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## Solubility of Litharge ( $\alpha$ -PbO) in Alkaline Media at Elevated Temperatures

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**SOLUBILITY OF LITHARGE (" -PbO)  
IN ALKALINE MEDIA AT ELEVATED TEMPERATURES**

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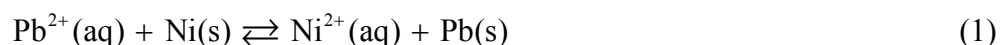
## **ABSTRACT**

An inert, flowing autoclave facility is used to investigate the solubility behavior of  $\alpha$ -PbO (litharge, tetragonal) in aqueous solutions of morpholine, ammonia and sodium hydroxide between 38 and 260°C. Lead solubilities increased from about 0.4 mmol kg<sup>-1</sup> at 38°C to about 4.5 mmol kg<sup>-1</sup> at 260°C and were relatively insensitive to the concentration and identity of the pH-reagent. The measured lead solubilities were interpreted using a Pb(II) ion hydroxocomplexing model and thermodynamic functions for these equilibria were obtained from a least-squares analysis of the data. A consistent set of thermodynamic properties for the species Pb(OH)<sup>+</sup>, Pb(OH)<sub>2</sub>(aq) and Pb(OH)<sub>3</sub><sup>-</sup> is provided to permit accurate lead oxide solubility calculations over broad ranges of temperature and alkalinity.

KEYWORDS: Lead(II) oxide; litharge, aqueous solutions; lead(II) ion hydrolysis; equilibrium constant; pressurized water; hydrothermal solutions

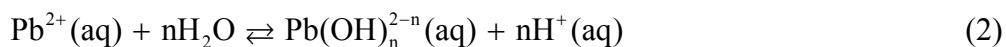
## INTRODUCTION

Lead is an aggressive, relatively soluble metal ion species that is capable of degrading nickel-base alloys in hydrothermal environments. For example, operation of PWR steam generators with water containing Pb(II) ion concentrations as low as 0.1 ppm can result in lead-induced stress corrosion cracking of tubing alloys 600 and 690.<sup>(1)</sup> Lead species may be introduced into the reactor coolant circuit by contaminants in the plant make-up water, main condenser cooling water leaks, or from the lead used in seals/gaskets for pumps and pipe fittings and bearings in pumps and turbines.<sup>(2)</sup> Although accumulation of lead-containing solids on tubing surfaces *at the* sludge-metal interface is indicative of the redox reaction



confirmatory chemical deposit analyses are presently lacking. Therefore, the extent of Pb(II) ion incorporation into the corrosion oxide layer(s) on the SG tubing surfaces is not known.

In order to correctly model the transport of Pb(II) ions in hydrothermal solutions as a function of temperature and pH it is necessary to know the thermodynamic properties of the stable, lead-containing solid phase as well as the equilibria for the series of hydrolysis reactions



Presently, litharge ( $\blacksquare$ -PbO, tetragonal, red) is known to be the thermodynamically stable oxide in the PbO-H<sub>2</sub>O binary, with respect to massicot ( $\blacklozenge$ -PbO, orthorhombic, yellow) and hydrous lead(II) oxide, from room temperature up to the critical point.<sup>(3,4)</sup> Although equilibrium constants for Eq. (2) are known at 25°C with a high degree of confidence, and a solubility investigation of litharge has been completed in sodium hydroxide at temperatures between 100

and 200°C,<sup>(5)</sup> the resulting log K vs. 1/T relationship for some of the Pb(II) ion hydrolytic equilibria exhibit non-linear behavior, which is inconsistent with that observed for isocoulombic hydrolysis reactions of other metal cations, see [Ref. 6]. Furthermore, litharge solubility predictions based on these results do not agree with PbO solubilities measured in a test facility that was used to investigate PbSCC.<sup>(7)</sup>

To resolve the above discrepancy, a solubility study of litharge was undertaken in morpholine, ammonia and sodium hydroxide solutions, covering the temperature range 38-260°C.

Regression analyses of the resulting solubility database allowed equilibrium constants for the Eq. (2) hydrolysis reactions to be determined for  $n = 1, 2$  and  $3$ .

## **EXPERIMENTAL**

### Materials

To minimize generation of fine particulate material, which could interfere with the solubility measurements, a coarse, granular form of lead(II) oxide was prepared using PbO certified by Cerac Incorporated to be 99.9% pure (metals basis). The coarsening process consisted of hot-pressing at 525°C, followed by attrition through a 20 mesh sieve onto a 70 mesh sieve. Although XRD analyses of this material showed it to be massicot (orthorhombic PbO), small satellite peaks indicative of minor amounts of a sulfur impurity were present: anglesite PbSO<sub>4</sub> or hokutolite BaPb(SO)<sub>2</sub>. A few grams of the coarsened material were subjected to hydrothermal treatment in pure water at 210°C for 14 days to confirm that it would indeed transform to litharge in the solubility apparatus. As expected, litharge (tetragonal PbO) was the only PbO phase detected.

Due to the extremely high solubilities of litharge measured during the initial series of tests at 260°C, significant amounts of PbO were lost from the bed via dissolution. Therefore, it was necessary to shut down the test facility after approximately 92 days of operation and refill the test column with a fresh charge of PbO. To eliminate the source of sulfur contaminants present in the initial PbO charge, a new batch of PbO was obtained from Aldrich-Alfa (Puratronic, 99.999% metals basis, lot no. 23028). X-ray diffraction analyses found only those peaks consistent with massicot; no additional peaks were present. The initial solubility data obtained using the second PbO solid were gathered at 260°C to demonstrate replicability (and hasten conversion of the yellow massicot phase to the red litharge phase). The massicot-litharge conversion was verified by comparing unit cell dimensions of the lead(II) oxide loaded into and removed from the solubility apparatus: orthorhombic ( $a = 5.484(2)$ ,  $b = 5.891(1)$ ,  $c = 4.751(2)$  Å) vs. tetragonal ( $a = 3.999(5)$ ,  $c = 5.036(18)$  Å). These values are consistent with those contained in the ICDD datafile for massicot (PDF 38-1477) and litharge (PDF 05-056).<sup>(8)</sup> In addition to visible color changes, distinct differences in crystalline morphology were observed by SEM: as-received massicot from Aldrich-Alfa consisted of polyhedral grains having a size of ~60 nm (see Fig. 1a), while the litharge removed from the solubility apparatus upon completion of testing exhibited tabular grains ~20 nm square x 6 nm thick (see Fig. 1b).

### Apparatus

The solubility measurements were made using the ORNL solubility apparatus. Details of its construction are given in Ref. (9). The essence of this facility is a test column containing the PbO, fabricated from Zircalloy-4, and equipped with submicron platinum/gold frits at its inlet and outlet to confine the PbO charge. Sampling is conducted through a platinum line which

allows for on-line acidification to prevent Pb losses by precipitation on the walls of the sampling line.

### Operational and Analytical Procedures

The test program consisted of a series of runs during which six different solution alkalinities were tested (three morpholine concentrations, two ammonia concentrations and one sodium hydroxide concentration). Pb(II) solubility measurements were taken in the temperature range 38-260°C at 27° intervals. Two initial measurements were conducted at 260°C using elevated sodium hydroxide concentrations that were aimed at possibly elevating the solubility of PbO and thereby preferentially dissolving fine particles that may have been present in the starting material. These results, however, failed to show an enhanced solubility that could be attributed to the presence of fine particulates.

All feed solutions were prepared using deionized water that had been sparged with helium to remove dissolved oxygen. A total pressure of 0.134 MPa He was maintained over the feed solutions in all tests. The feedwater He concentration was calculated to be 53 F mol kg<sup>-1</sup> based on the pressure in the feed reservoir and Henry's law coefficient for the solubility of helium in water at 25°C ( $\log K_H = 51.5$ ).<sup>(10)</sup>

To ensure *in situ* transformation to litharge, the initial experiments were conducted in an isothermal mode at 260°C, maintaining a flow rate of 0.2 mL min<sup>-1</sup> for each of the six different water chemistries. After the initial measurements were completed, it was found to be more expedient to maintain a constant feed solution composition and vary the temperature. This allowed for a much faster re-equilibration time following the completion of a given series of

samples. A flow rate of  $0.1 \text{ mL min}^{-1}$ , maintained by a high pressure liquid chromatography (HPLC) pump, was adopted for this portion of the program. Since the volume in the Zircalloy column packed with PbO is estimated to be approximately 18 to 20 mL, the residence time of solution under plug flow conditions was about 180 minutes at a flow rate of  $0.1 \text{ mL min}^{-1}$ . A flow of 0.2%  $\text{HNO}_3$  from a second HPLC pump was maintained into the saturated Pb(II) solution exiting the test bed (at the test temperature). This flow rate varied from 0.02 to  $0.05 \text{ mL min}^{-1}$ .

Sampling was conducted continuously throughout each run; sample masses were always  $> 10$  mL. Due to the ppm levels of Pb(II) ions in solution, a Perkin Elmer atomic absorption spectrometer (flame, Model 3110) was sufficient to measure all lead concentrations. Dilution with 0.2% (w/w)  $\text{HNO}_3$  was required in order to accommodate the 0.8-20 ppm linear response range of the instrument. The light source was a hollow cathode lamp operating at 10 mA using the resonance line 283.4 nm with a 0.7 nm spectral slit width. The oxidant/fuel combination was air-acetylene creating a lean-blue, oxidizing flame ( $\sim 2300^\circ\text{C}$ ). The standard solutions were also prepared by dilution of a 1000 ppb Pb stock solution with 0.1% (w/w)  $\text{HNO}_3$  (ULTREX II Ultrapure reagent - J. T. Baker).

## **RESULTS**

### Solubility Measurements/Reactions

Results from the experimental program, in terms of measured lead concentrations as a function of temperature, are summarized in Table I. The elemental lead concentrations represent averages based on 5-12 samples and are given in units of  $\text{mmol kg}^{-1}$  ( $10^{-3}$  moles of lead per kilogram of water). The listed uncertainties in the lead analyses correspond to the standard deviation about the mean of the number of values shown at each condition. The pressures listed in this table

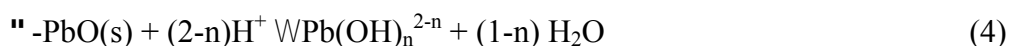


correspond to the average of those measured on the downstream transducer as each sample was removed. Total measured lead solubilities increased from about 0.4 mmol kg<sup>-1</sup> at 38°C to about 4.5 mmol kg<sup>-1</sup> at 260°C and were relatively insensitive to the amount and identity of the pH-reagent.

Given the hydrothermal environments in which lead(II) oxide was exposed, only one solid phase dissolution reaction is possible



As many as three stepwise hydrolysis reactions of the Pb(II) ion may occur, per Eq. (2), so that the overall lead(II) oxide dissolution reaction becomes the following sequence



where n refers to the state of hydrolysis, and may take on the values 0 through 3.

By expressing the concentration of each possible Pb(II) complex in terms of an equilibrium constant and calculable H<sup>+</sup> ion concentrations, the measured Pb(II) solubilities were separated into contributions from each of the individual complexes. The total molality of lead in solution (i.e., saturation solubility limit) was then calculable by summation over all mononuclear Pb(II) ion species present.

### pH Determination

Evaluation of the experimental solubilities listed in Table I in terms of concentrations of the possible hydrolyzed Pb(II) species present required that the pH (hydronium ion molality) be known at the existing solution conditions. This quantity depended on the molality of the alkaline reagent dissolved in solution (i.e., morpholine, ammonia or sodium hydroxide), as well as its

ionization constant and that of H<sub>2</sub>O. The latter parameters, which are functions of solution temperature, are defined below in terms of thermodynamic activities ( ) and tabulated in Table II.

$$K_w = (H^+) (OH^-) \quad (5)$$

$$K_B = (C_4H_9NOH^+)(OH^-)/(C_4H_9NO) \text{ or } (NH_4^+) (OH^-) / (NH_3) \quad (6)$$

with 
$$\log K = b_1 / T + b_2 + b_3 \ln T + b_4 T + b_5 / T^2 \quad (7)$$

Both  $K_w$  and  $K_B$  were pressure-corrected (to 6.43 MPa), as well as ionic strength-corrected, using the published correlations.<sup>(11 - 13)</sup>

Equilibrium constants for Eqs. (4) were corrected for small deviations from ideal solution behavior by distinguishing between ionic concentration (i.e., molality) and thermodynamic activity

$$(a_i) = \gamma_i [C_i] \quad (8)$$

where  $(a_i)$  is the thermodynamic activity,  $\gamma_i$  the ionic activity coefficient and  $[C_i]$  is the ionic concentration. Generally, it was assumed that ionic activity was related to ionic strength by an extended Debye-Hdckel expression,<sup>(14)</sup> which is applicable because the ionic strength was always  $< 10^{-3}$ :

$$\log \gamma_i = -SZ_i^2 \sqrt{I} / (1 + 1.5 \sqrt{I}) \quad (9)$$

where  $S$  is the temperature-dependent,<sup>(15)</sup> limiting Debye-Hdckel slope (0.51 at 298 K),  $Z_i$  is the ionic charge number, and  $I$  is the ionic strength ( $= \mathbf{2} \Sigma C_i Z_i^2$ ).

An overall ion electroneutrality balance was finally applied to determine  $[H^+]$  for each data point.

In ammonium hydroxide solutions, the balance is:

$$\sum_{n=0}^3 (2-n)[\text{Pb}(\text{OH})_n^{(2-n)+}] + [\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-] \quad (10)$$

Since all terms were expressible in terms of temperature and total dissolved ammonia (or morpholine or sodium hydroxide) concentrations, Eq. (10) was reduced to an algebraic equation in terms of the remaining unknown,  $[\text{H}^+]$ . To determine how a given scheme of Pb(II) complexes in solution could fit the results, a set of thermodynamic constants was substituted into the neutrality balance equation, and  $[\text{H}^+]$  concentrations were calculated by a Newton-Raphson iteration procedure. These  $[\text{H}^+]$  values were then used to compute all the soluble lead species which, after being summed, could be compared with the measured Pb solubilities. The differences were then minimized via a generalized, non-linear, least-squares curve-fitting routine based on Marquardt's algorithm.<sup>(16)</sup>

When the solubility data were analyzed, the importance of relative errors (i.e., percentage errors), rather than absolute errors, was accounted for by minimizing differences between the logarithms of the experimental and the predicted solubilities. The thermodynamic functions obtained were then resubstituted into the neutrality balance, and the two-step process was repeated. Because the high Pb(II) solubilities had significant impacts on solution pH, many iterative cycles were required to attain convergence, i.e., the condition when the calculated thermodynamic functions (and pH) ceased to change. Table III summarizes the calculated, initial pH values (soluble Pb(II) species absent) and the final solution pH values (effect of soluble Pb(II) determined via Eq. (10)).

### Thermodynamic Analysis

Equilibrium constants for the sequence of PbO dissolution reactions were calculated by applying the thermodynamic relationships

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

Generally, a three-parameter model was written to describe  $\Delta G^\circ(T)$ . This approximation assumes that the difference in heat capacities between reactants and products for each reaction is a constant (C). Integration of the applicable thermodynamic relationship gives

$$\Delta G^\circ(T) = A - BT - CT \ln T \quad (12)$$

where the constants A, B and C have the thermodynamic significance:  $A = \Delta H^\circ(298) - 298\Delta C_p^\circ$ ;  $B = \Delta S^\circ(298) - (1 + \ln 298)\Delta C_p^\circ$  and  $C = \Delta C_p^\circ$ . Normally, small values of  $\Delta C_p^\circ$  are expected ( $<20 \text{ J mol}^{-1} \text{ K}^{-1}$ ) for metal oxide dissolution reactions, when written in an isocoulombic form typified by the  $n = 0, 1$  and  $2$  forms of Eq. (4). As demonstrated previously by Mesmer et al. <sup>(17)</sup>,  $\Delta C_p^\circ$  for similar non-isocoulombic reactions where  $\Delta Z^2 = 2$  is expected to be equivalent to that of the water ionization reaction, i.e.,  $-223.8 \text{ J mol}^{-1} \text{ K}^{-1}$ . Therefore, C was constrained to zero ( $n = 1$  and  $2$ ) and  $-223.8 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $n = 3$ ) in Eq. (12) when fitting the Eq. (4) litharge dissolution reaction equilibria.

Results of the above data fitting procedure are shown in Figs. 2 - 4. These fits resulted in an overall standard deviation between measured and fitted Pb(II) ion solubilities of " 6% for a database consisting of 56 entries. This level of uncertainty is consistent with the expected analytical accuracies and replicability of the solubility measurements. Table IV presents the fitted thermodynamic parameters for the three litharge dissolution reactions identified in Eq. (4).

The litharge solubility database is thus explained by the quantitative presence of three Pb(II) hydrolytic species:  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}(\text{OH})_2(\text{aq})$  and  $\text{Pb}(\text{OH})_3^-$ . The hydrolytic behavior of the Pb(II) ion, together with the alkaline pH range covered by the solubility measurements, precluded significant contributions from the  $\text{Pb}^{2+}(\text{aq})$  ion. Attempts to eliminate the constraint imposed on C did not yield statistically-significant improvements, presumably reflecting the scatter in our solubility data. In addition, no evidence was found to suggest solubility enhancement of litharge by formation of Pb(II) ion-morpholino- or amminocomplexes for morpholine or ammonia concentrations as high as  $0.75 \text{ mmol kg}^{-1}$ .

## **DISCUSSION OF RESULTS**

### A. Comparison with Previous Litharge Solubility Studies

Previous litharge solubility measurements at elevated temperatures were reported by Sue et al.<sup>(18)</sup> in pure water and by Tugarinov et al.<sup>(5)</sup> in sodium hydroxide. The present results agree with those of Tugarinov et al. at lower temperatures, but diverge above  $100^\circ\text{C}$ , see Fig. 5. Since relatively good agreement exists at elevated temperatures between the present results and those of Sue et al., the lead ion solubilities reported by Tugarinov et al. appear to be too low at temperatures above  $100^\circ\text{C}$ .

Standard Gibbs energy changes for the litharge dissolution reactions, Eq. (4), as reviewed by Tugarinov et al.<sup>(5)</sup>, are  $-71.63 \pm 0.64$ ,  $-37.33 \pm 1.14$ ,  $25.12 \pm 0.57$  and  $87.45 \pm 0.57 \text{ kJ mol}^{-1}$ , respectively. The alkaline pH range employed by our investigation precluded determination of the equilibrium for the  $n = 0$  form of Eq. (4). However, Gibbs energy changes for the  $n = 1, 2$  and  $3$  forms of Eq. (4) were readily extracted from the litharge solubility database. Our room temperature results given in Table IV show nearly exact agreement for the  $n$

= 1 and 2 equilibria:  $-38.00 \pm 0.16$  and  $25.15 \pm 4.24$  kJ mol<sup>-1</sup>; while the n = 3 results differ by about 10 kJ mol<sup>-1</sup> (97.09 vs. 87.45 kJ mol<sup>-1</sup>).

As shown in Fig. 6, the equilibrium for litharge dissolution into the Pb(OH)<sup>+</sup> species is more sensitive to temperature changes than indicated by the results of Tugarinov et al.<sup>(5)</sup> This difference is caused by a higher value of standard partial molar entropy for Pb(OH)<sup>+</sup>: 111.8 vs. 70.6 J mol<sup>-1</sup> K<sup>-1</sup>. It is noteworthy that a reanalysis of the Tugarinov et al. solubility measurements by Shock et al. (see Table 7 in Ref. 19) gave  $S^\circ = 103.3$  J mol<sup>-1</sup> K<sup>-1</sup> and  $\Delta G_f^\circ = -225.73$  kJ mol<sup>-1</sup> for Pb(OH)<sup>+</sup>. The reason for the increase in  $S^\circ$  was not stated, although the effect of Pb(II) solution species on pH(T) may be a contributing factor.

Our result for the equilibrium for the n = 2 form of Eq. (4) at elevated temperatures is virtually the same as that reported by Tugarinov et al.; the calculated Gibbs energy changes differing by less than 2 kJ mol<sup>-1</sup> over the range of temperatures common to both studies. Therefore, the excessive curvature in the  $\Delta G^\circ(T)$  correlation indicated in Ref. 5 is unwarranted, so our recommended approximation  $\Delta C_p^\circ \approx 0$  remains valid.

As shown by Shock et al., the results of Tugarinov et al. for the n = 3 form of Eq. (4) are equivalent to

$$\Delta G^\circ(T), \text{ J mol}^{-1} = 192360 - 2711.56T + 414.0 T \ln T \quad (13)$$

Fig. 7 shows that our result differs from Eq. (13) by <5 kJ mol<sup>-1</sup> over the temperature interval 150-250°C, but larger differences are observed at lower temperatures. The cause of this deviation appears to be twofold: (1) the alkalinity range in our experimental program was too small to permit significant quantities of Pb(OH)<sub>3</sub><sup>-</sup> to be generated at low temperatures and (2) the

indicated  $\Delta C_p^\circ$  for Eq. (13) is nearly twice that expected by application of the isocoulombic principle, i.e., -414.0 vs. -223.8 J mol<sup>-1</sup> K<sup>-1</sup>.

It is noted that predictions of litharge solubility behavior in pure water based on the present results and those of Sue et al. deviate from each other by 34% at 260°C. A deviation of such magnitude is significantly beyond the individual experimental accuracies of ~ 7% and indicates the presence of unaccounted effects. At least two factors may be involved: (a) the deviation occurs (and increases) in a temperature region where pressure, as well as temperature and pH effects, are important, and (b) the absence of a pH-buffering agent makes the actual pH highly uncertain and subject to influence by unmeasured/unknown trace ionic contaminants. Because of these uncertainties (and a factor of five difference in pressure between the two studies) it is inappropriate to include the database of Sue et al. in our present analysis.

#### B. Compensation for Low Pb(OH)<sub>3</sub><sup>-</sup> Levels

To compensate for the lack of solubility measurements in the region where the Pb(OH)<sub>3</sub><sup>-</sup>(aq) species is a significant contributor to litharge solubility, two analytical modifications were made: (1)  $\Delta G^\circ(298)$  for the n = 3 form of Eq. (4) was constrained to the accepted literature value, 87.56 kJ mol<sup>-1</sup>, based on the work of Garrett et al.<sup>(20)</sup> and (2) a portion of the Tugarinov et al. database at 100°C, which included litharge solubility measurements at alkalinities beyond the range of our study, was combined with the Table I database. The added solubilities were 1.1, 1.2, 4.6 and 9.7 mmol Pb kg<sup>-1</sup> for sodium hydroxide concentrations of 9.5, 10, 40 and 100 mmol kg<sup>-1</sup>, respectively.

A refit of the expanded database (60 points), together with application of two thermodynamic constraints on  $\Delta G^\circ(T)$  for the  $n = 3$  form of Eq. (4) results in improved estimates for all three litharge dissolution reaction equilibria, see Table IV. Figure 7 shows that the refitted  $\Delta G^\circ(T)$  values for the  $n = 3$  equilibrium agree to within  $2 \text{ kJ mol}^{-1}$  with the Tugarinov et al. results over the temperature range 25-150°C, but diverge at higher temperatures. The divergence is caused by excessive curvature in the  $\Delta G^\circ(T)$  correlation, implied by lower PbO solubilities measured by Tugarinov et al. at temperatures  $>150^\circ\text{C}$ , see Fig. 4. Since this behavior has not been corroborated by our measurements, the discrepant  $\Delta C_p^\circ$  result of Tugarinov et al. is rejected. A probable explanation for the lower Pb(II) ion solubilities measured by Tugarinov et al. at temperatures  $>150^\circ\text{C}$  is precipitation of lead oxide/hydroxide in their sampling line, as observed in our experiments when the  $\text{HNO}_3$  flow was temporarily stopped. This effect would be expected to be less significant at lower temperatures, exactly as observed. By way of closure, Table V provides a summary of recommended thermochemical properties for aqueous species in the PbO- $\text{H}_2\text{O}$  binary.

### C. Thermochemical Properties of Pb(II) Ion Hydroxocomplexes

Lead is classified as a Group IVB element in the Periodic Table, having four electrons in its incomplete, outermost shell ( $6s^26p^2$ ). Other members of Group IVB include tin ( $5s^25p^2$ ), germanium ( $4s^24p^2$ ) and silicon ( $3s^23p^2$ ). The lighter members of this group (Si, Ge) achieve a stable +IV oxidation state in aqueous solutions by loss of two p-electrons as well as two s-electrons. Stability of these aquoions is such that no positively charged hydroxocomplexes are known; only the neutral and anionic species are stable. The neutral hydroxocomplexes exist as tetrahedral complexes and have standard partial molar entropies of 180 ( $\text{Si}(\text{OH})_4(\text{aq})$ ) and 200 ( $\text{Ge}(\text{OH})_4(\text{aq})$ )  $\text{J mol}^{-1} \text{ K}^{-1}$ .<sup>(6)</sup>



On the other hand, the heavier Group IVB members (Sn, Pb) can exhibit stable +II oxidation states in aqueous solutions, although the balance between the +II and +IV states is sensitive to the redox environment: the heavier the element, the greater the stability of its +II oxidation state. The aqueous chemistry of Pb(II) is, therefore, characterized by bonding in p-electron orbitals, which accommodate six electrons. The pair of s-electrons that is unused in hydrocomplexing is known to have important effects on stereochemistry, i.e., entropy. For example, a thermodynamic analysis of  $S^\circ(298)$  for the  $\text{Pb}^{2+}(\text{aq})$  ion indicates that its primary hydration shell contains approximately six ‘translationally-immobilized’, water molecules, i.e., water molecules that have lost their translational entropy.<sup>(25, 26)</sup> This behavior contrasts with that of divalent cations of the Period 3 transition metals, where 3d electron orbitals are involved and as many as ten water molecules are contained in the primary hydration shell.

The stepwise replacement of complexed water molecules by hydroxyl ions causes changes from an octahedrally-symmetric aquocomplex to a tetrahedrally-symmetric aquohydroxocomplex, with a concurrent increase in entropy (see Fig. 8). Standard partial molar entropies for  $\text{Ge}(\text{OH})_4(\text{aq})$  and  $\text{Ge}(\text{OH})_5^-(\text{aq})$  (tetrahedral entity is  $\text{HGeO}_2^- (\text{aq})$ ) are included for comparison in Fig. 8 to show that entropies for the higher order Pb(II) ion hydroxocomplexes approach those for hydroxocomplexes known to possess tetrahedral symmetry.

## **SUMMARY/CONCLUSIONS**

The solubility behavior of litharge ( $\text{PbO}$ ) was investigated in aqueous solutions of morpholine and ammonia using an inert, flowing autoclave system. To determine the importance of solubility enhancement via morpholino- and ammino-complexing, additional experiments were

conducted in sodium hydroxide. Based on the accumulated Pb(II) solubility database, and the subsequent thermodynamic analyses afforded the data, it is concluded that:

1. Litharge solubilities are controlled by the sequence of three dissolution reaction equilibria



where  $n = 1, 2$  and  $3$ .

2. Non-linear, least-squares regression analyses of the solubility database allowed Gibbs energy changes for the  $n = 1$  and  $2$  reactions to be determined with accuracies of  $\pm 0.16$  and  $\pm 4.24$   $\text{kJ mol}^{-1}$ , respectively, throughout the temperature range  $38$ - $260^\circ\text{C}$ . The standard Gibbs energy changes (i.e., values at room temperature) are in excellent agreement with recent literature.
3. Due to the limited pH range of the present study, the equilibrium for the  $n = 3$  form of the litharge dissolution reaction was determined with less accuracy and precision. However, by constraining this equilibrium constant to its accepted value at  $25^\circ\text{C}$  and including litharge solubility measurements at  $100^\circ\text{C}$  (obtained at higher sodium hydroxide concentrations by Tugarinov et al.), the precision of the fitted Gibbs energy change was improved to  $\pm 0.72$   $\text{kJ mol}^{-1}$  and accurate thermochemical properties were obtained for the  $\text{Pb(OH)}_3^-$  hydroxocomplex.
4. Pb(II) solubility enhancement due to formation of morpholino- or amino-complexes is insignificant for morpholine or ammonia levels as high as  $0.4$   $\text{mmol kg}^{-1}$ .

**REFERENCES**

1. R. W. Staehle, in Proc. 11<sup>th</sup> Int. Conf. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors (Eds. S. Bruemmer, P. Ford and G. Was, The Minerals, Metals and Materials Society, Warrendale, PA) pp. 381-424 (2003)
2. A. K. Agrawal and J. P. N. Paine, in Proc. 4<sup>th</sup> Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors (Ed. D. Cubicciotti, NACE, Houston) p. 7-1 (1990)
3. D. Risold, J. I. Nagata and R. O. Suzuki, *J. Phase Equil.* **19**, 213-233 (1998)
4. G. Todd and E. Parry, *Nature* **202**, 386-7 (1964)
5. I. A. Tugarinov, I. G. Ganeyev and I. L. Khodakovskiy, *Geochem. Int.* **12**, 47-55 (1975)
6. S. E. Ziemniak, *PPChem.* **3**, 193-200 (2001)
7. D. Feron and I. Lambert, in *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry*, Proc. 12<sup>th</sup> Int. Conf. on the Properties of Water and Steam (Eds. H. J. White, Begell House, New York) pp. 783-790 (1995)
8. Powder Diffraction File (PDF-4/Full File 2003), International Centre for Diffraction Data (ICDD), Newtown Square, PA (2003)
9. P. Benezeth, D. A. Palmer, D. J. Wesolowski and C. Xiao, *J. Solution Chem.* **31**, 947-72 (2002)
10. D. Krause and B. B. Benson, *J. Solution Chem.* **18**, 823-73 (1989)
11. F. H. Sweeton, R. E. Mesmer, and C. F. Baes, *J. Solution Chem.* **3**, 191 (1974)
12. R. E. Mesmer and B. F. Hitch, *J. Solution Chem.* **6**, 251-61 (1977)
13. B. F. Hitch and R. E. Mesmer, *J. Solution Chem.* **5**, 667 (1976)
14. W. L. Marshall, R. Slusher, and E. V. Jones, *J. Chem. Eng. Data* **9**, 187 (1964)
15. W. L. Marshall and E. V. Jones, *J. Phys. Chem.* **20**, 4028 (1966)
16. D. L. Marquardt, *J. Soc. Ind. Appl. Math.* **2**, 431 (1963)
17. R. E. Mesmer, W. L. Marshall, D. A. Palmer, J. M. Simonson, and H. F. Holmes, *J. Solution Chem.* **21**, 699 (1988)
18. K. Sue, Y. Hakuta, R. L. Smith Jr., T. Adschiri and K. Arai, *J. Chem. Eng. Data* **44**, 1422-26 (1999)

19. E. L. Shock, D. C. Sassani, M. Willis and D. A. Sverjensky, *Geochim. Cosmochim. Acta* **61**, 907-950 (1997)
20. A. B. Garrett, A. Vellenga and C. Fontana, *J. Am. Chem. Soc.* **61**, 367 (1939)
21. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nutall, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982)
22. I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, Weinheim (1989)
23. M. H. Abraham and Y. Marcus, *J. Chem. Soc., Faraday Trans.* **82**, 3255-74 (1986)
24. C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.* **86**, 5385-93 (1964)
25. Y. Marcus, *J. Chem. Soc., Faraday Trans. I.* **86**, 233-42 (1986)
26. Y. Marcus, *Biophys. Chem.* **51**, 111-27 (1994)

Table I

Measured Solubilities of Litharge ( $\text{PbO}$ ) in Aqueous Solutions

Temp. <sup>a</sup> °C	Pressure <sup>b</sup> bar	No. Samples	Pb Conc. mol kg <sup>-1</sup>	Temp. <sup>a</sup> °C	Pressure <sup>b</sup> bar	No. Samples	Pb Conc. mol kg <sup>-1</sup>
Run 1, 1 ppm morpholine				Run 2, 8 ppm morpholine			
260.0	67.5	7	(5.04±0.34)@0 <sup>-3</sup>	260.0	67.3	6	(4.51±0.14)@0 <sup>-3</sup>
232.0 <sup>c</sup>	63.1	8	(4.03±0.17)@0 <sup>-3</sup>	232.0 <sup>c</sup>	63.5	12	(4.03±0.42)@0 <sup>-3</sup>
204.0 <sup>c</sup>	64.0	8	(3.69±0.53)@0 <sup>-3</sup>	204.0 <sup>c</sup>	64.0	7	(3.31±0.09)@0 <sup>-3</sup>
177.0 <sup>c</sup>	59.7	7	(2.51±0.18)@0 <sup>-3</sup>	177.0 <sup>c</sup>	64.4	7	(2.73±0.13)@0 <sup>-3</sup>
149.0 <sup>c</sup>	63.6	7	(2.02±0.18)@0 <sup>-3</sup>	149.0 <sup>c</sup>	64.4	8	(2.09±0.13)@0 <sup>-3</sup>
121.0 <sup>c</sup>	65.8	8	(1.39±0.02)@0 <sup>-3</sup>	121.0 <sup>c</sup>	64.7	10	(1.42±0.08)@0 <sup>-3</sup>
93.0 <sup>c</sup>	63.7	8	(1.00±0.03)@0 <sup>-3</sup>	93.0 <sup>c</sup>	64.7	5	(9.64±0.10)@0 <sup>-4</sup>
66.0 <sup>c</sup>	63.8	6	(6.71±0.15)@0 <sup>-4</sup>	66.0 <sup>c</sup>	63.7	7	(6.52±0.22)@0 <sup>-4</sup>
38.0 <sup>c</sup>	64.9	7	(4.13±0.16)@0 <sup>-4</sup>	38.0 <sup>c</sup>	64.4	6	(3.99±0.03)@0 <sup>-4</sup>
Run 3, 67.9 ppm morpholine				Run 4, 1.20 ppm ammonia			
260.0	67.5	6	(4.59±0.57)@0 <sup>-3</sup>	260.0	68.0	7	(4.50±0.51)@0 <sup>-3</sup>
232.0 <sup>c</sup>	63.5	8	(3.89±0.37)@0 <sup>-3</sup>	232.0 <sup>c</sup>	65.2	8	(3.75±0.57)@0 <sup>-3</sup>
204.0 <sup>c</sup>	62.9	5	(3.51±0.13)@0 <sup>-3</sup>	204.0 <sup>c</sup>	61.0	7	(3.36±0.18)@0 <sup>-3</sup>
177.0 <sup>c</sup>	62.9	6	(2.76±0.13)@0 <sup>-3</sup>	177.0 <sup>c</sup>	56.7	12	(2.56±0.37)@0 <sup>-3</sup>
149.0 <sup>c</sup>	65.2	8	(1.93±0.07)@0 <sup>-3</sup>	149.0 <sup>c</sup>	64.8	9	(1.82±0.14)@0 <sup>-3</sup>
121.0 <sup>c</sup>	64.5	6	(1.33±0.06)@0 <sup>-3</sup>	121.0 <sup>c</sup>	64.9	9	(1.51±0.06)@0 <sup>-3</sup>
93.0 <sup>c</sup>	64.3	7	(9.62±0.24)@0 <sup>-4</sup>	93.0 <sup>c</sup>	64.7	10	(1.01±0.02)@0 <sup>-3</sup>
66.0 <sup>c</sup>	65.1	7	(6.24±0.06)@0 <sup>-4</sup>	66.0 <sup>c</sup>	65.3	7	(6.48±0.07)@0 <sup>-4</sup>
38.0 <sup>c</sup>	65.2	9	(3.68±0.08)@0 <sup>-4</sup>	38.0 <sup>c</sup>	67.0	5	(3.84±0.04)@0 <sup>-4</sup>
Run 5, 11.93 ppm ammonia				Run 6, 4.00 ppm sodium hydroxide			
257.6	64.3	7	(4.51±0.65)@0 <sup>-3</sup>	260.0 <sup>c</sup>	65.0	7	(4.42±0.25)@0 <sup>-3</sup>
232.0 <sup>c</sup>	64.2	8	(4.26±0.23)@0 <sup>-3</sup>	232.0	63.5	10	(3.85±0.32)@0 <sup>-3</sup>
204.0 <sup>c</sup>	63.6	8	(3.35±0.26)@0 <sup>-3</sup>	204.0	64.1	9	(2.92±0.51)@0 <sup>-3</sup>
177.0 <sup>c</sup>	61.4	7	(2.66±0.13)@0 <sup>-3</sup>	177.0	64.0	5	(2.73±0.08)@0 <sup>-3</sup>
149.0 <sup>c</sup>	65.3	6	(1.92±0.06)@0 <sup>-3</sup>	149.0 <sup>c</sup>	65.2	10	(1.91±0.10)@0 <sup>-3</sup>
122.0 <sup>c</sup>	64.4	7	(1.36±0.03)@0 <sup>-3</sup>	121.0 <sup>c</sup>	63.8	10	(1.35±0.07)@0 <sup>-3</sup>
93.0 <sup>c</sup>	63.6	9	(1.00±0.08)@0 <sup>-3</sup>	93.0	64.3	10	(8.28±0.16)@0 <sup>-4</sup>
66.0 <sup>c</sup>	63.3	7	(6.08±0.09)@0 <sup>-4</sup>	66.0	64.3	9	(5.28±0.04)@0 <sup>-4</sup>
38.0 <sup>c</sup>	64.2	10	(3.23±0.07)@0 <sup>-4</sup>	38.0	64.1	11	(2.89±0.32)@0 <sup>-4</sup>
Run 6A sodium hydroxide at 260°C							
370.4 <sup>d</sup>	67.8	8	(4.67±0.87)@0 <sup>-3</sup>				
64.4 <sup>d,c</sup>	68.6	12	(4.35±0.33)@0 <sup>-3</sup>				
4.70 <sup>d</sup>	68.4	6	(4.49±0.09)@0 <sup>-3</sup>				

<sup>a</sup> ± 0.2°C<sup>b</sup> ± 1.0 bar<sup>c</sup> PbO (Aldrich/Alfa Chemical Co.)<sup>d</sup> ppm NaOH

Table II  
Ionization Behavior of Selected Compounds via Eq. (7)

Compound	b <sub>1</sub>	b <sub>2</sub>	b <sub>3</sub>	b <sub>4</sub>	b <sub>5</sub>
Water <sup>a</sup>	31,286.0	-606.522	94.9734	-0.097611	-2,170,870
Morpholine <sup>b</sup>	20,332.7	-387.213	61.5622	-0.0724629	-1,390,320
Ammonia <sup>c</sup>	27,416.5	-513.761	81.2824	-0.0905795	-1,717,720

<sup>a</sup> Ref. 11; <sup>b</sup> Ref. 12; <sup>c</sup> Ref. 13

Table III  
Effect of Pb(II) Ion Solubility on Solution pH

Pb mmol kg <sup>-1</sup>	Temp. °C	pH <sub>i</sub> (T)	pH(T)	Pb mmol kg <sup>-1</sup>	Temp. °C	pH <sub>i</sub> (T)	pH(T)
Run 1, morpholine = 1 ppm				Run 2, morpholine = 8 ppm			
0.413	38	8.287	10.054	0.399	38	8.819	10.054
0.671	66	7.646	9.583	0.652	66	8.192	9.582
1.00	93	7.132	9.210	0.964	93	7.681	9.209
1.39	121	6.718	8.912	1.42	121	7.260	8.910
2.02	149	6.388	8.674	2.09	149	6.912	8.673
2.51	177	6.131	8.488	2.73	177	6.625	8.487
3.69	204	5.940	8.349	3.31	204	6.394	8.348
4.03	232	5.814	8.254	4.03	232	6.221	8.253
5.04	260	5.758	8.206	4.51	260	6.196	8.205
Run 3, Morpholine = 68 ppm				Run 4, ammonia = 1.2 ppm			
0.368	38	9.312	10.059	0.384	38	9.028	10.055
0.674	66	8.691	9.584	0.648	66	8.324	9.582
0.962	93	8.182	9.208	1.01	93	7.760	9.209
1.33	121	7.759	8.909	1.51	122	7.303	8.910
1.93	149	7.407	8.671	1.82	149	6.928	8.673
2.76	177	7.113	8.485	2.56	177	6.622	8.487
3.51	204	6.874	8.346	3.36	204	6.376	8.348
3.89	232	6.691	8.251	3.75	232	6.186	8.253
4.59	260	6.571	8.203	4.50	260	6.058	8.205
Run 5, ammonia = 12 ppm				Run 6, sodium hydroxide = 4 ppm			
0.323	38	9.600	10.078	0.289	38	9.564	10.118
0.608	66	8.893	9.589	0.528	66	8.870	9.619
1.00	93	8.324	9.210	0.828	93	8.336	9.233
1.36	122	7.858	8.909	1.35	121	7.924	8.929
1.92	149	7.473	8.671	1.91	149	7.612	8.690
2.66	177	7.156	8.485	2.73	177	7.386	8.504
3.35	204	6.897	8.346	2.92	204	7.239	8.366
4.26	232	6.692	8.251	3.85	232	7.165	8.270
4.51	257.6	6.554	8.205	4.42	260	7.164	8.215

Table IV

Thermodynamic Quantities for the Calculation of Litharge Solubility  
in Aqueous Media via Eq. (12)

Reaction	A <sup>a</sup>	B <sup>b</sup>	C <sup>b</sup>	$\Delta G^\circ(298)^a$
" -PbO(s) + H <sup>+</sup> WPb(OH) <sup>+</sup>	-17.88±1.39	67.50± 6.71	0	-38.00±0.16
" -PbO(s) + H <sub>2</sub> O WPb(OH) <sub>2</sub> (aq)	25.20±8.11	0.16±13.22	0	25.15±4.24
" -PbO(s) + 2H <sub>2</sub> O WPb(OH) <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	151.42±51.04	1457.37±48.37	-223.8	97.09±36.65
Reanalysis including Ref. 5 data at 100°C				
" -PbO(s) + H <sup>+</sup> WPb(OH) <sup>+</sup>	-18.68±0.83	64.70±3.06	0	-37.97±0.15
" -PbO(s) + H <sub>2</sub> O WPb(OH) <sub>2</sub> (aq)	29.86±5.52	7.57±9.49	0	27.60±2.70
" -PbO(s) + 2H <sub>2</sub> O WPb(OH) <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	136.83±0.72	1440.39	-223.8	87.56

<sup>a</sup> kJ mol<sup>-1</sup>

<sup>b</sup> J mol<sup>-1</sup> K<sup>-1</sup>



Table V  
Thermochemical Parameters for Selected Species in PbO-H<sub>2</sub>O System<sup>a</sup>

Species	$C_p^\circ$ (298)	$S^\circ$ (298)	$\Delta H_f^\circ$ (298)	$\Delta G_f^\circ$ (298)	Ref.
Pb(s)	26.44	64.81	0	0	[21]
PbO@0.4 H <sub>2</sub> O(s)	-	-	-	-282.3 <sup>c</sup>	[21]
"-PbO(s)	45.81	66.50	-218.99	-188.93	[21]
\$-PbO(s)	45.77	68.70	-217.32	-187.89	[21]
H <sub>2</sub> (g)	28.84	130.68	0	0	[22]
O <sub>2</sub> (g)	29.38	205.15	0	0	[22]
H <sub>2</sub> O(aq)	75.3	69.95	-285.83	-237.14	[22]
H <sup>+</sup> (aq)	-71.	-22.2	0	0	[23, 24]
Pb <sup>2+</sup> (aq)	-	-25.8 ± 0.8	1.21 ± 0.25	-23.97 ± 0.13	[5]
Pb(OH) <sup>+</sup> (aq)	-	109.1	-237.67	-226.90	b
Pb(OH) <sub>2</sub> (aq)	-	144.1	-474.96	-398.47	b
Pb(OH) <sub>3</sub> <sup>-</sup> (aq)	43.6	170.1	-720.55	-575.65	b

<sup>a</sup> Units:  $C_p^\circ$  and  $S^\circ$ , J mol<sup>-1</sup> K<sup>-1</sup>;  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$ , kJ mol<sup>-1</sup>

<sup>b</sup> This work

<sup>c</sup> Converted from tabulated value for PbO@1/3)H<sub>2</sub>O by adding (1/15)(-237.14) = -15.8 kJ mol<sup>-1</sup>.

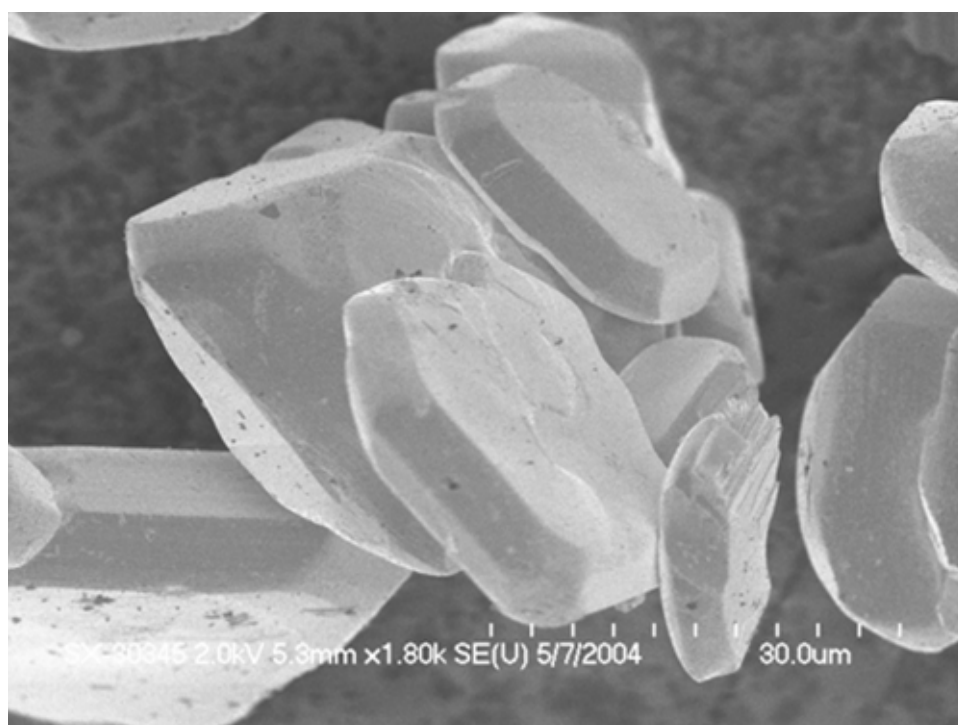
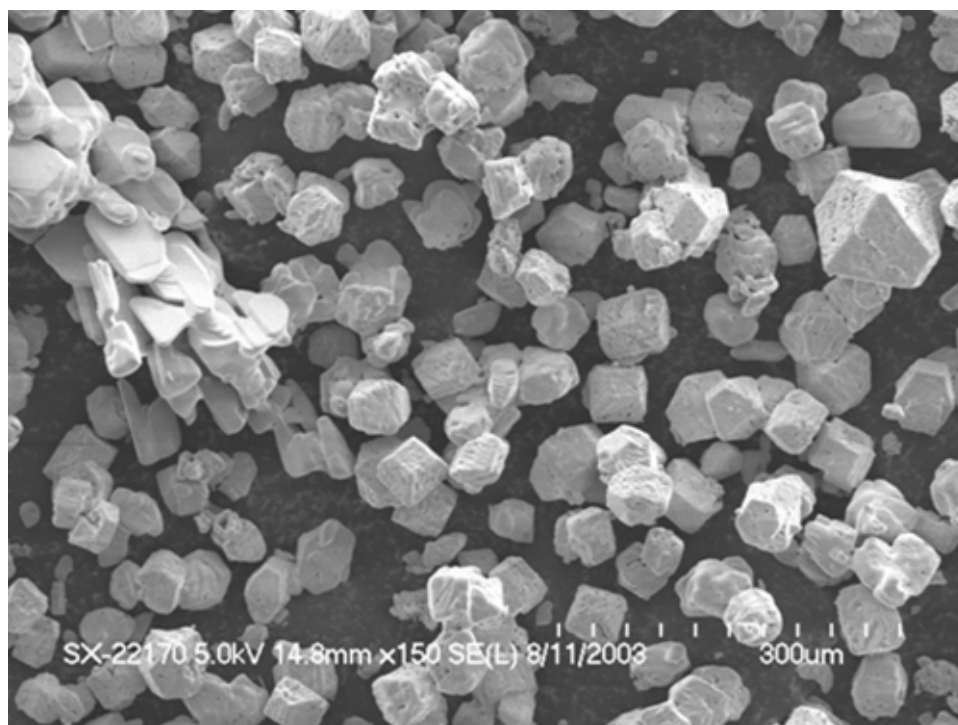


Fig. 1. Morphology of Pb(II) oxide crystals: (a) massicot, as-received from Aldrich-Alfa and (b) litharge, recovered from solubility apparatus.

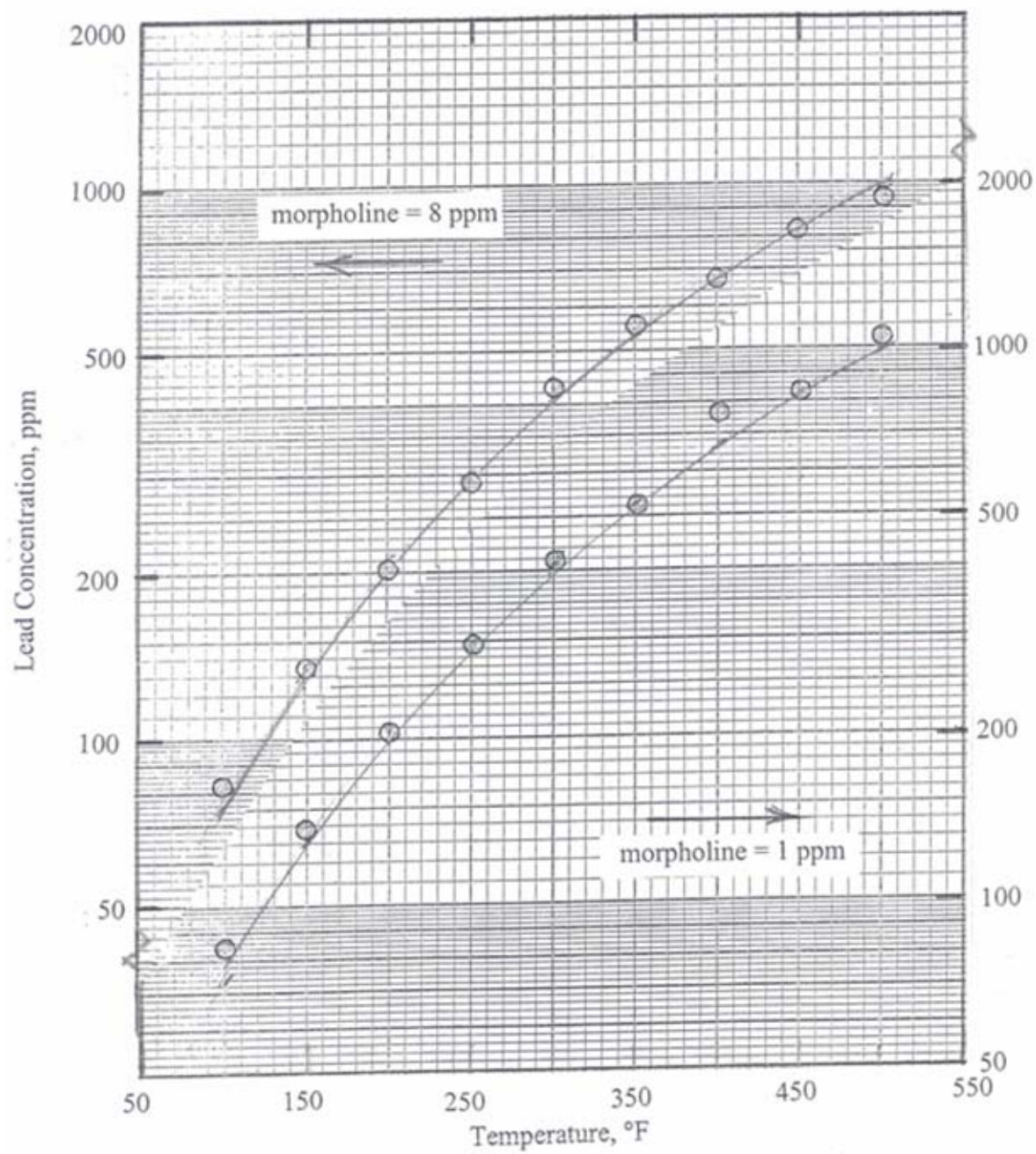


Fig. 2. Comparison of measured and fitted solubilities of litharge in morpholine solutions.

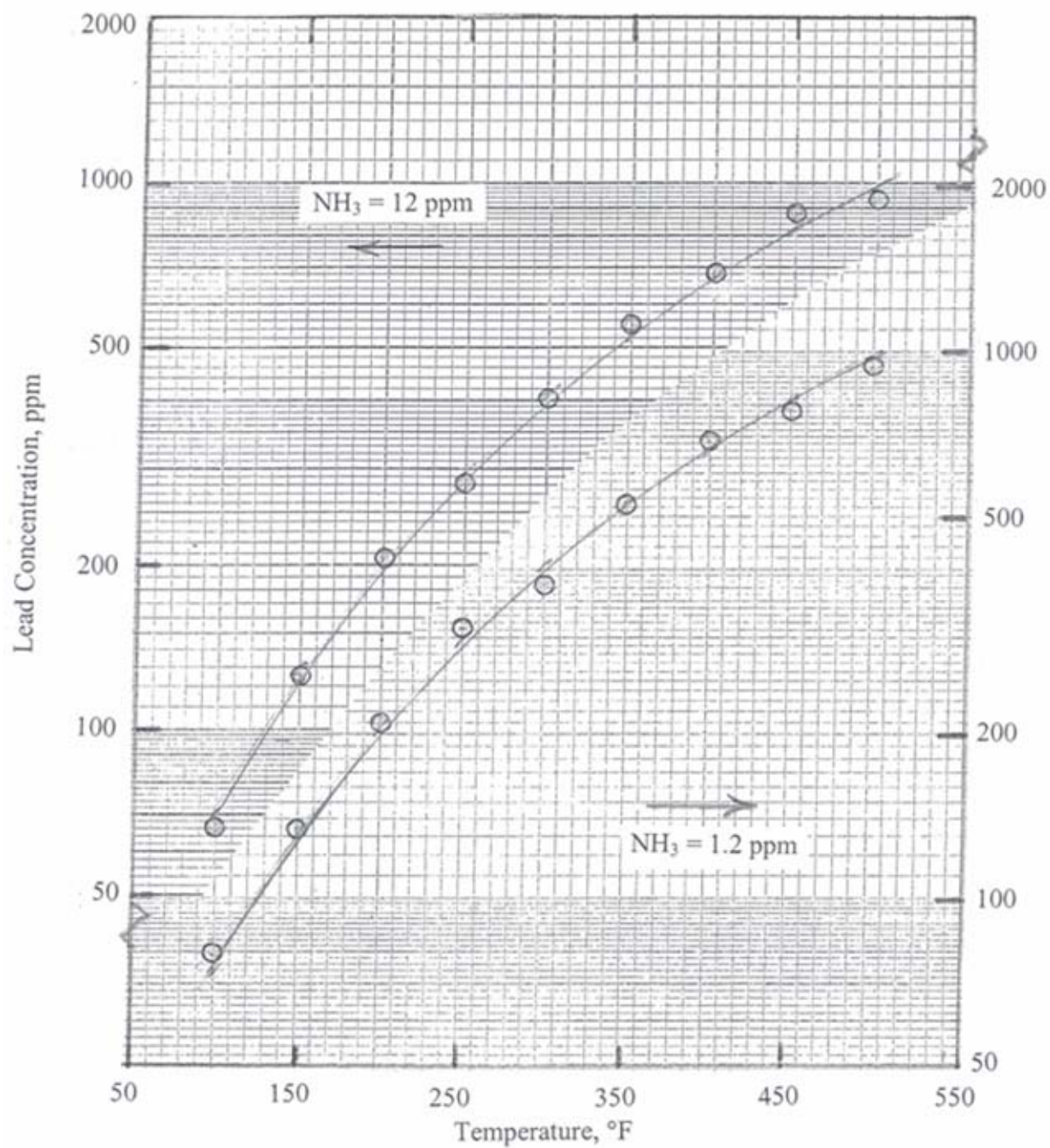


Fig. 3. Comparison of measured and fitted solubilities of litharge in ammonium hydroxide.

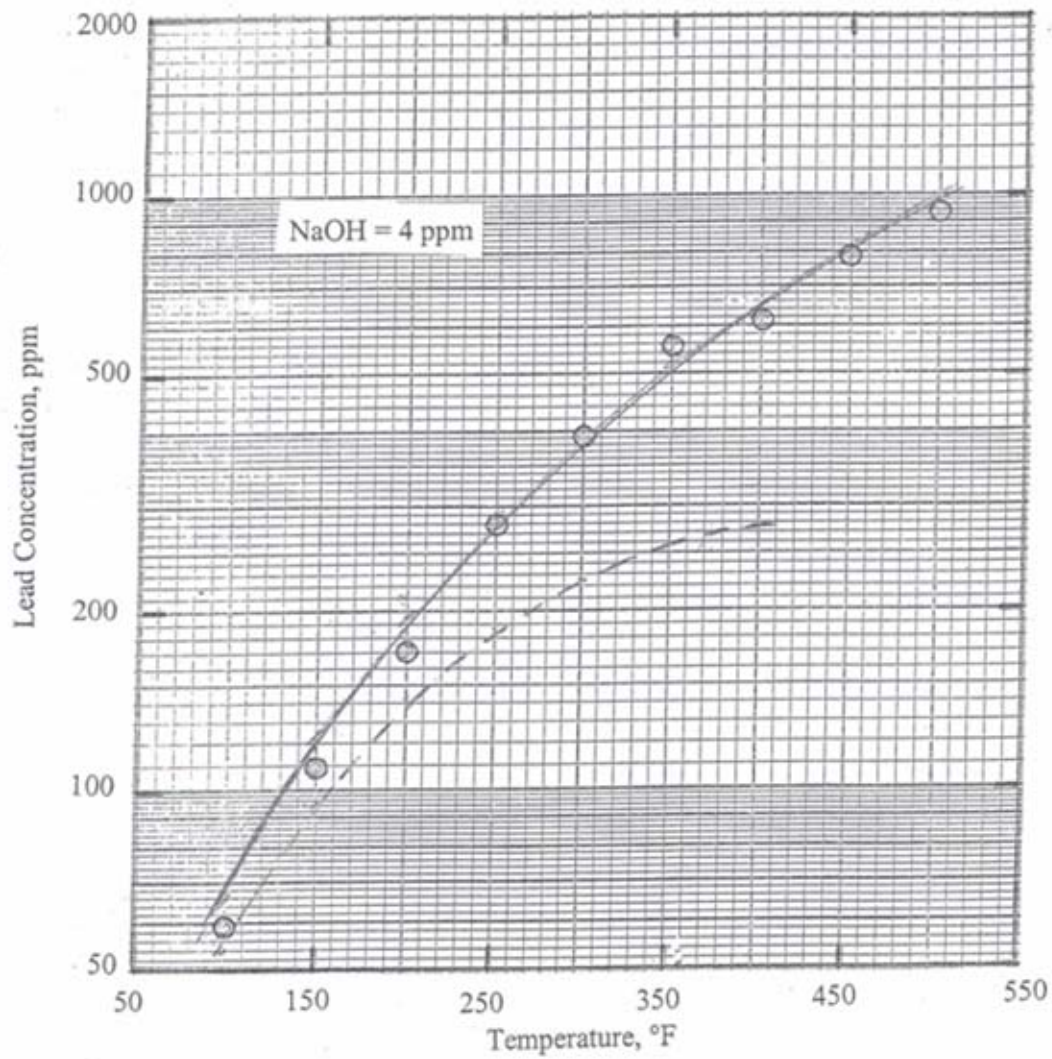


Fig. 4. Comparison of measured and fitted solubilities of litharge in sodium hydroxide. Results of Tugarinov et al.<sup>(5)</sup> plotted as dashed curve.

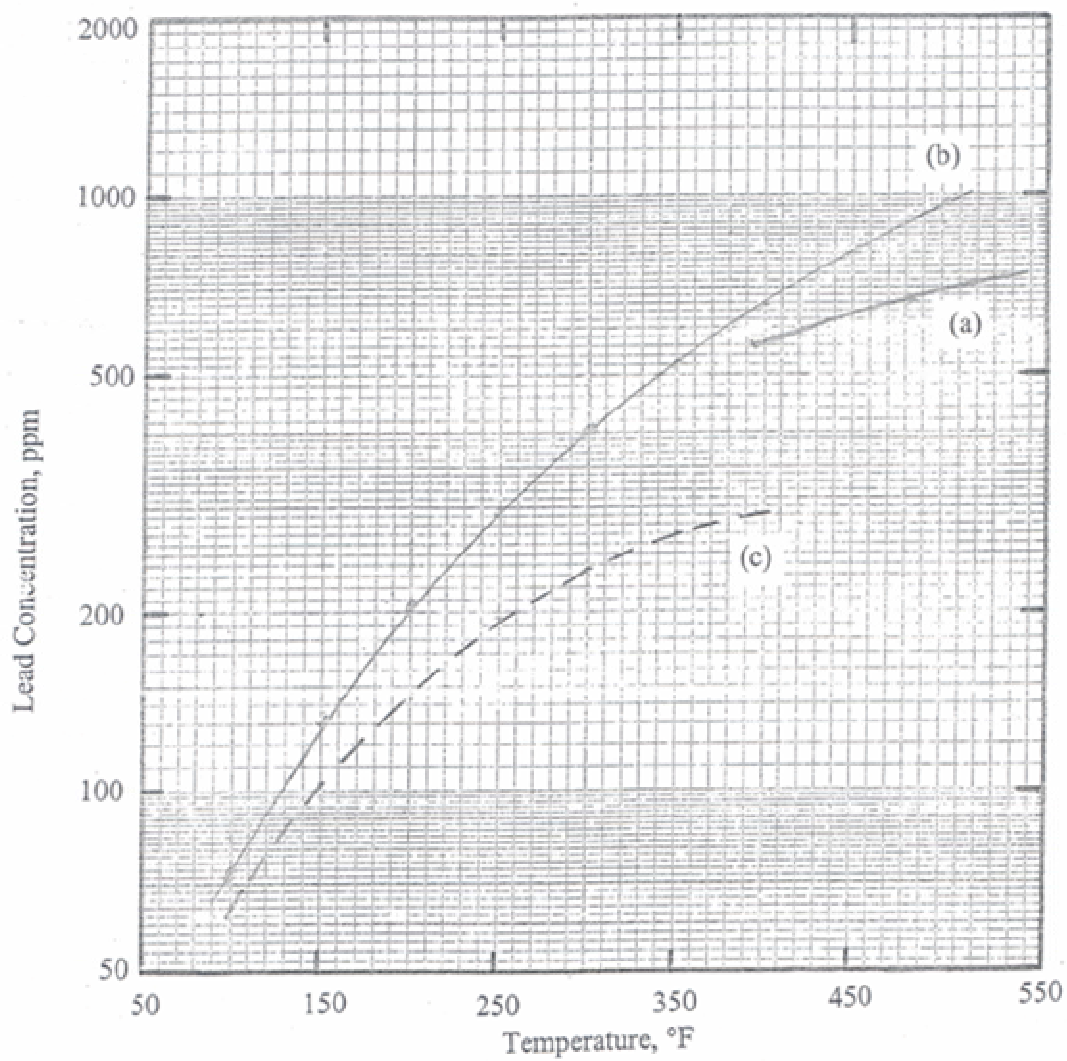


Fig. 5. Litharge solubilities in pure water: (a) measurements of Sue et al.<sup>(18)</sup> compared to predictions based on (b) present work and (c) results of Tugarinov et al.<sup>(5)</sup>

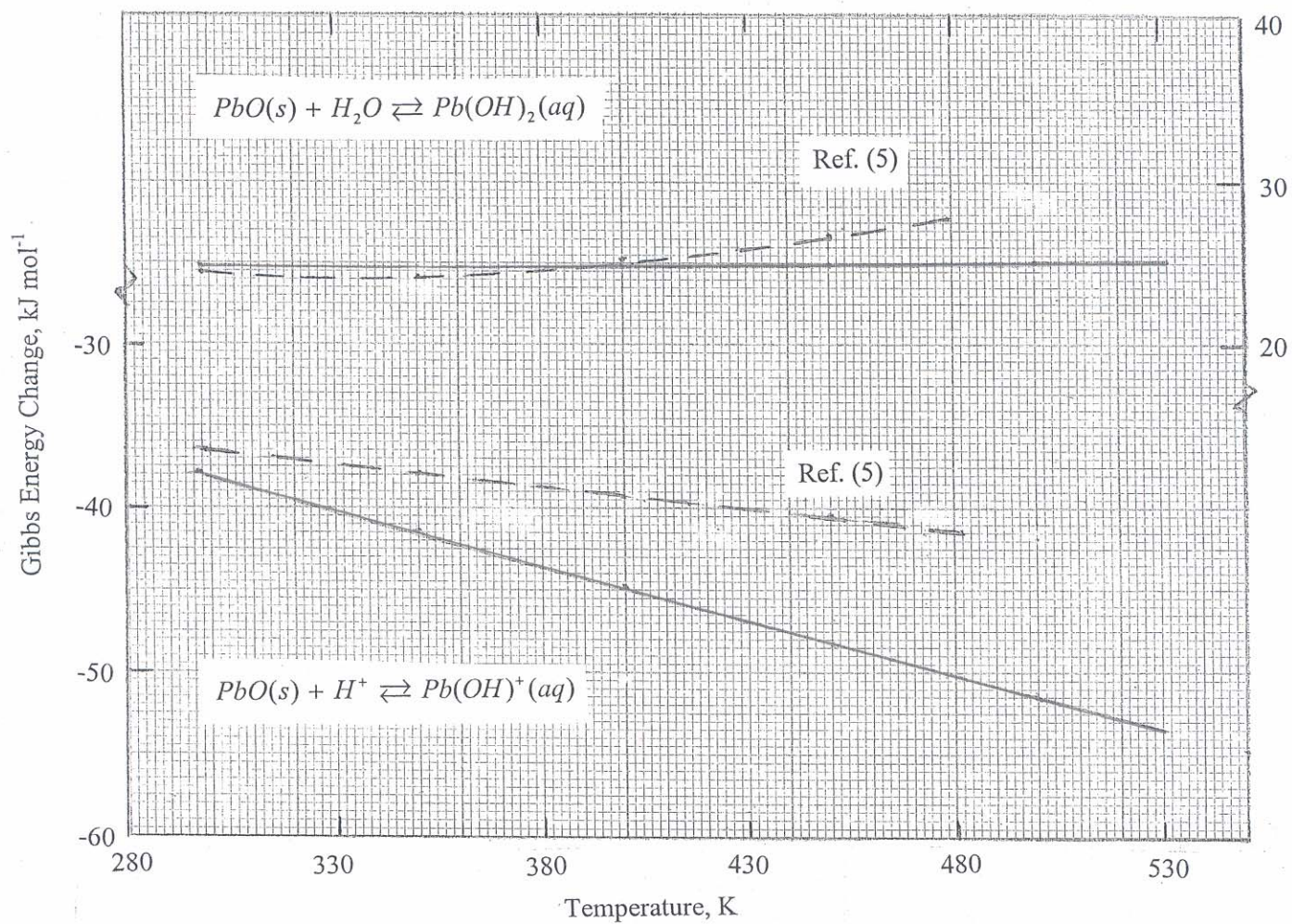


Fig. 6. Free energy changes determined for litharge dissolution reaction, Eq. (4), for  $n = 1$  and 2.

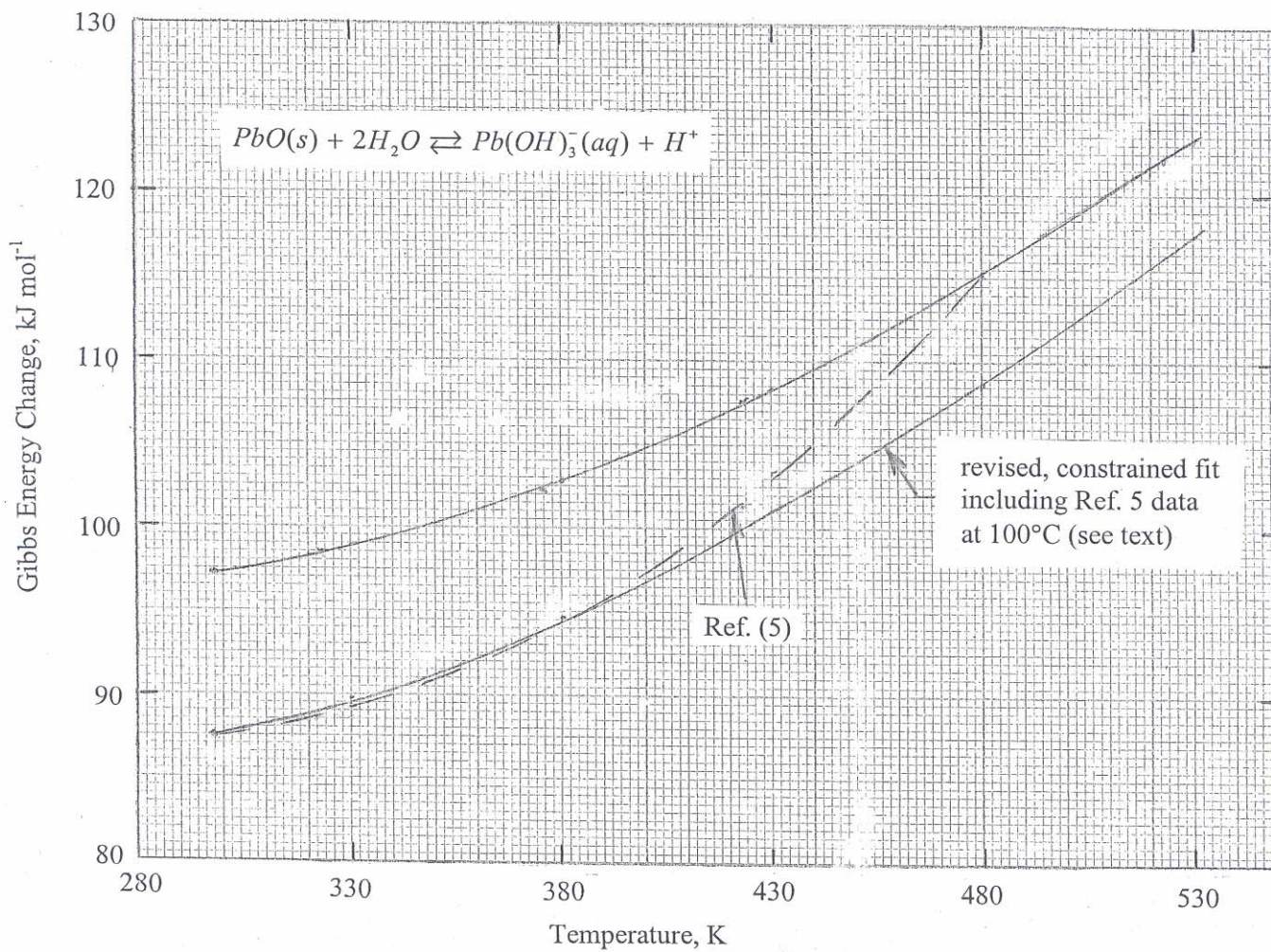


Fig. 7. Free energy changes determined for litharge dissolution reaction, Eq. (4), for  $n = 3$ .



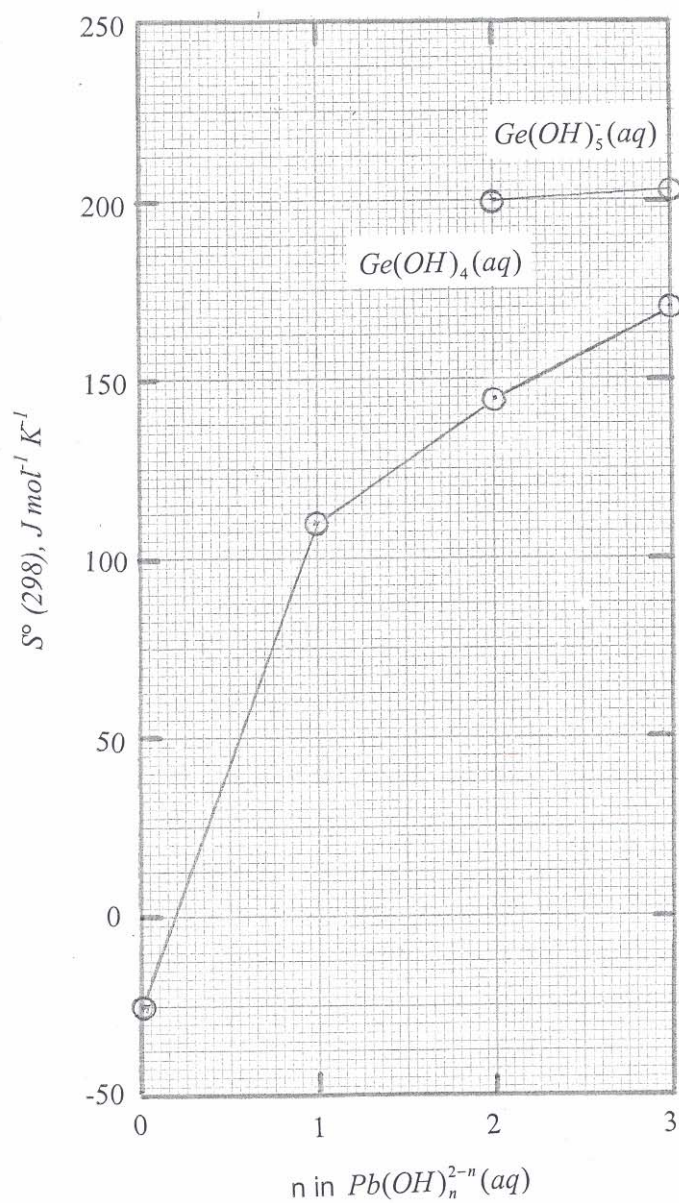


Fig. 8. Standard partial molar entropies for the Pb(II) aquoion and its hydroxocomplexes. Entropies for Ge(IV) hydroxocomplexes taken from Ref. (6).