The Solubility of Some Sparingly Soluble Lead Salts: An Evaluation of the Solubility in Water and Aqueous Electrolyte Solution

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The literature on the solubility of sparingly soluble lead salts in water and in aqueous electrolyte solution was reviewed. Solubility data were compiled and evaluated. Recommended and tentative values of the solubilities are presented. A partial compilation of solubility products and of complex ion formation constants are given. Where possible the solubility product values have been checked for consistency against thermodynamic data from sources other than solubility measurements.

Key words: Aqueous solubility of lead salts; lead carbonate; lead halides; lead nitrate; lead phosphates; lead sulfate; lead sulfide; solubility; solubility product; sparingly soluble lead salts.

Contents

List of Tables

Nomenclature

A	Debye-Huckel limiting law constant
A_1, A_2, A_3, and A_4	parameters of equation [10] and related equations
A, B, C, D, and E	parameters of equation [21]
B	Debye-Huckel constant
$B°$	specific ion interaction term, Scatchard deviation parameters
C_p°	heat capacity, constant pressure
E, $E°$, E_{jp}	electromotive force, potential, standard potential, junction potential
F	the Faraday constant
$G°$	Gibbs energy
$H°$	enthalpy
I	ionic strength
K_H	equilibrium constant, Henry's constant
K_n	equilibrium constant, ligand metal formation constant ($ML_{n-1}+L=ML_n$)
K_{s0}, K_{snm}°	equilibrium constant, solubility product (may be designated either concentration scale or molality scale) $ML(s)=M+L$; the superscript indicates the thermodynamic constant
K_{snm}, K_{snm}^0	equilibrium constant, solubility product when a complex M_mL_n is formed in solution. When $m=1$, the second subscript ($m=1$) is omitted; the notation also applies when a protonated ligand reacts with elimination of proton [3, supplement, p. xvi]. The superscript indicates the thermodynamic constant
K_1, K_2, K_3	equilibrium constant, weak acid dissociation
P	pressure
R	gas constant
$S°$	entropy
T	absolute 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	number of equivalents
z	ion charge
α	Harned rule coefficient
β_n	equilibrium constant, cumulative ligant metal formation constant ($M+nL=ML_n$), $\beta_n=\prod_{i=1}^{n} K_i$ (see K_n above)
ρ	density
γ	activity coefficient

1. Introduction

Equilibrium data of all kinds are required to model the transport and transformation of inorganic pollutants in natural, brackish, and sea water. Among the 20 or so metallic ions of concern in environmental studies is the lead ion. This report is a compilation and evaluation of stoichiometric solubility data of sparingly soluble lead salts in water and aqueous electrolyte solution.

The solubility data were compiled in two stages. Solubility data from before about 1955 were traced through standard compilations of solubility data [1–4].[1] Solubility data reported since 1955 were traced through a combined hand and computer search of Chemical Abstracts from 1955 into early 1978. The solubility data found were compiled and evaluated. Solubility values were recommended when the solubility data on a given lead salt over similar ranges of temperature from several laboratories agreed within estimates of experimental error. Information on the solid phase and on the speciation of complex ions in solution in equilibrium with the solid were included when available. Much of the information on the solid phase was taken from the Crystal Data Determinative Tables [5].

There is a listing of lead salt solubility products and a partial listing of lead complex ion formation constants. The evaluation of the stoichiometric solubility data is a preliminary step in the eventual evaluation of the solubility product constants. However, the evaluation of the solubility product constants will require compilation of other associated data and extensive calculations which we hope will be carried out later.

[1] Figures in brackets indicate literature references at the end of this paper.

2. Solubility Methods

There are several papers that summarize the factors important in the experimental determination of solubility [6–9]. However, for specific details of a method one usually has to consult the original research paper.

The solubility data found in the literature were determined by a variety of direct solubility methods, by emf methods for solubility products, and by standard electrode potential measurements, which are often evaluated for purposes other than the calculation of solubility products.

2.1. Direct Solubility Methods

Conductivity. Many measurements of the specific conductance of saturated aqueous solutions are reported in the early literature. The corrections for water conductivity and for hydrolysis products and complex ion products were often either not applied or inaccurately applied. The effect of a small concentration of a soluble electrolyte impurity is very large. In general, conductivity is not a good primary method of determining solubility. This is not to say that conductivity cannot be used to determine solubility. The work of Day and Gledhill [10] on Hg_2Cl_2 and of Little and Nancollas [11] on $PbSO_4$ illustrate successful application of conductivity techniques to the measurement of solubility.

Direct Physical Methods. The evaporation of the solvent from a known weight or volume of a saturated solution and the weighing of the solid residue is a successful classical method of determining solubility. However, there may be problems both in making a complete separation of the saturated liquid from finely divided suspended solid, and in the control of temperature during the separation process. In addition there can be loss of solid due to spattering during the drying process, and an incorrect weight of solid because of either incomplete drying or decomposition of the solid during the drying.

Another direct physical method is the synthetic method. Known weights of solid and liquid are sealed in a glass or silica tube. The tube and contents are agitated and the temperature is increased at such a rate as to maintain saturation. The temperature of the disappearance of the last solid is observed visually. The temperature at which the solid first reappears on cooling is also observed. The method can work well, especially at higher temperatures where the rates of solution and dissolution are rapid, but the sealed tube is required to keep the solvent in the liquid state. Benrath, Gjedebo, Schiffers, and Wunderlich [12] applied the technique to many salts over the 400–650 K temperature interval. Their solubility values for the lead halides, $PbCl_2$, $PbBr_2$, and PbI_2 appear to be low. A too rapid heating could lead to low solubility values. The method appears to have been successfully applied to silver sulfate solubilities in a series of papers by Lietzke and Stoughton [13].

Chemical Methods. The saturated liquid phase may be analyzed by a variety of chemical methods. Precipitation, colorimetric methods, acid-base and redox titrations have been used. Before a chemical method can be applied, the saturated solution and the solid must be separated with the problems noted above of complete separation of liquid and solid and of temperature control. In the hands of careful workers the proper chemical method can be reliable. Each paper must be carefully read to judge the reliability of the method and its application. Unfortunately, even the best workers do not always include all of the information required for a reliable evaluation of their work.

Other Methods. Radiochemical techniques, atomic absorption and other analytical methods are available, but seldom used in solubility of electrolyte determinations.

2.2. Electromotive Force Methods

The design of a cell in which the cell reaction is the solubility process, and the measurement of the cell emf as a function of ionic strength at one or more temperatures can be a successful method for the determination of the solubility product. A cell of the type,

M/MB (aq,m)/salt bridge/NaA (aq,m) MA(s)/M

where MA is the slightly soluble electrolyte and MB is a soluble electrolyte, is required. The standard potential of the cell, suitably corrected for liquid junction potential, is related to the solubility product

$$\ln K_{s0}^{0}=\frac{nF}{RT}\left(E_{\text{cell}}+\frac{RT}{nF}\ln a_2-E_{\text{junction potentials}}\right)=\frac{nF}{RT}E^{\circ}_{\text{cell}}. \tag{1}$$

To apply the method successfully, care must be taken to minimize or eliminate, either by experiment or extrapolation procedure, the liquid junction potential The standard potential is obtained after a choice of a suitable activity coefficient function to use in the extrapolation to zero ionic strength. Corrections for hydrolysis products and complex ions formed in the electrolyte may have to be taken into account.

Cells of this type have not been used often in the study of lead salts, but they have been extensively used for other metal salts, for example, mercury (I) salts [14].

2.3. Standard Electrode Potentials

Standard electrode potentials are often evaluated for purposes other than the calculation of solubility products. When the necessary standard electrode potentials are available, the calculation of the solubility product is a straightforward procedure of good accuracy, by the equation

$$\ln K_{s0}^{0}=\frac{nF}{RT}\left[E^{\circ}_{M/M^{n+}}-E^{\circ}_{M/MA(s)}\right] \tag{2}$$

where $E^{\circ}_{M/M^{n+}}$ is the standard potential of the reaction

$M^{n+}(aq)+ne^- \rightarrow M$ and $E^\circ_{M/MA(s)}$ is the standard potential of the reaction MA (s)$+ne^- \rightarrow M+A^{n-}$ (aq).

The standard potential for the reduction of the lead (II) ion in aqueous solution, $Pb^{2+}(aq)+2e^- \rightarrow Pb(s)$, has apparently been measured at only 298.15 K. The four modern values are −0.1263 [15a, b], −0.1203 [16, 17], −0.1274 [18, 19] and −0.1251 [20] volt. Earlier measured values are several millivolts higher [20]. A recent NBS compilation [21a] gives the thermodynamic functions of formation of lead (II) ion in aqueous solution as $\Delta G^\circ_f=(-24.39\pm0.04)$ kJ mol^{-1} and $\Delta H^\circ_f=(-1.7\pm0.4)$ kJ mol^{-1}. These values give $E^\circ_{Pb/Pb^{2+}}$ (298.15 K)$=(-0.1264\pm0.0002)$ V and $dE^\circ/dT=(-3.94\pm0.08)\times10^{-4}$ V K^{-1}. The calculated standard electrode potential value is about 0.1 mv higher than the average of the three highest measured values quoted above. We have found no emf data to check against the calculated dE°/dT value.

The equation

$$E^\circ_{Pb/Pb^{2+}}\,(T/\mathrm{K})/\mathrm{V}=(-0.1264-3.94\times10^{-4}\,\Delta T) \quad (3)$$

where $\Delta T=T/\mathrm{K}-298.15$ was used to calculate tentative values (table 1) of the electrode standard potential at several temperatures near 298.15 K. deBethune, Licht and Swendeman [22] calculate a value of dE°/dT of -4.51×10^{-4} V K^{-1} which would give $E^\circ_{Pb/Pb^{2+}}$ (273.15 K)$=-0.1151$ which is within our error range.

The values in table 1 are used later to calculate the solubility products of PbF_2 and $PbSO_4$ from the standard electrode potentials $E^\circ_{Pb/PbF_2(s)}$ and $E^\circ_{Pb/PbSO_4(s)}$. Further experimental work to confirm the values of table 1 would result in a better evaluation of the PbF_2 and $PbSO_4$ solubility products.

TABLE 1. Tentative values of the Pb/Pb^{2+} standard electrode potential

T/K	$E^\circ_{Pb/Pb^{2+}}$/V
273.15	−0.1166±0.0022
278.15	−0.1185±0.0018
288.15	−0.1225±0.0010
298.15	−0.1264±0.0002
308.15	−0.1303±0.0010
318.15	−0.1343±0.0018
323.15	−0.1363±0.0022

3. Treatment of the Solubility Data

There is no comprehensive literature source that describes in detail the treatment of electrolyte solubility data. The discussions of Bates [23], and of Leussing [24] are useful, but dated. A recent analytical chemistry textbook [25] and a monograph [26] on solid-liquid phase equilibria are helpful. Recently the International Union of Pure and Applied Chemistry (IUPAC) organized the Solubility Data Project (SDP). The SDP is a group of scientists who plan to prepare and to publish an extensive compilation and evaluation of the scientific literatures solubility data. Their planned [14, 27] and future publications will outline in good detail the treatment of solubility data. including electrolyte solubility data. In addition, standard textbooks on thermodynamics and on electrolyte theory should be consulted.

3.1 Stoichiometric Solubility

In the present work our principle objective is to compile and evaluate experimental solubility data. The mass of material dissolved at saturation is converted to an amount of substance, based on specified elementary entities, that describe the salt. Thus the solubility of lead fluoride, PbF_2, is given as either molality m_{PbF_2}/mol kg^{-1}, or concentration c_{PbF_2}/mol dm^{-3}. The used measure of solubility depends on whether the data in the original paper were based on a mass of solvent, or a volume of solution. For the systems for which reliable densities of the saturated solutions were reported, the solubility was calculated both as molality and concentration.

The stoichiometric solubility, henceforth called solubility, defined above is related to an arbitrarily chosen formula for the salt. It is a number which can be checked by the experiment of others. However, it tells the user nothing about the actual ionic and molecular species present in the solution.

In some cases solubility values are found at only one temperature, usually 298.15 K. In such cases, the values judged best are weighted and averaged, the standard deviation computed, and the value labelled either recommended or tentative depending on our judgment of the quality of the experimental data.

When solubility data from several laboratories agree within experimental error over the same temperature interval, and the data appear to be reliable, the data are fitted to an equation by a linear regression and a table of smoothed data is generated. For the solubility in molal units the equation is

$$\ln m_B=A_1+A_2/(T/100\,\mathrm{K}) + A_3 \ln (T/100\,\mathrm{K})+A_4(T/100\,\mathrm{K}) \quad (4)$$

A similar equation is used when the solubility is in molar units. Most of the solubility data are fitted within experimental error by a three constant equation, and often a two constant equation is adequate. Wilhelm, Battino and Wilcock [28] reference and briefly discuss the advantages of an equation of this form for representing equilibrium data. The particular form of the equation used here is due to Weiss [29]. The use of $T/100$ K has the advantage of making the A_i parameters of similar magnitude.

3.2. Solubility Product

In addition to the solubility, we also present some solubility product, ion ligand formation, and acid dissociation constants. These constants cannot be derived from either solubilities, or other data, without a model for the solution and certain basic assumptions. The ionic and molecular species and their amount in a solution can be calculated from the constants. However, the calculated results are subject to the same model and assumptions that were used to derive the constants. Sections 3.2 and 3.3 contain descriptions of several of the commonly used models used to obtain solubility product and other constants.

To obtain a value of the thermodynamic solubility product, K^0_{s0}, either the activity coefficients or some representation of the activity coefficients that allows extrapolation to zero ionic strength must be known.

To illustrate we assume the molal solubility, m_2, of a slightly soluble 1–1 electrolyte (MA) is known in the presence of a soluble 1–1 electrolyte (NB), m_3, at some temperature T.

$$\log K^0_{s0}(\mathrm{MA}) = \log (m_\mathrm{M} m_\mathrm{A}) + 2 \log \gamma_2 \tag{5}$$

where γ_2 is the mean ionic molality activity coefficient of the slightly soluble salt. If the total molality, m, is 0.1 or less the activity coefficient can be calculated from an extended Debye-Huckel-Bronsted-Guggenheim-type equation

$$\log \gamma_2 = -A \frac{m^{1/2}}{1+m^{1/2}} + m_2 B_\mathrm{MA} + 1/2\, m_3 (B^\circ_\mathrm{NA} + B^\circ_\mathrm{MB}) \tag{6}$$

where A is the Debye Huckel Limiting law constant, m is the total molality (ionic strength for other electrolyte types), and the B°'s are specific ionic interaction terms.

The specific interaction terms may not be known or the solubility may be measured in solutions of intermediate ionic strength. If that is the case, a Harned's rule type equation may be used

$$\log \gamma_2 = \log \alpha_\mathrm{KCl} + (\Delta B^\circ_\mathrm{MA} - \alpha f_\mathrm{NB})\, m \tag{7}$$

where α is the Harned rule coefficient, $\Delta B^\circ = B^\circ_\mathrm{MA} - B^\circ_\mathrm{KCl}$ and the B°'s are Scatchard deviation parameters, and f_NB is the fraction of the total molality due to the electrolyte NB. Since MA is slightly soluble, f_NB is approximately unity, and one can write

$$\log K^0_{s0} = \log (m_\mathrm{M}\, m_\mathrm{A}) + 2 \log \gamma_\mathrm{KCl} + 2 (\Delta B^\circ_\mathrm{NA} - \alpha)\, m \tag{8}$$

which rearranges to

$$\log (m_\mathrm{M}\, m_\mathrm{A}) + \log \gamma_\mathrm{KCl} = -\log K^0_{s0} + 2 (\Delta B^\circ_\mathrm{MA} - \alpha)\, m \tag{9}$$

Even when $\Delta B^\circ_\mathrm{MA}$ and α are not known the function $(\Delta B^\circ_\mathrm{MA} - \alpha)$ often remains nearly constant. Thus a plot of the left hand side of equation 9 against m (or ionic strength) will be linear with intercept equal to $-\log K^0_{s0}$. Lewis, Randall, Pitzer and Brewer [30] contains a good summary of ΔB° values. Equations 5 through 9 must be suitably modified for other electrolyte types.

When solubility product constants are known at several temperatures the values can be fitted to equation 4. It is then possible to write the thermodynamic functions $\Delta \bar{G}^\circ$, $\Delta \bar{H}^\circ$, $\Delta \bar{S}^\circ$, and $\Delta \bar{C}^\circ_p$ for the solution process of dissolving one mole of solute crystal to form a solution of unit activity. The equations are

$$\Delta \bar{G}^\circ = -RA_1 T - 100 RA_2 - RA_3 T \ln (T/100\ \mathrm{K}) - RA_4 T^2/100\ \mathrm{K} \tag{10}$$

$$\Delta \bar{S}^\circ = RA_1 + RA_3 \ln (T/100\ \mathrm{K}) + RA_3 + 2RA_4 T/100\ \mathrm{K} \tag{11}$$

$$\Delta \bar{H}^\circ = -100 RA_2 + RA_3 T + RA_4 T^2/100\ \mathrm{K} \tag{12}$$

$$\Delta \bar{C}^\circ_p = RA_3 + 2RA_4 T/100\ \mathrm{K} \tag{13}$$

In cases where the solubility product constants are known at only a few temperatures only the two constant equation

$$\ln K^0_{s0} = A_1 + A_2/(T/100\ \mathrm{K}) \tag{14}$$

can be justified, and then

$$\Delta \bar{G}^\circ = -RA_1 T - 100 RA_2 \tag{15}$$

$$\Delta \bar{S}^\circ = RA_1 \tag{16}$$

$$\Delta \bar{H}^\circ = -100 RA_2 \tag{17}$$

$$\Delta \bar{C}^\circ_p = 0 \tag{18}$$

3.3. Solubility Product and Complex Ion Formation Constants

The solubility of a slightly soluble electrolyte is often accompanied by the formation of complex ions in solution. The stoichiometric solubility can be expressed as a function of the varying concentration of a component ion of the complex ion in an equation that contains the solubility product constant and the complex ion formation constants. The constants can be evaluated when the stoichiometric solubility is fitted to the function of the complexing ion concentration under conditions at constant ionic strength.

For example, Nriagu and Anderson [31] suggest the system of interconnecting equilibria for $PbCl_2$ dissolved in aqueous $NaCl + NaClO_4$ of constant ionic strength is as follows:

$$PbCl_2\ (s) \rightleftarrows PbCl_2\ (aq)$$

$$PbCl_2\ (aq) \rightleftarrows Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

$$PbCl_2\ (aq) \rightleftarrows PbCl^+\ (aq) + Cl^-\ (aq)$$

$$PbCl_2\ (aq) + Cl^-\ (aq) \rightleftarrows PbCl_3^-\ (aq)$$

$$PbCl_2\ (aq) + 2Cl^-\ (aq) \rightleftarrows PbCl_4^{2-}\ (aq)$$

The solubility, $m_{PbCl_2}/\mathrm{mol\ kg^{-1}}$, is represented by the sum, S, which is

$$S = m_{Pb^{2+}} + m_{PbCl^-} + m_{PbCl_2} + m_{PbCl_3^-} + m_{PbCl_4^{-2}} \tag{19}$$

The cumulative formation constant for the complex ion $PbCl_n^{2-n}$ is

$$\beta_n = \frac{m_{PbCl_n^{2-n}}}{(m_{Pb^{2+}})\,(m^n_{Cl^-})},$$

where $\beta_0 = 1$.

The β_n constants can be solved for $m_{PbCl_n^{2-n}}$, substituted in the sum for S, and rearranged to give

$$S = \frac{m_{PbCl_2}}{\beta_2 m^2_{Cl^-}} \sum_{n=0}^{4} \beta_n\,(Cl^-)^n \qquad (20)$$

The equation takes the form

$$S = A/m^2_{Cl^-} + B/m_{Cl^-} + C + D m_{Cl^-} + E m^2_{Cl^-} \qquad (21)$$

where

$$A = C/\beta_2 = m_{PbCl_2}\,(aq)/\beta_2 = K_{s0} = C/K_1K_2 \qquad (22)$$

$$B = C\beta_1/\beta_2 = C/K_2 \qquad (23)$$

$$C = m_{PbCl_2}\,(aq) \qquad (24)$$

$$D = C\beta_3/\beta_2 = CK_3 \qquad (25)$$

$$E = C\beta_4/\beta_2 = CK_3K_4 \qquad (26)$$

where K_n are the consecutive formation contants,

$$K_n = \frac{m_{PbCl_n^{2-n}}}{m_{Cl^-}\, m_{PbCl_{n-1}^{3-n}}}$$

equation (21) is fitted to the stoichiometric solubility isotherm. The contants from the fitted equation are used to evaluate the β_n or K_n values.

Most workers believe the stoichiometric solubility fitted to the data by the graphical method of Haight and Peterson [32] gives more satisfactory values of β_n and K_n than when the equation is fitted by computer methods. A comparison of the constants obtained by using several techniques of fitting the experimental data has been published [33].

A solubility experiment is not the method preferred to obtain consecutive (K_n) and cumulative (β_n) formation constants. The use of polarography, conductivity, spectrophotometry, ion selective electrodes or other methods [3] may be more reliable. In general the consecutive or stepwise constants, K_n, are preferred, however the cumulative or gross constants, β_n, are used if they are the only quantities which were determined or if the sequence of consecutive constants is incomplete.

The equations developed above give formation constants. In cases where only one or two complex ions dominate in solution, modified equations including activity coefficients can be derived, and thermodynamic constants obtained.

3.4. The Solubility of Salts of Weak Acids

The solubility of sparingly soluble salts of weak acids depends on the hydrogen ion concentration. The stoichiometric solubility of compounds such as PbS and $PbCO_3$ may be calculated as follows.

Assume a sparingly soluble substance MA where the anion forms the acid H_2A. If there is no other source of the ions M^{2+} and A^{2-}, and if there is no complexing of the cation, the following equilibria describe the solution.

$$MA\,(s) \rightleftarrows M^{2+}\,(aq) + A^{2-}\,(aq) \quad K_{s0} = (a_{M^{2+}})\,(a_{A^{2-}}) = (m_{M^{2+}})\,(m_{A^{2-}})\gamma_{M^{2+}}\gamma_{A^{2-}}$$

$$H_2A\,(aq) \rightleftarrows HA^-\,(aq) + H^+\,(aq) \quad K_1 = a_{H^+}a_{HA^-}/a_{H_2A}$$

$$HA^-\,(aq) \rightleftarrows A^{2-}\,(aq) + H^+\,(aq) \quad K_2 = a_{H^+}a_{A^{2-}}/a_{HA^-}$$

The solubility, m_{MA}/mol kg^{-1}, is equal to $m_{M^{2+}}$. The value of $m_{M^{2+}}$ is equal to the sum, S, of the concentration of the A^{-2} species in the solution.

$$S = m_{M^{2+}} = \sum_{n=0}^{2} m_{H_nA^{n-2}} = m_{A^{2-}} + m_{HA^-} + m_{H_2A} \qquad (27)$$

$$S = m_{m^{2+}} = m_{A^{2-}} + \frac{a_{A^{2-}}a_{H^+}}{K_2\gamma_{HA^-}} + \frac{a_{A^{2-}}a_{H^+}}{K_1K_2\gamma_{H_2A}}$$

$$= m_{A^{2-}}\left(1 + \frac{\gamma_{A^{2-}}a_{H^+}}{K_2\gamma_{HA^-}} + \frac{\gamma_{A^{2-}}(a_{H^{2+}})^2}{K_1K_2\gamma_{H_2A}}\right). \qquad (28)$$

Substituting from the solubility product relation

$$m_{A^{2-}} = \frac{K_{s0}}{m_{M^{2+}}\gamma_{M^{2+}}\gamma_{A^{2-}}}$$

$$S = m_{M^{2+}} = \frac{K_{s0}}{m_{M^{2+}}\gamma_{M^{2+}}\gamma_{A^{2-}}}\left(1 + \frac{\gamma_{A^{2-}}a_{H^+}}{K_2\gamma_{HA^-}} + \frac{\gamma_{A^{2-}}(a_{H^+})^2}{K_1K_2\gamma_{H_2A}}\right)$$

$$S^2 = m^2_{M^{2+}} = \frac{K_{s0}}{\gamma_{M^{2+}}\gamma_{A^{2-}}}\left(1 + \frac{\gamma_{A^{2-}}a_{H^+}}{K_2\gamma_{HA^-}} + \frac{\gamma_{A^{2-}}(a_{H^+})^2}{K_1K_2\gamma_{H_2A}}\right). \qquad (29)$$

In the limit of infinite dilution the equation reduces to

$$S = K_{s0}^{1/2}[1 + m_{H^+}/K_2 + (m_{H^+})^2/K_1K_2]^{1/2}. \qquad (30)$$

If the weak acid H_2A is gaseous (e.g., H_2S or CO_2) the equilibrium

$$H_2A\,(g) \rightleftarrows H_2A\,(aq) \quad K_H = a_{H_2A\,(aq)}/f_{H_2A\,(g)}$$

allows the effect of gas pressure on the solubility to be taken into account.

Substitution of

$$m_{A^{2-}} = \frac{K_HK_1K_2f_{CO_2}}{a_{H^{2+}}\gamma_{A^{2-}}}$$

into equation (28) gives

$$S = \frac{K_HK_1K_2f_{H_2A}}{(a_{H^+})^2\gamma_{A^{2-}}}\left(1 + \frac{\gamma_{A^{2-}}a_{H^+}}{K_2\gamma_{HA^-}} + \frac{\gamma_{A^{2-}}(a_{H^+})^2}{K_1K_2\gamma_{H_2A}}\right)$$

$$S = f_{H_2A}\left(\frac{K_HK_1K_2}{(a_{H^+})^2\gamma_{A^{2-}}} + \frac{K_HK_1}{a_{H^+}\gamma_{HA^-}} + \frac{K_H}{\gamma_{H_2A}}\right).$$

In the limit of infinite dilution the equation becomes

$$S = P_{H_2A}K_H(K_1K_2/m_{H^{2+}} + K_1/m_{H^+} + 1).$$

The contribution of each term of the equation depends on the pH. Only the first term may be important in basic solutions, only the third term in acidic solutions. At intermediate pH values probably only two terms contribute significantly to the overall solubility.

The choice of the values of K_H, K_1, and K_2 to use in the equations is important. Berg and Vanderzee [134] recently selected values at 298.15 K for the carbonic acid system of $K_H=(0.03416\pm0.00015)$ mol kg^{-1} atm^{-1}, $K_1=(4.457\pm0.050)\times10^{-7}$ and $K_2=(4.688\pm0.075)\times10^{-11}$ which we recommend for use in carbonate solubility evaluation.

For the sulfide systems the choice of values for the H_2S dissolution and dissociation is more difficult. Ellis and Giggenbach [135, 136] present evidence that the second dissociation constant is smaller by a factor of 10^3 or 10^4 than the presently accepted values. However Krynlov et al [137] have also redetermined K_2 and found a value that agrees with older values. Our tentative recommendation is to use the values at 298.15 K of $K_H=0.102$, $K_1=1.02\times10^{-7}$ and $K_2=1.25\times10^{-14}$. The K_H value was used by Kivalo and Ringbom [138], the K_1 and K_2 values are suggested by Helgeson [139].

For a sparingly soluble electrolyte of the type M_3B_2, such as $Pb_3(PO_4)_2$, the equilibria are

$$M_3B_2(s)\rightleftarrows 3M^{2+}(aq)+2B^{3-}(aq)$$

$$K_{s0}=(a_{m^{2+}})^3(a_{B^{3-}})^2$$

$$=(m_{M^{2+}})^3(m_{B^{3-}})^2(\gamma_{m^{2+}})^3(\gamma_{B^{3-}})^2$$

$$H_3B(aq)\rightleftarrows H_2B^-(aq)+H^+(aq)$$

$$K_1=a_{H_2B^-}a_{H^+}/a_{H_3B}$$

$$H_2B^-(aq)\rightleftarrows HB^{2-}(aq)+H^+(aq)$$

$$K_2=a_{HB^{2-}}a_{H^+}/a_{H_2B^-}$$

$$HB^{2-}\rightleftarrows B^{3-}(aq)+H^+(aq)$$

$$K_3=a_{B^{3-}}a_{H^+}/a_{HB^{2-}}$$

If there is no complexing of the cation, the solubility, $m_{M_3B_2}$/mol kg^{-1}, is equal to the sum, S, in

$$S=\frac{m_{M^{2+}}}{3}=\frac{1}{2}\sum_0^3 m_{H_nB^{n-3}}=\frac{1}{2}(m_{B^{3-}}+m_{HB^{2-}}+m_{H_2B^-}+m_{H_3B})$$

$$S=\frac{m_{B^{3-}}}{2}\left(1+\frac{\gamma_{B^{3-}}a_{H^+}}{K_3\gamma_{HB^{2-}}}+\frac{\gamma_{B^{3-}}a_{H^+}^2}{K_2K_3\gamma_{H_2B}}+\frac{\gamma_{B^{3-}}a_{H^+}^3}{K_1K_2K_3\gamma_{H_3B}}\right). \quad (31)$$

From the solubility product,

$$m_{B^{3-}}=\left(\frac{K_{s0}}{m_{M^{2+}}^3\gamma_{M^{2+}}^3\gamma_{B^{3-}}^2}\right)^{1/2}$$

$$S=\frac{K_{s0}^{1/5}}{3^{3/5}2^{2/5}\gamma_{M^{2+}}^{3/5}}$$

$$\times\left(\frac{1}{\gamma_{B^{3-}}}+\frac{a_{H^+}}{K_3\gamma_{HB^{2-}}}+\frac{a_{H^+}^2}{K_2K_3\gamma_{H_2B^-}}+\frac{a_{H^+}^3}{K_1K_2K_3\gamma_{H_3B}}\right)^{2/5}. \quad (32)$$

In the limit of infinite dilution the equation becomes

$$S=\frac{K_{s0}^{1/5}}{3^{3/5}2^{2/5}}\left(1+\frac{m_{H^+}}{K_3}+\frac{m_{H^+}^2}{K_2K_3}+\frac{m_{H^+}^3}{K_1K_2K_3}\right)^{2/5}. \quad (33)$$

For phosphates, the last two terms predominate at pH 1, the middle two at pH 7, and the first two at pH 14. Suggested values for the orthophosphoric acid dissociation constants at 298.15 K are $pK_1=2.148$, $pK_2=7.198$, and $pK_3=12.32$ [140]. The same authors give a table of selected values at 278.15, 288.15, 298.15 and 310.65 K.

The solubility of sparingly soluble salts of weak acids is further complicated by complexing of the cation. The natural waters containing the weak acid anions are often slightly basic, and metal ion-hydroxide ion complexes may form, as well as complexes of the weak acid anion, and other anions that may be present. Thus the total cation concentration may be at least

$$[m^{2+}]_{total}=[m^{2+}]+\sum_0^n M(OH)_n^{2-n}+\sum_0^n MA_n^{2-Zn}$$

where Z is the charge on the anion, A^{Z-}. A good source of data on the metal hydroxide complexes is Feitknecht and Schindler [159]. Nriagu [141] has worked out expressions for the solubilities of metal sulfides in hydrothermal solutions that include complexing of the cation. General approaches to describing the species present in complex systems at equilibrium are an active area. For example see recent descriptions of the Ca^{2+} PO_4^{3-} system [140, 142]. The book of van Zeggeren and Storey [198] contains good general advice on the computation of chemical equilibria.

4. Solubility Data

This section contains data on lead salts dissolved in water and aqueous electrolyte solutions. Each lead compound is identified by its formula, Chemical Abstracts Registry Number, and formula weight. The 1975 atomic weights [34] were used. Although the atomic weight of lead is given as 207.2 we have given the molecular weights to one more significant figure. Thus the uncertainty in the molecular weights is of the order of ±0.10, mostly because of the known variations in the isotopic composition of normal terrestrial lead.

There is a brief description of the physical characteristics of each solid lead compound. This is followed by a table of recommended or tentative solubilities in water, an equation for the smoothed data, and a discussion of the sources of the solubility data used in the evaluation. There is a table of recommended or tentative solubility product values followed by a list of the experimental values and a discussion of the solubility product values. There is usually a list of some typical formation constants of complex ions, but the list is not intended to be comprehensive and critical except in a few cases which are noted.

The lead compounds in the following tables are arranged according to the Standard Order of Arrangement described in the NBS Technical Note Series [21].

4.1. Lead Fluoride

PbF_2, [7783-46-2]Formula Weight 245.20

Physical characteristics. Lead fluoride exists in two crystalline forms. The low temperature form, α-PbF_2, is an orthorhombic $PbCl_2$ type crystal with $Z=4$, and $a=6.441$, $b=7.648$, and $c=3.897\times10^{-10}$ m. The calculated density is 8431. kg m^{-3}. The high temperature form, β-PbF_2, is a cubic crystal with $Z=4$ and $a=5.93935\times10^{-10}$ m and a calculated density of 7772.1 kg m^{-3}. The transition temperature is 473 K. The high temperature crystal can exist in metastable form at room temperature. However, we assume that all of the solubility data below are for the low temperature α-PbF_2 form. Dundon [34] reports his solid PbF_2 was orthorhombic. There are no reports of hydrates of PbF_2 in the solubility studies. The unstable double salt PbF_2-2.5 HF has been reported [45] at 273.15 K in concentrated HF solution. There are solubility data on the mixed halide lead salts PbFCl [48] and PbFBr [49].

The recommended solubility of lead fluoride at 298.15 K in table 2 is from an average of the solubility values of Jaeger [35], Dundon [34], Carter [36], Messaric and Hume [37], and Talipov and Podogrnova [38]. The most recent determination of the solubility of PbF_2 is 2.69×10^{-3} mol dm^{-3} reported by Messaric and Hume [37]. Carter's value agrees with Messaric and Hume's value, but it has an uncertainty of at least $\pm0.05\times10^{-3}$. All of the other values at 298.15 range between $(2.73–2.78)\times10^{-3}$. Talipov and Podogrnova [38] report a density of 0.9964 g cm^{-3} for the saturated solution at 298.15 K. If the density is accepted, the recommended solubility of $2.73_5\times10^{-3}$ mol dm^{-3} becomes, in terms of molality $2.74_7\times10^{-3}$ mol kg^{-1} at 298.15 K.

The tentative values of PbF_2 solubility between 278.15 and 303.15 K in table 2 were calculated from the equation

$$\ln c_{PbF_2}/\text{mol dm}^{-3}=-0.60284/(T/100\text{ K})-3.8772$$

obtained from a linear regression of solubility data from the references mentioned above plus the data of Kohlrausch [39] with a standard deviation in ln c of 4.38×10^{-2}. An equation linear in temperature fitted the data equally well. The solubility data of Kohlrausch from conductivity measurements are the determining data for the temperature coefficient of solubility. The data of Jacek [40] were not used, the original paper was not available, the data in a secondary source [2] appears as if Jacek's data may be a restatement of Kohlracesch's earlier data. Solubility product values of PbF_2 are summarized in table 3. The Ivett and DeVries [41] solubility product values were calculated by us from their standard potential values, $E^{\circ}_{Pb/PbF_2(s)}$, and the tentative lead standard potentials in table 1. Broene and DeVries [42] used the solubility data of Kohlrausch [39], Dundon [34] and Carter [36] and activity coefficients calculated from the Debye-Huckel limiting law to obtain solubility product values at three temperatures. Messaric and Hume [37] used their water solubility value, an experimental activity coefficient, and their value of the PbF^+ formation constant at an ionic strength of 2.0 to calculate the K_{s0} value. They also recalculated the 298.15 K value of Broene and DeVries to take into account the formation of PbF^+. The recommended values at 288.15 and 309.15 K are from an average of the Ivett and DeVries and Broene and DeVries values with a weight of two to the first and a weight of one to the latter. The 298.15 K value is an average of the Ivett and DeVries, Broene and DeVries values as recalculated by Messaric and Hume and the Messaric and Hume value. The value of Scott [44] was quoted without any reference. The value calculated from data in the NBS-Technical Note 270–3 appears to be almost an order of magnitude too large.

The concentration solubility products, K_{s0}, of Messaric and Hume [37] and Gyunner and Federenko [43] in media of ionic strength 2.0, although of the same magnitude, differ by more than the experimental uncertainty claimed by the authors. The difference may be due to the strong $Pb^{2+}-NO_2^-$ complexes formed in the mixed electrolyte medium used by Gyunner and Federenko.

Table 4 summarizes the experimental values of the PbF_n^{2-n} complex ions. We believe the summary is fairly complete. There are not enough results over identical temperature and ionic strength ranges to recommend values.

In addition to the PbF_n^{2-n} complex ions Gyunner and Federenko [43] have interpreted the solubility data of PbF_2 in aqueous $NaNO_2+NaNO_3$ and $NaNO_2+NaNO_3+NaF$ at ionic strength 2.0 to obtain the following formation constants

$$PbNO_2^+\ (aq)\qquad \beta_1=344$$
$$Pb(NO_2)_2^{\circ}\ (aq)\qquad \beta_2=1480$$
$$Pb(NO_2)_3^-\ (aq)\qquad \beta_3=605$$

The data treatment required formation constants of $Pb^{2+}-NO_3^-$ complexes of

$$PbNO_3^+\ (aq)\qquad \beta_1=3.3$$
$$Pb(NO_3)_2^{\circ}\ (aq)\qquad \beta_2=3.2$$
$$Pb(NO_3)_3^-\ (aq)\qquad \beta_3=2.6$$

from Mironov [47].

TABLE 2. The solubility of lead fluoride in water

T/K	Solubility c_{PbF_2}/mol dm^{-3}
Recommended	
298. 15	$(2.73_5\pm0.035)\times10^{-3}$
Tentative	
278. 15	$(2.37\pm0.11)\times10^{-3}$
283. 15	$(2.46\pm0.11)\times10^{-3}$
288. 15	$(2.56\pm0.11)\times10^{-3}$
293. 15	$(2.65\pm0.12)\times10^{-3}$
298. 15	$(2.74\pm0.12)\times10^{-3}$
303. 15	$(2.83\pm0.12)\times10^{-3}$

TABLE 3. The solubility product constant of lead fluoride in aqueous solution

T/K	I/Electrolyte	K°_{s0}	K_{s0}	Reference
		Recommended values		
288.15	0	$(2.8\pm0.7)\times10^{-8}$		
298.15	0	$(3.3\pm0.5)\times10^{-8}$		
308.15	0	$(3.6\pm1.3)\times10^{-8}$		
		Literature values		
288.15	0	2.42×10^{-8} [a]		Ivett, DeVries [41]
	0	3.66×10^{-8}		Broene, DeVries [42]
293.15	2.0/$NaNO_2+NaNO_3$		1.47×10^{-7}	Gyunner, Fedorenko [43]
298.15	0	2.71×10^{-8} [a]		Ivett, DeVries [41]
	0	4.37×10^{-8} [b]		Broene, DeVries [42]
	?	7.1×10^{-8}		Scott [44]
	0	7.1×10^{-7}		NBS-270-3 [21]
	0	3.6×10^{-8}		Messaric, Hume [37]
	2.0/$NaClO_4$		2.5×10^{-7}	Messaric, Hume [37]
308.15	0	2.86×10^{-8} [a]		Ivett, DeVries [41]
	0	5.17×10^{-8}		Broene, DeVries [42]

[a] Values of K°_{s0} calculated from the emf data of Ivett and DeVries [41] for the cell Hg(Na)/NaF(aq) PbF_2(s)/Pb and the tentative $E^{\circ}_{Pb/Pb^{2+}}$ values in table 1.

[b] Messaric and Hume [37] corrected this value for PbF^+ formation and obtained 3.74×10^{-8}.

TABLE 4. Stability constants of PbF_n^{2-n} complex ions

Complex formula	T/K	Cumulative stability constant β_n	Ionic strength I/electrolyte	Method [a]	Reference
PbF^+	288.15	54 ± 5	0.1/$NaClO_4$	ise	Bond, Hefner [45]
		42 ± 3	1.0/$NaClO_4$	ise	Bond, Hefner [45]
		34 ± 5	1.0/$NaClO_4$	pol	Bond, Hefner [45]
	298.15	18	2.0/$NaClO_4$	pol	Messaric, Hume [37]
PbF_2	288.15	390 ± 30	1.0/$NaClO_4$	pol	Bond, Hefner [45]
	298.15	356	2.0/$NaClO_4$	pol	Messaric, Hume [37]
		188	var	pol	Talipov, Kutumova [46]
PbF_3^-	298.15	2.63×10^3	var	pol	Talipov, Kutumova [46]
PbF_4^{2-}	298.15	1.19×10^3	var	pol	Talipov, Kutumova [46]

[a] Method: ise=ion selective electrode, pol=polarography.

Several sources of PbF_2 solubility data that were not used include the solubility of PbF_2 in 0.1, 0.2, and 0.5 mol KNO_3 dm^{-3} solution over the temperature range of 291–293 K [50] and the solubility of PbF_2 in 20 to 50 volume percent ethanol in the presence of $NaNO_3$ [51].

4.2 Lead Chloride

$PbCl_2$, [7758-95-4] Formula Weight 278.11

Physical characteristics: Lead chloride crystallizes in an orthorhombic structure with Z=4, and a=7.605, b=9.027, and $c=4.520\times10^{-10}$ m. The calculated density is 5988 kg m^{-3} at 293.15 K. There are no mentions of hydrated lead chloride crystals in either the solubility or ternary system studies with water and lead chloride as components. The double salts $2PbCl_2\cdot KCl$, $2PbCl_2\cdot KCl\cdot 1/3\ H_2O$, and $PbCl_2\cdot KCl\cdot$

TABLE 5. The solubility of lead chloride in water

T/K	m_{PbCl_2}/mol kg^{-1}	T/K	m_{PbCl_2}/mol kg^{-1}
	Recommended value		
298. 15	(3. 907±0. 004)×10^{-2}		
	Tentative values		
273. 15	(2. 39±0. 13)×10^{-2}	373. 15	(0. 1272±0. 0036)
278. 15	2. 65 "	383. 15	0. 1455
283. 15	2. 93 "	393. 15	0. 1657
288. 15	3. 23 "	403. 15	0. 188
293. 15	3. 55 "	413. 15	0. 212
298. 15	(3. 89±0. 18)×10^{-2}	423. 15	(0. 239±0. 005)
303. 15	4. 26 "	433. 15	0. 268
308. 15	4. 65 "	443. 15	0. 300
313. 15	5. 08 "	453. 15	0. 334
318. 15	5. 53 "	463. 15	0. 371
323. 15	(6. 01±0. 24)×10^{-2}		
328. 15	6. 52 "	473. 15	(0. 411±0. 005)
333. 15	7. 07 "	498. 15	0. 526
338. 15	7. 64 "	523. 15	0. 662
343. 15	8. 25 "	548. 15	0. 823
348. 15	(8. 90±0. 30)×10^{-2}	573. 15	1. 011
353. 15	9. 59 "	598. 15	1. 23
358. 15	10. 31 "		
363. 15	11. 07 "	623. 15	(1. 48±0. 01)
368. 15	11. 88 "		
372. 15	(12. 72±0. 36) "		

TABLE 6. Experimental values of lead chloride solubility in water at 298.15 K

Saturated solution density/kg m^{-3}	m_{PbCl_2}/mol kg^{-1}	C_{PbCl_2}/mol dm^{-3}	Reference
	3.964×10^{-2}		Armstrong, Eyre [55]
	3.937×10^{-2}		Burrage [52]
1006.9	3.911×10^{-2}	3.896×10^{-2}	Flottman [56]
		3.895×10^{-2}	Herz, Hellebrandt [57]
	3.910×10^{-2}		Deacon [58]
	3.908×10^{-2}		Goulden, Hill [59]
	3.905×10^{-2}		Carmody [60]
1007.	(3.907±0.004)×10^{-2}	(3.892±0.005)×10^{-2}	Recommended
		3.880×10^{-2}	von Ende [61]
1007.25	3.899×10^{-2}	3.879×10^{-2}	Lichty [62]
		3.878×10^{-2}	Kendall, Sloan [63]
1006.	3.871×10^{-2}	3.853×10^{-2}	Talipov, Podgornova [38]
		3.851×10^{-2}	Dunning, Shutt [64]
		3.46×10^{-2}	Böttger [65]

1/3 H_2O [52] and PbOHCl, $3PbO \cdot PbCl_2 \cdot (2/3)H_2O$, and $6PbO \cdot PbCl_2 \cdot 2H_2O$ [53, 54] are known.

A recommended solubility of $PbCl_2$ in water at 298.15 K and tentative values of the solubility over the temperature interval of 273.15 to 623 K are given in table 5.

There are many more measurements of the solubility of lead chloride in water at 298.15 K than at any other temperature. Table 6 summarizes the values from the literature. All of the molal solubility values were averaged. The values [38, 52, 55] which were one standard deviation or more from the average were eliminated and a second average taken of the remaining values, which is given as the recommended value. The value corresponds to a concentration of $(3.892 \pm 0.005) \times 10^{-2}$ mol $PbCl_2$ dm^{-3} solution with a density of the saturated solution of 1007 kg m^{-3}. The recommended molar value agrees well with the measurements of Herz and Hellebrandt [57] and Flottman [56] and is within 0.40 percent of three other measurements [61, 62, 63].

The tentative values between temperatures of 273 and 623 K were calculated from the equation

$$\ln m_{PbCl_2}/\text{mol kg}^{-1} = -6.40476 - 5.43593/(T/100\text{ K}) + 3.64509 \ln (T/100\text{ K}) \quad (35)$$

and obtained by a linear regression of the data of Deacon [58], Flottman [56], and Goulden and Hill [59] with a weight of two, and the data of Lichty [62], Burrage [52], Carmody [60], Sowerby [69], and Malinin [66] with a weight of one, as a function of temperature. The standard error around the regression line is 1.4 percent of ln m at the middle of the temperature range. See the upper part of figure 1.

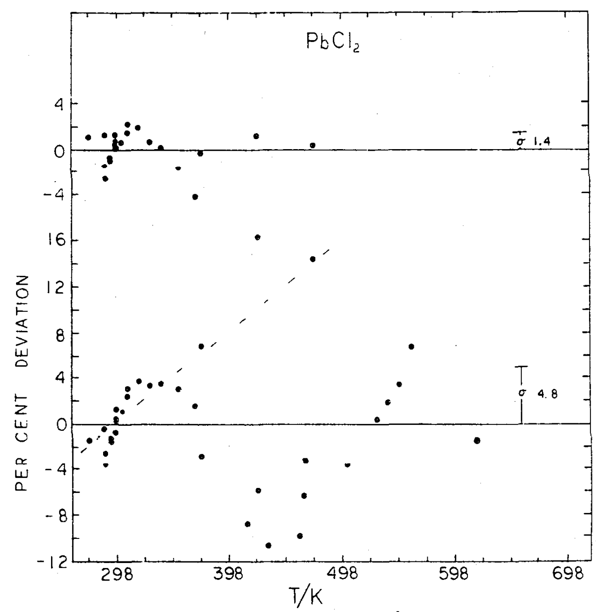

FIGURE 1. Lead chloride. Percent deviation of the stoichiometric solubility from the fitted equation. Bottom, all data; top, selected data and their deviation from eq 35.

The high temperature solubility values of Benrath, Gjedebo, Schiffers and Wunderlich [12] appear to be 20–25 percent low with a similar temperature coefficient as the other values. When the Benrath *et al.* data are included in the linear regression the standard error around the regression line is almost five percent of ln m. See the lower part of figure 1.

The equation gives a solubility value at 298.15 K that is 0.28 percent lower than the recommended solubility of 3.909×10^{-2} mol kg^{-1}.

At the higher temperatures hydrolysis may be a problem. Goulden and Hill [59] made the specific comment that they had no problems with hydrolysis at temperatures up to 308 K. Goulden and Hill's solubility determination over a 20 degree range around room temperature appears to have been carried out very carefully.

Table 7 summarizes experimental solubility values in various aqueous electrolyte solutions. There are many other values in the mixed electrolyte solutions of $Li(ClO_4,Cl)$ [67] and $Na(ClO_4,Cl)$ [31]. It appears that complexes of the type $PbCl_n^{2-n}$ are very important in concentrated chloride ion solution and that the effect is much greater in aqueous NaCl than in aqueous LiCl. Nriagu [31] states that x-ray examination showed the only solid to be $PbCl_2$.

Other solubility data on lead chloride in aqueous electrolyte solution are given by Kendall and Sloan [63] in aqueous HCl, NH_4Cl, LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, and $HgCl_2$, Burrage [52] in aqueous KCl, Deacon [58] in aqueous LiCl and aqueous NaCl and Katlov [70] in aqueous $ZnCl_2$ and NaCl.

The solubility data of Ditte [71] and of Demassiuex [72] are of poor quality and should not be used. The paper of Lewin, Vance and Nelson [73] quote the solubility of $PbCl_2$ in water from others. Noble and Garrett [74] measure the solubility of $PbCl_2$ in water + acetone mixtures, but accept the Carmody value for the water solubility of $PbCl_2$. Noonan [75] reports the solubility of $PbCl_2$ in 91.6 percent D_2O at 298.15 K from which he estimates a solubility of 0.0449 mol $PbCl_2$ per 100 mol D_2O (2.24×10^{-2} mol $PbCl_2$ per kg D_2O).

The solubility products of $PbCl_2$ are given in table 8. The recommended solubility product, K_{s0}°, at 298.15 is 1.70×10^{-5}. This is the value calculated from Gibbs energy of formation data given in NBS-Technical Note 270 3 [21a]. Thus the value is consistent with other thermodynamic information and it agrees within experimental error of several experimental values [60, 77]. The value of Lewis and Brighton [76] is from an early attempt to correct for activity effects. The treatment of data used by Nriagu and Anderson [31] was discussed in some detail in section 3.3. Vierling's [68] value appears to be high when compared to the others.

TABLE 7. Experimental solubility values of $PbCl_2$ in aqueous electrolyte solution

T/K	Ionic strength I/electrolyte	Molal solubility m_{PbCl_2}/mol kg^{-1}	Molar solubility c_{PbCl_2}/mol dm^{-3}	Reference
298.15	3.0/$LiClO_4$		19.2×10^{-3}	Mironov et al. [33]
298.15	3.0/LiCl		8.28×10^{-3}	Mironov et al. [33]
298.15	3.0/NaCl		17.1×10^{-3}	Mironov et al. [33]
288.15	3.0/LiCl		5.97×10^{-3}	Fedorov et al. [67]
298.15	3.0/LiCl		8.59×10^{-3}	Fedorov et al. [67]
318.15	3.0/LiCl		16.4×10^{-3}	Fedorov et al. [67]
301.15	3.0/$NaClO_4$	$16.\ \times10^{-3}$		Nriagu, Anderson [31]
301.15	3.0/NaCl	18.8×10^{-3}		Nriagu, Anderson [31]
313.15	3.0/$NaClO_4$	$19.\ \times10^{-3}$		Nriagu, Anderson [31]
313.15	3.0/NaCl	33.0×10^{-3}		Nriagu, Anderson [31]
333.15	3.0/$NaClO_4$	$22.\ \times10^{-3}$		Nriagu, Anderson [31]
333.15	3.0/NaCl	61.9×10^{-3}		Nriagu, Anderson [31]
363.15	3.0/$NaClO_4$	$36.\ \times10^{-3}$		Nriagu, Anderson [31]
363.15	3.0/NaCl	144.9×10^{-3}		Nriagu, Anderson [31]
298.15	4.0/NaCl		38.0×10^{-3}	Vierling [68]

TABLE 8. The solubility product of lead chloride

T/K	Ionic Strength I/electrolyte	Solubility Product K_{so}[d]	Reference
		Recommended value	
298.15	0	1.70×10^{-5}	
		Literature values	
298.15	0	1.63×10^{-5}	Carmody [60]
	0	1.70×10^{-5}	NBS-272-3 [21a]
	0	2.12×10^{-5}	Fromherz [18]
	0	2.29×10^{-5}	Lewis, Brighton [76]
298.15	1.0/Na(ClO_4,Cl)	$(1.73\pm0.04)\times10^{-5}$	Papoff et al. [77]
298.15	3.0/Li(ClO_4,Cl)	$(0.93-1.74)\times10^{-5}$	Mironov et al. [33][a]
288.15	3.0/Li(ClO_4,Cl)	$(0.75-1.46)\times10^{-5}$	Fedorov et al. [67][a]
298.15	3.0/Li(ClO_4,Cl)	$(1.06-1.80)\times10^{-5}$	Fedorov et al. [67][a]
318.15	3.0/Li(ClO_4,Cl)	$(1.88-2.04)\times10^{-5}$	Fedorov et al. [67][a]
301.15	3.0/Na(ClO_4,Cl)	$(0.70\pm0.10)\times10^{-5}$	Nriagu, Anderson [31][b]
313.15	3.0/Na(ClO_4,Cl)	$(0.76\pm0.10)\times10^{-5}$	Nriagu, Anderson [31][b]
333.15	3.0/Na(ClO_4,Cl)	$(0.90\pm0.15)\times10^{-5}$	Nriagu, Anderson [31][b]
363.15	3.0/Na(ClO_4,Cl)	$(1.10\pm0.20)\times10^{-5}$	Nriagu, Anderson [31][b]
298.15	4.0/Na(ClO_4,Cl)	$(47-97)\times10^{-5}$	Vierling [68][c]

[a] Molar scale, $K_{so}=a_{Pb^{2+}}(Cl^-)^2$ with $a_{Pb^{2+}}$ approximated by an emf method.
[b] Molar scale.
[c] Molar scale.
[d] K_{so} becomes K^0_{so} at $I=0$.

TABLE 9. Consecutive stoichiometric formation constants, K_n, for lead chloro complexes at ionic strength 3.0/Na (ClO_4, Cl) [31]

T/K	Complex $PbCl_n^{2-n}$	Stoichiometric constant, K_n
301. 15	$PbCl^+$	15. 7 ±3. 9
313. 15		19. 7 ±3. 4
333. 15		25. 5 ±3. 8
363. 15		40. 0 ±6. 2
301. 15	$PbCl_2$	8. 3 ±0. 9
313. 15		10. 4 ±1. 0
333. 15		13. 9 ±1. 1
363. 15		17. 7 ±2. 2
301. 15	$PbCl_3^-$	1. 6 ±0. 1
313. 15		2. 3 ±0. 2
333. 15		1. 2 ±0. 1
363. 15		0. 6 ±0. 1
301. 15	$PbCl_4^{2-}$	0. 6 ±0. 1
313. 15		0. 96±0. 1
333. 15		1. 5 ±0. 2
363. 15		3. 2 ±0. 4

There are more than 75 papers on the lead-chloro complexes $PbCl_n^{2-n}$ [3]. Rather than try to evaluate the literature on lead-chloro complex ions, we present, in table 9, a set of representative consecutive stoichiometric formation constants determined between 301 and 363 K at ionic strength 3.0 by Nriagu and Anderson in a solubility study. Nriagu and Anderson also present a comparison of their values and the values obtained from other studies [32, 77, 78, 79, 80] which include the methods of solubility, spectrophotometry and polarography. Some workers report constants for a $PbCl_6^{4-}$ complex [31,77]. At room temperature free Pb^{+2} exists only at concentrations <0.1 molal Cl^-, and at 1.0 molal Cl^- the lead is nearly equally distributed as $PbCl_2$, $PbCl_3^-$ and $PbCl_4^{2-}$ [31].

4.3 Lead Bromide

$PbBr_2$, [10031–22–8] Formula Weight 367.01

Physical characteristics: Lead bromide crystalizes in an orthorhombic structure with $Z=4$, and $a=8.038$, $b=9.518$ and $c=4.717\times10^{-10}$ m. The calculated density of the solid is 6714 kg m^{-3}. Lead bromide forms a solid solution with lead chloride. Ditte [71] has made the only report of the trihydrate 2 PbBr · $3H_2O$, and x-ray parameters are reported for it [5]. However, its existence in natural systems is questioned. There is no mention of a hydrated solid in the rest of the solubility literature.

The recommended solubility of lead bromide at 298.15 K and tentative values over the 273–328 K temperature interval are given in table 10. The molal value at 298.15 K is the average of four experimental values shown in table 11. The recommended molal value was converted to a molar value with a density of 1005.5 kg m^{-3} which agrees with the experimental molar solubility values of Lichty [62] and von Heveay and Wagner [81]. The value of Böttger [65] is much too low, the values of Herz and Hellebrandt [57] and von Ende [61] appear to be slightly low.

The tentative lead bromide solubility values were calculated from the equation

$$\ln m_{PbBr_2}/\text{mol kg}^{-1} = -2.0264 - 15.6393/(T/100\text{ K}) + 3.3410 \ln (T/100\text{ K}) \quad (36)$$

which resulted from a linear regression of nine solubility values from Burrage [52], Lichty [62], von Heveay and Wagner [81], and Randall and Veitti [82]. The 298.15 K values of Lichty and of von Heveay and Wagner were counted double weight, Lichty's values at 338, 353, and 368 K were not used. The standard deviation about the regression line was 1.35 percent at the middle of the temperature interval.

An attempt to use all of Lichty's data and the high temperature data of Beurath et al. [12] gave a standard error about the regression line of over 7 percent. Figure 2 shows the deviation of the regression line

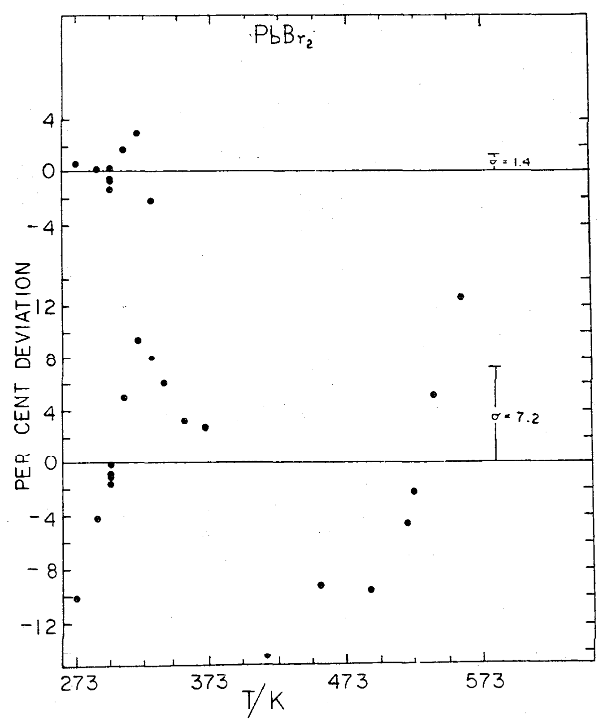

FIGURE 2. Lead bromide. Percent deviation of the stoichiometric solubility from the fitted equation. Bottom, all data, top, selected data and their percent deviation from eq 36.

fitted to all of the data (bottom) and the deviations of the data selected for the tentative equation (top). The only reports of the solubility of lead bromide in water at temperature other than 298.15 K are the data of Lichty [62] and of Benrath et al. [12]. Lichty's data scatter badly. The Benrath et al. data, as did their lead chloride data, appear to be 25–35 percent low. The lower values could be explained by a phase change in the solid, however, there is no independent evidence of the occurance of a phase change.

Table 12 summarizes experimental values of the solubility of lead bromide in aqueous electrolyte solution at several ionic strengths. The papers referenced in the table contain additional data on the solubility of $PbBr_2$ in the mixed electrolytes $Na(ClO_4, NO_3)$, $Li(ClO_4, Br)$ and $Na(ClO_4, Br)$.

There are only a few values of the lead bromide solubility product, K^0_{s0}. The value calculated from data in NBS Technical Note 270–3 is recommended. The value of Lewis and Brighton [76] was obtained with only poor approximations of activity effects. The work of Cann and Summer [88] appears to have been carefully carried out, but their value is 4 to 5 times the other values of K^0_{s0}.

TABLE 10. Solubility of lead bromide in water

T/K	m_{PbBr_2}/mol kg^{-1}
Recommended	
298. 15	$(2.659 \pm 0.014) \times 10^{-2}$
Tentative	
273. 15	$(1.23 \pm 0.07) \times 10^{-2}$
278. 15	1. 45 ,,
283. 15	1. 70 ,,
288. 15	1. 99 ,,
293. 15	2. 31 ,,
298. 15	$(2.67 \pm 0.13) \times 10^{-2}$
303. 15	3. 08 ,,
308. 15	3. 54 ,,
313. 15	4. 05 ,,
318. 15	4. 62 ,,
323. 15	5. 25 ,,
328. 15	$(5.95 \pm 0.22) \times 10^{-2}$

TABLE 11. Experimental solubilities of lead bromide in water at 298.15 K

Density/ kg m^{-3}	m_{PbBr_2}/mol kg^{-1}	c_{PbBr_2}/mol dm^{-3}	Reference
		2.625×10^{-2}	Herz, Hellebrandt [57]
		2.628×10^{-2}	von Ende [61]
	2.640×10^{-2}		Burrage [52]
1006. 08	2.655×10^{-2}	2.643×10^{-2}	Lichty [62]
1005.	2.659×10^{-2}	2.646×10^{-2}	von Heveay, Wagner [81]
1005. 5	$(2.659 \pm 0.014) \times 10^{-2}$	$(2.648 \pm 0.014) \times 10^{-2}$	Recommended
	2.680×10^{-2}		Randall, Veitti [82]

TABLE 12. Solubility of lead bromide in aqueous electrolyte solutions

T/K	Ionic strength I/electrolyte	Molar solubility c_{PbBr_2}/mol dm^{-3}	Reference
294	0. 4/$NaClO_4$	2.83×10^{-2}	Cooper [83]
	0. 4/$NaNO_3$	3.94×10^{-2}	Cooper [83]
298. 15	1. 0/KBr	0.81×10^{-2}	Kul'ba et al. [84]
	3. 0/$LiClO_4$	1.24×10^{-2}	Fedorov et al. [85]
	3. 0/$NaClO_4$	1.99×10^{-2}	Fedorov et al. [85]
	4. 0/$NaClO_4$	$(11.6–11.8) \times 10^{-2}$ (graph)	Kul'ba et al. [86]
	4. 0/NaBr	55.9×10^{-2}	Vierling [87]

TABLE 13. The solubility product of lead bromide at 298.15 K

Ionic strength I/electrolyte	Solubility product K_{s0} [c]	Reference
Recommended		
0	7.78×10^{-6}	
Literature values		
0	7.78×10^{-6}	NBS-270-3 [21a]
0	8.46×10^{-6}	Lewis, Brighton [76]
0	9.18×10^{-6}	Fromherz [18]
0	38.9×10^{-6}	Cann, Summer [88]
3.0/Li(ClO_4,Br)	3.50×10^{-6} [a]	Fedorov et al. [85]
3.0/Na(ClO_4,Br)	5.3×10^{-6} [a]	Fedorov et al. [85]
4.0/Na(ClO_4,Br)	$(1.7\text{–}2.4)\times10^{-6}$ [a]	Kul'ba et al. [86]
4.0/Na(ClO_4,Br)	$(121\text{–}1080)\times10^{-6}$ [b]	Vierling [87]

[a] Molar scale, solubility product defined as $K_{s0}=a_{Pb^{2+}}(Br^-)^2$ with the $a_{Pb^{2+}}$ from an emf method.
[b] Molar concentration scale.
[c] K_{s0} becomes K_{s0}° at $I=0$.

Stability Constants [3] lists over 30 papers on the lead-bromo stability constants. Table 14 lists the cumulative stoichiometric stability constants obtained by Mironov, Kul'ba, Fedorov, and Tikhomirov [89] in a potentiometric investigation of Pb^{2+} in 0.25 to 4.0 m Na(ClO_4,Br), Na(NO_3,Br) and Na(Cl,Br) solutions as representative values of the lead-bromo complex formation constants. In 1.0–6.0 m Na(ClO_4,Br) solutions, log β_n for the ions $PbBr_n^{2-n}$ is a linear function of the ionic strength.

4.4. Lead Iodide

PbI_2, [10101-63-0] Formula Weight 461.01

Physical characteristics: Solid lead iodide is the hexagonal $Cd(OH)_2$ type crystal with $Z=4$, and $a=4.54$ and $c=6.86\times10^{-10}$ m. The calculated density is 6211 kg m^{-3}. In the presence of water the solid is PbI_2. In ternary systems of PbI_2+MI+H_2O a double salt $PbI_2\cdot MI$ often forms, where M is Li, Na, K and NH_4.

Recommended and tentative solubilities of lead iodide in water are in table 15. The solubility at 298.15 K appears to be well established. Table 16 lists the experimental solubility values at 298.15 K from nine workers. The values of Lichty [62], Burrage [52], and Lanford and Kiehl [90] appear most reliable. The average of the three values is $(1.648\pm0.007)\times10^{-3}$ mol PbI_2 per kg H_2O which is taken as the recommended value. The average of the six values between 1.63 and 1.67×10^{-3} is $(1.649\pm0.013)\times10^{-3}$ mol kg^{-1}.

TABLE 14. Cumulative formation constants, β_n, for $PbBr_n^{2-n}$ at 298.15 K [89]

Ionic strength I/electrolyte	Constant β_n	Ionic strength I/electrolyte	Constant β_n	Ionic strength I/electrolyte	Constant β_n
$PbBr^+$					
0.25/$NaClO_4$	18±1				
0.5/$NaClO_4$	12±1			0.5/NaCl	3.0 ±0.6
0.75/$NaClO_4$	10.5+0.5	0.75/$NaNO_3$	5.2+0.5	0.75/NaCl	1.5 ±0.2
1.0/$NaClO_4$	11±2	1.0/$NaNO_3$	4.0±0.5	1.0/NaCl	1.1 ±0.2
2.0/$NaClO_4$	19±2	2.0/$NaNO_3$	4.0±0.5	2.0/NaCl	1.3 ±0.2
3.0/$NaClO_4$	20±2	3.0/$NaNO_3$	5.0±0.6	3.0/NaCl	1.35±0.10
4.0/$NaClO_4$	30±2	4.0/$NaNO_3$	5.2±0.5	4.0/NaCl	1.0 ±0.10
6.0/Na(ClO_4,Cl)	50				
$PbBr_2$					
0.25/$NaClO_4$	40±4				
0.50/$NaClO_4$	30±4			0.5/NaCl	2.0 ±1.5
0.75/$NaClO_4$	38±6	0.75/$NaNO_3$	8.0±2.0	0.75/NaCl	2.0 ±0.4
1.0/$NaClO_4$	28±8	1.0/$NaNO_3$	10.0±2.0	1.0/NaCl	2.2 ±0.2
2.0/$NaClO_4$	25±7	2.0/$NaNO_3$	5.0±2.0	2.0/NaCl	0.55±0.2
3.0/$NaClO_4$	80±8	3.0/$NaNO_3$	5.0±2.0	3.0/NaCl	0.4 ±0.2
4.0/$NaClO_4$	200±50	4.0/$NaNO_3$	7.0±2.0	4.0/NaCl	0.65±0.05
6.0/Na(ClO_4,Cl)	1900				

TABLE 14. Cumulative formation constants, β_n, for $PbBr_n^{2-n}$ at 298.15 K [89]—Continued

Ionic strength I/electrolyte	Constant β_n	Ionic strength I/electrolyte	Constant β_n	Ionic strength I/electrolyte	Constant β_n
$PbBr_3^-$					
0.25/$NaClO_4$	380±20				
0.5/$NaClO_4$	120±20			0.5/NaCl	14 ±4
0.75/$NaClO_4$	120±20	0.75/$NaNO_3$	23 ±7	0.75/NaCl	
1.0/$NaClO_4$	170±10	1.0/$NaNO_3$	18 ±3	1.0/NaCl	
2.0/$NaClO_4$	350±30	2.0/$NaNO_3$	9.0±1.0	2.0/NaCl	0.65±0.1
3.0/$NaClO_4$	750±50	3.0/$NaNO_3$	4.0±2.0	3.0/NaCl	0.3 ±0.15
4.0/$NaClO_4$	1800±200	4.0/$NaNO_3$	10 ±2	4.0/NaCl	0.02±0.01
6.0/Na(ClO_4,Cl)	7950				
$PbBr_4^{2-}$					
1.0/$NaClO_4$	35±4				
2.0/$NaClO_4$	110±10	2.0/$NaNO_3$	7.0±1.0		
3.0/$NaClO_4$	650±150	3.0/$NaNO_3$	12.0±2.0	3.0/NaCl	0.14±0.15
4.0/$NaClO_4$	2300±200	4.0/$NaNO_3$	8.5±1.5	4.0/NaCl	0.07±0.03
6.0/Na(ClO_4,Cl)	45,000				
$PbBr_5^{3-}$					
2.0/$NaClO_4$	30±5				
3.0/$NaClO_4$	200±50				
4.0/$NaClO_4$	400±150	4.0/$NaNO_3$	1.3±0.3		
$PbBr_6^{4-}$		4.0/$NaNO_3$	0.5±0.4		
$PbBr^+$					
4.0/Li(ClO_4,Cl)	35				
$PbBr_2$					
4.0/Li(ClO_4,Cl)	450				
$PbBr_3^-$					
4.0/Li(ClO_4,Cl)	2000				
$PbBr_4^{2-}$					
4.0/Li(ClO_4,Cl)	5800				
$PbBr_5^{3-}$					
4.0/Li(ClO_4,Cl)	300				
$PbBr_6^{4-}$					
4.0/Li(ClO_4,Cl)	160				

The solubility of lead iodide appears to be less certain than the solubility of the other lead halides at temperatures other than 298.15 K. At 273.15 K there are two values of 0.93×10^{-3} and 0.959×10^{-3} mol PbI_2 per kg H_2O. Above 298.15 K there are only the values of Lichty [62] up to 368.15 K, and the values of Benrath et al. [12] between 448.15 and 607.15 K. Linear regressions of three constant equations to each data set separately and combined had standard deviations of 6 to 8 percent. The available solubility data is just not very good. The tentative values of table 15 between 273.15 and 353.15 K were calculated from the equation

$$\ln m_{PbI_2}/\text{mol kg}^{-1} = -37.4645 + 32.5932/(T/100\ \text{K}) + 18.4290 \ln (T/100\ \text{K}) \quad (37)$$

obtained by a linear regression of selected data of Lichty (values at 273, 318, and 368 K not used), and the data of workers listed in table 16 except the values of von Ende, Böttger, and Menke. Data of Demassiux [72, 95] are unsatisfactory and were not used. The measurements of Duncan [96] appear low and were not used. The standard error about the regression line is 3.8 percent. Figure 3 shows the scatter of the data. The lower figure shows the scatter of Lichty and Benrath et al. data, the upper part of the figure shows the distribution of the data used to obtain equation (30). There are indications the Benrath et al. [12] data may be 20–25 percent low.

TABLE 15. The solubility of lead iodide in water

T/K	Solubility m_{PbI_2}/mol kg^{-1}
Recommended	
298.15	$(1.648 \pm 0.007) \times 10^{-3}$
Tentative values	
273.15	0.90
278.15	1.01
283.15	1.14
288.15	1.29
293.15	1.46
298.15	$(1.66 \pm 0.36) \times 10^{-3}$
303.15	1.88
308.15	2.14
313.15	2.43
318.15	2.76
323.15	$(3.14 \pm 0.62) \times 10^{-3}$
328.15	3.58
333.15	4.07
338.15	4.64
343.15	5.28
348.15	6.02
353.15	$(6.86 \pm 1.18) \times 10^{-3}$

TABLE 16. Experimental solubility of lead iodide in water at 298.15 K

Solubility m_{PbI_2}/mol kg^{-1}	Reference
1.84×10^{-3} [b]	Menke [91]
1.67×10^{-3} [a]	Rald, Gjaldbaek [92]
1.657×10^{-3}	Lichty [62]
1.65×10^{-3}	Fromherz [18]
1.65×10^{-3} [b]	Lewis, Brighton [76]
$(1.648 \pm 0.007) \times 10^{-3}$	Recommended
1.646×10^{-3}	Burrage [52]
1.641×10^{-3}	Lanford, Kiehl [90]
1.63×10^{-3}	van Klooster, Balon [93]
1.58×10^{-3}	von Ende [61]
1.52×10^{-3}	Fomin et al. [94]
1.31×10^{-3}	Böttger [65]

[a] Value at 298.00 K.
[b] c_{PbI_2}/mol dm^{-3}.

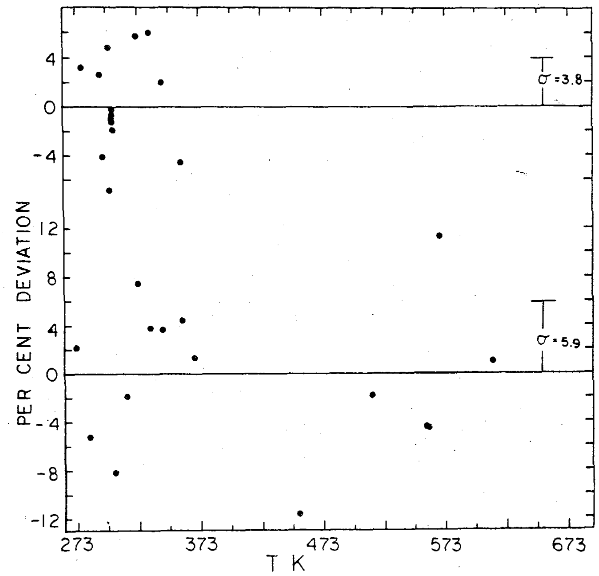

FIGURE 3. Lead iodide. Percent deviation of the stoichiometric solubility from the fitted equation. Bottom, all data; top, selected data and their percent deviation from eq 37.

Table 17 lists solubilities of lead iodide at several ionic strengths. In addition Rald and Gjaldbaek [92] determined the solubility of lead iodide between 0.02 and 0.12 and at 1.0 molar $NaClO_4$. Yatsimirskii and Shutov [97] determined lead iodide solubility in the presence of nitrates of Mg^{2+}, Ca^{2+}, Zn^{2+}, and Ca^{2+} and Pb^{2+}.

Tentative values of the lead iodide solubility product at 1.0 and 2.0 ionic strength and experimental values are given in table 18.

Nasanen [100, 101] made extensive measurements of the solubility product as a function of both ionic strength and temperature. At. 298.15 the equation

$$pK^{\circ}_{s0} = pK_{s0} + (3.04\ I^{1/2})/(1+1.80\ I^{1/2}) - 0.464\ I \quad (38)$$

where the ionic strength, I, varied from 0 to 1.54, fitted his data well. In the equation K°_{s0} is the thermodynamic solubility product and K_{s0} is the concentration solubility product. We have used the equation with a pK_{s0} value of 8.01 from the work of Rald and Gjaldbaek [92] to obtain the tentative values at 0, 1.0, and 2.0 ionic strength.

Values of cumulative formation constants, β_n, are given in table 19. Only two workers suggest the Pb_2I^{3+} ion is important. The values may be taken as representative values. There are not enough data under the same conditions of ionic strength to make intercomparisons and recommend values.

TABLE 17. The solubility of lead iodide as a function of ionic strength at 298 K

Ionic strength I/electrolyte	Solubility m_{PbI_2}/mol kg^{-1}	Reference
~0	1.648×10^{-3}	
1.0/nitrates	1.68×10^{-3}	Yatsimirskii, Shutov [97]
1.0/NaI	$(7.0\pm0.2)\times10^{-4}$ [a]	Kul'ba et al. [84]
2.0/$NaClO_4$	1.78×10^{-3}	Hsu, Tan, Yen [98]
3.0/$LiClO_4$	0.99×10^{-3} [a]	Fedorov et al. [85]

[a] c_{PbI_2}/mol dm^{-3}.

TABLE 18. The solubility product of lead iodide in aqueous solution

T/K	Ionic strength I/electrolyte	Solubility product [b] K_{s0}	pK_{s0}	Reference
		Tentative values		
298.15	0	9.8×10^{-9}	8.01	
	1.0	4.1×10^{-8}	7.38	
	2.0	1.9×10^{-8}	7.72	
		Experimental values		
273.15	0	6.8×10^{-10}	9.17	Nasanen [101]
298.15	0	6.3×10^{-9}		Nasanen [101]
	0	$(6.3\text{–}6.6)\times10^{-9}$		Nasanen [101]
	0	7.20×10^{-9}		Nasanen [100]
	0	8.49×10^{-9}		NBS-270-3 [21a]
	0	9.04×10^{-9}		Soulier, Gauthier [102]
	0	9.83×10^{-9}		Fromherz [18]
	0	9.9×10^{-9}		Rald, Gjaldbaek [92]
	0	11.9×10^{-9}		Lewis, Brighton [76]
318.15	0	3.0×10^{-8}		Nasanen [101]
333.15	0	8.3×10^{-8}		Nasanen [101]
298.15	1.0/nitrates	1.05×10^{-9}		Yatsimirskii, Shutov [97]
	1.0/KI [c]	1.07×10^{-9}		Korshunov, Budnov [103]
	1.0/(I^- & ClO_4^-)	3.4×10^{-8} [a]		Tur'yan [104]
	1.0/$NaClO_4$	6.1×10^{-8}		Rald, Gjaldbaek [92]
298.15	2.0/$NaClO_4$	2.48×10^{-8}		Hsu, Tan, Yen [98]
298.15	3.0/$LiClO_4$	3.17×10^{-8}		Fedorov et al. [99]

[a] Calculated from literature data [90, 97, 105].
[b] The K_{s0} and pK_{s0} values are K_{s0}^0 and pK_{s0}^0 values when the ionic strength, I=0.
[c] The authors are not clear as to whether the value is for KI only or for mixed electrolyte.

TABLE 19. Cumulative formation constants for lead-iodo complex ions in aqueous solution at 298.15 K

Complex ion	Ionic strength I/electrolyte	Formation constant, β_n	Method	Reference
PbI^+	0	83	spec	Briggs et al. [99]
	0	125	pot, sol	Nasanen [101]
	0	100 [a]	soly	Tur'yan [104]
	0. 375–3. 86	37 [b]	soly	Tur'yan [104]
	1. 0/$NaClO_4$	15	soly	Rald, Gjaldbaek [92]
	1. 0/	18	pot	Kivalo, Ekman [105]
	1. 0/	34 [c]		Tur'yan [104]
	2. 0/$NaClO_4$	19. 9	soly	Hsu, Tan, Yen [98]
	3. 0/	49 ± 5	soly	Fedorov et al. [85]
Pb_2I^{3+}	0. 375–3. 86	46 [d]	soly	Yatsimirskii, Shutov [97]
	3. 0/	90 ± 20 [d]	soly	Fedorov et al. [85]
PbI_2	0	1.43×10^3 [a]	soly	Tur'yan [104]
	1. 0/	6.20×10^2	pot	Kivalo, Ekman [105]
	1. 0/	4.75×10^2 [c]		Tur'yan [104]
	2. 0/	2.38×10^2	soly	Hsu, Tan, Yen [98]
PbI_3^-	0	8.3×10^3 [a]	soly	Tur'yan [104]
	1. 0/	2.6×10^3	pot	Kivalo, Ekman [105]
	2. 0/$NaClO_4$	1.38×10^3	soly	Hsu, Tan, Yen [98]
PbI_4^{-2}	0	2.9×10^4 [a]	soly	Tur'yan [104]
	1. 0/	0.83×10^4	pot	Kivalo, Ekman [105]
	2. 0/$NaClO_4$	2.66×10^4	soly	Hsu, Tan, Yen [98]

[a] Calculated from data of Lanford and Kiehl [90].
[b] Calculated from data of Kivalo and Ekman [105].
[c] Calculated from data of Yatsimirskii and Shutov [97].
[d] The cumulative formation constant is for the formation in solution of the complex M_mL_n. The constant is β_{nm} with $m=2$ and $n=1$.

4.5. Lead Sulfide

PbS, [1314–87–0] Galena, PbS, [12179–39–4] Formula Weight 239.26

Physical characteristics: Galena is a cubic crystal with $Z=4$ and $a=5.936\times10^{-10}$ m. Its density is 7596 kg m^{-3}. There is a high pressure orthorhombic form of PbS known at 25 kbar. There are numerous crystals containing lead, sulfur, and another element.

Neither tentative nor recommended values of the solubility of lead sulfide can be given at this time. Measured values of the solubility of lead sulfide in water by conductivity and by emf methods appear to be high. Weigel [143] reported values of 1.21×10^{-6} mol PbS per dm^3 solution at 291.15 K for crystalline PbS and 3.6×10^{-6} mol dm^{-3} for freshly precipitated PbS, which over 23 hours decreased to a value of 1.18×10^{-6}. Nims and Bonner [144] used a comparative emf method and reported a solubility of 0.94×10^{-6} mol dm^{-3} at 298.15K.

Calculation of the PbS solubility from

$$(K^0_{s0}(a_{H^+})^2/\gamma_{Pb^{2+}}\gamma_{H_2S}K_1K_2)^{1/2}=c_{PbS}/\text{mol dm}^{-3}$$

which assumes all the lead is present as Pb^{2+}, with $K^0_{s0}=2.69\times10^{-29}$, $K_1=1.02\times10^{-7}$, $K_1=1.25\times10^{-14}$ (Helgeson [139]), and γ's equal to unity gives

pH	2	3	4	5
10^9c_{PbS}/mol dm^{-3}	1500	150	15	1.5

The calculated solubilities are lower by about a factor of 5 than results calculated by Kapustinskii [145], and quoted in Seidell and Linke [1].

Nriagu [146] measured the solubility of PbS in 3.0 molal NaCl+HCl+H_2O at temperatures of 310.15, 333.15, 363.15, 393.15 and 473.15 K at pH's between 2.0 and 5.0. The results, when plotted as log (total Pb molality) vs pH, were linear with slope of near -1.0. In these solutions most of the lead is in the form of a $PBCl_n^{2-n}$ complex. Nriagu [146] showed that over the pH range of 2 to 5 the solubility of lead sulfide in the 3.0 molal NaCl can be calculated from the equation

$$\left(\frac{K^0_{s0}\left[\sum_0^4 \beta n(m_{Cl^-})^n\right](a_{H^+})^2}{\gamma_{Pb^{2+}}\gamma_{H_2S}K_1K_2}\right)^{1/2}-c_{PbS}/\text{mol dm}^{-3}$$

where K^0_{s0} is the PbS solubility product, β_n the formation constants of $PbCl_n^{2-n}$, and K_1 and K_2 the dissociation constants of H_2S. Taking β_n values in 3.0 molal NaCl from Nriagu and Anderson [31] (see sections 3.3 and 4.2) and $K^0_{s0}K_1$, and K_2 values from Helgeson [139] the equation reproduced the experimental results below 423 K within less than a factor of 2 and the results at 473 K within a factor of 4. Nriagu's experimental stoichiometric solubility values were given in a graph. He did state that the stoichiometric solubility at pH ~4.5 increases from about 1.0 ppm at

333 K to over 100 ppm at 473 K ($\sim 4\times 10^{-6}$ to $\sim 4\times 10^{-4}$ mol dm^{-3}).

Nriagu [146] cites other solubility studies at 353 and 371 K which are not available. Hemley, Meyer, Hodgson and Thatcher [147] determined the solbulity of PbS at 573–773 K and 1000 bar in a chemical environment buffered by silicate mineral equilibria. Kaz'nin and Karpov [148] calculated by Gibbs energy minimization the PbS-ZnS-NaCl-HCl-SiO_2-H_2O system as represented by 30 species. Up to 423 K Pb $(HS)_n^{2-n}$ complexes were important. Kuznetsov Efremova, and Kotelinikov [149] report results of their calculations on the Pb-S-H_2O system at 298 and 573 K.

Table 20 summarizes some solubility product values for lead sulfide. The tentative value is a pK_{s0}^{o} of 28.6 (K_{s0}^{o} of 2.5×10^{-29}) which is near the values calculated from thermodynamic data by Erdenbaeva [150] and by Helgeson [139], and the corrected value of Kivalo and Ringbom [138].

In a 1953 report to the Analytical section of IUPAC Ringbom [151] surveyed the literature on lead sulfide solubility products and recommended for the reactions the values

$$PbS\ (s) + 2H^+\ (aq) \rightleftarrows Pb^{2+}\ (aq) + H_2S\ (g)$$

$$PbS\ (s) \rightleftarrows Pb^{2+} + S^{2-} \qquad pK_{s0}^{o} = 5.6 \pm 0.5$$

$$dpK_{s0}^{o}/dT = -0.044$$

$$pK_{s0}^{o} = 26.6 \pm 0.7$$

In his survey, Ringbom accepted as probable values of the H_2S dissociation at 298.15 K

$$H_2S\ (g) \rightleftarrows H_2S\ (aq) \qquad pK_H = 0.99 \pm 0.01$$

$$H_2S\ (aq) \rightleftarrows HS^-\ (aq) + H^+\ (aq) \qquad pK_1 = 7.05 \pm 0.05$$

$$HS^-(aq) \rightleftarrows S^{2-}\ (aq) + H^+\ (aq) \qquad pK_2 = 12.9 \pm 0.1$$

Ringbom's recommendation gives too large a value of K_{s0}^{o} in part because the H_2S K_2 value he accepted was too large, and in part because of changes in the accepted Gibbs energy of formation of PbS.

The problem of the H_2S second dissociation is not settled yet. Recently Ellis and Giggenbach [135] and Giggenbach [136] reported experiments that strongly suggest the second ionization of H_2S is much smaller, with an upper limit at 298.15 of pK_2=17.1 (K_2=8×10^{-18}). However Krynknov, Starostina, Tarasenko and Primauchuk [137] have also redetermined the second ionization constant and report a value of pK_2 equal to 13.37 (K_2=4×10^{-13}) which does not confirm the lower value. Helgeson [139] accepts the value of 13.90 from Maronny [152]. All of these values are lower K_2 values than are calculated from thermodynamic data in either NBS Tech. Note 270 [21] or the Geological Survey Bulletin 1452 [153]. An evaluation of the H_2S dissociation equilibria must be made before metal sulfide solubility products can be evaluated.

In 1956 Kivalo and Ringbom [138] determined the thermodynamic solubility product of lead sulfide polarographically in a hydrochloric acid medium at 298.15 K. A correction was made for the effect of lead-chloro complex formation. The results of their study were

$$PbS(s) + 2H^+ \rightleftarrows Pb^{2+} + H_2S(g) \qquad pK_{s0}^{o} = 6.93$$

and

$$PbS(s) \rightleftarrows Pb^{2+}(aq) + S^{2-}(aq) \qquad pK_{s0}^{o} = 27.9$$

TABLE 20. Solubility product of lead sulfide

T/K	pK_{s0}^{o}	K_{s0}^{o}	Reference
		Tentative value	
298.15	28.6 [a]	2.5×10^{-29}	
		Experimental value	
298.15	28.8 [b]	1.6×10^{-29}	Kivalo, Ringbom [138]
		Values calculated from thermodynamic data	
298.15	28.05	8.9×10^{-29}	NBS-Tech Note 3 [21a]
298.15	27.59	2.6×10^{-28}	Geol. Sur. Bull. 1452 [153]
298.15	28.42	3.8×10^{-29}	Erdenbaeva [150]
298.15	28.57	2.8×10^{-29}	Helgeson [139]
323.15	26.67	2.1×10^{-27}	Helgeson [139]
333.15	26.14	7.2×10^{-27}	Helgeson [139]
373.15	23.96	1.1×10^{-24}	Helgeson [139]
423.15	21.93	1.2×10^{-22}	Helgeson [139]
473.15	20.36	4.4×10^{-21}	Helgeson [139]
523.15	19.14	7.2×10^{-20}	Helgeson [139]
573.15	18.31	4.9×10^{-19}	Helgeson [139]

[a] This is smaller by two orders of magnitude than the tentative value of Ringbom's 1953 IUPAC report, see Sillen and Martell[3].

[b] Kivalo and Ringbom reported pK_{s0}^{o}=27.9, they used the H_2S dissolution and dissociation of $K_HK_1K_2 = 10^{-20.94}$, we have revised their value by use of $K_HK_1K_2 = 10^{-21.88}$.

The use of the H_2S dissociation constants suggested by Helgeson [139] would change the pK_{s0}° value to 28.8. This agrees well with the values of 28. 42 [150] and 28. 57 [139] calculated from thermodynamic data.

Helgeson [139], in an important paper, has calculated a data base that is currently in active use by many geologists. Helgeson has used currently accepted approximations to calculate Gibbs energy (as log K values) at temperatures between 298 and 573 K for many dissociation, complexing, and solubility reactions of interest to the geologist. He has included temperature dependent heat capacities, activity coefficients and ionic strength effects in his calculations. His values for the PbS activity solubility product are in table 20. At 298.15 K the value of pK_{s0}° of Helgeson and the value of Erdenhaeva [150], also based on a thermodynamic calculation, agree closely. Their values, along with the experimental value of Kivalo and Ringbom, are the base of the tentative value of pK_{s0}° equal to 28.6. The K_{s0}° value is a smaller value of K_{s0}° than has been recommended in recent times.

4.6. Lead Sulfate

$PbSO_4$, [7446–14–2] Formula Weight 303.26 (Chem. Abstr. Index. $H_2O_4S \cdot Pb$, Sulfuric Acid, Lead (2^+) Salt (1:1).)

Physical characteristics: There have been several determinations of the x-ray structure of the mineral anglesite (lead sulfate) (5). A representative set of parameters for the orthorhombic crystal is Z=4 and a=6.958, b=8.480, and c=5.398$\times 10^{-10}$ m. The density is 6323 kg m^{-3} at 298.15 K. Hydrates of lead sulfate are not mentioned.

The recommended solubility of lead sulfate in water at 298.15 K is given in table 21. Tentative values are given at other temperatures. The recommended value is the average of the values in table 22 with Böttger's value excluded from the average. The single best experimental value at 298.15 K may be the value of Little and Nancollas [11]. In sodium perchlorate solution of ionic strength 0.2 Dyrssen et al. [118] report a solubility of 3.02$\times 10^{-4}$ mol dm^{-3} at 298. 15K.

TABLE 21. Recommended and tentative values of the solubility of lead sulfate in water

T/K	c_{PbSO_4}/mol dm^{-3}
Recommended value	
298.15	(1. 461 ± 0. 035) × 10^{-4}
Tentative values	
273.15	(1. 09 ± 0. 18) × 10^{-4}
278.15	1. 17 "
283.15	1. 24 "
288.15	1. 32 "
293.15	1. 395 "
298.15	(1. 47 ± 0. 25) "
303.15	1. 55 "
308.15	1. 64 "
313.15	1. 73 "
318.15	1. 81 "
323.15	(1. 90 ± 0. 32) "

TABLE 22. Experimental solubilities of lead sulfate in water at 298.15 K

c_{PbSO_4}/mol dm^{-3}	Reference
(1. 52 ± 0. 02) × 10^{-4}	Kolthoff et al. [113]
1. 481 "	Koisumi [114]
1. 47 "	Crockford, Brawley [112]
(1. 466 ± 0. 014) × 10^{-4}	Little, Nancollas [11]
(1. 461 ± 0. 035) × 10^{-4}	Recommended
1. 45 "	Beck, Stegmuller [106]
(1. 42 ± 0. 02) "	Huybrechts, de Langeron [108]
1. 42 "	Jager [115]
1. 34 "	Böttger [65]

The tentative values were calculated from the equation

$$\ln c_{PbSO_4}/\text{mol dm}^{-3} = -5.5600 - 0.97244/(T/100\ K) \tag{39}$$

obtained from a linear regression of the solubility values of Crockford and Brawley [112], Koizumi [114] and Little and Nancollas [119]. The standard deviation in ln c is 0.1558. The data from references [65, 106, 108, 110, 111, 113] were not used in the linear regression.

The lead sulfate solubility product values are summarized in table 23. The value of Böttger [65] is a concentration value with no corrections for activity or complexing effects. Jager [115] measured the solubility in pure water and nitric acid solutions. Debye-Huckel limiting law was used to calculate mean ionic activity coefficients to obtain a thermodynamic constant. The value of Dyrssen, Ivanova and Oren [118] is a concentration value in solutions of ionic strength 0.2 $Na^+ (SO_4^{2-}, ClO_4^-)$. Little and Nancollas [119] corrected for activity effects with an extended Debye-Huckel function to obtain a thermodynamic constant.

Egorov and Titova [116] developed a temperature dependent equation for ln K_{s0}° from thermodynamic data. Values calculated from their equation appear to be 3 to 4 times higher than the experimental values of Jager and of Little and Nancollas. Khodakovskii, Mishin and Zhogina [117] used tabulated solubility data to obtain the equation

$$\ln K_{s0}^{\circ} = 3.42 - 2009/T - 0.01492\ T \tag{40}$$

for the temperature interval of 273 to 573 K. The equation appears to be consistent with other thermodynamic data [21a] and to give values of K_{s0}° of near correct magnitude in the room temperature region. Several values calculated from the equation are given in table 23.

Helgeson [139] made calculations of log K_{s0}° from thermodynamic data for the temperature interval of

TABLE 23. The solubility product of lead sulfate

T/K	Ionic strength	Solubility product, K°_{s0} [a]	Reference
		Tentative values	
273.15	0	1.61×10^{-8}	Standard potential data from Pitzer [120] and table 1.
285.65	0	2.08×10^{-8}	
298.15	0	2.53×10^{-8}	
310.65	0	2.88×10^{-8}	
323.15	0	2.99×10^{-8}	
		Other calculated values	
273.15	0	0.98×10^{-8}	Khodakovskii et al. [117]
285.65	0	1.33×10^{-8}	
298.15	0	1.69×10^{-8}	
310.65	0	2.08×10^{-8}	
323.15	0	2.41×10^{-8}	
298.15	0	6.2×10^{-8}	Egorov, Titova [116]
298.15	0	1.78×10^{-8}	Helgeson [39]
323.15	0	2.0×10^{-8}	
333.15	0	2.0×10^{-8}	
373.15	0	1.4×10^{-8}	
423.15	0	5.5×10^{-9}	
473.15	0	1.3×10^{-9}	
523.15	0	2.5×10^{-10}	
573.15	0	3.6×10^{-11}	
		Experimental values	
293.15		1.32×10^{-8}	Böttger [65]
298.15		1.79×10^{-8}	Böttger [65]
	0	1.52×10^{-8}	
	0.2/Na(SO_4, ClO_4)	9.3×10^{-8}	Dyrssen et al. [118]
	0	1.72×10^{-8}	Little, Nancollas [11]
298.15	1.0/$NaClO_4$	0.63×10^{-8}	Ramette, Stewart [199]
	1.0/$LiClO_4$	0.63×10^{-8}	
	1.0/$HClO_4$	1.20×10^{-8}	

[a] K_{s0} becomes K°_{s0} at $I=0$.

298.15 to 573.15 K. The K°_{s0} values for $PbSO_4$ go through a maximum at 323–333 K, then decrease several orders of magnitude as the temperature increases to 573 K. Helgeson appears to have carefully selected his data base, and to have taken into account temperature dependent heat capacities, activity coefficients, and ionic strength effects. There apparently are no experimental data above 363 K. Thus his values between 289 and 373 K are probably much more reliable than his extrapolated values above 373 K.

Pitzer [119] has published a careful evaluation of the standard potential values for

$$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$$

The recommended E° values have been combined with the lead/lead ion standard potential values of table 1 to obtain the tentative K°_{s0} values of table 22. At 298.15 K the tentative K°_{s0} value is 50 to 65 percent higher than the direct experimental values w considered most reliable [115,11].

Values of the formation constant

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightleftarrows PbSO_4(aq)$$

have been reported by Dyrssen et al. [118] at an ioni strength 0.2/$NaClO_4$ as 118 and by Little and Nan collas [11] as 530. The values show that ion pai formation plays a role in determining solubility.

4.7. Lead Nitrate

$Pb(NO_3)_2$, [10099-74-8] Formula Weight 331.2 (Chem. Abstr. Index, Nitric Acid, Lead (2+) Salt $HNO_3 \cdot 1/2Pb$.)

Physical characteristics: Lead nitrate crystallizes a a colorless cubic crystal of $a=7.8568\times10^{-10}$ m with calculated density of 4535 kg m^{-3} at 298.15 K. Th solubility of lead nitrate in water gives no indication of a solid phase other than $Pb(NO_3)_2$.

Although the primary objective of this report is the sparingly soluble lead salts the soluble lead nitrate is included. The recommended solubility values in units of mol $Pb(NO_3)_2$ per kg water, g $Pb(NO_3)_2$ per kg water, and mass percent are given at 5 degree intervals from 273.15 to 373.15 K in table 24. The molal values were calculated from the equation

$$\ln m_{Pb(NO_3)_2}/\text{mol kg}^{-1}=11.70238 -22.52308/(T/100\text{ K})-3.2579\ln(T/100\text{ K}) \quad (41)$$

which was obtained from the linear regression of 26 solubility values starred (*) in table 25. The standard error about the regression line was 0.0241 in ln m which is 2.44 percent of the solubility value at the mid temperature value of 323.15 K.

Table 25 lists the experimental values of the lead nitrate solubility in water from 14 papers. Inspection of the data shows that above 303.15 K the values of Kremers [120] are always high and the values of Mulder [121] are usually the lowest. The values of Fishman and Bulkova [132] appear to be low. The values from these three papers were not used in the linear regression. Several other values that were one standard deviation or more from the first linear regression were also eliminated. The values of Motornaya, Ben'yash and Kristoforov [133] were obtained too late to include in the linear regression. The remaining starred (*) values were used.

The nitrate ion complexes the lead ion. The values of the formation constants found by Mironov [47] are given in the last paragraph of section 4.1.

TABLE 24. The recommended values of the solubility of lead nitrate in water between 273 and 373 K

T/K	$m_{Pb(NO_3)_2}$ mol kg^{-1}	g $Pb(NO_3)_2$ per kg H_2O	Mass percent
273. 15	1. 201	397. 8	28. 40
278. 15	1. 313	434. 8	30. 30
283. 15	1. 429	473. 3	32. 13
288. 15	1. 550	513. 4	33. 92
293. 15	1. 674	554. 4	35. 67
298. 15	1. 802	596. 8	37. 37
303. 15	1. 934	640. 5	39. 04
308. 15	2. 068	684. 9	40. 65
313. 15	2. 206	730. 6	42. 22
318. 15	2. 345	776. 7	43. 72
323. 15	2. 487	823. 7	45. 17
328. 15	2. 631	871. 4	46. 56
333. 15	2 776	919. 4	47. 90
338. 15	2. 923	968. 1	49. 19
343. 15	3. 070	1016. 8	50. 42
348. 15	3. 218	1065. 8	51. 59
353. 15	3. 367	1115. 2	52. 72
358. 15	3. 516	1164. 5	53. 80
363. 15	3. 664	1213. 5	54. 82
368. 15	3. 813	1262. 9	55. 81
373. 15	3. 961	1311. 9	56. 75

TABLE 25. Experimental values of lead nitrate solubility in water at temperature between 273 and 373 K

T/K	g $Pb(NO_3)_2$ per 100 g H_2O	Mass percent	mol $Pb(NO_3)_2$ per kg H_2O	Data source
273. 15	38. 8		1. 171*	Kremers [120]
	40. 25		1. 215*	Glasstone, Saunders [127]
		26. 9	1. 111	Kazantsen [130]
283. 15	48. 3	31. 6	1. 458*	Kremers [120]
		31. 6	1. 394	Kazantsen [130]
288. 15		32. 93	1. 482	Fishman, Bulakhova [132]
290. 15	54. 0		1. 630*	Kremers [120]
	52. 76		1. 593*	Euler [124]
293. 15	56. 5		1. 706	Kremers [120]
	55. 11		1. 664*	Fedotieff [125]
	55. 1		1. 685*	LeBlanc & Noyes [122]
		35. 7	1. 676*	Kazantsen [131]
		34. 31	1. 577	Fishman & Bulakhova [132]
298. 15	60. 6		1. 830*	Kremers [120]
	59. 6		1. 799*	Richards & Schumb [126]
	61. 2		1. 848*	Fock [123]
	59. 7		1. 802*	Akerlof & Turck [129]
	58. 9		1. 778*	Malquori [128]
		37. 4	1. 804*	Kazantsen [130]
		36. 8	1. 758	Motornaya, Ben'yash, Kristoforov [133]

TABLE 25. Experimental values of lead nitrate solubility in water at temperature between 273 and 373 K—Continued

T/K	g $Pb(NO_3)_2$ per 100 g H_2O	Mass percent	mol $Pb(NO_3)_2$ per kg H_2O	Data source
299.15		37.41	1.805*	Ferris [131]
303.15	66		1.993	Kremers [120]
		39.3	1.955*	Kazantsen [130]
313.15	75		2.264	Kremers [120]
	69.4		2.095	Mulder [121]
		42.3	2.213*	Kazantsen [130]
		42.16	2.201*	Ferris [131]
		41.8	2.168	Motornaya, Ben'yash, Kristoforov [133]
323.15	85		2.566	Kremers [120]
	81.1		2.449*	Glasstone & Saunders [127]
	78.7		2.376	Mulder [121]
		45.0	2.470*	Kazantsen [130]
333.15	95		2.868	Kremers [120]
	88		2.657	Mulder [121]
		47.8	2.764*	Kazantsen [130]
		48.0	2.787	Motornaya, Ben'yash, Kristoforov [133]
353.15	115		3.472	Kremers [120]
	107.6		3.249	Mulder [121]
		52.8	3.377*	Kazantsen [130]
		52.45	3.330*	Ferris [131]
371.95		56.7	3.954*	Kazantsen [130]
372.95		56.8	3.970*	Kazantsen [130]
373.15	138.8		4.191	Kremers [120]
	125.5		3.789	Glasstone & Saunders [127]
	127		3.834	Mulder [121]

4.8. Lead Phosphates

Primary Lead Orthophosphate, $Pb(H_2PO_4)_2$ [16180-04-4] Formula Weight 401.17 [Chem. Abstr. Index: Phosphoric Acid, Lead (2+) Salt (2:1) $H_3O_4P \cdot 1/2Pb$]

Secondary Lead Orthophosphate, $PbHPO_4$ [15845-52-0] Formula Weight 303.18 [Chem. Abstr. Index, Phosphoric Acid, Lead (2+) Salt (1:1)$H_3O_4P \cdot Pb$]

Tertiary Lead Orthophosphate, $Pb_3(PO_4)_2$ [7446-27-7] Formula Weight 811.54 [Chem. Abstr. Index, Phosphoric Acid, Lead (2+) Salt (2:3) $H_3O_4P \cdot 3/2Pb$]

Hydroxy Pyromorphite, $Pb_5(PO_4)_3OH$ [66732-49-8] Formula Weight 1337.92 [Chem. Abstr. Index: Pyromorphite, Hydroxy $HO_{13}P_3Pb_5$]

Tetraplumbite Ortho Phosphate, $Pb_4O(PO_4)_2$ [37295-08-2] Formula Weight 1034.74 [Chem. Abstr. Index: Lead Oxide Phosphate, $O_9P_2Pb_4$]

Lead Hydroxylapatite, $Pb_{10}(PO_4)_6(OH)_2$, [12207-55-5] Formula Weight 2675.84 [Chem. Abstr. Index: Lead Hydroxide Phosphate $HO_{13}P_3Pb_5$]

The thermodynamically stable solids of the $PbO-P_2O_5-H_2O$ system depend upon pH. According to Nriagu [154] at 298.15 K the stable phases and their range of pH are:

pH	very acid—? (~3.8)	$Pb(H_2PO_4)_2$
pH	?—4	$Pb_5(PO_4)_3OH$
pH	4—9.5	$Pb_4O(PO_4)_2$
pH	>9.5	$Pb(OH)_2$

Thus solid secondary lead orthophosphate, $PbHPO_4$ and tertiary lead orthophosphate, $Pb_3(PO_4)_2$ are metastable in contact with their solutions. However, the transition of $PbHPO_4$ to a stable solid is slow enough that $PbHPO_4$ solubility can be determined. Transformations to stable solid phases require about 100 hours in acid (pH ~4) solution and 200 hours in basic (pH ~10) solutions [154].

Secondary Lead Orthophosphate, $PbHPO_4$

Table 26 gives the solubility product values for secondary lead orthophosphate. The tentative recommendation is the value of Nriagu [154]. The Jowett and Price [155] value at 310.65 K agrees well with the Nriagu value. Earlier values at 298.15 and 310.65 K of Millet and Jowett [156] were declared erroneous

[155]. The value of Zharovskii [157] falls in the same range as the erroneous Millet and Jowett values. The value calculated from data in NBS–TN–270–3 [21a] appears to be several orders of magnitude too small. Nriagu suggests a ΔG°_{f298} value for $PbHPO_4(s)$ that is about 6 kcal less negative than the NBS–TN 270–3 value.

Nriagu [154] also reports values for the formation constants of $PbHPO_4$ and $PbH_2PO_4^+$ which are $10^{3.1\pm0.8}$ and $10^{1.5\pm0.5}$ respectively at 298.15 K.

The following equilibria are required to describe the saturated $PbHPO_4+H_2O$ system at 298.15 K.

1. $PbHPO_4(s) \rightleftarrows Pb^{2+} + HPO_4^{2-}$ $\quad K^\circ_{s0}=10^{-11.43}$
2. $Pb^{2+} + HPO_4^{2-} \rightleftarrows PbHPO_4$ $\quad K_2=10^{3.1}$
3. $Pb^{2+} + H_2PO_4^- \rightleftarrows PbH_2PO_4^+$ $\quad K_3=10^{1.5}$
4. $Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+$ $\quad K_4=10^{-6.18}$
5. $PbOH^+ + H_2O \rightleftarrows Pb(OH)_2 + H^+$ $\quad K_5=10^{-10.94}$
6. $Pb(OH)_2 + H_2O \rightleftarrows Pb(OH)_3^- + H^+$ $\quad K_6=10^{-10.94}$
7. $H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$ $\quad K_7=10^{-2.148}$
8. $H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$ $\quad K_8=10^{-7.198}$
9. $HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$ $\quad K_9=10^{-12.32}$

The sources of the constants are [154] for 1–3, [158,159] for 4–6 and [140] fcr 7–9.

Assuming the activity coefficients are unity, the above scheme has been used to calculate approximate water solubilities of $PbHPO_4$ as a function of pH at 298.15 K. See section 3.4.

pH	5	6	7	8	9
10^5 c/mol dm^{-3}	2.5	1.0	0.85	1.7	5.0

Tertiary Lead Orthophosphate, $Pb_3(PO_4)_2$

The crystal structure of $Pb_3(PO_4)_2$ is hexagonal with $Z=3$ and $a=9.66$ and $c=7.4\times10^{-10}$ m. The density is $6.99–7.03\times10^3$ kg m^{-3}.

Nriagu [154] carried out hydrolysis experiments in 0.0032 *M* H_3PO_4 and found the conversion reaction

$$3PbHPO_4(s) \rightleftharpoons Pb_3(PO_4)_2(s) + H_2PO_4^- + H^+$$

equilibrated in about 100 hours and that the equilibrium constant is $10^{-7.50}$ at 298.15 K. From this he obtained ΔG°_{f298} $[Pb_3(PO_4)_2(s)]$ as -565.0 kcal mol^{-1}, and calculated the $Pb_3(PO_4)_2$ K°_{s0} as $10^{-44.4}$, which is the recommended tentative value. It and other values are given in table 27.

As with $PbHPO_4$ the values of Millet and Jowett [156] were declared to be erroneous by Jowett and Price [155]. The report of a solubility product by a polargraphic method appears to result in much too high a value [160].

TAPLE 26. Solubility product values for secondary lead orthophosphate, $PbHPO_4$

T/K	pK^0_{s0}	Reference
Tentative value		
298.15	11.43±0.1	Nriagu [154]
Other literature values		
298.15	9.90	Millet, Jowett [155]
310.65	9.62	Millet, Jowett [155]
291–293	9.85	Zharovskii [157]
310.65	11.36	Jowett, Price [156]
298.15	15.6	NBS-270-3 [21]

TABLE 27. Values of the solubility product of tertiary lead phosphate, $Pb_3(PO_4)_2$

Temperature T/K	pK^0_{s0}	Reference
Tentative value		
298.15	44.4	Nriagu [154]
Other values		
298.15	42.10	Millet, Jowett [156]
310.65	42.00	Millet, Jowett [156]
310.65	43.53	Jowett, Price [155]
298	28.74	Skobets et al. [160]

We have used equation (33) of section 3.4 to calculate approximate $Pb_3(PO_4)_2$ solubilities in water at 298.15.

pH	4	5	6	7
10^7c/mol dm^{-3}	216.	34.	5.5	1.0

At higher pH values hydroxy lead complexes would need to be taken into account.

Hydroxy Pyromorphite, $Pb_5(PO_4)_3OH$ Nriagu's experiments on the alkaline hydrolysis of secondary lead orthophosphate gave a value of ΔG°_{f298} $[Pb_5(PO_4)_3OH(s)]=-902$ kcal mol^{-1} from which he calculated a $K^\circ_{s0}[Pb_5(PO_4)_3OH(s)]=10^{-76.8}$.

That and values of pK°_{s0} of several halo pyromorphites are summarized in table 28.

A recent study [163] shows the first precipitate from $PbCl_2+(K,Na)$ H_2PO_4 is Pb_2ClPO_4 but no solubility information is given.

Tetraplumbite Ortho Phosphate, $Pb_4O(PO_4)_2$ Nriagu [154] reports the $\Delta G^\circ_{f293}[PO_4O(PO_4)_2(s)]$ is -617.3 kcal mol^{-1}.

Lead Hydroxylapatite, $Pb_{10}(PO_4)_6(OH)_2$ Rao [164] measured the solubility of lead hydroxylapatite,

$Pb_{10}(PO_4)_6(OH)_2$ and its solid solutions with arsenate, $Pb_{10}(PO_4)_n(AsO_4)_{n-6}(OH)_2$ with $n=0,1...6$ as a function of pH between 5.0 and 8.0 at 303 K. The solubility data are presented in graphs. The solubility of $Pb_{10}(PO_4)_6(OH)_2$ decreased from about 10 to 3 mg dm^{-3} as the pH of acetic acid+sodium acetate and sodium diethyl barbiturate+hydrochloric acid buffers increased from 5.0 to 8.0 at 303 K. Substitution of AsO_4^{3-} for PO_4^{3-} caused the solubility to increase at the same pH.

TABLE 28. Solubility product values of lead hydroxy pyromorphite and several lead halo pyromorphites

Compound of lead	T/K	pK^0_{s0}	Reference
hydroxy pyromorphite	298. 15	76. 8	Nriagu [154]
chloro pyromorphite [a]	310. 65	79. 12	Jowett, Price [155]
chloro pyromorphite [a]	298. 15	84. 4	Nriagu [161]
fluoro pyromorphite [a]	298. 15	71. 6	Nriagu [162]
bromo pyromorphite [a]	298. 15	78. 1	Nriagu [162]

[a] The Chemical Abstracts Registry numbers are pyromorphite (chloro pyromorphite) [12190–77–1], fluoro pyromorphite [39422–50–9], and bromo pyromorphite [39422–29–2].

4.9. Lead Carbonate

$PbCO_3$[598–63–0] Formula Weight 267.21 [Chem. Abstr. Index, Carbonic Acid, Lead (2+) Salt (1:1), $CH_2O_3 \cdot Pb$]

Physical characteristics: The mineral cerussite (lead carbonate) has an orthorhombic crystal structure with $Z=4$ and $a=6.1302$, $b=8.4800$ and $c=5.17726\times10^{-10}$ m. The calculated density is 6559 kg m^{-3}. Synthetic lead carbonate has slightly different parameters and a density of 6583 kg m^{-3}. In addition to lead carbonate, crystals of lead calcium carbonate, lead bromide carbonate, lead chloride carbonate and lead hydroxy carbonate are known. There is no mention of hydrated lead carbonate.

Tentative values of the solubility of lead carbonate in water, the solubility product, and the formation constants of $PbCO_3$ (aq) and $Pb(CO_3)_2^{2-}$ at 298.15 K are given in table 29.

Böttger [65] and Kohlrausch and Rose [165] used electrical conductivity to measure the solubility of lead carbonate in water. Their results do not appear to be as reliable as the measurements of Pleissner [166] at 291.15 K, who studied the effect of the presence of dissolved carbon dioxide on the solubility of lead carbonate. Haehnel [167] reports a solubility of lead carbonate in water saturated with CO_2 at 1 atm pressure. The two sets of results are summarized in table 30.

There are several studies of the solubility of lead carbonate in the presence of sodium carbonate and other alkali carbonates [168a,b,169], but two are not readily available [168a,b]. The other which is a study of carbanato lead complex ions, is discussed ater.

TABLE 29. Tentative values of the solubility, the solubility product, and the complex ion formation constants of lead carbonate at 298.15 K

Solubility	6.55×10^{-5} c_{PbCO_3}/mol dm^{-3}	
Solubility product	K^0_{s0} 7.4×10^{-14}, pK^0_{s0} 13.13	
Formation constants		
$PbCO_3$(aq)	I/KNO_3=0.1,	$\beta_1=2\times10^6$
$Pb(CO_3)_2^{2-}$	I/KNO_3=0.1,	$\beta_2=6\times10^9$

TABLE 30. The solubility of lead carbonate in aqueous solution containing carbon dioxide at 291.15 K [166, 167]

Carbon dioxide		Lead carbonate [b]
c_{CO_2}/mol dm^{-3}	Pressure CO_2/mm Hg [a]	c_{PbCO_3}/mol dm^{-3}
0	0	0. 655$\times10^{-5}$
0. 64$\times10^{-4}$	1. 4	2. 25$\times10^{-5}$
1. 23$\times10^{-4}$	2. 7	2. 62$\times10^{-5}$
3. 28$\times10^{-4}$	7. 3	3. 07$\times10^{-5}$
5. 92$\times10^{-4}$	13	3. 70$\times10^{-5}$
9. 88$\times10^{-4}$	22	4. 08$\times10^{-5}$
24. 0$\times10^{-4}$	54	5. 70$\times10^{-5}$
(341. 6$\times10^{-4}$)	760	52. 3 $\times10^{-5}$

[a] Calculated by us from Henry's law constant $K_H=0.03416$.
[b] Calculated from tabulated values of mg $PbCO_3$ per dm^3 solution.

Nasanen, Merilainen, and Lippanen [170] applied a potentiometric method to determine the equilibrium constant at 298.15 K as a function of ionic strength of the reaction

$$PbCO_3(s)+2H^+(aq)\rightleftarrows Pb^{2+}(aq)+CO_2(aq)+H_2O$$

The equilibrium constant $K=K^0_{s0}/K_1K_2$ where K^0_{s0} is the solubility product of $PbCO_3$ and K_1 and K_2 are the first and second ionization constants of carbonic acid. They fitted their results to the equation

$$\log K=3.55+2.036\, I^{1/2}/(1+I^{1/2}) -1.018\, I^{1/2}/(1+2.20\, I^{1/2})+0.33\, I \quad (42)$$

where I is the ionic strength. When $I=0$, $\log K=3.55$, and for the values pK_1=6.35 and pK_2=10.33 the value of pK^0_{s0} is 13.13 ($K^0_{s0}=7.4\times10^{-14}$). The values of p$K_1$ and pK_2 agree well with the selected values of Berg and Vanderzee [134] discussed in section 3.4. The thermodynamic data in NBS Technical Note 270–3 [21a] results in pK^0_{s0}=12.83 ($K^0_{s0}=14.8\times10^{-14}$).

Egorov and Titova [116] analyzed thermodynamic data to derive the equation

$$\log K^0_{s0}= -24.04-805/T+5.86 \log T-2.41\times10^{-3}\, T \quad (43)$$

for K^0_{s0} between temperatures of 273 and 373 K. The magnitudes of the values of K^0_{s0} from their equation increase with increasing temperature (table 31).

TABLE 31. Lead carbonate solubility products

T/K	pK°_{s0}	K°_{s0}	Reference
Tentative value			
298.15	13.13	7.4×10^{-14}	
Experimental value			
298.15	13.13	7.41×10^{-14}	Nasanen et al. [170]
Calculated from thermodynamic data			
298.15	12.83	1.48×10^{-13}	NBS-270-3 [21a]
298.15	12.96	1.1×10^{-13}	Egorov, Titova [116]
323.15	12.60	2.5×10^{-13}	
333.15	12.48	3.3×10^{-13}	
373.15	12.03	9.3×10^{-13}	
298.15	13.45	3.55×10^{-14}	Helgeson [139]
323.15	13.19	6.45×10^{-14}	
333.15	13.16	6.9×10^{-14}	
373.15	13.21	6.2×10^{-14}	
423.15	13.54	2.9×10^{-14}	
473.15	14.30	5.0×10^{-15}	
523.15	15.31	4.9×10^{-16}	
573.15	16.50	3.2×10^{-17}	

Helgeson [139] made calculations of log K°_{s0} from thermodynamic data for the temperature interval of 298.15 to 573.15 K. His calculations give K°_{s0} values that go through a maximum and then decrease in magnitude as the temperature increase. Helgeson appears to have carefully selected his data base and to take into account temperature dependent heat capacities, activity coefficient and ionic strength effects. He does extrapolate to high temperatures but in the temperature interval of 298–373 K we have more confidence in his calculation than the calculatior of Egorov and Titova.

Baranova [169, 171] has determined formation constants for the complexes $Pb(HCO_3)_2$ and $Pb(HCO_3)_3^-$, by polarography, and $PbCO_3$ and $Pb(CO_3)_2^{2-}$ by solubility methods. There is some doubt about the existence of bicarbonato complexes. Bilinski, Huston and Stumm [172] show that the bicarbanato complex ion data can be equally well explained by a $Pb(CO_3)_2^{2-}$ complex. Bilinski et al. have redetermined the $PbCO_3$ and $Pb(CO_3)_2^{2-}$ formation constants. Their values are the tentative values of table 29. Table 32 reproduces part of the summary table from Bilinski et al. on formation constants of $PbCO_3$ and $Pb(CO_3)_2^{2-}$.

Baranova [169] approximates the formation constants at 298.15 K and $I=0$ as $\beta_1 \sim 1 \times 10^{10}$ and $\beta_2 \sim 1 \times 10^{11}$. From her measurements at 298, 473, 523, and 573 K she obtained the equation

$$\log \beta_1 \ (I=0) = +2484.0/T - 5.25 + 2.308 \times 10^{-2}\ T. \tag{44}$$

Although the temperature coefficient may be reliable, the values of β_1 appear to be high in view of the other values in table 32.

5. The Solubility Products of Some Other Sparingly Soluble Lead Salts

Table 33 summarizes solubility products and some other information found in a literature survey covering primarily Chemical Abstracts from 1955 to early 1978. Some earlier data are cited when they complement the information. In general, these data should be considered no better than tentative. The only values that may be considered recommended are the K°_{s0} value for $PbMoO_4$ of Dellien, McCurdy and Hepler [177], and of $Pb_2[Fe(CN)_6]$ of Rock and Powell [178].

TABLE 32. Summary of formation constants of the $PbCO_3$ and $Pb(CO_3)_2^{2-}$ complex ions at 298.15 K

Ionic strength I/electrolyte	Cumulative formation constants		Method [a]	Reference
	β_1	β_2		
0.1/KNO_3	2.5×10^6	6.3×10^9	a.s.v.	Bilinski et al. [172]
0.1/KNO_3	1.3×10^6	1.3×10^9	d.p.p.	Bilinski et al. [172]
0.1/KNO_3	2×10^6		d.p.p.	Ernst et al. [174]
0.3/$NaClO_4$	0.56×10^6	1.4×10^9	sol	Bilinski et al. [173]
0.7/$NaClO_4$	0.42×10^6		a.s.v.	Sipos [175]
1.0/$NaClO_4$	$10. \times 10^6$	1.0×10^9	sol	Baranova [169]
1.7/KNO_3		0.16×10^9 [b]	pol	Francherre [176]

[a] asv=anode stripping voltammetry, dpp=differential pulse polarography, pol=polarography, sol=solubility.

[b] Value at 291 K.

TABLE 33. The solubility products of some sparingly soluble lead electrolytes. Annotated bibliography 1955–1977

Substance	T/K	Solubility product K_{s0}	Comments	Reference
Lead iodate $Pb(IO_3)_2$ [25659-31-8]	308.15	3.3×10^{-12}	0.3 M (Na,H)ClO_4. The variation of solubility with pH is ascribed to Pb^{2+} hydrolysis, but it is in the direction expected for HIO_3 formation. See ref. [3].	Misra, Pani [179]
			Present evidence of polynuclear Pb^{2+} complex.	Herak et al. [180]
			$Pb(IO_3)_2$ the only solid precipitated when various concentrations of $Pb(NO_3)_2$ and KIO_3 mixed.	Gyunner et al. [181]
Lead thiosulfate PbS_2O_3 [13478-50-7]	298.15	1.24×10^{-7}	Recalculation from the data of Yatsimirskii [196] which takes into account three instead of two $Pb^{2+}-S_2O_3^{2-}$ complexes. β_1 2.26×10^3 β_2 4.35×10^5 β_3 7.19×10^6	Vol'dman [182]
Lead selenide PbSe [12069-00-0] [1314-90-5] Clausthalite	298.15	1×10^{-39}	Calculated from emf and thermodynamic data. Cites other literature values as 7.9×10^{-43} and 1×10^{-38}.	Erdenbaeva [150]
Lead selenite $PbSeO_3$ [7488-51-9]	293.15	3.4×10^{-12}	Average of five values from solubility in dil. HCl and dil. HNO_3 which ranged (1.9–5.2) $\times 10^{-12}$. Used H_2SO_3 dissociation constants $K_1 = 4 \times 10^{-3}$ and $K_2 = 1 \times 10^{-8}$.	Chukhlantsev, Tomashevsky [183]
	298.15	1.61×10^{-12}	Calculated from emf and thermodynamic data.	Erdenbaeva [150]
Lead selenate $PbSeO_4$ [7446-15-3]	273.15 288.15 298.15 308.15 323.15	0.83×10^{-7} 1.13×10^{-7} 1.45×10^{-7} 1.76×10^{-7} 2.30×10^{-7}	Solubility measured at temperatures between 273 and 373 K, data presented in small graph. Activity coefficients calculated from Debye-Huckel theory up to 323 K. Calculations not made for data above 323 K. The ΔH_{soln} is 3.78 kcal mol^{-1} from temperature dependence of K_{s0}. $PbSeO_4$ formed in the cold is microcrystalline and about 3 times more soluble than $PbSeO_4$ formed at higher temperatures or heat treated to form macrocrystalline material.	Selivanova et al. [184]
	298.15	1.27×10^{-7}	Calculated from emf and thermodynamic data.	Erdenbaeva [150]
Lead telluride PbTe [1314-91-6] [12037-86-4] Altaite	298.15	1.49×10^{-48}	Calculated from emf and thermodynamic data. Cites other literature values of 1×10^{-43} and 5×10^{-47}.	Erdenbaeva [150]
Lead tellurite $PbTeO_3$ [15851-47-5]	298.15	2.05×10^{-7}	Calculated from emf and thermodynamic data.	Erdenbaeva [150]
			The basic tellurite $5PbTeO_3 \cdot Pb(OH)_2$ forms at pH 9.6–9.7.	Ganelina [185]
Lead tellurate $PbTeO_4$ [13845-35-7]	298.15	2.2×10^{-9}	Calculated from emf and thermodynamic data.	Erdenbaeva [150]
Lead arsenite $PbAsO_3$ (AsO_2^-, $As(OH)_4^-$?)	293		Solubility 1.5×10^{-3} mol $Pb^{2+}dm^{-3}$ at pH 5.8, 7×10^{-3} at pH 5.0–5.4.	Chukhlantaev [186]

TABLE 33. The solubility products of some sparingly soluble lead electrolytes. Annotated bibliography 1955–1977—Continued

Substance	T/K	Solubility product K_{s0}	Comments	Reference
Lead arsenate $Pb_3(AsO_4)_2$ [3687–31–8]	291	2.1×10^{-36}		Karnaukbov et al. [187]
	294	$(4.1 \pm 3.6) \times 10^{-36}$		Chukhlantaev [188]
Lead oxalate PbC_2O_4 [814–93–7]			Stoichiometric solubility PbC_2O_4 in water+acetic acid (graph).	Babkin et al. [197]
	"Room"	3×10^{-11}	Polarographic method. Solubility of PbC_2O_4 in $NaNO_3$ and KNO_3 solutions shown in small graph.	Skobets et al. [160]
	288 291 298 308 318 328	1.4×10^{-11} 1.5×10^{-11} 2.1×10^{-11} 3.4×10^{-11} 8.1×10^{-11} 12.1×10^{-11}	Chronopotentiometric method.	Karnaukhov et al. [187]
Lead cyanamide $PbCN_2$ [20837–86–9]	298.15	3.2×10^{-14} 2.5×10^{-16}	1 M KNO_3, pH 5–7. 1 M KNO_3, pH 13–15. At the higher pH lead mostly $Pb(OH)_3^-$. Authors recommend their 3.2×10^{-14} value.	Kitaev, Sokolova [189]
Lead borate $Pb(BO_2)_2$ [14720–53–7] [10214–39–8] monohydrate	295	1.37×10^{-11} 3.00×10^{-11} 1.81×10^{-11}	0–0.54 M KNO_3. 0–0.49 M $Ba(NO_3)_2$. 0–1.81 M KCl. Use HBO_2 dissociation constant of 7.5×10^{-10}.	Schigol [190]
Lead ferrocyanide $Pb_2[Fe(CN)_6]$	298.15	3.5×10^{-15}	Comparative method with $PbSO_4$ as reference. Used Kolthoff et al. [193] value for $PbSO_4$ solubility.	Tananaev et al. [191]
	291	4.0×10^{-18}	Chronopotiometric method.	Karnaukhov et al. [187]
	298.15	9.6×10^{-19}	Emf and other thermodynamic data. This value recommended as $K_{s0}{}^0$.	Rock, Powell [178]
Basic lead permanganate $Pb(MnO_4)_{0.5}(OH)_{1.5}$		1.35×10^{-19}		Charreton [192]
Lead chromate $PbCrO_4$ [7758–97–6]	298	2.5×10^{-13}	Dellien et al. [177] suggest the value may be uncertain.	Kolthoff et al. [193]
	"Room"	6.4×10^{-13}	Polarographic method. Other literature value of 1.8×10^{-14} is cited.	Skoberts et al. [160]
	291	2.2×10^{-14}	Chromopotentiometric method	Karnaukhov et al. [187]
Basic lead chromate $Pn(CrO_4)_{0.5}OH$	298	1.35×10^{-16}	Kolthoff et al. [193] value for $PbCrO_4$ used in calculation of K_{s0}.	Charreton [192]
Lead molybdate $PbMoO_4$ [10190–55–3]	"Room"	3.3×10^{-12}	Polarographic method.	Skoberts et al. [160]
	298.15	2.4×10^{-10}	Thermodynamics data. Other values cited which range from 4×10^{-6} to 3.3×10^{-12}. Dellien et al. consider them high. This value recommended.	Dellien et al. [177]
	298.15	0.97×10^{-16}		NBS-270-3, 4 [21 ab]

TABLE 33. The solubility products of some sparingly soluble lead electrolytes. Annotated bibliography 1955–1977—Continued

Substance	T/K	Solubility product K_{s0}	Comments	Reference
	293.15		0.08 g $PbMoO_4$ per dm^3 solution.	Zelikman, Prosenkova [194]
			No evidence found of formation of mono or tri basic $PbMoO_4$.	Charreton [192]
Lead tungstate $PbWO_4$ [7759-01-5]	293	$(8.6 \pm 0.8)\times 10^{-17}$	$I=0.1$, pH 5, tetragonal form of $PbWO_4$. The conc. solubility product is 6.1×10^{-16}. Monoclinic $PbWO_4$ is more soluble. Its solubility product is 4.5×10^{-7}.	Bulatova et al. [195]
			No evidence found of formation of mono or tribasic $PbWO_4$.	Charreton [192]

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