

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

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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.

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| pH  | [Zn <sup>2+</sup> ]     | [Cd <sup>2+</sup> ]     | Total as [TeO <sub>3</sub> <sup>2-</sup> ] | Total as [TeO <sub>4</sub> <sup>2-</sup> ] |
|-----|-------------------------|-------------------------|--|--|
| 7.5 | 6.34 × 10 <sup>-5</sup> |                         | 9.71 × 10 <sup>-4</sup>                    |  |
| 7.5 |                         | 5.76 × 10 <sup>-6</sup> | 6.88 × 10 <sup>-4</sup>                    |  |
| 6   | 7.51 × 10 <sup>-3</sup> |                         |  | 9.97 × 10 <sup>-3</sup>                    |
| 6   |                         | 3.68 × 10 <sup>-3</sup> |  | 7.97 × 10 <sup>-3</sup>                    |

#### 4.9. Zinc and Cadmium Phosphates

##### 4.9.a. Zinc and Cadmium Metaphosphate

Zn(PO<sub>3</sub>)<sub>2</sub> [13566-15-9] Molecular weight 223.33  
 Cd(PO<sub>3</sub>)<sub>2</sub> [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.*<sup>179</sup> report on orthorhombic Cd(PO<sub>3</sub>)<sub>2</sub>, and Averbuch-Pouchot *et al.*<sup>180</sup> report on monoclinic Cd<sub>3</sub>(P<sub>3</sub>O<sub>9</sub>)·10H<sub>2</sub>O. These authors and others have published extensively in the area.

There is doubt that the mono-metaphosphate ion, PO<sub>3</sub><sup>-</sup>, has a stable existence in aqueous solution. However, condensed forms (PO<sub>3</sub>)<sub>n</sub><sup>-</sup>, with *n* = 2 to 8, 10 and 14, are known. The trimetaphosphate, (P<sub>3</sub>O<sub>9</sub>)<sup>3-</sup>, and the tetrametaphosphate, (P<sub>4</sub>O<sub>12</sub>)<sup>4-</sup>, 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<sup>10</sup>. 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 <sup>a</sup><br>c/mol L <sup>-1</sup> | Reference                    |
|------|--|--|------------------------------|
| room | Cd(P <sub>2</sub> O <sub>6</sub> )·H <sub>2</sub> O                              | 0.102  | Glatzel, 1880 <sup>181</sup> |
| room | Zn(P <sub>2</sub> O <sub>6</sub> )   | 1.12   | Glatzel, 1880 <sup>181</sup> |
| 293  | Zn <sub>3</sub> (P <sub>3</sub> O <sub>9</sub> ) <sub>2</sub> ·9H <sub>2</sub> O | 0.000120   | Tammann, 1892 <sup>182</sup> |
| room | Zn <sub>2</sub> (P <sub>4</sub> O <sub>12</sub> )·10H <sub>2</sub> O             | 0.029  | Glatzel, 1880 <sup>181</sup> |

<sup>a</sup>Values as quoted in Comey and Hahn<sup>10</sup>

##### 4.9.b. Zinc Orthophosphate

Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> [7779-90-0] molecular weight 386.08  
 Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O [15491-18-6] (hopeite) α and β forms  
 Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O [16842-47-0] (parahopeite)  
 (three forms) molecular weight 458.14

*Physical Characteristics:* Zinc orthophosphate, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, is monoclinic with *Z* = 2, *a*, *b*, and *c* = 7.548, 8.469 and 5.074 × 10<sup>-10</sup> m, respectively, and a calculated density of 3.964 × 10<sup>3</sup> kg m<sup>-3</sup>. 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<sup>-10</sup> m, respectively, and a calculated density of 3.08 × 10<sup>3</sup> kg m<sup>-3</sup>. Parahopeite is triclinic with *Z* = 1, *a*, *b* and *c* = 5.755, 7.535 and 5.292 × 10<sup>-10</sup> m, respectively, and a calculated density of 3.304 × 10<sup>3</sup> kg m<sup>-3</sup>.

Goloshchapov and Filatova<sup>184</sup> have confirmed and extended earlier work<sup>185,186</sup> on the ZnO + P<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O system. They find regions of stability of the solids Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, ZnHPO<sub>4</sub>·3H<sub>2</sub>O, ZnHPO<sub>4</sub>·H<sub>2</sub>O, Zn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O and Zn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>3</sub>PO<sub>4</sub>. Bek *et al.*<sup>187</sup> have also studied the system as well as a four component system containing these components plus N<sub>2</sub>O<sub>5</sub>, but their papers were not available to us. The system is further complicated in that the tetrahydrate can exist in the three crystalline forms α- and β-hopeite and parahopeite. Most workers have not characterized the solid. Nriagu<sup>188</sup> has characterized the equilibrium solid in his systems as the α-hopeite, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O.

There have been studies of the solubility in the presence of various electrolytes, and as a function of pH. Goloshchapov and Filatova<sup>184</sup> say that Zn(HPO<sub>4</sub>) and Zn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> dissolve incongruently to form Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Sigel *et al.*<sup>189</sup> identify the species ZnHPO<sub>4</sub> in aqueous solution and measure its formation constant at *I* = 0.1 NaClO<sub>4</sub> as 251 ± 1 at 298 K.

Machevskaya and Babakina<sup>190</sup> observed the onset of precipitation as a function of pH, and Zn<sup>2+</sup>(aq) and PO<sub>4</sub><sup>3-</sup>(aq) concentrations. They developed an equation, assumed to be for 298 K, for the pH of precipitation:

$$\text{pH}_{\text{ppt}} = 7.3 - C_{\text{Zn}^{2+}} / (0.127 + (C_{\text{Zn}^{2+}} / C_{\text{PO}_4^{3-}}) + 0.180C_{\text{Zn}^{2+}})$$

They present figures of pH<sub>ppt</sub> vs. ion concentration at 298, 323 and 348 K both in the absence and presence of Ni<sup>2+</sup>(aq).

Table 29 summarizes the literature reporting Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O solubility values in water. Some workers<sup>191,192,193</sup> used very short equilibration times in their solubility studies and appear to have made no tests to confirm saturation. Andrew<sup>196</sup> 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<sup>186</sup> and Salmon and Terrey<sup>185</sup> are reproduced in the Seidell-Linke Handbook<sup>6</sup>.

The solubility product values are in Table 31. No value is recommended, but the value of Nriagu<sup>188</sup> for the tetrahydrate solid, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (α-hopeite), is classed as tentative. The value of Trapeznikova *et al.*<sup>194</sup> 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<sup>12</sup> and the Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(s) Gibbs energy and its temperature coeffi-

cient of Yaglov and Marinova<sup>200a</sup> appears to depend on the  $K_{s0}$  value of Zharovskii<sup>199</sup>. The value of Comeaux<sup>200b</sup> is taken from an abstract and its background is unknown. The value used by Machevskaya and Babakina<sup>190</sup> 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<br>c/mol L <sup>-1</sup>                    | Method                                  | Reference  |
|-------------|--|---|--|
| ?           | $7.68 \times 10^{-4}$                                  | ?                                       | Fujiwara, Tatekawa,<br>1959 <sup>195</sup>           |
| 293         | $\sim 6 \times 10^{-6}$                                | Chronopotentiometry                     | Trapeznikova <i>et al.</i> ,<br>1983 <sup>194a</sup> |
| 298.2 ± 0.2 | as P <sub>2</sub> O <sub>5</sub>                       | Molybdate<br>reaction                   | Joshi, Jain, 1964 <sup>191b</sup>                    |
| 298.7 ± 0.5 | as Zn <sup>2+</sup> &<br>PO <sub>4</sub> <sup>3-</sup> | Molybdate reac. &<br>dithionate complex | Mukerji, 1979 <sup>193</sup>                         |
| 307.2       | as ZnO &<br>P <sub>2</sub> O <sub>5</sub>              | not specified                           | Pant, Pathak,<br>1976 <sup>192b</sup>                |

<sup>a</sup>Value for hopeite,  $Zn_3(PO_4)_2 \cdot 4H_2O$ , estimated from a small graph.

<sup>b</sup>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.*<sup>206</sup> report that  $Cd_3(PO_4)_2$  is orthorhombic with  $Z = 8$ ,  $a$ ,  $b$  and  $c = 15.65$ ,  $11.07$  and  $7.56 \times 10^{-10}$  m, respectively, and a calculated density of  $5.35 \times 10^3$  kg m<sup>-3</sup>. No crystallographic information was found on  $CdHPO_4$ .

Hata *et al.*<sup>207</sup> report cadmium hydroxyapatite,  $Cd_3(PO_4)_3(OH)$ , is hexagonal with  $Z = 2$ ,  $a$  and  $c = 9.335$  and  $6.664 \times 10^{-10}$  m, respectively, and a calculated density of  $5.694 \times 10^3$  kg m<sup>-3</sup>. Two other papers<sup>208,209</sup> also report hexagonal structures for the material. Akao and Iwai<sup>209</sup> 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  $9.675 \times 10^{-10}$  m, respectively. Averbuch-Pouchot and Durif<sup>210</sup> 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 electrolytes are listed in Table 33.

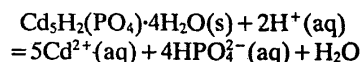
Ropp and Mooney<sup>211</sup> indicate the stable solid precipitated from mixing solutions of  $Cd(NO_3)_2$  and  $H_3PO_4$  at several concentrations over the 273 to 373 temperature interval and the pH range of 3 to 11 is

$Cd_5H_2(PO_4)_4 \cdot 4H_2O$ . 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  $Cd_5H_2(PO_4)_4 \cdot 4H_2O$  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<sup>212</sup> 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.*<sup>215,216</sup> 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<sup>214</sup> 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<sup>213</sup> report several equilibrium constants that may be useful in modeling cadmium phosphate solutions. They are



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

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

#### 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  $\alpha$  and  $\beta$  forms. The  $\alpha \rightarrow \beta$  transition occurs at  $405 \pm 1$  K. The  $\alpha$  form is a super-lattice which changes to the high temperature  $\beta$  form with a one-third decrease in the  $a$  dimension and a one-half change in the  $c$  dimension<sup>229</sup>. The  $\beta$  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<br>c/mol L <sup>-1</sup>                      | Method                   | Reference                                      |
|--------------|---|--|--------------------------|--|
| ?            | Peterman's soln.<br>NH <sub>4</sub> citrate, NaOH, HCl  |  |                          | Fujiwara, Tatekawa, 1959 <sup>195,a</sup>      |
| 284 ± 1      | HCl/pH = 6.85   | 2.88 × 10 <sup>-6</sup>                                  | molybdate reac.          | Atkins, 1924 <sup>201</sup>                    |
| 292 ± 1      | K phthalate, HCl,<br>pH = 3.6   | 2.3 × 10 <sup>-2</sup> Zn <sup>2+</sup>                  | hydroquinone             | Zharovskii, 1951 <sup>199</sup>                |
|              | pH = 3.8  | 1.7 × 10 <sup>-2</sup> "                                 | "                        | " "  |
|              | Na acetate, acetic acid<br>pH = 3.97  | 1.1 × 10 <sup>-2</sup> Zn <sup>2+</sup>                  | "                        | " "  |
|              | pH = 4.63   | 5.5 × 10 <sup>-3</sup> "                                 | "                        | " "  |
|              | pH = 5.57   | 1.5 × 10 <sup>-3</sup> "                                 | "                        | " "  |
| 297.15       | H <sub>2</sub> SO <sub>4</sub> /pH = 4.95   | Zn <sup>2+</sup> , PO <sub>4</sub> <sup>3-</sup> conc.   | molybdate                | Murkerji, 1979 <sup>193</sup>                  |
| 297.65       | NaOH/pH = 8.5   | " " "  | dithionate               | " "  |
| 298          | Na <sub>2</sub> HPO <sub>4</sub> /I = 0.075   | 6 × 10 <sup>-3</sup>                                     | electrochem.             | Immerwahr, 1901 <sup>202</sup>                 |
| 298          | ZnCl <sub>2</sub> ·H <sub>2</sub> PO <sub>4</sub> , NaOH<br>pH = 4.10–8.63  | Zn <sup>2+</sup> , PO <sub>4</sub> <sup>3-</sup> conc.   | dithionate               | Jurinack, Inouye, 1962 <sup>203,b</sup>        |
| 298.15       | pH = 5–14   | 1.47 × 10 <sup>-3</sup> – 4.14 × 10 <sup>-7</sup>        | calculation              | Jaulmes, Brun, 1965 <sup>204</sup>             |
| 298.2 ± 0.1  | several acid solns.   | P <sub>2</sub> O <sub>5</sub> reported                   | molybdate                | Joshi, Jain, 1964 <sup>191,c</sup>             |
| 298.15       | H <sub>3</sub> PO <sub>4</sub> /pH =<br>3.39–4.62   | 6.47 × 10 <sup>-3</sup><br>– 3.3 × 10 <sup>-4</sup>      | atomic absorp.           | Nriagu, 1973 <sup>188,b</sup>                  |
| 298 –<br>335 | ZnO + P <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O  | data table and<br>phase diagram                          | ferrocyanide             | Eberly, Gross, Crowell, 1920 <sup>186</sup>    |
| 298 –<br>373 | ZnO + P <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O<br>phase diagram   | data table and   | ferrocyanide             | Salomon, Terrey, 1950 <sup>185</sup>           |
| 273 –<br>333 | ZnO + P <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O<br>phase diagram   | data table and   | complexometric           | Golashchapov,<br>Filatova, 1969 <sup>184</sup> |
| 303.15       | 0.0012–0.0060 N<br>solutions of<br>NaOH, H <sub>2</sub> CO <sub>3</sub> ,<br>tartaric acid,<br>citric acid, Na <sub>2</sub> CO <sub>3</sub><br>and NaHCO <sub>3</sub> | g L <sup>-1</sup> P <sub>2</sub> O <sub>5</sub> reported |                          | Pathak, Pant, 1973 <sup>198,c</sup>            |
| 303.15       | NaOH/pH = 8.5   | Zn <sup>2+</sup> , PO <sub>4</sub> <sup>3-</sup> conc.   | Molybdate,<br>dithionate | Murkerji, 1979 <sup>193</sup>                  |
| 307.15       | H <sub>2</sub> SO <sub>4</sub> /pH = 5.00   | " " "  | " "                      | " "  |

\*Solubilities of ZnHPO<sub>4</sub> and Zn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> are also given.

<sup>b</sup>Solid Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O confirmed as solid by X-ray analysis.

<sup>c</sup>Unusually short equilibration times used, solutions may not be at equilibrium.

TABLE 31. The zinc orthophosphate solubility product constant

| T/K                                | Ionic Strength<br>I/Electrolyte | Ion Product Constant<br>K <sub>sp</sub> | Reference  |
|------------------------------------|---------------------------------|---|--|
| Calculated from thermodynamic data |                                 |   |  |
| 298.15                             | 0                               | 7.8 × 10 <sup>-33</sup>                 | "  |
| 323                                | 0                               | 3.0 × 10 <sup>-37</sup>                 | Yaglova, Marinova, 1976 <sup>200a,b</sup>        |
| From solubility studies            |                                 |   |  |
| 292 ± 1                            | c                               | 9.1 × 10 <sup>-33</sup>                 | Zharovskii, 1951 <sup>199</sup>                  |
| 293                                | ?                               | 1.2 × 10 <sup>-24</sup>                 | Trapeznikova <i>et al.</i> , 1983 <sup>194</sup> |
| 298.15                             | 0                               | 5.1 × 10 <sup>-36</sup>                 | Nriagu, 1973 <sup>188,d</sup>                    |
| 298.15                             | ?                               | 2 × 10 <sup>-33</sup>                   | Machevskaya, Babakina, 1982 <sup>190,e</sup>     |
| 298                                | ?                               | 1 × 10 <sup>-37</sup>                   | Comeaux, 1965 <sup>200b,f</sup>                  |

<sup>a</sup>Calculated by us using the ΔG<sub>f</sub><sup>o</sup> from Yaglov and Marinova<sup>200a</sup> and the aqueous ion Gibbs energies of formation from the NBS Tables<sup>12</sup>.

<sup>b</sup>Source of data and method of calculation not clear to us.

<sup>c</sup>An average of values determined at different pH's in buffered media.

<sup>d</sup>Solution reaction stated to be Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O(s) (α-hopeite) = 3Zn<sup>2+</sup>(aq) + 2PO<sub>4</sub><sup>3-</sup>(aq) + 4H<sub>2</sub>O(M).

<sup>e</sup>Value reported and used in this source, no references.

<sup>f</sup>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              | $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(s) = 3\text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{PO}_4^-(\text{aq}) + 4\text{OH}^-(\text{aq})$<br>$K = 6.3 \times 10^{-53}$ at $I = 0$ Nriagu, 1973 <sup>188</sup><br>$K = 1.3 \times 10^{-48}$ at $I \neq 0$ , pH = 7.48 | Jurinak, Inouye, 1967 <sup>203,a</sup>        |
| 298.15              | $\text{Zn}(\text{H}_2\text{PO}_4)_2(s) = \text{Zn}^{2+}(\text{aq}) + 2\text{H}_2\text{PO}_4^-(\text{aq})$<br>$K_{s0} = 1.72 \times 10^{-3}$ to $4.3 \times 10^{-12}$ at pH = 2.0-5.4.   | Tumanova, <i>et al.</i> , 1967 <sup>205</sup> |
| 298.15              | $\text{Zn}(\text{H}_2\text{PO}_4)_2(s) + 2\text{H}^+(\text{aq}) = \text{Zn}^{2+}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$<br>$K = 3.28 \times 10^{-2}$ to $1.31 \times 10^{-7}$ at pH 2.0 to 5.4  | " "   |
| 298.15              | $\text{Zn}^{2+}(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) = \text{ZnHPO}_4(\text{aq})$<br>$\beta = 251 \pm 1$ at $I = 0.1$  | Sigel <i>et al.</i> , 1967 <sup>189</sup>     |
| Solubility in water |   |   |
| ?                   | $\text{ZnHPO}_4$ $7.86 \times 10^{-5}$ mol L <sup>-1</sup>  | Fijiwara, Tatekawa, 1959 <sup>195,b</sup>     |
| ?                   | $\text{Zn}(\text{H}_2\text{PO}_4)_2$ $6.42 \times 10^{-4}$ mol L <sup>-1</sup>  | " "   |
| 291                 | $\text{Zn}(\text{H}_2\text{PO}_4)_2$ 0.03 mol L <sup>-1</sup>   | Travers, Perron, 1924 <sup>197,c</sup>        |

<sup>a</sup>The authors give this as an approximate value; Nriagu<sup>188</sup> questions the composition of the solid state in this work.

<sup>b</sup>There are additional solubility values in the paper for Peterson's solution, aqueous ammonium citrate and other aqueous solutions as a function of pH.

<sup>c</sup>Doubtful value.

TABLE 33. The solubility of several orthophosphates in aqueous solution

| T/K   | Ionic strength<br>I/electrolyte        | Phosphate  | Solubility<br>c/mol L <sup>-1</sup>     | Reference  |
|-------|--|--|---|--|
| (298) | 0.075/Na <sub>2</sub> HPO <sub>4</sub> | Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>                    | $4.2 \times 10^{-3}$                    | Immerwahr, 1901 <sup>202,a</sup>                 |
| 310   | 0.0045-0.165/                          | CdHPO <sub>4</sub>   | $(1.52 - 1.65) \times 10^{-3}$          | Mahapatra, <i>et al.</i> , 1982 <sup>216,b</sup> |
| 315   | NaNO <sub>3</sub>                      | "  | $(1.43 - 1.62) \times 10^{-3}$          | " " "  |
| 320   | " "                                    | "  | $(1.52 - 1.60) \times 10^{-3}$          | " " "  |
| 325   | " "                                    | "  | $(1.53 - 1.57) \times 10^{-3}$          | " " "  |
| 310   | pH = 6,7,8/?                           | Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> | graph                                   | Nayak, Rao, 1975 <sup>217</sup>                  |
| 310   | pH = 5.175-8.10<br>/°                  | "  | Cd <sup>2+</sup> &<br>total P reported. | Mahapatra, <i>et al.</i> , 1982 <sup>215</sup>   |

<sup>a</sup>Calculated relative to a CdCl<sub>2</sub>, KNO<sub>3</sub> half-cell with [Cd<sup>2+</sup>] assumed to be 0.5 mol L<sup>-1</sup>.

<sup>b</sup>The total ionic strength, all ions, ranges 0.0253 to 0.186.

<sup>c</sup>Electrolyte is NaNO<sub>3</sub>, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> + HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, or borax + boric acid. The solid phase reported to be CdHPO<sub>4</sub> at pH 5.0 to 7.0, and Cd<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> at pH 7.5 to 8.0.

and  $4.51 \times 10^{-10}$  m, respectively,  $\beta = 105.4^\circ$ , and a calculated density of  $4.241 \times 10^3$  kg m<sup>-3</sup>. 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<sup>221,225</sup>.

Neither the zinc pyrophosphate nor its hydrates exists alone with water. The hydrates exist in the equilibrium solid in a number of ternary systems<sup>220-223</sup>. Both the trihydrate and penta-hydrate are reported to have regions of stability in the ZnSO<sub>4</sub> + K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>O and the Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> + H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>O systems<sup>230</sup>. A number of potassium zinc pyrophosphate hydrates show regions as the equilibrium solid. The equilibrium solids in the Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> +

(NH<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>O system<sup>224</sup> at 298 K are the mixed hydrates Zn(NH<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O and Zn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O.

The solubility studies and some solubility values are given in Table 35. Selivanova *et al.*<sup>221</sup> observed the change of the pentahydrate to the trihydrate at about 351 K. Table 36 gives Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> solubility product values derived from solubility studies<sup>221,226</sup>. These have not been corrected to zero ionic strength, but they have been selectively corrected for complex ion formation. The formation constants of ZnP<sub>2</sub>O<sub>7</sub><sup>2-</sup>(aq) and Zn(P<sub>2</sub>O<sub>7</sub>)<sub>4</sub><sup>4-</sup>(aq) are given by Sillen and Martell<sup>6</sup>. The zero ionic strength values of Wolhoff and Overbeek<sup>227</sup> are

TABLE 34. Solubility product values for several cadmium phosphates

| T/K   | Media, pH or I/electrolyte                    | $K_{s0}$                        | $K_{sp}^0$            | Reference   |
|---|---|---------------------------------|-----------------------|---|
| Cadmium orthophosphate, $Cd_3(PO_4)_2$          |   |                                 |                       |   |
| 292.65<br>±0.5                                  | pH=4.9/HCl,HNO <sub>3</sub>                   | $(2.7 \pm 1.2) \times 10^{-33}$ |                       | Chukhlantsev, <i>et al.</i> , 1961 <sup>218</sup> |
| 298.15  | 0   |                                 | $2.5 \times 10^{-33}$ | NBS Tables <sup>12</sup>                          |
| 323.15  | 0   |                                 | $2.8 \times 10^{-37}$ | Yaglov, Marinova 1976 <sup>200a,a</sup>           |
| Cadmium hydrogen phosphate, $CdHPO_4$           |   |                                 |                       |   |
| 293.15  | 0   |                                 | $1.5 \times 10^{-7}$  | Omarkulova, Bliznyuk, 1974 <sup>214,b</sup>       |
| 310   | 0.0045-0.165/                                 | $(2.47-2.89) \times 10^{-9}$    |                       | Mahapatra <i>et al.</i> , 1982 <sup>216,c</sup>   |
| 315   | NaNO <sub>3</sub>                             | $(2.45-2.78) \times 10^{-9}$    |                       |   |
| 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 <sub>3</sub> ,borate           | $5.97 \times 10^{-97}$          |                       | Mahapatra <i>et al.</i> , 1982 <sup>215</sup>     |
|   | pH = 8.10/ " " "                              | $3.57 \times 10^{-97}$          |                       |   |
| 310-<br>325                                     | pH = 5.0/NaNO <sub>3</sub> ,acetate<br>buffer | values<br>reported <sup>d</sup> |                       | " " "   |

<sup>a</sup>Details of this calculation not clear to us.

<sup>b</sup>Calculated without consideration of any complex ion formation.

<sup>c</sup>Total ionic strength 0.00253-0.186; the authors report the  $K_{s0}$  value to five digits.

<sup>d</sup>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<br>$c/mol L^{-1}$     | Reference  |
|-------------------------|--|----------------------------------|--|
| 273.15<br>298.15        | Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> O<br>" " "   | 0.184-0.562<br>table/figure      | Selivanova <i>et al.</i> , 1978 <sup>220,a</sup><br>" " "  |
| 298.15 -<br>358.15      | 1/KNO <sub>3</sub> or NaNO <sub>3</sub>  | Zn <sup>2+</sup> conc.           | Selivanova, <i>et al.</i> , 1978 <sup>221</sup>  |
| 298.15<br>298.2<br>±0.2 | ZnSO <sub>4</sub> + K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> O<br>K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> + Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> O | figure<br>table/phase<br>diagram | Selivanova, <i>et al.</i> , 1974 <sup>222</sup><br>Morozova, <i>et al.</i> , 1976 <sup>223</sup> |
| 298.15                  | Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + (NH <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub><br>+ H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> O                     | table/figure                     | McCullough, <i>et al.</i> , 1972 <sup>224</sup>  |

<sup>a</sup>solid phase Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·5H<sub>2</sub>O.

|  | 298.15 K              | 313.15 K              |
|--|-----------------------|-----------------------|
| Zn <sup>2+</sup> (aq) + P <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (aq) = ZnP <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq)                  | $5.01 \times 10^8$    | $1.58 \times 10^9$    |
| Zn <sup>2+</sup> (aq) + 2P <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (aq) = Zn(P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> <sup>2-</sup> (aq) | $1.00 \times 10^{11}$ | $6.31 \times 10^{10}$ |

4.9.e. Cadmium Pyrophosphate

|   |                         |
|---|-------------------------|
| Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub> [15600-62-1]                    | molecular weight 398.76 |
| CdH <sub>2</sub> P <sub>2</sub> O <sub>7</sub> [52482-45-8]                   | molecular weight 288.37 |
| Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O [13477-18-4] | molecular weight 434.79 |

Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·2.5H<sub>2</sub>O [not found] molecular weight 443.80  
 Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·4H<sub>2</sub>O [not found] molecular weight 470.82

*Physical characteristics:* Calvo and Au<sup>228</sup> report cadmium pyrophosphate, Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, is monoclinic with Z = 2, a, b and c = 6.672, 6.623 and 6.858 × 10<sup>-10</sup> 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<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

Selivanova and Kudryavtsev<sup>229-232</sup> are the only workers to report Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> 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<br>I/Electrolyte | $K_{so}$              | Method     | Reference   |
|--------------------|---------------------------------|-----------------------|------------|---|
| 298.15             | 0.5/( $CH_3$ ) <sub>4</sub> Cl  | $2.5 \times 10^{-16}$ | solubility | Delannoy, <i>et al.</i> , 1979 <sup>226</sup>     |
| 298.2<br>$\pm 0.2$ | 1.0/ $KNO_3$ or<br>$NaNO_3$     | $0.7 \times 10^{-16}$ | solubility | Selivanova, <i>et al.</i> , 1978 <sup>221,a</sup> |

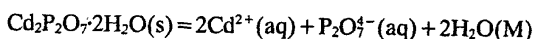
<sup>a</sup> Solid phase  $Zn_2P_2O_7 \cdot 5H_2O$

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

| Ionic strength<br>I/Electrolyte   | Solubility<br>$c/mol L^{-1}$   | References                                       |
|-----------------------------------|--------------------------------|--|
| 0 ( $H_2O$ )                      | $(2.7 \pm 0.2) \times 10^{-5}$ | Kudryavtsev, Selivanova, 1970 <sup>229</sup>     |
| 0.25–27.3/<br>$(NH_4)_4P_2O_7$    | $Cd^{2+}$ conc.                | Selivanova, Kudryavtsev, 1974 <sup>232</sup>     |
| 1/ $(NH_4)_4P_2O_7$ ,<br>$NaNO_3$ | table                          | " " , 1970 <sup>230</sup>                        |
| 0.12–30.0/<br>$K_4P_2O_7$         | $Cd^{2+}$ conc.                | Kudryavtsev, Selivanova, 1970 <sup>229,230</sup> |
| 0.112–2.3/<br>$Na_4P_2O_7$        | $Cd^{2+}$ conc.                | Selivanova, <i>et al.</i> , 1972 <sup>231</sup>  |

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<sup>233</sup> report a solubility for  $K_6Cd(P_2O_7)_2$  of  $5.5 \times 10^{-3} mol L^{-1}$  at 298 K with the solid identified as  $Cd_2P_2O_7 \cdot xH_2O$ . Selivanova and Kudryavtsev<sup>230</sup> report a solubility product of  $(19.6 \pm 2.7) \times 10^{-15}$  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  $27.7 \times 10^{-15}$  for the process



from the dihydrate Gibbs energy of formation of  $-2626 kJ \cdot mol^{-1}$  of Selivanova and Leshchinskaya<sup>234</sup> and data from the NBS Tables<sup>12</sup>. Both values must be viewed with caution if the equilibrium solid is the tetrahydrate.

Omarkulova and Bliznyuk<sup>214</sup> report solubility product values for several phosphates including  $CdH_2P_2O_7$ . Their value of  $8.1 \times 10^{-5}$  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<sup>8</sup> report complex ion formation constants. The values of Wolhoff and Overbeek<sup>227</sup> at zero ionic strength may be useful.

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

#### 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  $6.091 \times 10^{-10} m$ , respectively, and a calculated density is  $4.278 \times 10^3 kg m^{-3}$ .

$Zn_3(AsO_4)_2$  [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<sup>235</sup> with  $Z = 1$ ,  $\alpha$ ,  $\beta$  and  $\gamma = 940 18'$ ,  $910 12'$ , and  $920 6'$ , respectively,  $a$ ,  $b$  and  $c = 5.99$ ,  $7.63$ , and  $5.43 \times 10^{-10} m$ , respectively, and a calculated density is  $3.67$



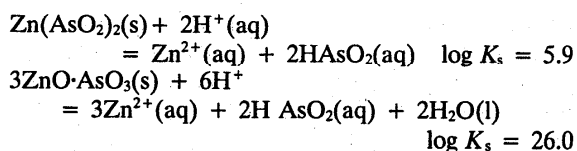
$\times 10^3 \text{ kg m}^{-3}$ . The mineral Koettigite,  $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is monoclinic with  $Z = 2$ ,  $\beta = 1030.05'$ ,  $a$ ,  $b$  and  $c = 10.08, 13.31, \text{ and } 4.70 \times 10^{-10} \text{ m}$ , respectively, and a calculated density of  $3.32 \times 10^3 \text{ kg m}^{-3}$ .

There are three zinc hydroxide arsenate minerals of formula  $\text{Zn}(\text{OH})\text{AsO}_4$  described in the Crystal Data Determinative Tables<sup>11</sup> but none has been identified as a solid phase in any of the solubility studies.

*Zinc Arsenite.* Kuperman, *et al.*<sup>236</sup> prepared both  $\text{Zn}(\text{AsO}_2)_2$  and  $\text{Zn}_3(\text{AsO}_3)_2$ . 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<sup>6</sup>.

Chukhlantsev<sup>237</sup> carried out two series of solubility experiments on  $\text{Zn}_3(\text{AsO}_3)_2$  at 293 K. His results are summarized in Table 38. In the first experiment he determined the  $\text{Zn}^{2+}$  concentration at saturation in dilute solutions of  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The solutions initially had a pH near 2, and after saturation the pH ranged from 5.90 to 6.30. If the  $\text{H}_3\text{AsO}_3$  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  $\text{AsO}_3^{2-}$  occurred, and its concentration was taken as 2/3 the  $\text{Zn}^{2+}$  concentration. The  $K_{s0}$  value (Table 38) is the average of four determinations.

Nishimura *et al.*<sup>238</sup> equilibrated  $\text{ZnO}$  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  $\log [\text{As}]$ -pH diagrams and gave  $\log K_s$  values for the two solubility equilibria:



*Zinc Arsenate* Kuperman *et al.*,<sup>236</sup> prepared both  $\text{Zn}_3(\text{AsO}_4)_2$  and  $\text{Zn}_3(\text{AsO}_4)_2 \cdot \text{Zn}(\text{OH})_2$ . 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<sup>239</sup> determined the  $\text{Zn}_3(\text{AsO}_4)_2$  solubility product at 298 K by two methods. In the first study he measured the stoichiometric solubility in dilute nitric and sulfuric acid solutions, using the literature dissociation constants of  $\text{H}_3\text{AsO}_4$  to calculate the actual  $\text{AsO}_4^{3-}$  concentration, and calculated the  $K_{s0}$  value. In the second experiment he used a radioactive tracer technique to measure the  $\text{Zn}^{2+}$  concentration in water, assumed the

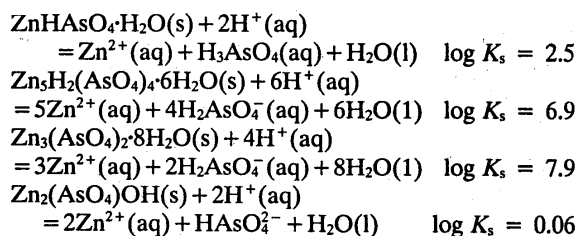
$\text{AsO}_4^{3-}$  concentration was 2/3 that value, and calculated  $K_{s0}$ . The two published values differ by one order of magnitude. However, there appears to be a decimal error in the radioactive tracer calculation, which makes the two values differ by two orders of magnitude. The values are in Table 39. In a later paper Chukhlantsev<sup>240</sup> uses the radioactive tracer  $K_{s0}$  values of  $\text{Zn}_3(\text{AsO}_4)_2$ ,  $\text{Sr}_3(\text{AsO}_4)_2$  and  $\text{Ag}_3\text{AsO}_4$  to determine new values of the acid dissociation constants of  $\text{H}_3\text{AsO}_4$ . The error mentioned above is repeated and may affect the dissociation constant values.

Sagadieva, Makhmetov, Malyshev and Maslennikova<sup>241</sup> 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  $\text{Zn}_3(\text{AsO}_4)_2$ . We have available only the Zh. Fiz. Khim. abstract which gives their fitted  $\Delta G_f^\circ$  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<sup>242</sup> have recalculated the solubility product values using activity coefficients. The paper is not presently available to us.

Takahashi and Sasaki<sup>243</sup> studied the system  $\text{ZnO} + \text{As}_2\text{O}_5 + \text{H}_2\text{O}$  at 303.15 K. They identified equilibrium solids as  $\text{ZnHAsO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Zn}(\text{H}_2\text{AsO}_4)_2$ . Only the phase diagram is given.

Nishimura *et al.*<sup>238</sup> equilibrated  $\text{ZnO}$  and arsenic acid solutions and analyzed the solid and solution in the same manner as the  $\text{ZnO}$  and arsenous acid solutions. They give equilibrium constants for the following solubility equilibria:



The NBS Tables<sup>12</sup> contain Gibbs energy data from which we calculate a  $K_{s0}$  value of  $2.8 \times 10^{-28}$  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  $\text{Zn}_3(\text{AsO}_4)_2$  solid he prepared as highly amorphous. He does not mention evidence for any of the known hydrates.

#### 4.10.b. Cadmium Arsenite and Arsenate



Physical characteristics: Engel and Klee<sup>245</sup> find cadmium arsenate,  $\text{Cd}_3(\text{AsO}_4)_2$ , to be monoclinic, a structure related to the mineral graffonite, with  $a$ ,  $b$  and  $c = 9.285, 11.936 \text{ and } 6.599 \times 10^{-10} \text{ m}$ , respectively,  $\beta = 98.45^\circ$ , and

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

| T/K | $10^5 C_{Zn^{2+}} / \text{mol L}^{-1}$ | pH      |       | Acid                           | References                        |
|-----|--|---------|-------|--------------------------------|-----------------------------------|
|     |  | Initial | Final |                                |                                   |
| 293 | 2.5                                    | 2.35    | 6.30  | H <sub>2</sub> SO <sub>4</sub> | Chukhlantsev, 1957 <sup>237</sup> |
|     | 3.1                                    | 2.35    | 6.25  | HNO <sub>3</sub>               |                                   |
|     | 6.1                                    | 2.10    | 6.20  | H <sub>2</sub> SO <sub>4</sub> |                                   |
|     | 5.8                                    | 2.15    | 6.10  | HCl                            |                                   |
|     | 7.4                                    | 2.00    | 6.05  | H <sub>2</sub> SO <sub>4</sub> |                                   |
|     | 1.1                                    | 1.90    | 6.00  | H <sub>2</sub> SO <sub>4</sub> |                                   |
|     | 6.8                                    | 1.98    | 5.95  | HNO <sub>3</sub>               |                                   |
|     | 9.9                                    | 1.90    | 5.90  | HCl                            |                                   |

Chukhlantsev's radioactive tracer study gave  $K_{s0} / \text{mol}^3 \text{L}^{-5} = (2.8 \pm 0.8) \times 10^{-20}$  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<br>298.15      | $2.8 \times 10^{-28} (K_{s0}^a)$  | Thermo data                                   | NBS Tables 1982 <sup>12</sup>                 |
| Experimental values<br>293 | $(1.3 \pm 0.4) \times 10^{-28} (6)$<br>$(108 \pm 11) \times 10^{-28} (4)$ | solubility <sup>a</sup><br>radioactive tracer | Chukhlantsev, 1956 <sup>239</sup>             |
| 298-346                    | <sup>b</sup>  | solubility                                    | Sagadieva <i>et al.</i> , 1976 <sup>241</sup> |

Number in ( ) is number of determinations.

<sup>a</sup>The dissociation constants of H<sub>3</sub>AsO<sub>4</sub> used were  $K_{1a} = 5.62 \times 10^{-3}$ ,  $K_{2a} = 1.7 \times 10^{-7}$  and  $K_{3a} = 1.95 \times 10^{-12}$ . (Britton and Jackson<sup>244</sup>).

<sup>b</sup>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<sup>11</sup> or through a Chem. Abst. search from 1962 to the present.

**Cadmium arsenite.** Chukhlantsev<sup>237</sup> 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<sup>239</sup> 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<sub>3</sub>AsO<sub>4</sub> to calculate the  $AsO_4^{3-}$  ion concentration. The six results range from  $(0.1 \text{ to } 6.2) \times 10^{-33}$  and average  $(2.2 \pm 2.7) \times 10^{-33} \text{ mol}^5 \text{L}^{-5}$  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<sup>246,247</sup>.

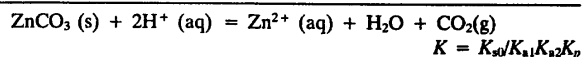
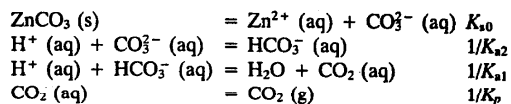
#### 4.11. Zinc and Cadmium Carbonate

##### 4.11.a. Zinc Carbonate

ZnCO<sub>3</sub> [3486-35-9] molecular weight 125.40  
Smithsonite [14476-25-6]

**Physical characteristics:** Zinc carbonate is a colorless hexagonal crystal with  $Z = 6$ ,  $a = 4.651 \times 10^{-10} \text{ m}$ ,  $c = 14.977 \times 10^{-10} \text{ m}$ , and a calculated density of  $4.425 \times 10^{-3} \text{ kg m}^{-3}$ . 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:



And in the acidic aqueous carbon dioxide solution:

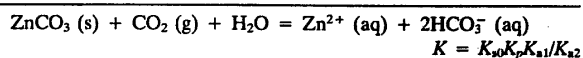
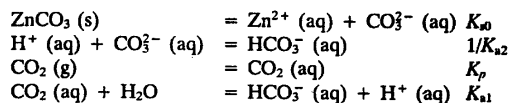


TABLE 40. Solubility of cadmium arsenite,  $\text{Cd}_3(\text{AsO}_3)_2$ 

| T/K | $10^3 C_{\text{Cd}^{2+}} / \text{mol L}^{-1}$ | pH      |       | Acid                    | Reference                         |
|-----|---|---------|-------|-------------------------|-----------------------------------|
|     |   | Initial | Final |                         |                                   |
| 293 | 2.8   | 2.35    | 7.00  | $\text{HNO}_3$          | Chukhlantsev, 1957 <sup>237</sup> |
|     | 2.8   | 2.35    | 7.00  | $\text{H}_2\text{SO}_4$ | " "                               |
|     | 6.9   | 1.98    | 6.60  | $\text{HNO}_3$          | " "                               |
|     | 7.0   | 2.00    | 6.60  | $\text{H}_2\text{SO}_4$ | " "                               |

 TABLE 41. Solubility product of cadmium arsenate,  $\text{Cd}_3(\text{AsO}_4)_2$ 

| T/K                 | $K_{s0}$                         | Method                  | Reference                         |
|---------------------|----------------------------------|-------------------------|-----------------------------------|
| Tentative<br>298.15 | $2.2 \times 10^{-33} (K_{s0}^0)$ | Thermo data             | NBS Tables <sup>12</sup>          |
| Experimental<br>293 | $(2.2 \pm 2.7) \times 10^{-33}$  | solubility <sup>a</sup> | Chukhlantsev, 1956 <sup>239</sup> |

<sup>a</sup> See Table 39 for  $\text{H}_3\text{AsO}_4$  dissociation constants used in study.

The second model is consistent with the increase in  $\text{ZnCO}_3$  solubility as carbon dioxide partial pressure increases and the observation the major solution species at high carbon dioxide partial pressure is  $\text{HCO}_3^-$ . 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<sup>248</sup>, Haehnel<sup>249</sup>, Piperaki and Hadjiioannou<sup>250</sup>, Grohmann<sup>251</sup>, Mann and Deutscher<sup>252</sup>, and Jaulmes and Brun<sup>204</sup> are doubtful because temperature or carbon dioxide pressure or details of calculation are lacking.

The paper of Ageno and Valla<sup>253</sup> contains apparent printing errors which causes some uncertainty of their values. The values of Smith<sup>254</sup> at 298.15 and 303.15 K are based on direct analysis of the saturated solutions. Smith reports solution concentrations of  $\text{H}_2\text{CO}_3$  and  $\text{Zn}(\text{HCO}_3)_2$ . We have estimated the carbon dioxide partial pressures from Henry's constant and the assumption the  $\text{H}_2\text{CO}_3$  concentration represents the dissolved  $\text{CO}_2$  concentration at 298.15 K.

At 298.15 K the tentative solubility values are the calculated solubility values from Kelley and Anderson<sup>255</sup> at a  $\text{CO}_2$  partial pressure of 1 kbar and the pure water value in air ( $\text{CO}_2$  partial pressure of about 0.00032 bar) given by Ageno and Valla<sup>253</sup>.

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<sup>261</sup>, Schindler *et al.*<sup>260</sup>, Ageno and Valla<sup>253</sup> and Smith<sup>254</sup>. There are recalculated values from the Smith data by Kelley and Anderson<sup>255</sup> and by us using more up-to-date auxiliary data. Several of these papers<sup>255,260</sup> report  $K_{s0}^0$  values extrapolated from the experimental data.

The  $K_{s0}^0$  values calculated from thermodynamic data are Latimer<sup>89</sup> who used data from 1949 NBS and 1935 Bureau of Mines data; Egorov and Titova<sup>262</sup> who used data from Latimer and from Kubaschewski and Evans<sup>93</sup>; Schindler *et al.*,<sup>260</sup> who used data from their own work and from NBS Circular 500<sup>110</sup>; Helgeson<sup>107</sup> who used 1968 NBS Technical Note 270-3 data and data from Wulff<sup>114</sup>; and Krestov *et al.*<sup>129</sup> 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<sup>262</sup> in Table 44 were calculated from their equation

$$\log K_{s0}^0 = 31.77 + 1480/(T/K) + 7.17 \log (T/K) - (2.82 \times 10^{-3})(T/K)$$

The values from the Krestov *et al.*<sup>129</sup> 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  $K_{s0}^0$  values is

$$\ln (K_{s0}^0 / \text{mol}^2 \text{L}^{-2}) = 109.5581 - 183.0211 (1/T/100 \text{ K}) - 64.8370 \ln(T/100 \text{ K}).$$

TABLE 42. The solubility of zinc carbonate in water

| T/K               | $P_{\text{CO}_2}$ /bar<br>( $c_{\text{CO}_2}$ /mol L <sup>-1</sup> )<br>or pH | Zinc Carbonate<br>Solubility<br>$c_{\text{ZnCO}_3}$ /mol L <sup>-1</sup>   | Method                  | Reference                                  |
|-------------------|---|--|-------------------------|--|
| Tentative values  |   |  |                         |  |
| 298.15            | 0.987   | $1.98 \times 10^{-3}$  |                         |  |
|                   | 0.00032 <sup>a</sup>  | $1.64 \times 10^{-4}$  |                         |  |
| Literature values |   |  |                         |  |
| 288.15            | 0.00032 <sup>a</sup>  | $8 \times 10^{-5}$   | —                       | von Essen 1897 <sup>248, c</sup>           |
| (291.15)          | 1   | $5.6 \times 10^{-5}$   | gravimetric             | Haehnel 1924 <sup>249</sup>                |
|                   | 56  | $6.7 \times 10^{-3}$   | gravimetric             | Haehnel 1924 <sup>249</sup>                |
| 298.1             | 1   | $1.98 \times 10^{-3}$  | calculated <sup>c</sup> | Kelley, Anderson 1935 <sup>255</sup>       |
| (298.15)          | 0.00032 <sup>a</sup>  | $2.05 \times 10^{-5}$  | titration               | Piperaki, Hadjiioannou 1977 <sup>250</sup> |
| (298.15)          | 0.00032   | figure   | calculated <sup>d</sup> | Grohmann 1976 <sup>251</sup>               |
| (298.15)          | 0.00032   | figure   | calculated <sup>c</sup> | Mann, Deutscher 1980 <sup>252</sup>        |
| 298.15            | 0.00032 <sup>a</sup>  | $1.64 \times 10^{-4}$  | electromagnetic         | Ageno, Valla 1911 <sup>253</sup>           |
|                   | 0.3641  | $1.84 \times 10^{-3}$  | titration               |  |
|                   | 0.5199  | $2.20 \times 10^{-3}$  |                         |  |
|                   | 0.7295  | $2.72 \times 10^{-3}$  |                         |  |
|                   | 0.9506  | $2.76 \times 10^{-3}$  |                         |  |
| 298.15            | 4.12 (0.1390) <sup>b</sup>  | $1.94 \times 10^{-3}$  | titration <sup>f</sup>  | Smith 1918 <sup>254</sup>                  |
|                   | 5.33 (0.1797) <sup>b</sup>  | $2.11 \times 10^{-3}$  |                         |  |
|                   | 7.64 (0.2579) <sup>b</sup>  | $2.42 \times 10^{-3}$  |                         |  |
|                   | 10.61 (0.3580) <sup>b</sup>   | $2.70 \times 10^{-3}$  |                         |  |
|                   | 12.16 (0.4103) <sup>b</sup>   | $2.78 \times 10^{-3}$  |                         |  |
|                   | 13.29 (0.4480) <sup>b</sup>   | $2.91 \times 10^{-3}$  |                         |  |
|                   | 19.73 (0.6657) <sup>b</sup>   | $3.17 \times 10^{-3}$  |                         |  |
| 298.15            | 20.65 (0.6969) <sup>b</sup>   | $3.19 \times 10^{-3}$  | titration <sup>f</sup>  | Smith <sup>254</sup>                       |
|                   | 22.56 (0.7610) <sup>b</sup>   | $3.42 \times 10^{-3}$  |                         |  |
|                   | 40.61 (1.3701) <sup>b</sup>   | $4.45 \times 10^{-3}$  |                         |  |
| 298.15            | 0.00032   | pH 6<br>pH 7<br>pH 8<br>pH 9<br>pH 10<br>pH 11<br>pH 12<br>pH 13   | calculated <sup>c</sup> | Jaulmes, Brun 1965 <sup>204</sup>          |
|                   |   | $1.05 \times 10^{-3}$<br>$1.99 \times 10^{-4}$<br>$5.74 \times 10^{-5}$<br>$1.83 \times 10^{-6}$<br>$6.86 \times 10^{-6}$<br>$4.07 \times 10^{-6}$<br>$4.0 \times 10^{-6}$<br>$4.0 \times 10^{-6}$ |                         |  |
| 303.15            | (0.1838) <sup>b</sup>   | $2.15 \times 10^{-3}$  | titration <sup>f</sup>  | Smith 1918 <sup>254</sup>                  |
|                   | (0.3838) <sup>b</sup>   | $2.77 \times 10^{-3}$  |                         |  |
|                   | (0.4038) <sup>b</sup>   | $2.86 \times 10^{-3}$  |                         |  |
|                   | (0.4601) <sup>b</sup>   | $3.08 \times 10^{-3}$  |                         |  |
|                   | (0.6064) <sup>b</sup>   | $3.24 \times 10^{-3}$  |                         |  |
|                   | (0.6257) <sup>b</sup>   | $3.37 \times 10^{-3}$  |                         |  |
|                   | (0.7470) <sup>b</sup>   | $3.52 \times 10^{-3}$  |                         |  |
|                   | (0.8351) <sup>b</sup>   | $3.76 \times 10^{-3}$  |                         |  |
|                   | (1.0840) <sup>b</sup>   | $3.39 \times 10^{-3}$  |                         |  |
|                   | (1.1275) <sup>b</sup>   | $4.29 \times 10^{-3}$  |                         |  |

<sup>a</sup>Carbon dioxide partial pressure not reported. Assumed to be an air atmosphere which is about 0.00032 bar CO<sub>2</sub>.

<sup>b</sup>Smith's experimentally determined carbonic acid concentration. Assuming it to represent the aqueous concentration of CO<sub>2</sub> 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.

<sup>c</sup>Calculated using thermodynamic data including carbonic acid dissociation constants.

<sup>d</sup>Calculations not explained in detail.

<sup>e</sup>Cited by Cantoni, Passamanik 1905<sup>257</sup> as from 1897 thesis, Geneva.

<sup>f</sup>Data in Seidel, Linke<sup>6</sup>.

TABLE 43. The solubility product constant for zinc carbonate

| T/K                      | Ionic Strength<br>I/Electrolyte               | Solubility Product                    |                                     | Reference   |
|--------------------------|---|---------------------------------------|-------------------------------------|---|
|                          |   | $K_{sp}^0/\text{mol}^2 \text{L}^{-2}$ | $K_{sp}/\text{mol}^2 \text{L}^{-2}$ |   |
| <b>Tentative values</b>  |   |                                       |                                     |   |
| 298.15                   | 0   | $1.46 \times 10^{-10}$                |                                     |   |
| 323.15                   | 0   | $9.02 \times 10^{-11}$                |                                     |   |
| 373.15                   | 0   | $1.59 \times 10^{-11}$                |                                     |   |
| 423.15                   | 0   | $1.5 \times 10^{-12}$                 |                                     |   |
| 473.15                   | 0   | $1.0 \times 10^{-13}$                 |                                     |   |
| 523.15                   | 0   | $6.2 \times 10^{-15}$                 |                                     |   |
| 573.15                   | 0   | $3.5 \times 10^{-16}$                 |                                     |   |
| <b>Literature values</b> |   |                                       |                                     |   |
| 291.15                   | 0.57/ $\text{Na}_2\text{CO}_3, \text{NaNO}_3$ |                                       | $2.6 \times 10^{-8}$                | Zhukova, Rachinskii 1972 <sup>261</sup>               |
| 293.15                   |   |                                       | $1.45 \times 10^{-11}$              | Sahli 1952 <sup>a</sup>                               |
| 298.1                    | 0   | $9.98 \times 10^{-11}$                |                                     | Kelly, Anderson 1935 <sup>255</sup>                   |
| 298.1                    | 0   | $7.1 \times 10^{-11}$                 |                                     | Saegusa 1950 <sup>263</sup>                           |
| 298.15                   |   | $8.7 \times 10^{-10}$                 |                                     | Agcino, Valla 1911 <sup>253</sup>                     |
| 298.15                   |   | $2.1 \times 10^{-11}$                 |                                     | Smith 1918 <sup>254</sup>                             |
| 298.15                   |   | $1.66 \times 10^{-11}$                |                                     | Kelley, Anderson 1935 <sup>255,b</sup>                |
| 298.15                   | 0.2/ $\text{NaClO}_4$                         |                                       |                                     | c   |
| 298.15                   |   | $1.61 \times 10^{-11}$                | $1.43 \times 10^{-10}$              | Schindler, Reinert, Gamsjaeger 1969 <sup>260, f</sup> |
| 298.15                   | 0   | $2 \times 10^{-10}$                   |                                     | Latimer 195 <sup>289</sup>                            |
| 298.15                   | 0   | $1.2 \times 10^{-10}$                 |                                     | Egorov, Titova 196 <sup>262,e</sup>                   |
| 298.15                   | 0   | $1.9 \times 10^{-10}$                 |                                     | Helgeson 1969 <sup>107</sup>                          |
| 298.15                   | 0   | $4.5 \times 10^{-11}$                 |                                     | Krestov, Kobenin, Sokolov 1977 <sup>129</sup>         |
| 298.15                   | 0   | $1.19 \times 10^{-10}$                |                                     | g   |
| 298.15                   | 0   | $4.30 \times 10^{-10}$                |                                     | h   |
| 323.15                   | 0   | $8.91 \times 10^{-11}$                |                                     | Helgeson 1969 <sup>107</sup>                          |
| 323.15                   | 0   | $7.78 \times 10^{-11}$                |                                     | Egorov, Titova 1962 <sup>262,d</sup>                  |
| 333.15                   | 0   | $6.45 \times 10^{-11}$                |                                     | Helgeson 1969 <sup>107</sup>                          |
| 333.15                   | 0   | $6.6 \times 10^{-11}$                 |                                     | Egorov, Titova 1962 <sup>262,d</sup>                  |
| 373.15                   | 0   | $1.3 \times 10^{-11}$                 |                                     | Helgeson 1969 <sup>107</sup>                          |
| 373.15                   | 0   | $3.85 \times 10^{-11}$                |                                     | Egorov, Titova 1962 <sup>262,d</sup>                  |
| 423.15                   | 0   | $1.7 \times 10^{-12}$                 |                                     | Helgeson 1969 <sup>107</sup>                          |
| 473.15                   | 0   | $1.3 \times 10^{-13}$                 |                                     | " " "   |
| 523.15                   | 0   | $6.6 \times 10^{-15}$                 |                                     | " " "   |
| 573.15                   | 0   | $3.0 \times 10^{-16}$                 |                                     | " " "   |

<sup>a</sup>Cited in Schindler *et al.*<sup>260</sup> as a dissertation, Bern, 1952.

<sup>b</sup>Recalculated from the data of Smith by the authors.

<sup>c</sup>Recalculated from the data of Smith by us. Used recent  $K_{a1}$  and  $K_{a2}$  values for  $\text{H}_2\text{CO}_3$ .

<sup>d</sup>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.

<sup>e</sup>Calculated from the equation in the paper (see d above). The author's report a value of  $2.1 \times 10^{-10}$  which may be a printing error.

<sup>f</sup>We were unable to duplicate this value from data in the paper.

<sup>g</sup>Calculated from Gibbs energy data in the NBS Tables, 1982<sup>12</sup> by us.

<sup>h</sup>Recalculation from data in Schindler *et al.*<sup>260</sup> and NBS Tables, 1982<sup>12</sup> by us to obtain a value of  $\Delta G^\circ$  for  $\text{ZnCO}_3(\text{s})$  which was used to calculate  $K_{sp}^0$ .

#### 4.11.b. Cadmium Carbonate

$\text{CdCO}_3$  [513–78–9] Molecular weight 172.42

Otavite [37428–30–1]

**Physical characteristics:** Cadmium carbonate is a colorless hexagonal crystal with  $Z = 6$ ,  $a = 4.913 \times 10^{-10} \text{ m}$ ,  $c = 16.24 \times 10^{-10} \text{ m}$ , and a calculated density of  $5.02 \times 10^3 \text{ kg m}^{-3}$ . 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 diox-

ide 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<sup>204</sup> values are for air with the natural  $\text{CO}_2$  content, but they do not say so. The Kelley and Anderson<sup>255</sup> 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<sup>264</sup> 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    | $P_{\text{CO}_2}/\text{bar}$<br>( $c_{\text{CO}_2}/\text{mol L}^{-1}$ )<br>or pH | Cadmium<br>solubility<br>$c/\text{CdCO}_3/\text{mol L}^{-1}$ | Method | Reference                               |
|--------|--|--|--------|---|
| 298.15 | 0.987  | $1.12 \times 10^{-4}$  | Calc.  | Kelley, Anderson 1935 <sup>255, a</sup> |
| 298.15 | 0.00032  | $4.18 \times 10^{-5}$ to<br>$1.57 \times 10^{-7}$            | Calc.  | Jaulmes, Brun 1965 <sup>204, b</sup>    |

<sup>a</sup>Calculated from thermodynamic data. Value reported in  $\text{mol kg}^{-1}$ .

<sup>b</sup>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 cadmium carbonate in aqueous electrolyte solutions

| T/K    | Ionic strength<br>$I/\text{Electrolyte}$ | Carbon dioxide<br>$P/\text{bar}$                | Cadmium carbonate<br>solubility<br>$c/\text{mol L}^{-1}$                | Reference   |
|--------|--|---|---|---|
| 298.15 | 0.075/ $\text{K}_2\text{CO}_3$           | 0.00032   | $2.5 \times 10^{-4}$  | Immewahr 1901 <sup>202, a</sup>                                 |
| 298.15 | 3.0/ $\text{NaClO}_4$                    | 0.167 pH 4.26<br>0.337 pH 4.11<br>0.908 pH 3.91 | $4.90 \times 10^{-2}$<br>$4.96 \times 10^{-2}$<br>$4.84 \times 10^{-2}$ | Gamsjaeger, Stuber, Schindler 1965 <sup>265</sup><br>" "<br>" " |
| 298.15 | 0.27–12.6/ $\text{CaCl}_2$               | ?   | $7.0 \times 10^{-4}$ to<br>1.623  | Ben'yash 1964 <sup>259, b</sup>                                 |
| 310.15 | gastric fluid<br>intestinal fluid        | ?<br>?  | $7.71 \times 10^{-4}$<br>$1.33 \times 10^{-7}$                          | Wada, Iijima, Ono, Toyokawa 1972 <sup>121, c</sup>              |

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

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

<sup>c</sup>These solutions may not have been saturated.

Until recently the most complete experimental study of the  $\text{CdCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$  system is that of Gamsjaeger, Stuber and Schindler<sup>265</sup>. They determined equilibrium constants at 298.15 K and ionic strengths of 0 and 3.0  $\text{NaClO}_4$  for the reactions below.

| Reaction   | Equilibrium constants  |                        |
|--|------------------------|------------------------|
|  | $I = 0$                | $I = 3.0$              |
| (1) $\text{CdCO}_3(\text{s}) + \text{H}_2\text{O} + \text{CO}_2(\text{g})$<br>$= \text{Cd}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq})$ | $3.16 \times 10^{-10}$ | $2.69 \times 10^{-10}$ |
| (2) $\text{CdCO}_3(\text{s}) + 2\text{H}^+$<br>$= \text{H}_2\text{O} + \text{CO}_2(\text{g}) + \text{Cd}^{2+}(\text{aq})$                | $1.38 \times 10^6$     | $2.95 \times 10^6$     |
| (3) $\text{CdCO}_3(\text{s})$<br>$= \text{Cd}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$   | $1.00 \times 10^{-12}$ | $6.60 \times 10^{-12}$ |

Their value of  $K_{s0}^\circ/\text{mol}^2 \text{L}^{-2} = 1.00 \times 10^{-12}$  is smaller than the value of  $6.18 \times 10^{-12}$  calculated from Gibbs energy of formation data in the NBS Tables<sup>12</sup>, but is confirmed by recent work of Stipp, Parks, Nordstrom and Leckie<sup>392</sup>. Using  $(\text{H}^+) = 1 \times 10^{-7}$  and  $P_{\text{CO}_2} = 3.2 \times 10^{-4}$  atm gives a solubility in water  $2.9 \times 10^{-5}$  and  $4.3 \times 10^{-5} \text{ mol L}^{-1}$  from equations (1) and (2), respectively.

A preprint of a paper under review by Stipp, Parks, Nordstrom and Leckie<sup>392, a</sup> was recently called to our attention. The paper contains an exhaustive literature search and evaluation of existing thermodynamic data on the components of the  $\text{Cd}^{2+}(\text{aq}) + \text{CO}_2(\text{aq, g}) + \text{H}_2\text{O}$  system, as well as an exceedingly careful new experimental determination of the  $\text{CdCO}_3$  solubility product at 278, 298 and 323 K ( $I < 0.1 \text{ mol L}^{-1} \text{KClO}_4$ ). The paper recommends new thermodynamic values for the formation of  $\text{CdCO}_3(\text{s})$  (synthetic otavite) which are consistent with the CODATA key values<sup>390</sup>. For  $\text{CaCO}_3(\text{s})$  at 209.15 K  $\Delta G_f^\circ = -(647.7 \pm 0.6) \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ = -(751.1 \pm 1.0) \text{ kJ mol}^{-1}$  and  $S^\circ = (109.1 \pm 1.0) \text{ J K}^{-1} \text{ mol}^{-1}$ . The solubility product is  $\text{p}K_{s0}^\circ = (12.1 \pm 0.1)$  or  $K_{s0}^\circ = 0.79 \times 10^{-12}$ . 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<sup>129</sup> and Egorov and Titova<sup>262</sup> have developed equations for  $K_{s0}^\circ$  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  $K_{s0}^\circ$  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<br>I/Electrolyte | Solubility product |                        | Reference                                       |
|---------------------------|---------------------------------|--------------------|------------------------|---|
|                           |                                 | $K_{s0}^{\circ}$   | $K_{s0}$               |   |
| Tentative value           |                                 |                    |                        |   |
| 298.15                    | 0                               |                    | $0.79 \times 10^{-12}$ | Stipp <i>et al.</i> , 199x <sup>392</sup>       |
| Literature values         |                                 |                    |                        |   |
| From thermodynamic data   |                                 |                    |                        |   |
| 298.15                    | 0                               |                    | $1.82 \times 10^{-14}$ | Kelley, Anderson 1935 <sup>255</sup>            |
| 298.15                    | 0                               |                    | $2.5 \times 10^{-12}$  | Saegusa 1950 <sup>263</sup>                     |
| 298.15                    | 0                               |                    | $5.2 \times 10^{-12}$  | Latimer 1952 <sup>89</sup>                      |
| 298.15                    | 0                               |                    | $5.1 \times 10^{-12}$  | Egorov, Titova 1962 <sup>262,a</sup>            |
| 298.15                    | 0                               |                    | $1.00 \times 10^{-12}$ | Gamsjaeger <i>et al.</i> , 1965 <sup>262</sup>  |
| 298.15                    | 0                               |                    | $0.87 \times 10^{-12}$ | Krestov, <i>et al.</i> , 1977 <sup>129,a</sup>  |
| 298.15                    | 0                               |                    | $6.18 \times 10^{-12}$ | NBS Tables 1982 <sup>12</sup>                   |
| From experimental studies |                                 |                    |                        |   |
| 278.15                    | 0.1/KClO <sub>4</sub>           |                    | $0.40 \times 10^{-12}$ | Stipp <i>et al.</i> , 199x <sup>392</sup>       |
| 291.15                    | 0.1/KNO <sub>3</sub>            |                    | $5.1 \times 10^{-12}$  | Karnaukhov, <i>et al.</i> , 1973 <sup>266</sup> |
| 298.15                    | 3.0/NaClO <sub>4</sub>          |                    | $6.60 \times 10^{-12}$ | Gamsjaeger <i>et al.</i> , 1965 <sup>265</sup>  |
| 298.15                    | 0.1/KClO <sub>4</sub>           |                    | $0.79 \times 10^{-12}$ | Stipp <i>et al.</i> , 199x <sup>392</sup>       |
| 323.15                    | 0.1/KClO <sub>4</sub>           |                    | $0.63 \times 10^{-12}$ | Stipp <i>et al.</i> , 199x <sup>392</sup>       |

<sup>a</sup>Authors give equations for  $K_{s0}^{\circ}$  for the 273–373 K interval.

tude to the tentative value at 298 K. The Egorov and Titova equation gives a  $K_{s0}^{\circ}$  value at 298.15 K 6.5 times larger than the tentative value. Their equation

$$\log K_{s0}^{\circ} = -28.06 + 619/(T/K) + 6.22 \log (T/K) - (2.35 \times 10^{-3})(T/K)$$

shows a shallow minimum in  $K_{s0}^{\circ}$  values in the 273.15 to 373.15 K temperature interval, while the work of Stipp *et al.*<sup>393</sup> shows a small maximum. Both imply a very small enthalpy of solution.

## 4.12. Zinc and Cadmium Oxalate

### 4.12.a. Zinc Oxalate

|  |                         |
|--|-------------------------|
| ZnC <sub>2</sub> O <sub>4</sub> [547–68–2]                     | molecular weight 153.40 |
| ZnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O [4255–07–6] | molecular weight 189.44 |
| ZnC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O [16788–40–2] | molecular weight 171.42 |

*Physical characteristics:* Anhydrous ZnC<sub>2</sub>O<sub>4</sub> exists in  $\alpha$  and  $\beta$  forms which have been characterized by Kondrashev *et al.*<sup>386</sup>

Deyrieux and Peneloux<sup>268</sup>, who have prepared and characterized both  $\alpha$ - and  $\beta$ -FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, were able to prepare only the  $\alpha$ -ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. They found its structure analogous to the monoclinic  $\alpha$ -FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, 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  $\alpha$ -ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in all cases. Agreement among the solubility values is poor. Early values derived from the

conductivity measurements of Kohlrausch *et al.*<sup>28,269</sup> appear to be too small and are rejected. Kunschert<sup>270</sup> measured a solubility product value. He derived a solubility value from his experiment by taking into account Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>2-</sup>(aq) and Zn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>4-</sup>(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<sub>2</sub>O<sub>4</sub> (aq). There is no modern evidence that the Zn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>4-</sup>(aq) species is of importance.

The values of Scholder, Gadenne and Niemann<sup>271</sup>, Osawa<sup>272</sup>, and Clayton and Vosburgh<sup>273</sup> fit a consistent pattern. The value of Piperaki and Hadjiioannou<sup>250</sup> 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.*<sup>271</sup>, Osawa<sup>272</sup>, and Clayton and Vosburgh<sup>273</sup> were treated by a linear regression to obtain the equation

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

with a standard error about the regression line of  $2.5 \times 10^{-6}$ . 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,  $K_{s0}^{\circ}/\text{mol}^2 \text{L}^{-2} = 1.38 \times 10^{-9}$ , was calculated from Gibbs energy data in the NBS Tables<sup>12</sup>. The value agrees well with the value recalculated by Vosburgh and Beckman<sup>274</sup> from the work of Clayton and Vosburgh<sup>273</sup>, and with the value given in the review of Zhuk<sup>275</sup>. There is no way to judge whether these

TABLE 47. The solubility of  $\alpha$ -zinc oxalate dihydrate in water

| T/K                 | Solubility<br>$10^4$ c/mol L <sup>-1</sup> | 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 <sup>269</sup>                |
| 291.07              | 0.338                                      | " "  |
| 291.15              | 1.10                                       | Scholder <i>et al.</i> , 1927 <sup>271</sup>   |
| 293.15              | 1.2  | Osawa, 1950 <sup>272</sup>                     |
| "Room"              | 1.43                                       | Piperaki and Hadjiioannou, 1977 <sup>250</sup> |
| 298.15              | 0.7 <sup>a</sup>                           | Kunschert, 1904 <sup>270</sup>                 |
|                     | 1.685                                      | Clayton and Vosburgh, 1937 <sup>273</sup>      |
|                     | 1.67                                       | " " " "  |
|                     | 2.99                                       | Brzyska and Bubela, 1982 <sup>386</sup>        |
| 299.30              | 0.377                                      | Kohlrausch, 1908 <sup>269</sup>                |

<sup>a</sup>Calculated by the author from his  $K_{40}$  value taking into account complex formation. The author also recalculated a value of  $0.77 \times 10^{-4}$  mol. L<sup>-1</sup> from earlier conductivity results of Kohlrausch *et al.*<sup>28</sup>

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

Money and Davies<sup>276</sup> were the first to suggest the low conductivity of saturated zinc oxalate solutions is due to the predominance of the non-conducting  $\text{ZnC}_2\text{O}_4(\text{aq})$  species. Their work suggested  $\text{ZnC}_2\text{O}_4(\text{aq})$  and  $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}(\text{aq})$  were the only important solution species. The conclusion was supported by the study of Clayton and Vosburgh<sup>273</sup>. Rowlands and Monk<sup>277</sup> studied the  $\text{Zn}^{2+} - \text{C}_2\text{O}_4^{2-}$  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  $\alpha$ - $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  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

$\text{CdC}_2\text{O}_4$  [814-88-0] molecular weight 200.43

$\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  [20712-42-9] molecular weight 254.48

**Physical characteristics:** No information on the anhydrous salt was found. Bridle and Lomer<sup>286</sup> report  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  is triclinic with  $a = 7.36 \times 10^{-10}$  m,  $b = 9.39 \times 10^{-10}$  m,  $c = 9.06 \times 10^{-10}$  m,  $\alpha = 135^\circ 32'$ ,  $\beta = 132^\circ 29'$ ,  $\gamma = 68^\circ 22'$ , and calculated density =  $2.73 \times 10^3$  kg m<sup>-3</sup>.

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  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in all cases.

The results of Kohlrausch<sup>269</sup> by a conductivity method are probably too small because account was not taken of the nonconducting  $\text{CdC}_2\text{O}_4(\text{aq})$  species. The values of Babkin *et al.*<sup>287,288</sup> 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<sup>273</sup> in 1937. Vosburgh and Beckman<sup>274</sup> 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<sup>-1</sup> and m/mol kg<sup>-1</sup> 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<sup>289</sup> 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<sup>12</sup> 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<sup>288</sup> value is a new experimental value. It is the same value as given by Zhuk<sup>275</sup> 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  $\text{CdC}_2\text{O}_4(\text{aq})$ ,  $\text{Cd}(\text{C}_2\text{O}_4)_2^{2-}(\text{aq})$ ,  $\text{Cd}(\text{C}_2\text{O}_4)_3^{4-}(\text{aq})$  and  $\text{Cd}_2(\text{C}_2\text{O}_4)^{2+}(\text{aq})$ . The paper of Olin and Wilmark<sup>290</sup> 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<sup>274</sup> discuss the possibility of the  $\text{Cd}_2(\text{C}_2\text{O}_4)^{2+}(\text{aq})$  species.

### 4.13. Zinc and Cadmium Cyanide

#### 4.13.a. Zinc Cyanide

$\text{Zn}(\text{CN})_2$  [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  $1.90 \times 10^3$  kg m<sup>-3</sup>.

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



TABLE 48. The solubility product of  $\alpha$ -zinc oxalate dihydrate

| T/K                    | I/Electrolyte   | $10^9 K_{sp}/\text{mol}^2\text{L}^{-2}$ | Reference   |
|------------------------|---|---|---|
| Tentative value        |   |   |   |
| 298.15                 | 0   | 1.38 ( $K_{sp}$ )                       |   |
| A. Experimental values |   |   |   |
| 298.15                 | 0   | 4.6                                     | Kunschert, 1904 <sup>270</sup>                      |
|                        | 0   | 2.47                                    | Clayton, Vosburgh, 1937 <sup>273</sup>              |
|                        | 0.02-0.33/K <sup>+</sup> (HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> ) | (2.79-3.77)                             | " " " " "   |
|                        | 0   | 1.28 <sup>a</sup>                       | Vosburgh, Beckman, 1940 <sup>274</sup>              |
|                        | ?   | 1.35 <sup>b</sup>                       | Zhuk, 1954 <sup>275</sup>                           |
|                        | NO  | 8.0 <sup>c</sup>                        | Lodzinska, Jablonski, Gornicki, 1965 <sup>278</sup> |
|                        | 1.5/NaNO <sub>3</sub>   | 11.2 <sup>d</sup>                       | " " " "   |
|                        | 3.0/NaNO <sub>3</sub>   | 215. <sup>d</sup>                       | " " " "   |
|                        | 6.0/NaNO <sub>3</sub>   | 436. <sup>d</sup>                       | " " " "   |
|                        | 9.0/NaNO <sub>3</sub>   | 511. <sup>d</sup>                       | " " " "   |
|                        | 0   | (0.6364 ± 0.0038)                       | Deyrieux, Peneloux, 1970 <sup>268</sup>             |
| Thermodynamic data     |   |   |   |
| 298.15                 | 0   | 1.38                                    | NBS Tables, 1982 <sup>12</sup>                      |

<sup>a</sup>A recalculated value of the result of Clayton and Vosburgh<sup>273</sup>

<sup>b</sup>Source unknown, but probably based on Vosburgh *et al.*<sup>273,274</sup> data.

<sup>c</sup>Value repeated in Gornicki and Jablonski, 1957<sup>281</sup> as  $I = 0$  value.

<sup>d</sup>Values repeated in Gornicki and Jablonski, 1957<sup>281</sup> with NaNO<sub>3</sub> clearly identified as the electrolyte.

TABLE 49. The solubility of cadmium oxalate trihydrate in water

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

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

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

A summary of the solubility studies carried out before 1931 is in Table 52. The early work of Joannis<sup>310</sup> did not

make clear the temperature or the added electrolyte concentration. Both Immerwahr<sup>202</sup> and Masaki<sup>311</sup> 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  $\text{ZnCl}_2$  to obtain a zinc ion activity which is reported as a molar solubility in Seidell<sup>6</sup>. Pines<sup>312</sup> measured the  $\text{Zn}^{2+}$  concentration over freshly precipitated  $\text{Zn}(\text{CN})_2$  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<sup>313</sup> studied the  $\text{KCN} + \text{Zn}(\text{CN})_2 + \text{H}_2\text{O}$  system at 298.15 K. He describes the  $\text{Zn}(\text{CN})_2$  solubility in water as a "trace". The values in Table 52 are the values for which he identified  $\text{Zn}(\text{CN})_2$  as the solid. Solutions at larger concentrations of  $\text{Zn}(\text{CN})_2$  and KCN are in equilibrium with solid  $\text{K}_2\text{Zn}(\text{CN})_4$  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<sup>312</sup> value in water was calculated by him from the polarographically determined  $\text{Zn}^{2+}$  concentration over freshly prepared  $\text{Zn}(\text{CN})_2$ . He took no account of hydrolysis or complex formation, and simply calculated  $K_{sp} = 4S^3$  using his  $\text{Zn}^{2+}$  concentration as the solubility. We judge the value to be too large by possibly several orders of magnitude. Persson<sup>314</sup> carried out the only modern day determination of the solubility product of  $\text{Zn}(\text{CN})_2$  in 3.0 molar

TABLE 50. The solubility product of cadmium oxalate trihydrate

| T/K                 | I/Electrolyte   | $10^6 K_{sp}/\text{mol}^2 \text{ L}^{-2}$ | Reference                                     |
|---------------------|---|---|---|
| Tentative value     |   |   |   |
| 298.15              | 0   | 1.42 ( $K_{sp}^0$ )                       |   |
| Experimental values |   |   |   |
| 291.15              | 0   | 1.53                                      | Zhuk, 1954 <sup>275</sup>                     |
| 298.15              | 0   | 2.78, 3.2                                 | Clayton and Vosburgh, 1937 <sup>273</sup>     |
|                     | 0   | 1.44 <sup>a</sup>                         | Vosburgh and Beckman, 1940 <sup>274</sup>     |
|                     | 0   | 1.64 <sup>b</sup>                         | Larson and Tomsicek, 1941 <sup>289</sup>      |
|                     | (0.02–0.33)/K <sup>+</sup> (HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> ) | (3.03–4.12)                               | Clayton and Vosburgh, 1937 <sup>273</sup>     |
|                     | ?   | 1.53                                      | Babkin <i>et al.</i> , 1985 <sup>287</sup>    |
|                     | ?   | 3.24                                      | Fridman <i>et al.</i> , 1963 <sup>295</sup>   |
|                     | ?   | 6.14                                      | Lodzinska <i>et al.</i> , 1965 <sup>278</sup> |
|                     | 1/KNO <sub>3</sub>  | (33.9 ± 0.8)                              | Olin, Wilmark, 1983 <sup>290</sup>            |
|                     | 3/NaNO <sub>3</sub>   | 174.                                      | Lodzinska <i>et al.</i> , 1965 <sup>278</sup> |
|                     | 6/NaNO <sub>3</sub>   | 521.                                      | " " "   |
| Thermodynamic data  |   |   |   |
|                     | 0   | 1.42                                      | NBS Tables 1982 <sup>12</sup>                 |

<sup>a</sup>Recalculation of Clayton and Vosburgh value.<sup>b</sup>Recalculation of Clayton and Vosburgh value.TABLE 51. Cumulative formation constants of Cd(C<sub>2</sub>O<sub>4</sub>)<sub>n</sub><sup>2(1-n)</sup> (aq) for n = 1, 2 and 3. Based on Table in Olin and Wikmark<sup>290</sup>

| T/K    | I/Electrolyte          | log β <sub>1</sub> | log β <sub>2</sub> | log β <sub>3</sub> | Method       | Reference  |
|--------|------------------------|--------------------|--------------------|--------------------|--------------|--|
| 298.15 | 0                      | 3.84               | —                  | —                  | <sup>a</sup> | Vosburgh <i>et al.</i> , 1936 <sup>296</sup> , 1940 <sup>274</sup> |
| —      | 0.25/KClO <sub>3</sub> | 2.05               | 4.55               | 5.15               | <sup>a</sup> | Oncescu <i>et al.</i> , 1969 <sup>297</sup>                        |
| 298.15 | 1.0/KNO <sub>3</sub>   | 2.66               | 4.29               | 5.00               | <sup>b</sup> | Olin, Wikmark, 1983 <sup>290</sup>                                 |
|        | 1.0/KNO <sub>3</sub>   | 3.20               | 4.57               | 5.53               | <sup>c</sup> | Kanemura, Watters, 1967 <sup>298</sup>                             |
|        | 1.0/NaClO <sub>4</sub> | 2.75               | —                  | —                  | <sup>a</sup> | Bottari, 1975 <sup>299</sup>                                       |
|        | 1.0/NaNO <sub>3</sub>  | 2.61               | 4.14               | 5.04               | <sup>d</sup> | Schaap <i>et al.</i> , 1961 <sup>300</sup>                         |
|        | 1.0/NaNO <sub>3</sub>  | 2.61               | 4.11               | 5.06               | <sup>d</sup> | McMasters <i>et al.</i> , 1962 <sup>301</sup>                      |
|        | 1.5/KNO <sub>3</sub>   | 2.72               | 4.16               | 5.14               | <sup>d</sup> | Arevalo <i>et al.</i> , 1974 <sup>302</sup>                        |
|        | 2.0/KNO <sub>3</sub>   | 2.78               | 4.00               | 5.20               | <sup>d</sup> | Dhuley <i>et al.</i> , 1975 <sup>303</sup>                         |
| 300.15 | 2.1/KNO <sub>3</sub>   | 2.90               | 4.00               | 5.08               | <sup>d</sup> | Khurana, Gupta, 1973 <sup>304</sup>                                |
| 298.15 | ?/CdSO <sub>4</sub>    | 3.52               | 4.61               | —                  | <sup>b</sup> | Ermolenko, 1975 <sup>305</sup>                                     |

Methods: <sup>a</sup>potentiometric <sup>b</sup>solubility <sup>c</sup>acidimetric <sup>d</sup>polarography

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

| T/K    | (c or m)/Electrolyte   | c/mol L <sup>-1</sup> or<br>m/mol Kg <sup>-1</sup> or<br>a/activity | Method      | Reference                      |
|--------|--|---|-------------|--------------------------------|
| 288(?) | conc. ZnSO <sub>4</sub>  | 0.01 <sub>7</sub> (c)   |             | Joannis, 1882 <sup>310</sup>   |
|        | conc. Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> | 0.03 <sub>4</sub> (c)   |             | " "                            |
| 298.15 | 0.05(c)/KCN  | 8.9 × 10 <sup>-9</sup> (a)  | emf         | Immerwahr, 1901 <sup>202</sup> |
| 298.15 | 0.403(m)/KCN   | 0.206 (m)   |             | Corbet, 1926 <sup>313</sup>    |
| 298.15 | 0.630(m)/KCN   | 0.305 (m)   |             | " "                            |
| 298.15 | 1.205(m)/KCN   | 0.688 (m)   |             | " "                            |
| "Room  | water  | 4 × 10 <sup>-5</sup> (c)  | polarograph | Pines, 1929 <sup>312</sup>     |
| 291.15 | water  | 4.49 × 10 <sup>-5</sup> (a)   | emf         | Masaki, 1931 <sup>311</sup>    |

NaClO<sub>4</sub> 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  $\beta_n$  for  $n = 1, 2, 3$  and 4 in 3.0 M NaClO<sub>4</sub> at 298.15 K. In an earlier study Izatt, Christensen, Hansen and Watt<sup>315</sup> reported values of the cumulative formation constants  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  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<sup>+</sup>(aq) in their system. The  $\beta$  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<sup>8</sup>.

TABLE 53. Solubility product constant of zinc cyanide

| T/K              | I/Electrolyte                   | $K_{s0}$  | Reference  |
|------------------|---------------------------------|---|--|
| "Room"<br>298.15 | water<br>3.0/NaClO <sub>4</sub> | $2.56 \times 10^{-13}$<br>$(3.3 \pm 1.3) \times 10^{-16}$ | Pines, 1929 <sup>312,a</sup><br>Persson, 1971 <sup>314</sup> |

<sup>a</sup> Calculated by Pines from solubility value in previous table by 4S<sup>3</sup>. Value probably too large.

 TABLE 54. Cumulative formation constants,  $\beta_n$ , for Zn(CN)<sub>n</sub><sup>2-n</sup> in aqueous solution at 298.15 K

| Cumulative formative constants, $\beta_n$ , at ionic strengths |   |   |
|--|---|---|
| $n$  | $I = 0^a$                                       | $I = 3.0/\text{NaClO}_4^b$                      |
| 1  |   | $(2.2 \pm 0.5) \times 10^5 \text{ m}^{-1}$      |
| 2  | $(1.17 \pm 0.05) \times 10^{11} \text{ m}^{-2}$ | $(1.06 \pm 0.06) \times 10^{11} \text{ m}^{-2}$ |
| 3  | $(1.12 \pm 0.06) \times 10^{16} \text{ m}^{-3}$ | $(4.8 \pm 0.5) \times 10^{16} \text{ m}^{-3}$   |
| 4  | $(4.2 \pm 0.6) \times 10^{19} \text{ m}^{-4}$   | $(3.7 \pm 0.8) \times 10^{21} \text{ m}^{-4}$   |

<sup>a</sup>Izatt *et al.*, 1965<sup>315</sup>

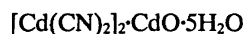
<sup>b</sup>Persson, 1971<sup>314</sup>

#### 4.13.b. Cadmium Cyanide

Cd(CN)<sub>2</sub>; [542-83-6] molecular weight 164.45

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

There are substances in addition to Cd(CN)<sub>2</sub> that may be important as equilibrium solids in contact with aqueous Cd(CN)<sub>2</sub>. The basic oxide



is known and is probably the solid phase when Cd(CN)<sub>2</sub> is dissolved in water. The salt  $K_2\text{Cd}(\text{CN})_4$  is the equilibrium solid in the KCN + Cd(CN)<sub>2</sub> + H<sub>2</sub>O 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  $a = 12.87 \times 10^{-10}$  m with a calculated density of  $1.836 \times 10^3 \text{ kg m}^{-3}$ . The salt NaCd(CN)<sub>3</sub>·1.5H<sub>2</sub>O may be important in NaCN + Cd(CN)<sub>2</sub> + H<sub>2</sub>O systems.

There is no definitive study on the solubility of cadmium cyanide in water and aqueous electrolyte solutions. Neither Pines<sup>312</sup> nor Persson<sup>314</sup>, who reported solubility products for Zn(CN)<sub>2</sub>, were able to obtain solubility product values for the more soluble Cd(CN)<sub>2</sub> in studies similar to those carried out for the zinc salt. Corbet<sup>313</sup> makes clear that Cd(CN)<sub>2</sub> 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)<sub>2</sub> in water reported by Joannis<sup>310</sup> is thought to be too large and is classed as doubtful. The values of Immerwahr<sup>202</sup> and Masaki<sup>311</sup> depend on emf measurements reversible to the Cd<sup>2+</sup> 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<sup>6</sup>. Corbet's study of the KCN + Cd(CN)<sub>2</sub> + H<sub>2</sub>O 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<sup>-3</sup> range at 298.15 K. The Corbet solubility values in Table 55 are the values for which he identifies the solid as Cd(CN)<sub>2</sub>. These values are footnoted with the comment that the solid is undoubtedly a basic cadmium cyanide. Joannis<sup>310</sup> earlier identified the basic oxide [Cd(CN)<sub>2</sub>]<sub>2</sub>·CdO·5H<sub>2</sub>O. Corbet found it impossible to prepare pure Cd(CN)<sub>2</sub> and identified his basic oxide as [Cd(CN)<sub>2</sub>]<sub>3</sub>·CdO·4H<sub>2</sub>O. NBS Tables<sup>12</sup> list thermodynamic data on a basic oxide of the Joannis formula. Solutions of larger concentrations of KCN and Cd(CN)<sub>2</sub> are in equilibrium with solid K<sub>2</sub>Cd(CN)<sub>4</sub> or KCN.

Persson<sup>314</sup> reports cumulative formation constants for cadmium cyanide complex ions in 3.0 M NaClO<sub>4</sub> at 298.15 K. They are  $(4.2 \pm 0.1) \times 10^5 \text{ m}^{-1}$ ,  $(6.9 \pm 0.5) \times 10^{10} \text{ m}^{-2}$ ,  $(5.3 \pm 0.3) \times 10^{15} \text{ m}^{-3}$ , and  $(1.6 \pm 0.4) \times 10^{19} \text{ m}^{-4}$  for  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  and  $\beta_4$ , respectively.

#### 4.14. Zinc and Cadmium Tetrathiocyanato Mercurate (2-)

##### 4.14.a. Zinc Tetrathiocyanato Mercurate (2-)

Zn[Hg(SCN)<sub>4</sub>] [15318-77-1] molecular weight 498.31

*Physical characteristics:* Zinc tetrathiocyanato mercurate (2-) is tetragonal with  $a = 7.823 \times 10^{-10}$  m and  $c = 4.319 \times 10^{-10}$  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<sup>316</sup> is much larger than any other reported value. It is rejected. The values reported by

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

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

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

| $T/\text{K}$ | $10^4 c/\text{mol L}^{-1}$ | Reference  |
|--------------|----------------------------|--|
| 288.15       | 48.                        | Robertson, 1907 <sup>316</sup>   |
| 291.15       | 1.75                       | Swinarski and Czakis, 1955 <sup>319</sup><br>Czakis and Swinarski, 1957 <sup>320</sup> |
| "Room"       | 3.7                        | Kolthoff and Stenger, 1947 <sup>318</sup>  |
| "Room"       | $4.7 \pm 0.4^a$            | Korenman <i>et al.</i> , 1956 <sup>317</sup>   |
| "Room"       | $4.9 \pm 0.4^a$            | " " "  |
| "Room"       | $6.7 \pm 0.3^a$            | " " "  |
| 303.15       | 6.90                       | Czakis and Swinarski, 1957 <sup>320</sup>  |
| 323.15       | 12.0                       | " " "  |
| 343.15       | 15.0                       | " " "  |

<sup>a</sup> The average of these values,  $(5.4 \pm 1.1) \times 10^{-4} \text{ mol L}^{-1}$ , is on Fig. 3a.

Korenman, Sheyanova, and Potapova<sup>317</sup> at an undefined temperature were determined with the aid of anisotropic radioactive indicators. They used  $^{65}\text{Zn}$ ,  $^{60}\text{Co}$ , and  $^{115}\text{Cd}$  to obtain the three values in the table. Kolthoff and Stenger<sup>318</sup> report a value in water and several  $\text{K}_2[\text{Hg}(\text{SCN})_4]$  aqueous solutions at an undefined temperature. Swinarski and Czakis<sup>319</sup> report the solubility in water at 291.15 K, and in a later paper Czakis and Swinarski<sup>320</sup> 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  $\ln(c/\text{mol L}^{-1})$  vs.  $1000/(T/\text{K})$  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 Swinarski papers. The values of Korenman *et al.*<sup>317</sup> and Kolthoff and Stenger<sup>318</sup> 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<sup>319</sup> report a solubility product calculated assuming  $K_{s0} = S^2$  ( $S$  = 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<sup>318</sup> show the solubility decreases to  $5 \times 10^{-6} \text{ mol L}^{-1}$  in the presence of  $3 \times 10^{-3} \text{ mol L}^{-1} \text{K}_2[\text{Hg}(\text{SCN})_4]$ , and Robertson<sup>316</sup> mentions the solubility is considerably reduced in the presence of zinc cation. Cuvelier<sup>321</sup> showed there is a seven fold increase in solubility as the ammonium chloride concentrations increase from 0.02 to 1.84  $\text{mol L}^{-1}$  at room temperature. Czakis and Swinarski<sup>320</sup> show the solubility of  $\text{Zn}[\text{Hg}(\text{SCN})_4]$  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-)

$\text{Cd}[\text{Hg}(\text{CNS})_4]$  [14878–23–0] molecular weight 545.33

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

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

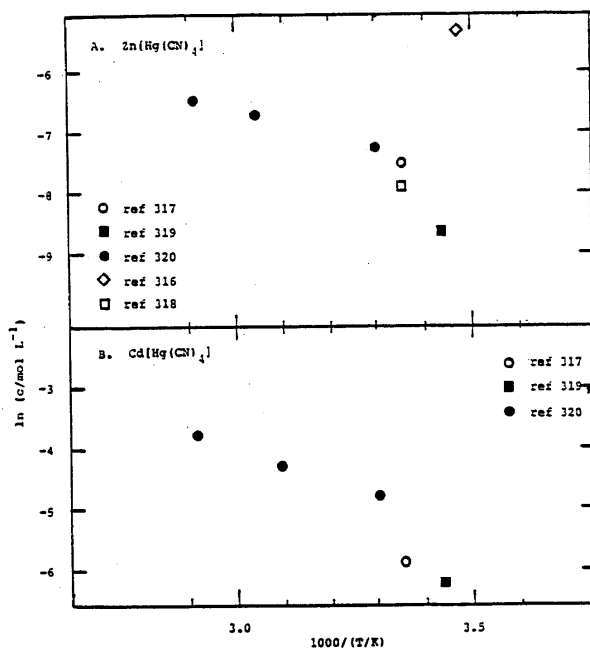


Fig 3. a. Solubility of  $\text{Zn}[\text{Hg}(\text{CN})_4]$  in water, 288–343 K.  
 b. Solubility of  $\text{Cd}[\text{Hg}(\text{CN})_4]$  in water, 291–343 K.  
 $\ln(c/\text{mol L}^{-1})$  vs.  $1000/(T/\text{K})$

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

| T/K    | $10^3 c/\text{mol L}^{-1}$ | Reference   |
|--------|----------------------------|---|
| 291.15 | 1.9                        | Swinarski and Czakis, 1955 <sup>319</sup> , 1957 <sup>320</sup> |
| "Room" | $4.0 \pm 0.5^a$            | Korenman <i>et al.</i> , 1956 <sup>317</sup>                    |
| "Room" | $3.3 \pm 0.3^a$            | " " "   |
| "Room" | $1.1 \pm 0.1^a$            | " " "   |
| 303.15 | 8.26                       | Czakis and Swinarski, 1957 <sup>320</sup>                       |
| 323.15 | 13.8                       | " " " "   |
| 343.15 | 23.0                       | " " " "   |

<sup>a</sup>Av. value of  $(2.8 \pm 1.5) \times 10^{-3} \text{ mol L}^{-1}$  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<sup>320</sup>.

Figure 3b shows that although the cadmium salt is about ten times more soluble than the zinc salt, the  $\ln(c/\text{mol L}^{-1})$  vs  $1000/(T/\text{K})$  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<sup>319</sup> 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 Ferricyanides

$\text{Zn}_2[\text{Fe}(\text{CN})_6]$  [14883–46–6] molecular weight 342.73

$\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$  [29730–24–3]

molecular weight 378.76

$\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 2.5 \text{H}_2\text{O}$  [not found]

molecular weight 387.77

$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  [15320–55–5] molecular weight 620.03

$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$  [not found]

molecular weight 836.26

$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$  [91947–27–2]

molecular weight 872.29

*Physical characteristics:* Zinc ferrocyanide. Kuznetsov *et al.*<sup>322</sup> report powder patterns of less than cubic symmetry for both  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$  and its dihydrate. Cola and Valentini<sup>323</sup> 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  $9.89 \times 10^{-10} \text{ m}$ , respectively, and a calculated density of  $1.73 \times 10^3 \text{ kg m}^{-3}$ . Siebert *et al.*<sup>324</sup> report the dihydrate is hexagonal with  $Z = 1$ ,  $a = 7.598 \times 10^{-10} \text{ m}$ ,  $c = 5.756 \times 10^{-10} \text{ m}$ , and a calculated density of  $2.18 \times 10^3 \text{ kg m}^{-3}$ .

*Zinc ferricyanide.* Weiser *et al.*<sup>325</sup> and Van Bever<sup>326</sup> found anhydrous  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  to be face centered cubic with  $a = 10.38 \times 10^{-10} \text{ m}$  from which we calculate a density of  $1.84 \times 10^3 \text{ kg m}^{-3}$ . Cola and Valentini<sup>323</sup> report the material to be monoclinic with  $Z = 4$ ,  $a$ ,  $b$  and  $c = 10.95, 13.16$  and  $18.12 \times 10^{-10} \text{ m}$ , respectively, and a calculated density of  $1.58 \times 10^3 \text{ kg m}^{-3}$ . Siebert and Jentsch<sup>327</sup> report a rhombohedral form with  $a = 13.17 \times 10^{-10} \text{ m}$ ,  $\alpha = 57.15^\circ$ , 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.*<sup>328</sup> report an unspecified hydrate of  $X$  moles of water which they later<sup>329</sup> identified as a cubic 14 water hydrate with  $a = 10.34 \times 10^{-10} \text{ m}$ ,  $Z = 4/3$ , and a calculated density of  $1.74 \times 10^3 \text{ kg m}^{-3}$ . It is possible that the dodecahydrate was misidentified and was really the tetradecahydrate.

Solubility data are reported for mixed ferrocyanides like  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  [15245–11–1],  $\text{K}_2\text{Zn}[\text{Fe}(\text{CN})_6]$  [15320–39–5],  $\text{Na}_2\text{Zn}[\text{Fe}(\text{CN})_6]$  [88560–56–9],  $(\text{NH}_4)_2\text{Zn}[\text{Fe}(\text{CN})_6]$  [79957–73–6], and  $(\text{NH}_4)_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  [79957–72–5].

The solubility of zinc ferrocyanide has been measured by five different methods by Tananaev *et al.*<sup>330</sup> and Basinski and co-workers<sup>331,332,333,1</sup> the conductivity method of Basinski *et al.*<sup>332</sup> 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<sup>334</sup> 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 $c/\text{mol L}^{-1}$ | Method       | Reference  |
|--|----------------------------------|--------------|--|
| Zinc ferrocyanide; $\text{Zn}_2[\text{Fe}(\text{CN})_6]$   |                                  |              |  |
| Recommended value  |                                  |              |  |
| 298.15   | $(9.7 \pm 1.7) \times 10^{-6}$   |              |  |
| Experimental values  |                                  |              |  |
| 293.15   | *                                |              | Dyulgerova, Zakharov, Songina 1983 <sup>337</sup>  |
| 298.15   | $7.4 \times 10^{-6}$             | phosphate    | Tananaev, Glushkova, Seifer 1956 <sup>330, f</sup> |
|  | $9.8 \times 10^{-6}$             | colorimetric | Basinski, Mucha 1960 <sup>331, b</sup>             |
|  | $11.4 \times 10^{-6}$            | polarography | " " " "  |
|  | $3.95 \times 10^{-6}$            | conductivity | Basinski, Szymanski, Bebnista 1961 <sup>332</sup>  |
|  | $(10.4 \pm 0.9) \times 10^{-6}$  | tracer       | Basinski, Szymanski, Bebnista 1961 <sup>333</sup>  |
| Zinc ferricyanide; $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ |                                  |              |  |
| Experimental values  |                                  |              |  |
| 289.15   | $1.24 \times 10^{-4}$            | iodometric   | Cuta 1929 <sup>338, c, d</sup>                     |
|  | $(1.65 \pm 0.05) \times 10^{-4}$ | colorimetric | Grieb, Cone 1950 <sup>336, e</sup>                 |

\*No solubility value for water. Do report solubilities in 0.1 and 0.5 mol L<sup>-1</sup> NH<sub>4</sub>OAc, H<sub>2</sub>SO<sub>4</sub>, and NH<sub>3</sub>.

<sup>b</sup>Also report solubility data in dilute HCl and HNO<sub>3</sub> (pH = 1.4).

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

<sup>d</sup>Paper also reports solubilities in solutions saturated at room temperature with 12 different electrolytes. Solubilities in mol kg<sup>-1</sup> at 289 K and in "hot" (348–353 K) water.

<sup>e</sup>Data appear in Seidell-Linke<sup>6</sup>.

TABLE 59. The solubility product constant of zinc ferrocyanide dihydrate  $\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ 

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

<sup>a</sup>Calculated for the process  $\text{Zn}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}(\text{s}) = 2 \text{Zn}^{2+}(\text{aq}) + [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) + 2\text{H}_2\text{O}$ .

among several workers is good. We recommend the value calculated from Gibbs energy of formation values from the NBS Tables<sup>12</sup>. The value is very near to the value of Rock and Powell<sup>334</sup> 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 Krlieza *et al.*<sup>335</sup> which according to the abstract may contain a value of the solubility product constant.

Grieb and Cone<sup>336</sup> report a solubility of  $1.2 \times 10^{-4}$  mol L<sup>-1</sup> for  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  at 298.15 K from electrode potential measurements and a comparative calculation method that depends on the solubility of  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ .

The solubilities of other mixed zinc-other cation ferrocyanides were measured in the presence of electrolytes with a common ion at  $293 \pm 1$  K by Dyulgerova, Zakharov and Songina<sup>337</sup>.

Cuta<sup>338</sup> 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<sup>-1</sup> gives  $1.24 \times 10^{-3}$  mol L<sup>-1</sup> 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-)]

|  |                         |
|--|-------------------------|
| $\text{Cd}_2[\text{Fe}(\text{CN})_6]$ [13755-33-4]                         | molecular weight 436.77 |
| $\text{Cd}_2[\text{Fe}(\text{CN})_6]\cdot 7\text{H}_2\text{O}$ [not found] | molecular weight 562.88 |
| $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ [15612-87-0]                       | molecular weight 761.14 |

*Physical characteristics:* Cadmium ferrocyanide. Kuznetsov *et al.*<sup>322</sup> report powder patterns of less than cubic symmetry for both  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  and its dihydrate. Siebert *et al.*<sup>324</sup>, report the crystal is trigonal (hexagonal) with  $Z = 1$ ,  $a$  and  $c = 6.35$  and  $6.361 \times 10^{-10}$  m, respectively, and a calculated density of  $3.28 \times 10^3 \text{ kg m}^{-3}$ . Cola *et al.*<sup>339</sup> give powder patterns for 1.5, 4 and 9 water hydrates. They report a cubic monohydrate  $\text{Cd}_{1.9}\text{H}_{0.2}[\text{Fe}(\text{CN})_6]\cdot\text{H}_2\text{O}$  with  $a = 15.50 \times 10^{-10}$  m,  $Z = 16$  and a calculated density of  $3.17 \times 10^3 \text{ kg m}^{-3}$ . No structural information was found for the heptahydrate.

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

Table 60 lists the values of the solubility of  $\text{Cd}_2[\text{Fe}(\text{CN})_6]$  in water. The tentative value at 298.15 K of  $(5.1 \pm 1.7) \times 10^{-6} \text{ mol L}^{-1}$  is the average of the results of Tananaev *et al.*<sup>330</sup>, Basinski and Poczopko<sup>340</sup>, and Basinski and Szymanski<sup>341</sup>. It is possible that the Basinski and Poczopko value is the average of the 293.15 K values of Balinski and Ledzinska<sup>342</sup> which would make the result more uncertain. The 298.15 K value reported by Bellomo *et al.*<sup>343</sup> 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.*<sup>344</sup>, Basinski and co-workers<sup>340,341,342</sup>, Tananaev *et al.*<sup>330</sup>, Rock and Powell<sup>334</sup>, and Bellomo *et al.*<sup>343</sup> report values of the solubility product,  $K_{s0}$ . Basinski and co-workers and Bellomo *et al.* obtained  $K_{s0} = 4 \text{ s}^3$  which assumes an ideal solution with no hydrolysis or association. Probably the work of Rock and Powell<sup>334</sup> 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.*<sup>339</sup> show a variable hydration of the solid depending on the conditions of precipitation. Thus, the nature of the solid is not fully settled. Krlezka *et al.*<sup>335</sup> 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.*<sup>343</sup> report solubilities of  $3.5 \times 10^{-6}$ ,  $6.1 \times 10^{-6}$  and  $6.9 \times 10^{-6} \text{ mol L}^{-1}$  at temperatures of 298.15, 308.15 and 318.15 K respectively for  $\text{K}_{12}\text{Cd}_8[\text{Fe}(\text{CN})_6]_7$ .

Only two papers were found on the solubility of cadmium ferricyanide. Piperaki and Hadjiioannou<sup>250</sup> report a room temperature value in water (see Table 60), and King<sup>345</sup> 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<br>10 <sup>6</sup> c/mol L <sup>-1</sup> | Method                 | Reference  |
|---|---|------------------------|--|
| Cadium ferrocyanide; Cd <sub>2</sub> [Fe(CN) <sub>6</sub> ]               |   |                        |  |
| Tentative value   |   |                        |  |
| 298.15  | (5.1 ± 1.7)   |                        |  |
| Literature values   |   |                        |  |
| 293.15  | 10.9  | Colorimetry (in light) | Basinski, Ledzinska 1957 <sup>242</sup>          |
|   | 6.98  | Colorimetry (in dark)  | " " " "  |
|   | 6.30  | Polarography           | " " " "  |
| 298.15  | 3.2   | Gravimetric            | Tananaev, Glushkova, Seifer 1956 <sup>330a</sup> |
|   | 6.62  | Calculated             | Basinski, Poczopko 1958 <sup>340</sup>           |
|   | 5.35  | Conductivity           | Basinski, Szymanski 1958 <sup>341</sup>          |
|   | 20.7  | Conductivity           | Bellomo, DeMarco, Casale 1972 <sup>343</sup>     |
| 308.15  | 47.6  | "                      | " " " "  |
| 318.15  | 48.2  | "                      | " " " "  |
| Cadmium ferricyanide; Cd <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> |   |                        |  |
| "Room"  | 44.   | Catalytic titration    | Piperaki, Hadjiioannou 1977 <sup>250</sup>       |
| 273.15 –<br>320.15  | <sup>b</sup>  |                        | King 1949 <sup>345, a</sup>                      |

<sup>a</sup>Data appear in Siedell-Linke<sup>6</sup>.

<sup>b</sup>No value in water, but solubility data for aqueous solutions containing ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, and H<sup>+</sup>.

TABLE 61. The solubility product constant of cadmium ferrocyanide heptahydrate, Cd<sub>2</sub>[Fe(CN)<sub>6</sub>]·7H<sub>2</sub>O

| T/K               | Ionic strength<br>I/Electrolyte | K <sub>s0</sub>          | Solubility product<br>K <sub>s0</sub> | Reference  |
|-------------------|---------------------------------|--------------------------|---------------------------------------|--|
| Tentative value   |                                 |                          |                                       |  |
| 298.15            | 0                               | 3.6 × 10 <sup>-18</sup>  |                                       | <sup>a</sup>                                       |
| Literature values |                                 |                          |                                       |  |
| 291.15            | 0.1/KNO <sub>3</sub>            |                          | 2.3 × 10 <sup>-17</sup>               | Karnaukhov, Grinevich, Skobets 1973 <sup>344</sup> |
| 293.15            | /                               |                          | 1.17 × 10 <sup>-15</sup>              | Basinski, Ledzinska 1957 <sup>242, b</sup>         |
| 298.15            |                                 |                          | 3.2 × 10 <sup>-17</sup>               | Tananaev, Glushkova, Seifer 1956 <sup>330</sup>    |
| 298.15            | 0                               | 9.62 × 10 <sup>-16</sup> |                                       | Basinski, Poczopko 1957 <sup>340</sup>             |
|                   |                                 |                          | 6.1 × 10 <sup>-16</sup>               | Basinski, Szymanski 1958 <sup>341</sup>            |
|                   | 0                               | 4.2 × 10 <sup>-18</sup>  |                                       | Rock, Powell 1964 <sup>334</sup>                   |
|                   | 0(?)                            | 3.6 × 10 <sup>-14</sup>  |                                       | Bellomo, DeMarco, Casale 1972 <sup>343</sup>       |
| 308.15            | 0(?)                            | 4.3 × 10 <sup>-13</sup>  |                                       | " " " "  |
| 318.15            | 0(?)                            | 4.5 × 10 <sup>-13</sup>  |                                       | " " " "  |

<sup>a</sup>Tentative value calculated from Gibbs energy of formation data in NBS Tables<sup>12</sup> for Cd<sub>2</sub>[Fe(CN)<sub>6</sub>]·7H<sub>2</sub>O(s) = 2Cd<sup>2+</sup>(aq) + Fe(CN)<sub>6</sub><sup>4-</sup>(aq) + 7 H<sub>2</sub>O.

<sup>b</sup>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<sup>3</sup> (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 <sup>-1</sup>   | 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(ClO <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O, 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 <sup>346</sup> . |
| Zn(ClO <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O   | 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 <sup>-1</sup>   |  |
| Cd(ClO <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O   | 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   |        |  | Titration method used. Feitknecht, Haberli, 1950 <sup>347</sup> .  |
| ZnCl <sub>0.3</sub> (OH) <sub>1.7</sub>   | 298.15 | $K_{s0} = 1.2 \times 10^{-15}$                                   |  |
| ZnCl <sub>0.4</sub> (OH) <sub>1.6</sub>   | 298.15 | $K_{s0} = 6 \times 10^{-15}$                                     | Potentiometric method used. Aksel'rud, Spivakovskii, 1958 <sup>348</sup> .   |
| Zn <sub>2</sub> Cl(OH) <sub>3</sub> [12381-00-9]  | 298.15 | $K_{s0} = 4.0 \times 10^{-14}$                                   |  |
| as ZnCl <sub>0.5</sub> (OH) <sub>1.5</sub>  | 298.15 | $K_{s0} = 1.6 \times 10^{-27}$                                   |  |
| as Zn <sub>2</sub> Cl(OH) <sub>3</sub>  | 298.15 | $K_{s0} = 1.57 \times 10^{-27}$                                  |  |
|   | 298.15 | Calculated graphs.   | Calculated by us from Gibbs energy data in NBS Tables <sup>12</sup> . Used literature equilibrium constants to show that at $f_{\text{CO}_2} = 10^{-3.5}$ in the presence of aqueous Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> the compound limits Zn <sup>2+</sup> solubility only at low sulfate ion activity. The solid is very soluble in acid solution. Mann, Deutscher, 1980 <sup>232</sup> .  |
|   | 298.15 |  |  |
| Cadmium chloride hydroxide  |        |  | Five solids were identified from a study of CdCl <sub>2</sub> + NaOH solutions. $K_{s0}$ calculated from analysis of solutions over solid. The solids formed and their crystal structures are discussed. Feitknecht, Gerber, 1937 <sup>350,351</sup> .   |
| CdCl(OH) [14031-46-9]   | 298.15 | $K_{s0} = 2 \times 10^{-11}$                                     |  |
| Zinc hydroxide perchlorate  |        |  | The solubilization reaction is formulated as Zn(ClO <sub>4</sub> ) <sub>1/4</sub> (OH) <sub>7/4</sub> (s) = Zn <sup>2+</sup> (aq) + (1/4)ClO <sub>4</sub> <sup>-</sup> (aq) + (7/4)OH <sup>-</sup> (aq). The Gibbs energy, enthalpy and entropy of formation of Zn(ClO <sub>4</sub> ) <sub>1/4</sub> (OH) <sub>7/4</sub> (s) are -512.16, 621.08, and 0.10157 (kJ). Gomez de Agüero, Ramirez Garcia, Garcia Martinez, Guerrero Laverat, 1988 <sup>349</sup> .  |
| Zn <sub>4</sub> ClO <sub>4</sub> (OH) <sub>7</sub> [118956-02-8]                                      | 298.15 | $K_{s0} = 3.84 \times 10^{-16}$                                  |  |
| Periodic acid (H <sub>5</sub> IO <sub>6</sub> ),<br>Cadmium salts<br>Cd <sub>2</sub> HIO <sub>6</sub> | 298.15 | $K_{s0} = 1.5 \times 10^{-21}$<br>at $I = 6.24 \times 10^{-3}$ . | Solubility product reaction is 0.5Cd <sub>2</sub> HIO <sub>6</sub> (s) + 1.5H <sub>2</sub> O = Cd <sup>2+</sup> + 1.5OH <sup>-</sup> + 0.5H <sub>4</sub> IO <sub>6</sub> <sup>-</sup> .  |

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 <sub>2</sub> HIO <sub>6</sub> ·1.25H <sub>2</sub> O [64265-91-4]<br>Cd <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub> [77308-33-9]                          | 298.15                                      | $K_{s0} = 1.0 \times 10^{-21}$<br>$K_{s0} = 2.0 \times 10^{-22}$<br>$K_{s0} = 1.26 \times 10^{-22}$                          | Solubility product reaction is $0.2\text{Cd}_5(\text{IO}_6)_2(\text{s}) + 1.6\text{H}_2\text{O} = \text{Cd}^{2+} + 1.6\text{OH}^- + 0.4\text{H}_4\text{IO}_6^-$ . Potentiometric method used to determine value for Cd <sub>2</sub> HIO <sub>6</sub> , which is the solid at pH < 3; the Cd <sub>5</sub> (IO <sub>6</sub> ) <sub>2</sub> value was estimated. It appears to exist at the higher pH's. Author states Cd <sub>2</sub> HIO <sub>6</sub> is anhydrous. Nasanen, 1955 <sup>352</sup> .         |
| Zinc hydroxide sulfate<br>Zn <sub>4</sub> SO <sub>4</sub> (OH) <sub>6</sub> [12027-98-4]<br>as ZnSO <sub>4</sub> ·3Zn(OH) <sub>2</sub>                       | 298.15<br>348.15                            | $K_{s0} = 2.51 \times 10^{-56}$<br>$K_{s0} = 6.31 \times 10^{-58}$   | 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 solutions and converts to Zn(OH) <sub>2</sub> . Dobrokhotov, 1954 <sup>353</sup> . Potentiometric titration of ZnSO <sub>4</sub> + NaOH. Solid the hydroxide at ZnSO <sub>4</sub> about $5 \times 10^{-4}$ mol L <sup>-1</sup> , sulfate hydroxide at ZnSO <sub>4</sub> > $7.4 \times 10^{-3}$ mol L <sup>-1</sup> . Hagsiwa, 1939 <sup>354</sup> . |
|  | 299.65                                      | $K_{s0} = 2 \times 10^{-17}(?)$  | Result of a ZnSO <sub>4</sub> = NaOH titration. Authors state the solid is the sulfate hydroxide, but the value appears to be for Zn(OH) <sub>2</sub> and they compare it with Zn(OH) <sub>2</sub> values. Quimby, McCune, 1957 <sup>225</sup> .  |
|  | 353   | 0.4 g L <sup>-1</sup>  | 3Zn(OH) <sub>2</sub> ·ZnSO <sub>4</sub> ·4H <sub>2</sub> O precipitates in a lime slurry at 70–80 °C. Sharma, 1990 <sup>395</sup> .   |
| as Zn(SO <sub>4</sub> ) <sub>0.25</sub> (OH) <sub>1.5</sub>  | 298.15                                      | Calculated solubility figures. Used pK <sub>s0</sub> = 13.9.   | pK <sub>s0</sub> value is Dobrokhotov's value (above). Authors calculated Zn ion activity for CO <sub>2</sub> fugacity of 10 <sup>-3.5</sup> and solutions containing OH <sup>-</sup> , Cl <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> . The compound is exceedingly soluble in acid solutions. Mann, Deutscher, 1980 <sup>252</sup> .   |
| Zinc sulfate<br>ZnSO <sub>4</sub> [7733-02-0]  | 298.15                                      | ZnSO <sub>4</sub> solubility decreases 3.512 m to 0.011 m as H <sub>2</sub> SO <sub>4</sub> conc. inc. 0 to 39.517 m.        | Study of ZnSO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O system 278.15, 288.15, and 298.15 K. In water the solid phase is ZnSO <sub>4</sub> ·7H <sub>2</sub> O [7446-20-0], and in H <sub>2</sub> SO <sub>4</sub> the solid is ZnSO <sub>4</sub> ·H <sub>2</sub> O [7446-19-7]. Pieniazek, Milewska, Masztalerz, 1982 <sup>355</sup> .  |
| Sodium chloride cadmium sulfate double salt<br>NaCl·CdSO <sub>4</sub> ·5H <sub>2</sub> O   | 298   | 2.491 mol/kg   | The compound has been isolated and identified in the 2NaCl + CdSO <sub>4</sub> = Na <sub>2</sub> SO <sub>4</sub> + CdCl <sub>2</sub> + H <sub>2</sub> O system. Rumyantsev and Charykov, 1989 <sup>393</sup> .  |
| (Ca, Zn) hydroxyapatite<br>(Ca,Zn) <sub>10</sub> (OH) <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub>   | 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 <sup>398</sup> .   |
| Zinc potassium phytate<br>Zn <sub>4</sub> K <sub>3</sub> [C <sub>6</sub> H <sub>4</sub> (PO <sub>4</sub> ) <sub>5</sub> (HPO <sub>4</sub> )]<br>[97726-59-8] | 298.15                                      | pK <sub>s</sub> = 30.4   | $K_s = [\text{Zn}^{2+}][\text{K}^+]^3[\text{Phy}^{11-}]$ Calculated from data obtained in a calorimetric study and knowledge of the ionization constants of phytic acid [83-86-3]. Evans, Marini, Martin, 1983 <sup>356</sup> .   |
| Zinc ammonium phosphate<br>ZnNH <sub>4</sub> PO <sub>4</sub> [15006-70-9]  | 283.15<br>290.65<br>boiling temp.<br>293.15 | $0.762 \times 10^{-4}$ mol L <sup>-1</sup><br>$0.813 \times 10^{-4}$ "<br>$1.26 \times 10^{-4}$ "<br>$0.84 \times 10^{-4}$ " | Solubility determined by gravimetric analysis. Artmann 1915 <sup>357</sup> . State compound water-insoluble but give no quantitative data. Travers, Perron, 1924 <sup>358</sup> , Vol'fkovich, Remen, 1955 <sup>359</sup> .   |

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  | $K_{s0} = 3.8 \times 10^{-15}$   | Value from a solubility and pH study. Sahli, 1952 <sup>360</sup>  |
| $Zn(CO_3)_{0.36}(OH)_{1.28}$ [51839-25-9]                      |         |  | Value quoted in Sillen and Martel, 1964-71 <sup>8</sup> .   |
| $Zn_5(OH)_6(CO_3)_2$<br>or<br>Hydrozincite<br>[12122-17-7]     | 298.15  | $K_{s0} = 2.0 \times 10^{-15}$<br>$I = 0.2 \text{ mol L}^{-1}$   | Sahli's value as given by Schindler, Reinert and Gamsjager, 1969 <sup>260</sup> .   |
|  | 298.15  | log K =<br>-9.417 0.040 (I = 0.2)<br>-9.199 0.050 (I = 0)<br>-5.743 (I = 0.2)<br>-6.433 (I = 0)<br>-14.011 (I = 0.2) 0.2<br>-14.859 (I = 0)              | $0.2Zn_5(OH)_6(CO_3)_2(s) + 2H^+ = Zn^{2+} + 0.4CO_2(g) + 1.6H_2O$<br>$0.2Zn_5(OH)_6(CO_3)_2(s) + 1.6CO_2(g) + 0.4H_2O = Zn^{2+} + 2HCO_3^-$<br>$Zn_5(OH)_6(CO_3)_2(s) = Zn^{2+}(aq) + 1.2OH^-(aq) + 0.4CO_3(aq)$<br>Schindler, Reinert and Gamsjager, 1969 <sup>260</sup> .  |
|  | 298 (?) |  | A study of the solubility of zinc at low concentration in basic solutions of $0.002 \text{ mol L}^{-1}$ 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 concentration was about $5 \times 10^{-7} \text{ mol L}^{-1}$ at pH 9.26 after 24 hours. Paulson, Benjamin and Ferguson, 1989 <sup>394</sup> .  |
| Cadmium stearate<br>$Cd[CH_3(CH_2)_{16}CO_2]_2$<br>[2223-93-0] | 310.15  | $6.4 \times 10^{-4} \text{ mol L}^{-1}$<br>(gastric juice,<br>pH = 1.47)<br>$1.93 \times 10^{-5} \text{ mol L}^{-1}$<br>(intestinal juice,<br>pH = 8.20) | Cd determined in the supernatant liquid by atomic absorption. Data for several Cd pigments also given. Wada, Iijima, Ono, Toyokawa, 1972 <sup>121</sup> .   |
| Zinc malonate<br>$ZnCH_2C_2O_4 \cdot 3H_2O$<br>[94649-52-2]    | 298.15  | $35.1540 \text{ g L}^{-1}$<br>$0.210 \text{ mol L}^{-1}$   | 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 <sup>361</sup> .   |
| Zinc succinate<br>$Zn(CH_2)_2C_2O_4$                           | 298.15  | $1.9954 \text{ g L}^{-1}$<br>$0.0110 \text{ mol L}^{-1}$<br>[6228-53-1]  |   |
| Zinc glutarate<br>$Zn(CH_2)_3C_2O_4$<br>[6426-46-6]            | 298.15  | $16.1230 \text{ g L}^{-1}$<br>$0.0825 \text{ mol L}^{-1}$  |   |
| Zinc adipinate<br>$Zn(CH_2)_4C_2O_4$ [3446-35-6]               | 298.15  | $0.7601 \text{ g L}^{-1}$<br>$0.00363 \text{ mol L}^{-1}$  |   |
| Zinc pimelinate<br>$Zn(CH_2)_5C_2O_4$ [61810-62-6]             | 298.15  | $0.8804 \text{ g L}^{-1}$<br>$0.00394 \text{ mol L}^{-1}$  |   |
| Zinc suberate<br>$Zn(CH_2)_6C_2O_4$ [85561-38-2]               | 298.15  | $0.5343 \text{ g L}^{-1}$<br>$0.00225 \text{ mol L}^{-1}$  |   |
| Zinc cyanamide<br>$ZnCN_2$ [20654-08-4]                        | 298.15  | $pK_{s0} = 14.1$   | Solubility of cyanamides determined in $1 \text{ mol L}^{-1} KNO_3$ 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 $CN_2^-$ 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, Yatlava, 1971 <sup>362</sup> . |
| Cadmium cyanamide<br>$CdCN_2$ [20654-10-8]                     | 298.15  | $pK_{s0} = 14.1$   |   |
| Zinc xanthate<br>$Zn(C_3H_5OS_2)_2$ [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 <i>et al.</i> , 1957 <sup>363</sup> .  |

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<br>$Zn(C_5H_8NS_2)_2$ [53632-23-8]                           | 298              | $pK_{s0} = 15.9 \pm 0.2$<br>$3.15 \times 10^{-6} \text{ mol L}^{-1}$  | 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 <sup>364</sup> .  |
| Cadmium pyrrolidine dithiocarbamate<br>$Cd(C_5H_8NS_2)_2$                                     | 298              | $pK_{s0} = 18.9 \pm 0.5$<br>$3.2 \times 10^{-7} \text{ mol L}^{-1}$   |  |
| Zinc diethyldithiocarbamate<br>$Zn(C_5H_{10}NS_2)_2$  | ?                | $K_{s0} = 3.05 \times 10^{-17}$   | Value quoted in Chem. Abstr.; Stepanyuk, 1958 <sup>365</sup> .   |
| Cadmium diethyldithiophosphate  | 291.15<br>293.15 | $2.4 \times 10^{-4} \text{ mol L}^{-1}$<br>$K_{s0} = 5.8 \times 10^{-11}$   | Soly by gravimetric method. Solubility product appears to be calculated from $4s^2$ . Busev, Ivanyutin, 1958 <sup>366</sup>  |
| $Cd[(C_2H_5O)_2PS_2]_2$   | 293.15           | $3.14 \times 10^{-4} \text{ mol L}^{-1}$<br>$K_{s0}^0 = 6.40 \times 10^{-11}$   | 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 <sup>367</sup> .   |
| Zinc sulfanilamides<br>Zinc sulfapyridazine<br>$Zn(C_{11}H_{11}N_4O_3S_2)_2$ ZnR <sub>2</sub> | 298.15           | $K_{s0} = 6.79 \times 10^{-11}$   | 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 <sup>-1</sup> metal acetate, 0.1 mol L <sup>-1</sup> sodium sulfanilamide and $2.5 \times 10^{-2}$ to $2.5 \times 10^{-5}$ mol L <sup>-1</sup> in HCl. |
| Zinc sulfadimenine<br>$Zn(C_{12}H_{13}N_4O_2S_2)_2$ ZnS <sub>2</sub>                          |                  | $K_{s0} = 3.50 \times 10^{-10}$   | 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 <sup>368</sup> .   |
| Zinc sulfadimethoxin<br>$Zn(C_{12}H_{13}N_4O_4S_2)_2$ ZnF <sub>2</sub>                        |                  | $K_{s0} = 4.08 \times 10^{-9}$  |  |
| Zinc norsulfazol<br>$Zn(C_9H_8N_3O_2S_2)_2$ ZnL <sub>2</sub>                                  |                  | $K_{s0} = 7.18 \times 10^{-7}$  |  |
| Cadmium sulfanilamides  | 298.15           |   |  |
| Cadmium sulfapyridazine<br>$Cd(C_{11}H_{11}N_4O_3S_2)_2$ CdR <sub>2</sub>                     |                  | $K_{s0} = 2.49 \times 10^{-11}$   |  |
| Cadmium sulfadimezine<br>$Cd(C_{12}H_{13}N_4O_2S_2)_2$ CdS <sub>2</sub>                       |                  | $K_{s0} = 2.28 \times 10^{-10}$   |  |
| Cadmium sulfadimethoxin<br>$Cd(C_{12}H_{13}N_4O_4S_2)_2$ CdF <sub>2</sub>                     |                  | $K_{s0} = 2.45 \times 10^{-9}$  |  |
| Cadmium norsulfazol<br>$Cd(C_9H_8N_3O_2S_2)_2$ CdL <sub>2</sub>                               |                  | $K_{s0} = 3.28 \times 10^{-7}$  |  |
| Zinc silicate<br>$ZnSiO_3$ [16871-71-9]   | ?                | $K_{s0}^0 = (1-3) \times 10^{-16}$<br>in 0.24 to 1.07<br>M NH <sub>3</sub><br><br>$K_{s0}^0 = 1 \times 10^{-16}$<br>in 0.41 M NH <sub>3</sub> | 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 $Zn(NH_3)_2^{2+}$ , $ZnOH^+$ , and $H_2SiO_3$ . Alekseeva, Dushina, Aleskovskii, 1968 <sup>369</sup> , 1972 <sup>370</sup> .   |
| Cadmium silicate<br>$CdSiO_3$ [12672-37-6]<br>$CdSiO_3 \cdot nH_2O$                           | ?                | $K_{s0} = (5.7 \text{ } 1.7) \times 10^{-15}$   | Study similar to $ZnSiO_3$ study described above. The data treatment required dissociation constants of $Cd(NH_3)_2^{2+}$ , $CdOH^+$ , $CdCl^+$ , 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. Alekseeva, Dushina, Aleskovskii, 1974 <sup>371</sup> .   |
| Zinc germanate<br>$Zn_2GeO_4$ [12025-29-5]  | 298.15           | 0.0153 mol ZnO<br>0.00234 mol GeO <sub>2</sub>  | 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 <sub>2</sub> solution ratio taken as evidence of decomposition on dissolution. Values given are for water and solid $Zn_2GeO_4$ . Additional data in paper. Zangieva, <i>et al.</i> , 1983 <sup>372</sup> .  |

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<br>Zn(BO <sub>2</sub> ) <sub>2</sub> [22588-98-3]                              | 295    | $K_{s0}^{\circ} = (6.5 \pm 3.5) \times 10^{-11}$                       | Crystalline Zn(BO <sub>2</sub> ) <sub>2</sub> · H <sub>2</sub> O and Cd(BO <sub>2</sub> ) <sub>2</sub> · 7H <sub>2</sub> O were prepared. Their solubilities were measured in water (initially 0.05 to 0.015 mol L <sup>-1</sup> HCl) and in 3% aqueous H <sub>3</sub> BO <sub>3</sub> . The solubility product was calculated from the water solutions after determination of M <sup>2+</sup> , H <sup>+</sup> and HBO <sub>2</sub> concentrations. The K <sub>a</sub> of the acid was taken as 7.5 × 10 <sup>-10</sup> and activity coefficients were calculated from extended Debye-Huckel theory to obtain the K <sub>s0</sub> <sup>o</sup> values. The solubilities in aqueous H <sub>3</sub> BO <sub>3</sub> were used to obtain instability constants for the complex ions Zn(BO <sub>2</sub> ) <sub>4</sub> <sup>2-</sup> , K = 1.6 × 10 <sup>-12</sup> ; and Cd(BO <sub>2</sub> ) <sub>4</sub> <sup>2-</sup> , K = 2.3 × 10 <sup>-11</sup> . Shchigol, 1959 <sup>373</sup> . |
|  | 298.15 | $K_{s0}^{\circ} = 6.47 \times 10^{-11}$<br>NBS table data              |   |
| Cadmium borate<br>Cd(BO <sub>2</sub> ) <sub>2</sub> [74153-66-5]                           | 295    | $K_{s0}^{\circ} = (2.3 \pm 1.1) \times 10^{-9}$                        | Determined using a photometric method. Swinarski, Lodzinska, 1958 <sup>374</sup> .  |
|  | 298.15 | $K_{s0}^{\circ} = 2.29 \times 10^{-9}$<br>NBS table data               |   |
| Zinc mercury (II) selenocyanate<br>Zn[Hg(SeCN) <sub>4</sub> ]                              | 291.15 | 1.126 × 10 <sup>-4</sup> mol L <sup>-1</sup>                           |   |
| Cadmium mercury (II) selenocyanate<br>Cd[Hg(SeCN) <sub>4</sub> ]                           | 291.15 | 5.395 × 10 <sup>-3</sup> mol L <sup>-1</sup>                           |   |
| Zinc cobalticyanide<br>Zn <sub>3</sub> [Co(CN) <sub>6</sub> ] <sub>2</sub> [14049-79-7]    | 293.15 | 3.645 × 10 <sup>-4</sup> mol L <sup>-1</sup><br>pK <sub>s</sub> = 9.71 | Conductivity method. Solubility reaction assumed to be M <sub>3</sub> [Co(CN) <sub>6</sub> ] <sub>2</sub> (s) = M <sup>2+</sup> (aq) + 2M[Co(CN) <sub>6</sub> ] <sup>-</sup> (aq).  |
| Cadmium cobalticyanide<br>Cd <sub>3</sub> [Co(CN) <sub>6</sub> ] <sub>2</sub> [25359-19-7] | 293.15 | 6.91 × 10 <sup>-5</sup> mol L <sup>-1</sup><br>pK <sub>s</sub> = 11.88 | Limiting eq. cond. of M[Co(CN) <sub>6</sub> ] <sup>-</sup> ion approximated. M = Zn, Cd. De Robertis, Bellomo, De Marco, 1982 <sup>375</sup> .  |
| Zinc chromate<br>ZnCrO <sub>4</sub> [13530-65-9]   |        | 10 <sup>3</sup> g/mol L <sup>-1</sup> 10 <sup>5</sup> K <sub>s0</sub>  | Solubility determined by a spectrophotometric method in aqueous NaNO <sub>3</sub> of ionic strength I = 0.025 – 1.00. Solubilities were extrapolated to total I = 0 and to NaNO <sub>3</sub> ionic strength, I = 0, at which the I would be four times the solubility. Coetzee, 1979 <sup>376</sup> .   |
|  | 293.15 | I = 0 I = 4S<br>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) × 10 <sup>-3</sup> mol L <sup>-1</sup>                     |   |
| Cadmium chromate<br>CdCrO <sub>4</sub> [14312-00-6]  | 298.15 | $K_{s0} = 7.6 \times 10^{-5}$<br>I/NaNO <sub>3</sub> = 0.1             | 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 <sup>377</sup> .   |
| Zinc chromate hydroxide<br>Zn(CrO <sub>4</sub> ) <sub>0.2</sub> (OH) <sub>1.6</sub>        | 293    | $K_{s0} = 5 \times 10^{-17}$   | Cadmium ion selective electrode method. He, Wang, 1983 <sup>378</sup> . Six values given between 283 and 308K which do not show constant temperature coefficient. Solid identified as CdCrO <sub>4</sub> ·2H <sub>2</sub> O. Three crystalline forms of varying hydration were prepared. Formula solubility product was found by titration curve and activity coefficients by Debye-Huckel theory. Feitknecht, Hugi-Carnes, 1954 <sup>379</sup> . Values were obtained by colorimetric and gravimetric analysis. Zelikman, Prosenkova, 1961 <sup>380</sup> .  |
| Zinc molybdate<br>ZnMoO <sub>4</sub> [13767-32-3]  | 293    | 6.93 × 10 <sup>-3</sup> mol L <sup>-1</sup>                            |   |
|  | 373    | 8.61 × 10 <sup>-3</sup> mol L <sup>-1</sup>                            |   |
| Cadmium molybdate<br>CdMoO <sub>4</sub>  | 298.15 | $K_{s0} = 2.2 \times 10^{-9}$<br>I/NaNO <sub>3</sub> = 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 <sup>378</sup> .  |
|  | ?      | $K_{s0} = 6.05 \times 10^{-8}$   | Titration study. Details of obtaining K <sub>s0</sub> not given. Rao, 1954 <sup>381</sup> .   |
| Cadmium tungstate<br>CdWO <sub>4</sub> [7790-85-4]   | 298.15 | $K_{s0} = 2.3 \times 10^{-10}$<br>I/NaNO <sub>3</sub> = 0.1            | Cadmium ion selective electrode method. Six values given between 283 and 308K which do not show constant temperature coefficient. Solid identified as CdWO <sub>4</sub> ·H <sub>2</sub> O. He, Wang, 1983 <sup>378</sup> .  |

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 <sup>382</sup> . Graph & Table.   |
|                        | 573–673 | Solubility in aq  | Gravimetric methods used. Up to 14–15 % LiCl, solid is LiCl solution. CdWO <sub>4</sub> ; at higher percent LiCl, the solid is Li <sub>2</sub> WO <sub>4</sub> . Graph and Table. Dem'yanets, 1968 <sup>383</sup> .  |
| Zinc in fertilizers    | ?       | <i>microg Zn/g fertilizer</i><br>total extracted by H <sub>2</sub> O                        | 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 <sup>-1</sup> CaCl <sub>2</sub> , and 0.1 mol L <sup>-1</sup> HCl. Only the results for water are given here. The Zn and Cd were determined by atomic absorption. Easterwood, Street, 1982 <sup>384</sup> . |
| 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 | ?       | <i>microg Cd/g fertilizer</i><br>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.<br>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 <sup>385</sup> .   |
| Cadmium in soils       |         | The solubility of Cd from soils of various total Cd content as a function of pH.<br>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 <sup>397</sup> .  |

## 6. Appendix

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

| T/K    | I/Electrolyte<br>or<br>Mass % / Nonelectrolyte   | Reference  |
|--------|--|--|
|        | 298.15   |  |
| 308.15 | 3/(Cd <sup>2+</sup> , Na <sup>+</sup> ) ClO <sub>4</sub> <sup>-</sup> )<br>3/Na <sup>+</sup> (Br, ClO <sub>4</sub> <sup>-</sup> ) <sup>k</sup> | Ramette, 1983 <sup>61</sup><br>Ramette, 1983 <sup>61</sup> |
| 323.15 | (8-78) /HIO <sub>3</sub>   | Lepeshkov <i>et al</i> ; 1979 <sup>54</sup>                |
| 298.15 | (0-45) Tetrahydrofuran   | Miyamoto, 1972 <sup>51</sup>                               |

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

| T/K            | Ionic strength<br>I/Electrolyte<br>or pH                 | Solubility<br><i>c</i> <sub>ZnS</sub> /mol L <sup>-1</sup>   | Method                               | Reference                                |
|----------------|--|--|--------------------------------------|--|
| 298.15         | pH = 3<br>pH = 5<br>pH = 9<br>pH = 11                    | 8.3 × 10 <sup>-6</sup><br>8.3 × 10 <sup>-8</sup><br>8.6 × 10 <sup>-11</sup><br>8.6 × 10 <sup>-12</sup> | Model calculation                    | Kapustinskii,<br>1940 <sup>85,a</sup>    |
| 298.15         | pH = 3<br>pH = 11  | 10.7 × 10 <sup>-6</sup><br>10.9 × 10 <sup>-12</sup>  | Model calculation                    | Czamanske,<br>1959 <sup>86,b</sup>       |
| 298.15-<br>473 | pH = 3<br>pH = 3   | 2 × 10 <sup>-6</sup> -<br>3X10 <sup>-4</sup>   | (?)                                  | Rafal'skii,<br>1966 <sup>88,c</sup>      |
| 298.15         | ?/H <sub>2</sub> S, 6.8atm                               | <1 × 10 <sup>-5</sup>  | polarography                         | Barnes, 1958 <sup>95</sup>               |
| 298.15         | 3/H <sub>2</sub> S, pH = 7.6<br>6/H <sub>2</sub> S, 1-3m | 9.34 × 10 <sup>-3</sup><br>2.80 × 10 <sup>-3</sup><br>NaCl   | Solubility<br>"                      | Barnes, Romberger,<br>1962 <sup>96</sup> |
| 298.15-<br>368 | ?/H <sub>2</sub> S, NaCl                                 | Table  | Atomic absorption                    | Barrett, Anderson,<br>1982 <sup>97</sup> |
| 298.15-<br>573 | ?/H <sub>2</sub> S, NaCl                                 | Table<br>1-3m  | Model calculation                    | Barrett, Anderson,<br>1982 <sup>97</sup> |
| 298.15-<br>648 | 0-2.0/NaCl   | Graph  | Colorimetry and<br>atomic absorption | Hennig, 1971 <sup>83</sup>               |
| 298.15         | 10.3/? , pH=8.2,   | (2.78 ± 0.04) × 10 <sup>-2</sup>   | Polarography                         | Barnes, 1960 <sup>98,99</sup>            |
| 323.15         | ?/H <sub>2</sub> S, satd at<br>35 atm                    | (1.1 ± 0.2) × 10 <sup>-4</sup><br>35 atm   | Polarography                         | Barnes, 1959 <sup>100</sup>              |
| 323.15         | ?/H <sub>2</sub> S satd<br>(at 1 atm ?)                  | 3.82 × 10 <sup>-5</sup>  | Colorimetry                          | Vukotic, 1961 <sup>63</sup>              |
| 348            | ?/H <sub>2</sub> S, satd at<br>20.4 atm                  | >1 × 10 <sup>-4</sup><br>20.4 atm  | Polarography                         | Barnes, 1958 <sup>95</sup>               |
| 353            | ?/H <sub>2</sub> S, satd at                              | 5 × 10 <sup>-5</sup>   | ?<br>1 atm                           | Hinners,<br>1964 <sup>101,d</sup>        |

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

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

<sup>a</sup>Calculated using their own thermodynamic data and H<sub>2</sub>S acid dissociation constants from Lewis and Randall<sup>91</sup>, and Wright and Maas<sup>92</sup>.

<sup>b</sup>Calculated using data from Latimer<sup>89</sup>, Kubaschewski and Evans<sup>93</sup> and Kury, Zielen and Latimer<sup>94</sup>.

<sup>c</sup>It is not clear to the reader whether this is calculated or experimental data. The data from 473 K may be from another paper.

<sup>d</sup>Unpublished dissertation cited by Barnes and Czaminske, 1967<sup>82</sup>

<sup>e</sup>The paper was not available to us; information is from abstract, Chem. Abstr. 68, 116355c.



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

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

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 auxiliary thermodynamic data.

<sup>a</sup>Solubility calculated for (hexagonal ?) CdS precipitated from CdCl<sub>2</sub> from value of Bruner and Zawadski, 1909<sup>116</sup>, 1910<sup>117</sup> assuming water saturated with atmospheric CO<sub>2</sub> ( $1.35 \times 10^{-5}$  mol L<sup>-1</sup>) at pH 5.8.

<sup>b</sup>Same as <sup>a</sup> above except for (cubic ?) CdS precipitated from CdSO<sub>4</sub> solution.

<sup>c</sup>See footnote<sup>d</sup> of Table 19.

<sup>d</sup>See footnote<sup>e</sup> of Table 19. <sup>e</sup>Corrected for Cd-Cl complex ion.

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

| T/K     | Ionic strength<br>I/Electrolyte                                    | Carbon<br>dioxide <sup>a</sup><br>p/bar | References  |
|---------|--|---|---|
| 287     | 0.7,0.8/Na <sub>2</sub> SO <sub>4</sub>                            | 2                                       | Ehlert, Hempel, 1912 <sup>256</sup>                 |
| 287     | 0.9,1.9,6/NaCl   | 2                                       | " " "   |
| 287     | 1.3,11/NaNO <sub>2</sub>   | 2                                       | " " "   |
| 287-353 | 1.0/NH <sub>4</sub> Cl   |   | Cantoni, Passamanik, 1905 <sup>257</sup>            |
| 287-353 | 1.0/NaCl   |   | " " "   |
| 287-353 | 1.0/KCl  |   | " " "   |
| 288     | 0.05/NH <sub>4</sub> Cl  |   | Ehlert, Hempel, 1912 <sup>256</sup>                 |
| 288     | 0.05/NaCl  |   | " " "   |
| 288     | 0.05/KCl   |   | " " "   |
| 291     | 0.57/NaNO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub>           |   | " " "   |
| 293     | 1.0/NH <sub>4</sub> Cl   |   | " " "   |
| 293     | ?/KHCO <sub>3</sub> (graph only)                                   |   | Taketatsu, 1963 <sup>258</sup>                      |
| 298     | 0.075/K <sub>2</sub> CO <sub>3</sub>                               |   | Immerwhar, 1901 <sup>202</sup>                      |
| 298     | (a <sub>Ca</sub> = a <sub>CO<sub>3</sub><sup>2-</sup></sub> = 0.1) | 0.01                                    | Mann, Deutscher, 1980 <sup>252,b</sup>              |
| 298     | 1.4-13.1/CaCl <sub>2</sub>   |   | Ben'yash, 1964 <sup>259,c</sup>                     |
| 298     | 0.2/NaClO <sub>4</sub>   | 0.18-0.90                               | Schindler, Reinert, Gamsjaeger, 1969 <sup>260</sup> |

<sup>a</sup>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.

<sup>b</sup>Calculated on the basis of a geological model.

<sup>c</sup>Solubility in mol kg<sup>-1</sup>, equilibrium solid is a CaCO<sub>3</sub>/ZnCO<sub>3</sub> mixture.

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

| T/K    | I/Electrolyte   | Reference   |
|--------|---|---|
| 291.15 | (0.03-0.74)/Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>(0.15-5.63)/H <sub>2</sub> SO <sub>4</sub>   | Britton and Jarrett, 1936 <sup>279</sup><br>" " " "   |
| 298.15 | (0.50-8.0) × 10 <sup>-3</sup> /H <sub>2</sub> SO <sub>4</sub><br>(0.21-1.10)/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>(0.01-0.11)/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>(0.005-0.08)/ZnSO <sub>4</sub><br>(0.45-17.3)/Na <sup>+</sup> (S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> )<br>(0.1-9.0)NH <sub>3</sub> , NaNO <sub>3</sub><br>(0.1-2)/KCN<br>(0.05-0.25)/(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub><br>KU-1, KU-2 ion exchangers | Deyrieux and Peneloux, 1970 <sup>268</sup><br>Metler and Vosburgh, 1933 <sup>280</sup><br>Clayton, Vosburgh, 1937 <sup>273</sup><br>" " "<br>Lodzinska <i>et al.</i> , 1965 <sup>278</sup><br>Gornicki, Jablonski, 1957 <sup>281</sup><br>" " 1978 <sup>282</sup><br>Kunschert, 1904 <sup>270</sup><br>Smyshlyaev <i>et al.</i> , 1968 <sup>283</sup> |
| 308.15 | (0.13-2.28)/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>(0.01-0.20)/NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub><br>(0.01-0.20)/KNO <sub>3</sub>  | Metler, 1934 <sup>284</sup><br>Bardhan and Aditya, 1955 <sup>285</sup><br>" " " "   |

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

| T/K    | I/Electrolyte   | Reference  |
|--------|---|--|
| ?      | (0.1-1.0)/KNO <sub>3</sub>  | Babkin, 1956 <sup>288</sup>  |
| ?      | ?/Cd(NO <sub>3</sub> ) <sub>2</sub>   | Babkin, <i>et al.</i> , 1955 <sup>287</sup>  |
| ?      | ?/(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>   | " " "  |
| ?      | /KCl  | " " "  |
| 293.15 | 2.1/NaX (X = Br <sup>-</sup> , I <sup>-</sup> , NCS <sup>-</sup> )<br>/C <sub>2</sub> H <sub>5</sub> OH, C <sub>3</sub> H <sub>7</sub> OH   | Czakis-Sulikowska and Kuznik, 1972 <sup>306</sup><br>Lebedeva <i>et al.</i> , 1978 <sup>307</sup>  |
| 298.15 | /HCl + Ethylenediamine<br>/HCl + K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + Ethylenediamine<br>(0.005-0.08)/CdSO <sub>4</sub><br>(0.005-0.04)/CdSO <sub>4</sub><br>(0.23-2.3)/MgSO <sub>4</sub><br>(0.19-3.1)/NaCl<br>(0.24-2.1)/Na <sub>2</sub> SO <sub>4</sub><br>(0.03-0.46)/NaNO <sub>3</sub><br>(0.3-11)/Na <sup>+</sup> (S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> )<br>(0.25-3.5)/KCl<br>(0.007-0.08)/KClO <sub>4</sub><br>(0.005-0.04)/K <sub>2</sub> SO <sub>4</sub><br>(0.03-0.19)/K <sub>2</sub> SO <sub>4</sub><br>(0.07-1.8)/KNO <sub>3</sub><br>(0.2-2.0)/KNO <sub>3</sub><br>1/KNO <sub>3</sub> (graph)<br>KNO <sub>3</sub> + Ethylenediamine(graph)<br>(0.006-0.09)/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub><br>(0-0.24)/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (graph)<br>/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + CdC <sub>2</sub> O <sub>4</sub><br>(phase diagram)<br>/K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + KNO <sub>3</sub> +<br>ethylenediamine | Fridman <i>et al.</i> , 1963 <sup>295</sup><br>" " "<br>Clayton and Vosburgh, 1937 <sup>273</sup><br>Vosburgh and Beckman, 1940 <sup>0274</sup><br>Pesce and Lago, 1944 <sup>291</sup><br>Accascina and Schiavo, 1953 <sup>293</sup><br>Pesce and Lago, 1944 <sup>291</sup><br>Accascina and Schiavo, 1953 <sup>293</sup><br>Lodzinska <i>et al.</i> , 1965 <sup>278</sup><br>Accascina and Schiavo, 1953 <sup>293</sup><br>Vosburgh and Beckman, 1940 <sup>274</sup><br>" " "<br>Accascina and Schiavo, 1953 <sup>293</sup><br>" " "<br>Cavigli, 1949 <sup>308</sup><br>Olin, Wikmark, 1983 <sup>290</sup><br>Fridman <i>et al.</i> , 1963 <sup>295</sup><br>Clayton and Vosburgh, 1937 <sup>273</sup><br>Barney <i>et al.</i> , 1951 <sup>292</sup><br><br>Vosburgh <i>et al.</i> , 1936 <sup>296</sup><br><br>Fridman <i>et al.</i> , 1963 <sup>295</sup> |
| 303.15 | 0.1/KNO <sub>3</sub>  | Gupta and Chatterjee, 1967 <sup>309</sup>  |
| 313.15 | 0.1/KNO <sub>3</sub><br>/C <sub>2</sub> H <sub>5</sub> OH, C <sub>3</sub> H <sub>7</sub> OH   | " " "<br>Lebedeva <i>et al.</i> , 1978 <sup>307</sup>  |
| 323.15 | 0.1/KNO <sub>3</sub>  | Gupta and Chatterjee, 1967 <sup>309</sup>  |
| 333.15 | (0.01-0.15)/NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub><br>(0.01-0.15)/KNO <sub>3</sub>  | Bardhan and Aditya, 1955 <sup>294</sup><br>" " " "   |

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## Nomenclature

|                          |  |
|--------------------------|--|
| $A$                      | Debye-Huckel constant  |
| $A_1, A_2, A_3$          | Parameters of regression equation for solubility and solubility product  |
| $B$                      | Debye-Huckel constant  |
| $C_p^\circ$              | Standard heat capacity at constant pressure  |
| $F$                      | Faraday constant, 96,485.309 C mol <sup>-1</sup>   |
| $G^\circ$                | Standard Gibbs energy  |
| $H^\circ$                | Standard enthalpy  |
| $I$                      | Ionic strength, $(1/2)\sum c_i z_i^2$ (molar scale)  |
| $K_H$                    | Equilibrium constant, Henry's constant   |
| $K_n$                    | Equilibrium constant, ligand metal formation constant ( $ML_{n-1} + L = ML_n$ )  |
| $K_{s0}, K_{s0}^\circ$   | 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   |
| $K_{snm}, K_{snm}^\circ$ | Equilibrium constant, solubility product constant when a complex $M_n L_n$ 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   |
| $S^\circ$                | 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  |
| $p, p_D$                 | Pressure, total pressure, partial pressure of substance B  |
| $x_B$                    | Mole fraction of substance B; $n_B/\sum n_i$   |
| $\gamma, \gamma_{\pm}$   | Activity coefficient, mean ionic activity coefficient, concentration (molar) scale   |
| $x$                      | Ion charge   |
| $\beta_n$                | Equilibrium constant, cumulative ligand metal formation constant ( $M + nL = ML_n$ )   |
|                          | $\beta_n = \prod_{i=1}^n K_i$ (see $K_n$ above)  |
| $\rho$                   | Density  |
| $\gamma, \gamma_{\pm}$   | Activity coefficient, mean ionic activity coefficient, molal scale   |

## 1. Introduction

Heavy metal salts contribute to environmental 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<sup>1</sup>, and metallic mercury and mercury salts<sup>2</sup>. 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<sup>3</sup> outline the problem for the FeS + NaCl + H<sub>2</sub>O 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<sup>-1</sup> 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)<sup>4</sup>, and sulfites, selenites, and tellurites (Vol. 26)<sup>5</sup> 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<sup>6</sup>, Stephen and Stephen<sup>7</sup>, Sillen and Martell<sup>8</sup>, Kir-

gintsev, Trushnikova and Lavent'eva<sup>9</sup> and Comey and Hahn<sup>10</sup>.

The Crystal Data Determinative Tables<sup>11</sup> 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<sup>12</sup>, the Geological Survey Bulletin on Thermodynamic Properties of Minerals<sup>13</sup>, the CODATA Key Values<sup>390</sup>, and the IUPAC sponsored Standard Potentials in Aqueous Solution<sup>14</sup> 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 Prokofev<sup>388</sup> 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<sup>15a,b</sup> 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<sup>14a,b</sup> 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<sup>12</sup>, but there are a few important differences.

**Zinc.** Brodd and Werth<sup>14a</sup> 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  $E^\circ$  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), respectively, differ even more from the NBS Table values. However, the recent CODATA<sup>390</sup> 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  $E^\circ$  of  $-0.7628$  volts at one atm pressure. The Gibbs energy and  $E^\circ$  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  $(dE^\circ/dT)$  values calculated by the method of de Bethune and co-

workers<sup>16,17</sup>, using data from Brodd and Werth's Table for the Zn species and from the NBS Tables<sup>12</sup> for other species. The use of the Brodd and Werth  $\Delta S^\circ$  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<sup>14b</sup>. We have confirmed the  $(dE^\circ/dT)$  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<sup>2</sup>. 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<sup>18</sup> 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  $(111 \pm 2)$  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 electrolyte solutions. Each sparingly soluble substance is identified by its formula, Chemical Abstracts Registry Number (when located) and formula weight. The 1985 atomic weights<sup>19</sup> were used. These are  $65.39 \pm 0.02$  for zinc and  $112.411 \pm 0.008$  for cadmium, based on terrestrial isotopic composition.

The physical characteristics of each sparingly soluble salt are briefly described when crystallographic information is available. The primary source is the Crystal Data Determinative Tables<sup>11</sup>. 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<sup>12</sup>. The zinc and cadmium substances are discussed by anion.

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

| Reaction  | $E^\circ/V$ | $(\partial E^\circ/\partial T)_p / \text{mV K}^{-1}$ |
|---|-------------|--|
| <b>Zinc</b>   |             |  |
| $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s})$   | -0.7626     | +0.096   |
| $\text{Zn}(\text{OH})_2(\text{s}) + 2\text{e}^- = \text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq})$  | -1.246      | -0.996   |
| $\text{Zn}(\text{OH})_4^{2-}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s}) + 4\text{OH}^-(\text{aq})$  | -1.285      | -  |
| $\text{ZnO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- = \text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq})$   | -1.248      | -1.162   |
| $\text{Zn}(\text{NH}_3)_4^{2+}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s}) + 4\text{NH}_3(\text{aq})$  | -1.04       | 0.286  |
| $\text{Zn}(\text{CN})_4^{2-}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s}) + 4\text{CN}^-(\text{aq})$  | -1.34       | 0.318  |
| $\text{ZnCO}_3(\text{s}) + 2\text{e}^- = \text{Zn}(\text{s}) + \text{CO}_3^{2-}(\text{aq})$   | -1.06       | -1.184   |
| $\text{ZnS}(\text{s})$ (wurzite) $+ 2\text{e}^- = \text{Zn}(\text{s}) + \text{S}^{2-}(\text{aq})$   | -1.44       | -0.836   |
| $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s}) + 2\text{C}_2\text{O}_4^{2-}(\text{aq})$                     | -0.99       | -  |
| $\text{Zn}(\text{C}_4\text{O}_6\text{H}_4)_4^{2-}(\text{aq}) + 2\text{e}^- = \text{Zn}(\text{s}) + 4\text{C}_4\text{O}_6\text{H}_4^{2-}(\text{aq})$ | -1.15       | -  |
| <b>Cadmium</b>  |             |  |
| $\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- = \text{Cd}(\text{s})$   | -0.4025     | -0.030   |
| $\text{Cd}^{2+} + \text{Hg} + 2\text{e}^- = \text{Cd}(\text{Hg})$   | -0.3515     | -0.229   |
| $\text{Cd}(\text{OH})_2(\text{aq}) + 2\text{e}^- = \text{Cd}(\text{s}) + 2\text{OH}^-$  | -0.824      | -1.018   |
| $\text{Cd}(\text{OH})_4^{2-} + 2\text{e}^- = \text{Cd}(\text{s}) + 4\text{OH}^-(\text{aq})$   | -0.670      | -  |
| $\text{CdO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- = \text{Cd}(\text{s}) + 2\text{OH}^-$  | -0.783      | -1.167   |
| $\text{Cd}(\text{NH}_3)_4^{2+}(\text{aq}) + 2\text{e}^- = \text{Cd}(\text{s}) + 4\text{NH}_3(\text{aq})$  | -0.622      | 0.155  |
| $\text{Cd}(\text{CN})_4^{2-}(\text{aq}) + 2\text{e}^- = \text{Cd}(\text{s}) + 4\text{CN}^-(\text{aq})$  | -0.943      | -0.127   |
| $\text{CdCO}_3(\text{s}) + 2\text{e}^- = \text{Cd}(\text{s}) + \text{CO}_3^{2-}(\text{aq})$   | -0.734      | -1.183   |
| $\text{CdS}(\text{s}) + 2\text{e}^- = \text{Cd}(\text{s}) + \text{S}^{2-}(\text{aq})$   | -0.255      | -0.821   |
| $\text{CdSe}(\text{s}) + 2\text{e}^- = \text{Cd}(\text{s}) + \text{Se}^{2-}(\text{aq})$   | -1.32       | -  |
| $\text{CdTe}(\text{s}) + 2\text{e}^- = \text{Cd}(\text{s}) + \text{Te}^{2-}(\text{aq})$   | -1.62       | -  |

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

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

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

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

Often the experimental solubility product constant,  $K_{\text{sp}}^\circ$ , is compared with the constant calculated from Gibbs energy values from the NBS Tables<sup>12</sup>. 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 ( $\text{ZnS}$ ) and 3A ( $\text{CdS}$ ) do contain solubility data values, but they are values based on older models no longer considered 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  $7.140 \times 10^3$   $\text{kg m}^{-3}$ ; and cadmium with  $Z = 2$ ,  $a = 2.9736 \times 10^{-10}$  m,  $c = 5.6058 \times 10^{-10}$  m, and a calculated density of  $8.642 \times 10^3$   $\text{kg m}^{-3}$ .

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,<br>R, Tentative, T | Table |
|--|--------|---|---------------------------------|-------|
| Zn(OH) <sub>2</sub>                                      | 298.15 | See equations and equilibrium constants in Sec. 4.2                           | T                               |       |
| Cd(OH) <sub>2</sub>                                      | 298.15 | See equations and equilibrium constants in Sec. 4.2                           | T                               |       |
| ZnF <sub>2</sub> ·4H <sub>2</sub> O                      | 298.15 | 0.1552 mol kg <sup>-1</sup>   | T                               | 3     |
| Zn(IO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O     | 298.15 | 0.01549 mol L <sup>-1</sup>   | T                               | 12    |
|  | 293.15 | $K_{s0}^{\circ} 3.5 \times 10^{-6} \text{ mol}^3 \text{ L}^{-3}$              | T                               | 13    |
|  | 298.15 | $(4.1 \pm 0.4) \times 10^{-6}$ "  | R                               | 13    |
|  | 303.15 | $5.2 \times 10^{-6}$ "  | T                               | "     |
|  | 308.15 | $6.2 \times 10^{-6}$ "  | T                               | "     |
|  | 313.15 | $7.4 \times 10^{-6}$ "  | T                               | "     |
|  | 318.15 | $8.8 \times 10^{-6}$ "  | T                               | "     |
| Cd(IO <sub>3</sub> ) <sub>2</sub>                        | 298.15 | $(1.97 \pm 0.13) \times 10^{-3} \text{ mol L}^{-1}$                           | T                               | 14    |
|  | 298.15 | $K_{s0}^{\circ} 2.5 \times 10^{-8} \text{ mol}^3 \text{ L}^{-3}$              | T                               | 15    |
| ZnS  |        |   |                                 |       |
| sphalerite   | 298.15 | $K_{s0}^{\circ} 1.3 \times 10^{-29} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 18    |
| wurtzite   | 298.15 | $K_{s0}^{\circ} 7.9 \times 10^{-27} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 18    |
| precipitated   | 298.15 | $K_{s0}^{\circ} 4.0 \times 10^{-26} \text{ mol}^2 \text{ L}^{-1}$             | T                               | 18    |
|  |        | See also equations, equilibrium constants and discussion in Sec. 4.5a.        |                                 |       |
| CdS  | 298.15 | $K_{s0}^{\circ} 5.0 \times 10^{-34} \text{ mol}^2 \text{ L}^{-1}$             | T                               | 20    |
| ZnSe   | 298.15 | $K_{s0}^{\circ} 3.6 \times 10^{-26} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 23    |
| ZnSeO <sub>3</sub> ·H <sub>2</sub> O                     | 298.15 | $K_{s0}^{\circ} 1.59 \times 10^{-7} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 24    |
| Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>         | 298.15 | $K_{s0}^{\circ} 2.8 \times 10^{-28} \text{ mol}^5 \text{ L}^{-5}$             | T                               | 39    |
| Cd <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>         | 298.15 | $K_{s0}^{\circ} 2.2 \times 10^{-33} \text{ mol}^5 \text{ L}^{-5}$             | T                               | 41    |
| ZnCO <sub>3</sub>  | 298.15 | $1.98 \times 10^{-3} \text{ mol L}^{-1}$<br>at P <sub>co2</sub> = 0.987 bar   | T                               | 42    |
|  | 298.15 | $1.64 \times 10^{-4} \text{ mol L}^{-1}$<br>at P <sub>co2</sub> = 0.00032 bar | T                               | 42    |
|  | 298.15 | $K_{s0}^{\circ} 1.46 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$            | T                               | 43    |
|  | 323.15 | $9.02 \times 10^{-11}$ " "  | "                               | "     |
|  | 373.15 | $1.59 \times 10^{-11}$ " "  | "                               | "     |
|  | 423.15 | $1.5 \times 10^{-12}$ " "   | "                               | "     |
|  | 473.15 | $1.0 \times 10^{-13}$ " "   | "                               | "     |
|  | 523.15 | $6.2 \times 10^{-15}$ " "   | "                               | "     |
|  | 573.15 | $3.5 \times 10^{-16}$ " "   | "                               | "     |
| CdCO <sub>3</sub>  | 298.15 | $K_{s0}^{\circ} 1.0 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 46    |
| a-ZnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O     | 283.15 | $0.64 \times 10^{-4} \text{ mol L}^{-1}$                                      | T                               | 47    |
|  | 288.15 | $0.89 \times 10^{-4}$ " "   | "                               | "     |
|  | 293.15 | $1.23 \times 10^{-4}$ " "   | "                               | "     |
|  | 298.15 | $1.67 \times 10^{-4}$ " "   | "                               | "     |
|  | 298.15 | $K_{s0}^{\circ} 1.38 \times 10^{-9} \text{ mol}^2 \text{ L}^{-2}$             | T                               | 48    |
| CdC <sub>2</sub> O <sub>4</sub> ·3H <sub>2</sub> O       | 298.15 | $(3.01 \pm 0.10) \times 10^{-4} \text{ mol L}^{-1}$                           | T                               | 49    |
|  | 298.15 | $K_{s0}^{\circ} 1.42 \times 10^{-8} \text{ mol}^2 \text{ L}^{-1}$             | T                               | 50    |
| Zn <sub>2</sub> [Fe(CN) <sub>6</sub> ]·2H <sub>2</sub> O | 298.15 | $(9.7 \pm 1.7) \times 10^{-6} \text{ mol L}^{-1}$                             | R                               | 58    |
|  | 298.15 | $K_{s0}^{\circ} 1.9 \times 10^{-16} \text{ mol}^3 \text{ L}^{-3}$             | R                               | 59    |
| Cd <sub>2</sub> [Fe(CN) <sub>6</sub> ]·7H <sub>2</sub> O | 298.15 | $(5.1 \pm 1.7) \times 10^{-6} \text{ mol L}^{-1}$                             | T                               | 60    |
|  | 298.15 | $K_{s0}^{\circ} 3.6 \times 10^{-18} \text{ mol}^3 \text{ L}^{-3}$             | T                               | 61    |

container material. Pariaud and Archinard<sup>20</sup> 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  $(700 \pm 50) \times 10^{-6} \text{ g L}^{-1}$  or  $(1.07 \pm 0.08) \times 10^{-5} \text{ mol L}^{-1}$ . The value is judged doubtful. It is of concern that the Zn solubility is nearly identical to the solubility of ZnO and  $\text{Zn(OH)}_2$ , 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

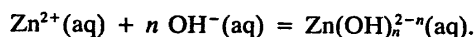
There are extensive data on the solubility of the oxides and hydroxides of zinc and cadmium. These data have been surveyed in detail in a recent Solubility Series volume edited by Dirkse<sup>4</sup>. Only a brief summary of Dirkse's evaluation is given here.

ZnO [1314-13-2] Molecular weight 81.38  
 $\text{Zn(OH)}_2$  [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  $Z = 2$ ,  $a = 3.24 \times 10^{-10} \text{ m}$ ,  $c = 5.176 \times 10^{-10} \text{ m}$ , and a density of  $5.70 \times 10^3 \text{ kg m}^{-3}$ . 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  $\text{Zn(OH)}_2$  and x-ray patterns of each are reported by Feitknecht<sup>21</sup>. The  $\epsilon$ -form is considered most stable. It is orthorhombic with  $Z = 4$ ,  $a = 5.170 \times 10^{-10} \text{ m}$ ,  $b = 8.547 \times 10^{-10} \text{ m}$ ,  $c = 4.93 \times 10^{-10} \text{ m}$ , and a density of  $3.03 \times 10^3 \text{ kg m}^{-3}$ . Other forms are described including a hexagonal form of density  $4.253 \times 10^3 \text{ kg m}^{-3}$ .

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

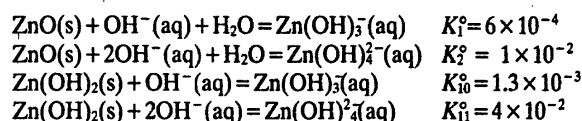
Gubeli and Ste-Marie<sup>22</sup> report cumulative formation constants ( $\text{mol L}^{-1}$ ) at unit ionic strength and 298.15 K for the zinc-hydroxide complex ions:



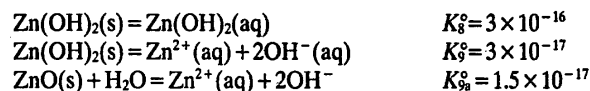
The values are  $2 \times 10^6$ ,  $1.5 \times 10^{11}$ ,  $2 \times 10^{14}$  and  $5 \times 10^{17}$  for  $n = 1, 2, 3$  and  $4$ , respectively.

Dirkse<sup>4</sup> gives the following as thermodynamic equilibrium constants for solid ZnO and  $\text{Zn(OH)}_2$  in contact with a saturated aqueous solution at 298.15 K. The equilibrium constant notation is that used by Dirkse.

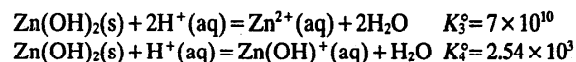
The acid character of ZnO and  $\text{Zn(OH)}_2$



Near minimum solubility



The basic character of  $\text{Zn(OH)}_2$



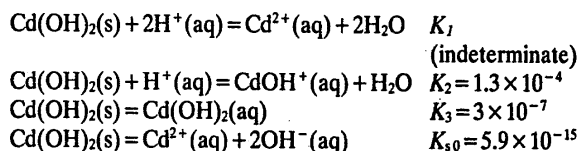
Data on a number of zinc basic salts are in Table 62. These include  $\text{Zn}_4(\text{OH})_7\text{ClO}_4$ ,  $\text{Zn}_4(\text{OH})_6\text{SO}_4$ , and  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  (hydrozincite).

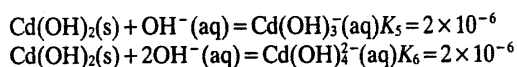
CdO [1306-19-0] Molecular weight 128.41  
 $\text{Cd(OH)}_2$  [21041-95-2] Molecular weight 146.42

*Physical characteristics:* Cadmium oxide is cubic with  $Z = 4$ ,  $a = 4.659 \times 10^{-10}$ , and a density of  $8.238 \times 10^3 \text{ kg m}^{-3}$ . Cadmium hydroxide exists in  $\alpha$ -,  $\beta$ - and  $\gamma$ -forms. Of these only the  $\beta$ - $\text{Cd(OH)}_2$  is stable in water suspensions. The  $\alpha$ -form is hexagonal with  $a = 3.36$  and  $c = 8$  (estimate)  $\times 10^{-10} \text{ m}$ . The  $\gamma$ - $\text{Cd(OH)}_2$  is monoclinic with  $Z = 4$ ,  $a = 5.67 \times 10^{-10} \text{ m}$ ,  $b = 10.25 \times 10^{-10} \text{ m}$ ,  $c = 3.41 \times 10^{-10} \text{ m}$ ,  $\beta = 91^{\circ}24'$ , and a density of  $4.908 \times 10^3 \text{ kg m}^{-3}$ . Another hexagonal form exists with  $Z = 1$ ,  $a = 3.47 \times 10^{-10} \text{ m}$ ,  $c = 4.71 \times 10^{-10} \text{ m}$  and a density of  $4.92 \times 10^3 \text{ kg m}^{-3}$ . We did not locate a structure specified to be the  $\beta$ -form. The aging of the  $\text{Cd(OH)}_2(\text{s})$  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<sup>4</sup> concludes that the solubilities of CdO and  $\text{Cd(OH)}_2$  in water are identical. He proposes a tentative solubility in water of  $5.4 \times 10^{-5} \text{ mol L}^{-1}$  at 298.15 K. An identical solubility of the two substances seems unlikely. It is more likely the CdO is relatively rapidly converted to  $\text{Cd(OH)}_2$  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<sup>4</sup>.

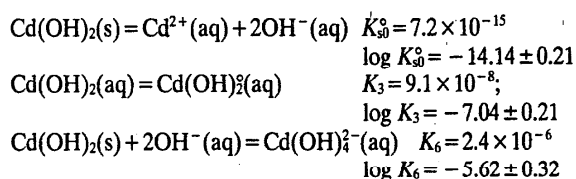




The  $K_3$  value represents the minimum solubility as a function of pH and probably appears at a pH of 11 to 13.

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<sup>4</sup>.

Since Dirkse's evaluation Rai, Felmy and Szelmeczka<sup>391</sup> have reported the solubility of  $\beta$ -Cd(OH)<sub>2</sub> in 0.01 NaClO<sub>4</sub> with the hydroxide ion varied from  $1 \times 10^{-6}$  to 1.0 mol L<sup>-1</sup>. Their results differ in a significant way from Dirkse's. They find the only dominant Cd(II) species required to explain the solubility of Cd(OH)<sub>2</sub>(s) are Cd<sup>2+</sup>(aq), Cd(OH)<sub>2</sub><sup>0</sup>(aq) and Cd(OH)<sub>3</sub><sup>-</sup>(aq). Thus, the required reactions and their equilibrium constants are:

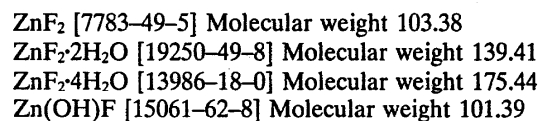


Only the  $K_3$  constant differs significantly from the values suggested by Dirkse. That difference is a direct consequence of Rai *et al.* considering the species Cd(OH)<sup>+</sup>(aq) and Cd(OH)<sub>3</sub><sup>-</sup>(aq) not significant. Rai *et al.*<sup>391</sup> also show that their constants 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<sub>4</sub>).

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.*<sup>391</sup> necessarily proves Cd(OH)<sup>+</sup> and Cd(OH)<sub>3</sub><sup>-</sup> 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)<sub>2</sub> system unless further experimental work reveals a better model.

### 4.3. Zinc and Cadmium Fluorides

#### 4.3.a. Zinc Fluoride



*Physical characteristics:* Zinc fluoride, ZnF<sub>2</sub>, is known in two crystal forms. The tetragonal form, with  $Z = 2$ ,  $a = 4.7034 \times 10^{-10}$  m,  $c = 3.1335 \times 10^{-10}$  m and a calculated density of 4952 kg m<sup>-3</sup>, 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  $5.01 \times 10^3$  kg m<sup>-3</sup>. The dihydrate, ZnF<sub>2</sub>·2H<sub>2</sub>O, 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<sup>23</sup> of  $3.07 \times 10^3$  kg m<sup>-3</sup>. The tetrahydrate, ZnF<sub>2</sub>·4H<sub>2</sub>O, 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<sup>-3</sup>. 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)<sub>1.5</sub>F<sub>0.5</sub> and Zn<sub>5</sub>(OH)<sub>8</sub>F<sub>2</sub>, were characterized by Feitknecht and Bucher<sup>24</sup> in precipitation studies reacting NaOH and ZnF<sub>2</sub>. An orthorhombic crystal structure of Zn(OH)F is reported<sup>25</sup>.

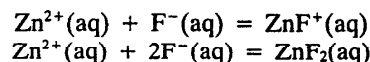
Literature values of the solubility of zinc fluoride tetrahydrate in water are given in Table 3. We have selected the value of Cook, Davies and Staveley<sup>26</sup> as the tentative value. Their value is reported as part of a careful emf study, but they did not give details of their solubility measurement.

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<sub>2</sub>·4H<sub>2</sub>O from the saturation molality and activity coefficient ( $\gamma_{\pm} = 0.312$ ) determined by Cook *et al.*<sup>26</sup>. A value was calculated for ZnF<sub>2</sub> from thermodynamic data<sup>12</sup>. The values lead to a  $\Delta G_{298}^0$  of -10.44 kJ for the hydration of ZnF<sub>2</sub>(s), which is consistent with the hydrated form being the stable thermodynamic form in water.

There are five studies on the solubility of ZnF<sub>2</sub> 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<sub>2</sub> solubility increases in the presence of moderate amounts of HF and SbF<sub>3</sub>, but decreases to a very small value in the presence of NH<sub>4</sub>F, KF and RbF.

The formation of the complexes



has been studied at several ionic strengths at 293 and 298 K. The reported values of  $\beta_1$  and  $\beta_2$  are given in Table 6. There is fair agreement among the  $\beta_1$  values in NaClO<sub>4</sub> media. Only Rodriguez Placeres *et al.*<sup>27</sup> have reported both  $\beta_1$  and  $\beta_2$  values.

#### 4.3.b. Cadmium Fluoride

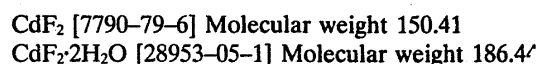


TABLE 3. Solubility of zinc fluoride tetrahydrate,  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ , in water

| T/K                       | $c/\text{mol L}^{-1}$ | $m/\text{mol kg}^{-1}$ | Reference  |
|---------------------------|-----------------------|------------------------|--|
| Tentative value           |                       |                        |  |
| 298.15                    | 0.1552                |                        | Cook, Davies, and Staveley, 1971 <sup>26</sup>                     |
| Other experimental values |                       |                        |  |
| 291                       | 0.15 <sub>5</sub>     |                        | Dietz quoted by Kohlrausch, Rose and Dolezalek, 1903 <sup>28</sup> |
| 293                       | 0.157                 |                        | Kurtenacker, Finger and Hey, 1933 <sup>29</sup>                    |
| 298.15                    | 0.1466                |                        | Carter, 1928 <sup>30</sup>   |
| 298.15                    |                       | 0.149                  | Gamburg, Deichman and Ikrami, 1976 <sup>31</sup>                   |

TABLE 4. Solubility product of zinc fluoride

| T/K    | $K/\text{mol}^3 \text{kg}^{-3}$ | Solid                                      | Reference                              |
|--------|---------------------------------|--|--|
| 298.15 | $4.54 \cdot 10^{-4}$            | $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}^a$ | Cook, <i>et al.</i> 1971 <sup>26</sup> |
| 298.15 | $3.0 \cdot 10^{-2}$             | $\text{ZnF}_2^a$                           | NBS Tables <sup>12</sup>               |

<sup>a</sup>Above data consistent with  $\text{ZnF}_2(\text{s}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{ZnF}_2 \cdot 4\text{H}_2\text{O}(\text{s})$   
 $\Delta G_{298}^\circ = -10.44 \text{ kJ}$

$\text{CdF}_2 \cdot 4\text{H}_2\text{O}$  [ ] Molecular weight 222.41

$\text{Cd}(\text{OH})\text{F}$  [16441-85-3] Molecular weight 148.42

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

The solubility of  $\text{CdF}_2$  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<sup>39</sup> and Feitknecht and Bucher<sup>24</sup> state they prepared the dihydrate,  $\text{CdF}_2 \cdot 2\text{H}_2\text{O}$ . Other authors make no mention of the hydration. The problem is complicated by the work of Kulikov and Mamaev<sup>40</sup>, who carried out kinetics of dissolution studies on the 100 face of cubic  $\text{CdF}_2$  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.*<sup>32</sup> identify the tetrahydrate,  $\text{CdF}_2 \cdot 4\text{H}_2\text{O}$ , 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<sup>30</sup> appears to be in error and is rejected. The values of Nuka<sup>39</sup> 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<sup>40</sup> at 283.15, 293.15 and 303.15 K, and the single point of Jaeger<sup>41</sup> because they seem a consistent data set in Fig. 1. The resulting equation is

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

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  $\text{CdF}_2$  in ternary systems containing HF, KF or  $\text{NH}_4\text{F}$  parallels the behavior of  $\text{ZnF}_2$  in these systems. Some of the values from Opalovskii *et al.*<sup>32</sup>, Kurtenacker *et al.*<sup>29,33</sup> and Jaeger<sup>41</sup> are given in Table 9. In

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

| T/K   | ZnF <sub>2</sub> , wt % | MF <sub>x</sub> , wt % | Solid Phase  | Reference   |                                     |   |
|---|-------------------------|------------------------|--|---|-------------------------------------|---|
| ZnF <sub>2</sub> + HF + H <sub>2</sub> O                |                         |                        |  |   |                                     |   |
| 273.  | 1.80                    | 0.40                   | ZnF <sub>2</sub> ·4H <sub>2</sub> O                      | Opalovskii <i>et al.</i> ,<br>1970 <sup>32</sup> .  |                                     |   |
|   | 5.17                    | 5.35                   | "  |   |                                     |   |
|   | 6.70                    | 10.70                  | "  |   |                                     |   |
|   | 7.03                    | 16.55                  | "  |   |                                     |   |
|   | 7.11                    | 20.60                  | ZnF <sub>2</sub> ·2H <sub>2</sub> O                      |   |                                     |   |
|   | 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 <sub>2</sub>   |   |                                     |   |
|   | 0.18–0.02               | 78.07–99.98            | ZnF <sub>2</sub> ·2HF <sup>b</sup>                       |   |                                     |   |
|   | 293                     | 2.54                   | 2.47   |   | ZnF <sub>2</sub> ·4H <sub>2</sub> O | Kurtenacker <i>et al.</i> ,<br>1933 <sup>29</sup> . |
|   |                         | 4.98                   | 3.69   |   |                                     |   |
| 9.53  |                         | 17.38                  |  |   |                                     |   |
| 11.40   |                         | 25.43                  |  |   |                                     |   |
| 11.84   |                         | 29.16                  |  |   |                                     |   |
| ZnF <sub>2</sub> + NH <sub>4</sub> F + H <sub>2</sub> O |                         |                        |  |   |                                     |   |
| 293   | 0.46                    | 4.0                    | ZnF <sub>2</sub> ·4H <sub>2</sub> O                      | Kurtenacker <i>et al.</i> ,<br>1933 <sup>33</sup> . |                                     |   |
|   | 0.31                    | 8.6                    |  |   |                                     |   |
|   | 0.16                    | 13.0                   | ZnF <sub>2</sub> ·2NH <sub>4</sub> F·2H <sub>2</sub> O   |   |                                     |   |
|   | 0.05                    | 20.4                   |  |   |                                     |   |
|   | 0.03                    | 28.0                   |  |   |                                     |   |
|   | 0.027                   | 39.8                   |  |   |                                     |   |
| ZnF <sub>2</sub> + KF + H <sub>2</sub> O                |                         |                        |  |   |                                     |   |
| 293   | 0.25                    | 1.5                    | ZnF <sub>2</sub> ·1.3KF·0.1H <sub>2</sub> O <sup>c</sup> | Kurtenacker <i>et al.</i> ,<br>1933 <sup>33</sup> . |                                     |   |
|   | 0.025                   | 10.0                   |  |   |                                     |   |
| ZnF <sub>2</sub> + RbF + H <sub>2</sub> O               |                         |                        |  |   |                                     |   |
| 298.15  | 1.52                    | 0                      | ZnF <sub>2</sub> ·4H <sub>2</sub> O                      | Gamburg <i>et al.</i> ,<br>1976 <sup>31</sup> .     |                                     |   |
|   | 0.002                   | 15                     | ZnF <sub>2</sub> ·RbF·2H <sub>2</sub> O <sup>d</sup>     |   |                                     |   |
| ZnF <sub>2</sub> + SbF <sub>3</sub> + H <sub>2</sub> O  |                         |                        |  |   |                                     |   |
| 298.15  | 2.1                     | 0                      | ZnF <sub>2</sub> ·4H <sub>2</sub> O                      | Shakhnazaryan <i>et al.</i> , 1983 <sup>34,e</sup>  |                                     |   |
|   | 13.7                    | 44.8                   |  |   |                                     |   |
|   | 14.6                    | 50.1                   | Zn[SbF <sub>4</sub> ] <sub>2</sub> ·6H <sub>2</sub> O    |   |                                     |   |
|   | 5.8                     | 68.4                   |  |   |                                     |   |
|   | 3.2                     | 74.1                   | SbF <sub>3</sub>   |   |                                     |   |

<sup>a</sup>Data range. There are 15 data points in this range where ZnF<sub>2</sub> solubility decreases as HF concentration increases.

<sup>b</sup>Data range. There are 8 data points in this range where ZnF<sub>2</sub> solubility decreases as HF concentration increases.

<sup>c</sup>Authors state solid compositions indeterminate.

<sup>d</sup>Two values given in paper, seven shown on small scale figure. The composition of the ZnF<sub>2</sub>·4H<sub>2</sub>O + ZnF<sub>2</sub>·RbF·2H<sub>2</sub>O mutual solubility point could not be read from the graph.

<sup>e</sup>The solvent composition is 2 wt % HF, 98 wt % water. The paper contains a table of 20 ZnF<sub>2</sub>/SbF<sub>3</sub> compositions for the system.



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

| T/K    | I/Electrolyte       | $\beta_n$      | n              | Reference  |
|--------|---------------------|----------------|----------------|--|
| 298.15 | 0                   | $18 \pm 4$     | 1 <sup>c</sup> | Connick, Paul, 1958 <sup>35,a</sup>                  |
| 298.15 | 0.01–0.155/ $ZnF_2$ | $13.6 \pm 1.6$ | 1              | Cook <i>et al.</i> , 1971 <sup>26</sup>              |
| 298.15 | 0.5/ $Na(F,ClO_4)$  | $5.4 \pm 1$    |                | Connick, Paul, 1958 <sup>35,b</sup>                  |
| 293.15 | 1.0/ $Na(F,ClO_4)$  | $5.9 \pm 0.6$  | 1              | Ahrland, Rosengren, 1956 <sup>36</sup>               |
| 298.15 | 2.0/ $Na(F,ClO_4)$  | $7.0 \pm 0.5$  | 1              | Mesaric, Hume, 1963 <sup>37</sup>                    |
| 298.15 | 0.5/ $K(F,NO_3)$    | 3              | 1              | Rodriguez Placeres, <i>et al.</i> 1980 <sup>27</sup> |
|        |                     | 11             | 2              |  |

<sup>a</sup>Estimated by method of R. Nasanen, *Acta Chem. Scand.* 4, 140 (1950).

<sup>b</sup>The authors report values of  $5.0 \pm 1$  and  $5.4 \pm 1$  at 288.15 and 308.15 K, respectively.

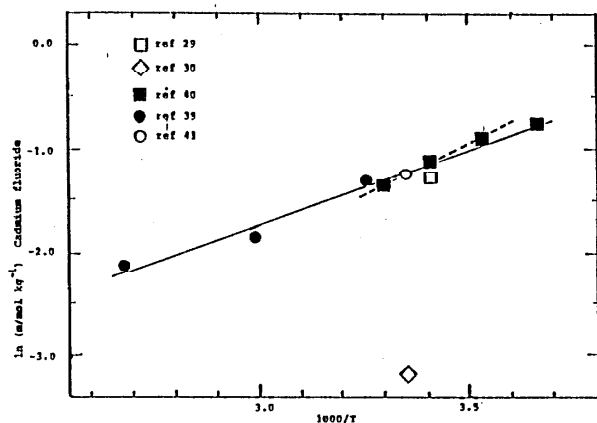


FIG. 1. Cadmium fluoride + water, 273–373 K.  $\ln(m/mol\ kg^{-1})$  vs.  $1000/T$

TABLE 7. The solubility of cadmium fluoride in water

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

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

| T/K    | Eq. (1)<br>m/mol kg <sup>-1</sup> | Eq. (2)<br>m/mol kg <sup>-1</sup> |
|--------|-----------------------------------|-----------------------------------|
| 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  $\beta_1$  for  $CdF^+$  are given in Table 10.

Feitknecht and Bucher<sup>24</sup> prepared the double salt  $Cd(OH)F$  and determined its solubility product to be  $2.2 \times 10^{-10}$  at 298 K. Gyunner *et al.*<sup>42</sup> 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<sup>47</sup> report  $Zn(IO_3)_2$  is monoclinic with  $Z = 2$ ,  $a$ ,  $b$  and  $c = 5.469$ , 10.938 and  $5.1158 \times 10^{-10}$  m, respectively, and an experimental density of  $5.08 \times 10^3$  kg m<sup>-3</sup>. 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<sup>48</sup>, Saegusa<sup>49</sup>, Spencer, Unger and Bailey<sup>50</sup> and Miyamoto<sup>51</sup> make no

TABLE 9. The solubility of cadmium fluoride in ternary systems  $\text{CdF}_2 + \text{MH} + \text{H}_2\text{O}$ .

| T/K                    | $\text{CdF}_2$ , wt %                                     | MF, wt %                       | Solid Phase   | Reference   |
|------------------------|---|--------------------------------|---|---|
| 273.15                 | $\text{CdF}_2 + \text{HF} + \text{H}_2\text{O}$           |                                | $\text{CdF}_2 \cdot 4\text{H}_2\text{O}$  | Opalovskii, <i>et al.</i> ,<br>1970 <sup>32</sup> . |
|                        | 9.77  | 3.75                           |   |   |
|                        | 12.27   | 6.71                           | $\text{CdF}_2 \cdot 2\text{H}_2\text{O}$  |   |
|                        | 14.05   | 7.39                           |   |   |
|                        | 14.44   | 9.47                           |   |   |
|                        | 14.99   | 10.81                          |   |   |
|                        | 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 <sup>a</sup>                                    | 32.97–66.76                    |   |   |
| 0.08–0.20 <sup>b</sup> | 71.31–97.80   | $\text{CdF}_2 \cdot \text{HF}$ |   |   |
| 293.15                 | 5.0   | 0.9                            | $\text{CdF}_2$  | Kurtenacker <i>et al.</i> , 1933 <sup>29</sup> .    |
|                        | 11.2  | 24.4                           |   |   |
|                        | 3.0   | 38.6                           |   |   |
| 298.15                 | 5.6   | 2.2                            |   | Jaeger, 1901 <sup>41,c</sup> .                      |
| 293.15                 | $\text{CdF}_2 + \text{NH}_4\text{F} + \text{H}_2\text{O}$ |                                | $\text{CdF}_2$  | Kurtenacker <i>et al.</i> , 1933 <sup>33</sup> .    |
|                        | 4.0   | 1.6                            |   |   |
|                        | 2.4   | 5.4                            |   |   |
|                        | 1.8   | 12.3                           | $\text{CdF}_2 \cdot 2\text{NH}_4\text{F} \cdot 2\text{H}_2\text{O}$                             |   |
|                        | 0.4   | 20.8                           |   |   |
|                        | 0.87  | 28.9                           |   |   |
|                        | 0.21  | 36.0                           |   |   |
| 0.57                   | 40.9  |                                |   |   |
| 293.15                 | $\text{CdF}_2 + \text{KF} + \text{H}_2\text{O}$           |                                | Variable composition<br>$\text{CdF}_2 \cdot (0.8-1.4)\text{KF} \cdot (0-1.0)\text{H}_2\text{O}$ | Kurtenacker <i>et al.</i> , 1933 <sup>33</sup> .    |
|                        | 2.4   | 3.4                            |   |   |
|                        | 0.6   | 13.6                           |   |   |
|                        | 0.18  | 24.1                           |   |   |
|                        | 0.05  | 32.5                           |   |   |
|                        | 0.024   | 33.1                           |   |   |
| —                      | 41.2  |                                |   |   |

<sup>a</sup>About 13 values.<sup>b</sup>About 8 values.<sup>c</sup>Did not identify solid.

mention of a hydrated solid. Both Fedorov *et al.*<sup>52</sup> and Lepeshkov, Vinogradov and Karataeva<sup>53,54,55</sup> used the wet residue method to prove their equilibrium solids were the dihydrate at both 298 and 323 K. It is clear that Rammelsberg<sup>56</sup> worked with the dihydrate. It is also clear that Ricci and Nesse<sup>48</sup>, Spencer *et al.*<sup>50</sup> and Miyamoto<sup>51</sup> 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  $\text{Zn}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$  in all of the solubility studies.

The data of Rammelsberg<sup>56</sup> 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 magni-

tude values agree very well. Their average is  $(1.549 \pm 0.007) \text{ mol L}^{-1}$ . 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.*<sup>50</sup> 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,  $K_s$ , values are in Table 13. The recommended value at 298.15 K is

TABLE 10. Formation constants of CdF<sup>+</sup> and CdF<sub>2</sub> in aqueous systems

| T/K    | I/Electrolyte               | β <sub>1</sub> | β <sub>2</sub> | Reference                                    |
|--------|-----------------------------|----------------|----------------|--|
| 289    | 0.05/NaNO <sub>3</sub>      | (13 ± 2)       |                | Bond, O'Donnell, 1970 <sup>43</sup> .        |
|        | 0.5/NaNO <sub>3</sub>       | (3.5 ± 0.4)    |                |  |
|        | 1.0/NaClO <sub>4</sub>      | 2.9            |                | Leden, 1943 <sup>44</sup> .                  |
| 298.15 | 2.0/Na(F,ClO <sub>4</sub> ) | (6.4 ± 0.5)    |                | Mesaric, Hume, 1963 <sup>37</sup> .          |
| 298.15 | 3.0/NaNO <sub>3</sub>       | (2.9 ± 0.2)    |                | Beutler <i>et al.</i> , 1976 <sup>45</sup> . |
| 303.15 | 1.0/NaClO <sub>4</sub>      | 5.8            | 4              | Bond, 1969 <sup>46</sup> .                   |

TABLE 11. The solubility of zinc iodate dihydrate in water

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

<sup>a</sup>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<sub>3</sub>)<sub>2</sub> value is shown. In the Russian handbook the dihydrate value is shown, but the number refers to amount of Zn(IO<sub>3</sub>)<sub>2</sub> dissolved. Both sets of data give the values above when the solid is properly identified.

<sup>b</sup>An interpolated value. No experiment carried out at this temperature by the authors.

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

TABLE 12. Solubility of zinc iodate dihydrate, Zn(±O<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, in water

| T/K             | Tentative values   |  |
|-----------------|--|--|
|                 | Concentration<br>10 <sup>2</sup> c <sub>1</sub> /mol L <sup>-1</sup> |  |
| 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   |  |

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<sup>12</sup>. 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

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

with a standard deviation about the regression line of 3.5 × 10<sup>-7</sup>.

The various papers listed in Table 12 contain solubility product, K<sub>s0</sub>, values as a function of ionic strength. Formation constants were calculated by Fedorov *et al.*<sup>57</sup> for Zn(IO<sub>3</sub>)<sub>n</sub><sup>(2-n)</sup>(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<sup>+</sup>(IO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>). 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<sup>32</sup>. The pK<sub>s0</sub> values found in the two Fedorov *et al.*<sup>52,57</sup> studies<sup>52,57</sup> differ by 0.24, which is considered satisfactory agreement.

## 4.4.b. Cadmium iodate

$\text{Cd}(\text{IO}_3)_2$  [7790-81-0] Molecular weight 462.22

*Physical characteristics:* Bach and Kueppers<sup>58</sup> report  $\text{Cd}(\text{IO}_3)_2$  is orthorhombic with  $Z = 4$ ,  $a$ ,  $b$  and  $c = 5.856$ ,  $17.470$  and  $5.582 \times 10^{-10}$  m, respectively, and a calculated density of  $5373 \text{ kg m}^{-3}$ . 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 ( $\text{mol L}^{-1}$ ) at 298.15 K is the average of the values of Saegusa<sup>49</sup> and Miyamoto<sup>51</sup>. Oelke and Wagner<sup>59</sup> measured the solubility of  $\text{Cd}(\text{IO}_3)_2$  at 298.15 K in the presence of KCl and  $\text{MgSO}_4$ . Their solubility values are presented in a graph from which the solubility ( $\text{mol kg}^{-1}$ ) 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.*<sup>54</sup> at 323 K suggests a negative temperature coefficient of solubility of cadmium iodate in water.

However, the work of Ramette<sup>60</sup> at ionic strength 3.0 ( $\text{Cd}^{2+}$ ,  $\text{Na}^+$ )  $\text{ClO}_4^-$  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<sup>12</sup>. It agrees well with the experimental values of Saegusa<sup>49</sup> and of Fedorov *et al.*<sup>57</sup>.

The formation of the complex ions,  $\text{Cd}(\text{IO}_3)_n^{(2-n)}(\text{aq})$  ( $n=1$  to 3), has been studied by Fedorov *et al.*<sup>57</sup>, Ramette<sup>60,61</sup> and Bond and Hefter<sup>62</sup>. The results are summarized in Table 16. The  $\beta_1$  values of Bond and Hefter and of Ramette agree well. Ramette does not work in a range where he can determine  $\beta_2$  values. Fedorov *et al.* give values of  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  as a function of ionic strength between 0.5 and 3.0  $\text{Li}^+(\text{IO}_3^-, \text{ClO}_4^-)$  at 298 K. Their values at  $I = 1.0$   $\text{LiClO}_4$  do not agree well with the results of the other workers. The results of Bond and Hefter<sup>62</sup> and of Ramette<sup>60,61</sup> 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

| $T/\text{K}$                | $10^6 K_{\text{sp}}/\text{mol}^2 \text{L}^{-3}$ | 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)                                   | $\text{KNO}_3$                               | Spencer <i>et al.</i> , 1974 <sup>50</sup>  |
| 298.15                      | 4.45 <sup>a</sup>                               |  | " " "                                       |
|                             | 3.905   | $\text{KNO}_3$                               | Saegusa, 1950 <sup>49</sup>                 |
|                             | 3.70 ± 0.56 <sup>b</sup>                        |  | Saegusa, recalculated <sup>50</sup>         |
|                             | 4.1   | $\text{Li}^+(\text{NO}_3^-, \text{ClO}_4^-)$ | Fedorov, <i>et al.</i> , 1976 <sup>57</sup> |
|                             | 4.3   | —  | NBS tables <sup>12</sup>                    |
|                             | 2.34 ± 0.40                                     | $\text{Li}^+(\text{IO}_3^-, \text{ClO}_4^-)$ | Fedorov <i>et al.</i> , 1983 <sup>57</sup>  |
| 301.55                      | 5.40 ± 0.20                                     | $\text{KNO}_3$                               | Spencer <i>et al.</i> , 1974 <sup>50</sup>  |
| 313.75                      | 7.39 ± 0.36                                     | $\text{KNO}_3$                               | " " "                                       |

<sup>a</sup>An interpolated value.

<sup>b</sup>Recalculated by Spencer *et al.*, 1974<sup>50</sup> from Saegusa's data.

TABLE 14. The solubility of cadmium iodate in water

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

<sup>a</sup>Read from a graph in the paper.

<sup>b</sup>Reported as 0.069 mass %, calculates as molality. (m) indicates molal unit, mol kg<sup>-1</sup>.

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

| <i>T/K</i>                    | <i>I/Electrolyte</i>   | Solubility product                       |   | Reference   |
|-------------------------------|--|--|---|---|
|                               |  | $10^8 K_{s0}/\text{mol}^3 \text{L}^{-3}$ | $10^8 K_s S(K_{s0}^0)/\text{mol}^3 \text{L}^{-3}$ |   |
| Tentative value<br>298.15     | 0  |  | 2.5   |   |
| Experimental values<br>298.15 | 0<br>0<br>1/(Cd <sup>2+</sup> , Na <sup>+</sup> )ClO <sub>4</sub> <sup>-</sup><br>3/(Cd <sup>2+</sup> , Na <sup>+</sup> )ClO <sub>4</sub> <sup>-</sup> | (6.94 ± 0.02)<br>(3.81 ± 0.03)           | 2.28<br>(3.72 ± 0.26)                             | Saegusa, 1950 <sup>49</sup><br>Fedorov <i>et al.</i> , 1983 <sup>57</sup><br>Ramette, 1981 <sup>60</sup><br>Ramette, 1983 <sup>61</sup> |
| 308.15                        | 3/(Cd <sup>2+</sup> , Na <sup>+</sup> )ClO <sub>4</sub> <sup>-</sup>   | (4.55 ± 0.03)                            |   | Ramette, 1983 <sup>61</sup>   |
| Thermodynamic data<br>298.15  | 0  |  | 2.49  | NBS Tables, 1982 <sup>12</sup>  |

 TABLE 16. Formation constants of Cd(IO<sub>3</sub>)<sub>n</sub><sup>2-n</sup> (aq)

| <i>T/K</i> | <i>n</i> | $\beta_n$   | <i>I/Electrolyte</i> | Reference                                  |
|------------|----------|-------------|----------------------|--|
| 298.15     | 1        | 3.2 ± 0.2   | 1/NaClO <sub>4</sub> | Bond and Hefter, 1972 <sup>62</sup>        |
|            | 2        | 33 ± 1      | 1/NaClO <sub>4</sub> |  |
|            | 1        | 3.27 ± 0.01 | 1/NaClO <sub>4</sub> | Ramette, 1981 <sup>60</sup>                |
|            | 1        | 3.25 ± 0.08 | 3/NaClO <sub>4</sub> | Ramette, 1983 <sup>61</sup>                |
| 308.15     | 1        | 3.36 ± 0.08 | 3/NaClO <sub>4</sub> | Ramette, 1983 <sup>61</sup>                |
| 298.15     | 1        | 0.036       | 1/LiClO <sub>4</sub> | Fedorov <i>et al.</i> , 1983 <sup>57</sup> |
|            | 2        | 0.0027      | 1/LiClO <sub>4</sub> | Fedorov <i>et al.</i> , 1983 <sup>57</sup> |
|            | 3        | 0.0091      | 1/LiClO <sub>4</sub> | Fedorov <i>et al.</i> , 1983 <sup>57</sup> |

## 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  $Z=4$ ,  $a=5.429 \times 10^{-10}$  m and a calculated density of  $4.096 \times 10^3$  kg m<sup>-3</sup>. The hexagonal wurtzite occurs in a number of structures of different  $Z$  and  $c$  values, but similar values. Synthetic wurtzite is hexagonal with  $Z=2$ ,  $a=3.811 \times 10^{-10}$  m,  $c=6.234 \times 10^{-10}$  m, and a calculated density of  $4.10 \times 10^3$  kg m<sup>-3</sup>. There are also naturally occurring mixed cation crystals such as (Zn<sub>0.584</sub>Cd<sub>0.415</sub>)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<sup>63</sup> 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<sup>64</sup> discuss the problem and point out the room temperature mixtures are metastable because the wurtzite component is stable only at high temperature.

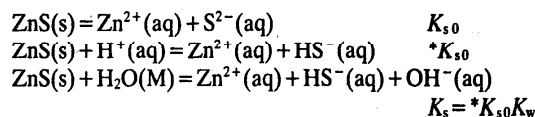
A common literature terminology is  $\alpha$ -ZnS and  $\beta$ -ZnS. These designations have different meanings to different workers. The original use of  $\alpha$ - and  $\beta$ -forms appears to have been that of Glixelli<sup>65</sup>, who called the ZnS precipitated from acid solution  $\alpha$ -ZnS and that precipitated from basic solution  $\beta$ -ZnS. From 1907 to about 1930 one could depend on this meaning for  $\alpha$ - and  $\beta$ -ZnS. Later authors have used the designation to distinguish between sphalerite and wurtzite. Ringbom<sup>66</sup> and Sillen and Martell<sup>18</sup> used  $\alpha$ -ZnS to refer to sphalerite and  $\beta$ -ZnS to refer to wurtzite. The CRC Handbook and the Crystal Data Determinative Tables<sup>11</sup> 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.*<sup>3</sup> 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<sub>2</sub>S. Licht<sup>18</sup> evaluated recent work and proposed a value of  $pK_{a2} = (17.3 \pm 0.3)$  for H<sub>2</sub>S(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<sup>-1</sup>. 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:

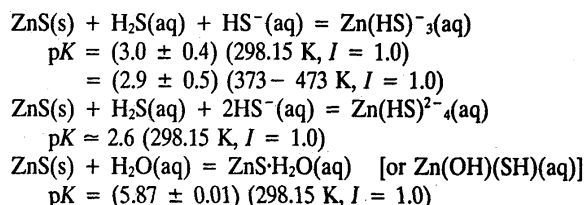


He gives the following  $pK$  values for each of these constants applied to sphalerite, wurtzite and precipitated ZnS at 298 K:

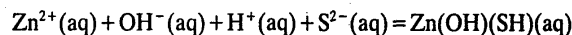
| Zinc sulfide     | $pK_{s,0}$ | $p^*K_{s,0}$ | $pK_s$ |
|------------------|------------|--------------|--------|
| ZnS(sphalerite)  | 28.9       | 11.5         | 25.5   |
| ZnS(wurtzite)    | 26.1       | 8.7          | 22.7   |
| ZnS(precipitate) | 25.4       | 8.0          | 22.0   |

The sulfide ion is of negligible concentration except in highly basic solutions. In many metal sulfide saturated solutions the HS<sup>-</sup> and OH<sup>-</sup> concentrations are nearly equal. Thus, one of the alternate solubility product expressions above may be more useful than the free ion product constant,  $K_{s,0}$ .

The zinc ion is probably present in these solutions as a complex ion, Zn(HS)<sub>*n*</sub><sup>(2-n)</sup>. Barnes<sup>67</sup> gives  $pK$  values for the following solution equilibria:



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



of 32.50. Use of Licht's<sup>18</sup> 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<sup>69,70,71,72</sup>, but only the Kolthoff<sup>72</sup> paper was available to us. More recent reviews are by Barnes<sup>57</sup> and by Rafal'skii<sup>73</sup>. Many of the available papers<sup>74-82,135</sup> 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<sup>83</sup> and Vukotic<sup>63</sup> 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<sup>136</sup> 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

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

goes through a maximum at 414 K.

Kuznetsov and Kostomarov<sup>137</sup> studied the ZnS + KOH + H<sub>2</sub>O system at 573 to 773 K. They found two solids, ZnS (sphalerite) and K<sub>2</sub>Zn<sub>3</sub>S<sub>4</sub>. As the temperature increased the ZnS region decreased and the K<sub>2</sub>Zn<sub>3</sub>S<sub>4</sub> region increased. The sphalerite dissolution mechanism is dependent on the KOH concentration. At low KOH concentration ZnS(OH)<sup>-</sup>(aq) predominates and at high KOH concentration Zn(OH)<sub>2</sub><sup>2-</sup>(aq) predominates in aqueous solution.

TABLE 17. Zinc sulfide (sphalerite) solubility in water

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

<sup>a</sup>Calculated using Gibbs energy data from Latimer<sup>89</sup> estimated heat capacity values, and H<sub>2</sub>S acid dissociation constants from Harned and Owen<sup>90</sup>.

<sup>b</sup>Calculated using their own thermodynamic data and H<sub>2</sub>S acid dissociation constants from Lewis and Randall<sup>91</sup>, and Wright and Maass<sup>92</sup>.

<sup>c</sup>Calculated from data Latimer<sup>89</sup>, Kubaschewski and Evans<sup>93</sup> and Kury, Zielen and Latimer<sup>94</sup>.

<sup>d</sup>These values appear to be calculated from the solubility ion product constant after taking various solutions complexes into account. The 473 K value may be from another source.

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

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

<sup>a</sup>Value probably not calculated by this author. Paper appears to be a compilation of data, but no references are given.

<sup>b</sup>Value calculated from data of Rossini *et al.*, 1950<sup>110</sup>.

<sup>c</sup>A best value for its time (1952). The average of several literature values with a standard deviation of 1.7.

<sup>d</sup>Calculated value using several sources of thermodynamic data including Latimer, 1952<sup>89</sup>, Kubaschewski and Evans<sup>93</sup>, Kelley, 1949<sup>111</sup>, and several Russian sources.

<sup>e</sup>Calculated value using data from Latimer, 1952<sup>89</sup>, Kubaschewski and Evans<sup>93</sup> and Kury, Zielen and Latimer<sup>94</sup>.

<sup>f</sup>Calculated values using estimated  $C_p$  values and data from Latimer, 1952<sup>89</sup>.

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

#### 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  $\alpha$ - or wurtzite form, is hexagonal with  $Z = 2$ ,  $a$  and  $c = 4.132$  and  $6.734 \times 10^{-10}$  m, respectively, and a calculated density of  $4.818 \times 10^3 \text{ kg m}^{-3}$ . The mineral hawleyite, sometimes called the  $\beta$ - or sphalerite form, is cubic with  $Z = 4$ ,  $a = 5.818 \times 10^{-10}$  m, and a calculated density of  $4.870 \times 10^3 \text{ kg m}^{-3}$ . Barton and Skinner<sup>64</sup> state that hawleyite is stable at low temperature and transforms to greenockite at an unknown higher temperature. Precipitated CdS may be either cu-

bic or hexagonal. Milligan<sup>115</sup> 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<sup>116,117</sup> 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 <sup>-1</sup>                | Method                         | Reference                                      |
|--------|--------------------------------------|--------------------------------|--|
| 290    | 6.6 × 10 <sup>-6</sup>               | ultramicroscope                | Biltz, 1907 <sup>118</sup>                     |
| 291.15 | 9.0 × 10 <sup>-6</sup>               | conductivity                   | Weigel, 1907 <sup>74</sup>                     |
| 291.15 | 3.2 × 10 <sup>-10</sup>              | calculation <sup>a</sup>       | Kolthoff, 1931 <sup>72</sup>                   |
|        | 0.87 × 10 <sup>-10</sup>             | calculation <sup>b</sup>       |  |
| 298.15 | 1.46 × 10 <sup>-10</sup>             | calculation                    | Ravitz, 1936 <sup>76</sup>                     |
| 298.15 | 1.51 × 10 <sup>-10</sup>             | calculation <sup>c</sup>       | van Rysselberghe,<br>Gropp, 1944 <sup>78</sup> |
| 298.15 | 1.5 × 10 <sup>-10</sup>              | calculation <sup>d</sup>       | Kapustinskii, 1940 <sup>85</sup>               |
| 298.15 | 1.19 × 10 <sup>-10</sup><br>(pH = 7) | model calculation <sup>e</sup> | Czaminske, 1959 <sup>86</sup>                  |
| 373.15 | 8.56 × 10 <sup>-10</sup><br>(pH = 7) | " "                            | " "  |
| 473    | 5.12 × 10 <sup>-9</sup><br>(pH = 7)  | " "                            | " "  |
| 673    | 4.29 × 10 <sup>-8</sup><br>(pH = 7)  | " "                            | " "  |
| 873    | 1.68 × 10 <sup>-7</sup><br>(pH = 7)  | " "                            | " "  |

<sup>a</sup>Recalculated from results of Bruner and Zawadski, 1909<sup>116</sup>, 1910<sup>117</sup> for (hexagonal ?) CdS precipitated from CdCl<sub>2</sub> solution.

<sup>b</sup>Recalculated from results of Bruner and Zawadski, 1909<sup>116</sup>, 1910<sup>117</sup> for (cubic ?) CdS precipitated from CdSO<sub>4</sub> solution.

<sup>c</sup>Recalculated from the data of Ravitz, 1936<sup>76</sup>.

<sup>d</sup>Calculation based on author's own thermodynamic data and H<sub>2</sub>S K<sub>a</sub> values from Lewis and Randall<sup>91</sup> and Wright and Maass, 1932<sup>92</sup>.

<sup>e</sup>Calculated from data of Latimer<sup>89</sup>, Kubaschewski and Evans<sup>93</sup>, and Kury, Zielen and Latimer<sup>94</sup>

<sup>f</sup>Calculated values using estimated C<sub>p</sub> values and data from Latimer, 1952<sup>89</sup>.

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

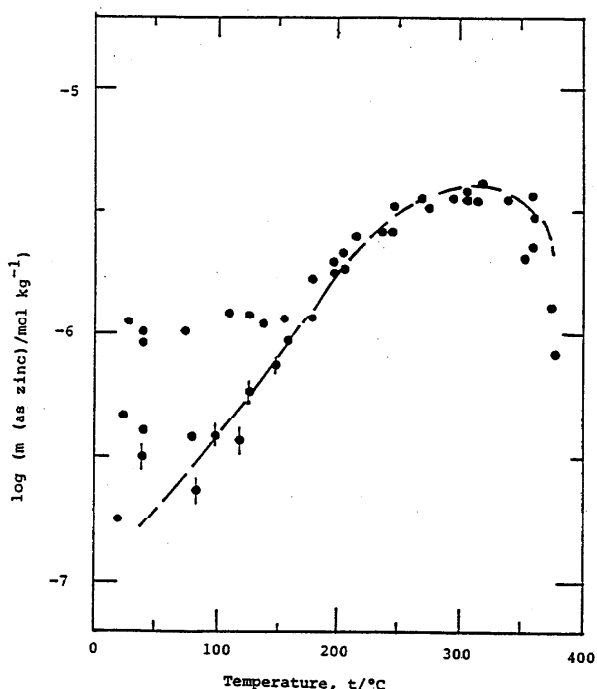
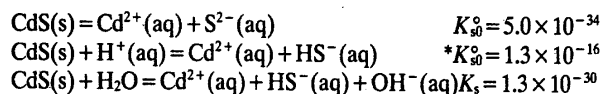
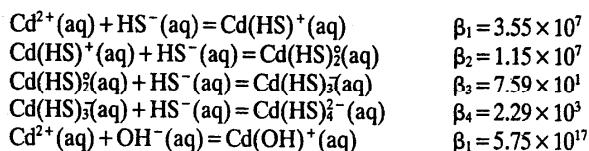


FIG. 2. Solubility of sphalerite (ZnS) in water, pH 5.4 at 20° C. Solutions analyzed either by atomic absorption, ●, or colorimetry, ◆. Original figure (Ref. 83) contains additional information as to use of water bath or sand bath, and whether equilibrium approached from high or low temperature.

The recent revision of the aqueous sulfide ion Gibbs energy has led Licht<sup>18</sup> to revised values of the solubility product constants for the reactions:



These values, along with the values of Ste-Marie, Torma and Gubeli<sup>119</sup> 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.



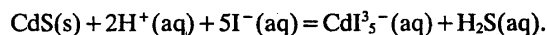
Neither Licht<sup>18</sup> nor Hampson and Latham<sup>15b</sup> identify the CdS solid for which they give standard potential values.

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<sub>2</sub>S as evaluated by Licht<sup>18</sup> are preferred.

Bruner and Zawadski<sup>116,117</sup>, Milligan<sup>115</sup>, Belcher, Townshend and Farr<sup>123</sup>, and Kraft, Gamsjaeger and Schwarzbekamp<sup>125</sup> are the only workers that discuss the nature of the solid CdS which is often a mixture of cubic and hexagonal. Kolthoff<sup>72</sup> rejects some early results<sup>74,118</sup> 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<sub>2</sub>S acid dissociation constants of an earlier time.

Golub<sup>134</sup> reported cadmium-halide ion dissociation constants at 293 ± 1 K. He used his dissociation constant for CdI<sub>3</sub><sup>-</sup> to obtain an equilibrium constant of 109.2 for



Egorov<sup>109</sup> used thermodynamic data to develop an equation for the temperature dependence of the ion product constant:

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

The equation gives values about an order of magnitude smaller than the values calculated by Czamanske<sup>86</sup>. Both

sets of values are probably too large in view of the recent evaluation of Licht<sup>18</sup>.

#### 4.6. Zinc and Cadmium Sulfites

In 1986 Masson, Lutz and Engelen<sup>138</sup> 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<sup>138</sup>.

##### 4.6.a. Zinc Sulfite

|   |                                       |
|---|---------------------------------------|
| ZnSO <sub>3</sub> [13597-44-9]                      | Molecular weight 145.45               |
| ZnSO <sub>3</sub> ·0.5H <sub>2</sub> O [65410-82-4] | Molecular weight 154.46               |
| ZnSO <sub>3</sub> ·H <sub>2</sub> O [66516-57-2]    | α and β forms Molecular weight 163.46 |
| ZnSO <sub>3</sub> ·2H <sub>2</sub> O [7488-52-0]    | Molecular weight 181.48               |
| ZnSO <sub>3</sub> ·2.5H <sub>2</sub> O [14460-28-7] | α, β, γ forms Molecular weight 190.49 |
| ZnSO <sub>3</sub> ·3H <sub>2</sub> O [75042-13-6]   | Molecular weight 199.50               |
| Zn(HSO <sub>3</sub> ) <sub>2</sub> [15457-98-4]     | Molecular weight 227.53               |

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

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

TABLE 20. The ion product constant of cadmium sulfide in aqueous solutions,  $\gamma_{\pm}$ . Continued

| T/K               | I/<br>Electrolyte    | $K_{s0}^a/\text{mol}^2 \text{L}^{-2}$ | $K_{s0}/\text{mol}^2 \text{L}^{-2}$ | Reference                                    |
|-------------------|----------------------|---------------------------------------|-------------------------------------|--|
| Calculated Values |                      |                                       |                                     |  |
| 298.15            | 0                    | $(7.9 \pm 5.9) \times 10^{-28i}$      |                                     | Kraft <i>et al.</i> ,<br>1966 <sup>125</sup> |
|                   | 1/NaClO <sub>4</sub> | $(1.6 \pm 1.2) \times 10^{-27i}$      |                                     |  |
|                   | 3/NaClO <sub>4</sub> | $(1.6 \pm 1.2) \times 10^{-27i}$      |                                     |  |
| 298.15            | 0                    | $1.4 \times 10^{-29m}$                |                                     | NBS Tables, 1982 <sup>12</sup>               |
| 298.15            | 0                    | $1.1 \times 10^{-27m}$                |                                     | Geol. Surv. Bull., 1978 <sup>13</sup>        |
| 298.15            | 0                    | $5.8 \times 10^{-28n}$                |                                     | Krestov, 1969 <sup>127</sup>                 |
| 298.15            | 0                    | $1.74 \times 10^{-28n}$               |                                     | Erdenbaeva, 1975 <sup>128</sup>              |
| 298.15            | 0                    | $5.6 \times 10^{-28n}$                |                                     | Krestov <i>et al.</i> , 1977 <sup>129</sup>  |
| 298.15            | ?                    |                                       | $7.1 \times 10^{-27c}$              | Simons, 1963 <sup>126</sup>                  |
| 298.15            | ?/pH=5.00            | $5.01 \times 10^{-18*}$               |                                     | Barnes, 1979 <sup>67</sup>                   |
|                   | ?/pH=6.12            | $9.33 \times 10^{-19*}$               |                                     | " "  |
|                   | ?/pH=7.00            | $5.01 \times 10^{-22*}$               |                                     | " "  |
| 373.15            | ?/pH=4.12            | $9.33 \times 10^{-15*}$               |                                     | " "  |
|                   | ?/pH=5.69            | $2.00 \times 10^{-16*}$               |                                     | " "  |
| 373.15            | 0                    | $4.79 \times 10^{-23k}$               |                                     | Czaminske, 1959 <sup>86</sup>                |
| 473               | 0                    | $5.63 \times 10^{-20k}$               |                                     | " "  |
| 473               | ?/pH=3.69            | $2.00 \times 10^{-12*}$               |                                     | Barnes, 1979 <sup>67</sup>                   |
| 673               | 0                    | $1.57 \times 10^{-16k}$               |                                     | Czaminske, 1959 <sup>86</sup>                |
| 873               | 0                    | $1.19 \times 10^{-14k}$               |                                     | " "  |

<sup>a</sup>CdS precipitated from CdCl<sub>2</sub> solution, probably hexagonal, see Milligan, 1934<sup>115</sup>  
<sup>b</sup>CdS precipitated from CdSO<sub>4</sub> solution, probably cubic, see Milligan, 1934<sup>115</sup>.  
<sup>c</sup>Used data from Goates, Gordon and Faux, 1952<sup>108</sup>, Latimer, 1952<sup>89</sup>, and his own data.  
<sup>d</sup>Source of data not clear, value probably not calculated by this author.  
<sup>e</sup>Recalculation of data of Bruner and Zawadski, 1909<sup>116</sup>1910<sup>117</sup>, first value for CdS from CdCl<sub>2</sub> and second value for CdS from CdSO<sub>4</sub>, see footnotes <sup>a,b</sup>.  
<sup>f</sup>Used data from Kelley, 1937<sup>111</sup>.  
<sup>g</sup>Used data from Rossini *et al.*, 1952<sup>110</sup>.  
<sup>h</sup>Apparently an average of several published values.  
<sup>i</sup>Used data from Makolkin, 1940<sup>130</sup>.  
<sup>j</sup>Used thermodynamic data from Latimer, 1952<sup>89</sup>, Kubashewskii and Evans<sup>93</sup>, and Kelley, 1949<sup>111</sup>.  
<sup>k</sup>Used thermodynamic data from Latimer, 1952<sup>89</sup>, Kubashewskii and Evans<sup>93</sup>, and Kury, Zielen and Latimer<sup>94</sup>.  
<sup>l</sup>Used their own electrochemical data at I = 1 and 3; at I = 0 they used data from Schindler, 1959<sup>131</sup>. Other data sources were Adami and King, 1964<sup>132</sup>, Sillen and Martell<sup>8</sup>, Latimer, 1952<sup>89</sup>, and NBS Technical Notes<sup>113</sup>.  
<sup>m</sup>Our calculation from thermodynamic data in reference cited.  
<sup>n</sup>Sources of thermodynamic data not given or unclear.  
<sup>o</sup>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<sup>+</sup>(aq) = Cd<sup>2+</sup>(aq) + H<sub>2</sub>S(g) equilibrium constant

| T/K    | I/Electrolyte        | K/atm L mol <sup>-1</sup>      | Reference  |
|--------|----------------------|--------------------------------|--|
| 289.15 | ?/HCl                | $1.06 \times 10^{-6a}$         | Aumeras, 1928 <sup>133</sup>                                     |
| 298.15 | 0                    | $1.3 \times 10^{-8b}$          |  |
|        |                      | $1.3 \times 10^{-9c}$          |  |
| 298.15 | ?                    | $3.4 \times 10^{-7}$           | Scheller, Treadwell,<br>1952 <sup>124</sup>                      |
| 298.15 | 0.4-1.2/HCl          | $(2.0-1.4) \times 10^{-7}$     | Kivalo, Ringbom,<br>1956 <sup>120</sup>                          |
| 298.15 | 0                    | $(7.9 \pm 5.9) \times 10^{-7}$ | Kraft, Gamsjaeger,<br>Schwarz-Bergkampff,<br>1966 <sup>125</sup> |
|        | 1/NaClO <sub>4</sub> | $(1.6 \pm 1.2) \times 10^{-7}$ |  |
|        | 3/NaClO <sub>4</sub> | $(1.6 \pm 1.2) \times 10^{-7}$ |  |

<sup>a</sup>Author wrote equation to form H<sub>2</sub>S(aq).  
<sup>b</sup>Calculated by us using CdS(s) + H<sup>+</sup>(aq) = Cd<sup>2+</sup>(aq) + HS<sup>-</sup>(aq) and \*K =  $1.3 \times 10^{-16}$  of Licht, 1988<sup>18</sup> and Gibbs energy of formation of HS<sup>-</sup>(aq) and H<sub>2</sub>S(g) from NBS Tables.  
<sup>c</sup>Calculated as in footnote <sup>b</sup> but for H<sub>2</sub>S(aq).

*Physical characteristics:* Lutz<sup>139</sup> reports the trihydrate crystallizes from water at temperatures below 275 K; the three forms of the 2.5 hydrate at ambient temperatures with the  $\alpha$ -form probably the thermodynamically stable form; the dihydrate at temperatures above 338 K; and the  $\alpha$ -monohydrate at temperatures above 363 K in the presence of excess sulfur dioxide.

Crystallographic information is from Lutz *et al.*<sup>139-142</sup> and Nyberg<sup>143</sup>. The ZnSO<sub>3</sub>·3H<sub>2</sub>O is orthorhombic with Z = 4, and a, b and c = 9.536, 5.530 and 9.419 × 10<sup>-10</sup> m, respectively. The hydrate ZnSO<sub>3</sub>·2.5H<sub>2</sub>O shows three crystalline forms. The  $\alpha$ -form is triclinic with Z = 4, and a, b and c = 7.651, 7.549, and 9.094 × 10<sup>-10</sup> m, respectively, angles  $\alpha$  = 90.06°,  $\beta$  = 88.53° and  $\gamma$  = 93.75°, and a density of 2.41 × 10<sup>3</sup> kg m<sup>-3</sup>. The  $\beta$ -form is tetragonal with Z = 8, and a, b and c = 9.521, 9.521 and 10.254 × 10<sup>-10</sup> m, respectively. The  $\gamma$ -form is orthorhombic with Z = 16, and a, b and c = 14.93, 18.12 and 7.53 × 10<sup>-10</sup> m, respectively. The dihydrate ZnSO<sub>3</sub>·2H<sub>2</sub>O 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

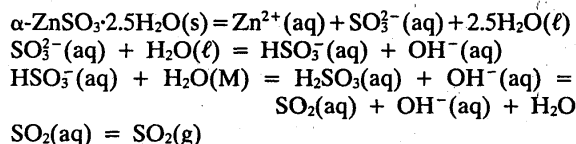
| <i>T/K</i> | Solubility<br>$m_{\text{ZnSO}_3}/\text{mol kg}^{-1}$ | Likely Hydration<br>of Solid | Reference                               |
|------------|--|------------------------------|---|
| "room"     | 0.011  | 2.5 <sup>a</sup>             | Heuston, Tichborne, 1890 <sup>144</sup> |
| 293.2      | 0.01230  | 2.5                          | Margulis, Rodin, 1981 <sup>149</sup>    |
| 298.2      | 0.01733  | 2.5                          | Murooka, Sato, 1937 <sup>148</sup>      |
| 323.2      | 0.01248  | 2.5                          | Margulis, Rodin, 1981 <sup>149</sup>    |
| 343.2      | 0.01290  | 2.0(?)                       | " " "                                   |
| 358.2      | 0.01314  | 2.0(?)                       | " " "                                   |
| 368.2      | 0.01336  | 2.0(?)                       | " " "                                   |

<sup>a</sup>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.

$\times 10^{-10}$  m, respectively, with  $\beta = 98.63^\circ$ , and a calculated density of  $2.943 \times 10^3 \text{ kg m}^{-3}$ .

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

The solubility of zinc sulfite in water has not been thoroughly studied. At temperatures at which  $\alpha\text{-ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$  is the equilibrium solid, the solubility process probably includes the steps



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

Analysis of the saturated solution by Murook and Sato<sup>148</sup> indicates that up to 75 % of the dissolved  $\text{SO}_3^{2-}$  is in the  $\text{HSO}_3^-$  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<sup>144</sup> and of Margulis and Rodin<sup>149</sup>. 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  $\log(\text{m/mol kg}^{-1})$  vs.  $1/(T/\text{K})$  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  $\text{ZnSO}_3$  has been studied in the systems  $\text{ZnSO}_3 + \text{SO}_2 + \text{H}_2\text{O}$ <sup>145-147</sup>,  $\text{ZnSO}_3 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$ <sup>147,148</sup> and  $\text{ZnSO}_3 + \text{ZnSO}_4 + \text{SO}_2 + \text{H}_2\text{O}$ <sup>146,147,149</sup>. Lutz<sup>138</sup> points out that in these systems the solubility of  $\text{ZnSO}_3$  increases with increasing concentration of sulfuric 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<sup>146</sup> and Terres and Ruhl<sup>145</sup> in a linear regression to obtain the relationship between the  $\text{ZnSO}_3$  solubility and the total  $\text{SO}_2$  content of the saturated solution at 293/298 K as

$$(m_{\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}}/\text{mol kg}^{-1}) = 0.035 + 0.463(m_{\text{SO}_2(\text{total})}/\text{mol kg}^{-1})$$

Lutz also used these data to show a linear relationship between  $\log(m_{\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}}/\text{mol kg}^{-1})$  and  $\log(P_{\text{SO}_2}/\text{Pa})$  at five temperatures between 283.1 and 351.6 K.

Margulis *et al.*<sup>389</sup> show the solubility of  $\text{ZnSO}_3$  in aqueous  $\text{ZnSO}_4$  increases with temperature and with  $\text{ZnSO}_4$  concentration. Diluting and cooling the  $\text{ZnSO}_3 + \text{ZnSO}_4 + \text{H}_2\text{O}$  solution gives a precipitate of  $\text{ZnSO}_3 \cdot \text{ZnSO}_4 \cdot x\text{H}_2\text{O}$  where  $x = 2$  or 3. The material is an unique compound which decomposes at 200–2600 °C to give  $\text{ZnSO}_3$  and  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ . The solubility data are shown in small graphs.

#### 4.6.b. Cadmium Sulfite

$\text{CdSO}_3$  [13477–23–1] Molecular weight 192.48

$\text{CdSO}_3 \cdot 1.5\text{H}_2\text{O}$  [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<sup>150</sup> have characterized the anhydrous forms and the hydrate. The thermodynamically stable  $\text{CdSO}_3\text{-I}$  is monoclinic with  $Z = 4$ ,  $a$ ,  $b$  and  $c = 4.439$ , 8.608, and 7.183  $\times 10^{-10}$  m, respectively, and  $\beta = 94.53^\circ$ . Kiers and Vos<sup>151</sup> show that  $\text{CdSO}_3 \cdot 1.5\text{H}_2\text{O}$  is monoclinic where  $a$ ,  $b$  and  $c$  are 122.19, 105.74 and 139.86  $\times 10^{-10}$  m, respectively, with  $\beta = 103.61^\circ$ .

The only solubility data found by us and by Lutz<sup>138b</sup> are the data of Margulis and Rodin<sup>152</sup> who studied the systems  $\text{CdSO}_3 + \text{H}_2\text{O}$ ,  $\text{CdSO}_3 + \text{CdSO}_4 + \text{H}_2\text{O}$ , and  $\text{CdSO}_3 + \text{Na}_2\text{SO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ . The solubility values in water are:

|  |         |         |
|--|---------|---------|
| <i>T/K</i>                             | 293.2   | 363.2   |
| $m_{\text{CdSO}_3}/\text{mol kg}^{-1}$ | 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<sup>138b</sup>.

#### 4.7. The Selenium Compounds of Zinc and Cadmium

There are few solubility data for the selenides,  $\text{Se}^{2-}$ , selenites,  $\text{SeO}_3^{2-}$ , and selenates,  $\text{SeO}_4^{2-}$ , of zinc and cad-

mium. 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  $5.261 \times 10^3$  kg m<sup>-3</sup>. 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 ( $\beta$ -CdSe) with  $Z = 4$  and  $a = 6.05 \times 10^{-10}$  m, has a calculated density of  $5.739 \times 10^3$ . A high pressure (30,000 kg/cm<sup>2</sup>) cubic form with  $Z = 4$ ,  $a = 5.54 \times 10^{-10}$  m and a calculated density of  $7.48 \times 10^3$  kg m<sup>-3</sup> 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<br>I/electrolyte | $K_{s0}$ or $K_{s0}^{\circ}$ | Reference                                     |
|------------------|---------------------------------|------------------------------|---|
| Zinc selenide    |                                 |                              |   |
| Tentative value  |                                 |                              |   |
| 298.15           | 0                               | $3.59 \times 10^{-26}$       | NBS Tables, 1982 <sup>12</sup>                |
| Other values     |                                 |                              |   |
| 298.15           | 0                               | $1 \times 10^{-31}$          | Latimer, 1952 <sup>89</sup>                   |
|                  | 0                               | $4.0 \times 10^{-30}$        | Buketov <i>et al.</i> , 1964 <sup>153,a</sup> |
|                  | ?                               | $2.6 \times 10^{-31}$        | Erdenbaeva, 1975 <sup>128</sup>               |
| Cadmium selenide |                                 |                              |   |
| 298.15           | 0                               | $6.3 \times 10^{-36}$        | Buketov <i>et al.</i> , 1964 <sup>153,a</sup> |
|                  | ?                               | $1.1 \times 10^{-32}$        | Erdenbaeva, 1975 <sup>128</sup>               |

<sup>a</sup>Calculated by authors using a combination of data from Latimer 1952<sup>89</sup> and Kubaschewski and Evans 1956<sup>93</sup>.

#### 4.7.b. Zinc and Cadmium Selenites

Zinc selenite ZnSeO<sub>3</sub> [13597-46-1]

molecular weight 192.34

Zinc selenite monohydrate ZnSeO<sub>3</sub>·H<sub>2</sub>O [23739-00-6]

molecular weight 210.36

Zinc selenite dihydrate ZnSeO<sub>3</sub>·2H<sub>2</sub>O [19527-79-8]

molecular weight 228.37

Zinc selenite dihydrate Zn(HSeO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O [71038-38-5]

molecular weight 357.35

Cadmium selenite CdSeO<sub>3</sub> [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.*<sup>154</sup>. Buketov *et al.*<sup>155</sup> found in a thermographic study that ZnSeO<sub>3</sub>·H<sub>2</sub>O loses water at 473 K to form  $\alpha$ -ZnSeO<sub>3</sub>, which changes at 589 K to  $\beta$ -ZnSeO<sub>3</sub>; the latter melts at 893–5 K, and decomposes above 936 K. No detailed crystallographic information was found for CdSeO<sub>3</sub>; however, x-ray powder patterns are given for three crystalline modifications of anhydrous CdSeO<sub>3</sub>.<sup>156,157</sup>

Ripan and Vericeanu<sup>158</sup>, Chukhlantsev<sup>159</sup>, and Redman and Harvey<sup>160</sup> report selenite solubility studies. Their data are evaluated by Masson, Lutz and Engelen<sup>138</sup>. 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<sup>161</sup>. 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<sub>3</sub> and CdSeO<sub>3</sub> in water

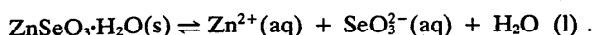
| T/K                                  | Ionic strength<br>I/Electrolyte                     | $K_{s0}$ or $K_{s0}^{\circ}$ | Reference                             |
|--------------------------------------|---|------------------------------|---------------------------------------|
| Zinc Selenite, ZnSeO <sub>3</sub>    |   |                              |                                       |
| Tentative value                      |   |                              |                                       |
| 298.15                               | 0   | $1.59 \times 10^{-7a}$       | NBS Tables, 1982 <sup>12</sup>        |
| Other values                         |   |                              |                                       |
| 291.15                               | sat. soln.  | $0.19 \times 10^{-7}$        | Ripan, Vericeanu, 1968 <sup>158</sup> |
| 293.15                               | ? HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> | $2.58 \times 10^{-7}$        | Chukhlantsev, 1956 <sup>159</sup>     |
| 298.15                               | 0 (?)   | $2.7 \times 10^{-7}$         | Erdenbaeva, 1975 <sup>128</sup>       |
| 298.15                               | 0   | $5.5 \times 10^{-11}$        | Essington, 1988 <sup>183</sup>        |
| Cadmium Selenite, CdSeO <sub>3</sub> |   |                              |                                       |
| Tentative value                      |   |                              |                                       |
| 298.15                               | 0   | $1.49 \times 10^{-9}$        | NBS Tables, 1982 <sup>12</sup>        |
| Other values                         |   |                              |                                       |
| 291.15                               |   | $6.0 \times 10^{-9}$         | Ripan, Vericeanu, 1968 <sup>158</sup> |
| 293.15                               |   | $1.29 \times 10^{-9}$        | Chukhlantsev, 1956 <sup>159</sup>     |
| "Room"                               |   | $0.40 \times 10^{-9b}$       | Redman, Harvey, 1967 <sup>160</sup>   |
| 298.15                               |   | $0.93 \times 10^{-9}$        | Erdenbaeva, 1975 <sup>128</sup>       |

<sup>a</sup>Value calculated from the Gibbs energy of the monohydrate, ZnSeO<sub>3</sub>·H<sub>2</sub>O(s). No other workers mention the hydration of the solid.

<sup>b</sup>Value calculated from the Redman, Harvey data by Masson<sup>138</sup>.

<sup>c</sup>Anhydrous salt

Ripan and Vericeanu<sup>158</sup> 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<sup>160</sup> at pH 6 and an undefined temperature was recalculated with suitable assumptions by Masson *et al.*<sup>138</sup>. Chukhlantsev<sup>159</sup> 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



Chukhlantsev's values are from the average of six  $pK_{s0}$  values. If the constants are averaged directly, values of  $(2.85 \pm 1.44) \times 10^{-7}$  and  $(1.38 \pm 0.66) \times 10^{-9}$  are obtained for  $ZnSeO_3$  and  $CdSeO_3$ , respectively. The sources of the data used by Erdenbaeva<sup>128</sup> are unknown. Essington<sup>183</sup> 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<sup>162</sup> 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  $ZnSeO_3 \cdot KH_2SeO_3$  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, Uchytlova and Ebert<sup>157</sup>. 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<sup>156</sup> have investigated the nature of  $CdSeO_3$  precipitates. A neutral, anhydrous, crystalline  $CdSeO_3$  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              |
| $K_2Cd(SeO_4)_2 \cdot 2H_2O$ [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  $4.905 \times 10^{-10} m$ , respectively, and a calculated density of  $2.722 \times 10^3 kg m^{-3}$ . Pistorius<sup>163</sup> reports the monohydrate to be monoclinic with  $Z = 4$ ,  $a$ ,  $b$  and  $c = 7.64, 7.98$  and  $7.07 \times 10^{-10} m$ , respectively, and  $\beta = 116^\circ 25'$ . Courtine<sup>164</sup> has also characterized the two solids. Palmer and Giles<sup>165</sup> report the hexahydrate to be tetragonal with  $Z = 4$ ,  $a$  and  $c = 6.953$  and  $18.33 \times 10^{-10} m$ , respectively, and a calculated density of  $2.371 \times 10^3 kg m^{-3}$ . 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  $8.219 \times 10^{-10} m$ , respectively,  $\beta = 120.83^\circ$  and an experimental density of  $4.22 \times 10^3 kg m^{-3}$  according to Herpin and Bregeault<sup>166</sup>. The Crystal Determinative Tables<sup>11</sup> list the dihydrate as orthorhombic with  $Z = 8$ ,  $a$ ,  $b$  and  $c = 10.42, 10.71$ , and  $9.365 \times 10^{-10} m$ , respectively, and a calculated density of  $3.68 \times 10^3 kg m^{-3}$ . 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<sup>128</sup> calculated values of  $K_{s0} = 3.0 \times 10^{-6}$  for  $ZnSeO_4$  and  $K_{s0} = 1.9 \times 10^{-7}$  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<sup>12</sup> data is  $5.75 \times 10^{-3}$ . 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<sup>169</sup> carried out a detailed study of solubility and characterized the equilibrium solid of both substances between about 265 K and 372 K. Gospodinov<sup>167</sup> 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 hex-

ahydrate, 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 dihydrate 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<sup>183</sup> has estimated the Gibbs energy formation of a number of selenates. He estimates the solubility product of anhydrous  $ZnSeO_4$  as  $1.9 \times 10^{-7}$ .

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

Gospodinov<sup>167</sup> 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<br>$\rho/g\ cm^{-3}$ | Molality <sup>a</sup><br>$m_{ZnSeO_4}/mol\ kg^{-1}$ | Solid<br>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 <sup>b</sup>                                  | "                        |
| 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 <sup>b</sup>                                  | $(ZnSeO_4 \cdot H_2O)^b$ |

<sup>a</sup>Molalities calculated from author's values of g  $ZnSeO_4$  per 100 g  $H_2O$ .

<sup>b</sup>The values at 298.15 and 373.15 K are from Gospodinov<sup>167</sup>. The remaining values are from Klein<sup>169</sup>. 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<sup>170</sup> 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)<sup>169</sup>

| T/K    | Density<br>$\rho/g\ cm^{-3}$ | Molality <sup>a</sup><br>$m_{CdSeO_4}/mol\ kg^{-1}$ | Solid<br>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   | "                          |

<sup>a</sup>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  $Z = 4$ ,  $a = 6.101 \times 10^{-10}$  m, and a calculated density of  $5.639 \times 10^3$  kg m $^{-3}$ ; and a hexagonal form with  $a$  and  $c = 4.31$  and  $7.09 \times 10^{-10}$  m, respectively. Cadmium telluride is cubic (sphalerite or zinc blend form) with  $Z = 4$ ,  $a = 6.478 \times 10^{-10}$ , and a calculated density of  $5.866 \times 10^3$  kg m $^{-3}$ ; and hexagonal (wurtzite form) with  $Z = 2$ ,  $a$  and  $c = 4.57$  and  $7.48 \times 10^{-10}$  m, and a calculated density of  $5.890 \times 10^3$  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<sup>89</sup> value is based on outdated information. The values of Buketov *et al.*<sup>153</sup> 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<sup>128</sup> 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 $K_{s0}^0$ | Reference                                       |
|-------------------------|------------------------------|------------------------|---|
| Zinc telluride, ZnTe    |                              |                        |   |
| 298.15                  | 0                            | $5.0 \times 10^{-34}$  | Buketov, Ugorets, Pashinkin 1964 <sup>153</sup> |
| 298.15                  | 0 (?)                        | $0.24 \times 10^{-34}$ | Erdenbaeva, 1975 <sup>128</sup>                 |
| Cadmium telluride, CdTe |                              |                        |   |
| 298.15                  | 0                            | $1 \times 10^{-42}$    | Latimer, 1952 <sup>89</sup>                     |
| 298.15                  | 0                            | $3.2 \times 10^{-42}$  | Buketov, Ugorets, Pashinkin 1964 <sup>153</sup> |
| 298.15                  | 0 (?)                        | $4.9 \times 10^{-44}$  | Erdenbaeva, 1975 <sup>128</sup>                 |

#### 4.8.b. Zinc and Cadmium Tellurites and Tellurates

Zinc tellurite ZnTeO<sub>3</sub> [15851-43-1] molecular weight 240.98

Cadmium tellurite CdTeO<sub>3</sub> [15851-44-2] molecular weight 288.00

Cadmium tellurite CdTe<sub>2</sub>O<sub>5</sub> [30180-70-2] molecular weight 447.60

Zinc tellurate ZnTeO<sub>4</sub> [not found] molecular weight 256.98

Cadmium tellurate CdTeO<sub>4</sub> [not found] molecular weight 304.00

Cadmium tellurate Cd<sub>3</sub>TeO<sub>6</sub> [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<sub>2</sub>Te<sub>2</sub>O<sub>5</sub>. Hanke<sup>171</sup> characterizes an orthorhombic ZnTeO<sub>3</sub> structure. No information was found for ZnTeO<sub>4</sub>.

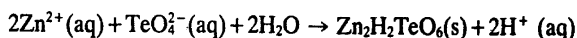
Two forms of CdTeO<sub>3</sub> are known: an  $\alpha$ -form stable to 973 K<sup>174</sup> or 1065 K<sup>173</sup> and a  $\beta$ -form stable at the higher temperature. Both forms are monoclinic. The crystal structure and transition temperature<sup>172</sup> are apparently in error. Markovskii and Pron<sup>172</sup> report a hexagonal form stable above 770 K. Recently Kramer and Brandt<sup>175</sup> restudied CdTeO<sub>3</sub> and found no transition and a structure similar to the  $\beta$ -form of Robertson *et al.*<sup>174</sup>. Sleight *et al.*<sup>176</sup>, report an orthorhombic form of CdTeO<sub>4</sub>. Erdenbaeva<sup>128</sup> carried out an experimental study of the emf of suspensions of the sparingly soluble salts in 0.5 molar Na<sub>2</sub>SO<sub>4</sub> 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 <sub>3</sub> | $3.56 \times 10^{-3}$ |
| CdTeO <sub>3</sub> | $3.6 \times 10^{-7}$  |
| ZnTeO <sub>4</sub> | $1.27 \times 10^{-6}$ |
| CdTeO <sub>4</sub> | $1.8 \times 10^{-8}$  |

The values are of doubtful usefulness. The compounds ZnTeO<sub>4</sub> and CdTeO<sub>4</sub> are probably not the thermodynamically stable solids in contact with aqueous solutions.

Redman and Harvey<sup>160</sup> 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<sub>3</sub> or CdTeO<sub>3</sub> with contamination by the metal hydroxide and TeO<sub>2</sub>. An early report of Lenher and Wolessky<sup>177</sup> identified the solid as 3CdTeO<sub>3</sub>·2H<sub>2</sub>O. Redman and Harvey misstate the Lenher and Wolessky 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<sub>4</sub> or CdTeO<sub>4</sub>; however, analysis of the precipitate showed 2 metal atoms to one tellurium atom corresponding to a formulation of Zn<sub>2</sub>H<sub>2</sub>TeO<sub>6</sub> or Cd<sub>2</sub>H<sub>2</sub>TeO<sub>6</sub>. The precipitation reaction is suggested to be:



with the end point shifted by the H<sup>+</sup> produced. Jander and Kienbaum<sup>178</sup> report Zn<sub>2</sub>H<sub>2</sub>TeO<sub>6</sub> as an intermediate and Zn<sub>3</sub>TeO<sub>6</sub> as the final product on reacting excess zinc solutions with tellurate solution at steam bath temperatures.

Redman and Harvey<sup>160</sup> report the following solution concentrations at the pH of the end point of their titration studies: