at unit ionic strength and 298.15 K for the zinc-hydroxide complex ions:

$$Zn^{2+}(aq) + n\ OH^-(aq) = Zn(OH)_n^{2-n}(aq).$$

The values are 2×10^6, 1.5×10^{11}, 2×10^{14} and 5×10^{17} for $n = 1, 2, 3$ and 4, respectively.

Dirkse[4] gives the following as thermodynamic equilibrium constants for solid ZnO and $Zn(OH)_2$ in contact with a saturated aqueous solution at 298.15 K. The equilibrium constant notation is that used by Dirkse.

The acid character of ZnO and $Zn(OH)_2$

$$ZnO(s) + OH^-(aq) + H_2O = Zn(OH)_3^-(aq) \qquad K_1^\circ = 6 \times 10^{-4}$$
$$ZnO(s) + 2OH^-(aq) + H_2O = Zn(OH)_4^{2-}(aq) \qquad K_2^\circ = 1 \times 10^{-2}$$
$$Zn(OH)_2(s) + OH^-(aq) = Zn(OH)_3^-(aq) \qquad K_{10}^\circ = 1.3 \times 10^{-3}$$
$$Zn(OH)_2(s) + 2OH^-(aq) = Zn(OH)_4^{2-}(aq) \qquad K_{11}^\circ = 4 \times 10^{-2}$$

Near minimum solubility

$$Zn(OH)_2(s) = Zn(OH)_2(aq) \qquad K_8^\circ = 3 \times 10^{-16}$$
$$Zn(OH)_2(s) = Zn^{2+}(aq) + 2OH^-(aq) \qquad K_9^\circ = 3 \times 10^{-17}$$
$$ZnO(s) + H_2O = Zn^{2+}(aq) + 2OH^- \qquad K_{9a}^\circ = 1.5 \times 10^{-17}$$

The basic character of $Zn(OH)_2$

$$Zn(OH)_2(s) + 2H^+(aq) = Zn^{2+}(aq) + 2H_2O \qquad K_3^\circ = 7 \times 10^{10}$$
$$Zn(OH)_2(s) + H^+(aq) = Zn(OH)^+(aq) + H_2O \qquad K_4^\circ = 2.54 \times 10^3$$

Data on a number of zinc basic salts are in Table 62. These include $Zn_4(OH)_7ClO_4$, $Zn_4(OH)_6SO_4$, and $Zn_5(OH)_6(CO_3)_2$ (hydrozincite).

CdO [1306–19–0] Molecular weight 128.41
$Cd(OH)_2$ [21041–95–2] Molecular weight 146.42

Physical characteristics: Cadmium oxide is cubic with $Z = 4$, $a = 4.659 \times 10^{-10}$, and a density of 8.238×10^3 kg m^{-3}. Cadmium hydroxide exists in α-, β- and γ- forms. Of these only the β-$Cd(OH)_2$ is stable in water suspensions. The α-form is hexagonal with a $= 3.36$ and $c = 8$ (estimate) $\times 10^{-10}$ m. The γ-$Cd(OH)_2$, is monoclinic with $Z = 4$, $a = 5.67 \times 10^{-10}$ m, $b = 10.25 \times 10^{-10}$ m, $c = 3.41 \times 10^{-10}$ m, $\beta = 91°24'$, and a density of 4.908×10^3 kg m^{-3}. Another hexagonal form exists with $Z = 1$, $a = 3.47 \times 10^{-10}$ m, $c = 4.71 \times 10^{-10}$ m and a density of 4.92×10^3 kg m^{-3}. We did not locate a structure specified to be the β-form. The aging of the $Cd(OH)_2(s)$ produces no change in the x-ray pattern, but it does affect the solubility. Aged precipitates produce better agreement in solubility studies than fresh precipitates.

Dirkse[4] concludes that the solubilities of CdO and $Cd(OH)_2$ in water are identical. He proposes a tentative solubility in water of 5.4×10^{-5} mol L^{-1} at 298.15 K. An identical solubility of the two substances seems unlikely. It is more likely the CdO is relatively rapidly converted to $Cd(OH)_2$ during the measurement. Dirkse points out the solubility depends on temperature, ionic strength, pH, method of preparation (anion and basic oxide contamination) and the age of the precipitate.

The dissolution process of cadmium hydroxide in acid and in alkaline aqueous solution may include a number of reactions. The following reaction scheme, notation and values at 298.15 K are from the review of Dirkse[4].

$$Cd(OH)_2(s) + 2H^+(aq) = Cd^{2+}(aq) + 2H_2O \qquad K_1 \ \text{(indeterminate)}$$
$$Cd(OH)_2(s) + H^+(aq) = CdOH^+(aq) + H_2O \qquad K_2 = 1.3 \times 10^{-4}$$
$$Cd(OH)_2(s) = Cd(OH)_2(aq) \qquad K_3 = 3 \times 10^{-7}$$
$$Cd(OH)_2(s) = Cd^{2+}(aq) + 2OH^-(aq) \qquad K_{s0} = 5.9 \times 10^{-15}$$

$$\mathrm{Cd(OH)_2(s) + OH^-(aq) = Cd(OH)_3^-(aq)}\, K_5 = 2\times10^{-6}$$
$$\mathrm{Cd(OH)_2(s) + 2OH^-(aq) = Cd(OH)_4^{2-}(aq)}\, K_6 = 2\times10^{-6}$$

The K_3 value represents the minimum solubility as a function of pH and probably appears at a pH of 11 to 13.

For the available experimental data, literature citations and other information on the zinc and cadmium oxide and hydroxide systems above, see the review of Dirkse[4].

Since Dirkse's evaluation Rai, Felmy and Szelmeczka[391] have reported the solubility of β-$Cd(OH)_2$ in 0.01 $NaClO_4$ with the hydroxide ion varied from 1×10^{-6} to 1.0 mol L^{-1}. Their results differ in a significant way from Dirkse's. They find the only dominante Cd(II) species required to explain the solubility of $Cd(OH)_2(s)$ are $Cd^{2+}(aq)$, $Cd(OH)_2^\circ(aq)$ and $Cd(OH)_4^{2-}(aq)$. Thus, the required reactions and their equilibrium constants are:

$$\mathrm{Cd(OH)_2(s) = Cd^{2+}(aq) + 2OH^-(aq)} \quad K_{s0}^\circ = 7.2\times10^{-15}$$
$$\log K_{s0}^\circ = -14.14\pm0.21$$
$$\mathrm{Cd(OH)_2(aq) = Cd(OH)_2^\circ(aq)} \quad K_3 = 9.1\times10^{-8};$$
$$\log K_3 = -7.04\pm0.21$$
$$\mathrm{Cd(OH)_2(s) + 2OH^-(aq) = Cd(OH)_4^{2-}(aq)} \quad K_6 = 2.4\times10^{-6}$$
$$\log K_6 = -5.62\pm0.32$$

Only the K_3 constant differs significantly from the values suggested by Dirkse. That difference is a direct consequence of Rai *et al.* considering the species $Cd(OH)^+(aq)$ and $Cd(OH)_3^-(aq)$ not significant. Rai *et al.*[391] also show that their constants along with ion-interaction parameters from the low ionic strength study are also consistent with the cadmium hydroxide solubility data obtained in solutions as concentrated as 10 M in NaOH or KOH and 7 M Na(OH, ClO_4).

Although it is satisfying to fit a system with as few parameters as possible, we do not believe the good fit found by Rai *et al.*[391] necessarily proves $Cd(OH)^+$ and $Cd(OH)_3^-$ negligible species. Their model does represent the data well, and we see no reason not to use it as the tentative model for the aqueous $Cd(OH)_2$ system unless further experimental work reveals a better model.

4.3. Zinc and Cadmium Fluorides

4.3.a. Zinc Fluoride

ZnF_2 [7783–49–5] Molecular weight 103.38
$ZnF_2{\cdot}2H_2O$ [19250–49–8] Molecular weight 139.41
$ZnF_2{\cdot}4H_2O$ [13986–18–0] Molecular weight 175.44
Zn(OH)F [15061–62–8] Molecular weight 101.39

Physical characteristics: Zinc fluoride, ZnF_2, is known in two crystal forms. The tetragonal form, with $Z = 2$, $a = 4.7034\times10^{-10}$ m, $c = 3.1335\times10^{-10}$ m and a calculated density of 4952 kg m^{-3}, is probably the thermodynamically stable form under standard conditions. The orthorhombic form exists at pressures above 50 kbar. It has $Z = 4$, a, b and c = 5.166, 5.658 and 4.683 $\times 10^{-10}$ m, respectively, and a calculated density of 5.01×10^3 kg m^{-3}. The dihydrate, $ZnF_2{\cdot}2H_2O$, is orthorhombic with $Z = 8$, a, b and c = 13.103, 3.120 and 15.080 $\times 10^{-10}$ m, respectively, and an experimental density[23] of 3.07×10^3 kg m^{-3}. The tetrahydrate, $ZnF_2{\cdot}4H_2O$, is orthorhombic with $Z = 4$, a, b and c = 7.598, 12.695 and 5.297 $\times 10^{-10}$ m, respectively, and a calculated density of 2291 kg m^{-3}. There is good evidence that the tetrahydrate is the equilibrium solid with water at 298 K, and that the dihydrate is the equilibrium solid in a number of concentrated aqueous ternary systems.

The sparingly soluble zinc hydroxide fluorides, $Zn(OH)_{1.5}F_{0.5}$ and $Zn_5(OH)_8F_2$, were characterized by Feitknecht and Bucher[24] in precipitation studies reacting NaOH and ZnF_2. An orthorhombic crystal structure of Zn(OH)F is reported[25].

Literature values of the solubility of zinc fluoride tetrahydrate in water are given in Table 3. We have selected the value of Cook, Davies and Staveley[26] as the tentative value. Their value is reported as part of a careful emf study, but they did not give details of their solubility measurement.

The system deserves further study. There are no solution density data available to allow conversion between concentration and molality. There are not enough reliable solubility data as a function of temperature to establish the temperature coefficient of solubility and thermodynamic changes for the solution process, and there are no studies to show whether or not the hydration of the solid changes with temperature. The data in Table 3 are weak evidence that the temperature coefficient of solubility is negative, as it is for cadmium fluoride.

A solubility product value (Table 4) was estimated for $ZnF_2{\cdot}4H_2O$ from the saturation molality and activity coefficient ($\gamma_\pm$ = 0.312) determined by Cook *et al.*[26]. A value was calculated for ZnF_2 from thermodynamic data[12]. The values lead to a ΔG_{298}° of -10.44 kJ for the hydration of $ZnF_2(s)$, which is consistent with the hydrated form being the stable thermodynamic form in water.

There are five studies on the solubility of ZnF_2 in the presence of fluorine-containing acids or salts. Some of these data are given in Table 5 along with composition of the equilibrium solid. The ZnF_2 solubility increases in the presence of moderate amounts of HF and SbF_3, but decreases to a very small value in the presence of NH_4F, KF and RbF.

The formation of the complexes

$$\mathrm{Zn^{2+}(aq) + F^-(aq) = ZnF^+(aq)}$$
$$\mathrm{Zn^{2+}(aq) + 2F^-(aq) = ZnF_2(aq)}$$

has been studied at several ionic strengths at 293 and 298 K. The reported values of β_1 and β_2 are given in Table 6. There is fair agreement among the β_1 values in $NaClO_4$ media. Only Rodriguez Placeres *et al.*[27] have reported both β_1 and β_2 values.

4.3.b. Cadmium Fluoride

CdF_2 [7790–79–6] Molecular weight 150.41
$CdF_2{\cdot}2H_2O$ [28953–05–1] Molecular weight 186.4

TABLE 3. Solubility of zinc fluoride tetrahydrate, $ZnF_2{\cdot}4H_2O$, in water

T/K	c/mol L^{-1}	m/mol kg^{-1}	Reference
Tentative value			
298.15	0.1552		Cook, Davies, and Staveley, 1971[26]
Other experimental values			
291	0.15_5		Dietz quoted by Kohlrausch, Rose and Dolezalek, 1903[28]
293	0.157		Kurtenacker, Finger and Hey, 1933[29]
298.15	0.1466		Carter, 1928[30]
298.15		0.149	Gamburg, Deichman and Ikrami, 1976[31]

TABLE 4. Solubility product of zinc fluoride

T/K	$K\mathcal{S}$mol^3 kg^{-3}	Solid	Reference
298.15	$4.54 \quad 10^{-4}$	$ZnF_2{\cdot}4H_2O$[a]	Cook, *et al.* 1971[26]
298.15	3.0×10^{-2}	ZnF_2[a]	NBS Tables[12]

[a]Above data consistent with $ZnF_2(s) + 4H_2O(l) \rightarrow ZnF_2{\cdot}4H_2O(s)$
$\Delta G^\circ_{298} = -10.44$ kJ

$CdF_2{\cdot}4H_2O$ [] Molecular weight 222.47
Cd(OH)F [16441–85–3] Molecular weight 148.42

Physical characteristics: Cadmium fluoride, CdF_2, is cubic with $Z = 4$, $a = 5.388 \times 10^{-10}$ m, and a calculated density of 6386 kg m^{-3}. The dihydrate $CdF_2{\cdot}2H_2O$ is known. Feitnecht and Bucher[24] show the lines of an x-ray powder photograph, but there is no definitive information on the structure. The cadmium fluoride hydroxide, Cd(OH)F, is reported by both Volkova *et al.*[25] and Staalhandskė[38] to be orthorhombic. Staalhandske's values are $Z = 4$, a, b and c = 4.8320, 5.5159, and 6.8559×10^{-10} m, respectively, and a calculated density of 5.15×10^3 kg m^{-3}. The mixed solids $CdF_2{\cdot}xCd(OH)_2$ with $x = 4$ to 6 and 2 to 9 were shown to be hexagonal by Feitknecht and Bucher[24].

The solubility of CdF_2 in water is given in Table 7 and in Fig. 1. The nature of the solid in equilibrium with the saturated solution is in question. Both Nuka[39] and Feitknecht and Bucher[24] state they prepared the dihydrate, $CdF_2{\cdot}2H_2O$. Other authors make no mention of the hydration. The problem is complicated by the work of Kulikov and Mamaev[40], who carried out kinetics of dissolution studies on the 100 face of cubic CdF_2 prepared from a high temperature melt. They report solubility values in water at several temperatures, but without experimental details. It is unlikely they used the 100 face of the single crystal for the solubility study, but they may have. Opalovskii *et al.*[32] identify the tetrahydrate, $CdF_2{\cdot}4H_2O$, as the solid at 273 K in equilibrium with aqueous 3.8 to 9.5 wt % HF, and the dihydrate at larger HF concentrations.

The solubility value of Carter[30] appears to be in error and is rejected. The values of Nuka[39] were determined by preparing solutions of known concentration and heating them until they appeared turbid. The method works because of the negative temperature coefficient of solubility. Nuka's values are higher than those reported by the other workers. They may be too large because of a too rapid heating rate and/or supersaturation. The values are classed as doubtful. The other results are classed tentative.

The data have been treated in two ways. A linear regression was applied to all of the data except the rejected value to obtain the equation

$$\ln (m/\text{mol kg}^{-1}) = -(6.0331 \pm 0.3218) + (14.3249 \pm 0.9750)/(T/100\ \text{K})$$

with a standard error about the regression line of 0.022. A second linear regression was applied to the three data points of Kulikova and Mamaev[40] at 283.15, 293.15 and 303.15 K, and the single point of Jaeger[41] because they seem a consistent data set in Fig. 1. The resulting equation is

$$\ln (\text{m/mol kg}^{-1}) = -(7.8061 \pm 0.1473) + (19.5854 \pm 0.4331)/(T/100\ \text{K})$$

with a standard error about the regression line of 0.0024. Both lines are shown on the Figure, and the smoothed solubility values are given in Table 8. We cannot recommend one smoothing equation over the other, but we do suspect the first equation may give too large a solubility at the higher temperatures because of the influence of Nuka's values on the linear regression.

It is tempting to speculate that there is a difference between the hydration of the solid at 273 K and the hydration at the other temperatures, but there is no convincing experimental evidence to support the idea. The possibility of tetrahydrate or dihydrate at 273 K and dihydrate or anhydrous salt at higher temperatures awaits further experiments.

The solubility of CdF_2 in ternary systems containing HF, KF or NH_4F parallels the behavior of ZnF_2 in these systems. Some of the values from Opalovskii *et al.*[32], Kurtenacker *et al.*[29,33] and Jaeger[41] are given in Table 9. In

TABLE 5. Solubility of zinc fluoride in ternary systems ZnF_2 + MF_x + H_2O

T/K	ZnF_2, wt %	MF_x, wt %	Solid Phase	Reference
	ZnF_2 + HF + H_2O			
273.	1.80	0.40	$ZnF_2{\cdot}4H_2O$	Opalovskii *et al.*, 1970[32].
	5.17	5.35	"	
	6.70	10.70	"	
	7.03	16.55	"	
	7.11	20.60	$ZnF_2{\cdot}2H_2O$	
	8.06	21.23	"	
	9.21	25.27	"	
	8.68	26.70	"	
	9.31	29.43	"	
	10.49–0.19	34.88–74.63	ZnF_2^a	
	0.18–0.02	78.07–99.98	$ZnF_2{\cdot}2HF^b$	
293	2.54	2.47	$ZnF_2{\cdot}4H_2O$	Kurtenacker *et al.*, 1933[29].
	4.98	3.69		
	9.53	17.38		
	11.40	25.43		
	11.84	29.16		
	ZnF_2 + NH_4F + H_2O			
293	0.46	4.0	$ZnF_2{\cdot}4H_2O$	Kurtenacker *et al.*, 1933[33].
	0.31	8.6		
	0.16	13.0	$ZnF_2{\cdot}2NH_4F{\cdot}2H_2O$	
	0.05	20.4		
	0.03	28.0		
	0.027	39.8		
	ZnF_2 + KF + H_2O			
293	0.25	1.5	$ZnF_2{\cdot}1.3KF{\cdot}0.1H_2O^c$	Kurtenacker *et al.*, 1933[33].
	0.025	10.0		
	ZnF_2 + RbF + H_2O			
298.15	1.52	0	$ZnF_2{\cdot}4H_2O$	Gamburg *et al.*, 1976[31].
	0.002	15	$ZnF_2{\cdot}RbF{\cdot}2H_2O^d$	
	ZnF_2 + SbF_3 + H_2O			
298.15	2.1	0	$ZnF_2{\cdot}4H_2O$	Shakhnazaryan *et al.*, 1983[34,e]
	13.7	44.8		
	14.6	50.1	$Zn[SbF_4]_2{\cdot}6H_2O$	
	5.8	68.4		
	3.2	74.1	SbF_3	

[a] Data range. There are 15 data points in this range where ZnF_2 solubility decreases as HF concentration increases.

[b] Data range. There are 8 data points in this range where ZnF_2 solubility decreases as HF concentration increases.

[c] Authors state solid compositions indeterminate.

[d] Two values given in paper, seven shown on small scale figure. The composition of the $ZnF_2{\cdot}4H_2O$ + $ZnF_2{\cdot}RbF{\cdot}2H_2O$ mutual solubility point could not be read from the graph.

[e] The solvent composition is 2 wt % HF, 98 wt % water. The paper contains a table of 20 ZnF_2/SbF_3 compositions for the system.

TABLE 6. Formation constants of ZnF^+ and ZnF_2 in aqueous systems

T/K	*I*/Electrolyte	β_n	*n*	Reference
298.15	0	18 ± 4	1'	Connick, Paul, 1958[35,a]
298.15	0.01–0.155/ZnF_2	13.6 ± 1.6	1	Cook *et al.*, 1971[26]
298.15	0.5/Na(F,ClO$_4$)	5.4 ± 1		Connick, Paul, 1958[35,b]
293.15	1.0/Na(F,ClO$_4$)	5.9 ± 0.6	1	Ahrland, Rosengren, 1956[36]
298.15	2.0/Na(F,ClO$_4$)	7.0 ± 0.5	1	Mesaric, Hume, 1963[37]
298.15	0.5/K(F,NO$_3$)	3	1	Rodriguez Placeres, *et al.* 1980[27]
		11	2	

[a] Estimated by method of R. Nasanen, Acta Chem. Scand. 4, 140 (1950).

[b] The authors report values of 5.0 ± 1 and 5.4 ± 1 at 288.15 and 308.15 K, respectively.

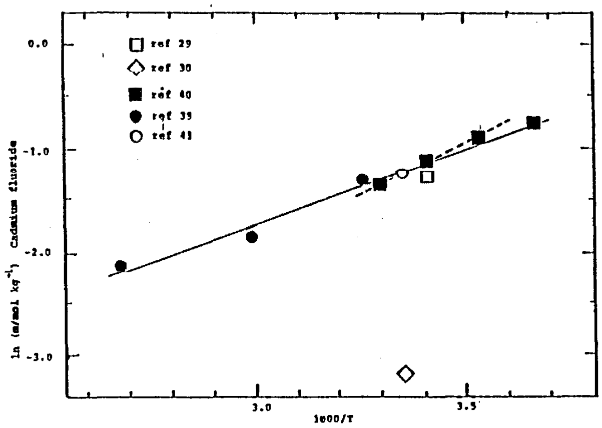

FIG. 1. Cadmium fluoride + water, 273–373 K. ln (*m*/mol kg^{-1}) vs. 1000/(*T*/K)

TABLE 7. The solubility of cadmium fluoride in water

T/K	*c*/mol L^{-1}	m/mol kg^{-1}	Reference
273.15	0.4725	0.4652	Kalikov *et al.*, 1973[40].
283.15	0.4114	0.4093	" " "
293.15	0.3282	0.3270	" " "
		0.281	Kurtenacker *et al.*, 1933[29].
298.15		0.291	Jaeger, 1901[41].
	0.0414		Carter, 1928[30].
303.15	0.2590	0.2589	Kalikov *et al.*, 1973[40].
307		0.272	Nuka 1929[39].
334		0.157	
373		0.12	

TABLE 8. The solubility of cadmium fluoride in water. Smoothed data

T/K	Eq. (1) m/mol kg^{-1}	Eq. (2) m/mol kg^{-1}
273.15	0.454	–
283.15	0.378	0.411
293.15	0.318	0.324
298.15	0.293	0.290
303.15	0.270	0.260
313.15	0.233	–
333.15	0.177	–
353.15	0.139	–
373.15	0.111	–

the presence of HF the CdF_2 solubility first increases, then decreases as the HF concentration increases. Several solids are identified. In the presence of NH_4F and KF the CdF_2 solubility decreases to very small values.

The only important complex ion in the cadmium fluoride solutions appears to be CdF^+. Earlier mentions in the literature of CdF_2^0 and Cd_2F^{3+} have not been substantiated by recent work. Values of β_1 for CdF^+ are given in Table 10.

Feitknecht and Bucher[24] prepared the double salt Cd(OH)F and determined its solubility product to be 2.2×10^{-10} at 298 K. Gyunner *et al.*[42] identified this solid in the $Cd(OAc)_2$ + NaF + NaOH + H_2O system at 293 K.

4.4. Zinc and Cadmium Iodates

4.4.a. Zinc Iodate

$Zn(IO_3)_2$ [7790–37–6] Molecular weight 415.19
$Zn(IO_3)_2 \cdot 2H_2O$ [ ] Molecular weight 451.22

Physical characteristics: Liang and Wang[47] report $Zn(IO_3)_2$ is monoclinic with $Z = 2$, *a*, *b* and c = 5.469, 10.938 and 5.1158 × 10^{-10} m, respectively, and an experimental density of 5.08 × 10^3 kg m^{-3}. No report of the $Zn(IO_3)_2 \cdot 2H_2O$ crystal structure was found.

The solubility of zinc iodate in water is given in Table 11. The solid in equilibrium with the saturated solution is in question. Ricci and Nesse[48], Saegusa[49], Spencer, Unger and Bailey[50] and Miyamoto[51] make no

TABLE 9. The solubility of cadmium fluoride in ternary systems CdF_2 + MH + H_2O.

T/K	CdF_2, wt %	MF, wt %	Solid Phase	Reference
	CdF_2 + HF + H_2O			
273.15	9.77	3.75	$CdF_2{\cdot}4H_2O$	Opalovskii, *et al.*, 1970[32].
	12.27	6.71		
	14.05	7.39		
	14.44	9.47		
	14.99	10.81	$CdF_2{\cdot}2H_2O$	
	13.27	11.01		
	12.93	16.45		
	13.59	17.59		
	13.31	19.09		
	11.28	24.05		
	11.64	24.92		
	9.76	30.32		
	5.30–0.07[a]	32.97–66.76	CdF_2	
	0.08–0.20[b]	71.31–97.80	$CdF_2{\cdot}HF$	
293.15	5.0	0.9	CdF_2	Kurtenacker *et al.*, 1933[29].
	11.2	24.4		
	3.0	38.6		
298.15	5.6	2.2		Jaeger, 1901[41,c].
	CdF_2 + NH_4F + H_2O			
293.15	4.0	1.6	CdF_2	Kurtenacker *et al.* 1933[33].
	2.4	5.4		
	1.8	12.3		
	0.4	20.8	$CdF_2{\cdot}2NH_4F{\cdot}2H_2O$	
	0.87	28.9		
	0.21	36.0		
	0.57	40.9		
	CdF_2 + KF + H_2O			
293.15	2.4	3.4	Variable composition $CdF_2{\cdot}(0.8\text{-}1.4)KF{\cdot}(0\text{-}1.0)H_2O$	Kurtenacker *et al.*,1933[33].
	0.6	13.6		
	0.18	24.1		
	0.05	32.5		
	0.024	33.1		
	–	41.2		

[a] About 13 values.
[b] About 8 values.
[c] Did not identify solid.

mention of a hydrated solid. Both Fedorov *et al.*[52] and Lepeshkov, Vinogradov and Karataeva[53,54,55] used the wet residue method to prove their equilibrium solids were the dihydrate at both 298 and 323 K. It is clear that Rammelsberg[56] worked with the dihydrate. It is also clear that Ricci and Nesse[48], Spencer *et al.*[50] and Miyamoto[51] prepared the anhydrous solid for their work. Whether or not the anhydrous salt converted to the dihydrate during the equilibration cannot be determined from their papers. However, we judge it likely that the equilibrium solid is $Zn(IO_3)_2{\cdot}2H_2O$ in all of the solubility studies.

The data of Rammelsberg[56] are rejected because they appear too large relative to more modern data, and they are at poorly defined temperatures. The other data are classed as tentative. At 298.15 K the three middle magnitude values agree very well. Their average is (1.549 ± 0.007) mol L^{-1}. This average value at 298.15 K was combined with the values at 293.35, 301.55 and 313.75 K of Spencer *et al.*[50] in a linear regression to obtain the equation

$$\ln\,(c/\text{mol L}^{-1}) = 105.1463 - 163.9227/(T/100\ \text{K}) - 49.7334\,\ln\,(T/100\ \text{K})$$

with a standard error about the regression line of 0.000093. The smoothed values of the solubility from the equation are in Table 12.

The zinc iodate dihydrate solubility product, K°_{s0}, values are in Table 13. The recommended value at 298.15 K is

TABLE 10. Formation constants of CdF^+ and CdF_2 in aqueous systems

T/K	*I*/Electrolyte	β_1	β_2	Reference
289	0.05/$NaNO_3$	(13 ± 2)		Bond, O'Donnell, 1970[43].
	0.5/$NaNO_3$	(3.5 ± 0.4)		
	1.0/$NaClO_4$	2.9		Leden, 1943[44].
298.15	2.0/Na(F,$C10_4$)	(6.4 ± 0.5)		Mesaric, Hume, 1963[37].
298.15	3.0/$NaNO_3$	(2.9 ± 0.2)		Beutler *et al*., 1976[45].
303.15	1.0/$NaClO_4$	5.8	4	Bond, 1969[46].

TABLE 11. The solubility of zinc iodate dihydrate in water

T/K	Concentration 10^2c/mol L^{-1}	Method	Reference
'cold'	1.95[a] (m)		Rammelsberg, 1838[56]
293.35	1.421 ± 0.006	radiotracer technique	Spencer *et al*., 1974[50]
298.15	1.548	titration analysis	Ricci and Nesse, 1942[48]
	1.457		Saegusa, 1950[49]
	1.556	iodometric	Miyamoto, 1972[51]
	1.542[b]	radiotracer technique	Spencer *et al*., 1974[50]
	1.63	amperometric titration	Fedorov *et al*., 1976[52]
301.55	1.654 ± 0.007	radiotracer technique	Spencer *et al*., 1974[50]
313.75	1.893 ± 0.008	radiotracer technique	Spencer *et al*., 1974[50]
323.15	1.63[c]	titration	Lepeshkov *et al*., 1977[53]
373	2.92[a] (m)		Rammelsberg, 1838[56]

[a] The Rammelsberg data are presented in an unclear way in several handbooks. In Seidell-Linke the mass refers to the dihydrate, but clearly the $Zn(IO_3)_2$ value is shown. In the Russian handbook the dihydrate value is shown, but the number refers to amount of $Zn(IO_3)_2$ dissolved. Both sets of data give the values above when the solid is properly identified.

[b] An interpolated value. No experiment carried out at this temperature by the authors.

[c] Authors reported the value as 0.68 mass % in this and two other papers[54,55]. The value above was calculated assuming the solution density is the same as the water density of 323.15 K.

the average of four values. They are the interpolated value of Spencer *et al*., Saegusa's value as recalculated by Spencer *et al*., the 1976 value of Fedorov *et al*., and the value calculated from Gibbs energy data in the NBS Tables[12]. The tentative values are from a linear regression of the recommended value at 298.15 weighted twice, and the experimental values of Spencer *et al*. between 293.35 and 317.75 K. The equation is

$$\log(K^\circ_{s0}/\mathrm{mol}^3\ \mathrm{L}^{-3}) = -(0.9455 \pm 1.4080) - (34.0358 \pm 4.2347)/T/(100\ \mathrm{K})$$

with a standard deviation about the regression line of 3.5×10^{-7}.

The various papers listed in Table 12 contain solubility product, K_{s0}, values as a function of ionic strength. Formation constants were calculated by Fedorov *et al*.[57] for $Zn(IO_3)_n^{(2-n)}(aq)$ for $n = 1-3$, and extrapolated to zero ionic strength using the solubility studies at 298 K and ionic strength of 0.5 and 3.0 of $Li^+(IO_3^-, ClO_4^-)$. The $n = 3$ species is important at ionic strengths of 2 or more. The authors make no mention of the dihydrate identified in an earlier paper[52]. The pK°_{s0} values found in the two Fedorov *et al*.[52,57] studies[52,57] studies differ by 0.24, which is considered satisfactory agreement.

TABLE 12. Solubility of zinc iodate dihydrate, $Zn(\pm 0_3)_2 \cdot 2H_2O$,in water

T/K	Tentative values Concentration 10^2c_1/mol L^{-1}
Tentative value	
298.15	(1.549 ± 0.007)
Smoothed data	
293.15	1.41
298.15	1.55
303.15	1.68
308.15	1.79
313.15	1.88
318.15	1.95
323.15	1.99

4.4.b. Cadmium iodate

$Cd(IO_3)_2$ [7790–81–0] Molecular weight 462.22

Physical characteristics: Bach and Kueppers[58] report $Cd(IO_3)_2$ is orthorhombic with $Z = 4, a, b$ and $c = 5.856$, 17.470 and 5.582×10^{-10} m, respectively, and a calculated density of 5373 kg m^{-3}. No mention of cadmium iodate hydrates was found in the solubility literature.

The cadmium iodate solubility values from the literature are in Table 14. The tentative value of the solubility (mol L^{-1}) at 298.15 K is the average of the values of Saegusa[49] and Miyamoto[51]. Oelke and Wagner[59] measured the solubility of $Cd(IO_3)_2$ at 298.15 K in the presence of KCl and $MgSO_4$. Their solubility values are presented in a graph from which the solubility (mol kg^{-1}) in water was read. Even allowing for the difference in the volume and mass units of solubility their result is low when compared with the other two workers. The solubility value reported by Lepeshkov *et al.*[54] at 323 K suggests a negative temperature coefficient of solubility of cadmium iodate in water. However, the work of Ramette[60] at ionic strength 3.0 (Cd^{2+}, Na^+) ClO_4^- at 298.15 and 308.15 K shows a positive temperature coefficient of solubility in that medium.

Table 15 summarizes the solubility product values. The tentative value is that calculated from the NBS Tables[12]. It agrees well with the experimental values of Saegusa[49] and of Fedorov *et al.*[57].

The formation of the complex ions, $Cd(IO_3)_n^{(2-n)}(aq)$ ($n = 1$ to 3), has been studied by Fedorov *et al.*[57], Ramette[60,61] and Bond and Hefter[62]. The results are summarized in Table 16. The β_1 values of Bond and Hefter and of Ramette agree well. Ramette does not work in a range where he can determine β_2 values. Fedorov *et al.* give values of β_1, β_2 and β_3 as a function of ionic strength between 0.5 and 3.0 $Li^+(IO_3^-, ClO_4^-)$ at 298 K. Their values at I = 1.0 $LiClO_4$ do not agree well with the results of the other workers. The results of Bond and Hefter[62] and of Ramette[60,61] are preferred.

Table 1A summarizes the solubility and complex ion studies of cadmium iodate solutions. One needs to consult the literature for complete details.

TABLE 13. The zinc iodate dihydrate solubility product

T/K	$10^6 K_{s0}^\circ$/mol^{3}L^{-3}	Added Electrolyte	Reference
Recommended			
298.15	(4.1 ± 0.4)		
Tentative values (Equation)			
293.15	3.5		
298.15	4.3		
303.15	5.2		
308.15	6.2		
313.15	7.4		
318.15	8.8		
Experimental values			
293.35	(3.57 ± 0.21)	KNO_3	Spencer *et al.*, 1974[50]
298.15	4.45[a]		" " "
	3.905	KNO_3	Saegusa, 1950[49]
	3.70 ± 0.56[b]		Saegusa, recalculated[50]
	4.1	$Li^+(NO_3^-, C10_4^-)$	Fedorov, *et al.*, 1976[52]
	4.3	–	NBS tables[12]
	2.34 ± 0.40	$Li^+(IO_3^-, C10_4^-)$	Fedorov *et al.*, 1983[57]
301.55	5.40 ± 0.20	KNO_3	Spencer *et al.*, 1974[50]
313.75	7.39 ± 0.36	KNO_3	" " "

[a] An interpolated value.

[b] Recalculated by Spencer *et al.*, 1974[50] from Saegusa's data.

TABLE 14. The solubility of cadmium iodate in water

T/K	Concentration $10^3\ c$/mol L^{-1}		Reference
298.15	(1.97 ± 0.13)	Tentative value	
298.15	(1.5–1.6) (m)[a]	Experimental values	Oelke and Wagner, 1939[59]
	2.104		Saegusa, 1950[49]
	1.840		Miyamoto, 1972[51]
323.15	1.49 (m)[b]		Lepeshkov *et al.*, 1979[54]

[a] Read from a graph in the paper.

[b] Reported as 0.069 mass %, calculates as molality. (m) indicates molal unit, mol kg-1.

TABLE 15. The solubility product of cadmium iodate in water and aqueous electroyte solution

		Solubility product		
T/K	I/Electrolyte	$10^8 K_{s0}$/mol^3 L^{-3}	$10^8 K_s S(K^\circ_{s0})$/mol^3 L^{-3}	Reference
Tentative value				
298.15	0		2.5	
Experimental values				
298.15	0		2.28	Saegusa, 1950[49]
	0		(3.72 ± 0.26)	Fedorov *et al.*, 1983[57]
	1/(Cd^{2+}, Na^+)$\mathrm{C10}_4^-$	(6.94 ± 0.02)		Ramette, 1981[60]
	3/(Cd^{2+}, Na^+)$\mathrm{C10}_4^-$	(3.81 ± 0.03)		Ramette, 1983[61]
308.15	3/(Cd^{2+}, Na^+)$\mathrm{C10}_4^-$	(4.55 ± 0.03		Ramette, 1983[61]
Thermodynamic data				
298.15	0		2.49	NBS Tables, 1982[12]

TABLE 16. Formation constants of $\mathrm{Cd(IO_3)}_n^{2-n}$ (aq)

T/K	n	β_n	I/Electrolyte	Reference
298.15	1	3.2 ± 0.2	1/$\mathrm{NaC10_4}$	Bond and Hefter, 1972[62]
	2	33 ± 1	1/$\mathrm{NaC10_4}$	
	1	3.27 ± 0.01	1/$\mathrm{NaC10_4}$	Ramette, 1981[60]
	1	3.25 ± 0.08	3/$\mathrm{NaC10_4}$	Ramette, 1983[61]
308.15	1	3.36 ± 0.08	3/$\mathrm{NaC10_4}$	Ramette, 1983[61]
298.15	1	0.036	1/$\mathrm{LiC10_4}$	Fedorov *et al.*, 1983[57]
	2	0.0027	1/$\mathrm{LiC10_4}$	Fedorov *et al.*, 1983[57]
	3	0.0091	1/$\mathrm{LiC10_4}$	Fedorov *et al.*, 1983[57]

4.5. Zinc and Cadmium Sulfides

4.5.a. Zinc Sulfide

ZnS [1314–98–3] Molecular weight 97.45
  sphalerite [12169–28–7] (also called zinc blende)
  wurtzite [12138–066]
  cleiophane [12210–80–9] (a white sphalerite)

Physical characteristics: Sphalerite, the naturally occurring cubic form of ZnS, is the thermodynamically stable form at standard conditions. Wurtzite, the naturally occurring hexagonal form, is the thermodynamically stable form above about 1300 K. The sphalerite to wurtzite transition occurs at 1286 to 1304 K depending on the zinc to sulfur ratio. Sphalerite is cubic with $Z=4$, $a=5.429\times10^{-10}$ m and a calculated density of 4.096×10^3 kg m^{-3}. The hexagonal wurtzite occurs in a number of structures of different Z and c values, but similar a values. Synthetic wurtzite is hexagonal with $Z=2$, $a=3.811\times10^{-10}$ m, $c=6.234\times10^{-10}$ m, and a calculated density of 4.10×10^3 kg m^{-3}. There are also naturally occurring mixed cation crystals such as $(Zn_{0.584}Cd_{0.415})S$. Other mixed sulfides of zinc with Fe, Co and Mn are known.

In addition to the mineral forms, a number of forms precipitated from aqueous solution are discussed in the literature. Their nature is still a matter of controversy. Vukotic[63] found laboratory precipitates are a metastable mixture of sphalerite and wurtzite. Some workers discuss the equilibria among sphalerite, the numerous polytypes and wurtzite forms. Barton and Skinner[64] discuss the problem and point out the room temperature mixtures are metastable because the wurtzite component is stable only at high temperature.

A common literature terminology is α-ZnS and β-ZnS. These designations have different meanings to different workers. The original use of α- and β-forms appears to have been that of Glixelli[65], who called the ZnS precipitated from acid solution α-ZnS and that precipitated from basic solution β-ZnS. From 1907 to about 1930 one could depend on this meaning for α- and β-ZnS. Later authors have used the designation to distinguish between sphalerite and wurtzite. Ringbom[66] and Sillen and Martell[8] used α-ZnS to refer to sphalerite and β-ZnS to refer to wurtzite. The CRC Handbook and the Crystal Data Determinative Tables[11] appear to use the opposite convention.

A problem of equal or greater importance than the nature of the solid is the control and measurement of solution variables during a solubility measurement. Crerar *et al.*[3] point out that in the study of the solubility of a metal oxide or sulfide in aqueous electrolyte solution at variable pH, Gibbs phase rule requires the knowledge of seven variables. The number may be reduced by knowledge of various connecting equilibria, but it is a larger number of variables than measured or controlled in solubility studies of the past. Most studies of the solubility of ZnS are useless as far as obtaining reliable values of thermodynamic equilibrium constants and thermodynamic changes. This is not to say that the many studies of the past are useless; many are of practical use for empirical applications under conditions similar to the conditions of the original solubility study.

Another problem is the value of the second ionization constant of H_2S. Licht[18] evaluated recent work and proposed a value of $pK_{a2} = (17.3 \pm 0.3)$ for $H_2S(aq)$, which leads to a Gibbs energy of formation of the aqueous sulfide ion, $\Delta G_f^\circ(S^{2-}(aq)) = (111 \pm 2)$ kJ·mol^{-1}. The value is almost 30% larger than the present NBS Table value of 85.8. The change makes the ZnS solubility product several orders of magnitude smaller than previously thought.

Licht suggests several ways of expressing the solubility product:

$$ZnS(s) = Zn^{2+}(aq) + S^{2-}(aq) \qquad K_{s0}$$
$$ZnS(s) + H^+(aq) = Zn^{2+}(aq) + HS^-(aq) \qquad {}^*K_{s0}$$
$$ZnS(s) + H_2O(M) = Zn^{2+}(aq) + HS^-(aq) + OH^-(aq)$$
$$K_s = {}^*K_{s0}K_w$$

He gives the following pK values for each of these constants applied to sphalerite, wurtzite and precipitated ZnS at 298 K:

Zinc sulfide	pK_{s0}	p$^*K_{s0}$	pK_s
ZnS(sphalerite)	28.9	11.5	25.5
ZnS(wurtzite)	26.1	8.7	22.7
ZnS(precipitate)	25.4	8.0	22.0

The sulfide ion is of negligible concentration except in highly basic solutions. In many metal sulfide saturated solutions the HS^- and OH^- concentrations are nearly equal. Thus, one of the alternate solubility product expressions above may be more useful than the free ion product constant, K_{s0}.

The zinc ion is probably present in these solutions as a complex ion, $Zn(HS)_n^{(2-n)}$. Barnes[67] gives pK values for the following solution equilibria:

$$ZnS(s) + H_2S(aq) + HS^-(aq) = Zn(HS)^-{}_3(aq)$$
$$pK = (3.0 \pm 0.4)\ (298.15\ \text{K}, I = 1.0)$$
$$= (2.9 \pm 0.5)\ (373-473\ \text{K}, I = 1.0)$$
$$ZnS(s) + H_2S(aq) + 2HS^-(aq) = Zn(HS)^{2-}{}_4(aq)$$
$$pK \simeq 2.6\ (298.15\ \text{K}, I = 1.0)$$
$$ZnS(s) + H_2O(aq) = ZnS{\cdot}H_2O(aq) \quad [\text{or } Zn(OH)(SH)(aq)]$$
$$pK = (5.87 \pm 0.01)\ (298.15\ \text{K}, I = 1.0)$$

The solid ZnS is assumed to be sphalerite. None of the above depends on the value of K_{a2}. Gubeli and Ste-Marie[68] report a pK value for the reaction

$$Zn^{2+}(aq) + OH^-(aq) + H^+(aq) + S^{2-}(aq) = Zn(OH)(SH)(aq)$$

of 32.50. Use of Licht's[18] Gibbs energy of formation of the sulfide ion changes the value to pK = 37.07.

The equations and equilibrium constants in the paragraphs above probably give as good an interpretation of ZnS solubility and solution equilibria as are presently available. We suggest their use as a tentative scheme to describe the aqueous zinc sulfide system.

The older ZnS solubility literature has been reviewed a number of times[69,70,71,72], but only the Kolthoff[72] paper was available to us. More recent reviews are by Barnes[67] and by Rafal'skii[73]. Many of the available papers[74–82,135] are of questionable value, usually because the solid and/or the equilibration conditions were poorly described. The literature on the solubility of zinc sulfide in various media are summarized in Table 17, for the solubility of ZnS in water; Table 2A, solubility of ZnS in aqueous electrolyte solutions; and Table 18, ZnS solubility product values in aqueous systems. It is likely that these values could be improved upon by recalculation of the data using today's accepted values of Gibbs energy of formation, hydrogen sulfide dissociation constants and other required auxiliary data. Such a project was beyond the resources of the present work.

Hennig[83] and Vukotic[63] report experimental solubilities. The other values in Table 17 are calculated from the solubility product or some other model. Hennig's results are presented in a graph which is reproduced as Fig 2. The total zinc in solution shows a maximum about 573 K.

Rafal'skii and Osipov[136] studied solutions of U, Cu and Fe sulfides in the presence of various minerals including ZnS (cleiophane). They estimated the solubility of ZnS at temperatures from 373 to 633 K. Their equation for the solubility product

$$\log K_{s0} = -4204.64/(T/\mathrm{K}) + 1.4882 - 0.024479\ (T/\mathrm{K})$$

goes through a maximum at 414 K.

Kuznetsov and Kostomarov[137] studied the ZnS + KOH + H_2O system at 573 to 773 K. They found two solids, ZnS (sphalerite) and $K_2Zn_3S_4$. As the temperature increased the ZnS region decreased and the $K_2Zn_3S_4$ region increased. The sphalerite dissolution mechanism is dependent on the KOH concentration. At low KOH concentration $ZnS(OH)^-(aq)$ predominates and at high KOH concentration $Zn(OH)_4^{2-}(aq)$ predominates in aqueous solution.

TABLE 17. Zinc sulfide (sphalerite) solubility in water

T/K	c/mol L^{-1}	Method	Reference
(293.15 −648)	graph	colorimetry, atomic absorp.	Hennig, 1971[83]
298.15	9×10^{-10}	model calculation	Ellis, 1959[84,a]
“	1.2×10^{-9}	model calculation	Kapustinskii,1940[85,b]
“	1.53×10^{-9}(pH = 7)	model calculation	Czamanske, 1959[86,c]
“	$<1\times10^{-5}$(p = 6.8 atm)	polarography	Barnes, 1957–58[87]
(298.15	3×10^{-10} (pH = 7)	model calculation	Rafal'skii, 1966[88,d]
−473)	4×10^{-8}	“ “	“ “
“			
373.15	1.2×10^{-8}	model calculation	Ellis, 1959[84,a]
“	2.5×10^{-9}(pH = 7)	“ “	“ “
“	4.29×10^{-9}(pH = 7)	model calculation	Czamanske, 1959[86,c]
“	$>1\times10^{-4}$(p = 34 atm)	polarography	Barnes, 1957–58[87]
383.15	3.00×10^{-6}	colorimetry	Vukotic, 1961[63]
473.15	4.70×10^{-6}		“ “
“	“		
“	1.0×10^{-7}	model calculation	Ellis, 1959[84,a]
“	7×10^{-9}(pH = 7)	“ “	“ “
“	1.24×10^{-8}(pH = 7)	model calculation	Czamanske, 1959[86,c]
523	1.7×10^{-7}	model calculation	Ellis, 1959[84,a]
	1.0×10^{-8}	“ “	“ “
573	3×10^{-7}	“ “	“ “
“	1.6×10^{-8}(pH = 7)	“ “	“ “
“	4.70×10^{-6}	colorimetry	Vukotic, 1961[63]
623	4.70×10^{-6}	“	“ “
673	4.22×10^{-8}(pH = 7)	model calculation	Czamanske. 1959[86,c]
873	1.03×10^{-7}(pH = 7)	“ “	“ “

[a] Calculated using Gibbs energy data from Latimer[89] estimated heat capacity values, and H_2S acid dissociation constants from Harned and Owen[90].

[b] Calculated using their own thermodynamic data and H_2S acid dissociation constants from Lewis and Randall[91], and Wright and Maass[92].

[c] Calculated from data Latimer[89], Kubaschewski and Evans[93] and Kury, Zielen and Latimer[94].

[d] These values appear to be calculated from the solubility ion product constant after taking various solutions complexe into account. The 473 K value may be from another source.

TABLE 18. The thermodynamic ion product constant of zinc sulfide in aqueous solution

T/K	K°_{s0}/mol^2 L^{-2}	Reference	T/K	K°_{s0}/mol^2 L^{-2}	Reference
		Sphalerite			
Tentative value					
298.15	1.3×10^{-29}	Licht, 1988[18]			
Literature Values					
298 (?)	1.6×10^{-24}	Shcherbina, 1972[106,a]	373	3.3×10^{-23}	Helgeson, 1969[107,g]
298.15	7.4×10^{-27}	Kapustinskii, 1940[85]	373	1.2×10^{-21}	Czamanske, 1959[86,e]
298.15	$8\ \times10^{-24}$	Goates, *et al*., 1952[108,b]	373	3×10^{-23}	Ellis, 1959[84,f]
298.15	7.0×10^{-26}	Latimer, 1952[89]	423	9.8×10^{-22}	Helgeson, 1969[107,g]
298.15	1.6×10^{-24}	Ringbom, 1953[66,c]	473	1.6×10^{-20}	" "
298.15	7.1×10^{-26}	Egorov, 1957[109,d]	473	3.3×10^{-19}	Czamanske, 1959[86,e]
298.15	1.5×10^{-24}	Czamanske, 1959[86,e]	473	2×10^{-21}	Ellis, 1959[84,f]
298.15	6×10^{-26}	Ellis, 1959[84,f]	523	6×10^{-21}	" "
298.15	1.9×10^{-26}	Helgeson, 1969[107,g]	523	1.4×10^{-19}	Helgeson, 1969[107,g]
298.15	2.9×10^{-25}	NBS Tables, 1982[12]	573	6.8×10^{-19}	" "
323	3.6×10^{-25}	Helgeson, 1969[107,g]	573	1.3×10^{-20}	Ellis, 1959[84,f]
333	9.3×10^{-25}		673	1.5×10^{-16}	Czamanske, 1959[86,e]
			873	4.5×10^{-15}	" "
		Wurtzite			
Tentative value					
298.15	7.9×10^{-27}	Licht. 1988[18]			
Literature values					
298.15	1.6×10^{-23}	Latimer, 1952[89]	373	1.1×10^{-21}	Helgeson, 1969[107,g]
298.15	2.5×10^{-22}	Ringbom, 1953[66,c]	423	1.9×10^{-20}	" "
298.15	2.2×10^{-24}	Helgeson, 1969[107,g]	473	1.9×10^{-19}	" "
323	2.6×10^{-23}	" "	523	1.1×10^{-18}	" "
333	5.8×10^{-23}	" "	573	4.1×10^{-18}	" "
Precipitated ZnS					
Tentative value					
298.15	4.0×10^{-26}	Licht, 1988[18]			

[a] Value probably not calculated by this author. Paper appears to be a compilation of data, but no references are given.

[b] Value calculated from data of Rossini *et al*., 1950[110].

[c] A best value for its time (1952). The average of several literature values with a standard deviation of 1.7.

[d] Calculated value using several sources of thermodynamic data including Latimer, 1952[89], Kubaschewski and Evans[93], Kelley, 1949[111], and several Russian sources.

[e] Calculated value using data from Latimer, 1952[89], Kubaschewski and Evans[93] and Kury, Zielen and Latimer[94].

[f] Calcuated values using estimated C_p values and data from Latimer, 1952[89].

[g] Calculated values using data from a number of sources including Robie and Waldbaum, 1968[112], Wagman, *et al*., 1968[113], Wulff, 1967[114] and Latimer, 1952[89].

4.5.b. Cadmium Sulfide

CdS [1306–23–6] Molecular weight 144.47
Greenockite [1317–58–4]
Hawleyite [24270–48–2]

Physical characteristics: The CdS mineral greenockite, sometimes called the α- or wurtzite form, is hexagonal with $Z = 2$, a and $c = 4.132$ and 6.734×10^{-10} m, respectively, and a calculated density of 4.818×10^3 kg m^{-3}. The mineral hawleyite, sometimes called the β- or sphalerite form, is cubic with $Z = 4$, $a = 5.818 \times 10^{-10}$ m, and a calculated density of 4.870×10^3 kg m^{-3}. Barton and Skinner[64] state that hawleyite is stable at low temperature and transforms to greenockite at an unknown higher temperature. Precipitated CdS may be either cubic or hexagonal. Milligan[115] has shown that CdS precipitated from solutions containing sulfate ion is predominately cubic, and CdS precipitated from solutions containing chloride ion is predominately hexagonal. The color of the precipitate, which ranges from red to yellow, is not a function of the crystal structure.

The solubility studies of cadmium sulfide are complicated by the possibility of more than one crystalline solid and by the presence of a number of complex ions in the aqueous solution. Relatively few workers have specified which solid they used. Bruner and Zawadski[116,117] worked 24 years before Milligan, but they must have sensed a difference in CdS precipitates as they identify their precipitates as from either sulfate (cubic form predominates) or chloride (hexagonal form predominates) ion containing solutions.

TABLE 19. Cadmium sulfide solubility in water

T/K	c/mol L^{-1}	Method	Reference
290	6.6×10^{-6}	ultramicroscope	Biltz, 1907[118]
291.15	9.0×10^{-6}	conductivity	Weigel, 1907[74]
291.15	3.2×10^{-10}	calculation[a]	Kolthoff, 1931[72]
	0.87×10^{-10}	calculation[b]	
298.15	1.46×10^{-10}	calculation	Ravitz, 1936[76]
298.15	1.51×10^{-10}	calculation[c]	van Rysselberghe, Gropp, 1944[78]
298.15	1.5×10^{-10}	calculation[d]	Kapustinskii, 1940[85]
298.15	1.19×10^{-10} (pH = 7)	model calculation[e]	Czamanske, 1959[86]
373.15	8.56×10^{-10} (pH = 7)	“ “	“ “
473	5.12×10^{-9} (pH = 7)	“ “	“ “
673	4.29×10^{-8} (pH = 7)	“ “	“ “
873	1.68×10^{-7} (pH = 7)	“ “	“ “

[a] Recalculated from results of Bruner and Zawadski, 1909[116], 1910[117] for (hexagonal ?) CdS precipitated from $CdCl_2$ solution.

[b] Recalculated from results of Bruner and Zawadski, 1909[116], 1910[117] for (cubic ?) CdS precipitated from $CdSO_4$ solution.

[c] Recalculated from the data of Ravitz, 1936[76].

[d] Calculation based on author's own thermodynamic data and H_2S K_{ai} values from Lewis and Randall[91] and Wright and Maass, 1932[92].

[e] Calculated from data of Latimer[89], Kubaschewski and Evans[93], and Kury, Zielen and Latimer[94]

[f] Calculated values using estimated C_p values and data from Latimer, 1952[89].

[g] Calculated values using data from a number of sources including Robie and Waldbaum, 1968[112], Wagman, *et al.*, 1968[113], Wulff, 1967[114] and Latimer, 1952[89].

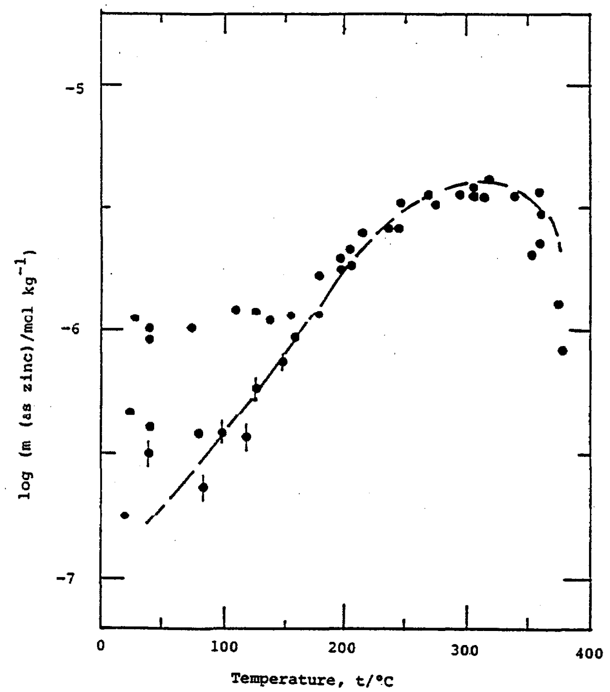

FIG. 2. Solubility of sphalerite (ZnS) in water, pH 5.4 at 20° C. Solutions analyzed either by atomic absorption, ●, or colorimetry, ɸ. Original figure (Ref. 83) contains additional information as to use of water bath or sand bath, and whether equilibrium approached from high or low temperature.

The recent revision of the aqueous sulfide ion Gibbs energy has led Licht[18] to revised values of the solubility product constants for the reactions:

$$CdS(s) = Cd^{2+}(aq) + S^{2-}(aq) \qquad K^{\circ}_{s0} = 5.0 \times 10^{-34}$$
$$CdS(s) + H^{+}(aq) = Cd^{2+}(aq) + HS^{-}(aq) \qquad {}^{*}K^{\circ}_{s0} = 1.3 \times 10^{-16}$$
$$CdS(s) + H_2O = Cd^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq) K_s = 1.3 \times 10^{-30}$$

These values, along with the values of Ste-Marie, Torma and Gubeli[119] at unit ionic strength for the formation of various hydroxide and hydrosulfide complex ions of cadmium, make a tentative working basis to model cadmium sulfide solubility and composition of the saturated solutions.

$$Cd^{2+}(aq) + HS^{-}(aq) = Cd(HS)^{+}(aq) \qquad \beta_1 = 3.55 \times 10^{7}$$
$$Cd(HS)^{+}(aq) + HS^{-}(aq) = Cd(HS)^{\circ}_{2}(aq) \qquad \beta_2 = 1.15 \times 10^{7}$$
$$Cd(HS)^{\circ}_{2}(aq) + HS^{-}(aq) = Cd(HS)^{-}_{3}(aq) \qquad \beta_3 = 7.59 \times 10^{1}$$
$$Cd(HS)^{-}_{3}(aq) + HS^{-}(aq) = Cd(HS)^{2-}_{4}(aq) \qquad \beta_4 = 2.29 \times 10^{3}$$
$$Cd^{2+}(aq) + OH^{-}(aq) = Cd(OH)^{+}(aq) \qquad \beta_1 = 5.75 \times 10^{17}$$

Neither Licht[18] nor Hampson and Latham[15b] identify the CdS solid for which they give standard potential values.

Table 19 summarizes values of the solubility of cadmium sulfide in water, and Table 3A the solubility in aqueous electrolyte solutions. We are unable to classify any of these values as recommended or even tentative. Table 20 gives ion product constant values and Table 21 equilibrium constants for dissolving CdS in acid solution.

The smaller values based on the smaller second dissociation constant of H_2S as evaluated by Licht[18] are preferred.

Bruner and Zawadski[116,117], Milligan[115], Belcher, Townshend and Farr[123], and Kraft, Gamsjaeger and Schwarz-Bergkampf[125] are the only workers that discuss the nature of the solid CdS which is often a mixture of cubic and hexagonal. Kolthoff [72] rejects some early results[74,118] and recalculates many of them, but he does not mention the nature of the solid, or take into account complex ion formation in solution, and he, of course, used H_2S acid dissociation constants of an earlier time.

Golub[134] reported cadmium-halide ion dissociation constants at 293 ± 1 K. He used his dissociation constant for CdI_5^{3-} to obtain an equilibrium constant of 109.2 for

$$CdS(s) + 2H^+(aq) + 5I^-(aq) = CdI^3{}_5{}^-(aq) + H_2S(aq).$$

Egorov[109] used thermodynamic data to develop an equation for the temperature dependence of the ion product constant:

$$\log K^\circ_{s0} = -5834/(T/K) - 2.973 - 2.020 \log(T/K) + 9.05 \times 10^{-4}(T/K).$$

The equation gives values about an order of magnitude smaller than the values calculated by Czamanske[86]. Both sets of values are probably too large in view of the recent evaluation of Licht[18].

4.6. Zinc and Cadmium Sulfites

In 1986 Masson, Lutz and Engelen[138] edited Volume 26 of the Solubility Series on the solubility of the sulfites, selenites and tellurites. Their evaluations have been used as the source of much of the following information on zinc and cadmium sulfites. For the complete experimental details and more comprehensive evaluations see Solubility Series Volume 26[138].

4.6.a. Zinc Sulfite

$ZnSO_3$ [13597–44–9]	Molecular weight 145.45
$ZnSO_3{\cdot}0.5H_2O$ [65410–82–4]	Molecular weight 154.46
$ZnSO_3{\cdot}H_2O$ [66516–57–2]	α and β forms Molecular weight 163.46
$ZnSO_3{\cdot}2H_2O$ [7488–52–0]	Molecular weight 181.48
$ZnSO_3{\cdot}2.5H_2O$ [14460–28–7]	α, β, γ forms Molecular weight 190.49
$ZnSO_3{\cdot}3H_2O$ [75042–13–6]	Molecular weight 199.50
$Zn(HSO_3)_2$ [15457–98–4]	Molecular weight 227.53

TABLE 20. The ion product constant of cadmium sulfide in aqueous solutions

T/K	I/ Electrolyte	K°_{s0}/mol^2 L^{-2}	K_{s0}/mol^2 L^{-2}	Reference
Tentative Value				
298.15	0	5.0×10^{-34}		Licht, 1988[18]
Experimental values				
291.15	?		7.0×10^{-28a}	Brunner,
	?		5.1×10^{-29b}	Zawadski, 1909[116]
	?		3.6×10^{-29b}	1910[117]
293.15	0.7/HCl		5.2×10^{-26}	Belcher, Townshend, Farr,
	2.1/$HClO_4$		7.2×10^{-28}	1969[123]
	9.6/H_2SO_4		6.5×10^{-28}	
298.15	?		3.7×10^{-29}	Scheller, Treadwell, 1952[124]
298.15	0		1.6×10^{-28}	Kivalo, Ringbom 1956[120]
298.15	0	$(500\text{-}5) \times 10^{-29}$		Belcher, Townshend, Farr, 1969[123]
	0.22/HCl		$(1.6\text{-}6.4) \times 10^{-27}$	
	0.92/$HClO_4$		$(1.3\text{-}3.9) \times 10^{-28}$	
	0.66/H_2SO_4		1.1×10^{-27}	" "
	1.08/H_2SO_4		$(6.9\text{-}22) \times 10^{-28}$	" "
298.15	1/$NaClO_4$		1.74×10^{-26}	St. Marie *et al.*, 1964[119]
333	3.3/Na_2S		1.10×10^{-4}	Polyvyanii, Milyutina, 1967[125b]
Calculated Values				
294–417	?		Graph[c]	Simons, 1963[126]
?			7.9×10^{-27d}	Shcherbina,1972[106]
298.15	0	1.14×10^{-28}		Ravitz, 1936[76]
	/H_2S, H^+		7.6×10^{-28e}	" "
	/H_2S, H^+		5.3×10^{-29e}	" "
298.15	0	1.2×10^{-28f}		Kapustinskii, 1940[85]
298.15	0	7×10^{-27g}		Goates, Gordon, Faux, 1952[108]
298.15	0	1.0×10^{-28}		Latimer, 1952[89]
298.15	0	$(1.3 \pm 0.9) \times 10^{-26h}$		Ringbom, 1953[66]
	0	1.62×10^{-26i}		" "
298.15	0	5.2×10^{-28j}		Egorov, 1957[109]
298.15	0	9.34×10^{-27k}		Czamanske, 1959[86]

TABLE 20. The ion product constant of cadmium sulfide in aqueous solutions — Continued

T/K	I/ Electrolyte	K°_{s0}/mol^2 L^{-2}	K_{s0}/mol^2 L^{-2}	Reference
Calculated Values				
298.15	0	$(7.9 \pm 5.9) \times 10^{-28}$[l]		Kraft *et al.*,
	1/$NaClO_4$	$(1.6 \pm 1.2) \times 10^{-27}$[l]		1966[125]
	3/$NaClO_4$	$(1.6 \pm 1.2) \times 10^{-27}$[l]		
298.15	0	1.4×10^{-29}[m]		NBS Tables, 1982[12]
298.15	0	1.1×10^{-27}[m]		Geol. Surv. Bull., 1978[13]
298.15	0	5.8×10^{-28}[n]		Krestov, 1969[127]
298.15	0	1.74×10^{-28}[n]		Erdenbaeva, 1975[128]
298.15	0	5.6×10^{-28}[n]		Krestov *et al.*, 1977[129]
298.15	?		7.1×10^{-27}[c]	Simons, 1963[126]
298.15	?/pH = 5.00	5.01×10^{-18}[o]		Barnes, 1979[67]
	?/pH = 6.12	9.33×10^{-19}[o]		" "
	?/pH = 7.00	5.01×10^{-22}[o]		" "
373.15	?/pH = 4.12	9.33×10^{-15}[o]		" "
	?/pH − 5.69	2.00×10^{-16}[o]		" "
373.15	0	4.79×10^{-23}[k]		Czamanske, 1959[86]
473	0	5.63×10^{-20}[k]		" "
473	?/pH = 3.69	2.00×10^{-12}[o]		Barnes, 1979[67]
673	0	1.57×10^{-16}[k]		Czamanske, 1959[86]
873	0	1.19×10^{-14}[k]		" "

[a] CdS precipitated from $CdCl_2$ solution, probably hexagonal, see Milligan, 1934[115]

[b] CdS precipitated from $CdSO_4$ solution, probably cubic, see Milligan, 1934[115].

[c] Used data from Goates, Gordon and Faux, 1952[108], Latimer, 1952[89], and his own data.

[d] Source of data not clear, value probably not calculated by this author.

[e] Recalculation of data of Bruner and Zawadski, 1909[116]1910[117], first value for CdS from $CdCl_2$ and second value for CdS from $CdSO_4$, see footnotes [a,b].

[f] Used data from Kelley, 1937[111].

[g] Used data from Rossini *et al.*, 1952[110].

[h] Apparently an average of several published values.

[i] Used data from Makolkin, 1940[130].

[j] Used thermodynamic data from Latimer, 1952[89], Kubashewskii and Evans[93], and Kelley, 1949[111].

[k] Used thermodynamic data from Latimer, 1952[89], Kubashewskii and Evans [93], and Kury, Zielen and Latimer[94].

[l] Used their own electrochemical data at $I = 1$ and 3; at $I = 0$ they used data from Schindler, 1959[131]. Other data sources were Adami and King, 1964[132], Sillen and Martell[8], Latimer, 1952[89], and NBS Technical Notes[113].

[m] Our calculation from thermodynamic data in reference cited.

[n] Sources of thermodynamic data not given or unclear.

[o] Used data from Naumov, Ryzhenko, and Khodakovsky, Handbook of Thermodynamic Data, 1971, as translated and published by Nat. Tech. Info. Service PB-226-722, 1974.

TABLE 21. The $CdS(s) + 2H^+(aq) = Cd^{2+}(aq) + H_2S(g)$ equilibrium constant

T/K	I/Electrolyte	K/atm L mol^{-1}	Reference
289.15	?/HCl	1.06×10^{-6}[a]	Aumeras, 1928[133]
298.15	0	1.3×10^{-8}[b]	
		1.3×10^{-9}[c]	
298.15	?	3.4×10^{-7}	Scheller, Treadwell, 1952[124]
298.15	0.4–1.2/HCl	$(2.0\text{–}1.4) \times 10^{-7}$	Kivalo, Ringbom, 1956[120]
298.15	0	$(7.9 \pm 5.9) \times 10^{-7}$	Kraft, Gamsjaeger,
	1/$NaClO_4$	$(1.6 \pm 1.2) \times 10^{-7}$	Schwarz-Bergkampf,
	3/$NaClO_4$	$(1.6 \pm 1.2) \times 10^{-7}$	1966[125]

[a] Author wrote equation to form $H_2S(aq)$.

[b] Calculated by us using $CdS(s) + H^+(aq) = Cd^{2+}(aq) + HS^-(aq)$ and $^*K = 1.3 \times 10^{-16}$ of Licht, 1988[18] and Gibbs energy of formation of $HS^-(aq)$ and $H_2S(g)$ from NBS Tables.

[c] Calculated as in footnote [b] but for $H_2S(aq)$.

Physical characteristics: Lutz[139] reports the trihydrate crystallizes from water at temperatures below 275 K; the three forms of the 2.5 hydrate at ambient temperatures with the α-form probably the thermodynamically stable form; the dihydrate at temperatures above 338 K; and the α-monohydrate at temperatures above 363 K in the presence of excess sulfur dioxide.

Crystallographic information is from Lutz *et al.*[139-142] and Nyberg[143]. The $ZnSO_3{\cdot}3H_2O$ is orthorhombic with $Z = 4$, and a, b and c = 9.536, 5.530 and 9.419 × 10^{-10} m, respectively. The hydrate $ZnSO_3{\cdot}2.5H_2O$ shows three crystalline forms. The α-form is triclinic with Z = 4,and a, b and c = 7.651, 7.549, and 9.094 × 10^{-10} m, respectively, angles α = 90.06°, β = 88.53° and γ = 93.75°, and a density of 2.41 × 10^3 kg m^{-3}. The β-form is tetragonal with Z = 8, and a, b and c = 9.521, 9.521 and 10.254 × 10^{-10} m, respectively. The γ-form is orthorhombic with Z = 16, and a, b and c = 14.93, 18.12 and 7.53 × 10^{-10} m, respectively. The dihydrate $ZnSO_3{\cdot}2H_2O$ is monoclinic with Z = 4, a, b and c = 6.421, 8.524 and 7.574

TABLE 22. The solubility of zinc sulfite in water

T/K	Solubility m_{ZnSO_3}/mol kg^{-1}	Likely Hydration of Solid	Reference
"room"	0.011	2.5[a]	Heuston, Tichborne, 1890[144]
293.2	0.01230	2.5	Margulis, Rodin, 1981[149]
298.2	0.01733	2.5	Murooka, Sato, 1937[148]
323.2	0.01248	2.5	Margulis, Rodin, 1981[149]
343.2	0.01290	2.0(?)	" " "
358.2	0.01314	2.0(?)	" " "
368.2	0.01336	2.0(?)	" " "

[a] The original authors identified the 2.0 hydrate, but modern results support the 2.5 hydrate at least up to temperatures of 323.2 K.

× 10^{-10} m, respectively, with β = 98.63°, and a calculated density of 2.943 × 10^3 kg m^{-3}.

Lutz[138a] evaluates and reports in detail the experimental solubility results of Heuston and Tichborne[144], Terres and Ruhl[145], Kuz'minykh and Kuznetsova[146], Peisakhov and Karmazina[147], Murooka and Sato[148] and Margulis and Rodin[149].

The solubility of zinc sulfite in water has not been thoroughly studied. At temperatures at which α-$ZnSO_3 \cdot 2.5H_2O$ is the equilibrium solid, the solubility process probably includes the steps

$$\alpha\text{-}ZnSO_3 \cdot 2.5H_2O(s) = Zn^{2+}(aq) + SO_3^{2-}(aq) + 2.5H_2O(\ell)$$
$$SO_3^{2-}(aq) + H_2O(\ell) = HSO_3^-(aq) + OH^-(aq)$$
$$HSO_3^-(aq) + H_2O(M) = H_2SO_3(aq) + OH^-(aq) = SO_2(aq) + OH^-(aq) + H_2O$$
$$SO_2(aq) = SO_2(g)$$

In addition the Zn^{2+}(aq) ion hydrolysis and complex ion formation will contribute to the process.

Analysis of the saturated solution by Murook and Sato[148] indicates that up to 75 % of the dissolved SO_3^{2-} is in the HSO_3^- form. The solubility value of Murooka and Sato at 298 K appears to be too large when compared with the results of Heuston and Tichborne[144] and of Margulis and Rodin[149]. See Table 22.

Margulis and Rodin do not make the nature of the solid clear. It is assumed to be the 2.5 mol water hydrate at room temperature and perhaps the 2.5 or 2.0 hydrate at higher temperatures. A plot of their solubility data as log(m/mol kg^{-1}) vs. 1/(T/K) indicates a possible change in slope between 323 and 343 K, which could be due to a hydration change of the solid.

The solubility of $ZnSO_3$ has been studied in the systems $ZnSO_3 + SO_2 + H_2O$[145–147], $ZnSO_3 + Na_2SO_3 + H_2O$[147,148] and $ZnSO_3 + ZnSO_4 + SO_2 + H_2O$[146,147,149]. Lutz[138] points out that in these systems the solubility of $ZnSO_3$ increases with increasing concetration of sulfurous acid or partial pressure of sulfur dioxide, and only slightly with increasing sulfate ion concentration.

Lutz combined the solubility values of Kuz'minykh and Kuznetsova[146] and Terres and Ruhl[145] in a linear regression to obtain the relationship between the $ZnSO_3$ solubility and the total SO_2 content of the saturated solution at 293/298 K as

$$(m_{ZnSO_3 \cdot 2.5H_2O}/\text{mol kg}^{-1}) = 0.035 + 0.463(m_{SO_2(\text{total})}/\text{mol kg}^{-1})$$

Lutz also used these data to show a linear relationship between log ($m_{ZnSO_3 \cdot 2.5H_2O}$/mol kg^{-1}) and log (P_{SO_2}/Pa) at five temperatures between 283.1 and 351.6 K.

Margulis *et al.*[389] show the solubility of $ZnSO_3$ in aqueous $ZnSO_4$ increases with temperature and with $ZnSO_4$ concentration. Diluting and cooling the $ZnSO_3 + ZnSO_4 + H_2O$ solution gives a precipitate of $ZnSO_3 \cdot ZnSO_4 \cdot xH_2O$ where x = 2 or 3. The material is an unique compound which decomposes at 200–2600 °C to give $ZnSO_3$ and $ZnSO_4 \cdot H_2O$. The solubility data are shown in small graphs.

4.6.b. Cadmium Sulfite

$CdSO_3$ [13477–23–1] Molecular weight 192.48
$CdSO_3 \cdot 1.5H_2O$ [60943–67–1] Molecular weight 219.50

Anhydrous cadmium sulfite exists in up to three forms. Both they and the hydrate with 1.5 moles of water crystallize from aqueous saturated solutions. Lutz and El-Suradi[150] have characterised the anhydrous forms and the hydrate . The thermodynamically stable $CdSO_3$-I is monoclinic with Z = 4, a, b and c = 4.439, 8.608, and 7.183 × 10^{-10} m, respectively, and β = 94.53°. Kiers and Vos[151] show that $CdSO_3 \cdot 1.5H_2O$ is monoclinic where a, b and c are 122.19, 105.74 and 139.86 × 10^{-10} m, respectively, with β = 103.61°.

The only solubility data found by us and by Lutz[138b] are the data of Margulis and Rodin[152] who studied the systems $CdSO_3 + H_2O$, $CdSO_3 + CdSO_4 + H_2O$, and $CdSO_3 + Na_2SO_3 + Na_2SO_4 + H_2O$. The solubility values in water are:

T/K	293.2	363.2
m_{CdSO_3}/mol kg^{-1}	0.00221	0.00207

The authors did not characterize the solid. All of the original data on the systems studied are reproduced in Solubility Series Volume 26[138b].

4.7. The Selenium Compounds of Zinc and Cadmium

There are few solubility data for the selenides, Se^{2-}, selenites, SeO_3^{2-}, and selenates, SeO_4^{2-}, of zinc and cadmium. There is no definitive study of the solubility of these salts which clearly defines the nature of the solid and controls enough solution variables to define the systems thermodynamically.

4.7.a. Zinc and Cadmium Selenides

Zinc selenide ZnSe [1315–09–9] molecular weight 144.35
Cadmium selenide CdSe [1306–24–7] molecular weight 191.37

Physical characteristics: Zinc selenide is known in both cubic and hexagonal forms. The cubic form stable at standard conditions has $Z = 4, a = 5.672 \times 10^{-10}$m and a calculated density of 5.261×10^3 kg m^{-3}. The metastable hexagonal form with $a = 4.00 \times 10^{-10}$m and $c = 6.54 \times 10^{-10}$m has not been further characterized. Cadmium selenide is also known in cubic and hexagonal forms. The usual cubic form (β-CdSe) with $Z = 4$ and $a = 6.05 \times 10^{-10}$, has a calculated density of 5.739×10^3. A high pressure (30,000 kg/cm^2) cubic form with $Z = 4, a = 5.54 \times 10^{-10}$ and a calculated density of 7.48×10^3 kg m^{-3} is known. The hexagonal form has $Z = 2$, $a = 4.30 \times 10^{-10}$m, and $c = 7.01 \times 10^{-10}$m. No hydrates of these substances are reported.

There are no solubility data for either zinc or cadmium selenide. There are several values of the solubility product for the $MSe(s) = M^{2+}(aq) + Se^{2-}(aq)$ process calculated from emf and other thermodynamic data. Even if the values prove to be reliable they are of little practical application until all ionic species and the equilibria among them in saturated solutions are characterized.

The solubility product values are given in Table 23. The solubility product of ZnSe calculated from the NBS Tables Gibbs energies is classed as a tentative value. The NBS Tables do not contain a Gibbs energy value for CdSe(s).

TABLE 23. Zinc selenide and cadmium selenide solubility product values

T/K	Ionic strength I/electrolyte	K_{s0} or K°_{s0}	Reference
		Zinc selenide	
Tentative value			
298.15	0	3.59×10^{-26}	NBS Tables, 1982[12]
Other values			
298.15	0	1×10^{-31}	Latimer, 1952[89]
	0	4.0×10^{-30}	Buketov *et al.*, 1964[153,a]
	?	2.6×10^{-31}	Erdenbaeva, 1975[128]
		Cadmium selenide	
298.15	0	6.3×10^{-36}	Buketov *et al.*, 1964[153,a]
	?	1.1×10^{-32}	Erdenbaeva, 1975[128]

[a] Calculated by authors using a combination of data from Latimer 1952[89] and Kubaschewski and Evans 1956[93].

4.7.b. Zinc and Cadmium Selenites

Zinc selenite $ZnSeO_3$ [13597–46–1] molecular weight 192.34
Zinc selenite monohydrate $ZnSeO_3 \cdot H_2O$ [23739–00–6] molecular weight 210.36
Zinc selenite dihydrate $ZnSeO_3 \cdot H_2O$ [19527–79–8] molecular weight 228.37
Zinc selenite dihydrate $Zn(HSeO_3)_2 \cdot H_2O$[71038–38–5] molecular weight 357.35
Cadmium selenite $CdSeO_3$ [13814–59–0] molecular weight 239.36

Physical characteristics: Zinc selenite synthesized at high temperatures and pressures is orthorhombic with $Z = 4$, a, b and c = 5.923, 7.665 and $= 5.040 \times 10^{-10}$ m, respectively, according to Kohn *et al.*[154]. Buketov *et al.*[155] found in a thermographic study that $ZnSeO_3 \cdot H_2O$ loses water at 473 K to form α-$ZnSeO_3$, which changes at 589 K to β-$ZnSeO_3$; the latter melts at 893–5 K, and decomposes above 936 K. No detailed crystallographic information was found for $CdSeO_3$; however, x-ray powder patterns are given for three crystalline modifications of anhydrous $CdSeO_3$[156,157].

Ripan and Vericeanu[158], Chukhlantsev[159], and Redman and Harvey[160] report selenite solubility studies. Their data are evaluated by Masson, Lutz and Engelen[138]. The selenous acid dissociation constants, $K_1 = 4 \times 10^{-3}$ and $K_2 = 1 \times 10^{-8}$ at 293 K, required to calculate solubility products, are from Rumpf[161]. In addition to the solubility product values from experimental studies there are values from emf and other thermodynamic data. All of the values are summarized in Table 24.

TABLE 24. Solubility product values of $ZnSeO_3$ and $CdSeO_3$ in water

T/K	Ionic strength I/Electrolyte	K_{s0} or K°_{s0}	Reference
		Zinc Selenite, $ZnSeO_3$	
Tentative value			
298.15	0	1.59×10^{-7a}	NBS Tables, 1982[12]
Other values			
291.15	sat. soln.	0.19×10^{-7}	Ripan, Vericeanu, 1968[158]
293.15	? HNO_3,H_2SO_4	2.58×10^{-7}	Chukhlantsev, 1956[159]
298.15	0 (?)	2.7×10^{-7}	Erdenbaeva, 1975[128]
298.15	0	5.5×10^{-11}	Essington, 1988[183]
		Cadmium Selenite, $CdSeO_3$	
Tentative value			
298.15	0	1.49×10^{-9}	NBS Tables, 1982[12]
Other values			
291.15		6.0×10^{-9}	Ripan, Vericeanu, 1968[158]
293.15		1.29×10^{-9}	Chukhlantsev, 1956[159]
"Room"		0.40×10^{-9b}	Redman, Harvey, 1967[160]
298.15		0.93×10^{-9}	Erdenbaeva, 1975[128]

[a] Value calculated from the Gibbs energy of the monohydrate, $ZnSeO_3 \cdot H_2O(s)$. No other workers mention the hydration of the solid.
[b] Value calculated from the Redman, Harvey data by Masson[138].
[c] Anhydrous salt

Ripan and Vericeanu[158] applied a conductivity method. They did not take into account selenite hydrolysis and their solubility product value is not considered particularly reliable. The value from the saturated solution study of Redman and Harvey[160] at pH 6 and an undefined temperature was recalculated with suitable assumptions by Masson *et al.*[138]. Chukhlantsev[159] directly determined the Zn^{2+} and Cd^{2+} ion concentrations in several aqueous HNO_3 and H_2SO_4 solutions saturated with the selenite. His K_{s0} values are average values from six experiments. His values agree well with those calculated from Gibbs energy data in the NBS Tables. The values may not be independent. None of the papers mentions a hydrated solid, but the NBS Tables value is for the monohydrate and the reaction

$$ZnSeO_3{\cdot}H_2O(s) \rightleftharpoons Zn^{2+}(aq) + SeO_3^{2-}(aq) + H_2O\ (l)\ .$$

Chukhlantsev's values are from the average of six pK_{s0} values. If the constants are averaged directly, values of $(2.85 \pm 1.44)\times10^{-7}$ and $(1.38 \pm 0.66)\times10^{-9}$ are obtained for $ZnSeO_3$ and $CdSeO_3$, respectively. The sources of the data used by Erdenbaeva[128] are unknown. Essington[183] has estimated the standard Gibbs energy of formation of $ZnSeO_3(s)$ and calculated a K_{s0} value. The solubility product values are summarized in Table 24.

Recently Gospodinov[162] has reported the $ZnO + SeO_3 + H_2O$ isotherm at 373 K. In the concentration interval of 1.19 to 59.79 mass % SeO_2 the stable phase is $ZnSeO_3$. Its solubility increases from 0.0905 to 1.88 mass % as ZnO. At larger SeO_2 concentrations the stable phase is $ZnSeO_3KH_2SeO_3$ and its solubility decreases to 0.42 mass % as ZnO at 80 mass % SeO_2.

A $CdSeO_3 + SeO_2 + H_2O$ isotherm at 298 K is reported by Micka, Uchytilova and Ebert[157]. They report no numerical data, but show a triangular phase diagram with regions of stability for the solids $CdSeO_3$, $CdSe_2O_5$ ($CdSeO_3{\cdot}SeO_2$), and $Cd_3H_2(SeO_3)_4$ or ($3CdSeO_3{\cdot}H_2SeO_3$).

Markovskii and Sapozhnikov[156] have investigated the nature of $CdSeO_3$ precipitates. A neutral, anhydrous, crystaline $CdSeO_3$ is formed on mixing aqueous $CdSO_4$ and aqueous M_2SeO_3 [$M^+ = Na^+, K^+, NH_4^+$, and H^+ (up to 30% excess acid)]. Reaction of $CdCO_3$ with 5–30% excess H_2SeO_3 gives a second form of solid $CdSeO_3$ which irreversibly converts to the first form on heating below 732 K. When $CdCO_3$ and $CdSeO_3$ are treated with a 4 to 10-fold excess of H_2SeO_3, $3CdSeO_3{\cdot}H_2SeO_3$ is formed. The authors were unable to prepare $CdSeO_3{\cdot}H_2SeO_3$, $2CdSeO_3{\cdot}H_2SeO_3$, $2CdSeO_3{\cdot}H_2SeO_3{\cdot}H_2O$, and $CdSeO_3{\cdot}1.5\ H_2O$ from aqueous solution at room temperature although the substances have been reported by others. Their existence is thus doubtful.

4.7.c. Zinc and Cadmium Selenates

Zinc selenate $ZnSeO_4$ [13597–54–1]
molecular weight 208.34
Zinc selenate monohydrate $ZnSeO_4{\cdot}H_2O$ [14912–28–0]
molecular weight 226.36
Zinc selenate trihydrate $ZnSeO_4{\cdot}3H_2O$ [55004–57–4]
molecular weight 262.39
Zinc selenate hexahydrate $ZnSeO_4{\cdot}6H_2O$ [7446–24–4]
molecular weight 316.43
Cadmium selenate $CdSeO_4$ [13814–62–5]
molecular weight 255.36
Cadmium selenate monohydrate $CdSeO_4{\cdot}H_2O$
[20861–74–9] molecular weight 273.38
Cadmium selenate dihydrate $CdSeO_4{\cdot}2H_2O$ [not found]
molecular weight 291.40
$Na_2Cd(SeO_4)_2{\cdot}2H_2O$ [31605–16–0]
molecular weight 480.33
$K_2Cd(SeO_4){\cdot}2H_2O$ [40472–13–7]
molecular weight 512.55

Physical characteristics: Zinc selenate is orthorhombic with $Z = 4$, a, b and c = 6.793, 9.012 and 4.905×10^{-10}m, respectively, and a calculated density of 2.722×10^3 kg m^{-3}. Pistorius[163] reports the monohydrate to be monoclinic with $Z = 4$, a, b and c = 7.64, 7.98 and 7.07×10^{-10}m, respectively, and $\beta = 116° 25'$. Courtine[164] has also characterized the two solids. Palmer and Giles[165] report the hexahydrate to be tetragonal with $Z = 4$, a and c = 6.953 and 18.33×10^{-10} m, respectively, and a calculated density of 2.371×10^3 kg m^{-3}. The *di*-, *tri*- and *penta*-hydrates are reported to exist.

Cadmium selenate. The monohydrate is monoclinic with $Z = 4$, a, b and c = 7.702, 7.749 and 8.219×10^{-10}m, respectively, $\beta = 120.83°$ and an experimental density of 4.22×10^3 kg m^{-3} according to Herpin and Bregeault[166]. The Crystal Determinative Tables[11] list the dihydrate as orthorhombic with $Z = 8$, a, b and c = 10.42, 10.71, and 9.365×10^{-10}m, respectively, and a calculated density of 3.68×10^3 kg m^{-3}. The dihydrate precipitates first from a saturated aqueous solution and converts to the monohydrate with agitation at all temperatures from 262 to 373 K.

The NBS Tables give enthalpy of formation values for $ZnSeO_4(s)$, $ZnSeO_4{\cdot}H_2O(s)$, $ZnSeO_4{\cdot}6H_2O(s)$, $CdSeO_4(s)$ and $CdSeO_4{\cdot}H_2O(s)$, but give a Gibbs energy of formation value only for $CdSeO_4$. Since the stable solid in contact with water is $CdSeO_4{\cdot}H_2O$, we are unable to calculate a useful solubility product value from the NBS Tables.

Erdenbaeva[128] calculated values of $K_{s0} = 3.0\times10^{-6}$ for $ZnSeO_4$ and $K_{s0} = 1.9\times10^{-7}$ for $CdSeO_4$ from measured emf and other thermodynamic data. The source of those data is not given and the hydration of the solid is not clear. The $CdSeO_4(s) = Cd^{2+}(aq) + SeO_4^{2-}(aq)$ K_{s0} value calculated from the NBS Tables[12] data is 5.75×10^{-3}. None of these values can be classed as even tentative values.

The Stoichiometric solubility of $ZnSeO_4$ and $CdSeO_4$ in water is relatively large. Klein[169] carried out a detailed study of solubility and characterized the equilibrium solid of both substances between about 265 K and 372 K. Gospodinov[167] measured the solubility of $ZnSeO_4$ at 298 and 373 K. Their values are in Tables 25 and 26. The two authors agree the equilibrium solid at 298.15 K is the hexahydrate, but Gospodinov's solubility value is nearly 5 per cent larger than Klein's value. At 373.15 K Gospodinov identified the solid as $ZnSeO_4 \cdot H_2O$ and Klein as $ZnSeO_4$. The Gospodinov solubility value is nearly 10 per cent larger. Thus, questions about the equilibrium solid in the $ZnSeO_4 + H_2O$ system remain, but Gospodinov's evidence for the monohydrate at 373 K is convincing. Klein found that on evaporation of water from $CdSeO_4$ solutions the dihyrate precipitated first. However, after a period of time with agitation the monohydrate forms as the thermodynamically stable state at all temperatures from 262 to 353 K. Only the monohydrate formed between 353 and 373 K.

Recently Essington[183] has estimated the Gibbs energy formation of a number of selenates. He estimates the solubility product of anhydrous $ZnSeO_4$ as 1.9×10^{-7}.

In saturated solutions near room temperature the predominant species is probably $ZnSeO_4^0$ (aq) or $CdSeO_4^0$ (aq). Aruga[168] gives formation constants at 298 K of 8.1 ± 0.3 and 9.8 ± 0.6 for the zinc and cadmium selenate ion pairs, respectively.

Gospodinov[167] reports a detailed study of the $ZnSeO_4 + H_2SeO_4 + H_2O$ system at both 298 and 373 K. At 298 K $ZnSeO_4 \cdot 6H_2O$, $ZnSeO_4 \cdot 5H_2O$, $ZnSeO_4 \cdot H_2O$, and $ZnSeO_4$ solids all have regions of stability as the H_2SeO_4 concentration increases. At 373 K only $ZnSeO_4 \cdot H_2O$ and $ZnSeO_4$ have regions as the stable solid.

TABLE 25. Solubility of zinc selenate, $ZnSeO_4$, in water

T/K	Density ρ/g cm^{-3}	Molality[a] m_{ZnSeO_4}/mol kg^{-1}	Solid Phase
271.15	–	1.01	Ice
267.15	–	1.967	"
265.35	–	2.276 (E)	Ice + hexahydrate
273.15	1.4835	2.370	$ZnSeO_4 \cdot 6H_2O$
284.65	1.5201	2.623	"
295.15	1.5588	2.922	"
298.15	–	3.189[b]	"
300.15	1.5796	3.13	"
307.55	–	3.45	"
301.15	–	3.26 (M)	$ZnSeO_4 \cdot 5H_2O$
302.15	–	3.31 (M)	"
313.45	–	3.63	"
316.55	1.6594	3.73	"
325.15	–	4.02 (M)	"
327.35	–	4.10 (M)	"
320.15	1.6250	3.61	$ZnSeO_4 \cdot H_2O$
329.35	1.5728	3.307	"
333.15	1.5611	3.259	"
325.15	1.6270	3.692 (M)	$ZnSeO_4$
333.15	1.5677	3.326 (M)	"
343.15	1.5061	2.978	"
353.15	–	2.657	"
364.15	–	2.40	"
371.65	1.3580	2.218	"
373.15	–	2.482[b]	$(ZnSeO_4 \cdot H_2O)$[b]

[a] Molalities calculated from author's values of g $ZnSeO_4$ per 100 g H_2O.
[b] The values at 298.15 and 373.15 K are from Gospodinov[167]. The remaining values are from Klein[169]. The authors disagree on the solid phase near 373 K. The Gospodinov values at 298 and 373 K are nearly 5 and 10 per cent greater, respectively, than the Klein values.
E = eutectic
M = metastable

4.8. The Tellurium Compounds of Zinc and Cadmium

The solubility data available for tellurium compounds of zinc and cadmium are meager and do not appear to be very reliable. The NBS tables do not contain sufficient Gibbs energy of formation values to allow any calculations of solubility products. There is a definitive and useful paper on the ionization and solubility properties of tellurous acid by Masson[170] which should be consulted by anyone working with tellurous, TeO_3^{2-}, compounds and their aqueous solutions.

TABLE 26. Solubility of cadmium selenate, $CdSeO_4$, in H_2O (Klein)[169]

T/K	Density ρ/g cm^{-3}	Molality[a] m_{CdSeO_4}/mol kg^{-1}	Solid Phase
269.95	–	1.541	Ice
267.35	–	2.188	"
265.35	1.5520	2.561	"
262.15	–	3.011 (M,E)	Ice + Dihydrate
273.15	1.6241	2.925 (M)	$CdSeO_4 \cdot 2H_2O$
283.15	1.5950	2.854 (M)	"
294.15	1.5950	2.680 (M)	"
313.15	1.5015	2.380 (M)	"
327.35	1.4520	2.164 (M)	"
333.35	1.4306	2.050 (M)	"
343.15	–	1.88	"
262.95	–	– (E)	Ice + $CdSeO_4 \cdot H_2O$
263.65	–	2.988	$CdSeO_4 \cdot H_2O$
268.35	1.6195	2.900	"
273.15	1.6048	2.837	"
283.15	1.5725	2.680	"
288.15	1.5555	2.561	"
290.15	1.5490	2.561	"
294.75	1.5337	2.492	"
299.15	1.5155	2.398	"
303.15	1.5012	2.306	"
308.35	1.4823	2.249	"
318.15	1.4412	2.057	"
321.15	1.4284	2.015	"
324.55	1.4074	1.917	"
329.15	1.3886	1.814	"
333.15	1.3664	1.731	"
335.65	1.3557	1.676	"
343.15	1.3158	1.517	"
353.15	1.2559	1.271	"
363.15	1.2035	1.064	"
371.65	–	0.862	"

[a] Molalities calculated from author's values of g $CdSeO_4$ per 100 g H_2O.
M = metastable
E = eutectic

4.8.a. The Zinc and Cadmium Tellurides

Zinc telluride ZnTe [1315–11–3]
molecular weight 192.99
Cadmium telluride CdTe [1306–25–8]
molecular weight 240.01

Physical characteristics: Zinc telluride exists in a cubic form with $Z = 4$, $a = 6.101\times10^{-10}$ m, and a calculated density of 5.639×10^{3} kg m^{-3}; and a hexagonal form with a and $c = 4.31$ and 7.09×10^{-10} m, respectively. Cadmium telluride is cubic (sphalerite or zinc blend form) with $Z = 4$, $a = 6.478\times10^{-10}$, and a calculated density of 5.866×10^{3} kg m^{-3}; and hexagonal (wurtzite form) with $Z = 2$, a and $c = 4.57$ and 7.48×10^{-10} m, and a calculated density of 5.890×10^{-3} kg m^{-3}. Several high pressure forms of CdTe are mentioned.

No direct measurements of the solubility or solubility products were found. Table 27 contains solubility products calculated from thermodynamic information. The Latimer[89] value is based on outdated information. The values of Buketov *et al.*[153] used information from Latimer and an empirical relationship proposed by the authors between the pK's of the telluride and sulfide. The source of data and method of calculation of Erdenbaeva[128] are not clear. The values are all classed as doubtful.

TABLE 27. Calculated solubility product constants of ZnTe and CdTe in water

T/K	Ionic strength I/Electrolyte	K_{s0} or K_{s0}°	Reference
		Zinc telluride, ZnTe	
298.15	0	5.0×10^{-34}	Buketov, Ugorets, Pashinkin 1964[153]
298.15	0 (?)	0.24×10^{-34}	Erdenbaeva, 1975[128]
		Cadmium telluride, CdTe	
298.15	0	1×10^{-42}	Latimer, 1952[89]
298.15	0	3.2×10^{-42}	Buketov, Ugorets, Pashinkin 1964[153]
298.15	0 (?)	4.9×10^{-44}	Erdenbaeva, 1975[128]

4.8.b. Zinc and Cadmium Tellurites and Tellurates

Zinc tellurite $ZnTeO_3$ [15851–43–1] molecular weight 240.98

Cadmium tellurite $CdTeO_3$ [15851–44–2] molecular weight 288.00

Cadmium tellurite $CdTe_2O_5$ [30180–70–2] molecular weight 447.60

Zinc tellurate $ZnTeO_4$ [not found] molecular weight 256.98

Cadmium tellurate $CdTeO_4$ [not found] molecular weight 304.00

Cadmium tellurate Cd_3TeO_6 [54954–11–9] molecular weight 560.82

Physical characteristics: Since there are no reliable solubility data for the tellurites and tellurates, the crystal structures are referenced but structural details are not given. The only data listed in the crystal determinative tables is for $Zn_2Te_2O_5$. Hanke[171] characterizes an orthorhombic $ZnTeO_3$ structure. No information was found for $ZnTeO_4$.

Two forms of $CdTeO_3$ are known: an α-form stable to 973 K[174] or 1065 K[173] and a β-form stable at the higher temperature. Both forms are monoclinic. The crystal structure and transition temperature[172] are apparently in error. Markovskii and Pron[172] report a hexagonal form stable above 770 K. Recently Kramer and Brandt[175] restudied $CdTeO_3$ and found no transition and a structure similar to the β-form of Robertson *et al.*[174]. Sleight *et al.*[176], report an orthorhombic form of $CdTeO_4$. Erdenbaeva[128] carried out an experimental study of the emf of suspensions of the sparingly soluble salts in 0.5 molar Na_2SO_4 solutions in contact with mercury. The results were combined with standard potential values or other accepted data to estimate the solubility product. The K_{s0} values are:

$ZnTeO_3$	3.56×10^{-3}
$CdTeO_3$	3.6×10^{-7}
$ZnTeO_4$	1.27×10^{-6}
$CdTeO_4$	1.8×10^{-8}

The values are of doubtful usefulness. The compounds $ZnTeO_4$ and $CdTeO_4$ are probably not the thermodynamically stable solids in contact with aqueous solutions.

Redman and Harvey[160] report experiments on the nature of zinc and cadmium precipitates and solution species of the tellurium compounds. The experiments were carried out at ambient temperature and several pHs by mixing zinc or cadmium solutions with potassium tellurite. The precipitates found were mainly $ZnTeO_3$ or $CdTeO_3$ with contamination by the metal hydroxide and TeO_2. An early report of Lenher and Wolesenky[177] identified the solid as $3CdTeO_3{\cdot}2H_2O$. Redman and Harvey misstate the Lenher and Wolesenky result.

The tellurates were studied by mixing solutions of zinc or cadmium salts with sodium tellurate at pH above 4. Titration curves showed no sharp end points, but indicated a precipitate composition near $ZnTeO_4$ or $CdTeO_4$; however, analysis of the precipitate showed 2 metal atoms to one tellurium atom corresponding to a formulation of $Zn_2H_2TeO_6$ or $Cd_2H_2TeO_6$. The precipitation reaction is suggested to be:

$$2Zn^{2+}(aq) + TeO_4^{2-}(aq) + 2H_2O \rightarrow Zn_2H_2TeO_6(s) + 2H^{+}\ (aq)$$

with the end point shifted by the H^+ produced. Jander and Kienbaum[178] report $Zn_2H_2TeO_6$ as an intermediate and Zn_3TeO_6 as the final product on reacting excess zinc solutions with tellurate solution at steam bath temperatures.

Redman and Harvey[160] report the following solution concentrations at the pH of the end point of their titration studies:

pH	$[Zn^{2+}]$	$[Cd^{2+}]$	Total as $[TeO_3^{2-}]$	Total as $[TeO_4^{2-}]$
7.5	6.34×10^{-5}		9.71×10^{-4}	
7.5		5.76×10^{-6}	6.88×10^{-4}	
6	7.51×10^{-3}			9.97×10^{-3}
6		3.68×10^{-3}		7.97×10^{-3}

4.9. Zinc and Cadmium Phosphates

4.9.a. Zinc and Cadmium Metaphosphate

$Zn(PO_3)_2$ [13566–15–9] Molecular weight 223.33
$Cd(PO_3)_2$ [14466–83–2] Molecular weight 270.35

Physical characteristics: There are a large number of condensed metaphosphates of zinc and cadmium. A number of these exist as hydrates. The results of several crystallographic studies on these compounds have been reported over the past twenty years. Only two studies are mentioned here: Bagieu-Beucher *et al.*[179] report on orthorhombic $Cd(PO_3)_2$, and Averbuch-Pouchot *et al.*[180] report on monoclinic $Cd_3(P_3O_9)\cdot10H_2O$. These authors and others have published extensively in the area.

There is doubt that the mono-metaphosphate ion, PO_3^-, has a stable existence in aqueous solution. However, condensed forms $(PO_3)_n^{n-}$, with $n = 2$ to 8, 10 and 14, are known. The trimetaphosphate, $(P_3O_9)^{3-}$, and the tetrametaphosphate, $(P_4O_{12})^{4-}$, are particularly stable anions of cyclic structure in which the oxygen atoms are shared in a tetrahedral arrangement about the phosphorus.

The only zinc and cadmium metaphosphate solubility data found were in the Comey and Hahn Handbook[10]. The data for the solubility in water of one cadmium and several zinc metaphosphates are given in Table 28. We class all of the values as doubtful.

TABLE 28. The solubility of some zinc and cadmium metaphosphates in water.

T/K	Formula	Solubility[a] *c*/mol L^{-1}	Reference
room	$Cd(P_2O_6)\cdot H_2O$	0.102	Glatzel, 1880[181]
room	$Zn(P_2O_6)$	1.12	Glatzel, 1880[181]
293	$Zn_3(P_3O_9)_2\cdot9H_2O$	0.000120	Tammann, 1892[182]
room	$Zn_2(P_4O_{12})\cdot10H_2O$	0.029	Glatzel, 1880[181]

[a] Values as quoted in Comey and Hahn[10]

4.9.b. Zinc Orthophosphate

$Zn_3(PO_4)_2$ [7779–90–0] molecular weight 386.08
$Zn_3(PO_4)_2\cdot4H_2O$ [15491–18–6] (hopeite) α and β forms
$Zn_3(PO_4)_2\cdot4H_2O$ [16842–47–0] (parahopeite)
(three forms) molecular weight 458.14

Physical Characteristics: Zinc orthphosphate, $Zn_3(PO_4)_2$, is monoclinic with $Z = 2, a, b$, and $c = 7.548$, 8.469 and 5.074 × 10^{-10} m, respectively, and a calculated density of 3.964 × 10^3 kg m^{-3}. The α- and β-hopeite differ in optical and dehydration properties. Hopeite is orthorhombic with $Z = 4$, a, b and $c = 10.64$, 18.32 and 5.03 × 10^{-10} m, respectively, and a calculated density of 3.08 × 10^3 kg m^{-3}. Parahopeite is triclinic with $Z = 1$, a, b and $c = 5.755$, 7.535 and 5.292 × 10^{-10} m, respectively, and a calculated density of 3.304 × 10^3 kg m^{-3}.

Goloshchapov and Filatova[184] have confirmed and extended earlier work[185,186] on the $ZnO + P_2O_5 + H_2O$ system. They find regions of stability of the solids $Zn_3(PO_4)_2\cdot4H_2O$, $ZnHPO_4\cdot3H_2O$, $ZnHPO_4\cdot H_2O$, $Zn(H_2PO_4)_2\cdot2H_2O$ and $Zn(H_2PO_4)_2\cdot2H_3PO_4$. Bek *et al.*[187] have also studied the system as well as a four component system containing these components plus N_2O_5, but their papers were not available to us. The system is further complicated in that the tetrahydrate can exist in the three crystaline forms α- and β-hopeite and parahopeite. Most workers have not characterized the solid. Nriagu[188] has characterized the equilibrium solid in his systems as the α-hopeite, $Zn_3(PO_4)_2\cdot4H_2O$.

There have been studies of the solubility in the presence of various electrolytes, and as a function of pH. Goloshchapov and Filatova[184] say that $Zn(HPO_4)$ and $Zn(H_2PO_4)_2$ dissolve incongruently to form $Zn_3(PO_4)_2$. Sigel *et al.*[189] identify the species $ZnHPO_4$ in aqueous solution and measure its formation constant at $I = 0.1$ $NaClO_4$ as 251±1 at 298 K.

Machevskaya and Babakina[190] observed the onset of precipitation as a function of pH, and Zn^{2+}(aq) and PO_4^{3-}(aq) concentrations. They developed an equation, assumed to be for 298 K, for the pH of precipitation:

$$pH_{ppt} = 7.3 - C_{Zn^{2+}}/(0.127 + (C_{Zn^{2+}}/C_{PO_4^{3-}}) + 0.180C_{Zn^{2+}})$$

They present figures of pH_{ppt} vs. ion concentration at 298, 323 and 348 K both in the absence and presence of Ni^{2+}(aq).

Table 29 summarizes the literature reporting $Zn_3(PO_4)_2\cdot4H_2O$ solubility values in water. Some workers[191,192,193] used very short equilibration times in their solubility studies and appear to have made no tests to confirm saturation. Andrew[196] indicates that zinc orthophosphate has a negative temperature coefficient of solubility, but he presents no quantitative data. Table 30 lists the solubility studies of zinc orthophosphate in various aqueous electrolyte solutions. The complete data sets of Eberly, Gross and Crowell[186] and Salmon and Terrey[185] are reproduced in the Seidell-Linke Handbook[6].

The solubility product values are in Table 31. No value is recommended, but the value of Nriagu[188] for the tetrahydrate solid, $Zn_3(PO_4)_2\cdot4H_2O$ (α-hopeite), is classed as tentative. The value of Trapeznikova *et al.*[194] is also stated to be for the tetrahydrate. It is not clear why the value is so large. The value calculated by us from the aqueous ion Gibbs energies of the NBS Tables[12] and the $Zn_3(PO_4)_2$(s) Gibbs energy and its temperature coefficient of Yaglov and Marinova[200a] appears to depend on the K_{s0} value of Zharovskii[199]. The value of Comeaux[200b] is taken from an abstract and its background is unknown. The value used by Machevskaya and Babakina[190] was not measured by them. Its source is not clear.

Some solubilities of other zinc phosphates and some equilibrium constants for other solubility reactions are given in Table 32.

TABLE 29. The solubility of zinc orthophosphate, probably $Zn_3(PO_4)_2{\cdot}4H_2O$, in water

T/K	Solubility c/mol L^{-1}	Method	Reference
?	7.68×10^{-4}	?	Fujiwara, Tatekawa, 1959[195]
293	$\sim 6 \times 10^{-6}$	Chronopotentiometry	Trapeznikova *et al.*, 1983[194,a]
298.2 ± 0.2	as P_2O_5	Molybdate reaction	Joshi, Jain, 1964[191,b]
298.7 ± 0.5 307.2	as Zn^{2+} & PO_4^{3-}	Molybdate reac. & dithionate complex	Mukerji, 1979[193]
303–333	as ZnO & P_2O_5	not specified	Pant, Pathak, 1976[192,b]

[a] Value for hopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$, estimated from a small graph.
[b] Short equilibration time, results may be too small.

4.9.c. Cadmium Orthophosphate

$Cd_3(PO_4)_2$ [13477–17–3]	molecular weight 527.17
$CdHPO_4$ [14067–62–0]	molecular weight 208.39
$Cd_{10}(PO_4)_6(OH)_2$ [12515–18–3]	molecular weight 1727.9
$Cd_5H_2(PO_4)_4{\cdot}4H_2O$ [15955–72–3]	molecular weight 1016.01

Physical Characteristics: Simonov *et al.*[206] report that $Cd_3(PO_4)_2$ is orthorhombic with $Z = 8$, a, b and c = 15.65, 11.07 and 7.56×10^{-10} m, respectively, and a calculated density of 5.35×10^3 kg m^{-3}. No crystallographic information was found on $CdHPO_4$.

Hata *et al.*[207] report cadmium hydroxyapatite, $Cd_5(PO_4)_3(OH)$, is hexagonal with $Z = 2$, a and c = 9.335 and 6.664×10^{-10} m, repectively, and a calculated density of 5.694×10^3 kg m^{-3}. Two other papers[208,209] also report hexagonal structures for the material. Akao and Iwai[209] report $Cd_5H_2(PO_4)_4{\cdot}4H_2O$ is monoclinic with $Z = 4$, and a, b and c = 17.889, 9.394 and 9.675×10^{-10} m, respectively. Averbuch-Pouchot and Durif[210] report similar results.

No solubility data were found for cadmium orthophosphate or cadmium hydrogen phosphate in water. Solubility data for these compounds in the presence of various dissolved elctrolytes are listed in Table 33.

Ropp and Mooney[211] indicate the stable solid precipitated from mixing solutions of $Cd(NO_3)_2$ and H_3PO_4 at several concentrations over the 273 to 373 temperature interval and the pH range of 3 to 11 is $Cd_5H_2(PO_4)_4(H_2O)_4$. They do not believe that this solid is a true crystalline hydrate. They also find that cadmium hydroxyapatite, $Cd_5(PO_4)_3(OH)$, does not form on precipitation, but that it does form slowly when $Cd_5H_2(PO_4)_4(H_2O)_4$ is refluxed with water. They found no evidence of either $Cd_3(PO_4)_2$ or $CdHPO_4$ as the solid in these systems.

Klement and Zureda[212] indicate they obtain an amorphous $Cd_3(PO_4)_2{\cdot}5H_2O$ as a precipitate from boiling solutions of $CdCl_2$ and Na_3PO_4. Mahapatra *et al.*[215,216] have evidence that the solid in equilibrium with cadmium hydroxyapatite solutions at 310 K is pH dependent. The predominant solid may be $CdHPO_4$ at pH 5.0 to 7.0 and $Cd_{10}(PO_4)_6(OH)_2$ at pH 7.5 to 8.0. The nature of the equilibrium solid in the systems described above needs further study.

The solubility product values for these compounds are of questionable reliability and usefulness. The available values for $Cd_3(PO_4)_2$, $CdHPO_4$ and $Cd_{10}(PO_4)_6(OH)_2$ are given in Table 34. Omarkulova and Bliznyuk[214] report a solubility product value for $CdH_3P_3O_{10}$ which we do not recommend because they do not appear to have considered other equilibria.

Hietanen, Sillen and Hogfeldt[213] report several equilibrium constants that may be useful in modeling cadmium phosphate solutions. They are

$$Cd_5H_2(PO_4){\cdot}4H_2O(s) + 2H^+(aq) = 5Cd^{2+}(aq) + 4HPO_4^{2-}(aq) + H_2O$$

with $K = 4.0 \times 10^{-26}$ at an ionic strength ($NaClO_4$) of 3. and

	I/Electrolyte	K
$Cd^{2+}(aq) + H^+(aq) + HPO_4^{2-} = CdH_2PO_4^+(aq)$	3/$NaClO_4$	1.10×10^7
$Cd^{2+}(aq) + HPO_4^{2-}(aq) = CdHPO_4(aq)$	3/$NaClO_4$	4.79×10^2
$Cd^{2+}(aq) + H_2PO_4^-(aq) = CdHPO_4(aq) + H^+(aq)$	1/$NaClO_4$	8.89×10^{-5}
	2/$NaClO_4$	6.04×10^{-5}
	3/$NaClO_4$	3.33×10^{-5}

4.9.d. Zinc Pyrophosphate

$Zn_2P_2O_7$ [7446–26–6]	molecular weight 304.72
$ZnH_2P_2O_7$ [54389–17–2]	molecular weight 241.35
$Zn_2P_2O_7{\cdot}H_2O$ [73356–02–2]	molecular weight 322.74
$Zn_2P_2O_7{\cdot}3H_2O$ [55852–32–9]	molecular weight 358.77
$Zn_2P_2O_7{\cdot}5H_2O$ [55303–37–0]	molecular weight 394.80

Physical characteristics: Zinc pyrophosphate exists in α and β forms. The α→β transition occurs at 405 ± 1 K. The α form is a super-lattice which changes to the high temperature β form with a one-third decrease in the a dimension and a one-half change in the c dimension[229]. The β form is monoclinic with $Z = 2$, a, b and c = 6.61, 8.30

TABLE 30. The solubility of zinc orthophosphate in aqueous solution

T/K	Medium	Solubility c/mol L^{-1}	Method	Reference
?	Peterman's soln. NH_4 citrate,NaOH,HCl			Fujiwara, Tatekawa, 1959[195,a]
284±1	HCl/pH=6.85	2.88×10^{-6}	molybdate reac.	Atkins, 1924[201]
292±1	*K* phthalate,HCl,			Zharovskii, 1951[199]
	pH=3.6	2.3×10^{-2} Zn^{2+}	hydroquinone	“ “
	pH=3.8	1.7×10^{-2} “	“	“ “
	Na acetate,acetic acid			“ “
	pH=3.97	1.1×10^{-2} Zn^{2+}	“	“ “
	pH=4.63	5.5×10^{-3} “	“	“ “
	pH=5.57	1.5×10^{-3} “	“	“ “
297.15	H_2SO_4/pH=4.95	Zn^{2+},PO_4^{3-} conc.	molybdate	Mukerji, 1979[193]
297.65	NaOH/pH=8.5	“ “ “	dithionate	“ “
298	Na_2HPO_4/I=0.075	6×10^{-3}	electrochem.	Immerwahr, 1901[202]
298	$ZnCl_2$,·H_2PO_4,NaOH pH=4.10–8.63	Zn^{2+},PO_4^{3-} conc.	dithionate	Jurinack, Inouye, 1962[203,b]
298.15	pH=5–14	$1.47\times10^{-3}-4.14\times10^{-7}$	calculation	Jaulmes, Brun, 1965[204]
298.2±0.1	several acid solns.	P_2O_5 reported	molybdate	Joshi, Jain, 1964[191,c]
298.15	H_3PO_4/pH = 3.39–4.62	6.47×10^{-3} -3.3×10^{-4}	atomic absorp.	Nriagu, 1973[188,b] “ “
298– 335	$ZnO+P_2O_5+H_2O$	data table and phase diagram	ferrocyanide	Eberly, Gross, Crowell, 1920[186]
298– 373	$ZnO+P_2O_5+H_2O$ phase diagram	data table and	ferrocyanide	Salomon, Terrey, 1950[185]
273– 333	$ZnO+P_2O_5+H_2O$ phase diagram	data table and	complexometric	Golashchapov, Filatova, 1969[184]
303.15	0.0012–0.0060 N solutions of NaOH, H_2CO_3, tartaric acid, citric acid, Na_2CO_3 and $NaHCO_3$	g L^{-1} P_2O_5 reported		Pathak, Pant, 1973[198,c]
303.15	NaOH/pH=8.5	Zn^{2+}, PO_4^{3-} conc.	Molybdate,	Murkerji, 1979[193]
307.15	H_2SO_4/pH=5.00	“ “ “	dithionate	“ “

[a] Solubilities of $ZnHPO_4$ and $Zn(H_2PO_4)_2$ are also given.

[b] Solid $Zn_3(PO_4)_2{\cdot}4H_2O$ confirmed as solid by X-ray analysis.

[c] Unusally short equilibration times used, solutions may not be at equilibrium.

TABLE 31. The zinc orthophosphate solubility product constant

T/K	Ionic Strength I/Electrolyte	Ion Product Constant K_{s0}	K_{s0}°	Reference
Calculated from thermodynamic data				
298.15	0		7.8×10^{-33}	[a]
323	0		3.0×10^{-37}	Yaglova, Marinova, 1976[200a,b]
From solubility studies				
292±1	[c]	9.1×10^{-33}		Zharovskii, 1951[199]
293	?	1.2×10^{-24}		Trapeznikova *et al.*, 1983[194]
298.15	0	5.1×10^{-36}		Nriagu, 1973[188,d]
298.15	?	2×10^{-33}		Machevskaya, Babakina, 1982[190,e]
298	?	1×10^{-37}		Comeaux, 1965[200b,f]

[a] Calculated by us using the $\Delta G_f^\circ{}_{298}$ from Yaglov and Marinova[200a] and the aqueous ion Gibbs energies of formation from the NBS Tables[12].

[b] Source of data and method of calculation not clear to us.

[c] An average of values determined at different pH's in buffered media.

[d] Solution reaction stated to be $Zn_3(PO_4)_2{\cdot}4H_2O(s)(\alpha\text{-hopeite}) = 3Zn^{2+}(aq) + 2PO_4^{3-}(aq) + 4H_2O(M)$.

[e] Value reported and used in this source, no references.

[f] Value reported in Chem. Abstr., original paper not available to us.

TABLE 32. Some zinc phosphate equilibria and solubility values

T/K	Process and Data	Reference
298.15	$Zn_3(PO_4)_2{\cdot}4H_2O(s) = 3Zn^{2+}(aq) + 2H_2PO_4^-(aq) + 4OH^-(aq)$ $K = 6.3 \times 10^{-53}$ at I = 0 Nriagu, 1973[188] $K = 1.3 \times 10^{-48}$ at I ≠ 0, pH = 7.48	Jurinak, Inouye, 1967[203,a]
298.15	$Zn(H_2PO_4)_2(s) = Zn^{2+}(aq) + 2H_2PO_4^-(aq)$ $K_{s0} = 1.72 \times 10^{-3}$ to 4.3×10^{-12} at pH = 2.0-5.4.	Tumanova, *et al.*, 1967[205]
298.15	$Zn(H_2PO_4)_2(s) + 2H^+(aq) = Zn^{2+}(aq) + H_3PO_4(aq)$ $K = 3.28 \times 10^{-2}$ to 1.31×10^{-7} at pH 2.0 to 5.4	" "
298.15	$Zn^{2+}(aq) + HPO_4^{2-}(aq) = ZnHPO_4(aq)$ β = 251 ± 1 at I = 0.1	Sigel *et al.*, 1967[189]
Solubility in water		
?	$ZnHPO_4$ 7.86×10^{-5} mol L^{-1}	Fijiwara, Tatekawa, 1959[195,b]
?	$Zn(H_2PO_4)_2$ 6.42×10^{-4} mol L^{-1}	" "
291	$Zn(H_2PO_4)_2^{1}$ 0.03 mol L^{-1}	Travers, Perron, 1924[197,c]

[a] The authors give this as an approximate value; Nriagu[188] questions the composition of the solid state in this work.
[b] There are additional solubility values in the paper for Peterson's solution, aqueous ammonium citrate and other aqueous solutions as a function of pH.
[c] Doubtful value.

TABLE 33. The solubility of several orthophosphates in aqueous solution

T/K	Ionic strength *I*/electrolyte	Phosphate	Solubility *c*/mol L^{-1}	Reference
(298)	0.075/Na_2HPO_4	$Cd_3(PO_4)_2$	4.2×10^{-3}	Immerwahr, 1901[202,a]
310	0.0045–0.165/	$CdHPO_4$	$(1.52-1.65) \times 10^{-3}$	Mahapatra, *et al.*, 1982[216,b]
315	$NaNO_3$	"	$(1.43-1.62) \times 10^{-3}$	
320	"	"	$(1.52-1.60) \times 10^{-3}$	" " "
325	" "	"	$(1.53-1.57) \times 10^{-3}$	" " "
310	pH = 6,7,8/?	$Cd_{10}(PO_4)_6(OH)_2$	graph	Nayak, Rao, 1975[217]
310	pH = 5.175 – 8.10 /[c]	"	Cd^{2+} & total P reported.	Mahapatra, *et al.*, 1982[215]

[a] Calculated relative to a $CdCl_2$, KNO_3 half-cell with $[Cd^{2+}]$ assumed to be 0.5 mol L^{-1}.
[b] The total ionic strength, all ions, ranges 0.0253 to 0.186.
[c] Electrolyte is $NaNO_3$, $NaC_2H_3O_2$ + $HC_2H_3O_2$, or borax + boric acid. The solid phase reported to be $CdHPO_4$ at pH 5.0 to 7.0, and $Cd_{10}(PO_4)_6(OH)_2$ at pH 7.5 to 8.0.

and 4.51×10^{-10} m, respectively, β = 105.4°, and a calculated density of 4.241×10^3 kg m^{-3}. A crystal structure is reported for a tetrahydrate, but we found no information on the other hydrates. The pentahydrate loses water to form the trihydrate at about 351 K[221,225].

Neither the zinc pyrophosphate nor its hydrates exists alone with water. The hydrates exist in the equilibrium solid in a number of ternary systems[220-223]. Both the trihydrate and penta- hydrate are reported to have regions of stability in the $ZnSO_4 + K_4P_2O_7 + H_2O$ and the $Zn_2P_2O_7 + H_4P_2O_7 + H_2O$ systems[230]. A number of potassium zinc pyrophosphate hydrates show regions as the equilibrium solid. The equilibrium solids in the $Zn_2P_2O_7$ + $(NH_4)_4P_2O_7 + H_4P_2O_7 + H_2O$ system[224] at 298 K are the mixed hydrates $Zn(NH_4)_2P_2O_7{\cdot}H_2O$ and $Zn_3(NH_4)_2(P_2O_7)_2{\cdot}2H_2O$.

The solubility studies and some solubility values are given in Table 35. Selivanova *et al.*[221] observed the change of the pentahydrate to the trihydrate at about 351 K. Table 36 gives $Zn_2P_2O_7$ solubility product values derived from solubility studies[221,226]. These have not been corrected to zero ionic strength, but they have been selectively corrected for complex ion formation. The formation constants of $ZnP_2O_7^{2-}(aq)$ and $Zn(P_2O_7)_2^{6-}(aq)$ are given by Sillen and Martell[8]. The zero ionic strength values of Wolhoff and Overbeek[227] are

TABLE 34. Solubility product values for several cadmium phosphates

T/K	Media, pH or I/electrolyte	K_{s0}	K°_{s0}	Reference
Cadmium orthophosphate, $Cd_3(PO_4)_2$				
292.65 ±0.5	pH≈4.9/HCl,HNO_3	$(2.7 \pm 1.2) \times 10^{-33}$		Chukhlantsev, *et al.*, 1961[218]
298.15	0		2.5×10^{-33}	NBS Tables[12]
323.15	0		2.8×10^{-37}	Yaglov, Marinova 1976[200a,a]
Cadmium hydrogen phosphate, $CdHPO_4$				
293.15	0		1.5×10^{-7}	Omarkulova, Bliznyuk, 1974[214,b]
310	0.0045–0.165/	$(2.47-2.89) \times 10^{-9}$		Mahapatra *et al.*, 1982[216,c]
315	$NaNO_3$	$(2.45-2.78) \times 10^{-9}$		
320	"	$(2.38-2.75) \times 10^{-9}$		" " "
325	"	$(2.36-2.65) \times 10^{-9}$		" " "
Cadmium hydroxyapatite, $Cd_{10}(PO_4)_6(OH)_2$				
310	pH = 7.60/$NaNO_3$,borate	5.97×10^{-97}		Mahapatra *et al.*, 1982[215]
	pH = 8.10/ " "	3.57×10^{-97}		
310–325	pH = 5.0/$NaNO_3$,acetate buffer	values reported[d]		" " "

[a] Details of this calculation not clear to us.
[b] Calculated without consideration of any complex ion formation.
[c] Total ionic strength 0.00253–0.186; the authors report the K_{s0} value to five digits.
[d] Not clear if the reported values are for this solid.

TABLE 35. Zinc pyrophosphate solubility studies in aqueous systems

T/K	System or media	Solubility c/mol L^{-1}	Reference
273.15	$Zn_2P_2O_7 + H_2P_2O_7 + H_2O$	0.184–0.562	Selivanova *et al.*, 1978[220,a].
298.15	" " "	table/figure	" " "
298.15–358.15	1/KNO_3 or $NaNO_3$	Zn^{2+} conc.	Selivanova, *et al.*, 1978[221]
298.15	$ZnSO_4 + K_4P_2O_7 + H_2O$	figure	Selivanova, *et al.*, 1974[222]
298.2 ±0.2	$K_4P_2O_7 + Zn_2P_2O_7 + H_2O$	table/phase diagram	Morozova, *et al.*, 1976[223]
298.15	$Zn_2P_2O_7 + (NH_4)_4P_2O_7 + H_2P_2O_7 + H_2O$	table/figure	McCullough, *et al.*, 1972[224]

[a] solid phase $Zn_2P_2O_7 \cdot 5H_2O$.

	298.15 K	313.15 K
$Zn^{2+}(aq) + P_2O_7^{4-}(aq) = ZnP_2O_7^{2-}(aq)$	5.01×10^{8}	1.58×10^{9}
$Zn^{2+}(aq) + 2P_2O_7^{4-}(aq) = Zn(P_2O_7)_2^{6-}(aq)$	1.00×10^{11}	6.31×10^{10}

4.9.e. Cadmium Pyrophosphate

$Cd_2P_2O_7$ [15600–62–1]	molecular weight 398.76
$CdH_2P_2O_7$ [52482–45–8]	molecular weight 288.37
$Cd_2P_2O_7 \cdot 2H_2O$ [13477–18–4]	molecular weight 434.79
$Cd_2P_2O_7 \cdot 2.5H_2O$ [not found]	molecular weight 443.80
$Cd_2P_2O_7 \cdot 4H_2O$ [not found]	molecular weight 470.82

Physical characteristics: Calvo and Au[228] report cadmium pyrophosphate, $Cd_2P_2O_7$, is monoclinic with $Z = 2$, a, b and $c = 6.672$, 6.623 and 6.858×10^{-10} m, respectively, and angles α, β and γ of 95.80, 115.38 and 82.38°, respectively. No crystallographic information was found on either of the hydrates or anhydrous $CdH_2P_2O_7$.

Selivanova and Kudryavtsev[229–232] are the only workers to report $Cd_2P_2O_7$ solubility values. They used titration methods to determine the ion concentrations in solution,

TABLE 36. *Zinc pyrophosphate*, $Zn_2P_2O_7$, solubility product constant

T/K	Ionic strength *I*/Electrolyte	K_{s0}	Method	Reference
298.15	0.5/$N(CH_3)_4Cl$	2.5×10^{-16}	solubility	Delannoy, *et al.*, 1979[226]
298.2 ±0.2	1.0/KNO_3 or $NaNO_3$	0.7×10^{-16}	solubility	Selivanova, *et al.*, 1978[221,a]

[a] Solid phase $Zn_2P_2O_7{\cdot}5H_2O$

TABLE 37. Cadmium pyrophosphate tetrahydrate, $Cd_2P_2O_7{\cdot}4H_2O$, solubility studies in aqueous solution at 298.15 K

Ionic strength *I*/Electrolyte	Solubility *c*/mol L^{-1}	References
0 (H_2O)	$(2.7\pm0.2)\times10^{-5}$	Kudryavtsev, Selivanova, 1970[229]
0.25–27.3/ $(NH_4)_4P_2O_7$	Cd^{2+} conc.	Selivanova, Kudryavtsev, 1974[232]
1/$(NH_4)_4P_2O_7$, $NaNO_3$	table	" " , 1970[230]
0.12–30.0/ $K_4P_2O_7$	Cd^{2+} conc.	Kudryavtsev, Selinanova, 1970[229,230]
0.112–2.3/ $Na_4P_2O_7$	Cd^{2+} conc.	Selivanova, *et al.*, 1972[231]

and x-ray diffraction and thermogravimetric methods to analyze the solid phase. Table 37 summarizes the systems they have studied. Some of the data are repeated in later publications without reference to these papers.

In the study of the solubility of cadmium pyrophosphate in water the solute was $Cd_2P_2O_7{\cdot}2H_2O$, but at equilibrium the solid was $Cd_2P_2O_7{\cdot}4H_2O$. In another study the authors[233] report a solubility for $K_6Cd(P_2O_7)_2$ of 5.5 × 10^{-3} mol L^{-1} at 298 K with the solid identified as $Cd_2P_2O_7{\cdot}xH_2O$. Selivanova and Kudryavtsev[230] report a solubility product of (19.6±2.7) × 10^{-15} for $Cd_2P_2O_7{\cdot}2.5H_2O$. It is not clear to us how this value was obtained from data in the paper. We obtain a value of 27.7 × 10^{-15} for the process

$$Cd_2P_2O_7{\cdot}2H_2O(s) = 2Cd^{2+}(aq) + P_2O_7^{4-}(aq) + 2H_2O(M)$$

from the dihydrate Gibbs energy of formation of −2626 kJ·mol^{-1} of Selivanova and Leshchinskaya[234] and data from the NBS Tables[12]. Both values must be viewed with caution if the equilibrium solid is the tetrahydrate.

Omarkulova and Bliznyuk[214] report solubility product values for several phosphates including $CdH_2P_2O_7$. Their value of 8.1 × 10^{-5} at 293 K appears to have been calculated on the basis of a model that does not take into account complex ions in solution. The value is classed as doubtful.

Sillen and Martell[8] report complex ion formation constants. The values of Wolhoff and Overbeek[227] at zero ionic strength may be useful.

	298.15 K	313.15 K
$Cd^{2+}(aq) + P_2O_7^{4-}(aq) \rightleftharpoons CdP_2O_7^{2-}(aq)$	5.00×10^{8}	3.98×10^{8}
$Cd^{2+}(aq) + OH^{-}(aq) + P_2O_7^{4-} \rightleftharpoons CdOHP_2O_7^{3-}(aq)$	6.33×10^{11}	2.51×10^{12}

4.10. Zinc and Cadmium Arsenites and Arsenates

4.10.a. Zinc Arsenite and Arsenate

$Zn(AsO_2)_2$ [10326–24–6] molecular weight 279.23
$Zn_3(AsO_3)_2$ [28837–97–0] molecular weight 442.00

Physical characteristics: The mineral Reinerite, $Zn_3(AsO_3)_2$, is orthorhombic with Z = 4, *a*, *b*, and *c* = 7.804, 14.397, and 6.091 × 10^{-10} m, respectively, and a calculated density is 4.278 × 10^3 kg m^{-3}.

$Zn_3(AsO_4)_2$ [13464–44–3] molecular weight 474.00
$Zn_3(AsO_4)_2{\cdot}H_2O$ [28347–85–5] molecular weight 492.02
$Zn_3(AsO_4)_2{\cdot}4H_2O$ [56280–71–8] molecular weight 546.06
$Zn_3(AsO_4)_2{\cdot}8H_2O$ [not found] molecular weight 618.13

Physical characteristics: Crystalline $Zn_3(AsO_4)_2{\cdot}4H_2O$ is triclinic[235] with Z = 1, α, β and γ = 940 18′, 910 12′, and 920 6′, respectively, a, b and c = 5.99, 7.63, and 5.43 × 10^{-10} m, respectively, and a calculated density is 3.67

× 10^3 kg m^{-3}. The mineral Koettigite, $Zn_3(AsO_4)_2 \cdot 8H_2O$, is monoclinic with $Z = 2$, $\beta = 1030\ 05'$, a, b and c = 10.08, 13.31, and 4.70 × 10^{-10} m, respectively, and a calculated density of 3.32 × 10^3 kg m^{-3}.

There are three zinc hydroxide arsenate minerals of formula $Zn(OH)AsO_4$ described in the Crystal Data Determinative Tables[11] but none has been identified as a solid phase in any of the solubility studies.

Zinc Arsenite. Kuperman, *et al.*[236] prepared both $Zn(AsO_2)_2$ and $Zn_3(AsO_3)_2$. They studied their solutions in both 5 and 10 per cent ammonia and acetic acid solutions at 298 and 343 K. The original paper is not available to us. We were unable to judge from the abstract whether or not the paper contained useful solubility data as stated by Seidell[6].

Chukhlantsev[237] carried out two series of solubility experiments on $Zn_3(AsO_3)_2$ at 293 K. His results are summarized in Table 38. In the first experiment he determined the Zn^{2+} concentration at saturation in dilute solutions of HCl, HNO_3 and H_2SO_4. The solutions initially had a pH near 2, and after saturation the pH ranged from 5.90 to 6.30. If the H_3AsO_3 dissociation constants are known, these data could be recalculated as K_{s0} values. The second experiment used a radioactive tracer method to determine the solubility product. The experiment was apparently done in pure water with care taken to exclude carbon dioxide. It was assumed that no hydrolysis of the AsO_3^{3-} occurred, and its concentration was taken as 2/3 the Zn^{2+} concentration. The K_{s0} value (Table 38) is the average of four determinations.

Nishimura *et al.*[238] equilibrated ZnO and arsenious acid solutions under a nitrogen atmosphere for one week to four months. The solid was filtered, the pH was measured and the arsenic (III) was analyzed. A portion of the precipitate was analyzed for Zn and another portion was analyzed by x-ray diffraction. The authors prepared log [As]-pH diagrams and gave log K_s values for the two solubility equilibria:

$$Zn(AsO_2)_2(s) + 2H^+(aq) = Zn^{2+}(aq) + 2HAsO_2(aq) \quad \log K_s = 5.9$$

$$3ZnO \cdot AsO_3(s) + 6H^+ = 3Zn^{2+}(aq) + 2H\,AsO_2(aq) + 2H_2O(l) \quad \log K_s = 26.0$$

Zinc Arsenate Kuperman *et al.*,[236] prepared both $Zn_3(AsO_4)_2$ and $Zn_3(AsO_4)_2 \cdot Zn(OH)_2$. They carried out studies on these compounds at 298 and 343 K in 5 and 10 per cent ammonia and acetic acid solutions. As mentioned above in the arsenite discussion we were unable to obtain the paper.

Chukhlantsev[239] determined the $Zn_3(AsO_4)_2$ solubility product at 298 K by two methods. In the first study he measured the stoichimetric solubility in dilute nitric and sulfuric acid solutions, using the literature dissociation constants of H_3AsO_4 to calculate the actual AsO_4^{3-} concentration, and calculated the K_{s0} value. In the second experiment he used a radioactive tracer technique to measure the Zn^{2+} concentration in water, assumed the AsO_4^{3-} concentration was 2/3 that value, and calculated K_{s0}. The two published values differ by one order of magnitude. However, there appears to be a decimal error in the radioactive tracer calculation, which makes the two values differ by two orders of magnitude. The values are in Table 39. In a later paper Chukhlantsev[240] uses the radioactive tracer K_{s0} values of $Zn_3(AsO_4)_2$, $Sr_3(AsO_4)_2$ and Ag_3AsO_4 to determine new values of the acid dissociation constants of H_3AsO_4. The error mentioned above is repeated and may affect the dissociation constant values.

Sagadieva, Makhmetov, Malyshev and Maslennikova[241] applied the acid solubility method at pH 5 at temperatures of 298, 310, 322, 334 and 346 K to obtain values of K_{s0} for $Zn_3(AsO_4)_2$. We have available only the Zh. Fiz. Khim. abstract which gives their fitted ΔG_T° equation. There appears to be an error in the equation and it cannot be used to obtain K_{s0} values.

Recently Malyshev, Sagadieva, and Makhmetov[242] have recalculated the solubility product values using activity coefficients. The paper is not presently available to us.

Takahashi and Sasaki[243] studied the system ZnO + As_2O_5 + H_2O at 303.15 K. They identified equilibrium solids as $ZnHAsO_4 \cdot H_2O$ and $Zn(H_2AsO_4)_2$. Only the phase diagram is given.

Nishimura *et al.*[238] equilibrated ZnO and arsenic acid solutions and analyzed the solid and solution in the same manner as the ZnO and arsenous acid solutions. They give equilibrium constants for the following solubility equilibria:

$$ZnHAsO_4 \cdot H_2O(s) + 2H^+(aq) = Zn^{2+}(aq) + H_3AsO_4(aq) + H_2O(l) \quad \log K_s = 2.5$$

$$Zn_5H_2(AsO_4)_4 \cdot 6H_2O(s) + 6H^+(aq) = 5Zn^{2+}(aq) + 4H_2AsO_4^-(aq) + 6H_2O(1) \quad \log K_s = 6.9$$

$$Zn_3(AsO_4)_2 \cdot 8H_2O(s) + 4H^+(aq) = 3Zn^{2+}(aq) + 2H_2AsO_4^-(aq) + 8H_2O(1) \quad \log K_s = 7.9$$

$$Zn_2(AsO_4)OH(s) + 2H^+(aq) = 2Zn^{2+}(aq) + HAsO_4^{2-} + H_2O(l) \quad \log K_s = 0.06$$

The NBS Tables[12] contain Gibbs energy data from which we calculate a K_{s0}°value of 2.8×10^{-28} at 298.15 K, which is in good agreement with Chukhlantsev's solubility product from the study of solubility in dilute acid. However, the values may not be independent. The value is apparently for the unhydrated salt. Chukhlantsev describes the $Zn_3(AsO_4)_2$ solid he prepared as highly amorphous. He does not mention evidence for any of the known hydrates.

4.10.b. Cadmium Arsenite and Arsenate

$Cd_3(AsO_3)_2$ [not found]	molecular weight 583.07
$Cd_3(AsO_4)_2$ [7778–44–1]	molecular weight 615.07

Physical characteristics: Engel and Klee[245] find cadmium arsenate, $Cd_3(AsO_4)_2$, to be monoclinic, a structure related to the mineral graftonite, with *a*, *b* and *c* = 9.285, 11.936 and 6.599 × 10^{-10} m, respectively, $\beta = 98.45°$, and

TABLE 38. Solubility of zinc arsenite, $Zn_3(AsO_3)_2$

T/K	$10^3C_{Zn^{2+}}$/ mol L^{-1}	pH Initial	pH Final	Acid	References
293	2.5	2.35	6.30	H_2SO_4	Chukhlantsev, 1957[237]
	3.1	2.35	6.25	HNO_3	
	6.1	2.10	6.20	H_2SO_4	
	5.8	2.15	6.10	HCl	
	7.4	2.00	6.05	H_2SO_4	
	1.1	1.90	6.00	H_2SO_4	
	6.8	1.98	5.95	HNO_3	
	9.9	1.90	5.90	HCl	

Chukhlantsev's radioactive tracer study gave K_{s0}/mol^{5}L^{-5} = $(2.8\pm0.8)\times10^{-20}$ as the average of four determinations.

TABLE 39. Solubility products of zinc arsenate, $Zn_3(AsO_4)_2$

T/K	K_{s0}	Method	Reference
Recommended			
298.15	$2.8\times10^{-28}(K^\circ_{s0})$	Thermo data	NBS Tables 1982[12]
Experimental values			
293	$(1.3\pm0.4)\times10^{-28}(6)$ $(108\pm11)\times10^{-28}(4)$	solubility[a] radioactive tracer	Chukhlantsev, 1956[239]
298–346	[b]	solubility	Sagadieva *et al.*, 1976[241]

Number in ( ) is number of determinations.

[a] The dissociation constants of H_3AsO_4 used were $K_{1a} = 5.62\times10^{-3}$, $K_{2a} = 1.7\times10^{-7}$ and $K_{3a} = 1.95\times10^{-12}$. (Britton and Jackson[244]).

[b] Unable to obtain paper by publication time.

$Z = 4$. No density is given. We were unable to obtain crystal structure information for cadmium arsenite, $Cd_3(AsO_3)_2$, through the Crystal Data Determination Tables[11] or through a Chem. Abst. search from 1962 to the present.

Cadmium arsenite. Chukhlantsev[237] measured the stoichiometric solubility of $Cd_3(AsO_3)_2$ in dilute nitric and sulfuric acid at 293 K. The results are in Table 40. No solubility product values were found.

Cadmium arsenate. Chukhlantsev[239] determined the solubility product by a study of solubility in dilute nitric and sulfuric acid solutions. He used literature values of the ionization constants of H_3AsO_4 to calculate the AsO_4^{3-} ion concentration. The six results range from $(0.1$ to $6.2)\times10^{-33}$ and average $(2.2\pm2.7)\times10^{-33}$ mol^5 L^{-5} at 293 K (Table 41). The same value is obtained from Gibbs energy data in the NBS Tables. Since the NBS Tables data are not referenced one cannot tell if the Gibbs energy value is independent. The value is in common use in the literature without its source being referenced[246,247].

4.11. Zinc and Cadmium Carbonate

4.11.a. Zinc Carbonate

$ZnCO_3$ [3486–35–9] molecular weight 125.40
Smithsonite [14476–25–6]

Physical characteristics: Zinc carbonate is a colorless hexagonal crystal with $Z = 6$, $a = 4.651\times10^{-10}$ m, $c = 14.977\times10^{-10}$ m, and a calculated density of 4.425×10^{-3} kg m^{-3}. The natural occurring zinc carbonate mineral is Smithsonite.

The solubility of zinc carbonate depends on temperature, ionic strength, pH, and partial pressure of carbon dioxide. The calculation of the zinc carbonate solubility requires reliable values of the carbonic acid dissociation constants and the carbon dioxide Henry's constant. In dilute strong acid media:

$$\begin{array}{lll}
ZnCO_3\ (s) & = Zn^{2+}\ (aq) + CO_3^{2-}\ (aq) & K_{s0} \\
H^+\ (aq) + CO_3^{2-}\ (aq) & = HCO_3^-\ (aq) & 1/K_{a2} \\
H^+\ (aq) + HCO_3^-\ (aq) & = H_2O + CO_2\ (aq) & 1/K_{a1} \\
CO_2\ (aq) & = CO_2\ (g) & 1/K_p \\
\hline
ZnCO_3\ (s) + 2H^+\ (aq) & = Zn^{2+}\ (aq) + H_2O + CO_2(g) & \\
 & & K = K_{s0}/K_{a1}K_{a2}K_p
\end{array}$$

And in the acidic aqueous carbon dioxide solution:

$$\begin{array}{lll}
ZnCO_3\ (s) & = Zn^{2+}\ (aq) + CO_3^{2-}\ (aq) & K_{s0} \\
H^+\ (aq) + CO_3^{2-}\ (aq) & = HCO_3^-\ (aq) & 1/K_{a2} \\
CO_2\ (g) & = CO_2\ (aq) & K_p \\
CO_2\ (aq) + H_2O & = HCO_3^-\ (aq) + H^+\ (aq) & K_{a1} \\
\hline
\multicolumn{2}{l}{ZnCO_3\ (s) + CO_2\ (g) + H_2O = Zn^{2+}\ (aq) + 2HCO_3^-\ (aq)} & \\
 & & K = K_{s0}K_pK_{a1}/K_{a2}
\end{array}$$

TABLE 40. Solubility of cadmium arsenite, $Cd_3(AsO_3)_2$

T/K	$10^3 C_{Cd^{2+}}$/	pH		Acid	Reference
T/K	mol L^{-1}	Initial	Final		
293	2.8	2.35	7.00	HNO_3	Chukhlantsev, 1957[237]
	2.8	2.35	7.00	H_2SO_4	" "
	6.9	1.98	6.60	HNO_3	" "
	7.0	2.00	6.60	H_2SO_4	" "

TABLE 41. Solubility product of cadmium arsenate, $Cd_3(AsO_4)_2$

T/K	K_{s0}	Method	Reference
Tentative			
298.15	$2.2\times10^{-33}(K_{s0}^{0})$	Thermo data	NBS Tables[12]
Experimental			
293	$(2.2\pm2.7)\times10^{-33}$	solubility[a]	Chukhlantsev, 1956[239]

[a] See Table 39 for H_3AsO_4 dissociation constants used in study.

The second model is consistent with the increase in $ZnCO_3$ solubility as carbon dioxide partial pressure increases and the observation the major solution species at high carbon dioxide partial pressure is HCO_3^-. Neither of the models necessarily represents a mechanism.

The values of zinc carbonate solubility in water from the literature are in Table 42. Both experimental and calculated values are found in the literature. The values of von Essen[248], Haehnel[249], Piperaki and Hadjiioannou[250], Grohmann [251], Mann and Deutscher[252], and Jaulmes and Brun[204] are doubtful because temperature or carbon dioxide pressure or details of calculation are lacking.

The paper of Ageno and Valla[253] contains apparent printing errors which causes some uncertainty of their values. The values of Smith[254] at 298.15 and 303.15 K are based on direct analysis of the saturated solutions. Smith reports solution concentrations of H_2CO_3 and $Zn(HCO_3)_2$. We have estimated the carbon dioxide partial pressures from Henry's constant and the assumption the H_2CO_3 concentration represents the dissolved CO_2 concentration at 298.15 K.

At 298.15 K the tentative solubility values are the calculated solubility values from Kelley and Anderson[255] at a CO_2 partial pressure of 1 kbar and the pure water value in air (CO_2 partial pressure of about 0.00032 bar) given by Ageno and Valla[253].

Table 4A lists the temperatures, carbon dioxide partial pressure, and non-saturating electrolyte in the various studies of zinc carbonate solubility in aqueous electrolyte solutions. Because temperature and carbon dioxide partial pressure are not always clearly defined the solubility values from these papers should be used with caution.

Table 43 lists values of the zinc carbonate solubility product, K_{s0}, from the literature. The table contains both values from experimental measurements and values calculated from thermodynamic data. The values at the higher temperatures are values calculated from thermodynamic data.

The experimental values are reported by Zhukova and Rachiuski[261], Schindler *et al.*[260], Ageno and Valla[253] and Smith[254]. There are recalculated values from the Smith data by Kelley and Anderson[255] and by us using more up-to-date auxiliary data. Several of these papers[255,260] report K_{s0}° values extrapolated from the experimental data.

The K_{s0}° values calculated from thermodynamic data are Latimer[89] who used data from 1949 NBS and 1935 Bureau of Mines data; Egorov and Titova[262] who used data from Latimer and from Kubaschewski and Evans[93]; Schindler *et al.*,[260] who used data from their own work and from NBS Circular 500[110]; Helgeson[107] who used 1968 NBS Technical Note 270–3 data and data from Wulff[114]; and Krestov *et al.*[129] who give a five constant equation for the 273–373 K interval but do not identify sources of data.

Values of the solubility product constant of Egorov and Titova[262] in Table 44 were calculated from their equation

$$\log K_{s0}^{\circ} = 31.77 + 1480/(T/\mathrm{K}) + 7.17 \log (T/\mathrm{K}) - (2.82\times10^{-3})(T/\mathrm{K})$$

The values from the Krestov *et al.*[129] equation calculated by us are nearly a factor of 10 smaller than the other values at 298.15, 323.15 and 373.15 K. Only Krestov's 298.15 K value is in Table 43 and the data were not used further.

The tentative values in Table 43 are from a linear regression of the values of Latimer, Egorov and Titova, and Helgeson given later in the table. A linear regression of other scientists' calculated values cannot be considered a satisfactory evaluation, but we had neither the time nor the resources to evaluate directly the thermodynamic data used in the calculations.

The equation for the tentative K_{s0}° values is

$$\ln (K_{s0}^{\circ}/\mathrm{mol}^2\ \mathrm{L}^{-2}) = 109.5581 - 183.0211\ (1/T/100\ \mathrm{K}) - 64.8370 \ln(T/100\ \mathrm{K}).$$

TABLE 42. The solubility of zinc carbonate in water

T/K	P_{CO_2}/bar (c_{CO_2}/mol L^{-1}) or pH	Zinc Carbonate Solubility c_{ZnCO_3}/mol L^{-1}	Method	Reference
Tentative values				
298.15	0.987	1.98×10^{-3}		
	0.00032[a]	1.64×10^{-4}		
Literature values				
288.15	0.00032[a]	8×10^{-5}	–	von Essen 1897[248, e]
(291.15)	1	5.6×10^{-5}	gravimetric	Haehnel 1924[249]
	56	6.7×10^{-3}	gravimetric	Haehnel 1924[249]
298.1	1	1.98×10^{-3}	calculated[c]	Kelley, Anderson 1935[255]
(298.15)	0.00032[a]	2.05×10^{-5}	titration	Piperaki, Hadjiioannou 1977[250]
(298.15)	0.00032	figure	calculated[d]	Grohmann 1976[251]
(298.15)	0.00032	figure	calculated[c]	Mann, Deutscher 1980[252]
298.15	0.00032[a]	1.64×10^{-4}	electromagnetic titration	Ageno, Valla 1911[253]
	0.3641	1.84×10^{-3}		
	0.5199	2.20×10^{-3}		
	0.7295	2.72×10^{-3}		
	0.9506	2.76×10^{-3}		
298.15	4.12 (0.1390)[b]	1.94×10^{-3}	titration[f]	Smith 1918[254]
	5.33 (0.1797)[b]	2.11×10^{-3}		
	7.64 (0.2579)[b]	2.42×10^{-3}		
	10.61 (0.3580)[b]	2.70×10^{-3}		
	12.16 (0.4103)[b]	2.78×10^{-3}		
	13.29 (0.4480)[b]	2.91×10^{-3}		
	19.73 (0.6657)[b]	3.17×10^{-3}		
298.15	20.65 (0.6969)[b]	3.19×10^{-3}	titration[f]	Smith[254]
	22.56 (0.7610)[b]	3.42×10^{-3}		
	40.61 (1.3701)[b]	4.45×10^{-3}		
298.15	0.00032 pH 6	1.05×10^{-3}	calculated[c]	Jaulmes, Brun 1965[204]
	pH 7	1.99×10^{-4}		
	pH 8	5.74×10^{-5}		
	pH 9	1.83×10^{-6}		
	pH 10	6.86×10^{-6}		
	pH 11	4.07×10^{-6}		
	pH 12	4.0×10^{-6}		
	pH 13	4.0×10^{-6}		
303.15	(0.1838)[b]	2.15×10^{-3}	titration[f]	Smith 1918[254]
	(0.3838)[b]	2.77×10^{-3}		
	(0.4038)[b]	2.86×10^{-3}		
	(0.4601)[b]	3.08×10^{-3}		
	(0.6064)[b]	3.24×10^{-3}		
	(0.6257)[b]	3.37×10^{-3}		
	(0.7470)[b]	3.52×10^{-3}		
	(0.8351)[b]	3.76×10^{-3}		
	(1.0840)[b]	3.39×10^{-3}		
	(1.1275)[b]	4.29×10^{-3}		

---

[a] Carbon dioxide partial pressure not reported.Assumed to be an air atmosphere which is about 0.00032 bar CO_2.

[b] Smith's experimentally determined carbonic acid concentration. Assuming it to represent the aqueous concentration of CO_2 the gas partial pressure was estimated at 298.15 K, but a reliable value of Henry's constant was not available to do the same calculation at 303.15 K.

[c] Calculated using thermodynamic data including carbonic acid dissociation constants.

[d] Calculations not explained in detail.

[e] Cited by Cantoni, Passamanik 1905[257] as from 1897 thesis, Geneva.

[f] Data in Seidel, Linke[6].

TABLE 43. The solubility product constant for zinc carbonate

T/K	Ionic Strength I/Electrolyte	Solubility Product K°_{s0}/mol^2 L^{-2}	K_{s0}/mol^2 L^{-2}	Reference
Tentative values				
298.15	0	1.46×10^{-10}		
323.15	0	9.02×10^{-11}		
373.15	0	1.59×10^{-11}		
423.15	0	1.5×10^{-12}		
473.15	0	1.0×10^{-13}		
523.15	0	6.2×10^{-15}		
573.15	0	3.5×10^{-16}		
Literature values				
291.15	0.57/Na_2CO_3,$NaNO_3$		2.6×10^{-8}	Zhukova, Rachinskii 1972[261]
293.15			1.45×10^{-11}	Sahli 1952[a]
298.1	0	9.98×10^{-11}		Kelly, Anderson 1935[255]
298.1	0	7.1×10^{-11}		Saegusa 1950[263]
298.15		8.7×10^{-10}		Ageno, Valla 1911[253]
298.15		2.1×10^{-11}		Smith 1918[254]
298.15		1.66×10^{-11}		Kelley, Anderson 1935[255,b]
298.15		1.6×10^{-11}		[c]
298.15	0.2/$NaClO_4$	1.61×10^{-11}	1.43×10^{-10}	Schindler, Reinert, Gamsjaeger 1969[260, f]
298.15	0	2×10^{-10}		Latimer 195 2[89]
298.15	0	1.2×10^{-10}		Egorov, Titova 196 2[262,e]
298.15	0	1.9×10^{-10}		Helgeson 1969[107]
298.15	0	4.5×10^{-11}		Krestov, Kobenin, Sokolov 1977[129]
298.15	0	1.19×10^{-10}		[g]
298.15	0	4.30×10^{-10}		[h]
323.15	0	8.91×10^{-11}		Helgeson 1969[107]
323.15	0	7.78×10^{-11}		Egorov, Titova 1962[262,d]
333.15	0	6.45×10^{-11}		Helgeson 1969[107]
333.15	0	6.6×10^{-11}		Egorov, Titova 1962[262,d]
373.15	0	1.3×10^{-11}		Helgeson 1969[107]
373.15	0	3.85×10^{-11}		Egorov, Titova 1962[262,d]
423.15	0	1.7×10^{-12}		Helgeson 1969[107]
473.15	0	1.3×10^{-13}		" " "
523.15	0	6.6×10^{-15}		" " "
573.15	0	3.0×10^{-16}		" " "

[a] Cited in Schindler *et al.*[260] as a dissertation, Bern, 1952.

[b] Recalculated from the data of Smith by the authors.

[c] Recalculated from the data of Smith by us. Used recent K_{a1} and K_{a2} values for H_2CO_3.

[d] Calculated from equation in the paper. The temperature range for the equation was not specified. Since no value in the paper at temperatures above 373 K was shown we assume this is the upper limit for the equation.

[e] Calculated from the equation in the paper (see d above). The author's report a value of 2.1×10^{-10} which may be a printing error.

[f] We were unable to duplicate this value from data in the paper.

[g] Calculated from Gibbs energy data in the NBS Tables, 1982[12] by us.

[h] Recalculation from data in Schindler *et al.*[260] and NBS Tables, 1982[12] by us to obtain a value of ΔG°_f for $ZnCO_3$(s) which was used to calculate K°_{s0}.

4.11.b. Cadmium Carbonate

$CdCO_3$ [513–78–9] Molecular weight 172.42
Otavite [37428–30–1]

Physical characteristics: Cadmium carbonate is a colorless hexagonal crystal with $Z = 6$, $a = 4.913 \times 10^{-10}$ m, $c = 16.24 \times 10^{-10}$ m, and a calculated density of 5.02×10^3 kg m^{-3}. The naturally occurring cadmium carbonate mineral is otavite.

The general comments in the first paragraph of the zinc carbonate evaluation above apply equally well to cadmium carbonate. Values of temperature, carbon dioxide partial pressure, pH and ionic strength need to be specified along with any solubility value.

Values of the solubility of cadmium carbonate in water and in aqueous electrolyte solutions are given in Tables 44 and 45. We have reservations about these values because the experimental conditions are not completely defined. We have assumed the Jaulmes and Brun[204] values are for air with the natural CO_2 content, but they do not say so. The Kelley and Anderson[255] value was calculated by them from their solubility product value which differs by several orders of magnitude from our tentative value. The results of Lake and Goodings[264] are not given here. Their graphically presented data are difficult to interpret because of a mislabelling.

TABLE 44. The solubility of cadmium carbonate in water

T/K	$P_{\mathrm{CO_2}}$/bar ($c_{\mathrm{CO_2}}$/mol L^{-1}) or pH	Cadmium solubility $c_{\mathrm{CdCO_3}}$/ol L^{-1}	Method	Reference
298.15	0.987	1.12×10^{-4}	Calc.	Kelley, Anderson 1935[255, a]
298.15	0.00032	4.18×10^{-5} to 1.57×10^{-7}	Calc.	Jaulmes, Brun 1965[204, b]

[a] Calculated from thermodynamic data. Value reported in mol kg^{-1}.

[b] Calculated from authors' equation which considered carbonate hydrolysis as a function of pH. Assumed to be for air containing normal amounts of carbon dioxide.

TABLE 45. The solubility of cadium carbonate in aqueous electrolyte solutions

T/K	Ionic strength I/Electrolyte	Carbon dioxide P/bar	Cadmium carbonate solubility c/mol L^{-1}	Reference
298.15	0.075/K2CO$_3$	0.00032	2.5×10^{-4}	Immewahr 1901[202, a]
298.15	3.0/NaClO$_4$	0.167 pH 4.26	4.90×10^{-2}	Gamsjaeger, Stuber, Schindler 1965[265].
		0.337 pH 4.11	4.96×10^{-2}	" "
		0.908 pH 3.91	4.84×10^{-2}	" "
298.15	0.27–12.6/CaCl2	?	7.0×10^{-4} to 1.623	Ben'yash 1964[259, b]
310.15	gastric fluid	?	7.71×10^{-4}	Wada, Iijima, Ono, Toyokawa 1972[121, c]
	intestinal fluid	?	1.33×10^{-7}	

[a] Calculated from emf measurement vs. a CdCl$_2$, KNO$_3$ half-cell with [Cd^{2+}] = 0.5 mol L^{-1}. System probably in equilibrium with air at 0.00032 bar CO$_2$.

[b] The solubility values are in mol kg^{-1}. The solid is a mixture of CaCO$_3$ and CdCO$_3$. There is no information about carbon dioxide partial pressure.

[c] These solutions may not have been saturated.

Until recently the most complete experimental study of the $CdCO_3(s) + CO_2(g) + H_2O$ system is that of Gamsjaeger, Stuber and Schindler[265]. They determined equilibrium constants at 298.15 K and ionic strengths of 0 and 3.0 NaClO$_4$ for the reactions below.

Reaction	Equilibrium constants I = O	I = 3.0
(1) $CdCO_3(s) + H_2O + CO_2(g) = Cd^{2+}(aq) + 2HCO_3^-(aq)$	3.16×10^{-10}	2.69×10^{-10}
(2) $CdCO_3(s) + 2H^+ = H_2O + CO_2(g) + Cd^{2+}(aq)$	1.38×10^6	2.95×10^6
(3) $CdCO_3(s) = Cd^{2+}(aq) + CO_3^{2-}(aq)$	1.00×10^{-12}	6.60×10^{-12}

Their value of K°_{s0}/mol^2 L^{-2} = 1.00×10^{-12} is smaller than the value of 6.18×10^{-12} calculated from Gibbs energy of formation data in the NBS Tables[12], but is confirmed by recent work of Stipp, Parks, Nordstrom and Leckie[392]. Using (H$^+$) = 1×10^{-7} and $P_{\mathrm{CO_2}} = 3.2 \times 10^{-4}$ atm gives a solubility in water 2.9×10^{-5} and 4.3×10^{-5} mol L^{-1} from equations (1) and (2), respectively.

A preprint of a paper under review by Stipp, Parks, Nordstrom and Lechie[392,a] was recently called to our attention. The paper contains an exhaustive literature search and evaluation of existing thermodynamic data on the components of the $Cd^{2+}(aq) + CO_2(aq, g) + H_2O$ system, as well as an exceedingly careful new experimental determination of the CdCO$_3$ solubility product at 278, 298 and 323 K (I < 0.1 mol L^{-1} KClO$_4$). The paper recommends new thermodynamic values for the formation of CdCO$_3$(s) (synthetic otavite) which are consistent with the CODATA key values[390]. For CaCO$_3$(s) at 209.15 K $\Delta G_f^\circ = -(647.7 \pm 0.6)$ kJ·mol^{-1}, $\Delta H_f^\circ = -(751.1 \pm 1.0)$ kJ·mol^{-1} and S0 = (109.1 ± 1.0) J K^{-1} mol^{-1}. The solubility product is pK°_{s0} = (12.1 ± 0.1) or $K^\circ_{s0} = 0.79 \times 10^{-12}$. We accept this as the tentative value in Table 46. The author's solubility product values at 278, 298 and 323 K are in Table 46.

A number of workers have calculated the ion product constant from thermodynamic data. Both Krestov, Kobenin, and Sokolov[129] and Egorov and Titova[262] have developed equations for K°_{s0} as a function of temperature between 273.15 and 373.13 K from thermodynamic data. They do not specify the source of all of the data they use. Only the K°_{s0} values at 298.15 K are given in Table 46. The equation of Krestov *et al*. gives values of similar magni-

TABLE 46. Solubility product constant of cadmium carbonate

T/K	Ionic strength I/Electrolyte	Solubility product K°_{s0} K_{s0}	Reference
Tentative value			
298.15	0	0.79×10^{-12}	Stipp *et al*., 199x[392]
Literature values			
From thermodynamic data			
298.15	0	1.82×10^{-14}	Kelley, Anderson 1935[255]
298.15	0	2.5×10^{-12}	Saegusa 1950[263]
298.15	0	5.2×10^{-12}	Latimer 1952[89]
298.15	0	5.1×10^{-12}	Egorov, Titova 1962[262,a]
298.15	0	1.00×10^{-12}	Gamsjaeger *et al*., 1965[262].
298.15	0	0.87×10^{-12}	Krestov, *et al*., 1977[129,a]
298.15	0	6.18×10^{-12}	NBS Tables 1982[12]
From experimental studies			
278.15	0.1/$KClO_4$	0.40×10^{-12}	Stipp *et al*.. 199x[392]
291.15	0.1/KNO_3	5.1×10^{-12}	Karnaukhov, *et al*., 1973[266]
298.15	3.0/$NaClO_4$	6.60×10^{-12}	Gamsjaeger *et al*., 1965[265]
298.15	0.1/$KClO_4$	0.79×10^{-12}	Stipp *et al*., 199x[392]
323.15	0.1/$KClO_4$	0.63×10^{-12}	Stipp *et al*., 199x[392]

[a] Authors give equations for K°_{s0} for the 273–373 K interval.

tude to the tentative value at 298 K. The Egorov and Titova equation gives a K°_{s0} value at 298.15 K 6.5 times larger than the tentative value. Their equation

$$\log K^\circ_{s0} = -28.06 + 619/(T/\mathrm{K}) + 6.22 \log (T/\mathrm{K}) - (2.35\times10^{-3})(T/\mathrm{K})$$

shows a shallow minimum in K°_{s0} values in the 273.15 to 373.15 K temperature interval, while the work of Stipp *et al*[393] shows a small maximum. Both imply a very small enthalpy of solution.

4.12. Zinc and Cadmium Oxalate

4.12.a. Zinc Oxalate

ZnC_2O_4 [547–68–2]	molecular weight 153.40
$ZnC_2O_4 \cdot 2H_2O$ [4255–07–6]	molecular weight 189.44
$ZnC_2O_4 \cdot H_2O$ [16788–40–2]	molecular weight 171.42

Physical characteristics: Anhydrous ZnC_2O_4 exists in α and β forms which have been characterized by Kondrashev *et al*.[386].

Deyrieux and Peneloux[268], who have prepared and characterized both α- and β-$FeC_2O_4 \cdot 2H_2O$, were able to prepare only the α-$ZnC_2O_4 \cdot 2H_2O$. They found its structure analogous to the monoclinic α-$FeC_2O_4 \cdot 2H_2O$, but do not give the cell measurements.

Experimental values of the solubility of zinc oxalate in water are given in Table 47. It is probable that the solid is the α-$ZnC_2O_4 \cdot 2H_2O$ in all cases. Agreement among the solubility values is poor. Early values derived from the conductivity measurements of Kohlrausch *et al*.[28,269] appear to be too small and are rejected. Kunschert[270] measured a solubility product value. He derived a solubility value from his experiment by taking into account $Zn(C_2O_4)_2^{2-}$(aq) and $Zn(C_2O_4)_3^{4-}$(aq) complex species. His result is also too small and is rejected. The results of Kohlrausch and of Kunschert are probably too small because it was not recognized at the time of their work that the predominant solution species is ZnC_2O_4 (aq). There is no modern evidence that the $Zn(C_2O_4)_3^{4-}$(aq) species is of importance.

The values of Scholder, Gadenne and Niemann[271], Osawa[272], and Clayton and Vosburgh[273] fit a consistent pattern. The value of Piperaki and Hadjiioannou[250] at an unspecified temperature fits the pattern of the other values at a temperature of about 296 K.

The solubility values of Scholder *et al*.[271], Osawa[272], and Clayton and Vosborgh[273] were treated by a linear regression to obtain the equation

$$\ln (c/\mathrm{mol\ L^{-1}}) = (9.3958 \pm 0.9916) - (53.9419 \pm 2.9263)/(T/100\ \mathrm{K})$$

with a standard error about the regression line of 2.5×10^{-6}. The tentative values in Table 47 were calculated from the equation.

The solubility product values are summarized in Table 48. The tentative value at 298.15 K, $K^\circ_{s0}/\mathrm{mol^2\ L^{-2}} = 1.38\times10^{-9}$, was calculated from Gibbs energy data in the NBS Tables[12]. The value agrees well with the value recalculated by Vosburgh and Beckman[274] from the work of Clayton and Vosburgh[273], and with the value given in the review of Zhuk[275]. There is no way to judge whether these

TABLE 47. The solubility of α-zinc oxalate dihydrate in water

T/K	Solubility 10^4c/mol L^{-1}	Reference
Tentative values		
283.15	0.64	
288.15	0.89	
293.15	1.23	
298.15	1.67	
Experimental values		
282.91	0.30	Kohlrausch, 1908[269]
291.07	0.338	" "
291.15	1.10	Scholder *et al.*, 1927[271]
293.15	1.2	Osawa, 1950[272]
"Room"	1.43	Piperaki and Hadjiioannou, 1977[250]
298.15	0.7[a]	Kunschert, 1904[270]
	1.685	Clayton and Vosburgh, 1937[273]
	1.67	" " " "
	2.99	Brzyska and Bubela, 1982[386]
299.30	0.377	Kohlrausch, 1908[269]

[a] Calculated by the author from his K_{s0} value taking into account complex formation. The author also recalculated a value of 0.77×10^{-4} mol. L^{-1} from earlier conductivity results of Kohlrausch *et al.*[28]

are independent values or relate back to the original Clayton and Vosburgh study.

Money and Davies[276] were the first to suggest the low conductivity of saturated zinc oxalate solutions is due to the predominance of the non-conducting $ZnC_2O_4(aq)$ species. Their work suggested $ZnC_2O_4(aq)$ and $Zn(C_2O_4)_2^{2-}(aq)$ were the only important solution species. The conclusion was supported by the study of Clayton and Vosburgh[273]. Rowlands and Monk[277] studied the $Zn^{2+} - C_2O_4^{2-}$ complexing by an extraction method. They combined their results with other literature values to obtain averages from which we obtain consecutive formation constants K_1 $(7.1 \pm 0.8) \times 10^4$ and K_2 $(3.2 \pm 1.5) \times 10^2$ at 298 K.

The literature on the solubility of $\alpha\text{-}ZnC_2O_4{\cdot}2H_2O$ in ternary aqueous systems is given in Table 5A. The ionic strength ranges are only rough estimates especially in cases where no weight per cent data were given in the paper.

4.12.b. Cadmium Oxalate

CdC_2O_4 [814–88–0] molecular weight 200.43
$CdC_2O_4{\cdot}3H_2O$ [20712–42–9] molecular weight 254.48

Physical characteristics: No information on the anhydrous salt was found. Bridle and Lomer[286] report $CdC_2O_4{\cdot}3H_2O$ is triclinic with $a = 7.36 \times 10^{-10}$ m, $b = 9.39 \times 10^{-10}$ m, $c = 9.06 \times 10^{-10}$m, $\alpha = 135°32'$, $\beta = 132°29'$, $\gamma = 68°22'$, and calculated density $= 2.73 \times 10^3$ kg m^{-3}.

The experimental solubility values are given in Table 49. Not all of the authors studied the composition of the solid, but those that did identified the trihydrate. Thus it is likely that the solid is the $CdC_2O_4{\cdot}3H_2O$ in all cases.

The results of Kohlrausch[269] by a conductivity method are probably too small because account was not taken of the nonconducting $CdC_2O_4(aq)$ species. The values of Babkin *et al.*[287,288] were at an undetermined room temperature. These values are rejected.

The tentative value at 298.15 K is the average of the seven experimental values. The average value is near the values reported by Clayton and Vosburgh[273] in 1937. Vosburgh and Beckman[274] imply their smaller value is possibly more accurate, but that is not borne out by subsequent work. We do not believe the difference in c/mol L^{-1} and m/mol kg^{-1} is significant in these dilute solutions.

Solubility product values are given in Table 50. The Clayton and Vosburgh values are defective because out-of-date activity coefficient data were used. Both Vosburgh and Beckman, and Larson and Tomsicek[289] recalculated the Clayton and Vosburgh data using more recent, but different, sources of activity coefficient data. The tentative value is based on the Gibbs energy data in the NBS[12] Tables and agrees well with the Vosburgh and Beckman recalculated value.

We do not know if these are independent values or not. It is not clear whether the Babkin[288] value is a new experimental value. It is the same value as given by Zhuk[275] from his literature survey. The value may be an average of the Vosburgh and Beckman, and the Larson and Tomsicek values.

Table 6A lists the above and other studies of the solubility of cadmium oxalate in aqueous systems. Some of these papers present only graphical data, and some present poorly interpreted data, for example solubility product values calculated without taking cadmium oxalate complex species in solution into account.

There have been a number of studies of the aqueous solution species $CdC_2O_4(aq)$, $Cd(C_2O_4)_2^{2-}(aq)$, $Cd(C_2O_4)_3^{4-}(aq)$ and $Cd_2(C_2O_4)^{2+}(aq)$. The paper of Olin and Wilmark[290] gives a good summary of the literature on the first three complexes. The data from their summary is in Table 51. Only Vosburgh and Beckman[274] discuss the possibility of the $Cd_2(C_2O_4)^{2+}(aq)$ species.

4.13. Zinc and Cadmium Cyanide

4.13.a. Zinc Cyanide

$Zn(CN)_2$ [557–21–1] molecular weight 117.42

Physical characteristics: Crystalline zinc cyanide is cubic with $Z = 2$ and $a = 5.91 \times 10^{-10}$ m. Its calculated density is 1.90×10^3 kg m^{-3}.

There are other several important equilibrium solids in addition to $Zn(CN)_2(s)$ in aqueous $Zn(CN)_2$ systems. The basic oxide $[Zn(CN)_2]_3{\cdot}ZnO$ is known and may be the equilibrium solid at certain pH's. The double salt $K_2Zn(CN)_4$ is the equilibrium solid in the KCN + $Zn(CN)_2$ + H_2O system at 298 K and aqueous KCN con-

TABLE 48. The solubility product of α-zinc oxalate dihydrate

T/K	I/Electrolyte	10^9K_{s0}/mol^{2}L^{-2}	Reference
Tentative value			
298.15	0	1.38 (K°_{s0})	
A. Experimental values			
298.15	0	4.6	Kunschert, 1904[270]
	0	2.47	Clayton, Vosburgh, 1937[273]
	0.02–0.33/$K^+(HC_2O_4^-,C_2O_42^-)$	(2.79–3.77)	" " " " "
	0	1.28[a]	Vosburgh, Beckman, 1940[274]
	?	1.35[b]	Zhuk, 1954[275]
	N0	8.0[c]	Lodzinska, Jablonski, Gornicki, 1965[278]
	1.5/$NaNO_3$	11.2[d]	" " " "
	3.0/$NaNO_3$	215.[d]	" " " "
	6.0/$NaNO_3$	436.[d]	" " " "
	9.0/$NaNO_3$	511.[d]	" " " "
	0	(0.6364 ± 0.0038)	Deyrieux, Peneloux, 1970[268]
Thermodynamic data			
298.15	0	1.38	NBS Tables, 1982[12]

[a] A recalculated value of the result of Clayton and Vosburgh[273]

[b] Source unknown, but probably based on Vosburgh *et al.*[273,274] data.

[c] Value repeated in Gornicki and Jablonski, 1957[281] as $I = 0$ value.

[d] Values repeated in Gornicki and Jablonski, 1957[281] with $NaNO_3$ clearly identified as the electrolyte.

TABLE 49. The solubility of cadmium oxalate trihydrate in water

T/K	10^4c/mol L^{-1}	Reference
Tentative value		
298.15	(3.01 ± 0.10)	
Experimental values		
284.28	1.11	Kohlrausch, 1908[269]
"Room"	1.2	Babkin *et al.*, 1955[287]
"Room"	1.5	Babkin, 1956[288]
291.15	1.96	Scholder *et al.*, 1927[271]
291.21	1.33, 1.32	Kohlrausch, 1908[269]
293.15	1.9	Osawa, 1950[272]
298.15	3.00, 2.97 (*m*)	Clayton and Vosburgh, 1937[273]
	2.89 (*m*)	Vosburgh and Beckman, 1940[274]
	3.09 (*m*)	Pesce and Lago, 1944[291]
	2.93	Barney *et al.*, 1951[292]
	3.20 (*m*)	Accascina and Schiavo, 1955[293]
	3.018	Bardhan and Aditya, 1955[294]
299.90	1.63	Kohlrausch, 1908[269]

Values with (m) are 10^4m/mol kg^{-1}

centrations between 6.7 and 41.1 weight per cent. It is a cubic crystal with $Z = 8$ and $a = 12.54 \times 10^{-10}$ m with an experimental density of 1.673×10^3 kg m^{-3}. The salt $Na_2Zn(CN)_4{\cdot}3H_2O$ is probably present in the NaCN + $Zn(CN)_2$ + H_2O system.

A summary of the solubility studies carried out before 1931 is in Table 52. The early work of Joannis[310] did not make clear the temperature or the added electrolyte concentration. Both Immerwahr[202] and Masaki[311] used emf methods which measured a mean ionic activity. Immerwahr's low value indicates that zinc cyanide complexing is important in the 0.05 M KCN solution. Masaki used a concentration cell method which depended on known solution properties of $ZnCl_2$ to obtain a zinc ion activity which is reported as a molar solubility in Seidell[6]. Pines[312] measured the Zn^{2+} concentration over freshly precipitated $Zn(CN)_2$ by a polarographic method. The good agreement between Masaki's and Pines' values does tempt one to identify the value as the stoichiometric solubility in water at 298.15 K, but the values should be used with caution.

Corbet[313] studied the KCN + $Zn(CN)_2$ + H_2O system at 298.15 K. He describes the $Zn(CN)_2$ solubility in water as a "trace". The values in Table 52 are the values for which he identified $Zn(CN)_2$ as the solid. Solutions at larger concentrations of $Zn(CN)_2$ and KCN are in equilibrium with solid $K_2Zn(CN)_4$ or KCN. Corbet was aware of the basic oxide from the earlier work of Joannis but he did not consider it in his study.

Solubility product values are in Table 53. Pines'[312] value in water was calculated by him from the polarographically determined Zn^{2+} concentration over freshly prepared $Zn(CN)_2$. He took no account of hydrolysis or complex formation, and simply calculated $K_{s0} = 4S^3$ using his Zn^{2+} concentration as the solubility. We judge the value to be too large by possibly several orders of magnitude. Persson[314] carried out the only modern day determination of the solubility product of $Zn(CN)_2$ in 3.0 molar

TABLE 50. The solubility product of cadmium oxalate trihydrate

T/K	I/Electrolyte	10^8K_{s0}/mol^2 L^{-2}	Reference
Tentative value			
298.15	0	1.42 (K_{s0}°)	
Experimental values			
291.15	0	1.53	Zhuk, 1954[275]
298.15	0	2.78, 3.2	Clayton and Vosburgh, 1937[273]
	0	1.44[a]	Vosburgh and Beckman, 1940[274]
	0	1.64[b]	Larson and Tomsicek, 1941[289]
	(0.02–0.33)/$K^+(HC_2O_4^-, C_2O_4^{2-})$	(3.03–4.12)	Clayton and Vosburgh, 1937[273]
	?	1.53	Babkin *et al.*, 1985[287]
	?	3.24	Fridman *et al.*, 1963[295]
	?	6.14	Lodzinska *et al.*, 1965[278]
	1/KNO_3	(33.9 ± 0.8)	Olin, Wilmark, 1983[290]
	3/$NaNO_3$	174.	Lodzinska *et al.*, 1965[278]
	6/$NaNO_3$	521.	" " "
Thermodynamic data			
	0	1.42	NBS Tables 1982[12]

[a] Recalculation of Clayton and Vosburgh value.
[b] Recalculation of Clayton and Vosburgh value.

TABLE 51. Cumulative formation constants of $Cd(C_2O_4)_n{}^{2(1-n)}$ (aq) for n = 1, 2 and 3. Based on Table in Olin and Wikmark[290]

T/K	I/Electrolyte	log β_1	log β_2	log β_3	Method	Reference
298.15	0	3.84	—	—	[a]	Vosburgh *et al.*, 1936[296], 1940[274]
—	0.25/$KClO_3$	2.05	4.55	5.15	[a]	Oncescu *et al.*, 1969[297]
298.15	1.0/KNO_3	2.66	4.29	5.00	[b]	Olin, Wikmark, 1983[290]
	1.0/KNO_3	3.20	4.57	5.53	[c]	Kanemura, Watters, 1967[298]
	1.0/$NaClO_4$	2.75	—	—	[a]	Bottari, 1975[299]
	1.0/$NaNO_3$	2.61	4.14	5.04	[d]	Schaap *et al.*, 1961[300]
	1.0/$NaNO_3$	2.61	4.11	5.06	[d]	McMasters *et al.*, 1962[301]
	1.5/KNO_3	2.72	4.16	5.14	[d]	Arevalo *et al.*, 1974[302]
	2.0/KNO_3	2.78	4.00	5.20	[d]	Dhuley *et al.*, 1975[303]
300.15	2.1/KNO_3	2.90	4.00	5.08	[d]	Khurana, Gupta, 1973[304]
298.15	?/$CdSO_4$	3.52	4.61	—	[b]	Ermolenko, 1975[305]

Methods: [a] potentiometric [b] solubility [c] acidimetric [d] polarography

TABLE 52. Solubility of zinc cyanide in water and in aqueous salt solutions

T/K	(c or m)/Electrolyte	c/mol L^{-1} or m/mol Kg^{-1} or a/activity	Method	Reference
288(?)	conc. $ZnSO_4$	0.01_7 (c)		Joannis, 1882[310]
	conc. $Zn(C_2H_3O_2)_2$	0.03_4 (c)		" "
298.15	0.05(c)/KCN	8.9×10^{-9} (a)	emf	Immerwahr, 1901[202]
298.15	0.403(m)/KCN	0.206 (m)		Corbet, 1926[313]
298.15	0.630(m)/KCN	0.305 (m)		" "
298.15	1.205(m)/KCN	0.688 (m)		" "
"Room "	water	4×10^{-5} (c)	polarograph	Pines, 1929[312]
291.15	water	4.49×10^{-5} (a)	emf	Masaki, 1931[311]

$NaClO_4$ at 298.15 K. He studied the system by potentiometric measurements using both zinc amalgam and glass electrodes vs. the Ag/AgCl electrode, taking great care to exclude oxygen. He reports values of K_{s0} and β_n for $n = 1,2,3$ and 4 in 3.0 m $NaClO_4$ at 298.15 K. In an earlier study Izatt, Christensen, Hansen and Watt[315] reported values of the cumulative formation constants β_2, β_3 and β_4 corrected to $I = 0$ at 298.15 K. They did not report a solubility product nor did they find evidence of the existence of $ZnCN^+(aq)$ in their system. The β values from the two papers are given in Table 54. Reference to earlier studies on zinc cyanide complex ion formation can be found in their papers and in Sillen and Martell[8].

TABLE 53. Solubility product constant of zinc cyanide

T/K	I/Electrolyte	K_{so}	Reference
"Room"	water	2.56×10^{-13}	Pines, 1929[312,a]
298.15	3.0/$NaC10_4$	$(3.3\pm1.3)x10^{-16}$	Persson, 1971[314]

[a] Calculated by Pines from solubility value in previous table by $4S^3$. Value probably too large.

TABLE 54. Cumulative formation constants, β_n, for $Zn(CN)_n{}^{2-n}$ in aqueous solution at 298.15 K

	Cumulative formative constants, β_n, at ionic strengths	
n	$I = 0$[a]	$I = 3.0/NaClO_4$[b]
1		$(2.2\pm0.5)\times10^5\ m^{-1}$
2	$(1.17\pm0.05)\times10^{11}\ m^{-2}$	$(1.06\pm0.06)\times10^{11}\ m^{-2}$
3	$(1.12\pm0.06)\times10^{16}\ m^{-3}$	$(4.8\pm0.5)\times10^{16}\ m^{-3}$
4	$(4.2\pm0.6)\times10^{19}\ m^{-4}$	$(3.7\pm0.8)\times10^{21}\ m^{-4}$

[a] Izatt *et al.*, 1965[315]
[b] Persson, 1971[314]

4.13.b. Cadmium Cyanide

$Cd(CN)_2$; [542–83–6] molecular weight 164.45

Physical characteristics: Solid cadmium cyanide is cubic with $Z = 2$ and $a = 6.33\times10^{-10}$ m. Its calculated density is 2.17×10^3 kg m^{-3}.

There are substances in addition to $Cd(CN)_2$ that may be important as equilibrium solids in contact with aqueous $Cd(CN)_2$. The basic oxide

$$[Cd(CN)_2]_2{\cdot}CdO{\cdot}5H_2O$$

is known and is probably the solid phase when $Cd(CN)_2$ is dissolved in water. The salt $K_2Cd(CN)_4$ is the equilibrium solid in the $KCN + Cd(CN)_2 + H_2O$ system at 298.15 K and aqueous KCN concentrations between 9.5 and 40.7 weight per cent. It is a cubic crystal with $Z = 8$ and $a = 12.87\times10^{-10}$ m with a calculated density of 1.836×10^3 kg m^{-3}. The salt $NaCd(CN)_3{\cdot}1.5H_2O$ may be important in $NaCN + Cd(CN)_2 + H_2O$ systems.

There is no definitive study on the solubility of cadmium cyanide in water and aqueous electrolyte solutions. Neither Pines[312] nor Persson[314], who reported solubility products for $Zn(CN)_2$, were able to obtain solubility product values for the more soluble $Cd(CN)_2$ in studies similar to those carried out for the zinc salt. Corbet[313] makes clear that $Cd(CN)_2$ is not the equilibrium solid even in the presence of traces of KCN.

Table 55 summarizes the solubility studies we have found. The solubility of $Cd(CN)_2$ in water reported by Joannis[310] is thought to be too large and is classed as doubtful. The values of Immerwahr[202] and Masaki[311] depend on emf measurements reversible to the Cd^{2+} ion. Immerwahr's small value in the presence of KCN indicates much of the cadmium is in complexed form. Masaki's value, although measured as an activity, is reported as the molar solubility in water (with an incorrect exponent) in Seidell[6]. Corbet's study of the $KCN + Cd(CN)_2 + H_2O$ system at 298.15 K may offer the most useful data. However, Corbet's lowest solubility value was measured in the presence of an undefined trace of KCN and is probably high as a water solubility value. We judge the solubility in water to be in the 0.023 to 0.0015 mol dm^{-3} range at 298.15 K. The Corbet solubility values in Table 55 are the values for which he identifies the solid as $Cd(CN)_2$. These values are footnoted with the comment that the solid is undoubtedly a basic cadmium cyanide. Joannis[310] earlier identified the basic oxide $[Cd(CN)_2)]_2{\cdot}CdO{\cdot}5H_2O$. Corbet found it impossible to prepare pure $Cd(CN)_2$ and identified his basic oxide as $[Cd(CN)_2]_3{\cdot}CdO{\cdot}4H_2O$. NBS Tables[12] list thermodynamic data on a basic oxide of the Joannis formula. Solutions of larger concentrations of KCN and $Cd(CN)_2$ are in equilibrium with solid $K_2Cd(CN)_4$ or KCN.

Persson[314] reports cumulative formation constants for cadmium cyanide complex ions in 3.0 M $NaC10_4$ at 298.15 K. They are $(4.2\pm0.1)\times10^5\ m^{-1}$, $(6.9\pm0.5)\times10^{10}\ m^{-2}$, $(5.3\pm0.3)\times10^{15}\ m^{-3}$, and $(1.6\pm0.4)\times10^{19} m^{-4}$ for β_1, β_2, β_3 and β_4, respectively.

4.14. Zinc and Cadmium Tetrathiocyanato Mercurate (2-)

4.14.a. Zinc Tetrathiocyanato Mercurate (2-)

$Zn[Hg(SCN)_4]$ [15318–77–1] molecular weight 498.31

Physical characteristics: Zinc tetrathiocyanato mercurate (2-) is tetragonal with $a = 7.823\times10^{-10}$ m and $c = 4.319\times10^{-10}$ m. The density and value of Z were not given.

Values of the experimental solubility of zinc tetrathiocyanato mercurate (2−) in water are in Table 56. The value of Robertson[316] is much larger than any other reported value. It is rejected. The values reported by

TABLE 55. The solubility of $Cd(CN)_2$ in water and aqueous electrolyte solution

T/K	c, m/Electrolyte	$Cd(CN)_2$ c or m	Method	Reference
288	water	0.103 (c)		Joannis, 1882[310]
298.15	0.66 (c)/KCN	7×10^{-5} (c)	emf	Immerwahr, 1901[202]
298.15	trace/KCN	0.022–0.023 (m)		Corbet, 1926[313]
	0.844 (m)/KCN	0.730 (m)		
	1.571 (m)/KCN	1.251 (m)		
	2.037 (m)/KCN	1.630 (m)		
291.2	water	1.51×10^{-3} (c)	emf	Masaki, 1931[311]

TABLE 56. Solubility of zinc tetrathiocyanato mercurate(2-) in water

T/K	10^4c/mol L^{-1}	Reference
288.15	48.	Robertson, 1907[316]
291.15	1.75	Swinarski and Czakis, 1955[319] Czakis and Swinarski, 1957[320]
“Room”	3.7	Kolthoff and Stenger, 1947[318]
“Room”	4.7±0.4[a]	Korenman *et al.*, 1956[317]
“Room”	4.9±0.4[a]	“ “ “
“Room”	6.7±0.3[a]	“ “ “
303.15	6.90	Czakis and Swinarski, 1957[320]
323.15	12.0	“ “ “
343.15	15.0	“ “ “

[a] The average of these values, $(5.4\pm1.1)\times10^{-4}$ mol L^{-1}, is on Fig. 3a.

Korenman, Sheyanova, and Potapova[317] at an undefined temperature were determined with the aid of anisotropic radioactive indicators. They used ^{65}Zn, ^{60}Co, and ^{115}Cd to obtain the three values in the table. Kolthoff and Stenger[318] report a value in water and several $K_2[Hg(SCN)_4]$ aqueous solutions at an undefined temperature. Swinarski and Czakis[319] report the solubility in water at 291.15 K, and in a later paper Czakis and Swinarski[320] repeat the 291.15 K value and report solubility values at three additional temperatures by a photometric method.

Figure 3a shows a problem with the data. The plot of ln(c/mol L^{-1}) vs. 1000/(T/K) is non-linear. The cadmium tetrathiocyanato mercurate(2−) is about 10 times more soluble than the zinc compound and shows a similar non-linear pattern. There are several possible explanations of the behavior. The solid may show a change in structure, with or without a change in hydration, near 298 K. There may have been temperature measurement and/or sampling errors especially at the higher temperature. The workers may have inadvertently had samples of different purity for the work reported in the two Czakis and Swinarzki papers. The values of Korenman *et al.*[317] and Kolthoff and Stenger[318] arbitrarily placed on the figure at temperatures of 293 K are of little help in resolving the problem.

Two lines are placed in Fig. 3a to suggest two possible explanations. The solid line is from a linear regression of the Czakis and Swinarski solubility values at 291.15, 323.15 and 343.15 K. It assumes the 308.15 K value is in error. The dotted line is arbitrarily drawn to suggest the 323 and 343 K values are too small because of temperature measurement or sampling errors. A third possibility is to put two straight lines through the data that intersect at a 1000/T value corresponding to near 298 K, suggesting a solid phase change at that point. These are all speculations. To obtain a better answer, the system will have to be restudied.

Swinarski and Czakis[319] report a solubility product calculated assuming $K_{s0}^{\circ} = S^2$ (S = solubility). No account was taken of ionic strength and activity effects.

The solubility responds to the common ion effect in dilute solutions. Kolthoff and Stenger[318] show the solubility decreases to 5×10^{-6} mol L^{-1} in the presence of 3×10^{-3} mol L^{-1} $K_2[Hg(SCN)_4]$, and Robertson[316] mentions the solubility is considerably reduced in the presence of zinc cation. Cuvelier[321] showed there is a seven fold increase in solubility as the ammonium chloride concentrations increase from 0.02 to 1.84 mol L^{-1} at room temperature. Czakis and Swinarski[320] show the solubility of $Zn[Hg(SCN)_4]$ at 291.15 K increases as ethanol is added to the aqueous solution. At 75 wt % ethanol the solubility is over five times its magnitude in water.

4.14.b. Cadmium Tetrathiocyanato Mercurate (2-)

$Cd[Hg(CNS)_4]$ [14878-23-0] molecular weight 545.33

Physical characteristics: The cadmium tetrathiocyanato mercurate (2−) is tetragonal with $a = 11.4403\times10^{-10}$ m, $c = 4.2043\times10^{-10}$ m, $Z = 2$, and a calculated density of 3.2746×10^3 kg m^{-3}.

Values of the experimental solubility of cadmium tetrathiocyanato mercurate (2−) in water are in Table 57. Korenman, Sheyanova, and Potapova[317] report, at an undefined room temperature, three values determined with the aid of anisotropic radioactive indicators ^{115}Cd, ^{60}Co, and ^{65}Zn. Swinarski and Czakis[319] report the solubility in

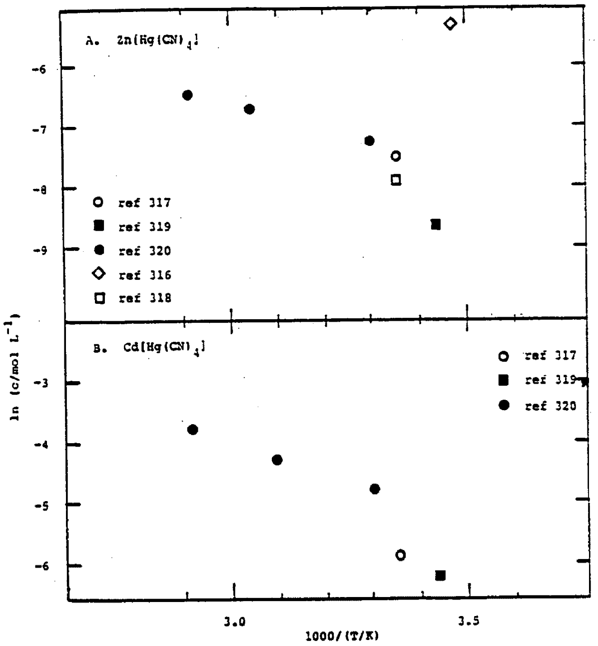

FIG 3. a. Solubility of $Zn[Hg(CN)_4]$ in water, 288–343 K.
b. Solubility of $Cd[Hg(CN)_4]$ in water, 291–343 K.
$\ln (c/\mathrm{mol\ L^{-1}})$ vs. $1000/(T/K)$

TABLE 57. The solubility of cadmium tetrathiocyanato mercurate(2−) in water

T/K	$10^3c/\mathrm{mol\ L^{-1}}$	Reference
291.15	1.9	Swinarski and Czakis, 1955[319], 1957[320]
"Room"	4.0 ± 0.5[a]	Korenman *et al.*, 1956[317]
"Room"	3.3 ± 0.3[a]	" " "
"Room"	1.1 ± 0.1[a]	" " "
303.15	8.26	Czakis and Swinarski, 1957[320]
323.15	13.8	" " " "
343.15	23.0	" " " "

[a] Av. value of $(2.8 \pm 1.5)\times10^{-3}$ mol L^{-1} shown in Fig. 3b.

water at 291.15 K, and in a later paper they repeat the 291.15 K value and report solubility values at three additional temperatures by a photometric method[320].

Figure 3b shows that although the cadmium salt is about ten times more soluble than the zinc salt, the $\ln(c/\mathrm{mol\ L^{-1}})$ vs $1000/(T/K)$ plots show a similar pattern. The same speculations made about the zinc salt data can be made about the cadmium salt data. The temperature coefficient of the solubility is in doubt and needs to be restudied. Swinarski and Cyakis[319] calculated a solubility product by squaring the stoichiometric solubility at 291.15 K.

4.15. Zinc and Cadmium Ferro- and Ferricyanides [hexakis(cyano-C) ferrate(3-) and (4-)]

4.15.a. Zinc Ferro- and Ferricycnaides

$Zn_2[Fe(CN)_6]$ [14883–46–6] molecular weight 342.73
$Zn_2[Fe(CN)_6]\cdot2H_2O$ [29730–24–3]
molecular weight 378.76
$Zn_2[Fe(CN)_6]\cdot2.5\ H_2O$ [not found]
molecular weight 387.77
$Zn_3[Fe(CN)_6]_2$ [15320–55–5] molecular weight 620.03
$Zn_3[Fe(CN)_6]_2\cdot12H_2O$ [not found]
molecular weight 836.26
$Zn_3[Fe(CN)_6]_2\cdot14H_2O$ [91947–27–2]
molecular weight 872.29

Physical characteristics: Zinc ferrocyanide. Kuznetsov *et al.*[322] report powder patterns of less than cubic symmetry for both $Zn_2[Fe(CN)_6]$ and its dihydrate. Cola and Valentini[323] report both the anhydrous salt and the 2.5 water hydrate to have identical powder patterns. They identified the crystals as orthorhombic with $Z = 4$, a, b and $c = 11.50$, 13,167 and 9.89×10^{-10} m, respectively, and a calculated density of 1.73×10^3 kg m^{-3}. Siebert *et al.*[324] report the dihydrate is hexagonal with $Z = 1$, $a = 7.598\times10^{-10}$ m, $c = 5.756\times10^{-10}$ m, and a calculated density of 2.18×10^3 kg m^{-3}.

Zinc ferricyanide. Weiser *et al.*[325] and Van Bever[326] found anhydrous $Zn_3[Fe(CN)_6]_2$ to be face centered cubic with $a = 10.38\times10^{-10}$ m from which we calculate a density of 1.84×10^3 kg m^{-3}. Cola and Valentini[323] report the material to be monoclinic with $Z = 4$, a, b and $c = 10.95$, 13.16 and 18.12×10^{-10} m, respectively, and a calculated density of 1.58×10^3 kg m^{-3}. Siebert and Jentsch[327] report a rhombohedral form with $a = 13.17\times10^{-10}$ m, $\alpha = 57.15°$, and $Z = 2$. The rhombohedral form appears to be stable and non-hygroscopic, but when it is dampened with water it transforms to the cubic form.

No crystallographic information was found for the 12 water hydrate, but Garnier *et al.*[328] report an unspecified hydrate of X moles of water which they later [329] identified as a cubic 14 water hydrate with $a = 10.34\times10^{-10}$ m, $Z = 4/3$, and a calculated density of 1.74×10^3 kg m^{-3}. It is possible that the dodecahydrate was misidentified and was really the tetradecahydrate.

Solubility data are reported for mixed ferrocyanides like $K_2Zn_3[Fe(CN)_6]_2$ [15245–11–1], $K_2Zn[Fe(CN)_6]$ [15320–39–5], $Na_2Zn[Fe(CN)_6]$ [88560–56–9], $(NH_4)_2Zn[Fe(CN)_6]$ [79957–73–6], and $(NH_4)_2Zn_3[Fe(CN)_6]_2$ [79957–72–5].

The solubility of zinc ferrocyanide has been measured by five different methods by Tananaev *et al.*[330] and Basinski and co-workers[331,332,333].The conductivity method of Basinski *et al.*[332] appears to give a low result. The other four values were averaged and the result given in Table 58 as a recommended value. The authors do not discuss hydration of the solid, but the work of Rock and Powell[334] strongly suggests the solid is the dihydrate.

Values of the zinc ferrocyanide dihydrate solubility product constant are given in Table 59. Agreement

TABLE 58. The solubility of zinc ferrocyanide and zinc ferricyanide in water

T/K	Solubility c/mol L^{-1}	Method	Reference
		Zinc ferrocyanide; $Zn_2[Fe(CN)_6]$	
Recommended value			
298.15	$(9.7 \pm 1.7) \times 10^{-6}$		
Experimental values			
293.15	[a]		Dyulgerova, Zakharov, Songina 1983[337]
298.15	7.4×10^{-6}	phosphate	Tananaev, Glushkova, Seifer 1956[330, f]
	9.8×10^{-6}	colorimetric	Basinski, Mucha 1960[331, b]
	11.4×10^{-6}	polarography	" " " "
	3.95×10^{-6}	conductivity	Basinski, Szymanski, Bebnista 1961[332]
	$(10.4 \pm 0.9) \times 10^{-6}$	tracer	Basinski, Szymanski, Bebnista 1961[333]
		Zinc ferricyanide; $Zn_3[Fe(CN)_6]_2$	
Experimental values			
289.15	1.24×10^{-4}	iodometric	Cuta 1929[338, c,d]
	$(1.65 \pm 0.05) \times 10^{-4}$	colorimetric	Grieb, Cone 1950[336, e]

[a] No solubility value for water. Do report solubilities in 0.1 and 0.5 mol L^{-1} NH_4OAc, H_2SO_4, and NH_3.

[b] Also report solubility data in dilute HCl and HNO3 (pH = 1.4).

[c] Solubility value in question. Paper says solubility is 0.770 g or 1.24×10^{-4} mol L^{-1}; 0.770 g L^{-1} is $1.24 \times 10-3$ mol L^{-1}. Cuta identified the solid as the dodecahydrate and had evidence it may dehydrate at about 343 K.

[d] Paper also reports solubilities in solutions saturated at room temperature with 12 different electrolytes. Solubilities in mol kg^{-1} at 289 K and in "hot" (348–353 K) water.

[e] Data appear in Seidell-Linke[6].

TABLE 59. The solubility product constant of zinc ferrocyanide dihydrate $Zn_2[Fe(CN)_6].2H_2O$

T/K	Ionic strength I/Electrolyte	Solubility product K_{s0}°	K_{s0}	Reference
Recommended value				
298.15	0	1.9×10^{-16}		
Literature values				
298.15			4.1×10^{-16}	Tananaev, Glushkova, Seifer 1956[330]
298.15			6.0×10^{-15}	Basinski and Mucha 1960[331]
298.15		2.1×10^{-16}		Rock, Powell 1964[334]
298.15		1.94×10^{-16}		NBS Tables 1982[12, a]

[a] Calculated for the process $Zn_2[Fe(CN)_6].2H_2O(s) = 2\,Zn^{2+}\,(aq) + [Fe(CN)_6]^{4-}\,(aq) + 2H_2O$.

among several workers is good. We recommend the value calculated from Gibbs energy of formation values from the NBS Tables[12]. The value is very near to the value of Rock and Powell[334] who confirmed the solid is the dihydrate. We cannot tell if the values are linked since we do not know the data source of the NBS Tables. We were unable to obtain the paper of Krleza *et al.*[335] which according to the abstract may contain a value of the solubility product constant.

Grieb and Cone[336] report a solubility of 1.2×10^{-14} mol L^{-1} for $K_2Zn_3[Fe(CN)_6]_2$ at 298.15 K from electrode potential measurements and a comparative calculation method that depends on the solubility of $Zn_3[Fe(CN)_6]_2$. The solubilities of other mixed zinc-other cation ferrocyanides were measured in the presence of electrolytes with a common ion at 293 ± 1 K by Dyulgerova, Zakharov and Songina[337].

Cuta[338] reports solid zinc ferricyanide is a dodecahydrate. The solubility measurements of Cuta and of Grieb and Cone appear to agree well. However, Cuta's value is in question because he gives two measures of the solubility which do not agree. His value of 0.770 g L^{-1} gives 1.24×10^{-3} mol L^{-1} which is ten times larger than the value in the paper. Although it may be only a decimal error (0.077 ?), for the present we suggest the use of the Grieb and Cone value.

4.15.b. Cadmium Ferro-and Ferricyanides [hexakis(cyano-C) Ferrate(3-) and (4-)]

$Cd_2[Fe(CN)_6]$ [13755–33–4] molecular weight 436.77
$Cd_2[Fe(CN)_6]\cdot 7H_2O$ [not found] molecular weight 562.88
$Cd_3[Fe(CN)_6]_2$ [15612–87–0] molecular weight 761.14

Physical characteristics: Cadmium ferrocyanide. Kuznetsov *et al.*[322] report powder patterns of less than cubic symmetry for both $Cd_2[Fe(CN)_6]$ and its dihydrate. Siebert *et al.*[324], report the crystal is trigonal (hexagonal) with $Z = 1$, a and $c = 6.35$ and 6.361×10^{-10} m, respectively, and a calculated density of 3.28×10^3 kg m^{-3}. Cola *et al.*[339] give powder patterns for 1.5, 4 and 9 water hydrates. They report a cubic monohydrate $Cd_{1.9}H_{0.2}[Fe(CN)_6]\cdot H_2O$ with $a = 15.50 \times 10^{-10}$ m, $Z = 16$ and a calculated density of 3.17×10^3 kg m^{-3}. No structural information was found for the heptahydrate.

Cadmium ferricyanide. Van Bever[326] reports cadmium ferricyanide is cubic with $a = 10.38 \times 10^{-10}$ m, and $Z = 2$, from which a density of 2.09×10^3 kg m^{-3} can be calculated. Weiser *et al.*[325] and Cola *et al.*[323] confirm the structure.

Table 60 lists the values of the solubility of $Cd_2[Fe(CN)_6]$ in water. The tentative value at 298.15 K of $(5.1 \pm 1.7) \times 10^{-6}$ mol L^{-1} is the average of the results of Tananaev *et al.*[330], Basinski and Poczopko[340], and Basinski and Szymanski[341]. It is possible that the Basinski and Poczopko value is the average of the 293.15 K values of Balinski and Ledzinska[342] which would make the result more uncertain. The 298.15 K value reported by Bellomo *et al.*[343] from a conductivity measurement is over three times larger than the other values and was not used. Their values at 308.15 and 318.15 K may also be too large and should be used with caution. Although Bellomo *et al.* carried out their conductivity measurements on oxygen- and carbon dioxide-free saturated solutions, small amounts of a highly conducting impurity can lead to high results. There is no convincing evidence this was a problem except the relatively good agreement of the other three values at 298.15 K.

Karnavkhov *et al.*[344], Basinski and co-workers[340,341,342], Tananaev *et al.*[330], Rock and Powell[334], and Bellomo *et al.*[343] report values of the solubility product, K°_{s0}. Basinski and co-workers and Bellomo *et al.* obtained $K_{s0} = 4\ s^3$ which assumes an ideal solution with no hydrolysis or association. Probably the work of Rock and Powell[334] reports the most carefully done experiment. Rock and Powell identified the solid as the heptahydrate, and we have specified it as the equilibrium solid in Table 61. However, Cola *et al.*[339] show a variable hydration of the solid depending on the conditions of precipitation. Thus, the nature of the solid is not fully settled. Krleza *et al.*[335] may also report a solubility product value, but their paper was not available to us.

Mixed cation ferrocyanides with cadmium are known. Bellomo *et al.*[343] report solubilities of 3.5×10^{-6}, 6.1×10^{-6} and 6.9×10^{-6} mol L^{-1} at temperatures of 298.15, 308.15 and 318.15 K respectively for $K_{12}Cd_8(Fe(CN)_6]_7$.

Only two papers were found on the solubility of cadmium ferricyanide. Piperaki and Hadjiioannou[250] report a room temperature value in water (see Table 60), and King[345] reports solubility values in aqueous electrolyte solution, but no value for pure water. King found evidence the solid is hydrated, but he did not determine the degree of hydration. No solubility product values were found.

TABLE 60. The solubility of cadmium ferrocyanide and cadmium ferricyanide in water

T/K	Solubility 10^6c/mol L^{-1}	Method	Reference
		Cadium ferrocyanide; $Cd_2[Fe(CN)_6]$	
Tentative value			
298.15	(5.1 ± 1.7)		
Literature values			
293.15	10.9	Colorimetry (in light)	Basinski, Ledzinska 1957[342]
	6.98	Colorimetry (in dark)	" " " "
	6.30	Polarography	" " " "
298.15	3.2	Gravimetric	Tananaev, Glushkova, Seifer 1956[330a]
	6.62	Calculated	Basinski, Poczopko 1958[340]
	5.35	Conductivity	Basinski, Szymanski 1958[341]
	20.7	Conductivity	Bellomo, DeMarco, Casale 1972[343]
308.15	47.6	"	" " "
318.15	48.2	"	" " "
		Cadmium ferricyanide; Cd3[Fe(CN)6]2	
"Room"	44.	Catalytic titration	Piperaki, Hadjiioannou 1977[250]
273.15 – 320.15	[b]		King 1949[345, a]

[a] Data appear in Siedell-Linke[6].

[b] No value in water, but solubility data for aqueous solutions containing ClO_4^-, Cl^-, and H^+.

TABLE 61. The solubility product constant of cadmium ferrocyanide heptahydrate, $Cd_2[Fe(CN)_6]\cdot 7H_2O$

T/K	Ionic strength I/Electrolyte	Solubility product K°_{s0}	K_{s0}	Reference
Tentative value				
298.15	0	3.6×10^{-18}		[a]
Literature values				
291.15	0.1/KNO3		2.3×10^{-17}	Karnaukhov, Grinevich, Skobets 1973[344]
293.15	/		1.17×10^{-15}	Basinski, Ledzinska 1957[242, b]
298.15			3.2×10^{-17}	Tananaev, Glushkova, Seifer 1956[330]
298.15	0	9.62×10^{-16}		Basinski, Poczopko 1957[340]
			6.1×10^{-16}	Basinski, Szymanski 1958[341]
	0	4.2×10^{-18}		Rock, Powell 1964[334]
	0(?)	3.6×10^{-14}		Bellomo, DeMarco, Casale 1972[343]
308.15	0(?)	4.3×10^{-13}		" " " "
318.15	0(?)	4.5×10^{-13}		" " " "

[a] Tentative value calculated from Gibbs energy of formation data in NBS Tables[12] for $Cd_2[Fe(CN)_6]\cdot 7H_2O(s) = 2Cd^{2+}(aq) + Fe(CN)_6^{4-}(aq) + 7 H_2O$.

[b] The value is an average of two values calculated from the authors' solubility in water values by a colorimetric and a polarographic method using $4s^3$ (see preceding table).

5. The Solubilities or Solubility Products of Some Other Sparingly Soluble Zinc and Cadmium Salts. Annotated Bibliography

Table 62 lists the solubility, solubility product, solution species and/or solid state species of additional sparingly soluble zinc and cadmium salts. There are data on salts of zinc or cadmium with about 35 anions. A number of weak acid organic anions have been included. We have tried to present an especially complete coverage of the literature from 1950 through 1991. Many data from earlier papers are also included.

Not enough information is available to classify these data as recommended, tentative or doubtful. We assume most of the data should be classed as tentative. The compounds containing weak acid anions may form mixed oxide or hydroxide solids whose composition depends on pH. Many such systems have not been studied in adequate detail.

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium

Substance	T/K	Solubility or solubility product	Comments/Reference
Zinc chlorite	274.15	51.4 g L^{-1}	Methods of preparing the Zn and Cd dihydrates are given. The solubility was determined at eight temperatures. The sat. soln. was analyzed for both cation and anion. The solubility values are the average of four values, two from cation analysis and two from anion analysis. The values appear to be for g of the dihydrate, $M(C10_2)_2$ $2H_2O$, rather than for the anhydrous salts. The cadmium salt shows an increase in solubility near 323 K that may indicate a change in hydration of the solid. Levi, Curti, 1956[346].
$Zn(C10_2)_2·2H_2O$	283.15	58.1 "	
	293.15	64.8 "	
	303.15	72.8 "	
	313.15	79.9 "	
	323.15	87.8 "	
	333.15	95.7 "	
	343.15	103.9 "	
Cadmium chlorite	274.15	48.9 g L^{-1}	
$Cd(C10_2)_2·2H_2O$	283.15	57.8 "	
	293.15	66.7 "	
	303.15	77.1 "	
	313.15	86.9 "	
	323.15	102.1 "	
	333.15	117.0 "	
	343.15	142.7 "	
Zinc chloride hydroxide			
$ZnCl_{0.3}(OH)_{1.7}$	298.15	$K_{s0} = 1.2 \times 10^{-15}$	Titration method used. Feitknecht, Haberli, 1950[347].
$ZnCl_{0.4}(OH)_{1.6}$	298.15	$K_{s0} = 6\times 10^{-15}$	
$Zn_2Cl(OH)_3$[12381–00–9]			
as $ZnCl_{0.5}(OH)_{1.5}$	298.15	$K_{s0} = 4.0 \times 10^{-14}$	Potentiometric method used. Aksel'rud, Spivakovskii, 1958[348].
as $Zn_2Cl(OH)_3$	298.15	$K_{s0} = 1.6 \times 10^{-27}$	
	298.15	$K^{\circ}_{s0} = 1.57 \times 10^{-27}$	Calculated by us from Gibbs energy data in NBS Tables[12].
	298.15	Calculated graphs.	Used literature equilibrium constants to show that at $f_{CO_2} = 10^{-3.5}$ in the presence of aqueous Cl^- and SO_4^{2-} the compound limits Zn^{2+} solubility only at low sulfate ion activity. The solid is very soluble in acid solution. Mann, Deutscher, 1980[252].
Cadmium chloride hydroxide CdCl(OH) [14031–46–9]	298.15	$K_{s0} = 2 \times 10^{-11}$	Five solids were identified from a study of $CdCl_2$ + NaOH solutions. K_{so} calculated from analysis of solutions over solid. The solids formed and their crystal structues are discussed. Feitknecht, Gerber, 1937[350,351].
Zinc hydroxide perchlorate $Zn_4ClO_4(OH)_7$ [118956–02–8]	298.15	$K_{s0} = 3.84 \times 10^{-16}$	The solubilization reaction is formulated as $Zn(ClO_4)_{1/4}(OH)_{7/4}(s) = Zn^{2+}(aq) + (1/4)ClO_4^-(aq) + (7/4)OH^-(aq)$ The Gibbs energy, enthalpy and entropy of formation of $Zn(ClO_4)_{1/4}(OH)_{7/4}(s)$ are -512.16, 621.08, and 0.10157 (kJ) Gomez de Aguero, Ramirez Garcia, Garcia Martinez, Guerrero Laverat, 1988 [349].
Periodic acid (H_5IO_6), Cadmium salts Cd_2HIO_6	298.15	$K_{s0} = 1.5 \times 10^{-21}$ at $I = 6.24 \times 10^{-3}$.	Solubility product reaction is $0.5Cd_2HIO_6(s)$ + $1.5H_2O = Cd^{2+} + 1.5OH^- + 0.5H_4IO_6^-$.

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium — Continued

Substance	T/K	Solubility or solubility product	Comments/Reference
$Cd_2HIO_6 \cdot 1.25H_2O$ [64265–91–4]		$K^\circ_{s0} = 1.0 \times 10^{-21}$	
$Cd_5(IO_6)_2$ [77308–33–9]	298.15	$K_{s0} = 2.0 \times 10^{-22}$ $K^\circ_{s0} = 1.26 \times 10^{-22}$	Solubility product reaction is $0.2Cd_5(IO_6)_2(s) + 1.6H_2O = Cd^{2+} + 1.60H^- + 0.4H_4IO_6^-$ Potentiometric method used to determine value for Cd_2HIO_6, which is the solid at pH <3; the $Cd_2(IO_6)_2$ value was estimated. It appears to exist at the higher pH's. Author states Cd_2HIO_6 is anhydrous. Nasanen, 1955[352].
Zinc hydroxide sulfate $Zn_4SO_4(OH)_6$ [12027–98–4] as $ZnSO_4 \cdot 3Zn(OH)_2$	298.15 348.15	$K_{s0} = 2.51 \times 10^{-56}$ $K_{s0} = 6.31 \times 10^{-58}$	The 348 K value determined by a potentiometric method. The 298 K value calculated from literature data. Author states the solid is unstable in dilute soutions and converts to $Zn(OH)_2$. Dobrokhotov, 1954[353]. Potentiometric titration of $ZnSO_4$ + NaOH. Solid the hydroxide at $ZnSO_4$ about 5×10^{-4} mol L^{-1}, sulfate hydroxide at $ZnSO_4$ $>7.4 \times 10^{-3}$ mol L^{-1}. Hagisawa, 1939[354].
	299.65	$K_{s0} = 2 \times 10^{-17}$(?)	Result of a $ZnSO_4$ = NaOH titration. Authors state the solid is the sulfate hydroxide, but the value appears to be for $Zn(OH)_2$ and they compare it with $Zn(OH)_2$ values. Quimby, McCune, 1957[225].
	353	0.4 g L^{-1}	$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ precipitaes in a lime slurry at 70–80 °C. Sharma, 1990 [395].
as $Zn(SO_4)_{0.25}(OH)_{1.5}$	298.15	Calculated solubility figures. Used $pK_{s0} = 13.9$.	pK_{sO} value is Dobrokhotov's value (above). Authors calculated Zn ion activity for CO_2 fugacity of $10^{-3.5}$ and solutions containing OH^-, Cl^- and SO_4^{2-}. The compound is exceedingly soluble in acid solutions. Mann, Deutscher, 1980[252].
Zinc sulfate $ZnSO_4$ [7733–02–0]	298.15	$ZnSO_4$ solubility decreases 3.512 *m* to 0.011 *m* as H_2SO_4 conc. inc. 0 to 39.517 m.	Study of $ZnSO_4 + H_2SO_4 + H_2O$ system 278.15, 288.15, and 298.15 K. In water the solid phase is $ZnSO_4 \cdot 7H_2O$ [7446–20–0], and in H_2SO_4 the solid is $ZnSO_4$ H_2O [7446–19–7]. Pieniazek, Milewska, Masztalerz, 1982[355].
Sodium chloride cadmium sulfate double salt $NaCl \cdot CdSO_4 \cdot 5H_2O$	298	2.491 mol/*k*g	The compound has been isolated and identified in the 2NaCl + $CdSO_4 = Na_2SO_4 + CdCl_2 + H_2O$ system. Rumyantsev and Charykov, 1989 [393].
(Ca, Zn) hydroxyapatite $(Ca,Zn)_{10}(OH)_2(PO_4)_6$	310		Solid solutions of calcium and zinc hydroxyapatite are formed from aqueous solution. A decrease in solubility occurs with increase in zinc content in the 5.0 to 7.5 pH range. The authors believe this indicates zinc incorporation increases the compactness of the apatite structure. Abstract only available) Chickerur, Dash, Nagak and Padhy, 1989 [398].
Zinc potassium phytate $Zn_4K_3[C_6H_6(PO_4)_5(HPO_4)]$ [97726–59–8]	298.15	$pK_s = 30.4$	$K_s = [Zn^{2+}]^4[K^+]^3[Phy^{11-}]$ Calculated from data obtained in a calorimetric study and knowledge of the ionization constants of phytic acid [83–86–3]. Evans, Marini, Martin, 1983[356].
Zinc ammonium phosphate $ZnNH_4PO_4$ [15006–70–9]	283.15	0.762×10^{-4} mol L^{-1}	Solubility determined by gravimetric analysis. Artmann 1915[357].
	290.65	0.813×10^{-4} "	
	boiling temp.	1.26×10^{-4} "	
	293.15	0.84×10^{-4} "	State compound water-insoluble but give no quantitative data. Travers, Perron, 1924[358], Vol'fkovich, Remen, 1955[359].

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium — Continued

Substance	T/K	Solubility or solubility product	Comments/Reference
Zinc hydroxide carbonate	298.15	$K_{s0}^{\circ} = 3.8 \times 10^{-15}$	Value from a solubility and pH study. Sahli, 1952[360]
$Zn(CO_3)_{0.36}(OH)_{1.28}$ [51839–25–9]			Value quoted in Sillen and Martel, 1964–71 [8].
$Zn_5(OH)_6(CO_3)_2$ or Hydrozincite [12122–17–7]	298.15	$K_{s0}^{\circ} = 2.0 \times 10^{-15}$ $I = 0.2$ mol L^{-1}	Sahli's value as given by Schindler, Reinert and Gamsjager, 1969 [260].
	298.15	log K = −9.417 0.040 (I = 0.2) −9.199 0.050 (I = 0)	$0.2Zn_5(OH)_6(CO_3)_2(s) + 2H^+ = Zn^{2+} + 0.4CO_2(g) + 1.6H_2O$
		−5.743 (I = 0.2) −6.433 (I = 0)	$0.2Zn_5(OH)_6(CO_3)_2(s) + 1.6CO_2(g) + 0.4H_2O = Zn^{2+} + 2HCO_3^-$
		−14.011 (I = 0.2) 0.2 −14.859 (I = 0)	$Zn_5(OH)_6(CO_3)_2(s) = Zn^{2+}(aq) + 1.2OH^-(aq) + 0.4CO_3(aq)$
			Schindler, Reinert and Gamsjager, 1969 [260].
		298 (?)	A study of the solubility of zinc at low concentration in basic solutions of 0.002 mol L^{-1} total dissolved CO_2 as a function of pH. pH < 8.2 crystalline hydrozincite forms, pH 8.2–10.5 poorly crystalline hydrozincate forms, and pH > 10.5 ZnO forms. The minimum dissolved zinc concetration was about 5×10^{-7} mol L^{-1} at pH 9.26 after 24 hours. Paulson. Benjamin and Ferguson, 1989 [394].
Cadmium stearate $Cd[CH_3(CH_2)_{16}CO_2]_2$ [2223–93–0]	310.15	6.4×10^{-4} mol L^{-1} (gastric juice, pH = 1.47) 1.93×10^{-5} mol L^{-1} (intestinal juice, pH = 8.20)	Cd determined in the supernatant liquid by atomic absorption. Data for several Cd pigments also given. Wada, Iijima, Ono, Toyokawa, 1972[121].
Zinc malonate $ZnCH_2C_2O_4 \cdot 3H_2O$ [94649–52–2]	298.15	35.1540 g L^{-1} 0.210 mol L^{-1}	Preparation and properties of zinc alkanedicarboxylates. In addition to solubility values the paper contains results of study of thermogravimetric decomposition and IR spectra of solids. In addition to salts listed here results are given for the zinc oxalate (see zinc oxalate section of this paper). Brzyska, Bubela, 1982[361].
Zinc succinate $Zn(CH_2)_2C_2O_4$	298.15	1.9954 g L^{-1} 0.0110 mol L^{-1} [6228–53–1]	
Zinc glutarate $Zn(CH_2)_3C_2O_4$ [6426–46–6]	298.15	16.1230 g L^{-1} 0.0825 mol L^{-1}	
Zinc adipinate $Zn(CH_2)_4C_2O_4$ [3446–35–6]	298.15	0.7601 g L^{-1} 0.00363 mol L^{-1}	
Zinc pimelinate $Zn(CH_2)_5C_2O_4$ [61810–62–6]	298.15	0.8804 g L^{-1} 0.00394 mol L^{-1}	
Zinc suberate $Zn(CH_2)_6C_2O_4$ [85561–38–2]	298.15	0.5343 g L^{-1} 0.00225 mol L^{-1}	
Zinc cyanamide $ZnCN_2$ [20654–08–4]	298.15	$pK_{s0} = 14.1$	Solubility of cyanamides determined in 1 mol L^{-1} KNO_3 with enough HNO_3 to adjust pH. Solubility shown on small figure. Both Zn and Cd cyanamide fall on the same solubility curve. The solubility product was calculated assuming the solubility equaled the metal ion concentration, and calculating the CN_2^{2-} ion conc. from the pH and the values of $K_{a1} = 5.25 \times 10^{-11}$ and $K_{a1}K_{a2} = 7.95 \times 10^{-23}$. Kitaev, Bol'shchikova, Yatlova, 1971[362].
Cadmium cyanamide $CdCN_2$ [20654–10–8]	298.15	$pK_{s0} = 14.1$	
Zinc xanthate $Zn(C_3H_5OS_2)_2$ [13435–48–8]	?	$K_{s0} = 6 \times 10^{-9}$	Value quoted in Chem. Abstr. from a study of the solubilities of heavy metal xanthates and dithiophosphates. Oyama *et al.*, 1957[363].

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium — Continued

Substance	T/K	Solubility or solubility product	Comments/Reference
Zinc pyrrolidine dithiocarbamate $Zn(C_5H_8NS_2)_2$ [53632–23–8]	298	pK_{s0} = 15.9 ± 0.2 3.15 × 10^{-6} mol L^{-1}	Total metallic ion conc. of sat. solution measured by atomic absorption. A conditional solubility product was calculated from the total metal ion conc. Authors mention solubility should be pH dependent, but they do not give pH of their sat. solutions. Arnac, Verboom, 1974[364].
Cadmium pyrrolidine dithiocarbamate $Cd(C_5H_8NS_2)_2$	298	pK_{s0} = 18.9 ± 0.5 3.2 × 10^{-7} mol L^{-1}	
Zinc diethyldithiocarbamate $Zn(C_5H_{10}NS_2)_2$	?	$K_{s0} = 3.05 \times 10^{-17}$	Value quoted in Chem. Abstr.; Stepanyuk, 1958[365].
Cadmium diethyldithiophosphate	291.15 293.15	2.4 × 10^{-4} mol L^{-1} $K_{s0} = 5.8 \times 10^{-11}$	Soly by gravimetric method. Solubility product appears to be calculated from $4s^3$. Busev, Ivanyutin, 1958[366]
$Cd[(C_2H_5O)_2PS_2]_2$	293.15	3.14 × 10^{-4} mol L^{-1} $K^{\circ}_{s0} = 6.40 \times 10^{-11}$	Solubility determined by a radiometric method in water, and several electrolyte solutions. Mean ionic activity coefficients found. In water $\gamma_{\pm} = 0.8024$. Value preferred over first value above. Busev, Byr'ko, 1958[367].
Zinc sulfanilamides	298.15		The solubility of the Zn and Cd sulfanilamides; sulfadimesine (SH) [57–68–1], pK_a = 7.37; sulfadimethoxine (FH) [122–11–2], pK_a = 7.23; sulfathiazole (LH) [72–14–0], pK_a = 7.12; and sulfamethoxypuridazine (RH) [80–35–3], pK_a = 7.85; was determined at 20 degree intervals from 298 to 358 K in solutions initially 0.1 mol L^{-1} metal acetate, 0.1 mol L^{-1} sodium sulfanilamide and 2.5 × 10^{-2} to 2.5 × 10^{-5} mol L^{-1} in HCl. Solubilities, g per 100 g water, are given for each of the four temperatures studied. Solubility product constants were derived from the solubility at 298 K. The effects of an excess of metal ion and sulfanilamide on the solubility were studied by the method of isomolar series. The authors imply the sparingly soluble solids are hydrated. Tskitishvili, Mikadze, Chrelashvili, 1983[368].
Zinc sulfapyridazine $Zn(C_{11}H_{11}N_4O_3S)_2$ ZnR_2		$K_{s0} = 6.79 \times 10^{-11}$	
Zinc sulfadimenine $Zn(C_{12}H_{13}N_4O_2S)_2$ ZnS_2		$K_{s0} = 3.50 \times 10^{-10}$	
Zinc sulfadimethoxin $Zn(C_{12}H_{13}N_4O_4S)_2$ ZnF_2		$K_{s0} = 4.08 \times 10^{-9}$	
Zinc norsulfazol $Zn(C_9H_8N_3O_2S_2)_2ZnL_2$		$K_{s0} = 7.18 \times 10^{-7}$	
Cadmium sulfanilamides	298.15		
Cadmium sulfapyridazine $Cd(C_{11}H_{11}N_4O_3S)_2$ CdR_2		$K_{s0} = 2.49 \times 10^{-11}$	
Cadmium sulfadimezine $Cd(C_{12}H_{13}N_4O_2S)_2$ CdS_2		$K_{s0} = 2.28 \times 10^{-10}$	
Cadmium sulfadimethoxin $Cd(C_{12}H_{13}N_4O_4S)_2$ CdF_2		$K_{s0} = 2.45 \times 10^{-9}$	
Cadmium norsulfazol $Cd(C_9H_8N_3O_2S_2)_2$ CdL_2		$K_{s0} = 3.28 \times 10^{-7}$	
Zinc silicate $ZnSiO_3$ [16871–71–9]	?	$K^{\circ}_{s0} = (1-3) \times 10^{-16}$ in 0.24to1.07 M NH_3 $K^{\circ}_{s0} = 1 \times 10^{-16}$ in 0.41 M NH_3	From a study of the sorption of zinc ions by silica gel from an ammonia solution by titration and colorimetric methods. The activity product of zinc and silicate ions was calculated taking into account the dissociation constants of $Zn(NH_3)_4^{2+}$, $ZnOH^+$, and H_2SiO_3. Alekseeva, Dushina, Aleskovskii, 1968[369], 1972[370].
Cadmium silicate $CdSiO_3$ [12672–37–6] $CdSiO_3$ nH_2O	?	K_{s0} = (5.7 1.7) × 10^{-15}	Study similar to $ZnSiO_3$ study described above. The data treatment required dissociation constants of $Cd(NH_3)_4^{2+}$, $CdOH^+$, $CdCl^+$, and H_2SiO_3. The acid dissociation constants used were $K_{a1} = 2.2 \times 10^{-10}$ and $K_{a2} = 1.0 \times 10^{-12}$. Hydration of the solid discussed, but not characterized. Alekeseeva, Dushina, Aleskovskii, 1974[371].
Zinc germanate Zn_2GeO_4 [12025–29–5]	298.15	0.0153 mol ZnO 0.00234 mol GeO_2	Study of $Zn_2GeO_4 + H_2SO_4 + H_2O$ system. Solution conc. of Ge and Zn by photometric and polarographic methods. per kg water. The large (6.5) ZnO/GeO_2 solution ratio taken as evidence of decomposition on dissolution. Values given are for water and solid Zn_2GeO_4. Additional data in paper.Zangieva, *et al.*, 1983[372].

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium — Continued

Substance	T/K	Solubility or solubility product	Comments/Reference
Zinc borate $Zn(BO_2)_2$ [22588–98–3]	295	$K^\circ_{s0} = (6.5 \pm 3.5) \times 10^{-11}$	Crystalline $Zn(BO_2)_2\ H_2O$ and $Cd(BO_2)_2\ 7H_2O$ were prepared. Their solubilities were measured in water (initially 0.05 to 0.015 mol L^{-1}HCl) and in 3% aqueous H_3BO_3. The solubility product was calculated from the water solutions after determination of M^{2+}, H^+ and HBO_2 concentrations. The K_a of the acid was taken as 7.5×10^{-10} and activity coefficients were calculated from extended Debye-Huckel theory to obtain the K°_{s0} values. The solubilities in aqueous H_3BO_3 were used to obtain instability constants for the complex ions $Zn(BO_2)_4^{2-}$, $K = 1.6 \times 10^{-12}$; and $Cd(BO_2)_4^{2-}$, $K = 2.3 \times 10^{-11}$. Shchigol, 1959[373].
	298.15	$K^\circ_{s0} = 6.47 \times 10^{-11}$ NBS table data	
Cadmium borate $Cd(BO_2)_2$ [74153–66–5]	295	$K^\circ_{s0} = (2.3 \pm 1.1) \times 10^{-9}$	
	298.15	$K^\circ_{s0} = 2.29 \times 10^{-9}$ NBS table data	
Zinc mercury (II) selenocyanate $Zn[Hg(SeCN)_4]$	291.15	1.126×10^{-4} mol L^{-1}	Determined using a photometric method. Swinarski, Lodzinska, 1958[374].
Cadmium mercury (II) selenocyanate $Cd[Hg(SeCN)_4]$	291.15	5.395×10^{-3} mol L^{-1}	
Zinc cobalticyanide $Zn_3[Co(CN)_6]_2$ [14049–79–7]	293.15	3.645×10^{-4} mol L^{-1} $pK_s = 9.71$	Conductivity method. Solubility reaction assumed to be $M_3[Co(CN)_6]_2(s) = M^{2+}(aq) + 2M[Co(CN)_6]^-(aq)$.
Cadmium cobalticyanide $Cd_3[Co(CN)_6]_2$ [25359–19–7]	293.15	6.91×10^{-5} mol L^{-1} $pK_s = 11.88$	Limiting eq. cond. of $M[Co(CN)_6]^-$ ion approximated. M = Zn, Cd. De Robertis, Bellomo, De Marco, 1982[375].
Zinc chromate $ZnCrO_4$ [13530–65–9]		10^3 c/mol L^{-1} $10^5 K_{s0}$ $I = 0$ $I = 4S$	Solubility determined by a spectrophotometric method in aqueous $NaNO_3$ of ionic strength $I = 0.025 - 1.00$. Solubilities were extrapolated to total $I = 0$ and to $NaNO_3$ ionic strength, $I = 0$, at which the I would be four times the solubility. Coetzee, 1979[376].
	293.15	1.738 2.938 0.8632	
	298.15	1.950 3.488 1.2166	
	303.15	2.163 3.950 1.5603	
	308.15	2.371 4.500 2.0250	
	?	$(0.43 - 0.63) \times 10^{-3}$ mol L^{-1}	Solutions equilibrated 2 min with ultrasound, both Zn and Cr determined by atomic absorption. Solubility also measured in various culture media. Value appears low, probably because equilibration time was so short. Koshi, Iwasaki, 1983[377].
Cadmium chromate $CdCrO_4$ [14312–00–6]	298.15	$K_{s0} = 7.6 \times 10^{-5}$ $I/NaNO_3 = 0.1$	Cadmium ion selective electrode method. He, Wang, 1983[378]. Six values given between 283 and 308K which do not show constant temperature coefficient. Solid identified as $CdCrO_4{\cdot}2H_2O$.
Zinc chromate hydroxide $Zn(CrO_4)_{0.2}(OH)_{1.6}$	293	$K_{s0} = 5 \times 10^{-17}$	Three crystaline forms of varying hydration were prepared. Formula solubility product was found by titration curve and activity coefficients by Debye-Huckel theory. Feitknecht, Hugi-Carmes, 1954[379].
Zinc molybdate $ZnMoO_4$ [13767–32–3]	293 373	6.93×10^{-3} mol L^{-1} 8.61×10^{-3} mol L^{-1}	Values were obtained by colorimetric and gravimetric analysis. Zelikman, Prosenkova, 1961[380].
Cadmium molydate $CdMoO_4$	298.15	$K_{s0} = 2.2 \times 10^{-9}$ $I/NaNO_3 = 0.1$	Cadmium ion selective electrode method. Six values given between 283 and 308K which do not show constant temperature coefficient. Solid anhydrous. He, Wang, 1983[378].
	?	$K_{s0} = 6.05 \times 10^{-8}$	Titration study. Details of obtaining K_{s0} not given. Rao, 1954[381].
Cadmium tungstate $CdWO_4$ [7790–85–4]	298.15	$K_{s0} = 2.3 \times 10^{-10}$ $I/NaNO_3 = 0.1$	Cadmium ion selective electrode method. Six values given between 283 and 308K which do not show constant. temperature coeficient. Solid identified as $CdWO_4{\cdot}H_2O$. He, Wang, 1983[378].

TABLE 62. The solubility or solubility product constant of some sparingly soluble compounds of zinc and cadmium — Continued

Substance	T/K	Solubility or solubility product	Comments/Reference
	473–673	Solubility in aq	Gravimetry and titrimetry methods used. Dem'yanets, NaCl and KCl solns. Ravich, 1972[382]. Graph & Table.
	573–673	Solubility in aq	Gravimetric methods used. Up to 14–15 % LiCl, solid is LiCl solution. $CdWO_4$; at higher percent LiCl, the solid is Li_2WO_4. Graph and Table. Dem'yanets, 1968[383].
Zinc in fertilizers	?	*microg Zn/g fertilizer* total extracted by H_2O	Various fertilizers and process intermediates from North Carolina phosphate rock were tested. One g of material was equilibrated 24 hours with 100 mL water, 0.1 mol L^{-1} $CaCl_2$, and 0.1 mol L^{-1} HCl. Only the results for water are given here. The Zn and Cd were determined by atomic absorption. Easterwood, Street, 1982[384].
Triple super phosphate		275.00 4.82	
Diammonium phosphate		233.75 0.11	
Calcinated rock		183.75 0.00	
Non-calcinated rock		160.00 0.02	
Gypsum		– 0.04	
Cadmium in fertilizers	?	*microg Cd/g fertilizer* total extracted by water	
Triple super phosphate		21.75 0.35	
Diammonium phosphate		17.25 0.06	
Calcinated rock		19.38 0.01	
Non-calcinated rock		18.13 0.01	
Gypsum		– 0.01	
Zinc in soils	?	The solubility of Zn from soils of various total Zn content as a function of pH. Figure.	A review of the authors earlier work. The solubility increases sharply at pH of about 5 and lower. Organic material decreases the equilibrium solution concentration. *Show also data for Cu and Pb. Bruemmer, Herms,* 1983[385].
Cadmium in soils		The solubility of Cd from soils of various total Cd content as a function of pH. Figure.	
Zinc in soils			Paper reports solubility of Al, Cr, Cu and Zn in soils from Finnish acid sulfate soil area. Abstract only available. Palko and Yli-Halla, 1990[397].

6. Appendix

TABLE 1A. Sources of cadmium iodate solubility data in aqueous electrolyte solutions

T/K	*I*/Electrolyte or Mass % / Nonelectrolyte	Reference
298.15	0–2.5/KCl (graph)	Oelke and Wagner, 1939[59]
	0–8/$MgS0_4$ (graph)	Oelke and Wagner, 1939[59]
	0.0025–0.95/KCl	Saegusa, 1950[49]
	0.5–3.0/$Li^+(IO_3^- C10_4^-)$ (graph)	Federov *et al.*, 1983[57]
	1/$(Cd^{2+}, Na^+)\ C10_4^-$	Ramette, 1981[60]
	3/$Cd^{2+}, Na^+)\ C10_4^-$	Ramette, 1983[61]
	3/Na^+ (Br, $C10_4^-$)	Ramette, 1983[61]
308.15	3/$(Cd^{2+}, Na^+)\ C104^-)$	Ramette, 1983[61]
	3/Na^+ (Br, $C10_4^-$)*k*	Ramette, 1983[61]
323.15	(8–78) /HIO_3	Lepeshkov et al; 1979[54]
298.15	(0–45) Tetrahydrofuran	Miyamoto, 1972[51]

TABLE 2A. The solubility of zinc sulfide (sphalerite) in aqueous electrolyte solutions

T/K	Ionic strength *I*/Electrolyte or pH	Solubility c_{ZnS}/mol L^{-1}	Method	Reference
298.15	pH = 3 pH = 5 pH = 9 pH = 11	8.3×10^{-6} 8.3×10^{-8} 8.6×10^{-11} 8.6×10^{-12}	Model calculation	Kapustinskii, 1940[85,a]
298.15	pH = 3 pH = 11	10.7×10^{-6} 10.9×10^{-12}	Model calculation	Czamanske, 1959[86,b]
298.15–473	pH = 3 pH = 3	2×10^{-6}– $3X10^{-4}$	(?)	Rafal'skii, 1966[88,c]
298.15	?/H_2S,6.8atm	$<1\times10^{-5}$	polarography	Barnes, 1958[95]
298.15	3/H_2S,pH=7.6 6/H_2S, 1–3m	9.34×10^{-3} 2.80×10^{-3} NaCl	Solubility "	Barnes, Romberger, 1962[96]
298.15–368	?/H_2S, NaCl	Table	Atomic absorption	Barrett, Anderson, 1982[97]
298.15–573	?/H_2S, NaCl	Table 1–3m	Model calulation	Barrett, Anderson, 1982[97]
298.15–648	0–2.0/NaCl	Graph	Colorimetry and atomic absorption	Hennig, 1971[83]
298.15	10.3/?, pH=8.2,	$(2.78\pm0.04)\times10^{-2}$	Polarography	Barnes, 1960[98,99]
323.15	?/H_2S, satd at	$(1.1\pm0.2)\times10^{-4}$ 35 atm	Polarography	Barnes, 1959[100]
323.15	?/H_2S satd (at 1 atm ?)	3.82×10^{-5}	Colorimetry	Vukotic, 1961[63]
348	?/H_2S, satd at	$>1\times10^{-4}$ 20.4 atm	Polarography	Barnes, 1958[95]
353	?/H_2S, satd at	5×10^{-5}	? 1 atm	Hinners, 1964[101,d]

TABLE 2A. The solubility of zinc sulfide (sphalerite) in aqueous electrolyte solutions — Continued

T/K	Ionic strength I/Electrolyte or pH	Solubility c_{ZnS}/mol L^{-1}	Method	Reference
373	?/H_2S, satd	3.35×10^{-5}	Colorimetry	Vukotic, 1961[63]
373	pH = 3	1.61×10^{-5}	Model calculation	Czamanske, 1959[86,b]
	pH = 11	5.30×10^{-11}		
373	2/KCl	$(2.4–2.6)\times10^{-5}$	?	Gororov, et al., 1966[105,b]
373	/NaOH, HCl pH = 3–5.5	5×10^{-6}– 5×10^{-7}	Atomic absorption	Ewald, Hladky, 1980[102]
	1/NaCl, pH = 3–5.5	4.6×10^{-5}– 2×10^{-6}	" "	" "
	3/NaCl, pH = 3–5.5	3.0×10^{-4}– 1.5×10^{-5}	" "	" "
373–573	?/Hydrothermal solutions	Graph	Model Calculation	Rafal'skii, 1982[73]
418	10.3/H_2S,satd at 2.48×10^{-2}		Polarography 12.2 atm	Barnes, 1960[99]
423	?/H_2S, satd	3.66×10^{-5}	Colorimetry	Vukotic, 1961[63]
473	?/H_2S, satd	3.66×10^{-5}	"	" "
473	pH = 3	2.29×10^{-5}	Model calculation	Czamanske, 1959[86,b]
	pH = 11	5.77×10^{-11}	" "	
473	/NaOH, HCl pH = 3–5.5	3.0×10^{-5}– 2.3×10^{-6}	Atomic absorption	Ewald, Hladky, 1980[102]
	1/NaCl, pH = 3–5.5	3.3×10^{-5}– 9×10^{-6}	" "	Ewald, Hladky, 1980[102]
	3/NaCl, pH = 3–5.5	3.8×10^{-3}– 1.1×10^{-4}	" "	Ewald, Hladky, 1980[102]
473	~3/H_2S,pH 7.6	8.42×10^{-3}	Solubility method	Barnes, Romberger 1962[96]
	~6/H_2S, NaCl	4.21×10^{-3}		
573	0.5/KCl,9900 atm	~2×10^{-2}	Gravimetry	Hemley, *et al.*, 1967[103]
573–723	0.5,2/KCl silicate buffered	Graph	" "	
573–723	/base, salts 543 atm	Graph	Gravimetry	Laudise, *et al.* 1965[104]
673	pH = 3	3.30×10^{-5}	Model calculation	Czamanske, 1959[86, b] 86
	pH = 11	1.23×10^{-11}	" "	
773	2/KCl, 9900 atm	~3×10^{-3}	Gravimetry	Hemley, *et al.*, 1967[103]
873	pH = 3	4.24×10^{-5}	Model calculation	Czamanske, 1959[86, b]
	pH = 11	6.72×10^{-8}		

---

[a] Calculated using their own thermodynamic data and H_2S acid dissociation constants from Lewis and Randall[91], and Wright and Maas[92].

[b] Calculated using data from Latimer[89], Kubaschewski and Evans[93] and Kury, Zielen and Latimer[94].

[c] It is not clear to the reader whether this is calculated or experimental data.The data from 473 K may be from another paper.

[d] Unpublished dissertation cited by Barnes and Czamanske, 1967[82]

[e] The paper was not available to us; information isfrom abstract, Chem. Abstr. **68**, 116355c.

TABLE 3A. The solubility of cadmium sulfide in aqueous electrolytesolutions

T/K	Ionic strength I/Electrolyte or pH	Solubility c_{CdS}/mol L^{-1}	Method	Reference
291.15	/CO_2, pH = 5.8	$34. \times 10^{-10}$	Calculation[a]	Kolthoff,
	/CO_2, pH = 5.8	9.3×10^{-10}	Calculation[b]	1931[72]
298.15	pH = 3	1.0×10^{-6}	Calculation[c]	Kapustinskii, 1940[85]
	pH = 5	1.1×10^{-8}	"	" "
	pH = 7	1.5×10^{-10}	"	" "
	pH = 9	1.1×10^{-11}	"	" "
	pH = 11	1.1×10^{-12}	"	" "
298.15	pH = 3	8.4×10^{-7}	Calculation[d]	Czamanske, 1959[86]
	pH = 7	1.2×10^{-10}	"	" "
	pH = 11	8.6×10^{-13}	"	" "
298.15	1.0/$NaClO_4$	Graph	Radiochemistry	St.Marie, Torma
	1.0/HCl or NaOH	"	"	Gubeli, 1964[119]
	several buffers	"	"	" "
298.15	0.4-1.2/HCl	2.0×10^{-4}	Polarography[e]	Kivalo, Ringbom
		1.1×10^{-4}		1956[120]
298.15	1 ?/HS^-, H_2S	1.04×10^{-3}	Barnes, Czaman-	
	(p = 5 atm)		ske, 1967[82]	
310.15	gastric juices (pH = 1.47)		More soluble in	Wada, Iijima,
	intestinal juices (pH = 8.20)		the more acid	Ono, Toyokawa
			juices	1972[121]
373	pH = 3	3.2×10^{-6}	Calculation[d]	Czamanske, 1959[86]
	pH = 7	8.6×10^{-10}	"	" "
	pH = 11	1.1×10^{-11}	"	" "
473	pH = 3	9.5×10^{-6}	"	" "
	pH = 7	5.1×10^{-9}	"	" "
	pH = 11	2.4×10^{-10}	"	" "
573	1-2/NH_4Cl	0.005-0.010	Measured up	Geletii,
			to 1000 atm	Chernyshev,
623	1/NH_4Cl	0.017	"	Pastushkova, 1981[122]
673	0.56-2/NH_4Cl	0.028-0.073	"	" "
	1.7-3.4/NaCl	0.0012-0.0015	"	" "
	2/NaCl, HCl	0.020-0.029	"	" "
	4/NaCl, NH_4Cl	0.017-0.039	"	" "
673	pH = 3	3.4×10^{-5}	Calculation[d]	Czamanske, 1959[86]
	pH = 7	4.3×10^{-8}	"	
	pH = 11	1.25×10^{-8}	"	" "
873	pH = 3	6.9×10^{-5}	"	" "
	pH = 7	1.7×10^{-7}	"	" "
	pH = 11	1.1×10^{-7}	"	" "

The values above indicate qualitative trends of solubility with temperature, pH, and ionic strength. Many of the values could be made more reliable by recalculation of the data using modern auxillary thermodynamic data.

[a] Solubility calculated for (hexagonal ?) CdS precipitated from $CdCl_2$ from value of Bruner and Zawadski, 1909[116], 1910[117] assuming water saturated with atmospheric CO_2 (1.35×10^{-5} mol L^{-1}) at pH 5.8.

[b] Same as[a] above except for (cubic ?) CdS precipitated from $CdSO_4$ solution.

[c] See footnote[d] of Table 19.

[d] See footnote[e] of Table 19.[e] Corrected for Cd-Cl complex ion.

TABLE 4A. Sources of zinc carbonate solubility data in aqueous electrolyte systems

T/K	Ionic strength I/Electrolyte	Carbon dioxide[a] p/bar	References
287	0.7,0.8/Na_2SO_4	2	Ehlert, Hempel, 1912[256]
287	0.9,1.9,6/NaCl	2	“ “ “
287	1.3,11/$NaNO_2$	2	“ “ “
287–353	1.0/NH_4Cl		Cantoni, Passamanik, 1905[257]
287–353	1.0/NaCl		“ “ “
287–353	1.0/KCl		“ “ “
288	0.05/NH_4Cl		Ehlert, Hempel, 1912[256]
288	0.05/NaCl		“ “ “
288	0.05/KCl		“ “ “
291	0.57/$NaNO_3$,Na_2CO_3		“ “ “
293	1.0/NH_4Cl		“ “ “
293	?/$KHCO_3$ (graph only)		Taketatsu, 1963[258]
298	0.075/K_2CO_3		Immerwhar, 1901[202]
298	($a_{Cl^-} = a_{SO_4^{2-}} = 0.1$)	0.01	Mann, Deutscher, 1980[252,b]
298	1.4–13.1/$CaCl_2$		Ben'yash, 1964[259,c]
298	0.2/$NaClO_4$	0.18–0.90	Schindler, Reinert, Gamsjaeger, 1969[260]

[a] Where no carbon dioxide pressure is given we assume the carbon dioxide partial pressure was about the 0.00032 bar of carbon dioxide in air.

[b] Calculated on the basis of a geological model.

[c] Solubility in mol kg^{-1}, equilibrium solid is a $CaCO_3$ /$ZnCO_3$ mixture.

TABLE 5A. Solubility studies of zinc oxalate in aqueous electrolyte solution

T/K	I/Electrolyte	Reference
291.15	(0.03–0.74)/$Na_2C_2O_4$	Britton and Jarrett, 1936[279]
	(0.15–5.63)/H_2SO_4	“ “ “ “
298.15	$(0.50–8.0) \times 10^{-3}$/$H_2SO_4$	Deyrieux and Peneloux, 1970[268]
	(0.21–1.10)/$K_2C_2O_4$	Metler and Vosburgh, 1933[280]
	(0.01–0.11)/$K_2C_2O_4$	Clayton, Vosburgh, 1937[273]
	(0.005–0.08)/$ZnSO_4$	“ “ “
	(0.45–17.3)/$Na^+(S_2O_3^{2-}, NO_3^-)$	Lodzinska *et al*., 1965[278]
	(0.1–9.0)NH_3, $NaNO_3$	Gornicki, Jablonski, 1957[281]
	(0.1–2)/KCN	“ “ 1978[282]
	(0.05–0.25)/$(NH_4)_2CO_3$	Kunschert, 1904[270]
	KU-1, KU-2 ion exchangers	Smyshlyaev *et al*., 1968[283]
308.15	(0.13–2.28)/$K_2C_2O_4$	Metler, 1934[284]
	(0.01–0.20)/$NaC_2H_3O_2$	Bardhan and Aditya, 1955[285]
	(0.01–0.20)/KNO_3	“ “ “ “

TABLE 6A. Solubility studies of cadmium oxalate in aqueous electrolyte solution

T/K	I/Electrolyte	Reference
?	(0.1–1.0)/KNO_3	Babkin, 1956[288]
?	?/$Cd(NO_3)_2$	Babkin, *et al.*, 1955[287]
?	?/$(NH_4)_2C_2O_4$	" " "
?	/KCl	" " "
293.15	2.1/NaX ($X=Br^-$, I^-, NCS^-)	Czakis-Sulikowska and Kuznik, 1972[306]
	/C_2H_5OH, C_3H_7OH	Lebedeva *et al.*, 1978[307]
298.15	/HCl + Ethylenediamine	Fridman *et al.*, 1963[295]
	/HCl + $K_2C_2O_4$ + Ethylenediamine	" " "
	(0.005–0.08)/$CdSO_4$	Clayton and Vosburgh, 1937[273]
	(0.005–0.04/$CdSO_4$	Vosburgh and Beckman, 1940[0274]
	(0.23–2.3)/$MgSO_4$	Pesce and Lago, 1944[291]
	(0.19–3.1)/NaCl	Accascina and Schiavo, 1953[293]
	(0.24–2.1)/Na_2SO_4	Pesce and Lago, 1944[291]
	(0.03–0.46)/$NaNO_3$	Accascina and Schiavo, 1953[293]
	(0.3–11)/$Na^+(S_2O_32^-, NO_3^-)$	Lodzinska *et al.*, 1965[278]
	(0.25–3.5)/KCl	Accascina and Schiavo, 1953[293]
	(0.007–0.08)/$KClO_4$	Vosburgh and Beckman, 1940[274]
	(0.005–0.04)/K_2SO_4	" " "
	(0.03–0.19)/K_2SO_4	Accascina and Schiavo, 1953[293]
	(0.07–1.8)/KNO_3	" " "
	(0.2–2.0)/KNO_3	Cavigli, 1949[308]
	1/KNO_3 (graph)	Olin, Wikmark, 1983[290]
	KNO_3 + Ethylenediamine(graph)	Fridman *et al.*, 1963[295]
	(0.006–0.09)/$K_2C_2O_4$	Clayton and Vosburgh, 1937[273]
	(0–0.24)/$K_2C_2O_4$ (graph)	Barney *et al.*, 1951[292]
	/$K_2C_2O_4$ + CdC_2O_4 (phase diagram)	Vosburgh *et al.*, 1936[296]
	/$K_2C_2O_4$ + KNO_3 + ethylenediamine	Fridman *et al.*, 1963[295]
303.15	0.1/KNO_3	Gupta and Chatterjee, 1967[309]
313.15	0.1/KNO_3	" " " "
	/C_2H_5OH, C_3H_7OH	Lebedeva *et al.*, 1978[307]
323.15	0.1/KNO_3	Gupta and Chatterjee, 1967[309]
333.15	(0.01–0.15)/$NaC_2H_3O_2$	Bardhan and Aditya, 1955[294]
	(0.01–0.15)/KNO_3	" " " "

7. Acknowledgements

We thank Francis J. Johnston and Steven Dekich who helped in the early literature searches for this paper. We appreciate the advice of the late Professor A. Steven Kertes and of other colleagues of the IUPAC Solubility Data Commission.

This work was carried out with the support of Contract No. NB81NADA2052 from the Office of Standard Reference Data of the National Institute of Science and Technology.

8. References

[1] H. L. Clever and F. J. Johnston, J. Phys. Chem. Ref. Data **9**, 751 (1980).

[2] H. L. Clever, S. A. Johnson and M. E. Derrick, J. Phys. Chem. Ref. Data **14**, 631 (1985).

[3] D. A. Crerar, N. J. Susak, M. Borcsik, and S. Schwartz, Geochim. Cosmochim. Acta **42**, 1427 (1979).

[4] T. P. Dirkse, The Solubility of Some Heavy Metal Oxides and Hydroxides, Solubility Series **23**, 156–269 (Zn), 270–306 (Cd) (1986).

[5] H. D. Lutz, Solubility Series **26**, 271, 286 (1986). See also[138].

[6] A. Seidell and W. F. Linke, Editors, Solubilities of Inorganic and Metal Organic Compounds (American Chemical Society, Washington, DC), Vol. I (1958); Vol II (1965).

[7] H. Stephen and T. Stephen, Editors, Solubilities of Inorganic and Organic Compounds (Pergamon Press, Ltd., Oxford and New York), Vol. I, Part 1 (1963); Vol. I, Part II (1965).

[8] L. G. Sillen and A. E. Martell, Chem. Soc. Special Publication **17** (1964); Suppl. 1, Special Publication **25** (1971).

[9] A. N. Krigintsev, L. N. Trushnikova and V. G. Lavent'eva, Rasvorimost Neorganicheskikh Veshchestv Vode. Spravochnik (Solubility of Inorganic Substances in Water Handbook) [Khimya, Leningrad Otd. (1972)].

[10] A. M. Comey and D. A. Hahn, A Dictionary of Chemical Solubilities – Inorganic (Macmillan, New York) (1921).

[11] J. D. H. Donnay and H. M. Ondik, Crystal Data Determinative Tables, 3rd Ed. [National Bureau of Standards, Washington, DC (1973)]. Vol. 2; H. M. Ondik and A. D. Mighell, Vol. 4, (1978).

[12] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, The NBS (now NIST) Tables of Chemical Thermodynamic Properties. J. Phys. Chem. Ref. Data 11, Suppl. 2 (1982).

[13] R. A. Robie, B. S. Hemingway and J. R. Fisher, Geol. Survey Bull. No. 1452 [US GPO, Washington, DC (1978)].

[14] A. J. Bard, R. Parsons and J. Jordan, Editors, Standard Potentials in Aqueous Solution [Marcel Dekker, Inc., New York and Basel (1985)],

(a) R. J. Brodd and J. Werth, Zinc, Chapter 10, p. 249; (b) Y. Okinaka, Cadmium, Chapter 10, p. 257.

[15] A. J. Bard, Editor, Encyclopedia of Electrochemistry of the Elements, (a) R. J. Brodd and V. E. Leger, Zinc, Vol. V, Chapter 1, p 1; (b) N. A. Hampson and R. S. Latham, Cadmium, Vol. I, Chapter 4, p. 155.

[16] A. J. de Bethune, T. S. Light and N. A. Swendeman, J. Electrochem. Soc. **106**, 616 (1959).

[17] A. J. de Bethune and G. R. Salvi, J. Electrochem. Soc. **108**, 672 (1961).

[18] S. Licht, J. Electrochem. Soc. **135**, 2971 (1988).

[19] Atomic Weight of the Elements 1985, Pure Appl. Chem. **52**, 1677 (1986).

[20] J. C. Pariaud and P. Archinard, Bull. Soc. Chim. France, 454 (1952).

[21] W. Feitknecht, Helv. Chim. Acta **13**, 314 (1930).

[22] A. O. Gubeli and J. Ste-Marie, Can. J. Chem. **45**, 827 (1967).

[23] M. Nierlich, P. Charpin and P. Herpin, C. R. Seances Acad. Sci., Ser. *C* **276**, 1 (1973).

[24] W. Feitknecht and H. Bucher, Helv. Chim. Acta **26**, 2177 and 2196 (1943).

[25] L. M. Volkova, L. V. Samarets, S. A. Polishchuk and N. M. Laptash, Kristallografiya **23**, 951 (1978).

[26] R. O. Cook, A. Davies and L. A. K. Stavely, J. Chem Thermodyn. **3**, 907 (1971).

[27] J. C. Rodriquez Placeres, A. Cabrera Gonzalez, J. A. Sanchez and A. Arevalo, An. Quim., Ser. A **76**, 219 (1980).

[28] F. Kohlrausch, F. Rose and F. Dolezalek, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **44**, 197 (1903).

[29] A. Kurtenacker, W. Finger and F. Hey, Z. Anorg. Allg. Chem. **211**, 83 (1933).

[30] R. H. Carter, Ind. Eng. Chem. **20**, 1195 (1928).

[31] N. Sh. Gamburg, E. N. Deichman and D. D. Ikrami, Dokl. Acad. Nauk. Tadzh. SSR **19**, 43 (1976).

[32] A. A. Opalovskii, T. D. Fedotova and G. S. Voronina, Izv. Akad. Nauk. SSSR, Ser. Khim. (9) 1940 (1970); Bull. Acad. Sci. USSR, Div. Chem. Sci. (9) 1827 (1970).

[33] A. Kurtenacker, W. Finger and F. Hey, Z. Anorg. Allg. Chem. **211**, 281 (1933).

[34] A. A. Shakhnazaryan, G. R. Mkhitaryan, G. S. Panosyan and G. G. Babayan, Arm. Khim. Zh. **36**, 433 (1983).

[35] R. E. Connick and A. D. Paul, J. Am. Chem. Soc. **80**, 2069 (1958).

[36] S. Ahrland and K. Rosengren, Acta Chem. Scand. **10**, 727 (1956).

[37] S. S. Mesaric and D. N. Hume, Inorg. Chem. **2**, 1063 (1963).

[38] C. Staalhandske, Acta Crystallogr., Sec. *B* **35**, 2184 (1979).

[39] P. Nuka, Z. Anorg. Allg. Chem. **180**, 235 (1929).

[40] B. A. Kulikov and N. A. Mamaev, Zh. Fiz. Khim. **47**, 91 (1973); Russ. J. Phys. Chem. **47**, 49 (1973).

[41] A. Jaeger, Z. Anorg. Chem. **27**, 22 (1901).

[42] E. A. Gyunner, L. M. Mel'nichenko and N. D. Yakhkind, Zh. Neorg. Khim. **25**, 919 (1980); Russ. J. Inorg. Chem. **25**, 511 (1980).

[43] A. M. Bond and T. A. O'Donnell, J. Electroanal. Chem. Interfacial Electrochem. **26**, 137 (1970).

[44] I. Leden, Dissertation, Lund (1943), p. 43 (quoted in Ref 8).

[45] P. Beutler, K. Christen and H. Gamsjaeger, Chimia **30**, 104 (1976).

[46] A. M. Bond, J. Electroanal. Chem. Interfacial Electrochem. **20**, 223 (1969).

[47] J. K. Liang and C. Wang, Huaxue Xuebao **40**, 985 (1982).

[48] J. E. Ricci and G. J. Nesse, J. Am. Chem. Soc. **64**, 2305 (1942).

[49] F. Saegusa, Nippon Kagaku Zasshi *71, 223 (1950).*

[50] J. N. Spencer, E. A. Unger and D. N. Bailey, J. Chem. Eng. Data **19**, 140 (1974).

[51] H. Miyamoto, Nippon Kagaku Kaishi (3), 659 (1972).

[52] V. A. Fedorov, A. M. Robov, I. I. Shmyd'ko, T. N. Koneva, L. S. Simaeva and V. A. Kukhtina, Zh. Fiz. Khim. **50**, 2213 (1976);[Russ. J. Phys. Chem. **50**, 1330 (1976)].

[53] I. N. Lepeshkov, E. E. Vinogradov and I. M. Karataeva, Zh. Neorg. Khim. **22**, 2277 (1977); [Russ. J. Inorg. Chem. **22**, 1232 (1977)].

[54] I. N. Lepeshkov, E. E. Vinogradov and I. M. Karataeva, Zh. Neorg. Khim. **24**, 2540 (1979); [Russ. J. Inorg. Chem. **24**, 1412 (1979)].

[55] E. E. Vinogradov and I. M. Karataeva, Zh. Inorg. Khim. *24, 2529* (1979);[Russ. J. Inorg. Chem. **24**, 1406 (1979)].

[56] C. Rammelsberg, Ann. Phys. Chem. (Leipzig) **44**, 545 (1838).

[57] V. A. Fedorov, G. S. Dezhina, I. I. Shmyd'ko and L. I. Shmyd'ko, Koord. Khim. **9**, 1661 (1983);

[58] H. Bach and H. Kueppers, Acta Crystallogr. **B34**, 263 (1978).

[59] W. C. Oelke and C. Wagner, Proc. Iowa Acad. Sci. **46**, 187 (1939).

[60] R. W. Ramette, Anal. Chem. **53**, 2244 (1981).

[61] R. W. Ramette, Anal. Chem., **55**, 1232 (1983).

[62] A. M. Bond and G. Hefter, J. Electroanal. Chem. Interfacial Electrochem. **34**, 227 (1972).

[63] S. Vukotic, Bull. Bur. Rech. Geol. Min. (Fr.) (no. 3), 11 (1961).

[64] P. B. Barton and B. J. Skinner, "Sulfide Mineral Stabilities" in Geochemistry of Hydrothermal Ore Deposits, Second Ed. H. L. Barnes, Editor (John Wiley and Sons, Inc., New York 1979).

[65] S. Glixelli, Z. Anorg. Chem. **55**, 297 (1907).

[66] A. Ringbom, "Solubilities of Sulfides" Report to the Analytical Sec. IUPAC, July (1953).

[67] H. L. Barnes, "Solubilities of Ore Minerals" in Geochemistry of Hydrothermal Ore Deposits, 2nd Ed, H. L. Barnes, Editor (John Wiley and Sons, Inc., New York, 1979).

[68] A. O. Gubeli and J. Ste-Marie, Can. J. Chem. **45**, 2101 (1967).

[69] B. N. Melent'yev, V. V. Ivanenko and L. A. Pamfilova, The Solubilities of Some Ore-Forming Sulfides under Hydrothermal Conditions (Nauka, Moscow, 1968).

[70] R. P. Rafalskii, Hydrothermal Equilibria and Processing of Mineral Formation (Atomizdat, Moscow, 1973).

[71] Ya. I. Olshanskii, Tr. Inst. Geol. Rudn. Mestorozhd., Petrogr., Mineral. Geokhim., Acad. Nauk SSSR, (No. 6), 26 (1956).

[72] I. M. Kolthoff, J. Phys. Chem. **35**, 2711 (1931).

[73] R. P. Rafal'skii, Geokhimya (No. 12) 1780 (1982); Geochem. Int. (No. 12) 152 (1982).

[74] O. Weigel, Z. Phys. Chem., Stoechiom. Verwandschaftsl. **58**, 293 (1907).

[75] L. Moser and M. Behr, Z. Anorg. Allg. Chem. **134**, 49 (1924).

[76] S. F. Ravitz, J. Phys. Chem. **40**, 61 (1936).

[77] J. Verhoogen, Econ. Geol. **33**, 34 and 775 (1938).

[78] P. Van Rysselberghe and A. H. Group, J. Chem. Ed. **21**, 96 (1944).

[79] T. Y. Li, Hua Hsueh Tung Pao (No. 5), 59 (1962).

[80] B. N. Melent'ev, V. V. Ivanenko and L. A. Pamfilova, Dokl. Akad. Nauk SSSR **153**, 184 (1963).

[81] S. Guy, C. P. Broadbent, D. J. D. Jackson and G. J. Lawson, Hydrometallurgy **8**, 251 (1982).

[82] H. L. Barnes and G. K. Czamanske, "Solubilities and Transport of Ore Minerals" in Geochemistry of Hydrothermal Ore Deposits, 1st Ed., H. L. Barnes, Editor, (John Wiley and Sons, Inc., New York, 1967).

[83] W. Hennig, Neues Jahrb. Mineral., Abh. **116**, 61 (1971).

[84] A. J. Ellis, Econ. Geol. **54**, 1035 (1959).

[85] A. F. Kapustinskii, Dokl. Akad. Nauk SSSR **28**, 140 (1940).

[86] G. K. Czamanske, Econ. Geol. **54**, 57 (1959).

[87] H. L. Barnes, "Ore Solutions", Carnegie Inst. Wash. Yearbook **57**, 234 (1957–58).

[88] R. P. Rafal'skii, Geol. Rudn. Mestorozhd. **8**, 31 (1966).

[89] W. Latimer, Oxidation Potentials, (Prentice Hall, New York, 1952).

[90] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, (Reinhold Publishing Co., 2nd Ed., 1952).

[91] G. N. Lewis and M. Randall, Thermodynamics (McGraw-Hill Co., New York, 1923).

[92] R. H. Wright *and* O. Maass, *Can. J. Research* **6**, *94 and 588 (1932).*

[93] O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry (John Wiley and Sons, Inc., New York, 1956).

[94] J. W. Kury, A. J. Zielen and W. L. Latimer, US AEC, UCLR-2108 (1953); J. Electrochem. Soc. **100**, 468 (1953).

[95] H. L. Barnes, Econ. Geol. **53**, 914 (1958).

[96] H. L. Barnes and S. B. Romberger, Econ. Geol. **57**, 1017 (1962).

[97] T. J. Barrett and G. M. Anderson, Econ. Geol. **77**, 1923 (1982).

[98] H. L. Barnes, Geol. Soc. Am. Bull. **71**, 1821 (1960).

[99] H. L. Barnes, Year Book– Carnegie Inst., Washington DC **59**, 137 (1959–60).

[100] H. L. Barnes, Year Book– Carnegie Inst., *Washington, DC,* **58**, *163* (1958–59).

[101] N. W. Hinners, Dissertation, Princeton University, (1964).

[102] A. H. Ewald and G. Hladky, Invest. Rep. – CSIRO Inst. Earth Resources (No. 136) (1980).

[103] J. J. Hemley, C. Meyer, C. J. Hodgson and A. B. Thatcher, Science **158**, 1580 (1967).

[104] R. A. Laudise, E. D. Kolb and J. P. DeNeufville, Am. Mineral **50**, 382 (1965).

[105] I. N. Gororov, N. S. Blagodareva and Z. L. Mukoseeva, "Role of Alkali Carbonates and Halides in Hydrothermal Transfer of Lead and Zinc" in Geokhim. Mineral. Magmatogennykh Obraz., I. N. Gororov, Editor (Akademiia Nauk SSSR, 1966).

[106] V. V. Shcherbina, Geokhimya (No. 9), 1035 (1972).

[107] H. C. Helgeson, Am. J. Sci. **267**, 729 (1969).

[108] J. R. Goates, M. B. Gordon and N. D. Faux, J. Am. Chem. Soc. **74**, 835 (1952).

[109] A. M. Egorov, Zh. Neorg. Khim. **2**, 460 (1957); J. Inorg. Chem. (USSR)(Engl. Transl.) **2**(2), 358 (1957).

[110] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Selected Values of Thermodynamic Properties, NBS Circular **500**, 1952 (reprinted 1961).

[111] K. K. Kelley, US Bur. Mines, Bull. No. **476**, 241 pp (1949).

[112] R. A. Robie and D. R. Waldbaum, Thermodynamic Properties of Minerals, US Geological Survey Bulletin **1259**, (1968).

[113] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau Standards, Technical Note **270–3**, 264 pp (1968).

[114] C. A. Wulff, J. Chem. Eng. Data **12**, 82 (1967).

[115] W. O. Milligan, J. Am. Chem. Soc. **38**, 797 (1934).

[116] L. Bruner and J. Zawadski, Z. Anorg. Chem. **65**, 136 (1909).

[117] L. Bruner and J. Zawadski, Z. Anorg. Chem. **67**, 454 (1910).

[118] W. Biltz, Z. Phys. Chem., Stoechiom. Verwandschaftsl. **58**, 288 (1907).

[119] J. St. Marie, A. E. Torma and A. O. Gubeli, Can. J. Chem. **42**, 662 (1964).

[120] P. Kivalo and A. Ringbom, Suom. Kemistil. **29B**, 109 (1956).

[121] O. Wada, M. Iijima, T. Ona and K. Toyokawa, Ind. Health **10**, 122 (1972).

[122] V. F. Geletii, L. V. Chernyshev and T. M. Pastushkova, Geokhimya (**10**), 1463 (1981).

[123] R. Belcher, A. Townshend and J. P. G. Farr, Talanta **16**, 1089 (1969).

[124] W. Scheller and W. D. Treadwell, Helv. Chim. Acta **35**, 754 (1952).

[125a] W. Kraft, H. Gamsjaeger and E. Schwarz-Bergkampf, Monatsh. Chem. **97**, 1134 (1966).

[125b] I. R. Polyvyannyi and N. A. Milyutina, Tr. Inst. Met. Obogashch., Akad. Nauk Kaz. SSR **21**, 3 (1967).

[126] C. S. Simons, Met. Soc. Conf. **24**, 592 (1963).

[127] G. A. Krestov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **12**, 733 (1969).

[128] M. I. Erdenbaeva, Vestn. Akad. Nauk Kaz. SSR (2), **51** (1975).

[129] G. A. Krestov, V. A. Kobenin and V. N. Sokolov, Zh. Neorg. Khim. **22**, 2864 (1977); Russ. J. Inorg. Chem. (Engl. Transl.) **22**, 1556 (1977).

[130] I. A. Makolkin, Acta Physicochim. URSS **13**, 361 (1940).

[131] P. W. Schindler, Helv. Chim. Acta **42**, 2736 (1959).

[132] L. H. Adami and E. G. King, Rep. Invest. -US Bur. Mines **RI–6495** (1964).

[133] M. Aumeras, J. Chim. Phys. Phys. -Chim. Biol. **25**, 727 (1928).

[134] A. M. Golub, Ukr. Khim. Zh. (Russ. Ed.) **19**, 205 (1953).

[135] B. H. Relly, Econ. Geol. **54**, 1496 (1959).

[136] R. P. Rafal'skii and B. S. Osipov, Geol. Rudn. Mestorozhd. **9**, 44 (1967).

[137] V. A. Kuznetsov and D. V. Kostomarov, Kristallografiya **28**, 151 (1983); Sov. Phys. -Crystallogr. **28**, 83 (1983).

[138] M. R. Masson, H. D. Lutz and B. Engelen, Editors, Sulfites, Selenites and Tellurites, in A. S. Kertes, Editor,IUPAC Solubility Series **26**, (a) H. D. Lutz, pp 271–85 ($ZnSO_3$), (b) H. D. Lutz, pp 286–90 ($CdSO_3$), (1986); (c) M. R. Masson, pp 388–90 ($ZnSeO_3$); (d) M. R. Masson, pp 391–3 ($CdSeO_3$).

[139] H. D. Lutz, W. Eckers and B. Engelen, Z. Anorg. Allg. Chem. **475**, 165 (1981).

[140] H. D. Lutz, S. M. El-Suradi, Ch. Mertins and B. Engelen, Z. Naturforsch. Teil B. **35**, 808 (1980).

[141] B. Engelen Habilitationsschrift, Univerity Siegen, (1983).

[142] H. D. Lutz, W. Eckers, J. Henning, M. Jung and W. Buchmeir, Thermochim. Acta **74**, 323 (1984).

[143] B. Nyberg, Acta Chem. Scand. **26**, 857 (1971); **27**, 1541 (1972).

[144] F. T. Heuston and C. R. Tichborne, Br. Med. J., **1063** (1890).

[145] E. Terres and G. Ruhl, Angew. Chem. **47**, 332 (1934).

[146] I. N. Kuz'minykh and A. G. Kuznetsova, Zh. Prikl. Khim. **27**, 816 (1954); J. Appl. Chem. USSR (Engl. Transl.) **27**, 765 (1954).

[147] I. L. Peisakhov and V. D. Karmazina, Zh. Prikl. Khim. **32**, 70 (1959); J. Appl. Chem. USSR (Engl. Transl.) **32**, 71 (1959).

[148] T. Murooka and H. Sato, Bull. Inst. Phys. Chem. Res. (Tokyo) **16**, 636 (1937).

[149] E. V. Margulis and I. V. Rodin, Zh. Neorg. Khim. **26**, 2269 (1981); Russ. J. Inorg. Chem. (Engl. Transl.) **26**, 1221 (1981).

[150] H. D. Lutz and S. M. El-Suradi, Z. Anorg. Allg. Chem. **425**, 134 (1976).

[151] C. T. Kiers and A. Vos, Cryst. Struct. Commun, **7**, 399 (1978).

[152] E. V. Margulis and I. V. Rodin, Zh. Neorg. Khim. **26**, 1428 (1981); Russ. J. Inorg. Chem. (Engl. Transl.) **26**, 767 (1981).

[153] E. A. Buketov, M. Z. Ugorets and A. S. Pashinkin, Zh. Neorg. Khim. **9**, 526 (1964); Russ. I. Inorg. Chem. **9**, 292 (1964).

[154] K. Kohn, K. Inoue, O. Horie and S. Akimoto, J. Solid State Chem. **18**, 27 (1976).

[155] E. A. Buketov, M. Z, Ugorets, R. A. Muldagaliva and A. B. Dzhirenchina, Tr. Khim. -Metall. Inst., Akad. Nauk Kaz. SSR **1**, 201 (1963).

[156] L. Ya. Markovskii and Y. P. Sapozhnikov, Zh. Neorg Khim. **6**, 1592 (1961); Russ. J. Inorg. Chem. (Engl. Transl.) **6**, 816 (1961).

[157] Z. Micka, M. Uchytilova and M. Ebert, Chem. Zvesti **38**, 759 (1984).

[158] R. Ripan and G. Vericeanu, Stud. Univ. Babes-Bolyai, Ser. Chem. **13**, 31 (1968).

[159] V. G. Chukhlantsev, Zh. Neorg. Khim. **1**, 2300 (1956); J. Inorg Chem. USSR (Engl. Transl.) **1**(**10**), 132 (1956).

[160] M. J. Redman and W. W. Harvey, J. Less-Common Met. **12**, 395 (1967).

[161] P. Rumpf, Compt. Rendu **197**, 686 (1933).

[162] G. Gospodinov, Thermochim. Acta **77**, 439 (1984).

[163] C. W. F. T. Pistorius, Z. Anorg. Allg. Chem. 347, 233 (1966).

[164] P. Courtine, Ann. Chim. (Paris) **1**, 303 (1966).

[165] R. A. Palmer and H. F. Giles, J. Chem. Soc., Dalton Trans. **977** (1980).

[166] P. Herpin and J. M. Bregeault, Bull. Soc. Fr. Mineral. Cristallogr. **91**, 296 (1968).

[167] G. Gospodinov, Z. Anorg. Allg. Chem. **517**, 223 (1984).

[168] R. Aruga,Inorg. Chem. **17**, 2503 (1978).

[169] A. Klein, Ann. Chim. (Paris) **14**, 263 (1940).

[170] M. R. Masson, J. Inorg. Nucl. Chem. **38**, 545 (1976).

[171] K. Hanke, Naturwissenschaften **54**, 199 (1967).

[172] L. Ya. Markovskii and G. J. Pron', Zh. Neorg. Khim. **13**, 2640 (1968); Russ. J. Inorg. Chem. (Engl. Transl.) **13**, 1361 (1968).

[173] J. Wroblewska, A. Erb, J. Dobrowolski and W. Freundlich, Rev. Chim. Miner. **16**, 112 (1979).

[174] D. S. Robertson, N. Shaw and I. M. Young, J. Mater. Sci. **13**, 1986 (1978).

[175] V. Kramer and G. Brandt, Acta Crystallogr., Sect. C. : Cryst. Struct. Commun. **41**, 1152 (1985).

[176] A. W. Sleight, C. M. Foris and M. S. Licis, Inorg. Chem. **11**, 1157 (1972).

[177] V. Lenher and E. Wolesenky, J. Am. Chem. Soc. **35**, 718 (1913).

[178] I. G. Jander and F. Kienbaum, Z. Anorg. Allg. Chem. **316**, 41 (1962).

[179] M. Bagieu-Beucher, M. Brunel-Laugt and J. C. Guitel, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **35**, 292 (1979).

[180] M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **32**, 1894 (1976).

[181] Glatzel, Dissertation, 1880 cited in Comey and Hahn[10].

[182] G. Tammann, J. Prackt. Chem. [2] **45**, 417 (1892).

[183] M. E. Essington, Soil Sci. Soc. Am. J. **52**, 1574 (1988).

[184] M. V. Golashchapov and T. N. Filatova, Zh. Neorg. Khim. **14**, 814 (1969); Russ. J. Inorg. Chem. (Engl. Transl.) **14**, 424 (1969).

[185] J. E. Salmon and H. Terrey, J. Chem. Soc., **2813** (1950).

[186] N. E. Eberly, C. V. Gross and W. S. Crowell, J. Am. Chem. Soc. **42**, 1433 (1920).

[187] R. Y. Bek, Z. M. Mel'nikova and L. I. Borodikhina, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (5), **142** (1980); (1), **153** (1981).

[188] J. O. Nriagu, Geochim. Cosmochim. Acta **37**, 2357 (1973).

[189] H. Sigel, K. Becker and D. B. McCormick, Biochim. Biophys. Acta **148**, 655 (1967).

[190] R. V. Machevskaya and N. A. Babakina, Zh. Prikl. Khim. (Leningrad) 55, 2194 (1982); J. Appl. Chem. (USSR)(Engl. Transl.) **55**, 2008 (1982).

[191] D. P. Joshi and D. V. Jain, J. Indian Chem. Soc. **41**, 683 (1964).

[192] G. N. Pant and D. N. Pathak, Fet. Technol. **13**, 296 (1976).

[193] D. Mukerji, J. Indian Chem. Soc. **56**, 212 (1979).

[194] L. V. Trapeznikova, N. L. Shestidesyatnaya and A. I. Kamaukhov, Zh. Neorg. Khim 28, 2394 (1983); Russ. J. Inorg. Chem. (Engl. Transl.) **28**, 1359 (1983).

[195] A. Fujiwara and H. Tatekawa, Nippon Dojo Hiryogaku Zasshi **30**, 278 (1959).

[196] H. G. Andrew, School Sci. Rev. **44**, 405 (1963).

[197] M. Travers and Perron, Ann Chim. (Paris) **1**, 298 (1924).

[198] D. N. Pathak and G. N. Pant, Technology (Sindri, India) **10**, 305 (1973).

[199] F. G. Zharovskii, Trudy Komissii Anal. Khim. Akad. Nauk SSSR **3**, 101 (1951).

[200a] V. N. Yaglov and L. A. Marinova, Khim. Khim. Teckhnol. (Minsk) **10**, 26 (1976).

[200b] R. V. Comeaux, Am. Chem. Soc. Div. Water Waste Chem., Preprints **5**, 119 (1965); Chem. Abstr. **65**, 18334e (1966).

[201] W. R. G. Atkins, Nature **114**, 275 (1924).

[202] C. Immerwahr, Z. Elektrochem. **7**, 477 (1901).

[203] J. J. Jurinak and T. S. Inouye, Soil Sci. Soc. Am. Proc. **26**, 144 (1962).

[204] P. Jaulmes and S. Brun, Trav. Soc. Pharm. Montpellier **25**, 98 (1965).

[205] T. A. Tumanova, M. S. Pasechnik and I. A, Volodina, Nauch. Tr. Leningrad. Lesotekh. Akad., No. **108**, 149 (1967).

[206] M. A. Simonov, Yu. K. Egorov-Tismenko and N. V. Belov, Dokl. Akad. Nauk SSSR **239**, 1101 (1978).

[207] M. Hata, K. Okada, S. Iwai, M. Akao and H. Aoki, Acta Crystallogr., Sect. **B** **B34**, 3062 (1978).

[208] G. Engel, Z. Anorg. Chem. **378**, 49 (1970).

[209] M. Akao and S. Iwai, Iyo Kizai Kenkyusho Hokoku, Tokyo Ika Shika Daigaku **10**, 63 (1976).

[210] M. -T. Auerbach-Pouchot and A. Durif, Bull. Soc. Fr. Mineral et Cristollgr. **93**, 123 (1970).

[211] R. C. Ropp and R. W. Mooney, J. Am. Chem. Soc. **82**, 4848 (1960).

[212] R. Klement and F. Zureda, Z Anorg. Allg. Chem. **245**, 229 (1940).

[213] S. Hietanen, L. G. Sillen and E. Hogfeldt, Chem. Scr. **3**, 65 (1973).

[214] K. O. Omarkulova and V. M. Bliznyuk, Prikl. Teor. Khim. **5**, 11 (1974).

[215] P. P. Mahapatra, H. Mishra and N. S. Chickerur, Thermochim. Acta **54**, 1 (1982).

[216] P. P. Mahapatra, H. Mishra and N. S. Chickerur, Thermochim. Acta **59**, 383 (1982).

[217] N. Nayak and S. V. C. Rao, J. Indian Chem. Soc. **52**, 903 (1975).

[218] V. G. Chukhlantsev and K. V. Alyamouskaya, Izv. Vys. Uchebn. Zaved., Khim. Khim. Tekhnol. **4**, 706 (1961).

[219] Number not used.

[220] N. M. Selivanova, N. Yu. Morozova and G. A. Selivanova, Zh. Neorg. Khim. **23**, 1206 (1978); Russ. J. Inorg. Chem. **23**, 665 (1978).

[221] N. M. Selivanova, N. Yu. Morozova and G. A. Selivanova, Izv. Vyssh. Uchebn. Zaved., Khim. Khim Tekhnol. **21**, 311 (1978).

[222] N. M. Selivanova and N. Yu. Morozova, Tr. Mosk. Khim. Tekhnol. Inst. **81**, 13 (1974).

[223] N. Yu. Morozova and N. M. Selivanova, Zh. Neorg. Khim. **21**, 1606 (1976); Russ. J. Inorg. Chem. **21**, 878 (1976).

[224] J. F. McCullough and J. D. Hatfield, J. Chem. Eng. Data **17**, 344 (1972).

[225] O. T. Quimby and H. W. McCune, Anal. Chem. **29**, 248 (1957).

[226] A. Delannoy, J. Hennion, J. C. Bavay and J. Nicole, C. R. Hebd. Seances Acad. Sci., Ser. **C** **289**, 401 (1979).

[227] J. A. Wolhoff and J. Th. G. Overbeek, Rec. Trav. Chim. **78**, 759 (1959).

[228] C. Calvo and P. K. L. Au, Can. J. Chem. **43**, 1147 (1965); **47**, 3409 (1969).

[229] N. T. Kudryavtsev and G. A. Selivanova, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **13**, 932 (1970).

[230] G. A. Selivanova and N. T. Kudryavtsev, Tr. Mosk. Khim. Tekhnol. Inst., No. **67**, 79 (1970).

[231] G. A. Selivanova, N. T. Kudryavtsev and Y. M. Khozhainov, Zh. Neorg. Khim. **17**, 1560 (1972); Russ. J. Inorg. Chem. (Engl. Transl.) **17**, 806 (1972).

[232] G. A. Selivanova and N. T. Kudryavtsev, Zh. Neorg. Khim. **19**, 1951 (1974); Russ. J. Inorg. Chem. (Engl. Transl.) **19**, 1067 (1974).

[233] G. A. Selivanova and N. T. Kudryavtsev, Zh. Neorg. Khim. **15**, 2129 (1970); Russ. J. Inorg. Chem. (Engl. Transl.) **15**, 1097 (1970).

[234] G. A. Selivanova and Z. L. Leshchinskaya, Zh. Fiz. Khim. **45**, 2393 (1971); Russ. J. Phys. Chem. (Engl. Transl.) **45**, 1360 (1971); Deposited Document. VINITI 2941–71.

[235] M. A. Nabar and V. S. Patkar, Bull. Fr. Mineral. Cristallogr. **97**, 479 (1974).

[236] M. E. Kuperman, V. I. Orlov, M. N. Krutitskaya and N. I. Trushkina, Issled. Prikl. Khim., 236 (1955); Chem. Abstr. **50**, 4687g (1956).

[237] V. G. Chukhlantsev, Zh. Neorg. Khim. **2**, 1190 (1957); J. Inorg. Chem. (USSR) 2(5), 314 (1957).

[238] T. Nishimura, C. T. Itoh and K. Tozawa, Arsenic Metall. Fundam. Appl., Proc. Symp. **77** (1988), Edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, Metall. Soc. : Warrendale, PA USA.

[239] V. G. Chukhlantsev, Zh. Neorg. Khim. **1**, 1975 (1956); J. Inorg. Chem. (USSR) 1(9), 41 (1956).

[240] V. G. Chukhlantsev, Zh. Fiz. Khim. **33**, 3 (1959).

[241] A. K. Sagadieva, M. Zh. Makhmetov, V. P. Malyshev and L. I. Maslennikova, Zh. Fiz. Khim. **50**, 2163 (1976); Russ. J. Phys. Chem. (Engl. Transl.) 50, 1302 (1976); Deposited Doc. : VINITI 1564–76.

[242] V. P. Malyshev, A. K. Sagadieva and M. Zh. Makhmetov, Deposited Doc. : VINITI 872–83, 27 pp.

[243] T. Takahashi and K. Sasaki, Kogyo Kagaku Zasshi **56**, 843 (1953).

[244] H. J. Britton and P. Jackson, J. Chem. Soc., **1048** (1934).

[245] G. Engel and W. E. Klee, Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem. **132**, 332 (1970).

[246] T. B. Shakhtakhtinskii, B. S. Valiev, G. A. Aslanov and M. M. Mamatkulov, Med. Zh. Uzb. (4), **76** (1970).

[247] M. Qureshi and S. D. Sharma, Anal. Chem. **45**, 1283 (1973).

[248] von Essen, thesis, Geneva (1897). cited by Cantoni and Passamanik[257].

[249] O. Haehnel, J. Prakt. Chem. **187**, 187 (1924).

[250] E. A. Piperaki and T. P. Hadjiioannou, Chem. Chron. **6**, 375 (1977).

[251] A. Grohmann, Wasserwirtschaft **66**, 133 (1976).

[252] A. W. Mann and R. L. Deutscher, Chem. Geol. **29**, 293 (1980).

[253] F. Ageno and E. Valla, Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend. **20**, 706 (1911).

[254] H. J. Smith, J. Am. Chem. Soc. **40**, 883 (1918).

[255] K. K. Kelley and C. T. Anderson, US Bur. Mines **384**, (1935).

[256] H. Ehlert and W. Hempel, Z. Elektrochem. Angew. Phys, Chem. **18**, 727 (1912).

[257] H. Cantoni and J. Passamanik, Ann. Chim. Anal. Rev. Chem. Anal. Reunics **10**, 258 (1905).

[258] T. Taketatsu, Bull. Chem. Soc. Jpn. **36**, 549 (1963).

[259] E. Ya. Ben'yash, Zh. Neorg. Khim. **9**, 2726 (1964); Russ. J. Inorg. Chem. (Engl. Transl.) **9**, 1469 (1964).

[260] P. Schindler, M. Reinert and H. Gamsjaeger, Helv. Chim. Acta **52**, 2327 (1969).

[261] L. A. Zhukova and V. V. Rachinskii, Izv. Timiryazevsk. Skh. Akad. **(6)**, 204 (1972).

[262] A. M. Egorov and T. P. Titova, Zh. Neorg. Khim. **7**, 275 (1962); Russ. J. Inorg. Chem. (Engl. Transl.) **7**, 141 (1962).

[263] F. Saegusa, Sci. Rep. Tohoku Univ. Ser. **1** **34**, 55 (1950).

[264] P. E. Lake and J. M. Goodings, Can. J. Chem. **36**, 1089 (1958).

[265] H. Gamsjaeger, H. U. Stuber and P. Schindler, Helv. Chim. Acta **48**, 723 (1965).

[266] A. I. Karnaukhov, V. V. Grinevish and E. M. Skobets, Zh. Anal. Khim. **28**, 2298 (1973); J. Anal. Chem. (USSR) **28**, 2042 (1973).

[267] Yu. D. Kondrashev, V. S. Bogdanov, S. N. Golubev and G. F. Pron, Zh. Strukt. Khim. **26**, 90 (1985); J. Struct. Chem. (Engl. Transl.) **26**, 74 (1985).

[268] R. Deyrieux and A. Peneloux, Bull. Soc. Chim. Fr. (8), **2675** (1969); (6), 2160 (1970).

[269] F. Kohlrausch, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **64**, 129 (1908).

[270] F. Kunschert, Z. Anorg. Chem. **41**, 337 (1904).

[271] R. Scholder, E. Gadenne and H. Niemann, Ber. Dtsch. Chem. Ges. **60B**, 1510 (1927).

[272] T. Osawa, Bull. Chem. Soc. Jpn. **23**, 244 (1950).

[273] W. J. Clayton and W. C. Vosburgh, J. Am. Chem. Soc. **59**, 2414 (1937).

[274] W. C. Vosburgh and J. F. Beckman, J. Am. Chem. Soc. **62**, 1028 (1940).

[275] N. P. Zhuk, Zh. Fiz. Khim. **28**, 1690 (1954).

[276] R. W. Money and C. W. Davies, Trans. Faraday Soc. **28**, 609 (1932).

[277] D. L. G. Rowlands and C. B. Monk, Trans. Faraday Soc. **62**, 945 (1966).

[278] A. Lodzinska, Z. Jablonski and J. Gornicki, Rocz. Chem. **39**, 151 (1965).

[279] H. T. S. Britton and M. E. D. Jarrett, J. Chem. Soc., **1489** (1936).

[280] V. Metler and W. C. Vosburgh, J. Am. Chem. Soc. **55**, 2625 (1933).

[281] J. Gornicki and Z. Jablonski, Rocz. Chem. **31**, 1101 (1957).

[282] J. Gornicki and Z. Jablonski, Pr. Nauk Politech Szczecin. **90**, 105 (1978).

[283] S. I. Smyshlyaev, L. M. Voitko and L. A. Vashchenko, Izv. Vyssh. Ucheb. Zaved. Pishch. Tekhnol. (1), **64** (1968).

[284] V. Metler, J. Am. Chem. Soc. **56**, 1509 (1934).

[285] S. Bardham and S. Aditya, J. Indian Chem. Soc. **32**, 105 (1955).

[286] C. Bridle and T. R. Lomer, Acta Crystallogr. **19**, 483 (1965).

[287] M. P. Babkin, L. N. Nozhenko and E. I. Shevchenko, Ukr. Khim. Zh. (Russ. Ed.) **21**, 93 (1955).

[288] M. P. Babkin, Zh. Obshch. Khim. **26**, 1025 (1956); J. Gen. Chem. USSR 26, 1167 (1956).

[289] W. D. Larson and W. J. Tomsicek, J. Am. Chem. Soc. **63**, 3329 (1941).

[290] A. Olin and G. Wikmark, Anal. Chem. **55**, 1402 (1983).

[291] B. Pesce and M. V. Lago, Gazz. Chim. Ital. **74**, 145 (1944).

[292] J. E. Barney II, W. J. Argersinger and C. A. Reynolds, J. Am. Chem. Soc. **73**, 3785 (1951).

[293] F. Accascina and S. Schiavo, Ann. Chim. (Rome) **43**, 873 (1953).

[294] S. Bardhan and S. Aditya, *J* Indian Chem. Soc. **32**, 102 (1955).

[295] Ya. D. Fridman, R. A. Veresova, N. V. Dolgashova and R. I. Sorochan, Zh. Neorg. Khim. **8**, 676 (1963); Russ. J. Inorg. Chem. (Engl. Transl.) 8, 344 (1963).

[296] W. C. Vosburgh, L. G. Newlin, L. A. Puette, R. L. Peck and R. Dick, J. Am. Chem. Soc. **58**, 2079 (1936).

[297] T. Oncescu and M. Macovshi, An. Univ. Bucuresti, Ser. Stint. Nat., Chim. **16**, 77 (1967); Chem. Abstr. **70**, 118674 (1969).

[298] Y. Kanemura and J. I. Waters, J. Inorg. Nucl. Chem. **29**, 1701 (1967).

[299] E. Bottari, Monatsh. Chem. **106**, 451 (1975).

[300] W. B. Schaap and D. L. McMasters, J. Am. Chem. Soc. **83**, 4699 (1961).

[301] D. L. McMasters, J. C. DiRaimondo, L. H. Jones, R. P. Lindley and E. W. Zeitmann, J. Phys. Chem. **66**, 249 (1962).

[302] A. Arevalo, J. C. Rodriguez, A. Cabrena Gonzalez and J. Segura, An. Quim. **70**, 824 (1974).

[303] D. G. Dhuley, D. V. Jahagirdar and D. D. Khanolkar, J. Inorg. Nucl. Chem. **37**, 2135 (1975).

[304] S. C. Khurana and C. M. Gupta, J. Inorg. Nucl. Chem. **35**, 209 (1973).

[305] V. I. Ermolenko and G. I. Ermolenko, Dopov. Akad. Nauk. Ukr. RSR, Ser. B: Geol., Geofiz., Khim. Biol. (11), 996 (1975); Chem. Abstr. **84**, 127321 (1976).

[306] D. M. Czakis-Sulikowska and B. Kuznik, Rocz. Chem. **46**, 331 (1972).

[307] M. I. Lebedeva, B. I. Isaeva and L. S. Demchenko, Zh. Fiz. Khim. 52, 1553 (1978); Russ. J. Phys. Chem. (Engl. Transl.) **52**, 901 (1978); Deposited Doc. : VINITI 3896–77.

[308] M. Cavigli, Atti Soc. Toscana Sci. Nat. Pisa, Mem., Ser. **A 56**, 111 (1949).

[309] S. L. Gupta and M. K. Chatterjee, Trans. SAEST **2**, 9 (1967); Chem. Abstr. **70**, 23512c (1967).

[310] A. Joannis, Ann. Chim. Phys. [5] **26**, 482 (1882).

[311] K. Masaki, Bull. Chem. Soc. Jpn. **6**, 143 (1931).

[312] I. Pines, Coll. Czech. Chem. Commun. **1**, 387 and 429 (1929).

[313] A. S. Corbet, J. Chem. Soc. **129**, 3190 (1926).

[314] H. Persson, Acta Chem. Scand. **25**, 543 (1971)

[315] R. M. Izatt, J. J. Christensen, J. W. Hansen and G. D. Watt, Inorg. Chem. **4**, 718 (1965).

[316] P. W. Robertson, News J. Phys. Sci. **95**, 253 (1907).

[317] I. M. Korenman, F. P. Sheyanova and M. A. Potapova, Zh. Obshch. Khim. **26**, 2114 (1956); J. Gen. Chem. USSR **26**, 2359 (1956).

[318] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis (Interscience Publishers, Inc., New York, 1947), Vol. II, p. 341.

[319] A. Swinarski and M. Czakis, Przem. Chem. **11**, 384 (1955).

[320] M. Czakis and A. Swinarski, Rocz. Chem. **47**, 1985 (1957).

[321] B. V. J. Cuvelier, Z. Anal. Chem. **102**, 16 (1935).

[322] V. G. Kuznetsov, Z. V. Popova and G. B. Seifer, Zh. Neorg. Khim. **15**, 2077 (1970); Russ. J. Inorg. Chem. (Engl. Transl.) **15**, 1071 (1970).

[323] M. Cola and M. T. G. Valentini, Inorg. Nucl. Chem. Lett. **8**, 5 (1972).

[324] H. Siebert, B. Nuber and W. Jentsch, Z. Anorg. Allg. Chem. **474**, 96 (1981).

[325] H. B. Weiser, W. O. Milligan and J. B. Bates, J. Phys. Chem. **46**, 99 (1942).

[326] A. K. Van Bever, Recl. Trav. Chim. Pays-Bas 57, 1259 (1938).

[327] H. Siebert and W. Jentsch, Z. Naturforsch., *B: Anorg. Chem., Org.* Chem., Biochem., Biophys., Biol. **36B**, 123 (1981).

[328] E. Garnier, P. Gravereau, K. Ahmadi and A. Hardy, Rev. Chim. Miner **21**, 144 (1984).

[329] P. Gravereau and E. Garnier, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **C40**, 1306 (1984).

[330] I. V. Tananaev, M. A. Glushkova and G. B. Seifer, Zh. Neorg. Khim. **1**, 72 (1956); J. Inorg. Chem. (USSR) **1**(1), 72 (1956).

[331] A. Basinski and J. Mucha, Rocz. Chem. **34**, 811 (1960).

[332] A. Basinski, W. Szymanski and Z. Bebnista, Rocz. Chem. **35**, 59 (1961).

[333] A. Basinski, W. Szymanski and R. Tyszka, Rocz. Chem. **35**, 63 (1961).

[334] P. A. Rock and R. E. Powell, Inorg. Chem. **3**, 1593 (1964).

[335] F. Krleza, M. Avlijas and G. Dokovic, Glas. Hem. Technol. Bosne Hercegovine **23/34**, 7 (1976)(publ. 1977).

[336] M. W. Grieb and W. H. Cone, J. Phys. Colloid Chem. **54**, 658 (1950).

[337] A. S. Dyulgerova, V. A. Zakharov and O. A. Songina, Izv. Akad. Nauk. Kaz. SSR, Ser. Khim. (6), 1 (1983).

[338] F. Cuta, Coll. Czech. Chem. Commun. **1**, 538 (1929).

[339] M. Cola, M. T. Ganzerli-Valentini and P. A. Borroni, J. Inorg. Nucl. Chem. **40**, 1041 (1978).

[340] A. Basinski and S. Poczopko, Rocz. Chem. **31**, 449 (1958).

[341] A. Basinski and W. Szymanski, Rocz. Chem. **32**, 23 (1958).

[342] A. Basinski and U. Ledzinska, Rocz. Chem. **31**, 457 (1957).

[343] A. Bellomo, D. DeMarco and A. Casale, Talanta **19**, 1236 (1972).

[344] A. I. Karnavkhov, V. Grinevich and E. M. Skobets, Zh. Anal. Khim. **28**, 2298 (1973); Russ. J. Anal. Chem. (Engl. Transl.) **28**, 2042 (1973).

[345] E. L. King, J. Am. Chem. Soc. **71**, 319 (1949).

[346] G. R. Levi and M. Curti, Gazz. Chim. Ital. **86**, 1022 (1956).

[347] W. Feitknecht and E. Haberli, Helv. Chim. Acta **33**, 922 (1950).

[348] N. V. Aksel'rud and V. B. Spivakovskii, Zh. Neorg. Khim. **3**, 269 (1958); J. Inorg. Chem. (USSR) 3(2), 38 (1958).

[349] M. L. Gomez de Aguero, A. Ramirez Garcia, O. Garcia Martinez and A. Guerrero Laverat, An. Quim., Ser. **B 84**, 207 (1988).

[350] W. Feitknecht and W. Gerber, Helv. Chim Acta **20**, 1344 (1937).

[351] W. Feitknecht and W. Gerber, Z. Krist. **98**, 168 (1937).

[352] R. Nasanen, Suom. Kemistil. B. **28**, 111 (1955).

[353] G. N. Dobrokhotov, Zh. Prikl. Khim. 27, 1056 (1954); J. Appl. Chem. USSR (Engl. Transl.) 27, 995 (1954).

[354] H. Hagisawa, Bull. Inst. Phys. Chem. Res. Tokyo **18**, 368 (1939).

[355] T. Pieniazek, A. Milewska and P. Masztalerz, Chem. Stosow. **26**, 419 (1982).

[356] W. J. Evans, M. A. Marini and C. J. Martin, Thermochim. Acta **67**, 287 (1983).

[357] P. Artmann, Z. Anal. Chem. **54**, 89 (1915).

[358] Travers and Perron, Ann. Chim. (Paris) [10] **2**, 43 (1924).

[359] S. I. Vol'fkovitch, R. E. Remen, Issled. po Prikl. Khim., Akad. Nauk SSSR, Otd. Khim. Nauk, **149** (1955).

[360] M. Sahli, Dissertation, Bern (1952), cited by Schindler *et al.* [260]

[361] W. Brzyska and G. Bubela, Biul. Lubel. Tow. Nauk., Mat. -Fiz. -Chem. **24**, 15 (1982)(Pub. 1984).

[362] G. A. Kitaev, T. P. Bol'shchikova and L. E. Yatlova, Zh. Neorg. Khim **16**, 3173 (1971); Russ. J. Inorg. Chem. (Engl. Transl.) **16**, 1683 (1971).

[363] T. Oyama, J. Shimoizaka, S. Usui, A. Ohba and T. Yamasaki, Tohoku Kozan **4**(1), 22 (1957).

[364] M. Arnac, G. Verboom, Anal. Chem. **46**, 2059 (1974).

[365] O. M. Stepanyuk, Sb. Nauchn. Tr., Dnepropetr. Gos. Med. Inst. **6**, 447 (1958).

[366] A. I. Busev and M. I. Ivanyutin, Zh. Anal. Khim. **13**, 312 (1958); J. Anal. Chem. (USSR) (Engl. Transl.) **13**, 351 (1958).

[367] A. I. Busev and V. M. Byr'ko, Trudy Komissii Anal. Khim., Akad Nauk SSSR, Inst. Geokhim., Anal. Khim. **9**, 59 (1958).

[368] M. G. Tskitishvili, I. I. Mikadze and M. V. Chrelashvili, Izv. Akad. Nauk Gruz. SSR, Ser. Khim. **9**(2), 95 (1983).

[369] I. P. Alekseeva, A. P. Dushina and V. B. Aleskovskii, Zh. Obshch. Khim. **38**, 1428 (1968); J. Gen. Chem. (USSR) (Engl. Transl.) **38**, 1382 (1968).

[370] I. P. Alekseeva, A. P. Dushina and V. B. Aleskovskii, Zh. Obshch. Khim. **42**, 249 (1972); J. Gen Chem. (USSR)(Engl. Transl.) **42**, 237 (1972).

[371] I. P. Alekseeva, A. P. Dushina and V. B. Aleskovskii, Zh. Obshch. Khim. **44**, 477 (1974); J. Gen. Chem. (USSR)(Engl. Transl.) **44**, 459 (1974).

[372] Z. G. Zangieva, N. I. Kaloev, B. I. Bashkov, V. E. Burlakova and L. M. Kubalova, Zh. Neorg. Khim. **28**, 2631 (1983); Russ. J. Inorg. Chem. **28**, 1494 (1983).

[373] M. B. Shchigol, Zh. Neorg. Khim. **4**, 2014 (1959); Russ. J. Inorg. Chem. (Engl. Transl.) **4**, 913 (1959).

[374] A. Swinarski and A. Lodzinska, Rocz. Chem. **32**, 1053 (1958).

[375] A. DeRobertis, A. Bellomo, D. DeMarco, Bull. Soc. Chim. Fr., (1-2, Pt. 1), 23 (1982).

[376] C. J. Coetzee, J. Inorg. Nucl. Chem. **41**, 254 (1979).

[377] K. Koshi and K. Iwasaki, Ind. Health **21**(2), 57 (1983).

[378] Y. He and Y. Wang, Youse Jinshu **35**(3), 59 (1983).

[379] W. Feitknecht and L. Hugi-Carmes, Helv. Chim. Acta **37**, 2093 (1954).

[380] A. N. Zelikman and T. E. Prosenkova, Zh. Neorg. Khim. **6**, 212 (1961); Russ. J. Inorg. Chem. (Engl. Transl.) **6**, 105 (1961).

[381] D. V. R. Rao, J. Sci. Ind. Res., Sect. B: **13**, 309 (1954).

[382] L. N. Dem'yanets and M. I. Ravich, Zh. Neorg. Khim. **17**, 2816 (1972); Russ. J. Inorg. Chem. (Engl. Transl.) **17**, 1476 (1972).

[383] L. N. Dem'yanets, Kristallografiya **13**, 859 (1968).

[384] G. W. Easterwood and J. J. Street, Proc. -Soil Crop Sci. Fla. **41**, 214 (1982).

[385] G. Bruemmer and U. Herms, Eff. Accumulation Air Pollut. For. Ecosgst., Proc. Workshop 1982 [Edited by B. Ulrich and J. Pankrath. Reidel: Dordrecht, Netherlands, publ. 1983], pp. 233–43.

[386] Yu. D. Kondrashev, V. S. Bogdanov, S. N. Golubev and G. F. Pron, Zh. Strukt. Khim. **26**, 90–3 (1985); J. Struct. Chem. (Engl. Transl. **26**, (1985).

[387] W. Brzyska amd G. Bubela, Biul. Lubel. Tow. Nauk, Mat. -Fiz. -Chem. **24**(1), 15–20 (1982, publ. 1984).

[388] A. K. Prokof'ev, Usp. Khim. **50**, 54–84 (1981); Russ. Chem. Rev. (Engl. Transl.) **50**, 32–62 (1981).

[389] E. V. Margulis, R. N. Yaremenko, B. I. Bashkov, Zh. Neorg. Khim. **34**, 2962–65 (1989); Russ. J. Inorg. Chem. (Engl. Transl.) **34**, 1692–95 (1989).

[390] J. D. Cox, D. D. Wagman and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corporation, New York and Washington, 1989.

[391] D. Rai, A. R. Felmy and R. W. Szelmeczka J. Solution Chem. **20**, 375–90 (1991).

[392] S. L. Stipp, G. A. Parks, D. K. Nordstron and J. O. Leckie, Preprint (in review).

[392a] Private communication, D. K. Nordstrom, US Geological Survey, Boulder, CO.

[393] A. V. Rumyantsev and N. A. Charykov Zh. Neorg. Khim. 34, 3174 (1989); Russ. J. Inorg. Chem. **20** 1815 (1989).

[394] A. J. Paulson, M. M. Benjamin and J. F. Ferguson Water Res. **23**(12), 1563 (1989).

[395] K. D. Sharma Hydrometallurgy 24(3), 407–15 (1990).

[396] J. Li, H. Tang and H. Xuei Huanjing Huaxue 8(16), 1–10 (1987). [Chem. Abstr. **113**, 102911s (1990)].

[397] J. Palko and M. Yli-Halla Acta Agric. Scand. 40(2), 117–42 (1990). [Chem. Abstr. **114**, 22892s (1991)].

[398] N. S. Chickerur, H. M. Dash, G. H. Nayak and B. P. Padhy Proc. Natl. Acad. Sci., India, Sect. A. 59(3), 401–5 (1989). [Chem. Abstr. **114**, 151443v (1991)].