J. Chem. Eng. Data **2005,** *50,* 1109−1113

Reviews

Thermodynamics of the LiOH + H_2O System

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Literature data for the solubility of anhydrous lithium hydroxide and lithium hydroxide monohydrate in pure water have been compiled and critically evaluated. The selected data have been represented by empirical temperature−molality expressions from which the coordinates of the eutectic and of the peritectic have been calculated. The phase diagram of the LiOH + H_2O system is presented. A model using Pitzer's ion interaction approach for the calculation of the thermodynamic properties of aqueous LiOH solutions is built by fitting literature values for the osmotic coefficient obtained from isopiestic and from freezing point depression measurements from the eutectic point (255 K) to 473 K. Heat capacities of aqueous LiOH solutions are then calculated using the first and second derivatives with respect to temperature of these expressions and are compared to direct measurements. The solubility products of LiOH(s) and of $LiOH \cdot H_2O(s)$ are calculated from their solubilities in pure water. Standard entropies, enthalpies, and heat capacities of formation of solid lithium hydroxides retrieved from fits of their solubility products with respect to temperature are compared to literature values, which are mainly derived from calorimetric measurements.

1. Introduction

The main industrial use for lithium is in ceramics, glass, and aluminum production, but its use in electric batteries and as a heat carrier in atomic fusion reactors will increase the demand. Its main sources are the Li-bearing brines of salt deposits in the Andean and the Li-bearing minerals in pegmatites. (See the USGS web site http://minerals.usgs.gov/minerals-/pubs/commodity/lithium/450303.pdf.) Therefore, there is a need for a better understanding of lithium behavior in the earth's crust. This requires knowledge of the interactions between aqueous lithium and the main ligands found in natural waters over large ranges of solution composition, temperature, and pressure.

The present study reviews experimental data[1−4] on thermodynamic properties of aqueous lithium hydroxide solutions and models[5−7] based on Pitzer's ion interaction model generated from these data. A new model that is valid over an extended range of temperature (from 255 K to 473 K) is presented. Apparent heat capacities calculated by the model are compared to those calculated using Pitzer parameters obtained by fitting heat capacity data.[8]

Critically evaluated solubilities of $LiOH \cdot H_2O(s)$ and LiOH(s) in pure water were then used to calculate their solubility products. Standard enthalpies, entropies, and heat capacities of these solids were obtained from a regression of their solubility products versus temperature and compared to literature values.

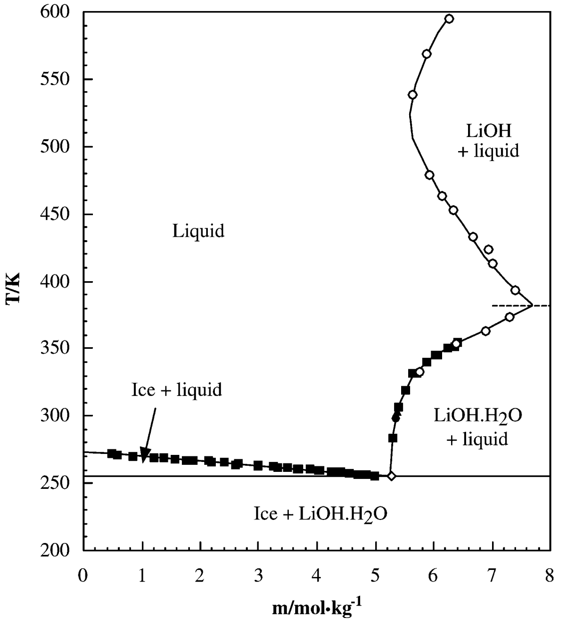

Figure 1. Phase diagram for the LiOH + H_2O system. The solid lines are fitted to the data (Table 1 and eq 1). ■ Pickering;[2] ▲, Donk;[24] ●, Van Moeurs;[4] ○, Stephan and Miller;[3] ◇, Ennan and Lapshin[1].

2. Phase Diagram of the LiOH + H_2O System

Literature solubility data for LiOH(s) and $LiOH \cdot H_2O(s)$ and the ice melting curve are plotted versus temperature in Figure 1. Several data sets[26−29] have not been retained because of their inconsistency with the general trend depicted by more extensive measurements.[1−4,24] The old

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10.1021/je0495482 CCC: $30.25

Table 1. Parameters of the Solubility−Temperature Relationships (Eq 1) for Ice and for the Lithium Hydroxide Salts

	a_0	a_1	a_2	a_3	temp range of fit/K	no. of points
ice	−3.834	−0.27828	-1.06952×10^{-6}	0	255−272	31
$LiOH \cdot H_2O$	−39.568	0.48784	-1.7670×10^{-3}	2.1431×10^{-6}	255−373	18
LiOH	−6.561	0.1442	-4.13238×10^{-4}	3.48232×10^{-7}	393−595	10

Table 2. Coordinates of the Eutectic and Perictectic Points in the H_2O + LiOH System

	experimental		calculated (this work)	
	m/mol·kg^{-1}	T/K	m_l/mol·kg^{-1}	T/K
eutectic	5.267[4,22] 5.271[1]	255.15 255.15	5.274	254.91
peritectic		382.05[22]	7.704	378.29

freezing point depression data of Pickering[2] extrapolate within 0.5 K into the position of the eutectics determined more recently by Ennan and Lapshin.[1] The selected data[1−4,24] have been fitted to simple polynomials

$$m = \sum_{i=0}^{3} a_i (T/\mathrm{K})^i \tag{1}$$

in which T is the absolute temperature and m is the LiOH molality. The a_i parameters are given in Table 1. The coordinates of the eutectics and of the peritectics are given in Table 2.

3. Literature Data for the Thermodynamic Properties of LiOH Aqueous Solutions

Published measurements yielding thermodynamic data for aqueous LiOH are surprisingly very scarse.[2,9−11] Several sets of Pitzer interaction parameters for LiOH(aq) have nevertheless been determined at 298.15 K by different authors.[5−7] Pitzer and Mayorga[6] fitted the emf data of Harned and Swindell,[9] whereas Covington et al.[5] gave their own values from a reanalysis of the same data.[9] Kim and Frederick[7] used the osmotic coefficient values at rounded molalities generated by Hamer and Wu[12] from the data of Harned and Swindell.[9] Pitzer and Mayorga[6] had noted "small but troublesome" problems with the Harned−Swindell data calling for further experiments. Robinson and Stokes[13] also report osmotic coefficient values at rounded molalities without mentioning how these values were obtained. Figure 2 displays the osmotic coefficient of aqueous LiOH solutions at 298.15 K calculated using alternate values of Pitzer parameters along with data generated in various compilations.[11−13] At molalities lower than 3 mol·kg^{-1}, the data of Kangro and Groneveld[11] is slighly lower that the values given by Hamer and Wu.[12] The Hamer−Wu values do not extrapolate smoothly to the Kangro and Groneveld[11] value at 5 mol·kg^{-1}. It is surprising to see the discrepancies between osmotic coefficient values generated with alternate sets of Pitzer interaction parameters (Figure 2), although the data used to obtain the parameters is the same most of the time. Such discrepancies are not as large for the LiOH(aq) activity coefficient values (Figure 3). According to the various estimates, the LiOH(aq) activity coefficient at 298.15 K becomes almost constant at values between 0.4 and 0.5 for molalities above 2 mol·kg^{-1}.

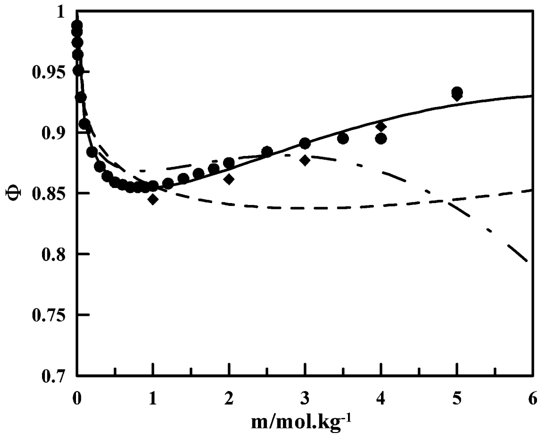

Figure 2. Osmotic coefficient of LiOH aqueous solutions at 298.15 K. Solid line, this work; short dashes, Pitzer and Mayorga;[6] long dashes, Covington et al.;[5] ◆, Kangro and Gronenveld;[11] ●, Hamer and Wu.[12]

At high temperatures, Holmes and Mesmer[10] report highly accurate isopiestic measurements at (393, 413, and 443) K to molalities of 7 mol·kg^{-1}.

The condition for equilibrium between ice and an aqueous LiOH solution is

$$K_{\mathrm{ice}}(T) = a_{\mathrm{w}}(T, m) \tag{2}$$

a_{w} is the activity of water of the aqueous solution of molality m at temperature T. K_{ice} is the water−ice equilibrium constant. It has been determined to 199 K from data for the LiCl + H_2O system.[14] The osmotic coefficients of LiOH solutions below 273.15 K can be calculated from freezing point depression data[2] using eq 2.

The information we retained to build a model to estimate the thermodymanic properties of LiOH(aq) are the rounded values of the osmotic coefficient of Hamer and Wu[12] (including the datum at 5 mol·kg^{-1}), the high-temperature data of Holmes and Mesmer,[10] and the freezing point depression data of Pickering.[2] The collected data extends to high concentrations but is quite restricted in temperature. The only values retained between 273.15 K and 373.15 K are those for 298.15 K. It does provide some constraints on the thermodynamic model for LiOH(aq). The present work highlights the need for new data.

4. Model for the Thermodynamic Properties of Aqueous Lithium Hydroxide

The osmotic coefficient of an aqueous solution of LiOH can be written in Pitzer's formalism as

$$\Phi - 1 = f^{\Phi} + mB^{\Phi}_{\mathrm{LiOH}} + m^2 C^{\Phi}_{\mathrm{LiOH}} \tag{3}$$

with

$$f^{\Phi} = -\frac{A_{\Phi} I^{1/2}}{1 + 1.2 I^{1/2}} \tag{4}$$

and

$$B^{\Phi}_{\mathrm{LiOH}} = \beta^{(0)}_{\mathrm{LiOH}} + \beta^{(1)}_{\mathrm{LiOH}} \exp(-2I^{1/2}) \tag{5}$$

I is the ionic strength, and m is the LiOH molality. $\beta^{(0)}$,

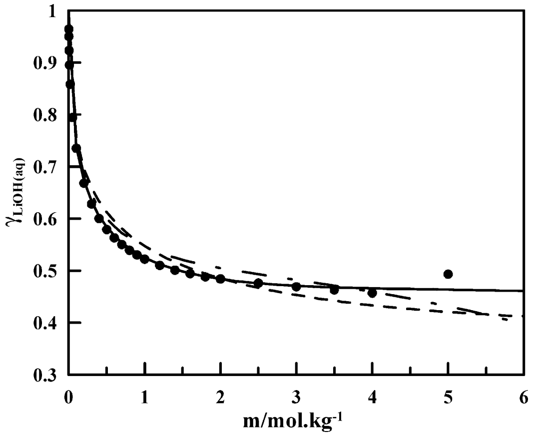

Figure 3. Activity coefficient of LiOH(aq) as a function of the LiOH molality at 298.15 K. Solid curve, this work; short dashes, Pitzer and Mayorga;[6] long dashes, Covington et al.;[5] ●, Hamer and Wu.[12]

Table 3. Parameters of Equations 6 and 7 for the Temperature Variation of the Debye−Hückel Slope for the Osmotic and Activity Coefficients

i	q_i	r_i
1	86.683649	0.36901532
2	0.0848795	$-6.3210043 \times 10^{-4}$
3	-8.88878×10^{-5}	9.1452359
4	4.88096×10^{-8}	$-1.35143986 \times 10^{-2}$
5	−1327.31477	$2.26089488 \times 10^{-3}$
6	−17.6460	$1.92118597 \times 10^{-6}$
7	0	45.2586464

$\beta^{(1)}$, and C^{Φ} are empirical parameters specific to a given aqueous electrolyte, here LiOH(aq).

Previous works on LiCl + H_2O[14] and on CsCl + H_2O[15] have shown that the thermodynamic properties of aqueous binary systems could be calculated at temperatures below ambient down to the eutectics (199 K for LiCl + H_2O and 248 K for CsCl + H_2O) using Pitzer's ion interaction model[16] with values for the Debye−Hückel slope A_{Φ} for the activity and osmotic coefficients[17] given by the following expression:

$$A_{\Phi} = q_1 + q_2(T/\text{K}) + q_3(T/\text{K})^2 + q_4(T/\text{K})^3 + \frac{q_5}{(T/\text{K})} + q_6 \ln(T/\text{K}) \quad (6)$$

At temperatures above 298.15 K, an alternate expression[18] can be used:

$$A_{\Phi} = r_1 + r_2(T/\text{K}) + \frac{r_3}{(T/\text{K})} + r_4 \ln(T/\text{K}) + \frac{r_5}{(T/\text{K}) - 263} + r_6(T/\text{K})^2 + \frac{r_7}{680 - (T/\text{K})} \quad (7)$$

The values of the q_i and r_i parameters are given in Table 3. Clegg and Brimblecombe[19] have noted in their work on sulfuric acid that the choice of the Debye−Hückel slope values is not critical for calculations at high concentrations and at T lower than 273.15 K.

The osmotic coefficient data[2,10,12] was first fitted at each temperature, which allowed an estimate of the experimental dispersion of the data and of the weight to be given to each data set. The standard deviations of fit in the osmotic coefficient at each temperature are 0.05 for the freezing point depression data[2], 0.005 for the Hamer−Wu osmotic coefficients[12] at 298.15 K, and 0.001 for the high-temperature data.[10] After numerous trials, it was found that the whole data set[2,10,12] could be fitted using expression 3 for the temperature dependency of Pitzer's ion interaction parameters.

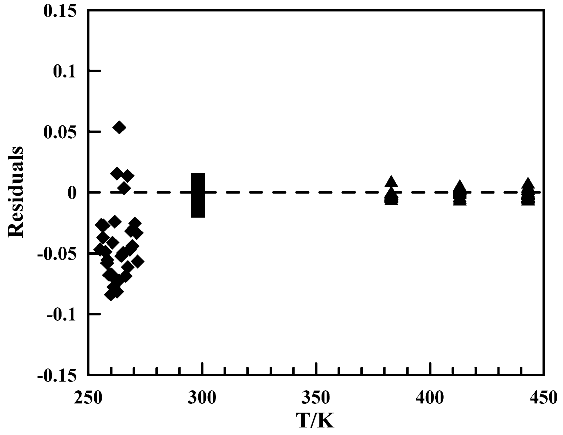

Figure 4. Residuals (calculated minus experimental values) of the fit of the LiOH(aq) osmotic coefficients versus temperature. ◆, Pickering;[2] ■, Hamer and Wu;[12] ▲, Holmes and Mesmer.[10]

Table 4. Parameters of Equation 8 for the Variation of Pitzer's Parameters as a Function of Temperature

	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
a_1	3.689298×10^{-1}	−2.201838	-1.491614×10^{-2}
a_2	-1.262427×10^{-3}	1.119177×10^{-2}	2.707400×10^{-5}
a_3	7.422313×10^{-7}	-1.403500×10^{-5}	3.591966×10^{-8}
a_4	-3.968190×10^{-1}	0	0

$$X = a_1 + a_2(T/\text{K}) + a_3(T/\text{K})^2 + \frac{a_4}{(T/\text{K}) - 240} \quad (8)$$

The last term of eq 8 was included to allow a better representation of the freezing point depression data in the region of the eutectics. It is nonzero only for the $\beta^{(0)}$ parameter and is sensitive only at temperature close to freeezing. As such, eq 8 allows a quadratic representation of the variation of Pitzer parameters with temperature. It avoids undue inflection points that more complex empirical expressions[17,18] may introduce. Because of the paucity of the data between (273 and 373) K, this choice implies a smooth variation of the parameters with temperature and hence some constraint on the value of derivative properties such as the heat capacity. The a_i parameters (eq 8) for $X = \beta^{(0)}, \beta^{(1),}$ and C^{Φ} are given in Table 4. The residuals are depicted in Figure 4.

In Pitzer's formalism,[8,16] the apparent heat capacity of aqueous LiOH solutions is

$$\Phi_{C_p} = \bar{C}_p^0(\text{LiOH}) + 2\left(\frac{A_J}{2.4}\right)\ln(1 + 1.2I^{1/2}) - 2RT^2 m(B^J_{\text{LiOH}} + mC^J_{\text{LiOH}}) \quad (9)$$

with

$$B^J_{\text{LiOH}} = \beta^{(0),J}_{\text{LiOH}} + \beta^{(1),J}_{\text{LiOH}} g(2I^{1/2})$$

and

$$g(x) = \frac{2[1 - (1 + x)\exp(-x)]}{x^2}$$

A_J is the Debye−Hüchel slope. A_J/R is equal to 3.94 at 298

Table 5. Parameters of Equation 12 for the Variation of the Solubility Products as a Function of Temperature and Standard Properties of Compounds in the LiOH + H_2O System[a]

	LiOH(aq)	H_2O(l)	LiOH(s)	LiOH·H_2O(s)
A			126.4 ± 0.4	105.9 ± 0.1
B			-3560 ± 23	-3939.9 ± 4.9
C			-19.53 ± 0.05	-15.94 ± 0.02
$\Delta_f H°$/kJ·mol^{-1}	-508.4^b	-285.83^b	-489.58 ± 0.24^e -484.93^b -487.50^d	-787.47 ± 0.58^e -788.01^b
$S°$/J·mol^{-1}·K^{-1}	7.1^b	69.91^b	43.6 ± 0.9^e 42.8^b 42.81^d	84.41 ± 0.3^e 71.21^b
$C_p°$/J·mol^{-1}·K^{-1}	-77.67^c	75.291^b	84.7 ± 0.5^e 49.66^b 49.58^d	130.2 ± 0.2^e 79.5^b

[a] The uncertainties are those of the reaction properties calculated from the A, B, and C parameters. Because they include the uncertainties of the NBS standard properties of LiOH(aq) and H_2O(l), they are only estimates of the errors of the standard properties of compounds. [b] NBS. [c] Criss and Millero.[8] [d] Gurvich et al.[21] [e] This work.

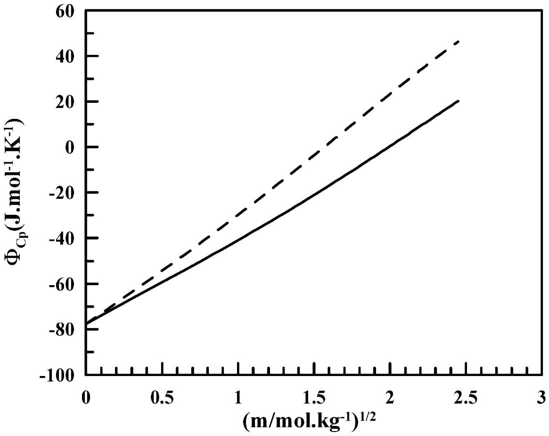

Figure 5. Apparent heat capacity of aqueous LiOH solutions at 298.15 K as a function of the square root of the LiOH molality. Dashed curve, Criss and Millero;[8] solid curve: this work.

K.[8] $\bar{C}_p{}^0$(LiOH) is the standard molal heat capacity of aqueous LiOH. It is -77.67 J·mol^{-1}·K^{-1} at 298.15 K.[8] Criss and Millero[8] report values of $\beta^{(0),J}$, $\beta^{(1),J}$, and C^Φ for the apparent heat capacity determined directly by a fit of calorimetric data. These parameters involve first and second derivatives with respect to temperature of Pitzer's interaction parameters for the osmotic and activity coefficients:

$$\beta^{(0),J} = \left(\frac{\partial^2 \beta^{(0)}}{\partial T^2}\right) + \frac{2}{T}\left(\frac{\partial \beta^{(0)}}{\partial T}\right) \tag{10}$$

(with a corresponding expression for $\beta^{(1),J}$) and

$$C^J = \frac{1}{2}\left(\frac{\partial^2 C^\phi}{\partial T^2}\right) + \frac{1}{T}\left(\frac{\partial C^\phi}{\partial T}\right) \tag{11}$$

$\beta^{(0),J}$, $\beta^{(1),J}$, and C^Φ can be calculated from the derivatives of eq 3 with respect to temperature. The agreement (Figure 5) between the apparent heat capacity calculated by both parameter sets is satisfactory if one keeps in mind that it is difficult to obtain accurate values of the first and second derivatives of a function from the values of the function itself and that the Gibbs free energy data used in the fit is very scarce between (273 and 373) K, thus providing loose constraints on thermal functions.

5. Calculation of the LiOH·H_2O(s) and LiOH(s) Solubility Products and Their Standard Thermodynamic Properties from Their Solubilities in Pure Water

LiOH·H_2O(s) is the stable form of solid lithium hydroxide from (255 to 383) K. It dehydrates to anhydrous LiOH(s) at temperatures above that of the peritectics (Table 2). The solubility products of these two salts have been calculated for each temperature from the aqueous LiOH concentration, from the aqueous LiOH activity coefficient, and from the activity of water given by the LiOH(aq) model described above. These values then have be fitted to the following expression

$$\ln K_{sp} = A + \frac{B}{(T/\mathrm{K})} + C \ln(T/\mathrm{K}) \tag{12}$$

which assumes that the heat capacity of the reaction is constant over the considered temperature range. Parameters A, B, and C are reported in Table 5. If it is assumed that eq 12 is valid over the temperature range including the standard conditions (298.15 K), then the standard thermodynamic properties of the dissolution reaction can be retrieved from the A, B, and C parameters[25] (Table 5).

The standard enthalpy of formation of LiOH·H_2O(s) determined in this work is in agreement with the NBS[20] value within the estimated uncertainty, whereas the agreement between the values of the entropy and the heat capacity is only fair. The LiOH·H_2O(s) solubility product calculated using the NBS data is about 4 times higher than the values determined in this work at all temperatures (Figure 6). It was noticed that changing the sign of the entropy of the reaction of dissolution (i.e., using a value of -5.8 J·mol^{-1}·K^{-1} instead of the NBS value of 5.8 J·mol^{-1}·K^{-1}) brings the NBS values into very good agreement with the values determined in this work. This amounts to increasing the NBS value of the standard entropy of LiOH·H_2O(s) from 71.21 J·mol^{-1}·K^{-1} to 82.81 J·mol^{-1}·K^{-1}, in very close agreement with the value determined in this work (Table 5). This may be due to a sign error in the elaboration of the NBS tables or simply a coincidence.

The entropy of LiOH(s) determined here is in very good agreement with previous evaluations,[20,21] whereas the heat capacity value is about twice that determined from direct measurements. The discrepancies between the LiOH·H_2O(s) and LiOH(s) heat capacity values determined in this work and the literature values may reflect the loose constraints on the thermal functions calculated by the

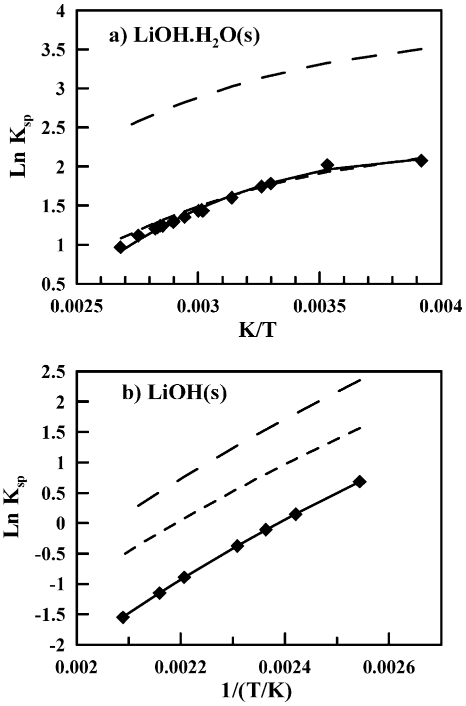

Figure 6. Arrhenius plot of the solubility products of the lithium hydroxides. (a) LiOH·H$_2$O(s). ■, Values calculated from the experimental solubilities and the LiOH(aq) model; solid curve, the fit to these values; long dashes, Wagman et al.;[20] short dashes, calculated using a corrected value for the enthalpy of dissolution. See the text. (b) LiOH(s). ■, Values calculated from the experimental solubilities and the LiOH(s) model; solid curve, fit to these values; long dashes, Wagman et al.;[20] short dashes, Gurvich et al.[21]

present model. (See above the discussion of the apparent heat capacity and Figure 5.) There is a noticeable discrepancy between the enthalpy values for LiOH(s). This results in values of the LiOH(s) solubility product that again show parallel trends when plotted versus temperature (Figure 6) but are offset by a factor of about 3 (difference between the values determined here and the NBS[20] values) or 5 (difference with the Gurvich et al.[21] values).

It then follows that the solubilities of either LiOH·H$_2$O(s) or LiOH(s) would be 2 to 5 times too large if consistency between the aqueous solution model for LiOH(aq) proposed in this work and the solubility products (or the standard thermodynamic properties) of the solid lithium hydroxides is not maintained.

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Received for review December 20, 2004. Accepted May 18, 2005.

JE0495482