Journal of Physical and Chemical Reference Data

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Cite as: Journal of Physical and Chemical Reference Data **14**, 631 (1985); https://doi.org/10.1063/1.555732
Published Online: 15 October 2009

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

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The literature on the solubility of mercury and of the sparingly soluble salts of mercury-(I) and mercury (II) in water and in aqueous electrolyte solutions has been reviewed. The solubility data have been compiled and evaluated. Recommended and tentative values of the solubilities are presented when warranted. Auxiliary thermodynamic data and crystallographic data useful in the interpretation of solubility data are given. An annotated bibliography on the solubility of some of the less common inorganic mercury compounds, with emphasis on the solubility literature published since 1950, is given.

Key words: mercury; mercury carbonate; mercury halides; mercury phosphate; mercury reproportionation constant; mercury sulfate; mercury sulfide; mercury thiocyanate; solubility; solubility product.

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Nomenclature

A	Debye–Hückel constant
$A_1, A_2, A_3,$ and A_4	Parameters of regression equation for solubility and solubility product constants
B	Debye–Hückel constant
C_p°	Standard heat capacity at constant pressure
E, E°	Electromotive force, potential, standard potential
F	Faraday constant
G°	Standard Gibbs energy
H°	Standard enthalpy
I	Ionic strength, $I = 1/2\Sigma c_i z_i^2$ (molar scale)
K_H	Equilibrium constant, Henry's constant
K_n	Equilibrium constant, ligand metal formation constant ($ML_{n-1} + L = ML_n$)
K_{s0}, K_{s0}°	Solubility ion product constant (may be designated either concentration scale or molality scale) $ML(s) = M^{z+} + L^{z-}$; the superscript indicates the free lattice ion activity product
K_{snm}, K_{snm}°	Equilibrium constant, solubility product constant when a complex $M_m L_n$ 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 proton (Ref. 8, supplement, p. xvi). The superscript indicates the thermodynamic constant
K_{a1}, K_{a2}, K_{a3}	Equilibrium constant, weak acid dissociation
R	Gas constant
S°	Standard entropy
T	Thermodynamic temperature
Z	Molecules per unit cell
a, b, and c	Unit cell dimensions
a	Activity
c_B	Amount-of-substance concentration of substance B (amount of B divided by the volume of the solution)
f	Fugacity
m_B	Molality of solute substance B (amount of B divided by the mass of solvent)
n	Amount of substance
p_1, p_B	Pressure, total pressure, partial pressure
x_B	Mole fraction of substance B: $n_B/\Sigma n_i$
$y, y_\pm$	Activity coefficient, mean ionic activity coefficient, molar scale
z	Ion charge
β_n	Equilibrum constant, cumulative ligand metal formation constant ($M + nL = ML_n$), $\beta_n = \prod_{i=1}^{n} K_i$ (see K_n above)
ρ	Density
$\gamma, \gamma_\pm$	Activity coefficient, mean ionic activity coefficient, molal scale

1. Introduction

Metallic mercury and the salts of mercury (I) and mercury (II) contribute to environmental problems in natural, brackish, and seawater. A knowledge of solubility and related solution equilibria is needed by the scientists who model the transport and transformation of inorganic pollutants in aqueous systems. This paper presents a critical evaluation of the stoichiometric solubilities and the solubility product constants, and information on many of the equilibrium constants related to solubility that are useful in understanding the behavior of mercury and mercury salts in aqueous electrolyte solutions.

The sparingly soluble mercury salt systems are much

more complex in their chemistry than the sparingly soluble lead salt systems evaluated in an earlier paper.[1] There are several reasons for the complexity of the sparingly soluble mercury salt systems. They include

(i) the reproportionation equilibrium $Hg(l) + Hg^{2+}(aq) = Hg_2^{2+}(aq)$;
(ii) the tendency of solid mercury salts to hydrolyze to stable basic solid salts under certain conditions of pH and temperature;
(iii) the acid nature of the mercury cations, especially the Hg^{2+} ion, which results in a number of hydrolysis products;
(iv) the tendency of the mercury cations, again, especially the Hg^{2+} ion, to form stable complexes in aqueous solution;
(v) the acid–base nature of anions in the case of mercury salts of weak acids; and
(vi) the activity effects due to ionic strength on the solubility, reproportionation, hydrolysis, complexing, and other equilibria associated with the solution process.

These points are discussed further in Sec. 3 on auxiliary thermodynamic data and in Sec. 4 on solubility as they apply to specific systems. Some examples of specific problems encountered in reading the literature on the solubility of mercury salts, which illustrate the points above as well as additional problems, are discussed below.

The dimeric nature of the mercury (I) ion has been recognized since the turn of the century. In spite of this, some papers give a solubility product value for mercury (I) compounds based on the Hg^{+} ion rather than the Hg_2^{2+} ion. Some of these values have been cited by others who have mistakenly assumed the value applied to the Hg_2^{2+} formulation. We have converted literature solubility product values based on the Hg^{+} ion to values based on the dimeric Hg_2^{2+} ion.

Many workers did not do the experiments required to clearly define the nature of the solid phase. They assumed the solid phase existed as the simplest unhydrated formula of the salt. However, many mercury compounds either precipitate as stable basic salts or convert to stable basic salts under certain conditions of pH and temperature. Hydroxide and oxide forms of the mercury halides are known. Salts also coprecipitate with other salts, either as separate crystals (eutectic) or as solid solutions. The solid may be a hydrate that has not been identified. The mercury (II) tellurate that precipitates on mixing dilute acid solutions of mercury (II) nitrate and potassium tellurate has the formula $Hg_2H_2TeO_6$. Some of the papers that discuss the solubility of mercury (I) oxalate do not mention that the solid is the monohydrate.

The conventional solubility product constant K_{s0} gives the composition of the solid phase in terms of the species with which it is in equilibrium in solution. Often the solubility process is described by a series of steps, of which the K_{s0} step is only one of many in the experimentally studied equilibrium.

For example, when mercury (I) chloride dissolves in an aqueous medium containing even a small concentration of chloride ion, the principal mercury species in solution is the tetrachloromercury (II) complex ion. The overall solution process may be represented by the following equilibria:

$Hg_2Cl_2(s)$	$= Hg_2^{2+}(aq) + 2Cl^{-}(aq)$	K_{s0}
$Hg_2^{2+}(aq)$	$= Hg^{2+}(aq) + Hg(l)$	$1/K_r$
$Hg^{2+}(aq) + 4Cl^{-}(aq)$	$= HgCl_4^{2-}(aq)$	β_4
$Hg_2Cl_2(s) + 2Cl^{-}(aq)$	$= HgCl_4^{2-}(aq) + Hg(l)$	$K_e = \beta_4 K_{s0}/K_r$

The conventional solubility product at the limit of zero ionic strength (thermodynamic constant) K_{s0}° can be calculated if the other constants have been evaluated at the limit of zero ionic strength to obtain the thermodynamic value. The evaluation of K_e° is itself a challenging problem[2,3] because of the dissociation of $HgCl_4^{2-}$ as the solution approaches zero ionic strength. Marcus[3] shows that it is necessary to use

$$\log K_{s0}^{\circ} = \log K_e^{\circ} + \log K_r^{\circ} - \log \beta_4 - \log y_{\text{NaCl in NaClO}_4}.$$

Another example is the solubility of mercury (II) carbonate in an acid solution saturated with carbon dioxide gas at a known partial pressure. The solubility depends on both the pH and the carbon dioxide partial pressure. Thus

$HgCO_3(s)$	$= Hg^{2+}(aq) + CO_3^{2-}(aq)$	K_{s0}
$H^{+}(aq) + CO_3^{2-}(aq)$	$= HCO_3^{-}(aq)$	$1/K_{a1}$
$H^{+}(aq) + HCO_3^{-}(aq)$	$= H_2O + CO_2(aq)$	$1/K_{a2}$
$CO_2(aq)$	$= CO_2(g)$	K_p
$HgCO_3(s) + 2H^{+}(aq)$	$= Hg^{2+}(aq) + H_2O + CO_2(g)$	$K_e = K_{s0}K_p/K_{a1}K_{a2}$.

Again the conventional solubility product at the limit of zero ionic strength can be calculated from a knowledge of the other constants as

$$\log K_{s0}^{\circ} = \log K_e^{\circ} + \log (K_{a1}^{\circ} K_{a2}^{\circ}) - \log K_p^{\circ}.$$

The determination of each of the constants is in itself a major research project unless evaluated data are available. Note that K_p is the inverse of Henry's constant as defined for CO_2 (Sec. 3.3). This type of system was discussed from a somewhat different viewpoint in our paper on lead salts (Sec. 3.4).[1]

The solubility products calculated from thermodynamic data independent of solubility data are frequently smaller than the solubility products obtained from the analysis of a model devised to explain the directly determined solubility of a compound in terms of solution species. This suggests that in many cases the solution species and the equilibrium constants that relate them to the simple ions of the salt are not completely known or understood. A model may be giving too large a concentration of free Hg_2^{2+} or Hg^{2+} and the free anion, and thus too large a value of the solubility product.

A better knowledge of the nature of the solid phase, the equilibria important in the solution process, and the solution species and the equilibria that relate them may well make many of the values of the solubility products presented here obsolete within the foreseeable future. This should not be true of the stoichiometric solubility data, which represent the amount of material dissolved on the basis of an arbitrary formula.

2. Scope and Approach

The present review includes the solubility of mercury and of the sparingly soluble salts of mercury (I) and mercury (II) in water and aqueous electrolyte solutions. By sparingly soluble we generally mean salts of solubilities of 0.1 mol dm^{-3} or less. Thus the nitrates, perchlorates, and other soluble salts are not included. The review also does not include the oxides and hydroxides of mercury, although they are important sparingly soluble salts. Some information on the oxides and hydroxides can be found in earlier reviews by Feitknecht and Schindler[4] and Hepler and Olofsson.[5] A comprehensive review of mercury oxide and hydroxide solubility data is in preparation by Dirkse.[291]

The solubility data were compiled in two stages. Solubility data reported since about 1950 were traced by a combined hand and computer search through *Chemical Abstracts* through June of 1983. The earlier data were traced through *Chemical Abstracts* and inspection of the standard compilations of solubility data, including Seidell and Linke,[6] Stephen and Stephen,[7] Sillen and Martell,[8] Kirgintsev *et al.*,[9] and Comey and Hahn.[10] Other recent compilations of evaluated solubility data that we did not use, but that may be useful to others, are Broul, Nyvlt, and Söhnel[11] and Freier.[12]

The *Crystal Data Determinative Tables*[13] were the major source of crystallographic and density values given in the sections on physical characteristics of the salts.

There are several sources of evaluated thermodynamic data on the mercury salts, their ions, and complex ions. The National Bureau of Standards Technical Notes[14] and the Geological Survey Bulletin on Thermodynamic Properties of Minerals[15] are very useful. The review of Hepler and Olofsson[5] on the thermodynamic properties of mercury and its compounds is indispensible to anyone working with mercury compounds. The IUPAC set of selected reduction potentials,[16] in which there are recommended E° values that do not depend in any way on experimentally determined solubility data, provides a useful cross check on some of the solubility product values. The book edited by McAuliffe[294] summarizes information on the chemistry of mercury.

3. Auxiliary Thermodynamic Data

To understand the solubility and the aqueous solution chemistry of sparingly soluble mercury salts requires a knowledge of the mercury reproportionation equilibrium, the formation constants of mercury (I) and mercury (II) complex ions, the dissociation constants of weak acids whose anions form sparingly soluble salts, and Henry's constant for the gases CO_2 and H_2S. In addition, reliable standard potential data for the $Hg(l)/Hg_2^{2+}(aq)$ and $Hg(l)/Hg^{2+}(aq)$ electrode systems, when combined with standard potentials of Hg(l)/insoluble salt electrodes, give thermodynamic values of the solubility product constants which are independent of directly measured solubility data. These topics, with some recommended values of useful constants, are discussed below.

3.1. The Reproportionation Constant

Many mercury (I) compounds (e.g., Hg_2O, Hg_2S, etc.) are not stable in the presence of water. The corresponding mercury (II) compounds are so insoluble in water that mercury (I) disproportionation converts the solid mercury (I) compound to the mercury (II) compound. Even in cases where the solid mercury (I) salt is stable in contact with water, the aqueous solution species are often mercury (II) species due to the disproportionation of mercury (I) and the strong complexes formed by the mercury (II) ion.

The equilibrium constant for the reproportionation reaction

$$Hg(l) + Hg^{2+}(aq) = Hg_2^{2+}(aq)$$

was carefully evaluated by Vanderzee and Swanson.[17] Their recommended value is $\log K_r^\circ = (1.944 \pm 0.009)$ or $K_r^\circ = (87.9 \pm 1.8)$ at 298.15 K. Vanderzee and Swanson[17] recalculated the data of Schwarzenbach and Anderegg[18] and of Hietanen and Sillen[19] with special attention to the corrections for hydrolysis and to the extrapolation to zero ionic strength using an extended Debye–Hückel equation. Both Hepler and Olofsson[5] and Marcus[3] have accepted Vanderzee and Swanson's value.

The work of Hietanen and Sillen[19] clearly shows that K_r is a function of the ionic strength. The effect is much more pronounced in perchlorate ion media than in nitrate ion media. Vanderzee and Swanson show that the effect is related to the ion size parameter in the extended Debye–Hückel equation used to obtain the activity coefficients of the mercury ions.

Table 1 gives the values of K_r calculated by Vanderzee and Swanson from the data of Hietanen and Sillen at ionic strengths up to 2 in both perchlorate ion and nitrate ion media. In addition, three experimental values[20–22] of K_r are included at a perchlorate medium ionic strength of 3.

Schwarzenbach and Anderegg[18] studied the effect of temperature on the reproportionation equilibrium at an ionic strength of 0.1 in aqueous sodium nitrate. The decrease in value of the constant with temperature between 273.15 and 313.15 K corresponds to an entropy change of 25.9 $J\,K^{-1}$ for the reproportionation. The constants have not been corrected for hydrolysis, as pointed out by Vanderzee and Swanson.

Recently, Malyszko and Malyszko[297] reported a study of the reproportionation equilibrium at 298.2 ± 0.2 K in concentrated magnesium and calcium perchlorate solutions. Their value of the constant at infinite dilution in water is 126, which agrees with the older value of Hietanen and Sillen.[19] The apparent constant K_r increases to 3.0×10^3 in 2.5 molar $Ca(ClO_4)_2$. Watters and Dunnigan[303] report a value of $K_r = 98.8$ at unit ionic strength KNO_3 at 298.15 K. The value is about 8% smaller than the value for unit ionic strength $NaNO_3$ in Table 1.

Moser and Voigt[23] point out that, below the metallic mercury solubility limit, the reproportionation constant takes the form

$$K_r^\circ = a_{Hg_2^{2+}}/a_{Hg}a_{Hg^{2+}},$$

with the metallic mercury activity in solution now a part of

Table 1. The mercury reproportionation constant, K_r, at 298.15 K as a function of ionic strength in perchlorate and in nitrate ion media.

Ionic Strength	Reproportionation Constant, K_r	
	Sodium Perchlorate	Sodium Nitrate
0	87.9	87.9
0.10	100	90
0.25	112	92
0.50	131	97
1.00	172	107
2.00	277	129
3.00	430 [20]	
	461 ± 4 [21]	
	480 ± 10 [22]	

the expression. They determined the solubility of mercury at 298.15 K in 0.1 M H_3PO_2 solution (reducing medium) to be $(3.0 \pm 0.3) \times 10^{-7}$ mol dm^{-3}. Assuming unit activity coefficients for metallic mercury at concentrations below its solubility value, the reproportionation constant including the metallic mercury concentration is 1.8×10^8. In the same study, Moser and Voight found no direct evidence of the dissociation of the mercury (I) dimer Hg_2^{2+} into Hg^+. They inferred from their results that the dimer dissociation constant is less than 10^{-7}.

Baltisberger *et al.*[283] have found conditions under which Hg_2Cl_2 does not undergo disproportionation with a measurable rate in acidic media; however, disproportionation is rapid above pH 7.0.

3.2. Mercury (II) Complex Ion Formation Constants

The literature on the formation constants of mercury(II) complex ions is too extensive for us to compile and evaluate in this study. Recently, Hepler and Olofsson[5] have reviewed and evaluated the thermodynamic data on mercury, its compounds, and aqueous solution species. We accept their values as the most reliable values available at present. Reproduced in Table 2 are their recommended values of the formation constants (K_i°, β_4) of the halide, cyanide, and thiocyanate complexes of mercury (II).

In addition to the values in Table 2, Arnek[22] summarizes the effect of ionic strength at 0.5 and 3.0 on the concentration constants, and Hansen, Izatt, and Christensen[24] report the formation constants of the halide complexes at several temperatures between 280.15 and 313.15 K. Values of formation constants of other anions with mercury (II) are mentioned at appropriate places in the paper. Recent reviews of the coordination chemistry of mercury are concerned principally with nonaqueous systems.[25,26]

3.3. Weak Acid Dissociation Constants

The solubilities of salts of weak acids are pH dependent. In the case of carbonates and sulfides, the solubility depends on carbon dioxide or hydrogen sulfide partial pressure as well as the pH. To obtain values of the solubility product K_{s0} from the experimental data requires knowledge of the weak acid dissociation constants as well as Henry's constant if a gas is involved.

In the carbonate case, we have reliable data at 298.15 K from the work of Berg and Vanderzee.[27] We suggest the use of their values when evaluating carbonate solubility data. The values are

$$K_{a1} = (4.457 \pm 0.050) \times 10^{-7} \text{ mol kg}^{-1},$$

$$K_{a2} = (4.688 \pm 0.075) \times 10^{-11} \text{ mol kg}^{-1},$$

$$K_p = (0.033\,71 \pm 0.000\,15) \text{ mol kg}^{-1} \text{ bar}^{-1}.$$

The K_p value is a form of Henry's constant for the reaction $CO_2(g) \rightleftarrows CO_2(aq)$.

The choice of values to represent the hydrogen sulfide dissolution and dissociation in evaluation of metal sulfide solubility is more difficult. Ellis and Giggenbach[28,29] presented evidence in 1971 that the second dissociation constant of H_2S is 8×10^{-18} at 298 K. The value is much smaller than the usually accepted value of 1×10^{-13}, which is a value consistent with the NBS Technical Note 270[14] data, or the value near 1×10^{-14} used in the evaluation of Stephens and Cobble.[32] In our earlier paper,[1] we suggested use of the value of Maronny,[30] which is a little smaller than the accepted value above.

Rao and Hepler[31] have compiled and evaluated the dissociation constant data for hydrogen sulfide. Although they

Table 2. Formation constants at 298 K for mercury(II) complexes [5].

Reaction	Formation constants					
	F^-	Cl^-	Br^-	I^-	CN^-	SCN^-
$Hg^{2+}(aq) + X^-(aq) = HgX^+(aq)$ K_1	38	5.8×10^6	1.1×10^9	6.4×10^{12}	2.0×10^{17}	1×10^9
$HgX^+(aq) + X^-(aq) = HgX_2(aq)$ K_2		2.5×10^6	2.5×10^8	1.3×10^{11}	1.7×10^{17}	1×10^8
$HgX_2(aq) + X^-(aq) = HgX_3^-(aq)$ K_3		6.7	1.5×10^2	6.2×10^3	5.5×10^3	7×10^2
$HgX_3^-(aq) + X^-(aq) = HgX_4^{2-}(aq)$ K_4		13	23	1.1×10^2	1.0×10^3	7×10^1
$Hg^{2+}(aq) + 4X^-(aq) = HgX_4^{2-}(aq)$ β_4		1.3×10^{15}	9.2×10^{20}	5.6×10^{29}	1.9×10^{41}	5×10^{21}

cannot completely reject the results of Ellis and Giggenbach,[28,29] Rao and Hepler find that the calorimetric values of the enthalpy of neutralization of aqueous H_2S are not consistent with a $\log K_{a2}$ value as negative as -17.

The problem is still not solved. The recent evaluations of Tsonopoulos, Coulson, and Inman[298] and Brewer[299] support the smaller value of K_{a2} of H_2S. The experimental work of Meyer *et al.*[300] also supports the smaller value. Meyer *et al.* converted their Raman spectra data in 16.9 *M* NaOH, 0.1 *M* $NaClO_4$ and 0.5 *M* H_2S to a pK_{a2} value of 17.0 ± 1.0. The value required estimations of water dissociation properties and OH^-, HS^-, and S^{2-} activity coefficients in the concentrated solution.

Although the dissociation constant values suggested by Tsonopoulos *et al.* and Rao and Hepler differ, they probably agree within the experimental uncertainties of the measurements. We suggest the use of the Rao and Hepler values for K_{a1} since their evaluation covers a larger temperature interval. The values at 298.15 K are

$$K_{a1} = 1.02\times10^{-7} \quad \text{or} \quad \log K_{a1} = -6.99$$

$$\Delta\bar{H}^\circ_1 = 22.2\ \text{kJ mol}^{-1}, \quad \Delta\bar{C}^\circ_{p1} = -314\ \text{J K}^{-1}\ \text{mol}^{-1}.$$

For temperatures between 288 and 308 K,

$$\log K_{a1} = -3.10 - 1158/(T/\text{K})$$

and for temperatures up to 550 K,

$$\log K_{a1} = 106.67 - 6045.2/(T/\text{K}) - 37.744 \log (T/\text{K}).$$

For the value of pK_{a2}, we suggest either 17.0 ± 1.0 from Meyer *et al.*[300] or use of the approximation of Tsonopoulos *et al.*[298] of $K_{a2} \cong 0.018\ K_w$, where K_w is the ion product constant of water under similar conditions of temperature and pressure. A Henry's constant of $K_p = 0.099$ mol kg^{-1} bar^{-1} follows from data in NBS Technical Note 270.[14]

Gregory, Moreno, and Brown[33] selected dissociation constants of orthophosphoric acid at temperatures of 278.15, 288.15, 298.15, and 310.65 K that appear reliable. Because there are questions as to whether mercury orthophosphate salts are the stable solid at any pH, the values may have little application in interpreting solubility data.

Other useful evaluations of dissociation constants at high temperatures and pressures include that of Barnes and Ellis[34] for some ten acids, bases, and salts, and that of Marshall and Franck[35] for the ion product constant of water from 0 to 1000 °C and 1 to 10 000 bar.

3.4. Standard Electrode Potential Values

Hepler and Olofsson[5] recommend use of Vanderzee and Swanson's[17] evaluation of the reduction potentials at 298.15 K. Vanderzee and Swanson took into account contributions of liquid junction potentials and hydrolysis reactions in an examination that made use of the Debye–Hückel equation and existing activity coefficients to obtain the values

$$Hg_2^{2+}(aq) + 2e^- \rightleftarrows 2Hg(l) \qquad E^\circ_{298} = 0.7960\ \text{V}$$

$$Hg^{2+}(aq) + 2e^- \rightleftarrows Hg(l) \qquad E^\circ_{298} = 0.8535\ \text{V}$$

$$2Hg^{2+}(aq) + 2e^- \rightleftarrows Hg_2^{2+} \qquad E^\circ_{298} = 0.9110\ \text{V}.$$

We concur that these are the best values currently available. The value of the Hg/Hg_2^{2+} potential suggested by Charlot *et al.*[16] is smaller by about 0.5% and should not be used.

Choudhary and Prasad[276] published a paper in 1982 in which they report Hg/Hg_2^{2+} potential values as a function of temperature between 278 and 308 K:

T/K	278.15	283.15	288.15	293.15	298.15	303.15	308.15
E°/V	0.8014	0.8003	0.7991	0.7978	0.7965	0.7952	0.7938

These are suggested as tentative values for use over the 278–308 K temperature interval. The 298 K value agrees within 0.06% of the recommended value.

4. Solubility Data

This section contains solubility data on mercury and on the sparingly soluble salts of mercury (I) and mercury (II) in water and in aqueous electrolyte solutions. Each mercury compound is identified by its formula, Chemical Abstracts Registry Number, and formula weight. The 1979 atomic weights[36] were used. Terrestrial mercury is composed of the seven isotopes of mass number (at.%) 196(0.2), 198(10.1), 199(17.0), 200(23.1), 201(13.2), 202(29.6), and 204(6.8). The atomic weight is 200.59 ± 0.03.

The physical characteristics of each solid mercury compound are described briefly when crystallographic information is available. The primary source is the *Crystal Data Determinative Tables*.[13] This section is followed by a discussion of the available experimental solubility data used in the evaluation, a table of recommended or tentative solubilities in water, and, if appropriate, an equation for the smoothed data. The solubility product values are treated similarly. An uncritical list of some typical formation constants of complex ions formed in the system is often given.

In some cases, a table is included that summarizes the available literature on the solubility of the salt in aqueous electrolyte solution. These tables are a guide to the solubility literature that has not been tabulated in standard handbooks. These tables are collected in the Appendix (Sec. 8).

The mercury compounds in the following tables are arranged according to the "Standard Order of Arrangement" described in the NBS Technical Note series.[14]

4.1. Mercury

Mercury

Hg [7439-97-6] Atomic weight 200.59 ± 0.03

Physical characteristics: Density and vapor pressure are two properties of mercury that have relevance to solubility. Ambrose, Brown, and Herington[37] give recommended density values of liquid mercury from 253 to 573 K. Ambrose and Sprake[38] should be consulted for the most up-to-date survey of liquid mercury vapor pressures.

Mercury dissolved in air-free water is monatomic and unionized with the zero-valent mercury atom in the spherically symmetric $^1S_0$ ground state.[39a–c] The molal and mole fraction solubilities increase with temperature and decrease with pressure. Henry's constant, as $K_p/\text{bar} = (p_{Hg}/\text{bar})/x_{Hg}$, goes through a maximum with temperature at about 460 K. Experimental values of the solubility of mercury in

Table 3. Experimental values of the solubility of mercury in water

Temperature T/K	10^7 Molality m_{Hg}/mol kg^{-1}	10^9 Mole Fraction x_{Hg}	Henry's Constant K/atm	Henry's Constant K/bar	Reference
273.15	1.20*	2.16	121	123	Spencer, Voigt [42]
277.45	2.27*	4.09	97.4	98.7	Glew, Hames [44]
278.15	0.957*	1.72	248	251	Sanemasa [46]
283.15	1.37*	2.46	277	281	Sanemasa [46]
284.56	2.31*	4.15	187	189	Glew, Hames [44]
288.12	2.14*	3.86	277	281	Glew, Hames [44]
288.65	2.10*	3.77	298	302	Spencer, Voigt [42]
292.95	2.44*	4.40	372	377	Glew, Hames [44]
293.15	2.25*	4.04	412	417	Sanemasa [46]
	2.40*	4.33	384	389	Spencer, Voigt [42]
298.15	2.81*	5.06	502	509	Spencer, Voigt [42]
	3.00*	5.42	469	475	Moser, Voigt [23]
	3.06*	5.51	461	467	Onat [45]
	3.15*	5.67	448	454	Choi, Tuck [43]
298.17	2.99*	5.39	472	478	Glew, Hames [44]
301.15	1.50	2.70	1200	1216	Pariaud et al. [41]
303.15	1.25	2.26	1690	1710	Stock et al. [40]
	2.91*	5.25	728	738	Spencer, Voigt [42]
	4.07*	7.33	522	529	Sanemasa [46]
303.17	3.59*	6.47	592	600	Glew, Hames [44]
303.24	3.47*	6.25	616	624	Glew, Hames [44]
308.15	3.42*	6.16	922	934	Spencer, Voigt [42]
	5.43*	9.79	580	588	Choi, Tuck [43]
312.31	4.39*	7.90	989	1002	Glew, Hames [44]
313.15	5.16*	9.30	895	907	Onat [45]
	6.88*	12.4	671	680	Sanemasa [46]
318.22	4.54*	8.16	1480	1500	Glew, Hames [44]
322.95	5.48*	9.88	1720	1740	Glew, Hames [44]
323.15	7.52*	13.5	1280	1295	Onat [45]
	8.82	15.9	1090	1105	Choi, Tuck [43]
	11.0	19.8	872	884	Sanemasa [46]
323.39	4.95*	8.92	1970	1995	Glew, Hames [44]
326.86	5.38*	9.70	2310	2340	Glew, Hames [44]
333.13	6.52*	11.8	2710	2745	Glew, Hames [44]
333.15	11.0	19.8	1730	1755	Onat [45]
	18.7	33.6	1020	1035	Sanemasa [46]
335.43	7.38*	13.3	2990	3030	Glew, Hames [44]
338.15	10.8	19.5	2490	2525	Choi, Tuck [43]
341.34	8.72*	15.7	3710	3760	Glew, Hames [44]
343.15	13.6	24.6	2650	2685	Onat [45]
345.59	9.71*	17.5	4330	4385	Glew, Hames [44]
353.15	13.0*	23.14	5110	5180	Choi, Tuck [43]
	16.8	30.3	3950	4000	Onat [45]
358.15	15.4*	27.8	5750	5825	Stock et al. [40]
363.15	16.7*	30.0	7070	7165	Choi, Tuck [43]
373.15	31.2	56.2	6480	6565	Stock et al. [40]
393.15	52.9*	95.2	10400	10550	Reichardt et al. [39c]
573.15	-	36300[a]	8970[a]	9090	Sorokin [47a]
673.15	-	369000[a]	5620[a]	5695	Sorokin [47a]
773.15	-	2790000[a]	2900[a]	2940	Sorokin [47a]

[a] Hypothetical 1 atm values extrapolated from Sorokin's experimental values.

* Values used in linear regression.

water range from 2.7×10^{-5} g kg^{-1} at 273 K and 1 bar to 24 g kg^{-1} at 773 K and 507 bar, decreasing to about 15 g kg^{-1} at 773 K and 1013 bar.

The solubility of metallic mercury in water has been measured by a variety of experimental techniques by Bonhoeffer and Reichardt,[39c] Stock *et al.*,[40] Pariaud and Archinard,[41] Moser and Voight,[23] Spencer and Voight,[42] Choi and Tuck,[43] Glew and Hames,[44] Onat,[45] Sanemasa,[46] Sorokin,[47a] Kawahara *et al.*,[47b] Gjessing and Rogne,[277] and Baltisberger *et al.*[283] Their solubility values, recalculated where necessary as molality, mole fraction, and Henry's constant K_p/bar are given in Table 3. The recent value determined by Gjessing and Rogne[277] is very small. It is only about 15% of the value reported by others and is not given here. Baltisberger *et al.*[283] report a mercury solubility in water at 303 K that agrees well with the other workers. Their paper was discovered too late to include the value in Fig. 1. The solubility values at 298.15 K of six of these workers agree with a standard deviation that is 4% of the average solubility value, but at lower and higher temperatures, the results do not agree nearly as well.

The recommended value of the solubility of mercury in water is $(3.03 \pm 0.12)\times10^{-7}$ mol kg^{-1} at 298.15 K. The value is the average of the experimental values of Moser and Voight,[23] Spencer and Voight,[42] Choi and Tuck,[43] Glew and Hames,[44] and Onat[45] and the value interpolated from the data of Sanemasa.[46]

Choi and Tuck,[43] Glew and Hames,[44] and Sanemasa[46] each carried out their measurements over about a 60° temperature interval. The three used widely differing experimental techniques. The values of Choi and Tuck do not fall on a smooth solubility-temperature curve, but in general

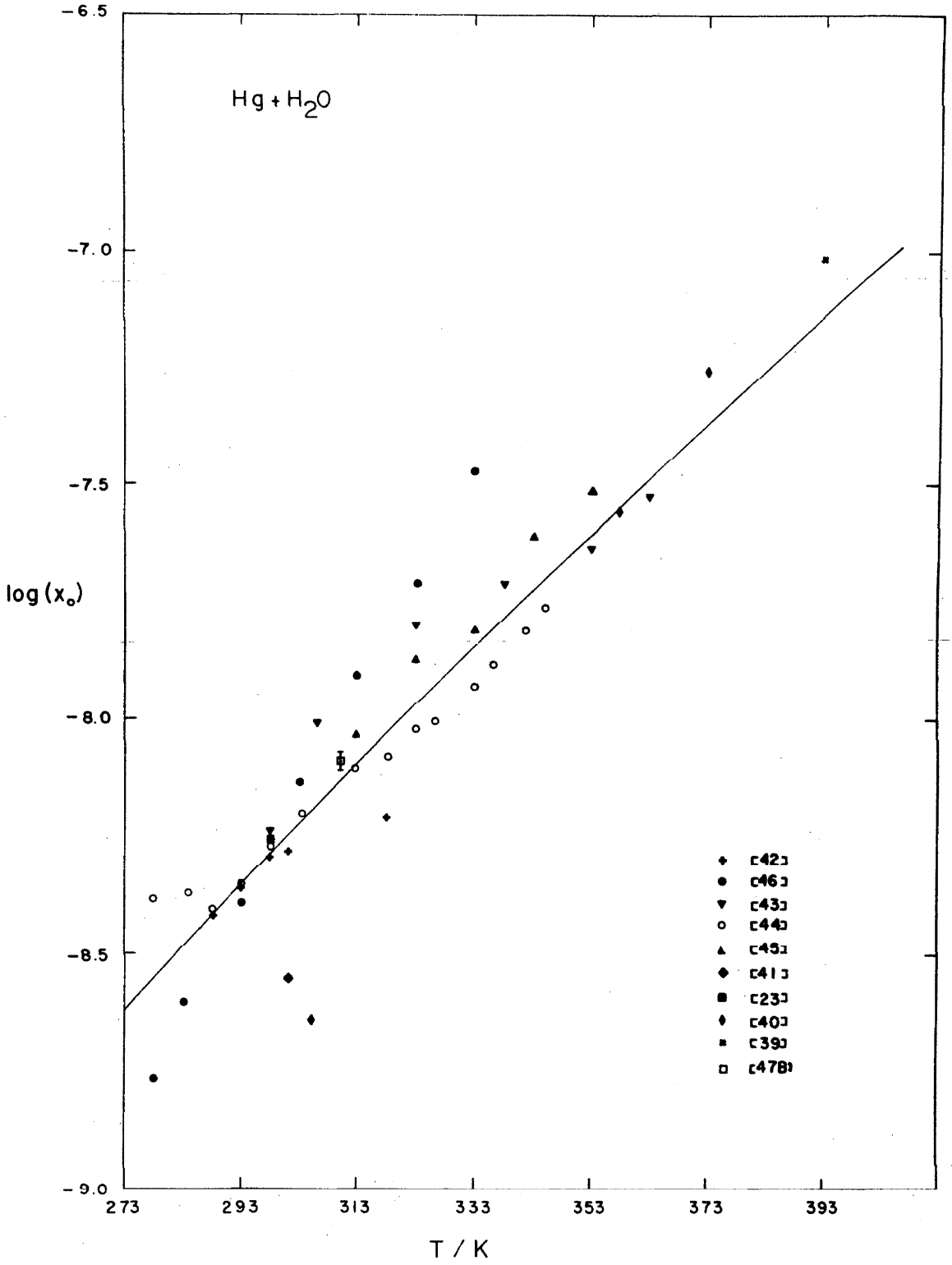

FIG. 1. The solubility of mercury in water. $\log(x_{Hg})$ vs T/K

Experimental mole fraction solubility values from Moser and Voight (Ref. 23), Bonhoeffer and Reichardt (Ref. 39c), Stock *et al.* (Ref. 40), Pariaud and Archinard (Ref. 41), Spencer and Voight (Ref. 42), Choi and Tuck (Ref. 43), Glew and Hames (Ref. 44), Onat (Ref. 45), Sanemasa (Ref. 46), and Kawahara *et al.* (Ref. 47b). See text for comments about other literature values (Refs. 277, 283, 309–311).

they fall between the values of the other two. The values of Glew and Hames and of Sanemasa do fall on smooth but different curves. The solubility values of the three agree fairly well at 298.15 K, but at 278 K, Sanemasa's value is only one-half the value of Glew and Hames, while at 333 K, Sanemasa's value is three times as large as that of Glew and Hames. All of the workers except Sanemasa equilibrated liquid mercury with liquid water. Sanemasa equilibrated mercury vapor with the liquid water.

The question of oxidation of mercury has been extensively discussed. Choi and Tuck[43] and Voight and co-workers[23,42] used radioactive mercury, which generates oxidizing agents that can react with mercury to form mercury (II). Voight and co-workers found that the apparent mercury solubility slowly increased with time unless they used a reducing medium. In the presence of a small amount of hypophosphorous acid as a reducing agent, their solubility values were reproducible and independent of time. Other workers pointed out the possibility of air oxidation of mercury and were careful to use air-free water.

Glew and Hames[44] used nonradioactive mercury, deoxygenated water, and a reducing medium. At temperatures greater than 298 K, their solubility values are smaller than others.

Sanemasa[46] disputes the possibility of air oxidation. He bases his conclusion that air oxidation of mercury is not a problem on two experiments. First, the same solubility of mercury in water is obtained under both nitrogen and air atmospheres. Second, his analytical method depends on a direct detection of metallic mercury by atomic absorption. As normally applied, the method contains a step at which any mercury (II) present is reduced to mercury by stannous chloride. He obtains the same solubility value within 2% when the reduction step is omitted as when it is used. This indicates that negligible mercury (II) as an oxidation product is present. Sanemasa does not state whether those tests were made at all temperatures or at just one or two temperatures.

In the Sanemasa experiment, the water is saturated with mercury vapor in nitrogen as a carrier gas. The gas is bubbled into a 100–200 cm^3 water sample. Sanemasa states that the gas phase, without liquid water in the apparatus, is saturated with Hg vapor in 5–30 min. With liquid water present, the circulating gas is saturated within 10–30 min. The liquid water is expected to reach saturation equilibrium with the mercury vapor within 60 min.

We have taken thermodynamic data from the NBS Technical Notes,[14] from Hepler and Olofsson,[5] and oxygen solubility data from Battino[48] to calculate equilibrium yields of mercury (II) due to air oxidation by several models. The results are not definitive, but they strongly suggest that air oxidation of mercury may be a problem at the temperatures of these experiments.

The evaluation of the mercury + water system solubility presents problems that can be settled only by new experimental work. For the present we classify all of the experi-

Table 4. Tentative Values of the solubility of mercury in water.

Temperature T/K	Mercury Solubility: Molality $10^7\ m_{Hg}$/mol kg^{-1}	Mercury Solubility: Mol Fraction $10^9\ x_{Hg}$	Henry's Constant[b] K/atm	Henry's Constant[c] K/bar
273.15	1.36	2.45	108	109
278.15	1.58	2.84	151	153
283.15	1.83	3.30	208	211
288.15	2.12	3.83	282	286
293.15	2.46	4.43	376	381
298.15	2.85[a]	5.14	495	502
303.15	3.30	5.95	642	651
308.15	3.82	6.89	823	834
313.15	4.42	7.97	1040	1054
318.15	5.11	9.21	1310	1327
323.15	5.91	10.6	1620	1641
328.15	6.82	12.3	1980	2006
333.15	7.87	14.2	2400	2432
338.15	9.08	16.3	2890	2928
343.15	10.5	18.8	3450	3495
348.15	12.0	21.7	4.07×10^3	4.12×10^3
353.15	13.8	24.9	4.77×10^3	4.83×10^3
358.15	15.9	28.6	5.56×10^3	5.63×10^3
363.15	18.3	32.9	6.42×10^3	6.51×10^3
368.15	21.0	37.7	7.36×10^3	7.46×10^3
373.15	24.0	43.3	8.39×10^3	8.50×10^3
378.15	27.5	49.6	9.5×10^3	9.63×10^3
383.15	31.5	56.8	10.7×10^3	10.84×10^3
388.15	36.0	64.9	12.0×10^3	12.16×10^3
393.15	41.2	74.2	13.3×10^3	13.48×10^3

[a] The recommended value at 298.15 K is $(3.03 \pm 0.12) \times 10^{-7}$ mol kg^{-1}. The value here is a tentative value that is consistent with the full set of smoothed data.

[b] Henry's constant, $K_H/atm = (p_{Hg}/atm)/x_{Hg}$.

[c] Henry's constant, $K_H/bar = (P_{Hg}/bar)/x_{Hg}$.

Table 5. Solubility of mercury in water at elevated temperatures and pressures. Sorokin [47a].

	Pressure		Mercury Solubility		
T/K	p/atm	p/bar	m/g kg^{-1}	m_1/mol kg^{-1}	mol fraction 10^3 x_1
573	500	507	0.29	0.0014	0.0260
573	640	648	0.24	0.0012	0.0216
571	900	912	0.19	0.0009	0.0171
673	400	405	3.37	0.0168	0.302
673	500	507	2.76	0.0138	0.248
673	495	502	3.22	0.0161	0.289
673	700	709	2.47	0.0123	0.222
673	700	709	2.80	0.0140	0.251
671	920	932	2.23	0.0111	0.200
674	910	922	2.13	0.0106	0.191
773	500	507	24.12	0.1202	2.16
775	510	517	23.71	0.1182	2.12
773	520	527	20.21	0.1008	1.81
768	755	765	18.45	0.0920	1.65
780	700	709	19.90	0.0992	1.78
771	990	1003	16.36	0.0816	1.47
776	960	972	13.41	0.0667	1.20

mental values as tentative. However, we have a preference for the smaller solubility values of Glew and Hames and the other data that approach the Glew and Hames curve (Fig. 1). New experiments may show that the Sanemasa data are the most reliable, but at present we have two reservations about them. First, we are concerned about the time of saturation. We have extensive experience in saturating liquids with gases. In thin films, liquids saturate in seconds; in bulk liquid, saturation may take hours. An interval of 60 min to establish vapor equilibrium ($Hg + N_2$) and solution equilibrium ($Hg + H_2O$) throughout a closed circulating system seems too short a time. We would expect the solubility values to be too small. Compared to the results of other workers, the Sanemasa values are too small at temperatures of 278, 283, and 293 K. Second, we are concerned about the problem of the oxidation of mercury during the experiment. This is a problem that needs further study. Our rather crude thermodynamic calculations indicate that oxygen partial pressures as low as 10^{-3} bar could oxidize enough mercury to mercury (II) in aqueous solution to affect the solubility results. There may be a kinetic aspect to the problem. At temperatures below room temperature, the reaction rate may be negligible, but at temperatures above about 303 K, the rate may be large enough to quickly attain the equilibrium yield of mercury (II) if either oxygen is not rigorously excluded or a reducing environment is not maintained.

We have fitted 36 solubility values, marked "*" in Table 3, by a linear regression to obtain the smoothed values of molality, mole fraction, and Henry's constant between 273.15 and 393.15 K in Table 4. The Henry's constants were calculated from the mole fraction solubilities and the mercury vapor pressures, calculated from Eq. (36) in Douglas, Ball, and Ginnings.[49] These are tentative values, which we believe represent the lower range of acceptable values of the solubility of metallic mercury in water. Future experiments may justify the larger solubility values. Those modeling the solubility of liquid mercury may want to take the Glew and Hames data as the lower bound and Sanemasa's data as the upper bound of mercury solubility values at 298 K and above.

The smoothed solubility data equations for the 273.15–393.15 K temperature interval are

$$\ln(m_{Hg}/\text{mol kg}^{-1}) = -39.0991 + 20.5648/(T/100\text{ K}) + 15.6815\ln(T/100\text{ K}) \quad (1)$$

with a standard error about the regression line of 2.2×10^{-7},

$$\ln(x_{Hg}) = -43.3343 + 20.9053/(T/100\text{ K}) + 15.7778\ln(T/100\text{ K}) \quad (2)$$

with a standard error about the regression line of 3.9×10^{-9}, and

$$\ln(K_H/\text{bar}) = 55.7339 - 95.4036/(T/100\text{ K}) - 16.0477\ln(T/100\text{ K}) \quad (3)$$

with a standard error about the regression line of 561.

Sorokin[47a] has measured the solubility of mercury in

Table 6. Henry's constant for mercury at 573, 673, and 773 K as a function of pressure. Sorokin [47a].

	Total Pressure		Henry's Constant	
T/K	p/atm	p/bar	10^{-4} K/atm	10^{-4} K/bar
573	1	1.013	0.90	0.91
	500	507	1.56	1.58
	750	760	2.06	2.09
	1000	1013	2.72	2.76
673	1	1.013	0.56	0.57
	500	507	0.90	0.91
	750	760	1.18	1.20
	1000	1013	1.53	1.55
773	1	1.013	0.290	0.294
	500	507	0.464	0.470
	750	760	0.591	0.599
	1000	1013	0.756	0.766

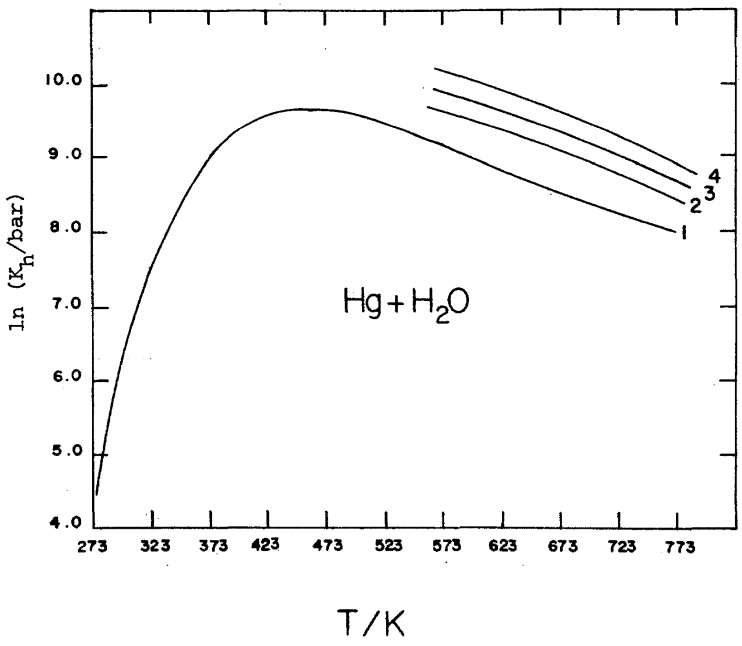

FIG. 2. The solubility of mercury in water. $\ln(K_H/\text{bar})$ vs T/K.
(1) 1 bar, (2) 507 bar, (3) 760 bar, and (4) 1013 bar. Curves based on data of Glew and Hames (Ref. 44) and of Sorokin (Ref. 47a).

oxygen-free water at temperatures of about 573, 673, and 773 K, and at total pressures between 507 and 1013 bar (argon + water vapor + mercury). His experimental values are given in Table 5. Sorokin calculated Henry's constants with corrections for the fugacity of the mercury vapor. Those values plus values extrapolated to a hypothetical 1-bar total pressure are given in Table 6.

We have combined the Henry's constants calculated from the data of Glew and Hames[44] with the hypothetical 1-bar values of Sorokin[47a] to obtain the equation

$$\ln(K_H/\text{bar}) = 157.119 - 242.287/(T/100\text{ K}) - 79.863\ln(T/100\text{ K}) + 5.896(T/100\text{ K}) \quad (4)$$

for use between 393 and 773 K. The equation reproduces the data with an average deviation of 6%. Figure 2 shows $\ln(K_H/\text{bar})$ versus T and includes the values of Sorokin at 507, 760, and 1013 bar. The 1-bar values of Henry's constant show a maximum at (458 ± 3) K (185 °C).

Papers of Khodakovsky, Popova, and Ozerova,[309] Sorokin, Alekhin, and Dadze,[310] and Okouchi and Sasaki[311] arrived too late to be included in the present evaluation. Their data will not materially change the recommendations made above.

Several papers report the solubility of mercury in aqueous electrolyte solution. Glew and Hames[50] measured the solubility of mercury in 6.10 mol kg^{-1} sodium chloride solution at temperatures between 278.39 and 332.92 K. Their data show that mercury is salted out below 324 K but salted in at higher temperatures. Chviruk and Koneva[51] determined the vapor pressure of mercury over a 3.82 mol dm^{-3} sodium chloride solution, undersaturated, saturated, and supersaturated with mercury at temperatures of 293, 313, 333, and 353 K. The data have an uncertainty of ± 20%. The authors give a smoothed equation for Henry's constant in the form

$$K_H = (p_{Hg}/\text{mg dm}^{-3})/(c_{Hg}/\text{mg dm}^{-3}),$$

which is

$$\log K_H = 4.276 - 0.515\log(T/\text{K}) - 937.4/(T/\text{K}). \quad (5)$$

The pressure is actually the function Mp/RT, which is the vapor density in mg dm^{-3}.

Sanemasa, Haraguchi, and Nagai[52] report salt effect parameters for mercury in aqueous solutions of 11 electrolytes at 298.15 K. Sanemasa *et al.* use the salt effect parameter in the form

$$k_{scc}/\text{dm}^3\text{ mol}^{-1} = [1/(c_s/\text{mol dm}^{-3})]\log(c^\circ_{Hg}/c_{Hg}),$$

where c_s is the electrolyte concentration and c°_{Hg} and c_{Hg} are the molar mercury solubilities in pure water and in the salt solution, respectively. Glew and Hames use the salt effect parameter

$$k_{smm}/\text{kg mol}^{-1} = [1/(m_s/\text{mol kg}^{-1})]\log(m^\circ_{Hg}/m_{Hg}),$$

where the salt and solubility values are in molal units. The salt effect parameters determined by Sanemasa *et al.* and the 298.15 K value of Glew and Hames are given in Table 7. All of the values are classed as tentative.

Both Sanemasa[46] and Baltisberger *et al.*[283] report solubilities of mercury in seawater. The values are consistent with the salting out properties of the electrolytes in seawater.

Table 7. Salt effect parameters for the Hg + salt + water system at 298.15 K. Sanemasa et al. [52].

Electrolyte	Salt Effect Parameter[a]	
	k_{scc}/dm^3 mol^{-1}	k_{scx}/dm^3 mol^{-1}
NaCl	0.079	0.087
	0.056[b]	-
$NaNO_2$	0.062	0.065
Na_2SO_4	0.308	0.319
NaBr	0.017	0.023
NaSCN	-0.035	-0.034
NaF	0.157	0.174
$NaClO_4$	0.117	0.114
KCl	0.070	0.074
$BaCl_2$	0.115	0.121
$(CH_3)_4NBr$	-0.078	-0.112
$(C_2H_5)_4NBr$	-0.116	-0.176
NaI[c]	-	-

[a] K_{scc}/mol dm^{-3} = $(1/c_s)\log(c^\circ_{Hg}/c_{Hg})$, K_{scx} = $(1/c_s)\log(x^\circ_{Hg}/x_{Hg})$, and K_{smm}/mol kg^{-1} = $(1/m_s)\log(m^\circ_{Hg}/m_{Hg})$.

[b] Glew and Hames [50]. k_{smm}/mol kg^{-1} = 0.041. The paper contains k_{smm} values at 5 degree intervals from 278-343 K for Hg in 6.10 molal NaCl. The salt effect parameter changes in sign at 325 K and salts in at the higher temperatures.

[c] Chemical interaction, no measurement possible.

4.2. Mercury Fluoride

a. Mercury (I) Fluoride

Hg_2F_2 [13967-25-4] Molecular weight 439.18

b. Mercury (II) Fluoride

HgF_2 [967-25-4] Molecular weight 238.59

$HgF_2 \cdot 2H_2O$ [26453-89-4] Molecular weight 274.61

Physical characteristics: the dihydrate is an orthorhombic crystal with $Z = 8$, $a = 10.00 \times 10^{-10}$ m, $b = 7.15 \times 10^{-10}$ m, and $c = 8.89 \times 10^{-10}$ m. The density is 5720 kg m^{-3}.[295]

No references to the solubility of either mercury (I) fluoride or mercury (II) fluoride in water or aqueous electrolyte solutions were found. There are solubility data in anhydrous HF at several temperatures for both salts.[53] Jaeger[296] studied the HgO + HF + H_2O system at 298.2 K in dilute HF (up to 4.3 wt.%) and reported HgO as the solid phase. Polyshchuk *et al.*[295] extended the study to the 5.9–100 wt. % HF range and found the stable solids to be HgOHF between 5.9 and 18.4 wt.% HF, and $HgF_2 \cdot 2H_2O$ over the 23.6–76.7 wt.% HF range. The solubility, as HgO, decreases from 15.0 to 2.8 wt.% as the weight percent HF increases from 23.6 to 76.7.

Cotton and Wilkinson[54] state that mercury (I) fluoride is unstable toward water, being hydrolyzed to HF and unisolatable mercury (I) hydroxide, which disproportionates to mercury and mercury (II) hydroxide. Mercury (II) fluoride, which is essentially ionic and crystalline in the fluoride structure, is almost completely decomposed by cold water. Durrant and Durrant[55] state that the solubility of mercury (II) fluoride in water is decreased by the presence of potassium fluoride, but they give no reference for the statement. They suggest that the behavior indicates weak or nonexistent complexing between Hg(II) and F^-. Paul[56] reports weak mercury (II)–fluoride complexes with formation constants of a magnitude of about 10, which is of similar magnitude to the value recommended in Table 2. Solid mercury (II) fluoride normally exists as the dihydrate $HgF_2 \cdot 2H_2O$. The *Kirk–Othmer Encylopedia of Chemical Technology*[308] contains a summary of the physical properties of the mercury fluorides.

4.3. Mercury Chloride

a. Mercury (I) Chloride

Hg_2Cl_2 [10112-91-1] Molecular weight 472.09

Physical characteristics: Solid mercury (I) chloride is a tetragonal crystal with $Z = 2$, $a = 4.45 \times 10^{-10}$ m, and $c = 10.89 \times 10^{-10}$ m. The calculated density is 7225 kg m^{-3}. Several oxychloride minerals are known. There is no mention of hydrate formation.

Marcus recently evaluated the solubility of mercury (I) chloride for this journal.[3] We accept his evaluation and summarize it briefly here.

Marcus recommends the solubility product K°_{s0}/mol^3 kg^{-3} between 278.15 and 318.15 K calculated from the equation

$$\log(K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3}) = -(17.884 \pm 0.017) + (0.0622 \pm 0.0002)\Delta T - (3.0 \pm 0.2) \times 10^{-4}(\Delta T)^2, \quad (6)$$

where $\Delta T = T/\text{K} - 298.15$. Values calculated from the equation agree most closely with the experimental values of Galloway.[57] Solubility product values at several temperatures are given below.

T/K	K°_{s0}/mol^3 kg^{-3}
278.15	$(5.65 \pm 0.22) \times 10^{-20}$
298.15	$(1.43_3 \pm 0.05_6) \times 10^{-18}$
318.15	$(1.73_8 \pm 0.06_8) \times 10^{-17}$

Dry and Gledhill[58] measured the total concentration of soluble mercury species in a saturated aqueous Hg_2Cl_2 solution at 298.15 K to be $(7.5 \pm 0.3) \times 10^{-6}$ mol dm^{-3}. Marcus[3] calculated a value of $(8.4 \pm 1.0) \times 10^{-6}$ mol dm^{-3} from a set of five equations, which took into account equilibria among the mercury species $Hg(OH)_2$, $HgCl_2$, $HgOH^+$, $HgCl^+$, Hg_2^{2+}, and Hg_2OH^+, in addition to H^+ and Cl^- ions. Values at other temperatures cannot be calculated, since the temperature coefficients of the various constants and of the pH are unknown.

b. Mercury (II) Chloride

$HgCl_2$ [7487-94-7] Molecular weight 271.50

Physical characteristics: Solid mercury (II) chloride is orthorhombic with $Z = 4$, and with a, b, and c equal to 5.963, 12.735, and 4.325×10^{-10} m, respectively. The calculated density is 5457 kg m^{-3}. There are crystallographic data on mixed crystals HgClBr and HgClSCN. Several ox-

Table 8. Solubility of mercury(II) chloride in water.

T/K	Molality m_{HgCl_2}/mol kg^{-1}	Reference
273.15	0.21	Ditte, 1881 [62]
	0.151	Schreinemakers, 1910 [63]
	0.16	Aslanov and Blidin, 1959 [64]
273.25	0.149	Étard, 1894 [60]
274.05	0.173	Eddy and Menzies, 1940 [59]
277.65	0.185	Étard, 1894 [60]
278.15	0.1707	Mikhailov and Grigor'eva, 1968 [65]
280.65	0.197	Étard, 1894 [60]
283.15	0.1920	Mikhailov and Grigor'eva, 1968 [65]
283.15	0.193	Aslanov, 1963 [66]
286.95	0.201	Étard, 1894 [60]
288.15	0.2164	Mikhailov and Grigor'eva, 1968 [65]
288.15	0.211	Flöttmann, 1928 [67]
288.71	0.206	Greenish and Smith, 1903 [68]
289.15	0.26	Ditte, 1881 [62]
288/291	0.20	Pélabon and Delwaulle, 1930 [69]
291.15	0.229	Laird, 1920 [70]
293.15	0.272	Tikhomirov, 1907 [71]
293.15	0.242	Flöttmann, 1928 [67]
293.15	0.320	Aslanov, 1963 [66]
293.15	0.2407	Mikhailov and Grigor'eva, 1968 [65]
294.05	0.244	Eddy and Menzies, 1940 [59]
room	0.272	Rohland, 1898 [72]
298.15	0.266	Morse, 1902 [73]
	0.272	Foote, 1903 [74]
	0.273	Sherrill, 1903 [75]
	0.267	Osaka, 1903/08 [76]
	0.271	Herz and Anders,1907 [77]
	0.269	Herz and Paul, 1913 [78]
	0.267	Moles and Marquina, 1924 [79]
	0.2596	Benrath, 1927 [80]
	0.268	Flöttmann, 1928 [67]
	0.2658	Benrath and Ammer, 1929 [81]
	0.272	Bassett and Croucher, 1930 [82]
	0.2658	Thomas, 1939 [83]
	0.269	Eddy and Menzies, 1940 [59]
	0.27	Laurent et al., 1955 [84]
	0.273	Blidin, 1957 [85]
	0.265	Lilich, 1959 [86]
	0.2711	Mikhailov and Grigor'eva, 1968 [65]
	(0.2616 mol dm^{-3})	Abraham et al., 1970 [87]
	0.263	Anderson et al., 1973 [88]
	0.257	Fridman et al., 1974 [89]
	0.262	Kartzmark, 1982 [90]
298.25	0.281	Étard, 1894 [60]
302.65	0.302	Étard, 1894 [60]
303.15	0.305	Meerburg, 1908 [91,92]
	0.305	Schreinemakers, 1910 [63]
307.15	0.344	Tourneux, 1919 [93]
308.15	0.342	Schreinemakers and Thonus, 1912 [94]
	0.345	Toda, 1922 [95]
	0.331	Lilich, 1959 [86]
311.15	0.401	Étard, 1894 [60]
312.35	0.380	Eddy and Menzies, 1940 [59]
317.15	0.45	Ditte, 1881 [62]
318.15	0.424	Lilich, 1959 [86]
	(0.375 mol dm^{-3})	Abraham et al., 1970 [87]
322.15	0.467	Étard, 1894 [60]
328.95	0.566	Eddy and Menzies, 1940 [59]
329.15	0.581	Torneux, 1919 [93]
334.15	0.651	Étard, 1894 [60]
335.85	0.687	Eddy and Menzies, 1940 [59]
348.55	0.995	Eddy and Menzies, 1940 [59]
353.15	1.13	Étard, 1894 [60]
353.15	1.12	Tourneux, 1913 [93]
360.15	1.44	Étard, 1894 [60]
364.75	1.612	Eddy and Menzies, 1940 [59]
372.85	2.110	Eddy and Menzies, 1940 [59]
373.15	2.38	Étard, 1894 [60]
	2.07	Tourneux, 1919 [93]
378.2	2.35	Benrath et al., 1937 [61]
378.8	2.773	Eddy and Menzies, 1940 [59]
389	3.54	Benrath et al., 1937 [61]
394	5.45	Étard, 1894 [60]
396	4.56	Benrath et al., 1937 [61]
400	8.47	Étard, 1894 [60]
402	5.88	Benrath et al., 1937 [61]
406	6.87	Benrath et al., 1937 [61]
413	12.3	Étard, 1894 [60]
414	8.84	Benrath et al., 1937 [61]
418	10.06	Benrath et al., 1937 [61]
423	13.3	Étard, 1894 [60]
430	14.7	Benrath et al., 1937 [61]
432	14.9	Étard, 1894 [60]
433	16.4	Étard, 1894 [60]
437	17.5	Benrath et al., 1937 [61]
438	16.5	Étard, 1894 [60]
448	23.6	Benrath et al., 1937 [61]
455	29.2	Benrath et al., 1937 [61]
468	39.1	Benrath et al., 1937 [61]
479	48.9	Benrath et al., 1937 [61]
496	67.1	Benrath et al., 1937 [61]
508	88.4	Benrath et al., 1937 [61]

Table 9. Recommended and tentative values of the solubility of mercury(II) chloride in water.

T/K	Solubility, m_{HgCl_2}/mol kg^{-1}
Recommended value	
298.15	0.269 ± 0.003
Tentative values	
273.15	0.163
278.15	0.178
283.15	0.196
288.15	0.217
293.15	0.242
298.15	0.270
303.15	0.304
308.15	0.343
313.15	0.388
318.15	0.441
323.15	0.503
328.15	0.575
333.15	0.659
338.15	0.758
343.15	0.873
348.15	1.009
353.15	1.167
358.15	1.353
363.15	1.571
368.15	1.827
373.15	2.128
378.15	2.481
390	3.34
418	9.95
438	17.5
458	29.4
478	47.2
498	73.
508	90.

ychloride mercury (II) minerals are known. There is no mention of hydrate formation in the solubility literature, but Durrant and Durrant[55] state that a dihydrate does exist.

The solubility of mercury (II) chloride in water and in various aqueous electrolyte solutions has been reported in about 60 papers since 1881. The solubility values in water are summarized in Table 8. The recommended solubility at 298.15 is (0.269 ± 0.003) mol kg^{-1}, which is the average and standard deviation of 19 of the 22 values in the table. The value agrees with the value recommended by Eddy and Menzies[59] in 1940.

The solubility data at other temperatures have been fitted by a linear regression to two equations: from 273.15 to 378.15 K,

$$\ln(m_{HgCl_2}/\text{mol kg}^{-1}) = -56.7732 + 68.4481/(T/100\text{ K}) + 29.7574\ln(T/100\text{ K}) \quad (7)$$

with a standard error about the regression line of 0.051 mol kg^{-1}, and from 383 to 508 K,

$$\ln(m_{HgCl_2}/\text{mol kg}^{-1}) = 14.7003 - 51.8426/(T/100\text{ K}). \quad (8)$$

Tentative values of the solubility of mercury (II) chloride in water calculated from Eqs. (7) and (8) are given in Table 9. Eddy and Menzies[59] showed that the International Critical Table solubility values for $HgCl_2$ were up to 16% too small at temperatures from 333 to 353 K. The present evaluation

Table 10. Solubility of mercury(II) chloride in deuterium oxide. Eddy and Menzies, [59].

T/K	Molality m_{HgCl_2}/mol kg^{-1}
281.25	0.129
291.85	0.170
300.35	0.213
322.05	0.369
330.55	0.463
340.45	0.605
364.35	1.212
378.25	2.024

confirms the observation. Values from Eqs. (7) and (8) are smaller at temperatures below 298.15 K, larger between temperatures of 303.15 and 368.15 K, and smaller again at temperatures of 373 and 378 K than the values of Eddy and Menzies. The differences range from zero to 3.5%.

At temperatures above 378 K there are two sets of data, the 1894 data of Étard[60] and the 1937 data of Benrath, Gjedebo, Schiffers, and Wunderlich.[61] At the lower and higher temperatures the two data sets agree, but at intermediate temperatures they differ by as much as a factor of 2. A graph of the data indicates that Étard's[60] values are too large, especially at the temperatures of 394, 400, 413, and 423 K. These data have been omitted in obtaining the 388–478 K equation above.

Eddy and Menzies[59] also measured the solubility of mercury (II) chloride in water–d_2, D_2O. The results are in Table 10. The solubility in D_2O is smaller than in H_2O, being about 75% of the H_2O solubility value at all temperatures between 281 and 378 K.

Table 1A (see Appendix) presents a survey of papers that contain $HgCl_2$ solubility data in aqueous electrolyte solution. Some of these data appear in Seidell and Linke.[6] The compound is relatively soluble and the solution species numerous, the predominant species probably being $HgCl_2$ in water.

One can calculate the following constants from the thermodynamic data in the NBS Technical Note series[14]:

$$HgCl_2(s) \rightleftarrows Hg^{2+}(aq) + 2Cl^-(aq) \quad K^\circ_{s0} = 7.1\times10^{-15}$$

$$HgCl_2(s) \rightleftarrows HgCl_2(aq) \quad K_s = 0.11$$

The $HgCl_2 + H_2O$ system can be modelled further by use of the formation constants in Table 2.

4.4. Mercury Bromide

a. Mercury (I) Bromide

Hg_2Br_2 [15385-58-7] Molecular weight 560.988

Physical characteristics: Solid mercury (I) bromide is a tetragonal crystal with two molecules per unit cell. The unit cell dimensions are $a = 4.65\times10^{-10}$ and $c = 11.10\times10^{-10}$ m. The calculated density is 7710 kg m^{-3}, but the measured density is only 7307 kg m^{-3}. No hydrates of mercury (I) bromide are mentioned.

The stoichiometric solubility values of mercury (I) bromide reported in the literature have been rejected as unreliable. The values are from early work in which the experimental methods and calculations are unclear or erroneous,[96–99] or they are calculated from the solubility product without taking into account the complex nature of the species in solution.[75]

A number of workers have determined the solubility product constant of mercury (I) bromide. Their results are given in Table 11 and Fig. 3. Only the data of Brodsky[100] and of Read[101] have been corrected to zero ionic strength. Their values agree fairly well, but we have a preference for the more modern careful work of Read,[101] which gives a self-consistent set of data over a large temperature interval. The recommended value at 298.15 K is the solubility product value,

$$K^\circ_{s0}/\text{mol}^3\ \text{kg}^{-3} = 6.40\times10^{-23},$$

calculated from NBS Technical Note[14] thermodynamic data. It agrees within 0.5% of Read's experimental value at 298.15 K. The tentative values of the zero ionic strength solubility product constant were calculated from the equation

$$\ln(K^\circ_{s0}/\text{mol}^3\ \text{kg}^{-3}) = 55.306 - 235.22/(T/100\ \text{K}) - 25.192\ \ln(T/100\ \text{K}), \quad (9)$$

obtained by a linear regression of Read's experimental data.

The values of Hansen *et al.*[24] at 280.15 and 313.15 K and the value of Bethge *et al.*[102] at 298.15 K make a tentative set of solubility products for use at an ionic strength of 0.5 (H, Na)ClO_4.

There are five solubility product values at 298.15 K calculated from thermodyamic data. In general these values do not depend on experimentally determined solubility data. The result of Latimer[103] appears to be too large. The more modern values fall within about a 40% range of each other.

Table 11. Mercury(I) bromide solubility product constants.

T/K	Ionic Strength I/electrolyte	Solubility Product K°_{s0}	Reference
		Recommended value	
298.15	0	6.40×10^{-23}	
		Tentative values	
288.15	0	0.97×10^{-23}	
293.15	0	2.54×10^{-23}	
298.15	0	6.37×10^{-23}	
303.15	0	15.4×10^{-23}	
308.15	0	35.9×10^{-23}	
313.15	0	81.0×10^{-23}	
318.15	0	$177. \times 10^{-23}$	
		Experimental values	
283.95	0	0.545×10^{-23}	Brodsky [100]
288.05	0	1.00×10^{-23}	Brodsky [100]
288.15	0	0.968×10^{-23}	Read [101]
292.35	0	3.89×10^{-23}	Brodsky [100]
293.15	0	2.56×10^{-23}	Read [101]
298.15	0	5.50×10^{-23}	Brodsky [100]
	0	6.43×10^{-23}	Read [101]
299.65	0	6.95×10^{-23}	Brodsky [100]
303.15	0	15.21×10^{-23}	Read [101]
308.15	0	35.85×10^{-23}	Read [101]
313.15	0	81.33×10^{-23}	Read [101]
318.15	0	177.6×10^{-23}	Read [101]
280.15	0.5/(H,Na)ClO_4	$(1.4 \pm 0.1) \times 10^{-23}$	Hansen et al.[24]
298.15	?	5×10^{-23}	Balyatinskaya[a][114]
	0.05/KBr	9.12×10^{-23}	Brodsky[b] [100]
	0.5/(H,Na)ClO_4	$(5.2 \pm 0.5) \times 10^{-22}$	Bethge et al.[102]
	1.0/KBr	1.3×10^{-21}	Sherrill [75]
	3.1/(H,Na)ClO_4	1.55×10^{-22}	Arnek [22]
313.15	0.5/(H,Na)ClO_4	$(6.7 \pm 0.1) \times 10^{-21}$	Hansen et al.[24]
		Calculated from emf/thermodynamic data	
298.15	0	5.78×10^{-23}	Bethge et al.[c][102]
	0	6.22×10^{-23}	Hepler, Olofsson [5]
	0	6.40×10^{-23}	NBS Tech. Note 270[14]
	0	8.40×10^{-23}	Charlot et al.[16]
	0	$13. \times 10^{-23}$	Latimer [103]

[a] Calculation of this value not made clear in the paper. It may be for zero ionic strength.

[b] Calculated by Brodsky using data from Immerwahr [98].

[c] Calculated by the authors from literature standard potential data.

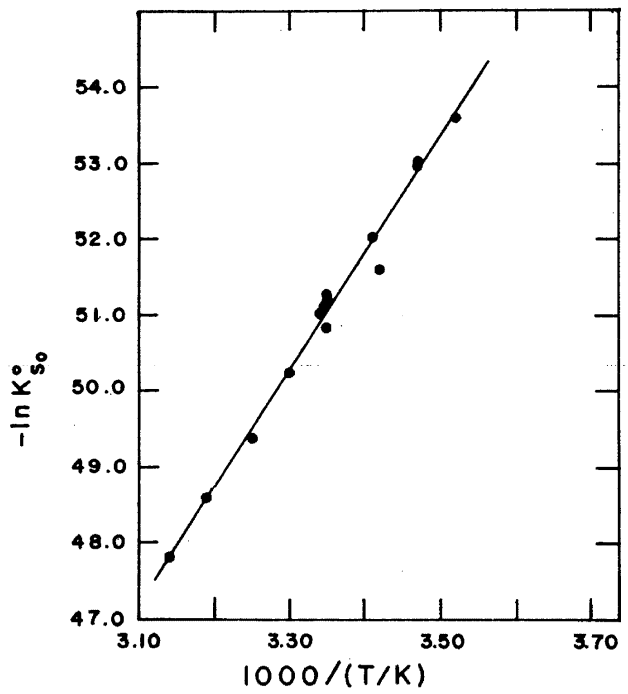

FIG.3. The solubility product constant of mercury(I) bromide in water. $\ln(K^\circ_{so}/\text{mol}^3\,\text{kg}^{-3})$ vs $1000/(T/\text{K})$.

b. Mercury (II) Bromide

$HgBr_2$ [7789-47-1] Molecular weight 360.40

Physical characteristics: Solid mercury (II) bromide is an orthorhombic crystal with four $HgBr_2$ units per unit cell. The unit cell dimensions are $a = 6.79\times10^{-10}$, $b = 12.445\times10^{-10}$, and $c = 4.624\times10^{-10}$ m. The calculated density is 6081 kg m^{-3}. Mixed anion compounds like mercury (II) chloride bromide and mercury (II) oxide bromide are known. There is no mention of hydrate formation of solid $HgBr_2$.

The values of the solubility of mercury (II) bromide in water at temperatures between 273 and 474 K are given in Table 12. No data were found on the density of the solutions. It is safe to assume that the difference between molar and molal values is negligible at the magnitude of the solubilities at temperatures below 323 K.

The aqueous solutions of mercury (II) bromide are complex. The species Hg^{2+}, Br^-, $HgBr^+$, $HgBr_2^\circ$, $HgBr_3^-$, $HgBr_4^{2-}$, and $HgOH^+$ are present. Probably $HgBr_2^\circ$ predominates. Often $HgBr_2$ is recrystallized from HBr solution. If only a trace of HBr remains the sample will give too large a water solubility, due to complexing of Hg^{2+} and Br^-.

Rejected literature data include the early work of Lassaigne,[106] who reported solubility values that are too large; that of Abegg *et al.*,[99] who did not indicate the temperature, although comparison with other papers from Abegg's laboratory suggests the temperature was probably 298.15 K; that of Bodländer,[97] whose results are orders of magnitude smaller than the other values [it is a calculated value that may represent the free mercury (II) ion concentration]; and that of Piperaki and Hadjiioannou,[105] who did not report a temperature.

The other values over the 273–353 K temperature interval show satisfactory agreement except for the value of Zajdler and Czakis-Sulikowska[104] at 293 ± 1 K, which is an order of magnitude smaller than other data at about the

Table 12. Experimental values of the solubility of mercury(II) bromide in water.

T/K	Molarity$_{\Sigma 3}$ c/mol dm	Molality$_{\Sigma 1}$ m/mol kg	Reference
273.15		0.008[a]	Pernot [107]
277.65		0.0075[a]	Tyrell, Richards [108]
283.55		0.0119[a]	Tyrell, Richards [108]
293.15 ± 1	0.00223		Zajdler, Czakis-Sulikowska [104]
room	0.0209		Piperaki, Hadjiioannou [105]
(298.15)	0.017		Abegg, Immerwahr, Jander [99]
298.15	7.6×10^{-8}		Bodländer [97]
298.15	0.017		Sherrill [75]
298.15		~0.011	Morse [73]
298.15	0.0167		Herz, Anders [77]
298.15	0.017		Herz, Paul [78]
298.15	0.017		Moles, Marquina [79]
298.15		0.0170	Garrett [109]
298.15		0.0170[a]	Tyrell, Richards [108]
298.15	0.017		Fridman et al. [89]
307.15		0.02[a]	Pernot [107]
353.15		0.08[a]	Pernot [107]
415		0.378[b]	Benrath et al. [61]
437		0.801[b]	Benrath et al. [61]
446		1.40[b]	Benrath et al. [61]
458		4.01[b]	Benrath et al. [61]
460		8.72[b]	Benrath et al. [61]
461		16.4[b]	Benrath et al. [61]
462		54.8[b]	Benrath et al. [61]
466		166.[b]	Benrath et al. [61]
474		641.[b]	Benrath et al. [61]

[a] Used to obtain low temperature equation.

[b] Used to obtain high temperature equation.

Table 13. Recommended and tentative values of the solubility of mercury(II) bromide in water.

T/K	Solubility[a], m/mol kg^{-1}
	Recommended
298.15	$(1.70 \pm 0.00) \times 10^{-2}$
	Tentative[b]
273.15	7.23×10^{-3}
283.15	1.04×10^{-2}
293.15	1.46×10^{-2}
298.15	1.71×10^{-2}
303.15	2.00×10^{-2}
313.15	2.69×10^{-2}
323.15	3.55×10^{-2}
348.15	6.63×10^{-2}
373.15	1.14×10^{-1}

[a] These values will differ negligibly from c/mol dm^{-3} values at temperatures up to 323 K.

[b] Calculated from equation 10. The standard error about the regression line is 0.21×10^{-2} which is about 6 percent of the solubility value at the mid point of the temperature range.

same temperature. Zajdler and Czakis-Sulikowska analyze their solubility value in terms of known complex ion dissociation constants to obtain a fifth power equation in the free Br^- concentration. Their calculated values of the free Br^- and free Hg^{2+} give a solubility product value that agrees well with solubility product values from other sources.

The solubility values at 298.15 K agree well and a value of 1.70×10^{-2} mol kg^{-1} (or mol dm^{-3}) is accepted as the tentative value of the solubility of $HgBr_2$ in water at 298.15 K. The molality data between 273 and 353 K, footnoted "a" in Table 12, were fitted by the method of least squares to the equation

$$\ln(m_{HgBr_2}/\text{mol kg}^{-1}) = 5.3570 - 28.096/(T/100\text{ K}). \quad (10)$$

Values calculated from the equation are given in Table 13 as tentative values of the solubility of $HgBr_2$ in water.

The data of Benrath *et al.*[61] at temperatures from 415 to 474 K begin as a logical extension of the lower temperature data, but as the temperature increases they show a much larger temperature coefficient of solubility than do the solubility values of lower temperatures. The values footnoted "b" in Table 12 were fitted by a linear regression to obtain the equation

$$\ln(m_{HgBr_2}/\text{mol kg}^{-1}) = 85.918 - 380.791/(T/100\text{ K}). \quad (11)$$

Figure 4 shows the data points and the lines calculated from Eqs. (10) and (11). The lines intersect at a temperature of 437 K.

Figure 4 points up some problems with the $HgBr_2 + H_2O$ system data. The abrupt change in the temperature coefficient of solubility at 437 K is much larger than the change observed in the HgI_2 system, where a known solid–solid transition occurs. We are not aware of any reports of a solid–solid transition at any temperature of mercury (II) bromide. It would appear that we are too far below the 509 K melting point for this to be a premelting effect, although the possibility exists.

There are questions about the solubility data that cannot be answered without further experimental work. As

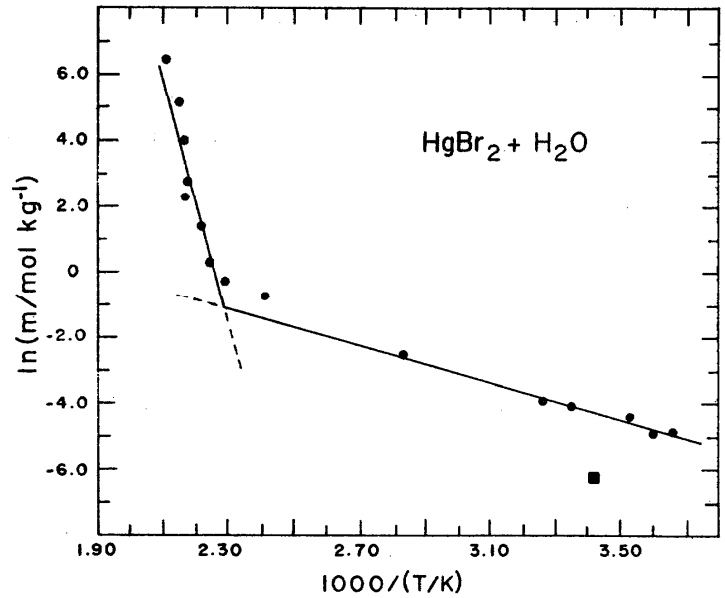

FIG. 4. Solubility of mercury(II) bromide in water.

$\ln(m_{HgBr_2}/\text{mol kg}^{-1})$ vs $1000/(T/\text{K})$.

■ Value of Zajdler and Czakis-Sulikowska (Ref. 104). Line to left, values of Benrath *et al.* (Ref. 61).

Table 14. Solubility product constant for mercury(II) bromide in aqueous solution.

T/K	I/Electrolyte	Solubility Product K°_{s0}	Solubility Product K_{s0}	Reference
		Tentative value		
298.15	0	6.2×10^{-20}		
		Literature values		
293.15	0	2.94×10^{-20}		Zajdler,Czakis-Sulikowska[104]
298.13	0	6.2×10^{-20}		NBS Technical Note 270 [14]
293.15	2.0/Na(ClO_4^-, NO_2^-)		1.26×10^{-19}	Zajdler,Czakis-Sulikowska[104]
298.15	? /KBr		8.0×10^{-20}	Sherrill [75][a]

[a] Data used to calculate this value determined at several concentrations of KBr.

mentioned earlier, contamination of $HgBr_2$ with HBr leads to solubilities that are too large. It is possible that all of the values are too large and that the smaller value of Zajdler and Czakis-Sulikowska is the nearest correct value in the room-temperature region. Another factor to consider is time of saturation. Zajdler and Czakis-Sulikowska used 24 h, while Garrett[109] presents data obtained from both under- and supersaturation to show that 72 h are needed to establish equilibrium. All of the high-temperature values with the very large temperature coefficient of solubility came from the paper of Benrath *et al.*[61] Their data may be in error.

The thermodynamic data of the NBS Technical Notes[14] have been used to calculate a tentative value of the thermodynamic solubility product constant of $HgBr_2$ at 298.15 K. The value of

$$K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3} = 6.2\times10^{-20}$$

agrees satisfactorily with the values of Zajdler and Czakis-Sulikowska[104] at 293 ± 1 K and the value of Sherrill,[75] obtained from a study of the solubility in dilute KBr solution (see Table 14). However, the small stoichiometric solubility of $HgBr_2$ reported by Zajdler and Czakis-Sulikowska casts some doubt on their results.

Table 2A summarizes the sources of mercury (II) bromide solubility studies in aqueous electrolyte systems. Some, but not all, of these papers were discussed above. The data from the papers footnoted "a" are listed in Seidell and Linke.[6]

4.5. Mercury Iodide

a. Mercury (I) Iodide

Hg_2I_2 [15385-57-6] Molecular weight 654.989

Physical characteristics: Solid mercury (I) iodide is a tetragonal crystal with $Z=2$, $a=4.92\times10^{-10}$, and $c=11.61\times10^{-10}$ m. The calculated density is 7680 kg m^{-3}. There is no mention of hydrate formation.

The only solubilities for Hg_2I_2 reported in the literature are from three early sources[75,98,99] or have been calculated from solubility products without taking the complex ions and other solution species into account.[75,97] These solubility values are all for dilute KI solutions, not water. Since both experimental methods and calculations are unclear and assumptions about solution species erroneous, these values have been rejected.

There are four experimental studies of the mercury (I) iodide solubility product. Values of the solubility product from these studies are given in Table 15 and Fig. 5. Several values of the solubility product calculated from thermodynamic, including emf, data are also given in Table 15. The solubility products calculated from metal/cation (aq) and metal/insoluble salt/anion (aq) standard electrode potentials obtained from emf studies are independent of experimentally determined solubilities.

The recommended value of the solubility product constant,

$$K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3} = 5.2\times10^{-29} \text{ at } 298.15\text{ K},$$

is the value calculated from thermodynamic data given in Hepler and Olofsson.[5] It agrees well with the value calculated from NBS Technical Note 270[14] data and with the experimental value of Brodsky.[100]

The experimental values of K°_{s0} of Brodsky[100] and the values of K_{s0} at an ionic strength of 0.5 $(H^+,Na^+)ClO_4$ of Hansen, Izatt, and Christensen[24] and of Qvarfort and Sillen[116] are accepted as tentative values over 15°–30° temperature intervals near 298 K. Brodsky gives the equation

$$\log K^\circ_{s0} = -30.72 + 0.094\,(t/^\circ\text{C}) \qquad (12)$$

for the 283–298 K temperature interval.

Egorov[117] used thermodynamic data to develop an equation for use between 273.15 and 373.15 K,

$$\log (K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3}) = -3.5483 - 7347/(T/\text{K}) + 0.0044\log(T/\text{K}) + 0.293\times10^{-3}\,(T/\text{K}). \qquad (13)$$

Several values of K°_{s0} from the equation are given in Table 15. The values are about twice the magnitude of Brodsky's experimental values and they have a larger temperature coefficient. Zhuk[118] presents a graph of $\log K^\circ_{s0}$ versus $1/T$, which is linear, but he does not give numerical data or an equation.

Table 15. The solubility product constant for mercury(I) iodide in aqueous solution.

T/K	Ionic strength I/Electrolyte	Solubility Product K°_{s0}	Solubility Product K_{s0}	Reference
		Recommended value		
298.15	0	5.2×10^{-29}		
		Experimental values		
283.15	0	2.01×10^{-30}		Brodsky [100]
288.05	0	5.10×10^{-30}		Brodsky [100]
292.35	0	1.05×10^{-29}		Brodsky [100]
298.15	0	4.95×10^{-29}		Brodsky [100]
298.15	0(?)	5×10^{-29}		Balyatinskaya[a] [114]
280.15	0.5/(H^+,Na^+)ClO_4		$(4.6 \pm 0.1) \times 10^{-30}$	Hansen et al. [24]
298.15	0.04/KI		1.2×10^{-28}	Sherrill & Abegg[75,115]
298.15	0.05/KI		6.3×10^{-29}	Brodsky [100][b]
298.15	0.5/(H^+,Na^+)ClO_4		$(3.43 \pm 0.08) \times 10^{-28}$	Qvarfort et al.[116]
313.15	0.5/(H^+,Na^+)ClO_4		$(3.5 \pm 0.1) \times 10^{-27}$	Hansen et al.[24]
		Calculated from thermodynamic data		
283.15	0	3.96×10^{-10}		Egorov [117][c]
288.15	0	1.12×10^{-29}		Egorov [117][c]
293.15	0	3.06×10^{-29}		Egorov [117][c]
298.15	0	8.09×10^{-29}		Egorov [117][c]
	0	4.5×10^{-29}		Latimer [103]
	0	5.16×10^{-29}		Hepler,Olofsson[5]
	0	5.34×10^{-29}		NBS Tech. Note 270 [14]
	0	7.46×10^{-29}		Charlot et al.[16]

[a] Value given in paper without reference. May be a restatement of Brodsky's [100] value.

[b] Calculated by Brodsky from data of Immerwahr [98].

[c] Calculated from the equation developed by Egorov [117], Eqn. 13.

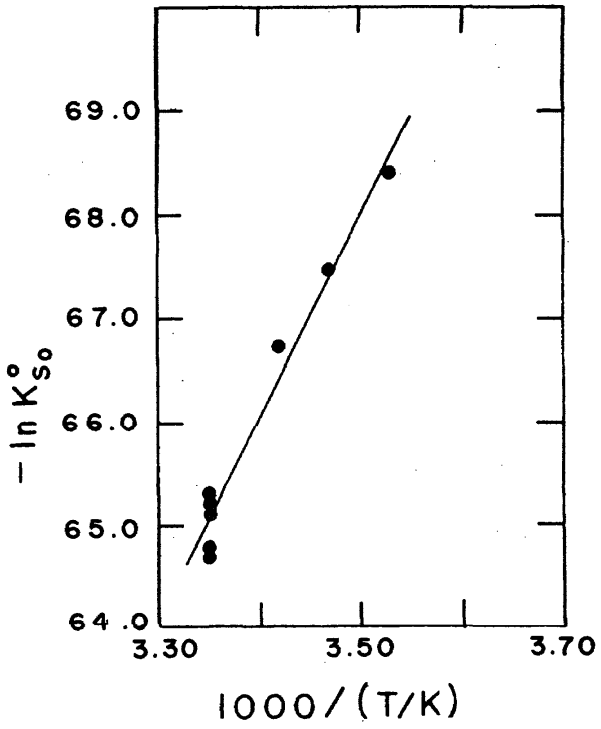

FIG. 5. Solubility product constant of mercury(I) iodide in water. $\ln(K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3})$ vs $1000/(T/\text{K})$.

b. Mercury (II) Iodide

HgI_2 [7774-29-0] Molecular weight 454.40

Physical characteristics: Solid mercury (II) iodide exists in three crystalline forms. A dark red tetragonal crystal is stable up to 400 K (127 °C) with $Z = 2$, $a = 4.36 \times 10^{-10}$, and $c = 12.45 \times 10^{-10}$ m; the calculated density is 6327 kg m^{-3}. Above 400 K, the stable form is a yellow orthorhombic crystal with $Z = 4$, $a = 7.432 \times 10^{-10}$, $b = 13.872 \times 10^{-10}$, and $c = 4.702 \times 10^{-10}$ m; its density is 6225 kg m^{-3}. There is also an orange metastable cubic crystal with $Z = 128$, $a = 24.85 \times 10^{-10}$ m, and a calculated density of 6293 kg m^{-3}; it is an ordered form of the red tetragonal crystal. There is no mention of hydrates of HgI_2. Nozhko and Tishina[301] report that yellow-orange HgBrI separates from $HgBr_2 + HgI_2 + H_2O$ solution at 20 °C. The compound dissolves incongruently with separation of solid HgI_2.

Experimental values of the solubility of mercury (II) iodide in water are given in Table 16. Several values are rejected: Tananaev and Pilipenko,[119] because of uncertainties in equilibrium conditions and temperature; Kohlrausch[120] and Morse[73], because of the approximate nature of the results as indicated by the authors; and Abegg, Immerwahr, and Jander,[99] because of uncertainty in the temperature. A value by Bodländer[97] is also rejected because of the assumptions made in calculating his value.

We found no density data for the saturated solutions. However, for the magnitude of the solubilities found near

Table 16. Experimental values of the solubility of mercury(II) iodide in water.

T/K	Solubility		Reference
	c_{HgI_2}/mol dm^{-3}	m_{HgI_2}/mol kg^{-1}	
291 ± 2	7.4 x 10^{-5}		Tananaev, Pilipenko [119][a]
290.65	8.87 x 10^{-5}		Bourgoin [121]
291.15	(6 ± 2) x 10^{-7}		Kohlrausch [120]
295.15	1.18 x 10^{-4}		Bourgoin [121]
295.65		2.2 x 10^{-4}	Naudé [122]
(298.15)	1 x 10^{-4}		Abegg et al. [99]
298.15	∿ 1.3 x 10^{-4}		Morse [73]
	9.77 x 10^{-5}		de Bruijn [123]
	(1.05 ± 0.055) x 10^{-4}		Biedermann, Sillen [124][b]
	1.3 x 10^{-4}		Fridman et al. [89][c]
373.15		4 x 10^{-3}	Hietanen, Sillen [125]
469		8.1 x 10^{-2}	Benrath et al. [61]
502		0.21	Benrath et al. [61]
514		0.25	Benrath et al. [61]

[a] Tananaev and Pilipenko's value has been misquoted in several papers because readers mistakenly took a table in the paper as containing the experimental data when it merely reproduced a table from Sherrill [75].

[b] The average of six determinations.

[c] Fridman et al. [89] report water solubilities of 0.103 mol dm^{-3} for HgClBr, 0.010 mol dm^{-3} for HgICl, and 0.0029 mol dm^{-3} for HgBrI at 298 K.

room temperature, we would expect a negligible difference in molar and molal values.

Table 17 gives tentative values of the solubility of mercury (II) iodide in water. The values in the table come from two equations. For temperatures of 288–323 K, the equation

$$\ln (m_{HgI_2}/\text{mol kg}^{-1}) = 7.608 - 49.576/(T/100\ \text{K}) \quad (14)$$

was used. The equation was generated from the solubility data between 290.65 and 298.15 K and the fact that the curve should meet the high-temperature curve at the tetragonal to orthorhombic transition of about 400 K.

The solubility values at temperatures of 463–513 K for the orthorhombic crystalline form were calculated from the equation

$$\ln (m_{HgI_2}/\text{mol kg}^{-1}) = 10.751 - 62.134/(T/100\ \text{K}). \quad (15)$$

The equation was obtained from a linear regression of the three solubility values reported by Benrath *et al.*[61]

The change in the temperature coefficient of solubility at the tetragonal to orthorhombic transition is small. The slopes of the equations above imply a change in the enthalpy of solution from 41 kJ mol^{-1} for the tetragonal crystal to 52 kJ mol^{-1} for the orthorhombic crystal (see Fig. 6).

At 514 K the $HgI_2 + H_2O$ system goes from a solid–liquid system to a liquid–liquid system. The upper consolute point of the liquid–liquid region is at 611 K and 77 wt.%

Table 17. Tentative values of the solubility of mercury(II) iodide in water.

T/K	Solubility[a] m_{HgI_2}/mol kg^{-1}	Crystal Form
288.15	0.68 x 10^{-4}	Tetragonal (red)
293.15	0.91 x 10^{-4}	"
298.15	1.21 x 10^{-4}	"
303.15	1.59 x 10^{-4}	"
308.15	2.08 x 10^{-4}	"
313.15	2.68 x 10^{-4}	"
318.15	3.44 x 10^{-4}	"
323.15	4.38 x 10^{-4}	"
400	Tetragonal ⇌ orthorhombic transition	
463.15	0.070	Orthorhombic (yellow)
473.15	0.092	"
483.15	0.12	"
493.15	0.16	"
503.15	0.20	"
513.15	0.26	"
514	Two liquid phases	
611	One liquid phase	

[a] The values at temperatures below 323 K probably differ negligibly from c/mol dm^{-3} values.

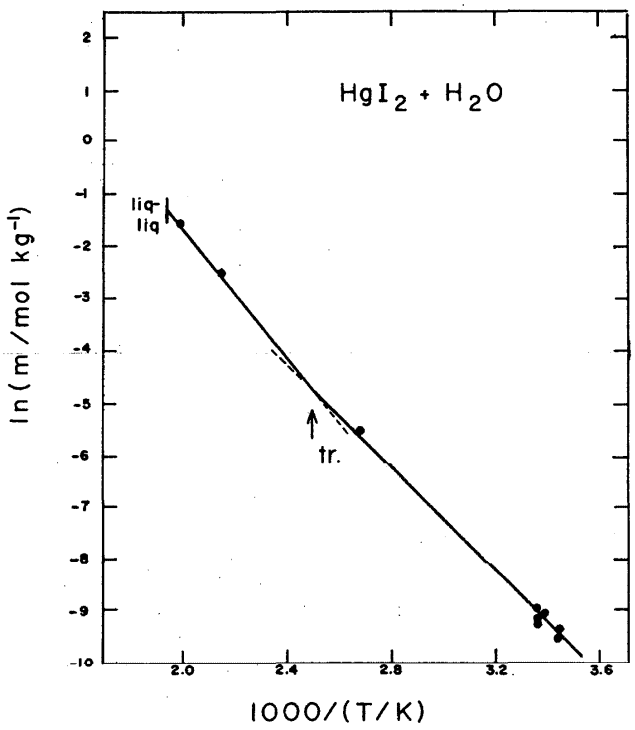

FIG. 6. The solubility of mercury(II) iodide in water.

$\ln(m_{HgI_2}/\text{mol kg}^{-1})$ vs $1000/(T/\text{K})$.

The tetragonal to orthorhombic transition is designated by "tr."

HgI_2; at higher temperatures it is a single liquid phase. The compositions in the two-phase region and the consolute temperature conditions measured by Benrath *et al.*[61] are given in Table 18. Mercury (II) chloride, bromide, or cyanide + water systems show similarly shaped solubility curves according to Benrath *et al.* The mercury (II) iodide solubility

Table 18. Composition of the liquid-liquid $HgI_2 + H_2O$ system between 514 and 611 K. Benrath et al. [61].

T/K	Water Rich Phase HgI_2, wt%	HgI_2 Rich Phase HgI_2, wt%
514	11.5	98.
516	12.0	-
529	15.5	-
530	15.7	-
535	-	97.4
545	18.7	-
558	23.7	-
566	-	95.3
568	27.5	-
573	30.5	-
587	41.0	-
595	-	90.5
597	48.0	-
599	49.7	-
601	53.8,54.4	-
607	65.5	-
609	68.0	82.7
610	74.3	-
611	75.0	-
(611)[a]	77	77

[a] Upper consolute temperature.

curve starts in similar fashion at low temperatures, but then goes to a liquid–liquid region. Benrath *et al.*[61] make the statement that no liquid–liquid regions are observed in the mercury (II) chloride, bromide, or cyanide + water systems

There are two values of the mercury (II) iodide solubility product calculated from thermodynamic data. The value calculated from the NBS Technical Note[14] of $K^\circ_{s0}/\text{mol}^3\,\text{kg}^{-3} = 2.9\times10^{-29}$ is given in Table 19 as the tentative value. The value of Yatsimirskii and Shutov[126] is of similar magnitude, but their source of thermodynamic data and the conditions are not clear.

Four laboratories report experimental values of the solubility product at various ionic strengths. The value given by Czakis-Sulikowska[127] appears to have been calculated from

Table 19. The solubility product constant for mercury(II) iodide in aqueous solution.

T/K	Ionic strength I/electrolyte	Solubility Product K°_{s0}	K_{s0}	Reference
		Tentative value		
298.15	0	2.9×10^{-29}		
		Calculated values		
298.15	0	2.9×10^{-29}		NBS Tech Note 270 [14]
	0	1×10^{-29}		Yatsimirskii, Shutov [126]
		Experimental values		
280.15	$0.5/(Na^+,H^+)ClO_4^-$		1.6×10^{-30}	Hansen et al. [24]
298.15	?		6.4×10^{-29}	Czakis-Sulikowska [127,128][a]
298.15	0.2/KI		3.2×10^{-29}	Sherrill [75]
298.15	$0.5/(Na^+,H^+)ClO_4^-$		1.12×10^{-28}	Qvarfort,Sillen [116]
313.15	$0.5/(Na^+,H^+)ClO_4^-$		1.5×10^{-27}	Hansen et al. [24]

[a] Value appears to have been calculated from data in earlier papers.

literature data. The conditions under which it applies are not clear. Values from Hansen, Izatt, and Christensen[24] and from Qvarfort and Sillen[116] apply to 0.5 ionic strength $NaClO_4 + 0.01$–$0.1\,M$ $HClO_4$. The three values at temperatures of 280.15, 298.15, and 313.15 K were fitted by a linear regression to the equation

$$\ln (K^\circ_{s0}/\text{mol}^3\,\text{dm}^{-9}) = -3.2764 - 182.765/(T/100\,\text{K}), \quad (16)$$

which reproduces the three values to about 15%.

Table 3A is a bibliography of papers on the solubility of mercury (II) iodide in various aqueous electrolyte solutions. Papers listed in Seidell and Linke[6] are footnoted.

4.6. Mercury (II) Sulfide

HgS [1344-18-5]

Cinnabar, red HgS [19122-79-3]

Metacinnabar, black HgS [23333-45-1] Molecular weight 232.65

Physical characteristics: Mercury (II) sulfide exists in several crystalline forms. At room temperature, the stable form is red HgS, α-HgS, or cinnabar. It is a hexagonal crystal of $Z = 3$, $a = 4.15 \times 10^{-10}$, and $c = 9.51 \times 10^{-10}$ m. The calculated density is 8129 kg m^{-3}. The high-temperature form is black HgS, β-HgS, or metacinnabar. Black HgS is a cubic crystal with $Z = 4$, $a = 5.858 \times 10^{-10}$ m, and a calculated density of 7676 kg m^{-3}. In addition, hypercinnabar, a form of HgS deficient in mercury, has been characterized at even higher temperatures. It is hexagonal with $Z = 12$, $a = 7.01 \times 10^{-10}$, and $c = 14.13 \times 10^{-10}$ m, and a calculated density of 7540 kg m^{-3}.

Potter and Barnes[143] report the Hg–S phase diagram. The accepted transition from cinnabar to metacinnabar at 1 bar occurs at 618 ± 2 K, but in the presence of molten sulfur it occurs at 588 ± 3 K. The metacinnabar to hypercinnabar transition occurs at 754 ± 3 K, but in the presence of molten sulfur it occurs at 743 ± 3 K.

Craig and Barton[144] report Gibbs energy equations for the reactions

$$2\text{Hg(l)} + \text{S}_2\text{(g)} = 2\text{HgS(cinnabar)}$$

$$\Delta G^\circ/\text{kJ} = -239\,070 + 212.5(T/\text{K}), \quad 298\text{–}618\ \text{K}$$

$$2\text{Hg(l)} + \text{S}_2\text{(g)} = 2\text{HgS(metacinnabar)}$$

$$\Delta G^\circ/\text{kJ} = -234\,180 + 205.0(T/\text{K}), \quad 618\text{–}753\ \text{K}.$$

It is important to note that precipitation reactions at room temperature yield the metastable black form of HgS.

The nonstoichiometric nature of many mercury (II) sulfide samples, the uncertainty of the values of the H_2S dissociation constants, and of the $HgS(H_2S)_2$, $Hg(HS)_3^-$, $HgS(HS)_2^{2-}$, and HgS_2^{2-} formation constants, and the lack of information about the pH and the partial pressures of H_2S and O_2 in the reported experimental studies make it difficult to give even tentative values of the solubility of mercury (II) sulfide in aqueous systems.

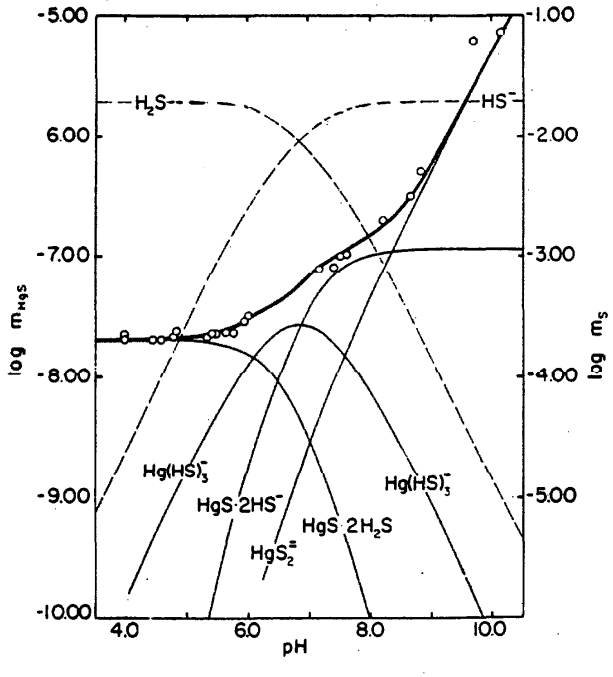

FIG. 7. The solubility of mercury(II) sulfide (metacinnabar) as a function of pH at 293 K. Circles, data of Schwarzenbach and Widmer (Ref. 160); heavy line, calculated solubilities based on the summation of the concentrations of the complexes as outlined by the light curves. The total sulfide concentration, $H_2S + HS^-$, is 0.02 mol kg^{-1}. The concentrations of the complexes were calculated from the equilibrium constants at 293 K given in Table 23. [Figure reproduced from Barnes, Romberger, and Stemprok (Ref. 153) by permission of the Economic Geology Publishing Co.]

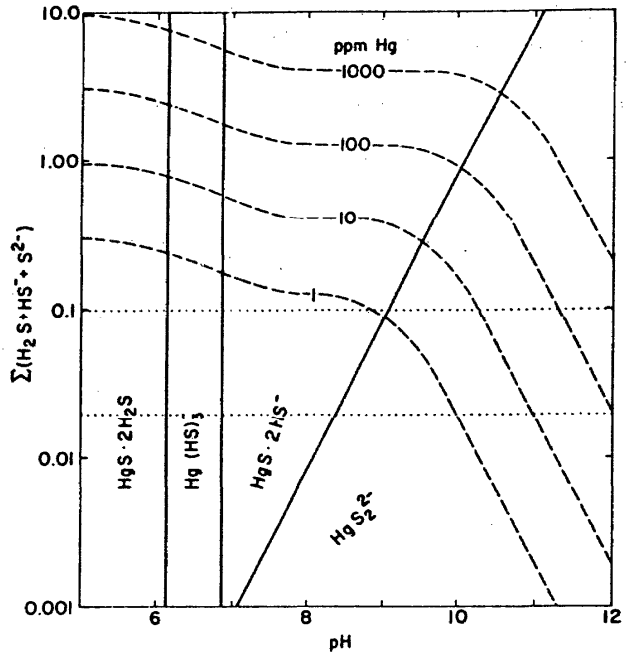

FIG. 8. The stoichiometries of mercury sulfide complexes at different acidities and sulfide activities at 293 K. The solubility contours are for metacinnabar and may be converted to those for cinnabar by multiplying by 0.8. The lower horizontal dotted line represents a total sulfide concentration of 0.02 mol kg^{-1}, as in Fig. 7. [Barnes, Romberger, and Stemprok (Ref. 153), Barnes (Ref. 34). Reproduced from Ref. 153 by permission of the Economic Geology Publishing Co.]

Table 20. The stability constants of mercury bisulfide complexes [34b]

Reaction	Ionic Strength	Pressure p/bar	-log K 293 K	298 K	373 K	423 K	473 K	523 K
Cinnabar								
$HgS(s) + 2H_2S(aq) = HgS(H_2S)_2(aq)$	0		4.31		3.0			
$HgS(s) + H_2S(aq) + HS^-(aq) = Hg(HS)_3^-(aq)$	1.0		-3.59 ± 0.3		-3.3 ± 0.4			
$HgS(s) + 2HS^-(aq) = HgS(HS)_2^{2-}$	1.0		3.60					
$HgS(s) + S^{2-}(aq) = HgS_2^{2-}(aq)$	1.0		-0.48					
Metacinnabar								
$HgS(s) + 2H_2S(aq) = HgS(H_2S)_2(aq)$	1.0		4.25					
$HgS(s) + H_2S(aq) + HS^-(aq) = Hg(HS)_3^-(aq)$	1.0		3.50					
$HgS(s) + 2HS^-(aq) = HgS(HS)_2^{2-}(aq)$	1.0		3.51					
$HgS(s) + S^{2-}(aq) = HgS_2^{2-}(aq)$	1.0		-0.57					
$HgS(s) + HS^-(aq) + OH^-(aq) = HgS_2^{2-}(aq) + H_2O$	0	1	-	0.31	0.49	0.57	0.63	0.69
	0	250	-	0.38	0.53	0.61	0.64	0.71
	0	500	-	0.44	0.58	0.68	0.69	0.74

The temperature range and aqueous electrolyte media of the mercury (II) sulfide solubility studies found in the literature are summarized in Table 4A. It does not appear that a new treatment of the solubility data based on existing data would improve upon the model last outlined by Barnes[34] in 1979. Only new studies with careful attention to the experimental difficulties pointed out by Barnes[145] and in the previous paragraph will advance our knowledge of the solubility of mercury (II) sulfide in water and in various aqueous electrolyte solutions.

Barnes's[34] model relates the solubility of black HgS (metacinnabar) to regions of stability of the complexes $HgS(H_2S)_2$, $Hg(HS)_3^-$, $HgS(HS)_2^{2-}$, and HgS_2^{2-} in aqueous solution as a function of pH at 293 K (Figs. 7 and 8). Barnes[34,153] relied heavily on the solubility data of Schwarzenbach and Widmer.[160] Barnes's recommendation of values of the formation constants of the mercury bisulfide complexes for both cinnabar and metacinnabar are given in Table 20. The values at the higher temperatures are based on the recent work of Khodakovskii, Popova, and Ozerova.[168]

Although Barnes's[34] model is satisfactory for metacinnabar at 293 K, it should be used with caution at higher temperatures. As the temperature increases, water acidity increases, and the HS^- species and its complexes will be less important. Hydrogen sulfide becomes more important, and HgS itself degrades to $Hg + H_2S$.[304]

A recent paper[305] not yet available to us reports the solubility of red mercury (cinnabar) in aqueous NaHS solution at temperatures of 453–543 K as a function of pH (9–13) and of NaHS concentration (0.54–2.11 mol kg^{-1}). The abstract states that at pH 9–11.4 the solubility is independent of pH, but as the pH increases from 11.4 to 13 the solubility increases rapidly.

Table 21 summarizes solubility product values from experimental studies and from thermodynamic data calculations. We accept as tentative values the solubility product of red (cinnabar) and black (metacinnabar) HgS given by Hepler and Olofsson.[5] For red HgS, their value is the same as that calculated from the thermodynamic data in Ref. 14. In both Tables 4A and 21 there is a section on unspecified forms of solid HgS. In most cases these data are probably for black HgS, but one cannot be certain.

Of the references that appear in Tables 4A and 21, many contain incorrect data or use out-of-date information. For example, the direct gravimetric determinations of the solubility of cinnabar and metacinnabar in water by Aidin'yan[147] and the solubility of metacinnabar in water by the conductivity studies of Weigel[157,158] give values that are too large by orders of magnitude. The extensive calculations of Krauskopf,[169] Czamanske,[170] and Jaulmes and Brun[171] are of little value today. They used values of the mercury sulfide solubility product and of the hydrogen sulfide dissociation constants that are not those currently accepted. In addition, much more is now known about HS^- complexes of mercury, which their work ignored.

Table 21. Mercury(II) sulfide solubility product constant

T/K	Ionic strength I/electrolyte	Solubility Product K°_{s0} or K_{s0}	Reference
	Cinnabar, red HgS, tentative value		
298.15	0	2.0×10^{-53}	NBS Tech. Note 270 [14] Hepler,Olofsson, 1975 [5]
	Metacinnabar, black HgS, tentative value		
298.15	0	2×10^{-52}	Hepler,Olofsson, 1975 [5]
	Experimental and calculated values - cinnabar, red HgS		
298.15	0.08/Na_2S	2.8×10^{-54}	Knox, 1906 [150]; 1908 [151]
	0.08/Na_2S	1.0×10^{-53}	Bruner,Zawadski,1909[172];1910[173][a]
	0.08/Na_2S	3×10^{-54}	Kolthoff, 1931 [174][a]
	0	7×10^{-53}	Treadwell,Schaufelberger,1946[159]
	0	$(2.0 \pm 5.7) \times 10^{-53}$	Ringbom, 1953 [175][b]
	0	1.88×10^{-53}	Czamanske, 1959 [170][c]
	0	2.10×10^{-54}	Helgeson, 1969 [176][f]
	0	2.0×10^{-53}	NBS Tech. Note 270-3,4 [14][e]
	0	2.0×10^{-53}	Geol.Survey Bull. 1452 [15][e]
(?)	?	7×10^{-53}	Shcherbina, 1972 [177][d]
323.15	0	9.60×10^{-51}	Helgeson, 1969 [176][f]
333.15	0	1.90×10^{-49}	Helgeson, 1969 [176][f]
373.15	0	3.98×10^{-44}	Czamanske, 1959 [170][c]
	0	5.60×10^{-43}	Helgeson, 1969 [176][f]
423.15	0	1.23×10^{-40}	Helgeson, 1969 [176][f]
473.15	0	2.69×10^{-36}	Czamanske, 1959 [170][c]
	0	3.10×10^{-37}	Helgeson, 1969 [176][f]
523.15	0	1.50×10^{-34}	Helgeson, 1969 [176][f]
573	0	1.90×10^{-32}	Helgeson, 1969 [176][f]
673	0	1.30×10^{-27}	Czamanske, 1959 [170][c]
873	0	6.92×10^{-23}	Czamanske, 1959 [170][c]
	Experimental and calculated values - metacinnabar, black HgS		
293.15	1.0/KCl	1.1×10^{-51}	Schwarzenbach,Widmer, 1963[160]
298.15	0	3×10^{-52}	Treadwell,Schaufelberger,1946[159]
	0	9×10^{-52}	Goates,Cole,Gray,1951 [178][g]
	0	8×10^{-52}	Goates,Cole,Gray,1951 [178][h]
	0	3×10^{-52}	Goates,Gordon,Faux,1952 [179][g,i]
	0	$(1.6 \pm 4.5) \times 10^{-52}$	Ringbom, 1953 [175][b]
	0	4.30×10^{-53}	Helgeson, 1969 [176][f]
	0	2×10^{-52}	Hepler,Olofsson, 1975 [5][j]
	0	6.5×10^{-53}	NBS Tech.Note 270-3,4 [14][e]
	0	3.76×10^{-52}	Geol.Survey Bull. 1452 [15][e]
323.15	0	1.45×10^{-49}	Helgeson, 1969 [176][f]
333.15	0	2.30×10^{-48}	Helgeson, 1969 [176][f]
373.15	0	4.40×10^{-44}	Helgeson, 1969 [176][f]
423	0	5.90×10^{-40}	Helgeson, 1969 [176][f]
473	0	1.05×10^{-36}	Helgeson, 1969 [176][f]
523	0	3.80×10^{-34}	Helgeson, 1969 [176][f]
573	0	3.60×10^{-32}	Helgeson, 1969 [176][f]
	HgS, solid form unspecified or questionable		
298.15	0	2.0×10^{-49}	Bruner,Zawadzki,1909[172];1910[173][k]
	0	4.0×10^{-52}	Bruner,Zawadzki,1909[172];1910[173][k]
	0.05/NaHS	6.7×10^{-48}	Bruner,Zawadzki,1909[172];1910[173][l]

Table 21 (continued)

T/K	Ionic strength I/electrolyte	Solubility product K°_{s0} or K_{s0}	Reference
	0	4.5×10^{-45}	Brodsky, 1929 [100]
	0.05/NaHS	2.95×10^{-45}	Brodsky, 1929 [100][k]
	0.05/NaHS	1×10^{-47}	Kolthoff, 1931 [174][k]
	0	1.00×10^{-47}	Verhoogen, 1938 [180][m]
	0	1.62×10^{-52}	Ringbom, 1953 [175][n]
	0	4×10^{-52}	Ringbom, 1953 [175][o]
	?	1.46×10^{-55}	Krestov, 1969 [181][p]
	1/?	$(1.26 \pm 1.88) \times 10^{-52}$	Mehra,Gubeli, 1971 [182]
	0	6.22×10^{-55}	Erdenbaeva, 1975 [183]
373	0	2.80×10^{-46}	Verhoogen, 1938 [180][m]
473	0	7.95×10^{-43}	Verhoogen, 1938 [180][m]
573	0	1.26×10^{-40}	Verhoogen, 1938 [180][m]
673	0	6.16×10^{-39}	Verhoogen, 1938 [180][m]

[a] Calculated using data from Knox [150].

[b] Value recommended in 1953 IUPAC report [175].

[c] Calculated by Csamanoke [170] from thermodynamic data obtained from Kury, Zeilen, and Latimer [184], Latimer [103], and Kubaschewski and Evans [185].

[d] Appears to be a compilation of literature data, but no references are given.

[e] Calculated by us from evaluated thermodynamic data in the reference cited.

[f] Calculated from critically evaluated thermodynamic data from several sources cited in the paper.

[g] Erroneously listed in Seidell, Linke [6] as Hg_2S.

[h] Calculated value using data from Kolthoff [174].

[i] Recalculated value from Goates, Cole and Gray [178] using H_2S ionization values from [179].

[j] Calculated by these authors from their recommended thermodynamic values and values in NBS-TN-270 [14].

[k] Calculated value based on thermodynamic values cited in paper.

[l] Calculated using data from Immerwahr [98] who lists the compound as Hg_2S.

[m] Calculated using literature thermodynamic data; source unclear, as the source cited in paper is erroneous.

[n] Calculated using data from Kryukova [186] who lists the compound as Hg_2S.

[o] Calculated using thermodynamic data from Makolkin [187].

[p] Calculated from thermodynamic data; source not clear.

4.7. Mercury Sulfate

a. Mercury (I) Sulfate

Hg_2SO_4 [7783-36-0] Molecular weight 497.24

[Chem. Abstr. Index Sulfuric acid, dimercury (1 +) salt (2:1), $H_2O_4S{\cdot}2Hg$]

Physical characteristics: Mercury (I) sulfate is monoclinic with $Z = 2$, $a = 6.2802 \times 10^{-10}$ m, $b = 4.4273 \times 10^{-10}$ m, $c = 8.367 \times 10^{-10}$ m, and $\beta = 91.76°$. The calculated density is 7100 kg m^{-3}, according to Dorm.[306]

Values for the solubility of mercury(I) sulfate in water from six references are given in Table 22. There are no density data for these solutions. The difference between molar and molal solubility values is estimated to be less than 0.5%, which is negligible considering the uncertainty of the solubility data.

The following data were rejected: those of Wright and Thompson,[188] because of uncertainty in both the temperature and the units; Wilsmore's[189] value, because it was calculated from outdated free-energy data; and the value of Leden,[190] because it was estimated from a curve fit, which included data used in the present analysis. The remaining data, with the Craig *et al.* data weighted twice and the other data once, were fitted by a linear regression to obtain the tentative equation

$$\ln(c_{Hg_2SO_4}/\text{mol dm}^{-3}) = -3.8586 - 9.0142/(T/100\ \text{K}). \quad (17)$$

Although the solubility is designated as molarity, the values may be used as molality with negligible error. A summary of the tentative solubility values calculated from the equation is given in Table 23.

Table 22. The solubility of mercury(I) sulfate in water.

T/K	Solubility		Reference
	$c_{Hg_2SO_4}$/mol dm^{-3}	$m_{Hg_2SO_4}$/mol kg^{-1}	
273.15	$(7.08 \pm 0.12) \times 10^{-4}$		Craig,Vinal,Vinal [191]
289.65		1.1×10^{-3}	Barré [192]
291.15	$\sim 9.5 \times 10^{-4}$		Wright, Thompson [188][a]
	7.8×10^{-4}		Wilsmore [189][b]
298.15	1.171×10^{-3}		Drucker [193]
	1.20×10^{-3}		Leden [190][c]
301.15	$(1.01 \pm 0.01) \times 10^{-3}$		Craig,Vinal,Vinal [191]
306		1.2×10^{-3}	Barré [192]
323		1.3×10^{-3}	Barré [192]
348		1.5×10^{-3}	Barré [192]
364		1.7×10^{-3}	Barré [192]
373		1.9×10^{-3}	Barré [192]

[a] Units and temperature unclear.

[b] Calculated from early free energy data of Bugarsky [194]

[c] Value derived from other work [191,192,193].

Mercury (I) sulfate solubility product values are listed in Table 24. The recommended value of 6.5×10^{-7} at 298.15 K is from the evaluation of mercury compound data of Hepler and Olofsson.[5] The value is smaller than those calculated from evaluated data in NBS Technical Note 270[14] and in Charlot *et al.*[16] Hepler and Olofsson point out that an accurate value of the standard potentials, from which the solubility product is calculated, must take into account both the second ionization constant of sulfuric acid, and the ion size parameter in the Debye–Hückel equation.

There is fairly good agreement on the value of the HSO_4^- ionization constant. Sharma and Prasad[195] give a summary of some of the HSO_4^- ionization constant values up to 1969; additional data have been published since 1969. The data are compared in Table 25. The more recent evaluations favor a value of $K_{a2} = 1.05 \times 10^{-2}$ at 298.15 K. Larson, Zeeb, and Hepler[196] measured heat capacities and volumes of dissociation. They evaluated other data and give an equation that reproduces accurately the constant between 273 and 373 K and yields moderately accurate values at temperatures up to 473 K. A form of their equation for HSO_4^- K_{a2} is

$$\ln K_{a2} = -(\Delta H^\circ_{298.15}/RT) + (\Delta S^\circ_{298.15}/R) - (\Delta C^\circ_p/RT)(T - 298.15) + (\Delta C^\circ_p/R)\ln(T/298.15)$$

with

$$\Delta H^\circ_{298.15} = -22.6 \times 10^3 \text{ J mol}^{-1},$$

$$\Delta S^\circ_{298.15} = -113.7 \text{ J K}^{-1} \text{ mol}^{-1},$$

and

$$\Delta C^\circ_p = -300 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Infeldt and Sillen[202] show that at 298.15 K and ionic

Table 23. Tentative values of the solubility of mercury(I) sulfate in water.

T/K	Solubility c/mol dm^{-3}	T/K	Solubility c/mol dm^{-3}
273.15	$(0.78 \pm 0.11) \times 10^{-3}$	313.15	$(1.19 \pm 0.11) \times 10^{-3}$
283.15	$(0.87 \pm 0.11) \times 10^{-3}$	323.15	$(1.30 \pm 0.11) \times 10^{-3}$
293.15	$(0.97 \pm 0.11) \times 10^{-3}$	333.15	$(1.41 \pm 0.11) \times 10^{-3}$
		343.15	$(1.53 \pm 0.11) \times 10^{-3}$
298.15	$(1.03 \pm 0.11) \times 10^{-3}$	353.15	$(1.64 \pm 0.11) \times 10^{-3}$
		363.15	$(1.76 \pm 0.11) \times 10^{-3}$
303.15	$(1.08 \pm 0.11) \times 10^{-3}$	373.15	$(1.88 \pm 0.11) \times 10^{-3}$

Table 24. The solubility product constant of mercury(I) sulfate.

T/K	Ionic strength I/electrolyte	Solubility Product K°_{so}/mol^2 dm^{-6}	K_{so}/mol^2 dm^{-6}	Reference
	Tentative value			
298.15	0	6.5×10^{-7}		
	Experimental values			
288.15	0	7.42×10^{-7}		Sharma, Prasad [197]
298.15	0	4.68×10^{-7}		Brodsky [100]
	0	4.8×10^{-7}		Hass, Jellinek [198]
	0	6.81×10^{-7}		Brown, Land [199]
		8.08×10^{-7}		Sharma, Prasad [197]
	0	7.6×10^{-7}		Edrissi [200]
308.15	0	8.73×10^{-7}		Sharma, Prasad [197]
278.15	$(0.02-0.06)/H_2SO_4$		[a]	Sharma, Prasad [201]
288.15	$(0.02-0.06)/H_2SO_4$		[a]	Sharma, Prasad [201]
298.15	$(0.02-0.05)/H_2SO_4$		[a]	Sharma, Prasad [201]
	$3/Na^+(SO_4^{2-} + ClO_4^-)$		$(3.5 \pm 0.5) \times 10^{-5}$	Infeldt, Sillen [202]
308.15	$(0.02-0.05)/H_2SO_4$		[a]	Sharma, Prasad [201]
	Calculated from thermodynamic data			
298.15	0	1×10^{-6}		Latimer [103]
	0	7.5×10^{-7}		Leden [190][b]
	0	4.8×10^{-7}		Zhuk [118][c]
	0	6.5×10^{-7}		Hepler,Olofsson [5]
	0	6.2×10^{-7}		Infeldt,Sillen [202][d]
	0	9.6×10^{-7}		Charlot et al. [16]
	0	8.0×10^{-7}		NBS Tech.Note 270[14]

[a] Authors give the equation $\log(K_{so}/\text{mol}^2\text{dm}^{-6}) = \log[Hg_2^{2+}][SO_4^{2-}] - 8AI^{\frac{1}{2}} + 2\beta I$. Values of A and β at the various temperatures are in the original paper.

[b] Calculated using cell potentials of Berecki, Biedermann and Sillen [203].

[c] Original source unknown. May be the Hass, Jellinck [198] value.

[d] Calculated using cell data of Harned and Hamer [204].

Table 25. The ionization constant of HSO_4^- in water, $10^2 K_{a2}$.

278.15 K	288.15 K	298.15 K	308.15 K	Reference
1.43	1.34	1.20[a]	1.05	Hamer, 1934 [205]
1.73	1.43	1.03[b]	0.78	Davies et al.,1952 [206]
2.31	1.59	1.10	0.82	Nair, Nancollas,1958[207]
		1.09		Covington et al.,1965[208]
2.30	1.60	1.10	0.83	Sharma,Prasad,1969[195]
		1.29		Lietzke et al., 1961[209]
		1.03		Marshall,Jones,1966[210]
1.85	1.39	1.04	0.77	Young et al.,1978 [211]
		1.05		Larson et al.,1982[196]

a Recalculated by Sharma and Prasad as 1.10×10^{-2}.

b Recalculated by Nair and Nancollas as 1.09×10^{-2}.

strength 0.5, the stepwise formation constants for the complexes $[Hg_2SO_4]^\circ$ and $[Hg_2(SO_4)_2]^{2-}$ are 20 and 12.5, respectively. Brown and Land[199] give good evidence for the existence of the complex $[Hg_2(SO_4)(HSO_4)]^-$. Table 5A is a guide to mercury(II) sulfate solubility studies in aqueous electrolytes.

b. Mercury(II) Sulfate

$HgSO_4$ [7783-35-9] Molecular weight 296.65

[Chem. Abstr. Index Sulfuric acid, mercury (2 +) salt (1:1), H_2O_4S·Hg]

$HgSO_4$·H_2O Molecular weight 314.66

$HgSO_4$·2HgO [51069-05-7] Molecular weight 729.83

$2HgSO_4$·HgO·$2H_2O$ Molecular weight 845.92

Physical characteristics: Solid mercury(II) sulfate is reported as orthorhombic and as pseudo-orthorhombic monoclinic. The latter designation probably is the accurate description. As a monoclinic lattice $Z = 2$, $a = 6.574 \times 10^{-10}$ m, $b = 4.783 \times 10^{-10}$ m, $c = 4.817 \times 10^{-10}$ m, and $\beta = 90°$. The calculated density is 6503 kg m^{-3}. The monohydrate is orthorhombic with $Z = 4$, and a, b, and c are 7.874, 8.964, and 5.416×10^{-10} m, respectively. The calculated density is 5466 kg m^{-3}. The basic salt $HgSO_4$·2HgO (Schuetteite) is

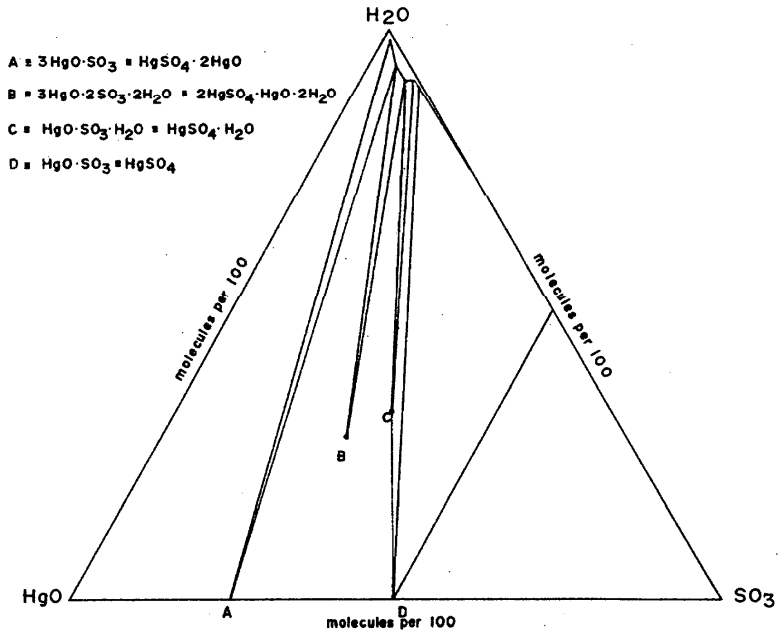

FIG. 9. Solubility of mercury(II) sulfate in water. The HgO + SO_3 + H_2O phase diagram at 298 K, based on the data of Hoitsema (Ref. 215). The solid $HgSO_4$·H_2O is not stable at 323 K.

hexagonal with $Z = 3$, $a = 7.03 \times 10^{-10}$ m, and $c = 9.98 \times 10^{-10}$ m. The calculated density is 8520 kg m^{-3}. The hydrated basic salt $2HgSO_4 \cdot HgO \cdot 2H_2O$ is monoclinic with a calculated density of 6140 kg m^{-3}. The unit cell dimensions are $a = 14.55 \times 10^{-10}$ m, $b = 8.94 \times 10^{-10}$ m, $c = 7.13 \times 10^{-10}$ m, and $\beta - 99° 30'$.

According to Cotton and Wilkinson[54] mercury(II) sulfate is completely ionic and highly dissociated in aqueous solution. Parks and Nordstrom,[214] who present thermodynamic formation data for several of the solid species, say that $HgSO_4$ is too soluble and requires too acid an environment to exist in nature.

In 1895, Hoitsema[215] extended earlier work of Ditte[216] and of Le Chatelier[217] on the $HgO + SO_3 + H_2O$ system at temperatures of 298 and 323 K. He prepared mixtures of $HgSO_4$ and/or $HgSO_4 \cdot 2HgO$ with H_2SO_4 and water. The mixtures were agitated continuously for 3 h at temperatures of 298 or 323 K. The fluid phase was analyzed and the solid phase identified. At 298 K all four solids, $HgSO_4$, $HgSO_4 \cdot H_2O$, $2HgSO_4 \cdot HgO \cdot 2H_2O$, and $HgSO_4 \cdot 2HgO$, have regions of stability. There may also be a $HgSO_4 + HgSO_4 \cdot H_2O$ solid solution region (see Fig. 9). At 323 K, $HgSO_4 \cdot H_2O$ does not exist as a stable solid. About one-half of Hoitsema's data are reproduced in Seidell and Linke.[6] The hydrogen ion concentration can be estimated only roughly from the data.

Vosburgh and Lackey[218] made several room-temperature (298–303 K) determinations of the solubility of $HgSO_4 \cdot 2HgO$ in dilute sulfuric acid solution with the following results:

$c_{H_2SO_4}$/mol dm^{-3}	0.011 94	0.0954	0.1450
c_{HgO}/mol dm^{-3}	0.001 03	0.0131	0.0203 .

The complexes $HgSO_4$ and $Hg(SO_4)_2^{2-}$ are important solution species. Infeldt and Sillen[202] report $K_1 = 22$ at $I = 0.5$ and 298.15 K; Posey and Taube[219] report $K_1 = 26$ at $I = 0.33$ to 0.38 and 298.15 K. Infeldt and Sillen also give a K_2 value of 12 at $I = 0.5$ and 298.15 K.

Erdenbaeva[183] gives a value of $K_{so} = 4.9 \times 10^{-3}$ for the solubility product of $HgSO_4$ in Na_2SO_4 solution at ionic strength 3 at 298.15 K. The value should be used with caution until the solid state is identified as $HgSO_4$ at this temperature and ionic strength.

4.8. Mercury Phosphates

a. Mercury(I) Phosphates

Hg_2HPO_4 [7782-67-4] Molecular weight 497.16

[Chem. Abstr. Index Phosphoric acid, dimercury (1 +) salt, $H_3O_4P \cdot 2Hg$]

$(Hg_2)_3(PO_4)_2$ [13465-20-8] Molecular weight 1393.48

[Chem. Abstr. Index Phosphoric acid, trimercury (1 +) salt, $H_3O_4P \cdot 3Hg$]

Physical characteristics: The *Crystal Data Determinative Tables*[13] contain no information on mercury (I) phosphates.

Mercury–phosphate systems can be understood only by knowledge of the complicated equilibria that exist therein. The older data are meager and sometimes contradictory. At present, the 1975 paper of Qvarfort-Dahlman[20] is the definitive work on both mercury (I) phosphate and mercury (II) phosphate systems.

Qvarfort-Dahlman[20] studied the $Hg_2^{2+} - HPO_4^{2-}$ aqueous system in oxygen-free 3 mol dm^{-3} $NaClO_4$ solution over the 1.7–7.2 pH interval at 298.15 K by titration studies of mercury(I) perchlorate with Na_2HPO_4. The precipitate Hg_2HPO_4 forms at pH's between 1.8 and 2.6. At higher pH's, $(Hg_2)_3(PO_4)_2$ is the stable solid phase. The pH at which the two solids are in equilibrium ranges from 2 to 3, depending on the concentration of total residual phosphate ion in the solution:

$$2Hg_2HPO_4(s) + Hg_2^{2+}(aq) = (Hg_2)_3(PO_4)_2(s) + 2H^+(aq).$$

No evidence of complex formation was found in the system. The tentative values of the solubility equilibria in 3 mol dm^{-3} $NaClO_4$ at 298.15 K from Qvarfort-Dahlman[20]

Table 26. Solubility product constants for the aqueous Hg_2^{2+}–HPO_4^{2-} system at 298.15 K.

Ionic strength I/electrolyte	Reaction	Solubility Product K°_{s0} or K_{s0}	Reference
	Tentative values		
0	$Hg_2HPO_4(s) \rightleftarrows Hg_2^{2+}(aq) + HPO_4^{2-}$	$(3.3 \pm 0.6) \times 10^{-13}$	a
3/$NaClO_4$		$(2.0 \pm 0.5) \times 10^{-11}$	Qvarfort-Dahlman[20]
3/$NaClO_4$	$(Hg_2)_3(PO_4)_2(s) + 2H^+(aq) \rightleftarrows 3Hg_2^{2+}(aq) + 2HPO_4^{2-}(aq)$	$(4.0 \pm 0.3) \times 10^{-22}$	Qvarfort-Dahlman[20]
	Other values		
0	$Hg_2HPO_4(s) \rightleftarrows Hg_2^{2+}(aq) + HPO_4^{2-}(aq)$	3.0×10^{-15}	Brodsky [100]
0.05/$NaClO_4$		2.1×10^{-15}	Brodsky [100]

[a] Calculated from standard potential [220,221] and ionization data [33].

are

$$Hg_2HPO_4(s) \rightleftarrows Hg_2^{2+}(aq) + HPO_4^{2-}(aq) \qquad \log K_{s0} = -10.70 \pm 0.10$$

$$(Hg_2)_3(PO_4)_2(s) + 2H^+(aq) \rightleftarrows 3Hg_2^{2+}(aq) + 2HPO_4^{2-}(aq), \qquad \log K = -21.40 \pm 0.03.$$

A value of K°_{s0} for Hg_2HPO_4 can be obtained by combining emf and ionization constant data at 298.15 K. Thus

$$2Hg(l) = Hg_2^{2+}(aq) + 2e^-, \qquad E^\circ = -0.796 \text{ V}$$

$$Hg_2HPO_4(s) + H^+(aq) + 2e^- = 2Hg(l) + H_2PO_4^-(aq), \qquad E^\circ = 0.638 \text{ V}$$

$$H_2PO_4^-(aq) = H^+(aq) + HPO_4^{2-}(aq), \qquad K^\circ_{a2} = 6.36\times10^{-8}$$

$$Hg_2HPO_4(s) = Hg_2^{2+}(aq) + HPO_4^{2-}(aq) \qquad K^\circ_{s0} = (3.3 \pm 0.6)\times10^{-13}, \quad \log K^\circ_{s0} = -12.48 \pm 0.07.$$

The E° for the reduction of $Hg_2HPO_4(s)$ is the average of the values of DeVries and Cohen[220] and Larson[221]; the second ionization constant of H_3PO_4 is from Gregory *et al.*[33]

The results of Brodsky,[100] based on measurements of his own and of Immerwahr,[98] are not well defined and are of doubtful value. The calculated values of the solubility of Hg_2HPO_4, as a function of pH from 6 to 14 using K°_{s0} and K_{a1}, K_{a2}, K_{a3} values, by Jaulmes and Brun[171] are also questionable since the solid is not stable in that pH range. The solubility product constant data are summarized in Table 26.

Although mercury(I) does not form complexes in the presence of HPO_4^{2-}, it does form complexes which are stable toward disproportionation to mercury(II) complexes and mercury, with pyrophosphate, $P_2O_7^{4-}$; tripolyphosphate, $P_3O_{10}^{5-}$; and tetrapolyphosphate, $P_4O_{13}^{6-}$. Both Yamane and Davidson[222] and Watters and Simonaitis[223] report formation constants at an ionic strength of 1 at 298.15 K for the various Hg_2^{2+}–$P_2O_7^{4-}$ complexes.

$$Hg_2^{2+}(aq) + P_2O_7^{4-}(aq) = Hg_2P_2O_7^{2-}(aq)$$

$$Hg_2^{2+}(aq) + 2P_2O_7^{4-}(aq) = Hg_2(P_2O_7)_2^{6-}(aq)$$

$$Hg_2^{2+}(aq) + OH^-(aq) + P_2O_7^{4-}(aq) = Hg_2OH(P_2O_7)^{3-}(aq)$$

$$Hg_2^{2+}(aq) + 2OH^-(aq) + P_2O_7^{4-}(aq) = Hg_2(OH)_2(P_2O_7)^{4-}(aq)$$

$$Hg_2^{2+}(aq) + HP_2O_7^{3-}(aq) = Hg_2HP_2O_7^-(aq).$$

The formation constants are summarized in Sillen and Martell.[8]

There are scattered data on several other aqueous Hg_2^{2+}–phosphorous-containing anion systems. Kryukova[186] reports a solubility of 3.5×10^{-7} mol dm^{-3} at 298 K for $Hg_2(PO_3)_2$ by a polarographic method. However, it is unlikely that a compound of this formula exists. Lange[224] reports a solubility of 5×10^{-4} mol dm^{-3} at 293 K for Hg_2PO_3F. Schulz, Matijevic, and Kerker[225] give figures showing the variation in solubility with pH of $Hg_2HPW_{12}O_{44}$ and $(Hg_2)_3P_2W_{18}O_{62}$ at 298 K.

b. Mercury(II) Phosphates

$HgHPO_4$ [7782-66-3] Molecular weight 296.57

[Chem. Abstr. Index Phosphoric acid, mercury(2 +) salt (1:1), $H_3O_4P{\cdot}Hg$]

$Hg_3(PO_4)_2$ [13464-28-3] Molecular weight 791.71

[Chem. Abstr. Index Phosphoric acid, mercury (2 +) salt (2:3), $H_3O_4P{\cdot}3/2\ Hg$]

$Hg_3(PO_4)_2{\cdot}2H_2O$ [37001-84-6] Molecular weight 827.74

[Chem. Abstr. Index Phosphoric acid, mercury (2 +) salt (2:3), dihydrate, $H_3O_4P{\cdot}H_2O{\cdot}3/2Hg$]

$(HgOH)_3PO_4$ [57363-76-5] Molecular weight 747.76

[Chem. Abstr. Index Mercury hydroxide phosphate, $Hg_3(OH)_3PO_4$]

Physical characteristics: Qvarfort-Dahlman[20] reports that $HgHPO_4$ forms as a low-density amorphous white material on mixing mercury(II) perchlorate and a phosphate solution near pH = 2. Solid $Hg_3(PO_4)_2$ forms a denser (7390 kg m^{-3}) white, finely grained crystal at pH = 5–6. Aurivillius and Nilsson[226] report that $Hg_3(PO_4)_2$ is monoclinic with $a = 9.737\times10^{-10}$ m, $b = 11.466\times10^{-10}$ m, $c = 6.406\times10^{-10}$ m, $\beta = 99.51°$, and $Z = 4$. Gyunner and Orlova[227] report obtaining the dihydrate, $Hg_3(PO_4)_2{\cdot}2H_2O$ on mixing mercury(II) nitrate with a 1.5 molar excess of NaH_2PO_4. At pH = 6–8, a mixture of $Hg_3(PO_4)_2$(s) and yellow $(HgOH)_3PO_4$(s) forms on mixing mercury(II) perchlorate and Na_2HPO_4 in 3 *M* $NaClO_4$.[20] The two solids can be separated easily. At more basic pH values, HgO is precipitated. In the 2–5 pH range, a second yellow precipitate forms along with $Hg_3(PO_4)_2$.[20] It was not identified, but it may be a basic mercury(II) phosphate or a mixture of basic mercury- (II) phosphates as reported by Mehta and Patel.[228] They proposed that $Hg_3(PO_4)_2{\cdot}HgO$, $Hg_3(PO_4)_2{\cdot}1.5HgO$, $Hg_3(PO_4)_2{\cdot}2HgO$, and $Hg_3(PO_4)_2{\cdot}2.5$ HgO form on mixing $Hg(NO_3)_2$ and Na_2HPO_4. They also report mixed HgNa phosphates and showed that $Hg_3(PO_4)_2$ decomposes to $Hg_2P_2O_7$ with evolution of oxygen at 903–953 K.

As is the case for the mercury(I)–phosphate system, the definitive work on the mercury(II)–phosphate system is the 1975 paper of Qvarfort-Dahlman.[20] As discussed above, she has shown that four solids predominate in the system in 3 mol dm^{-3} $NaClO_4$ at 298.15 K, at different ranges of pH. They are $HgHPO_4$ (amorphous solid at low pH), $Hg_3(PO_4)_2$ (dense, finely grained crystal, pH 5–6), $(HgOH)_3PO_4$ (yellow solid, pH 6–8), and HgO (at the higher pH's). More than one solid phase forms at a given pH. Between pH 2 and 5 there is evidence of another yellow solid that may be a basic mercury (II) phosphate.

According to Qvarfort–Dahlman,[20] at 298.15 K in 3 *M* aqueous sodium perchlorate the following solubility products, complex formation constants, and auxiliary equilibria describe the Hg^{2+}–HPO_4^{2-} system in the 2–9 pH range:

$$HgHPO_4(s) = Hg^{2+}(aq) + HPO_4^{2-}(aq) \qquad \log K_{s101} = -13.1 \pm 0.1$$

$$2Hg_3(PO_4)_2(s) + 2H^+(aq) = 3Hg^{2+}(aq) + 2HPO_4^{2-}(aq) \qquad \log K_{s322} = -24.6 \pm 0.6$$

$$(HgOH)_3PO_4(s) + 4H^+(aq)$$

$= 3Hg^{2+}(aq) + HPO_4^{2-}(aq) + 3H_2O$

$\log K_{s341} = -9.4 \pm 0.8$

$HgO(s) + 2H^+(aq) = Hg^{2+}(aq) + H_2O$

$\log K_s^* = 3.8 \pm 0.1$

$Hg^{2+}(aq) + HPO_4^{2-}(aq) = HgHPO_4(aq)$

$\log \beta_{101} = 8.80 \pm 0.20$

$Hg^{2+}(aq) + HPO_4^{2-}(aq) = HgPO_4^-(aq) + H^+(aq)$

$\log \beta_{111} = 3.25 \pm 0.20$

$Hg^{2+}(aq) + Hg(l) = Hg_2^{2+}(aq)$

$\log K_r = 2.63 \pm 0.02$

$H_2O = H^+(aq) + OH^-(aq)$

$\log K_w = -14.17 \pm 0.05.$

Gyunner and Orlova[227] obtained a solubility product value of 8×10^{-46} for what they identified as the dihydrate solid, $Hg_3(PO_4)_2 \cdot 2H_2O$, from isomolar solutions of about 0.28 mol dm^{-3} $Hg(NO_3)_2$ and NaH_2PO_4 at 293 K. The $Hg_3(PO_4)_2 \cdot 2H_2O$ is an ivory-colored finely divided crystalline powder of density 6370 kg m^{-3} that forms when the $Hg(NO_3)_2$:NaH_2PO_4 ratio is equal to or greater than 3:2. When more NaH_2PO_4 is present, a precipitate of variable composition is formed.

The solubility product value of Gyunner and Orlova can be combined with phosphoric acid ionization data:

$Hg_3(PO_4)_2(s) = 3Hg^{2+}(aq) + 2PO_4^{3-}(aq)$

$K_{s0} = 8 \times 10^{-46}$

$2PO_4^{3-}(aq) + 2H^+(aq) = 2HPO_4^{2-}(aq) \quad (1/K_{a3})^2$

to obtain

$Hg_3(PO_4)_2(s) + 2H^+(aq) = 3Hg^{2+}(aq) + 2HPO_4^{2-}(aq)$

$\log K_{s???} = -20.4.$

The result is several orders of magnitude larger than Qvarfort-Dahlman's value, but considering differences in ionic strength, temperature, and possible hydration of the solid, the agreement is better than one might expect.

Drivotina-Prodan *et al.*[229] report finding a 2:3 compound of $P_3O_{10}^{5-}$ and Hg^{2+} of low solubility. There are no quantitative data, only a small phase diagram of the system. Yamane and Davidson[222] report formation of the complex

$Hg^{2+}(aq) + OH^-(aq) + P_4O_7^{4-}(aq) = Hg(OH)P_4O_7^{3-}(aq)$

at 300.6 K in 0.5 mol dm^{-3} $HClO_4$/0.25 mol dm^{-3} $NaClO_4$.

4.9. Mercury Carbonate

a. Mercury(I) Carbonate

Hg_2CO_3 [6824-78-8] Molecular weight 461.189

[Chem. Abstr. Index Carbonic acid, dimercury (1 +) salt, $CH_2O_3 \cdot 2Hg$]

Physical characteristics: We found no crystallographic information on mercury(I) carbonate.

The solubility of mercury(I) carbonate is a function of pH and carbon dioxide partial pressure as well as ionic strength and temperature. The process is well described by the equation

$Hg_2CO_3(s) + 2H^+(aq) = Hg_2^{2+}(aq) + H_2O + CO_2(g) \quad K_e$

which is a sum of the steps

$Hg_2CO_3(s) = Hg_2^{2+}(aq) + CO_3^{2-}(aq) \quad K_{s0}$

$H^+(aq) + CO_3^{2-}(aq) = HCO_3^-(aq) \quad 1/K_{a2}$

$H^+(aq) + HCO_3^-(aq) = H_2O + CO_2(aq) \quad 1/K_{a1}$

$CO_2(aq) = CO_2(g) \quad K_H.$

Thus the equilibrium constant is $K_e = K_{s0}K_H/K_{a1}K_{a2}$, where K_{s0} is the traditional solubility product constant, K_H is Henry's constant for carbon dioxide, and K_{a1} and K_{a2} are the carbonic acid dissociation constants.

There are only a few studies of the mercury(I) carbonate system. Brodsky[100] used the earlier data of Immerwahr[98] to obtain a solubility product, $K^\circ_{s0} = 9.0 \times 10^{-17}$ at 298.15 K. Brodsky applied an activity coefficient correction and an arbitrary correction based on his own data for the Hg_2Cl_2 solubility product to obtain the value. This value has been quoted by many others, including Zhuk[230] and Latimer.[103] Kryukova[186] measured a solubility of 8.8×10^{-9} mol dm^{-3} by a polarographic method. The conditions of pH, ionic strength, carbon dioxide partial pressure, and temperature were not defined.

Saegusa[231] determined the Gibbs energy of formation of $Hg_2CO_3(s)$ by an emf study. He combined the result with Gibbs energy values from Latimer[103] to obtain the solubility product, K°_{s0}/mol^2 dm$^{-6} = 1.1 \times 10^{-17}$. A recalculation, using values from NBS Technical Note 270 (Sec. 3.4),[14] by Hepler and Olofsson,[5] and by us, gives the value K°_{s0}/mol^2 dm$^{-6} = 3.6 \times 10^{-17}$. This is accepted as the tentative value at 298.15 K (see Table 27).

Table 27. Tentative values of the mercury(I) carbonate solubility product constant at 298.15 K.

Ionic strength I/electrolyte	Solubility Product K°_{s0} or K_{s0}	Reference
0	$(3.6 \pm 0.5) \times 10^{-17}$	
3/$NaClO_4$	$(4.3 \pm 0.5) \times 10^{-14}$	Hietanen,Högfeldt [21]

Hietanen and Högfeldt[21] studied the mercury(I) carbonate system at an ionic strength of 3 in $NaClO_4$ solution at 298.15 K. They confirmed that the solid phase is Hg_2CO_3 over the pH range of 5–6. At pH 2–3, on mixing $NaHCO_3 + Hg(I)$ in 3 mol dm^{-3} $NaClO_4$, the solid obtained is $Hg_2(OH)_{0.75}(ClO_4)_{1.25}$. At an ionic strength of 3 at 298.15 K their emf measurements lead to the following values:

	Reaction	log K
(1)	$Hg_2CO_3(s) + 2H^+(aq) - Hg_2^{2+}(aq) + H_2O + CO_2(aq)$	4.19 ± 0.03
(2)	$CO_2(g) + H_2O = HCO_3^-(aq) + H^+(aq)$	-8.00 ± 0.03
(3)	$HCO_3^-(aq) = CO_3^{2-}(aq) + H^+(aq)$	-9.56 ± 0.02
(4)	$Hg_2CO_3(s) = Hg_2^{2+}(aq) + CO_3^{2-}(aq)$	-13.37 ± 0.05

or K_{s0}/mol^2 dm$^{-6} = (4.3 \pm 0.5) \times 10^{-14}$ at $I = 3$ and 298.15 K.

If one uses zero ionic strength values for reactions (2), (3), and (4) above, a value of $K^\circ = 51$ is obtained for reaction (1), compared to $(1.55 \pm 0.11) \times 10^4$ at $I = 3$.

b. Mercury(II) Carbonate

$HgCO_3$ [13004-83-6] Molecular weight 260.60

[Chem. Abstr. Index Carbonic acid, mercury (2 +) salt (1:1), $CH_2O_3 \cdot Hg$]

$HgCO_3 \cdot 2HgO$ [58800-00-3] Molecular weight 693.78

[Chem. Abstr. Index Mercury [carbonato (2 −)] dioxotri-, CHg_3O_5]

Physical characteristics: No crystallographic information was found for mercury(II) carbonate.

The solubility of mercury(II) carbonate depends on pH, carbon dioxide partial pressure, ionic strength, and temperature. Hydrolysis in both the solid and aqueous phases, and complex ion formation in the aqueous phase, are important steps in the solution process.

Over the pH range of 2.2–8.1 in 3 M $NaClO_4$ solution the solid phase is $HgCO_3 \cdot 2HgO$. The solution process is best described as

$$HgCO_3 \cdot 2HgO(s) + 6H^+(aq) = 3Hg^{2+}(aq) + CO_2(g) + 3H_2O.$$

Hietanen and Högfeldt[21,232] studied the system in 3 mol dm^{-3} sodium perchlorate solution. Bilinski, Markovic, and Gessner[233] studied the system in 0.5 mol dm^{-3} sodium perchlorate solution. They revised values reported earlier by Hietanen and Högfeldt and estimated zero ionic strength values of the equilibrium constants.

The studies in 0.5 ionic strength $NaClO_4$ solution show that at pH's greater than 9.5, solid ochre-yellow HgO forms; at pH's of 7 or smaller, the solid is $HgCO_3 \cdot 2HgO$; and at intermediate pH values, depending on the Hg^{2+} concentration, an orange-yellow precipitate of variable composition, which may contain some $HgCO_3 \cdot HgO$, forms. At 1 bar partial pressure of carbon dioxide, the variable composition precipitate slowly converts to $HgCO_3 \cdot 2HgO$.

In solution the species Hg^{2+}, $HgOH^+$, $Hg(OH)_2^\circ$, $HgHCO_3^+$, and $HgCO_3^\circ$ predominate. At more basic pH's, the species $Hg(CO_3)_2^{2-}$ is also observed.

Table 28 summarizes Bilinski, Markovic, and Gessner's[233] values of the various homogeneous and heterogeneous equilibrium constants in the Hg(II)–carbonate–water system. Auxiliary data from other sources have been added. These values give a self-consistent set of data to describe the system.

Table 28. Equilibria in the mercury(II) carbonate + water + sodium perchlorate system at 298.15 K.

Eqn. No.	Equilibrium	log K		
		I = 0	I = 0.5	I = 3.0
1	$H_2O = H^+(aq) + OH^-(aq)$	-13.995[d]	-13.73	-14.03
2	$CO_2(g) + H_2O = H^+(aq) + HCO_3^-(aq)$	-7.82[e]	-7.56	-8.00
3	$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq)$	-10.329[e]	-9.93	-9.56
4	$Hg^{2+}(aq) + H_2O = HgOH^+(aq) + H^+(aq)$	-	-3.38 ± 0.20[a]	-3.55
5	$HgOH^+(aq) + H_2O = Hg(OH)_2^\circ(aq) + H^+(aq)$	-	-2.56 ± 0.10[a]	-
	$Hg^{2+}(aq) + 2H_2O = Hg(OH)_2^\circ(aq) + 2H^+(aq)$	-	-	-6.21
6	$Hg^{2+}(aq) + H^+(aq) + CO_3^{2-}(aq) = HgHCO_3^+(aq)$	-	15.08 ± 0.10[a]	14.72[b]
7	$Hg^{2+}(aq) + CO_3^{2-}(aq) = HgCO_3^\circ(aq)$	-	11.01 ± 0.20[a]	11.00[b]
8	$Hg^{2+}(aq) + H_2O + CO_3^{2-}(aq) = Hg(OH)CO_3^-(aq) + H^+(aq)$	-	4.40 ± 0.10[a]	4.40[b]
9	$Hg^{2+}(aq) + 2CO_3^{2-}(aq) = Hg(CO_3)_2^{2-}(aq)$	-	14.50 ± 0.20[a]	14.00[a]
10	$HgCO_3 \cdot 2HgO(s) + 6H^+(aq) = 3Hg^{2+}(aq) + CO_2(g) + 3H_2O$	7.02 ± 0.25	5.40 ± 0.25[a]	7.12 to 7.26[c]
11	$HgO(s) + H_2O = Hg^{2+}(aq) + 2OH^-(aq)$	-	-24.87 ± 0.05[a]	-25.59

[a] Values determined by Bilinski, Markovic and Gessner [233].

[b] Values recalculated by Bilinski, et al.,[233] from Hietanen and Högfeldt [21,232].

[c] See references [21], [232], and ref. 4 of [233].

[d] From Marshall and Franck [35].

[e] From Berg and Vanderzee [27].

Table 29. Mercury(I) thiocyanate solubility in water.

T/K	Solubility $c_{Hg_2(SCN)_2}$/mol dm^{-3}	Reference
	Tentative value	
298.15	2.7×10^{-7}	
	Experimental and calculated values	
298.15	1.3×10^{-7}	Immerwahr, 1901 [98][a]
	1.5×10^{-7}	Grossmann, 1905 [234][b]
	1.7×10^{-7}	Sherrill,Skowronski, 1905 [235][b]
	3.1×10^{-7}	Brodsky, 1929 [100][a]
	1.38×10^{-7}	Kolthoff, 1931 [174][a]
	2.7×10^{-7}	Kryukova, 1939 [186][c]

[a] Calculated by Kryukova [186].

[b] Calculated from K_{s0}° value without taking into account complex formation.

[c] Incorrectly listed in Seidell, Linke [6] as g dm^{-3}.

4.10. Mercury Thiocyanate

a. Mercury(I) Thiocyanate

$Hg_2(SCN)_2$ [13465-37-7] Molecular weight 517.33

[Chem. Abstr. Index Thiocyanic acid, mercury (1 +) salt, CHNS·Hg]

Physical characteristics: The *Crystal Data Determinative Tables* contain no information on mercury(I) thiocyanate.

Both the disproportionation of Hg_2^{2+} to Hg and Hg^{2+} (Sec. 3.1) and the formation of the complexes $HgSCN^+$, $Hg(SCN)_2$, $Hg(SCN)_3^-$, and $Hg(SCN)_4^{2-}$ (Sec. 3.2) must be taken into account in any analysis of the solubility of mercury(I) thiocyanate.

Table 29 lists values for the solubility of mercury(I) thiocyanate in water. These values were determined indirectly, either by calculation from the solubility product constant or from an analysis of emf, including polarographic, measurements. Grossman[234] and Sherrill and Skowronski[235] were aware of ionic strength and complexing effects. However, it is not clear that these effects were properly taken into account in their calculations of solubility from solubility product values. The tentative value of 2.7×10^{-7} mol dm^{-3} for the solubility of mercury(I) thiocyanate in water at 298.15 K is the same as that determined by Kryukova[186] in a polarographic study.

There is good agreement on the magnitude of the solubility product values shown in Table 30. The value given as

Table 30. Mercury(I) thiocyanate solubility product constant

T/K	Ionic strength I/electrolyte	K_{s0} or K_{s0}°	Reference
	Tentative value		
298.15	0	3.2×10^{-20}	
	Experimental and calculated values		
298.15	0	1.8×10^{-20}	Sherrill, Skowronski, 1905 [235]
	0	1.44×10^{-20}	Grossman, 1905 [234]
	0	3×10^{-20}	Brodsky, 1929 [100]
	0.05/KSCN	1.66×10^{-20}	Brodsky, 1929 [100][a]
	0	3×10^{-20}	Balyatinskaya, 1978 [114][b]
	0	3.2×10^{-20}	NBS Tech. Note 270 [14][c]

[a] Calculated using data from Immerwahr [98].

[b] Probably Brodsky's value but not cited.

[c] Calculated from thermodynamic data in the reference cited.

Table 31. Mercury(II) thiocyanate solubility in water.

T/K	Solubility $c_{Hg(SCN)_2}$/mol dm^{-3}	Reference
	Tentative value	
298.15	2.2×10^{-3}	
	Literature values	
293.15	1.75×10^{-3}	Czakis, 1960 [236]
298.15	2.2×10^{-3}	Sherrill, Skowronski, 1905 [235]
298.15	2×10^{-3}	Mason, Forgeng, 1931 [237][a]

[a] Referenced as a handbook value. It may be a restatement of the Sherrill and Skowronski value.

the tentative value is calculated from thermodynamic data given in the NBS Technical Notes.[14]

b. Mercury(II) Thiocyanate

$Hg(SCN)_2$ [592-85-8] Molecular weight 316.74

[Chem. Abstr. Index Thiocyanic acid, mercury (2 +) salt, CHNS·1/2 Hg].

Physical characteristics: Mercury(II) thiocyanate is monoclinic with $a = 10.884 \times 10^{-10}$ m. $b = 4.050 \times 10^{-10}$ m, $c = 6.446 \times 10^{-10}$ m, $\beta = 95° 21'$, and $Z = 2$. The calculated density is 3759 kg m^{-3}.

Mercury(II) thiocyanate is more soluble in water than mercury(I) thiocyanate. As with the mercury(I) compound, mercury(II) thiocyanate complexes must be taken into account in analyzing $Hg(SCN)_2$ solubility data. The cumulative and stepwise formation constants recommended by Hepler and Olofsson[5] were given earlier (Sec. 3.2).

The tentative value for the solubility of mercury(II) thiocyanate in water at 298.15 K is 2.2×10^{-3} mol dm^{-3}.

Table 32. Solubility of $M[Hg(SCN)_4]$ salts.

Compound	Comments	Reference
$Co[Hg(SCN)_4]$	Tables and graphs of weight percent solubility as a function of t(37–80 °C) and NH_4Cl concentration (0.02–3.0 mol dm^{-3})	Cuvelier, 1936 [241]
$Zn[Hg(SCN)_4]$	1.75×10^{-4}	Swinarski, Czakis, 1955 [242]
$Cu[Hg(SCN)_4]$	1.82×10^{-4} solubility (mol dm^{-3}) at 291 K	
$Co[Hg(SCN)_4]$	$5.37\ z\ 10^{-4}$ in water	
$Cd[Hg(SCN)_4]$	19.0×10^{-4}	
	The four values above are repeated, but the temperature given at 293 K	Czakis, 1960 [236]
$Zn[Hg(SCN)_4]$	$[(4.7 \pm 0.4)-(6.7 \pm 0.6)] \times 10^{-4}$ mol dm^{-3}	Korenman et al, 1956 [243]
$Cd[Hg(SCN)_4]$	$[(1.1 \pm 0.1)-(4.0 \pm 0.5)] \times 10^{-4}$ mol dm^{-3}	
$Cu[Hg(SCN)_4]$	$[(4.4 \pm 0.4)-(8.6 \pm 1.1)] \times 10^{-4}$ mol dm^{-3}	
	temperature not defined, probably 293 K.	
$Co[Hg(SCN)_4]$	T/K Solubility/mol dm^{-3}	Korenman et al., 1956 [244]
	283 1.09×10^{-3}	
	293 1.46×10^{-3}	
	303 1.98×10^{-3}	
	313 2.68×10^{-3}	
$Pb[Hg(SCN)_4]$	293 9.72×10^{-3}	Czakis, 1960 [236]
$Mn[Hg(SCN)_4]$	293 0.660	

This value was determined by Sherrill and Skowronski[235] by a direct analytical method (Table 31).

A value for the mercury(II) thiocyanate solubility product of 2.15×10^{-8} appears to be calculated from Czakis's[236] solubility value with no account taken of activity coefficients or complexes.

A summary of sources of other solubility studies in aqueous electrolyte systems, with and without common ion, is given in Table 6A. Most of these studies were carried out at 293.15 K.

The divalent heavy metal ions Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, and Mn^{2+} form sparingly soluble salts with the $[Hg(SCN)_4]^{2-}$ anion. Analytical procedures have been developed for the determination of these ions as $M[Hg(SCN)_4]$ precipitates. Solubility values for these compounds are given in Table 32.

5. The Solubility Products of Some Other Sparingly Soluble Mercury Salts. Annotated Bibliography

Table 33 lists the solubility, solubility product, or information about the nature of the solid state of additional sparingly soluble mercury salts. There are data on sparingly soluble salts of mercury(I) or mercury(II) with over 20 anions. The goal was to cover the literature since 1950 thoroughly, but many data from earlier papers are also included.

Only a few of these data can be classed as recommended. Most values are classed as tentative and some are of only questionable usefulness. Included are references that contain little or no solubility data, but which contain information on solution species and on the nature of the solid state. Many of the sparingly soluble mercury compounds of anions of weak acids form mixed oxide or hydroxide solids whose exact composition is a function of pH. Many of these systems are just beginning to be understood.

Most of the solubility product values in Table 33 were obtained from experimental studies that used molar (c/mol dm^{-3}) concentrations. The values from Suzuki[260] and Rock,[270] and values calculated from the NBS tables[14] are on a molal (m/mol kg^{-1}) scale. Values from Erdenbaeva[183] and Zhuk[230] depend upon thermodynamic data from a variety of sources. Most of their values are probably on a molal basis. For applications to aqueous solutions of small ionic strengths in the room-temperature range, the difference in the molar and molal concentrations is negligible.

Table 33. The solubility or solubility product constant of some sparingly soluble mercury salts. Annotated Bibliography.

Substance	T/K	Solubility or solubility product	Comments/Reference
Mercury(I) chlorite $Hg_2(ClO_2)_2$			Too unstable in aqueous solution for quantitative measurement. Stated to be less soluble than mercury(II) chlorite. Levi, Bisi, 1956 [245].
Mercury(II) chlorite $Hg(ClO_2)_2$	273 282 292	0.046 g per 100 ml 0.050 g per 100 ml 0.066 g per 100 ml	Saturated aqueous solutions analyzed by iodimetric method. Levi, Bisi, 1956 [245]
Mercury(II) bromate $Hg(BrO_3)_2$			Solubility in hot and cold water. Rammelsberg, 1842 [2761]
$Hg(BrO_3)_2 \cdot 2H_2O$ [26522-91-8]	298.15	Acid, c/mol dm^{-3} | g $Hg(BrO_3)_2$ per 100 cm^3 $HClO_4$ | HNO_3 2.0 | 6.58 | 14.66 2.5 | 5.22 | - 3.0 | 4.13 | 15.00 3.5 | 3.40 | - 4.0 | 2.58 | 14.99 5.0 | 1.55 | 14.75	$Hg(BrO_3)_2$ completely hydrolyzed in aqueous solution to $Hg(OH)BrO_3$ in 36 h or less. Stable in 2M acid. No mention of the dihydrate by Smith. Nature of the solid uncertain. Smith, 1924 [247]. Grams of salt per 100 cm^3 of $HClO_4$ solution (column 2) and HNO_3 solution (column 3).
Mercury(II) bromate hydroxide $Hg(OH)BrO_3$ [11092-91-4]	298.15	g $Hg(OH)BrO_3$ per 100 cm^3 0 | 0.081 | 0.081 1.0 | 4.34 | 12.52 2.0 | 5.94 | - 2.5 | 6.06 | 21.30 3.0 | 6.06 | -	Smith 1924 [247,. see comment above.
Mercury(I) iodate $Hg_2(IO_3)_2$ [13465-35-5]	298	6.0×10^{-7} mol dm^{-3}	Value based on the result of a polarographic study. Mistakenly given units of g dm^{-3} in Seidell, Linke [6]. Kryukova, 1939 [186].
	298	K_s 1.3×10^{-18}	Value based on early emf results of Spencer [250]. Brodsky, 1929 [100].
		K_s° 1.94×10^{-14}	Study of cell with $Hg/Hg_2(IO_3)_2(s)$ electrode in media of varying IO_3 concentration. Takács, 1943 [248].
		K_s 3.0×10^{-20}	Original source not clear, may be from Russian Chemists Handbook. Zhuk, 1954 [230].
	298	K_s° 3.0×10^{-14}	Calculated by us from recommended E° values. Probably the most reliable value. Charlot et al., 1971 [16].
Mercury(II) iodate $Hg(IO_3)_2$ [7783-32-6]	298		Confirmed that only solid formed on mixing $Hg(NO_3)_2$ and KIO_3 is $Hg(IO_3)_2$. Gyunner, Poltavtseva, 1970 [249].
	Room	1×10^{-4} mol dm^{-3}	Catalytic titration. The authors compare their value with a reported value of 4.15×10^{-5} but no source is given. Piperaki, Hadjiioannou, 1977 [105].
Mercury(I) thiosulfate $Hg_2S_2O_3$	298	2.2×10^{-15} mol dm^{-3}	Value based on the results of a polarographic study. Mistakenly given units of g dm^{-3} in Seidell [6]. Kryukova, 1939 [186].
Mercury(II) selenide HgSe [20601-83-6]	298.15	K_s 10^{-59}	Calculated from data obtained in a polargraphic study. Lingane, Niedrach, 1948 [251].
	298.15	K_s $(2.5 \pm 1.5) \times 10^{-57}$	Studied solubility of HgSe as a function of pH by radiometric and potentiometric methods at I = 1 M $NaClO_4$. Solubility constant in acid medium up to pH = 3, increased but constant to pH = 6, constantly increasing with slope of one (log C_{Hg} vs. pH) in alkaline medium. Used values of H_2Se dissociation of $K_{a1} = 10^{-3.48}$ and $K_{a2} = 10^{-11.60}$ to obtain K_s value. Mehra, Gubeli, 1971 [182].

Table 33. (continued)

Substance	T/K	Solubility or solubility product	Comments/Reference
	298.15	K_s 10^{-58}	Measured $E^\circ = -0.83$ v for $HgSe + 2e^- \rightarrow Hg + Se^{2-}$. Combined with other thermodynamic data to calculate K_s. Gladyshev, Kireeva, 1972 [252].
	298.15	K_s 3.2×10^{-65}	Calculated value based on pre-1956 thermodynamic data. Buketov et al., 1964 [253].
	298.15	K_s 4.63×10^{-66}	Calculated from emf and thermodynamic data. Erdenbaeva, 1975 [183].
	Room	pH / mol L^{-1} Hg_2^{2+} 2.2 / 4.57×10^{-4} 3.4 / 4.97×10^{-4}	White, granular ppt. with composition near Hg_2SeO_3. Soluble in 4 M nitric acid. Redman Harvey, 1967 [254].
Mercury(I) selenite Hg_2SeO_3 [15855-76-2]	293.15	K_s 2.3×10^{-15}	From average of five measurements in dilute sulfuric and nitric acid solutions. Authors report K_s of $(3.8 \pm 2.2) \times 10^{-19}$ for $[Hg^+]^2[SeO_3^{2-}]$. Value given recalculated by us for Hg_2SeO_3. Authors used H_2SeO_3 dissociation constants of $K_{a1}=4 \times 10^{-3}$ and $K_{a2} = 1 \times 10^{-8}$. Second paper appears to be a summary of the first. Chukhlantsev,Tomashevsky, 1957 [255]. Chukhlantsev, 1962 [256].
	298.15	K_s 1.49×10^{-19}	Calculated from emf and thermodynamic data. Not clear if used Hg^+ or Hg_2^{2+} to calculate K_s. A more recent paper of the author [279] was not available to us. Erdenbaeva, 1975 [183].
	298.15	K_s 6×10^{-15}	Calculated from data in NBS Tech. Note 270 [14].
Mercury(II) selenite $HgSeO_3$ [14459-36-0]	298.15		Solubility increased from 5.5×10^{-3} to 83.5×10^{-3} normal as the conc. of Na_2SeO_3 increased from 0.0625 to 2 normal. The complex $Hg(SeO_3)_2^{2-}$ was reported. Rosenheim, Pritze, 1909 [257].
	298.15	K_s 1.4×10^{-14}	Measured solubility in 1 M $NaNO_3$ solution. Used H_2SeO_4 dissociation constants of $K_{a1} = 3.5 \times 10^{-3}$ and $K_{a2} = 5 \times 10^{-8}$ to obtain K_s. Toropova, 1957 [258].
	Room		$HgSeO_3$ identified as precipitate obtained on mixing 0.02 M $Hg(NO_3)_2$/0.01 M HNO_3 and 0.05 M K_2SeO_3. Aqueous phase contained 1.20×10^{-5} mol L^{-1} Hg^{2+} and 7.83×10^{-4} mol L^{-1} SeO_3^{2-} at pH 2.2. Solid somewhat soluble in 3-4 N acid. Redman, Harvey, 1967 [254].
	298.15	K_s 1.75×10^{-14}	Calculated from emf and thermodynamic data. Erdenbaeva, 1975 [183].
Mercury(I) selenate Hg_2SeO_4 [15513-59-4]	Room		Formed as yellow-white ppt. from acidified $Hg_2(NO_3)_2$ and Na_2SeO_4 solutions. Soluble in 5-6 $MHNO_3$. Analysis of solid indicated a basic salt of composition near $5Hg_2SeO_4 \cdot Hg_2O$. Redman, Harvey, 1967 [254].
Mercury(II) selenate $HgSeO_4$ [13870-15-0] $HgSeO_4 \cdot H_2O$ [61204-28-2] $HgSeO_4 \cdot HgO$ $HgSeO_4 \cdot 2HgO$	Room		Dark orange ppt. forms when Na_2SeO_4 soln added to acidified $Hg(NO_3)_2$ solution. On reverse addition, a yellow ppt. forms which turns orange on standing. Appreciably soluble at pH 1.2. Evidence that solid phase is a mixture of $HgSeO_4$, $HgSeO_4 \cdot HgO$, and $HgSeO_4 \cdot 2HgO$. At pH 2, the solution in equilibrium with the solid contains 0.46 g L^{-1} as Hg^{2+}. Redman, Harvey, 1967 [254].

Table 33. (continued)

Substance	T/K	Solubility or solubility product	Comments/Reference
	298.15	K_s 1.08×10^{-9}	Calculated from emf and thermodynamic data. Erdenbaeva, 1975 [183].
Mercury(II) telluride HgTe [12068-90-5]	298.15	K_s 2.5×10^{-70}	Calculated value based on pre-1956 thermodynamic data. Buketov et al., 1964 [253].
	298.15	K_s 10^{-68}	HgTe formed in the polarographic reduction of M_4TeO_4 cmpds. Zhdanov, Pats, 1965 [259].
	298.15	K_s 10^{-64}	Measured $E^\circ = -1.02$ v for $HgTe + 2e^- \rightarrow Hg + Te^{2-}$, combined result with other thermodynamic data to calculate K_s. Gladyshev, Kireeva, 1972 [252].
	298.15	K_s 9.24×10^{-74}	Calculated from emf and thermodynamic data. Erdenbaeva, 1975 [183].
Mercury(I) tellurite Hg_2TeO_3 [15851-46-4]	Room	0.070 g L^{-1} pH 5.5	On adding 0.05 M K_2TeO_3 to acidified $Hg_2(NO)_3$ a stable yellow ppt. forms. The ppt. becomes appreciably soluble at pH 1.25. TeO_2 coprecipitates as $Hg_2(NO_3)_2$ solution becomes less acidic. Redman, Harvey, 1967 [254].
Mercury(II) tellurite $HgTeO_3$ [15851-45-3]	Room	0.345 g L^{-1} pH 5.5	On adding 0.05 M K_2TeO_3 to acidified $Hg(NO_3)_2$ a white ppt. forms which is a mixture of $HgTeO_3$ and TeO_2. The ppt. becomes appreciable soluble at pH 1.2. Redman, Harvey, 1967 [254].
Mercury(I) tellurate Hg_2TeO_4 [15852-16-1]	Room	0.22 g L^{-1} pH 2	Mixing mercury(I) and tellurate solutions gives a yellow ppt. identified as Hg_2TeO_4. The ppt. is appreciably soluble at pH 0.8. Redman, Harvey, 1967 [254].
Mercury(II) tellurate $HgTeO_4$ [15852-15-0] $Hg_2H_2TeO_6$ [15980-01-5] Hg_3TeO_6 [13977-62-2]	Room	0.26 g L^{-1} pH 1.6	Mixing 0.02 M $Hg(NO_3)_2$/0.01 M HNO_3 with 0.05 M Na_2TeO_4 gives a yellow ppt. identified as $Hg_2H_2TeO_6$. It becomes appreciably soluble at pH 1.1-1.2. The precipitation reaction is probably $2Hg^{2+} + TeO_4^{2-} + 2H_2O \rightarrow Hg_2H_2TeO_6 + 2H^+$. Redman, Harvey, 1967 [254].
	298.15	K_s 6.1×10^{-8}	Calculated from emf and other thermodynamic data for $HgTeO_4$. Erdenbaeva, 1975 [183].
Mercury(I) azide $Hg_2(N_3)_2$ [38232-63-2]	298.15	K_s 0.81×10^{-18}	Emf study. Author calculated K_s 7×10^{-10} for HgN_3. We recalculated for $Hg_2(N_3)_2$ and used more modern auxiliary thermodynamic data. Suzuki, 1952 [260].
	298.15	K_s 1×10^{-18}	Sign of E° value in error in Charlot et al. Value taken from Suzuki and rounded. Thus the two values of K_s are not independent. Charlot et al. [16].
Mercury(I) monofluoro-phosphate Hg_2PO_3F	293.15	$\sim 5 \times 10^{-4}$ mol dm^{-3}	Compound hydrolyses in water so exact solubility could not be determined. The molar solubility value squared has been reported as the K_s value by others. Lange, 1929 [224].
Mercury(II) arsenite $Hg(AsO_2)_2$	Room	K_s $\sim 10^{-35}$	Polarographic study in alkaline solution. Vasil'eva et al., 1968 [261].
Mercury(I) arsenate $(Hg_2)_3(AsO_4)_2$ [13465-32-2]	293.15	K_s 7.5×10^{-51}	Determined directly both mercury and arsenic in saturated solutions in nitric and sulfuric acid. Author gave value of $(1.9 \pm 0.6) \times 10^{-31}$ for solubility product of Hg_3AsO_4. Value given was recalculated by us for $(Hg_2)_3(AsO_4)_2$. Arsenic acid dissociation constants used were 5.62×10^{-3}, 1.7×10^{-7}, and 2.9×10^{-12} for K_{a1}, K_{a2}, and K_{a3}, respectively. Chukhlantsev, 1956 [262].
Mercury(II) arsenate $Hg_3(AsO_4)_2$	298	K_s 2.5×10^{-39}	Thin layer chromatography of ion on stannic arsenate in aq. HCl system. Sharma et al., 1983 [302].

Table 33. (continued)

Substance	T/K	Solubility or solubility product	Comments/Reference
	298.15		Prepared stability diagram for mercury(I), arsenate and air with CO_2 partial pressure of $10^{-3.46}$ bar. Used Gibbs energy of formation of Hg_2^{2+}(aq) 36.7, Hg_2OH^+(aq) -12.76, Hg_2CO_3(s) -111.9, and Hg_3AsO_4(s) -141.86 kcal mol^{-1}. Robins, 1983 [278].
Mercury(I) oxalate		soly/mg L^{-1}	Determined solubility of $Hg_2C_2O_4 \cdot H_2O$ in water and in 0.8 M $NaNO_3$ solution. The presence of $NaNO_3$ in the solution had no effect on the solubility. Other authors do not mention the hydrated solid. The solubility is apparently based on the $Hg_2C_2O_4 \cdot H_2O$ formula. Jantsch,Schuster, 1936[263].
$Hg_2C_2O_4$ [2949-11-3]	291.2	2.61	
	293.2	2.84	
$Hg_2C_2O_4 \cdot H_2O$	295.4	2.90	
	297.2	3.36	
	299.7	4.01	
	301.6	4.52	
	303.6	5.17	
	309.2	7.56	
	313.4	9.50	
	291	K_s 2×10^{-13}	This value calculated by Brodsky [100] from data of Behrend [96] and stated to be at temperature of 298 K. Both Le Blanc and Harnapp [264] and Zhuk [230] quote the same value but identify the temperature as 291 K.
	298	K_s 1.8×10^{-13}	Value obtained from tabulated thermodynamic value in NBS Tech. Note and Charlot et al., [14], [16].
	291	k_s 3×10^{-14}	From measurements of emf of a cell with a Hg/Hg_2^{2+}-$C_2O_4^{2-}$-CaC_2O_4-Ca^{2+} electrode. Le Blanc,Harnapp, 1933 [264].
Mercury(II) oxalate	293	0.0107 g HgC_2O_4 in 100 g H_2O	Studied $K_2C_2O_4$ + HgC_2O_4 + H_2O system. Identified five regions where solids HgC_2O_4, $K_2C_2O_4 \cdot HgC_2O_4 \cdot 2H_2O$, $2K_2C_2O_4 \cdot HgC_2O_4 \cdot 3H_2O$, $3K_2C_2O_4 \cdot HgC_2O_4 \cdot 4H_2O$ or $K_2C_2O_4$ exist. Trifonov, 1924 [265].
HgC_2O_4 [3444-13-1]			
	298	K_s 4.7×10^{-9}	Value for aqueous media of I = 1.5 $NaNO_3$/NaCl. Measured solubility of HgC_2O_4 at I = 1.5 as NaCl conc. varied from 0.1 to 1.0 M. Also measured solubility of HgC_2O_4 at I = 3.0 KNO_3/$K_2C_2O_4$ as $K_2C_2O_4$ conc. varied from 0.2 to 1.0 M. Lodzińska et al., 1963 [266].
	293 ± 1	K_s 1.95×10^{-10}	In aq media of I = 1.0 $HClO_4$/$NaClO_4$. Used acid dissociation constants of oxalic acid (ethanedioic acid) of $K_{a1} = 5.9 \times 10^{-2}$ and $K_{a2} = 6.4 \times 10^{-5}$. Zajdler,Czakis-Sulikowska,1975 [267].
	Room	4.7×10^{-5} mol L^{-1}	Catalytic titration method. Piperaki,Hadjiioannou, 1977 [105].
Mercury(I) cyanide $Hg_2(CN)_2$	298	8.1×10^{-14} mol L^{-1}	Based on a polarographic measurement. Mistakenly given units of g L^{-1} in Seidell, Linke [6]. Kryukova, 1939 [186].
	298	K_s 5×10^{-40}	Brodsky recalculated Immerwahr's [98] value of 3×10^{-40}. Zhuk [230] also quotes the value. Brodsky, 1929 [100].
		D_2O/% mol(100 mol)$^{-1}$	
Mercury(II) cyanide	278	0 0.537	Measured $Hg(CN)_2$ solubility in H_2O and 91.43 per cent D_2O. Noonan, 1948 [268].
		91.43 0.434	
$Hg(CN)_2$ [592-04-1]		100 0.424 (est.)	
Mercury(II) cyanamide $HgCN_2$ [20837-85-8]	298.15	K_s 8×10^{-29}	Solubility measured in 1 M KNO_3 as a function of pH (HNO_3). The ionization constants of cyanamide, H_2NCN, used are K_{a1} 5.25×10^{-11} and cumulative constant 7.95×10^{-23}. Kitaev et al., 1971 [269].

Table 33 (continued)

Substance	T/K	Solubility or solubility product	Comments/Reference
Mercury(II) cyanate $Hg(OCN)_2$ [3021-39-4]	273	3.7 g per 100 ml	
	293	7.5 g per 100 ml	Söderbäck, 1957 [293]
Mercury(II) fulminate $Hg(CNO)_2$ [626-86-4]	285	0.693 and 0.710 g per liter	Precipitated and weighed as HgS. Holleman, 1896 [292].
	322	1.784 and 1.738 g per liter	
	291	0.74 g per 100 ml	Footnoted value for $Hg(ONC)_2$. Not clear if this is author's value or from literature. Söderbäck,1957 [293].
			There is confusion in the older literature on the salts of cyanic, isocyanic, fulminic, and isofulminic acids. Most now believe the ions cyanate-isocyanate and fulminate-isofulminate are indistinguishable.
Mercury(I) cobalticyanide $(Hg_2)_2[Co(CN)_6]_2$ [15521-63-8]	298.15	K_s 3.7×10^{-38}	Determined standard potential of electrode reaction $6Hg(\ell) + 2\ Co(CN)_6^{3-}\ (aq, a = 1) = (Hg_2)_3[Co(CN)_6]_2(s) + 6\ e^-$ and combined result with Latimer's [103] value of Hg/Hg_2^{2+} standard potential to obtain $K_s = 1.9 \times 10^{-37}$. The value given was calculated by us using Vanderzee and Swanson's Hg/Hg^{2+} $E°$ value. Rock, 1965 [270].
Mercury(I) ferrocyanide $(Hg_2)_2[Fe(CN)_6]$	298.15	K_s 1.12×10^{-12}	Determined by a method which is based on the distribution of the cation between two anions both of which form sparingly soluble precipitates. The reference salt was Hg_2SO_4. The authors used a K_s of 6.2×10^{-7} for Hg_2SO_4. Bukowska,Basinska, 1962 [271].
Mercury(II) ferrocyanide $Hg_2[Fe(CN)_6]$ [55578-07-9]	Room	K_s 6.2×10^{-11}	Predicted from paper chromatography studies of rate of movement of ions and their relationship to known K_s values. Varshney,Varshney, 1977 [280].
			Abstract states paper had K_s value. The paper is not available to us. Krleža et al., 1976 [281].
Mercury(I) ferricyanide $(Hg_2)_3[Fe(CN)_6]_2$	298.15	K_s 8.5×10^{-21}	See comment at mercury(I) ferrocyanide above. Bukowska, Basinska, 1962 [271].
Mercury(I) chromate Hg_2CrO_4 [13465-34-4]	298	K_s 2×10^{-9}	Brodsky recalculated Immerwahr's [98] value of 1.07×10^{-9}. The value is quoted by Zhuk [230]. Brodsky, 1929 [100].
			Paper chromatography study shows Hg_2CrO_4 less soluble than $HgCrO_4$. Paper gives order of solubility for 13 inorganic chromates. Hg_2^{2+} the least soluble of the group. No quantitative data. Kulaev, 1959 [272].

Table 33. (continued)

Substance	T/K	Solubility or solubility product	Comments/Reference
Mercury(II) chromate $HgCrO_4$ [13444-75-2] $HgCrO_4 \cdot 2HgO$ [11062-59-2]			Paper gives order of solubility for up to 17 cations of SiO_3^{2-}, HPO_4^{2-}, AsO_3^{3-}, $[Fe(CN)_6]^{4-}$, and CrO_4^{2-}. Mercury(II) ion is the least soluble silicate, arsenite, and hydrogen phosphate, and the third least soluble chromate. No quantitative values. Kulaev, 1959 [272].
	Room	1.28×10^{-4} mol L^{-1}	Catalytic titration method. Authors give a reported solubility which appears to be based on Hg_2CrO_4 solubility product value by mistake. Piperaki, Hadjiioannou, 1977 [105].
	293		The only sparingly soluble solid obtained on mixing $Hg(NO_3)_2$ and Na_2CrO_4 or K_2CrO_4 solutions is $HgCrO_4 \cdot 2HgO$. Gyunner, Orlova, 1971 [273].
Mercury(I) tungstate Hg_2WO_4 [38705-19-0]	291	K_s 1.1×10^{-17}	Study of $Hg/Hg_2WO_4 - CaWO_4 - Ca^{2+}$ electrode. Le Blanc, Harnapp, 1933 [264].
	298.15	$(2.2 \pm 0.2) \times 10^{-6}$ mol L^{-1}	Average of six measurements. Yatsimirskii, Rigin, 1958 [274].
Mercury(I) metavanadate $Hg_2(VO_3)_2$ [38688-96-9]	291	K_s 4.3×10^{-13}	A comparative method where solution analyzed contains two cations and one anion which form sparingly soluble precipitates. Author's result referenced to K_s of 5×10^{-7} for $AgVO_3$. Author reports value of 6.9×10^{-16} for $HgVO_3$. We recalculated given value for $Hg_2(VO_3)_2$. Zolotavin, 1947 [275].
Mercury(II) metavanadate $Hg(VO_3)_2$ [19402-46-1] $Na_2Hg(VO_3)_4$ [19320-90-2]	291	K_s 1.2×10^{-12}	Comparative method described above. Zolotavin, 1947 [275]. Mixing $Hg(NO_3)_2$ and $Na_2O \cdot V_2O_5$ solutions gives $HgO \cdot V_2O_5$ at pH 4.5-5.5 and $(HgO \cdot Na_2O)2V_2O_5$ at pH 6.4-6.9. Saxena et al., 1967 [282].
Mercury(I) hydroxide perchlorate $Hg_2(OH)_{1.3}(ClO_4)_{0.7}$ [61512-35-4]	298	$\log K_s = 2.35 \pm 0.01$ in 3 M $NaClO_4$	Solubility reaction $Hg_2(OH)_{1.3}(ClO_4)_{0.7}(s) + 1.3H^+ \rightleftharpoons Hg_2^{2+}(aq) + 0.7\ ClO_4^-(aq) + 1.3\ H_2O$ Hietanen, Högfeldt, 1976 [307].

6. Acknowledgments

We wish to acknowledge and thank Francis J. Johnston and Steven Dekich who helped with the preliminary stages of this manuscript, and Ms. Beth Boozer for technical assistance. We appreciate the advice of Professor A. Steven Kertes and other colleagues of the IUPAC Solubility Data Commission. Both L. H. Gevantman and T. P. Dirkse read preliminary drafts of the manuscript. David A. Crerar gave useful advice on the mercury sulfide section.

This work was carried out with the support of Contract No. NB81NADA2052 from the office of Standard Reference Data of the National Bureau of Standards.

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8. Appendix. Guide to the Literature on Additional Solubility Data Emphasizing Salt Effects

Table 1A. Sources of mercury(II) chloride solubility data in aqueous electrolyte solutions.

T/K	System	Reference
273,289,317	$HgCl_2 + HCl + H_2O$	Ditte, 1881 [62]
?	$HgCl_2 + HCl + H_2O$	Engel, 1889 [288]
298.15	$HgCl_2 + HCl + H_2O$	Richards, Archibald, 1902 [287][a]
298.15	$HgCl_2 + HCl + H_2O$	Thomas, 1939 [83][a]
298.2,308.2,318.2	$HgCl_2 + HCl + H_2O$	Lilich, 1959 [86]
298.15	$HgCl_2 + HCl + H_2O$	Anderson et al., 1974 [88]
298.2	$HgCl_2 + HCl + H_2O$	Kartzmark, 1982 [90]
303.2	$HgCl_2 + NH_4Cl + H_2O$	Meerberg, 1908 [91,92][a]
298.15	$HgCl_2 + AlCl_3 + H_2O$	Thomas, 1939 [83][a]
297	$HgCl_2 + InCl_2 + H_2O$	Kartzmark, 1980 [284]
298.2	$HgCl_2 + InCl_3 + H_2O$	Kartzmark, 1982 [90]
298.2	$HgCl_2 + TlCl + H_2O$	Benrath, Ammer, 1927 [81][a]
298.2,308.2,318.2	$HgCl_2 + Hg(ClO_4)_2 + H_2O$	Lilich, 1959 [86]
308.2	$HgCl_2 + CuCl_2 + H_2O$	Schreinemakers,Thonus, 1912 [94][a]
288-291	$HgCl_2 + CuCl_2 + H_2O$	Pélabon,Delwaulle,1930 [69]
298.2,308.2	$HgCl_2 + CuCl_2 + H_2O$	Bassett et al., 1933 [286][a]
298.2	$HgCl_2 + CoCl_2 + H_2O$	Benrath, 1927 [80][a]
298.2	$HgCl_2 + CoCl_2 + H_2O$	Bassett, Croucher, 1930 [82]
298.15	$HgCl_2 + BeCl_2 + H_2O$	Blidin, 1957 [85][a]
298.2	$HgCl_2 + MgCl_2 + H_2O$	Herz, Paul, 1913 [78][a]
298.2	$HgCl_2 + MgCl_2 + H_2O$	Bassett et al., 1933 [286]
298.15	$HgCl_2 + CaCl_2 + H_2O$	Richards, Archibald, 1902 [287][a]
298.2	$HgCl_2 + CaCl_2 + H_2O$	Herz, Paul, 1913 [78][a]
298.2	$HgCl_2 + CaCl_2 + H_2O$	Bassett et al., 1933 [286][a]
298.15	$HgCl_2 + CaCl_2 + H_2O$	Thomas, 1939 [83][a]
298.2	$HgCl_2 + SrCl_2 + H_2O$	Herz, Paul, 1913 [78][a]
291.2	$HgCl_2 + SrCl_2 + H_2O$	Krasikov, Ivanov, 1928[285]
298.2	$HgCl_2 + SrCl_2 + H_2O$	Bassett et al., 1933 [286][a]
298.15	$HgCl_2 + BaCl_2 + H_2O$	Richards, Archibald, 1902[287][a]
273,303.2	$HgCl_2 + BaCl_2 + H_2O$	Schreinemakers, 1910 [63]
298.2	$HgCl_2 + BaCl_2 + H_2O$	Herz, Paul, 1913 [78][a]
291.2	$HgCl_2 + BaCl_2 + H_2O$	Krasikov, Ivanov, 1928 [285]
298.2	$HgCl_2 + BaCl_2 + H_2O$	Bassett et al.,1933 [286][a]
298.2	$HgCl_2 + LiCl + H_2O$	Herz, Paul, 1913 [78][a]
298.15	$HgCl_2 + LiCl + H_2O$	Thomas, 1939 [83][a]
273	$HgCl_2 + LiCl + H_2O$	Aslanov, Blidin, 1959 [64]
203-293	$HgCl_2 + LiCl + H_2O$	Aslanov, 1963 [66]
298.15	$HgCl_2 + LiCl + AlCl_3 + H_2O$	Thomas, 1939 [83][a]
298.15	$HgCl_2 + LiCl + CaCl_2 + H_2O$	Thomas, 1939 [83][a]
288,338,373	$HgCl_2 + NaCl + H_2O$	Homeyer, Ritsert, 1888 [289][a]
298.2	$HgCl_2 + NaCl + H_2O$	Herz, Paul, 1913 [78][a]
298.15	$HgCl_2 + NaCl + H_2O$	Richards, Archibald, 1902 [287][a]
291.2	$HgCl_2 + NaCl + H_2O$	Krasikov, Ivanov, 1928 [285]

Table 1A (continued)

T/K	System	Reference
293	$HgCl_2 + KCl + H_2O$	Tikhomirov, 1907 [71][a]
298.2	$HgCl_2 + KCl + H_2O$	Herz, Paul, 1913 [78][a]
307,329,353,373	$HgCl_2 + KCl + H_2O$	Tourneux, 1919 [93][a]
291.2	$HgCl_2 + KCl + H_2O$	Krasikov, Ivanov, 1928 [285]
298.2	$HgCl_2 + KCl + H_2O$	Kartzmark, 1982 [90]
291.2	$HgCl_2 + KNO_3 + H_2O$	Krasikov, Ivanov, 1928 [285]
298.2	$HgCl_2 + CsCl + H_2O$	Foote, 1903 [74][a]
298.2	$HgCl_2$ + sea water	Ferry, Riley, 1946 [290][a]

[a] Referenced in Seidell, Linke [6].

Table 2A. Sources of mercury(II) bromide solubility data in aqueous electrolyte solutions.

T/K	Ionic strength/electrolyte	Reference
273.15	(0-5.7)/KBr (diagram only)	Pernot, 1932 [107][a]
277.65	(0-10.11)/$BaBr_2$	Tyrell, Richards, 1953 [108]
281.15	(∿1-5)/NaBr (diagram only)	Contet, 1943 [110]
283.55	(0-10.29)/$BaBr_2$	Tyrell, Richards, 1953 [108]
286.15	(∿3-18)/$BaBr_2$ (diagram only)	Delwaulle, Van Heems, 1952[111]
288.15	(∿1-5)/NaBr (diagram only)	Contet, 1943 [110][a]
293 ± 1	2.0/($NaNO_2$ + $NaClO_4$)	Zajdler, Czakis-Sulikowska, 1974 [104]
293.15 ± .05	2.2/($Hg(NO_3)_2$ + $Ca(NO_3)_2$ + HNO_3 (diagram only)	Gyunner, Yakhkind, 1968 [112]
298.15	0.05/KBr	Sherrill, 1903 [75][a]
298.15	∿0.3/$Hg(NO_3)_2$	Morse, 1902 [73]
298.15	(0-5.2)/NaBr	Herz, Paul, 1913 [78]
298.15 ± 0.02	(0.003-0.04)/KBr	Garrett, 1939 [109]
(298.15)	(0.1-3.0)/KBr	Abegg, Immerwahr, Jander, 1902 [99][a]
298.15	(0-3.5)/KBr	Herz, Paul, 1913 [78][a]
298.15	(0.2-11.3)/$CaBr_2$	Herz, Paul, 1913 [78][a]
298.15	(0.2-5.6)/$SrBr_2$	Herz, Paul, 1913 [78][a]
298.15	(0-3.3)/$BaBr_2$	Herz, Paul, 1913 [78][a]
298.15	(0-10.29)/$BaBr_2$	Tyrell,Richards, 1953 [108]
306.65	0.0275/KBr	Tourneux, Pernot, 1925 [113][a]
307.15	(0-9.6)/KBr (diagram only)	Pernot, 1932 [107][a]
328.65	0.0273/KBr	Tourneux, Pernot, 1925 [113][a]
351.15	0.0260/KBr	Tourneux, Pernot, 1925 [113][a]
353.15	(0-9.1)/KBr (diagram only)	Pernot, 1932 [107][a]
369.65	0.0271/KBr	Tourneux, Pernot, 1925 [113][a]

[a] The data appear in Seidell, Linke [6].

Table 3A. Sources of mercury(II) iodide solubility data in aqueous electrolyte solutions.

T/K	Ionic strength I/electrolyte	Reference
273.15-353.15	(~0.5-3.7)/KI	Pernot, 1927[129][a];1931[130][a]
273.15-351.15	(~0-2.5)/CsI (diagram only)	Pernot, 1936[131]; 1938[132]
281.15	0.5/$(Na^+,H^+)ClO_4^-$	Hansen et al., 1963 [24]
293.15	(~0.9-3)/KI	Dunningham, 1914 [133][a]
	5.2/$(Hg^{2+},Ca^{2+},H^+)NO_3^-$	Gyunner, Yakhkind, 1970 [134]
294.15	0.01/$HClO_4$	Belevantsev, Shuvaev, 1981 [135]
295.65	(~0.1-3.6)/KI	Naudé, 1927 [122][a]
298.15	0.03/KI	Sherrill, 1903 [75][a]
	0.5/$NaClO_4$	Belevantsev et al., 1973 [136]
	0.5/$(Na^+,H^+)ClO_4^-$	Biedermann, Sillen, 1949 [124]
	0.5/$(Na^+,H^+)ClO_4^-$	Hansen et al., 1963 [24]
	0.5/$Na^+(Cl^-,ClO_4^-)$	Belevantsev et al., 1973 [136]
	0.5/$Na^+(Br^-,ClO_4^-)$	Belevantsev et al., 1973 [136]
	0.5/$Na^+(I^-,ClO_4^-)$	Belevantsev et al., 1973 [136]
	1/$Na^+(I^-,ClO_4^-)$	Czakis-Sulikowska, 1964 [127]
	1/$Na^+(NCS^-,ClO_4^-)$	Czakis-Sulikowska, 1964 [137]
	1/$(Na^+,H^+)(NCSe^-,ClO_4^-)$	Czakis-Sulikowska, 1965 [138]
	1/$Na^+(ClO_4^-,S_2O_3^{2-})$	Czakis-Sulikowska, 1964 [127]
	1/$NH_4^+(Br^-,NO_3^-)$	Czakis-Sulikowska, 1966 [128]
	1/LiBr	Czakis-Sulikowska, 1966 [128]
	1/$Li^+(Br^-,NO_3^-)$	Czakis-Sulikowska, 1966 [128]
	1/NaBr	Czakis-Sulikowska, 1966 [128]
	1/$Na^+(Br^-,NO_3^-)$	Czakis-Sulikowska, 1966 [128]
298.15	1/KBr	Czakis-Sulikowska, 1966 [128]
	1/$K^+(Br^-,NO_3^-)$	Czakis-Sulikowska, 1966 [128]
	1/RbBr	Czakis-Sulikowska, 1966 [128]
	1/$Rb^+(Br^-,NO_3^-)$	Czakis-Sulikowska, 1966 [128]
	1.2/$Hg(CN)_2$	Coleman et al., 1968 [139]
	1.5/$Hg(NO_3)_2$	Morse, 1902 [73]
	(0.1-1.0)/NH_4Br	Czakis-Sulikowska, 1966 [128]
	(0.79-2.2)/NaI	Herz, Paul, 1913 [78][a]
	(0.004-1.2)/KI	Garrett, 1939 [109]
	(0.3-2.5)/KI	Herz, Paul, 1913 [78][a]
	(0.15-1.5)/$MgBr_2$	Czakis-Sulikowska, 1966 [128]
	(0.16-5.4)/CaI_2	Herz, Paul, 1913 [78][a]
	(0.15-1.5)/$SrBr_2$	Czakis-Sulikowska, 1966 [128]
	(0.75-1.8)/$SrBr_2$	Herz, Paul, 1913 [78][a]
	(0.15-1.5)/$BaBr_2$	Czakis-Sulikowska, 1966 [128]
	(0.3-4.5)/BaI_2	Herz, Paul, 1913 [78][a]
	(0.08-5.6)/$Hg(NO_3)_2$	Yatsimirskii, 1951[140][a], Yatsimirskii, Shutov, 1952 [126][a]
	(~0.3-2.6)/$(Na^+,H^+)(ClO_4^-,SO_3^{2-})$	Czakis-Sulikowska, 1966 [126]
(298)	0.1-1/KI	Abegg et al., 1902 [99]
303.15	(~1.8-3.7)/KI	Dunningham, 1914 [133][a]
	(0.25-0.95)/$HgCl_2$	Sugden, 1929 [141]
307.15	(~0.2-3)/RbI (diagram only)	Pernot, 1940 [142][a]
313.15	0.5/$(Na^+,H^+)ClO_4^-$	Hansen et al., 1963 [24]
343.15	(0.46-2.9)/$HgCl_2$	Sugden, 1929 [141]

[a] The data appear in Seidell, Linke [6].

Table 4A. Sources of mercury(II) sulfide solubility data in aqueous electrolyte solutions.

T/K	Ionic strength I/electrolyte	Reference
	Cinnabar, red HgS	
?	?/dil HCl	Dorenfeldt-Holtan, 1932 [146]
?	water	Aidin'yan, 1960 [147]
298.15	0.36-4.41/Na_2S	Dickson, Tunell, 1954 [148], 1958 [149]
	0.30-6.09/Na_2S	Knox, 1906 [150], 1908 [151]
	0.30-10.7/Na_2S + NaOH	Knox, 1906 [150], 1908 [151]
	0.51-13.6/Na_2S + Na_2O	Dickson, Tunell, 1954 [148], 1958 [149]
	0.3-6.0/Na_2S_2	Knox, 1906 [150], 1908 [151]
	~5/Na_2S_2 + NaOH	Knox, 1906 [150], 1908 [151]
	0.75-3.0/K_2S	Knox, 1906 [150], 1908 [151]
	1.75 - 7.1/K_2S + KOH	Knox, 1906 [150], 1908 [151]
	1.25 - 1.75/K_2S + NaOH	Knox, 1906 [150], 1908 [151]
306.15	0.30-2.3/Na_2S	Knox, 1906 [150], 1908 [151]
323.15	0.48-5.07/Na_2S	Dickson, Tunell, 1954 [148], 1958 [149]
348.15	0.36-4.56/Na_2S	Dickson, Tunell, 1954 [148], 1958 [149]
	1.26-8.44/Na_2S + Na_2O	Dickson, Tunell, 1954 [148], 1958 [149]
363.15	?/H_2S (diagram only)	Shikina, Zotov, Khodakovskii, 1981 [152]
423.15	?/H_2S (diagram only)	Shikina, Zotov, Khodakovskii, 1981 [152]
294.15-474	3.7/NaHS, 4.4-58.6 bar	Barnes, Romberger, Stemprok, 1967 [153]
298.15-474	0.4/NaHS, 18.9-88.3 bar	Barnes, Romberger, Stemprok, 1967 [153]
297.15-471	~8.4/NaHS + H_2S + NH_4Cl,	Barnes, Romberger, Stemprok, 1967 [153]
	20.1-142 bar	Barnes, Romberger, Stemprok, 1967 [153]
322.15-471	~1/H_2S, 13.9-44.5 bar	Barnes, Romberger, Stemprok, 1967 [153]
323.15-523	0.26-1.5/Na_2S, 1.00-1517 bar	Dickson, 1964 [154]; 1966 [155]
423 ± 2	0.4-2.7/Na_2S + Sb_2S_3, 100 ± 4 bar	Learned, Tunell, Dickson, 1974 [156]
473 ± 2	0.4-2.7/Na_2S + Sb_2S_3, 100 ± 4 bar	Learned, Tunell, Dickson, 1974 [156]
523 ± 2	0.4-2.7/Na_2S + Sb_2S_3, 100 ± 4 bar	Learned, Tunell, Dickson, 1974 [156]
	Metacinnabar, black HgS	
?	water	Aidin'yan, 1960 [147]
?	?/dil HCl	Dorenfeldt-Holtan, 1932 [146]
291.15	water	Weigel, 1906 [157]; 1907 [158]
291.15	~1/$HClO_4$ sat with H_2S	Treadwell, Schaufelberger, 1946 [159]
293.15	1/NaHS + KCl + buffer	Schwarzenbach, Widmer, 1963 [160]
298.15	0.30-6.09/Na_2S	Knox, 1906 [150]; 1908 [151]
	0.20-6.15/Na_2S	Dickson, Tunell, 1954 [148];1958 [149]
	~2/Na_2S + NaOH	Martin, 1950 [161]
	~9/Na_2S + NaOH	Martin, 1950 [161]
	?/CO_3^{2-} (diagram only)	Bilinski, Jusufi, 1980 [162]
	?/CO_3^{2-} + SO_4^{2-} (diagram only)	Bilinski, Jusufi, 1980 [162]
	?/CO_3^{2-} + PO_4^{3-} (diagram only)	Bilinski, Jusufi, 1980 [162]
	?/sea water (diagram only)	Bilinski, Jusufi, 1980 [162]
	0.75-3.0/K_2S	Knox, 1906 [150]; 1908 [151]
	0.42-4.77/Na_2S	Dickson, Tunell, 1954 [148];1958 [149]
	0.68-3.60/Na_2S	Dickson, Tunell, 1954 [148];1958 [149]

Table 4A (continued)

T/K	Ionic strength I/electrolyte	Reference
	Form of solid HgS unspecified	
?	~0.4-0.6/Na_2S	Dubey, Ghosh, 1959 [163]
?	0.4-2.5/Na_2S + NaOH	Dubey, Ghosh, 1959 [163]
?	?/Na_2S + NaOH	Becker, 1887 [164]; 1888 [165
?	~0.05-0.5/K_2S	Dubey, Ghosh, 1959 [163]
?	~3-4/K_2S + KOH	Dubey, Ghosh, 1959 [163]
290.15	?/Na_2S	Behrend, 1893 [96]
298.15	0.48-4.58/Na_2S	Milyutina, Polyvyannyi, Sysoev, 1967 [166]
	?/$(NH_4)_2S_X$ + metal ions	Beardsley et al., 1970 [167]
313.15	?/$(NH_4)_2S_X$ + Sn^{4+}	Beardsley et al., 1970 [167]
	0.5/KOH + metal ions	Beardsley et al., 1970 [167]
	~1/LiOH + KNO_3 + Sn^{4+}	Beardsley et al., 1970 [167]
353	~0.5/KOH + metal ions	Beardsley et al., 1970 [167]
368	~2/KOH + metal ions	Beardsley et al., 1970 [167]
	~1/LiOH + KNO_3 + metal ions	Beardsley et al., 1970 [167]

Table 5A. Sources of mercury(I) sulfate solubility data in aqueous electrolyte solutions.

T/K	Ionic strength I/electrolyte	Reference
273.15	0.003-12.00/H_2SO_4	Craig et al., [191][a]
278.15	0.021-0.063/H_2SO_4	Sharma, Prasad, [201]
288.15	0.020-0.058/H_2SO_4	Sharma, Prasad, [201]
288.15	1.16-4.05/K_2SO_4	Barré, [192][a]
(291)	4.4, 12.8/$ZnSO_4$	Wright, Thompson [188]
298.15	0.006-6.00/H_2SO_4	Brown, Land [199]
298.15	0.012-12.0/H_2SO_4	Hulett, [212]
298.15	0.019-0.054/H_2SO_4	Sharma, Prasad, [201]
298.15	0.060-0.300/H_2SO_4	Drucker, [193][a]
298.15	0.006/(H_2SO_4 + HCl)	Sharma, Prasad, [197]
298.15	0.300/K_2SO_4	Drucker, [193][a]
301.15	0.003-12.00/H_2SO_4	Craig et al., [191][a]
306.15	1.17-5.25/K_2SO_4	Barré, [192][a]
308.15	0.018-0.051/H_2SO_4	Sharma, Prasad, [201]
308.15	0.006/(H_2SO_4 + HCl)	Sharma, Prasad, [197]
323.15	1.17-4.67/K_2SO_4	Barré, [192][a]
348.15	1.24-8.16/K_2SO_4	Barré, [192][a]
373.15	~1.5-15/H_2SO_4 (diagram only)	Summers, Gardiner, [213]

[a] Data in Seidell, Linke [6].

Table 6A. Sources of mercury(II) thiocyanate solubility data in aqueous electrolyte solutions.

T/K	Ionic Strength I/electrolyte	References
273.15	0.13-0.25/KSCN	Sherrill, Skowronski, 1905 [235]
293.15	0.06-0.60/$NaNO_2$	Czakis-Sulikowska, Swinarski, 1962 [238]
	0.5/$Na^+(NO_2^- + NO_3^-)$	Czakis-Sulikowska, Swinarski, 1962 [238]
	2.0/$Na^+(NO_2^- + NO_3^-)$	Yakhkind, Gyunner, 1968 [239]
	0.5/$NaNO_3$	Czakis, 1960 [236]
	2.0/$NaNO_3$	Yakhkind, Gyunner, 1968 [239]
	0.4/NaCl	Czakis-Sulikowska, Swinarski, 1962 [238]
	0.1-0.5/NaBr	Czakis-Sulikowska, Swinarski, 1962 [238]
	2.0/NaBr	Yakhkind, Gyunner, 1968 [239]
	2.0/$Na^+(Br^- + NO_3^-)$	Yakhkind, Gyunner, 1968 [239]
	0.4/NaSCN	Czakis-Salikowska, Swinarski, 1962 [238]
	0.5/$Na^+(SCN^- + NO_3^-)$	Czakis, 1960 [236]
	1.4/NH_4NO_3	Czakis, 1960 [236]
	4.6/$(Hg^{2+} + Ca^{2+} + H^+ + K^+)NO_3^-$	Gyunner, Belykh, 1966 [240]
	4.6/$(Hg^{2+} + Ca^{2+} + H^+ + K^+)NO_3^-$	Gyunner, Yakhkind, 1968 [112]
?	0.1-0.54/KSCN	Abegg, Immerwahr, Jander, 1902 [99]
298.15	0.1-0.77/KSCN	Sherrill, Skowronski, 1905 [235]
298.15	0.20-6.8/KSCN	Mason, Forgeng, 1931 [237]