

## ENTHALPY OF DISSOLUTION OF LiCl AND LiCl · H<sub>2</sub>O IN WATER AT 25 °C AT LOW CONCENTRATIONS

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### ABSTRACT

Enthalpy of dissolution of LiCl and LiCl·H<sub>2</sub>O in water was measured at 25 °C at low concentrations. The molar enthalpy of dissolution extrapolated to infinite dilution is  $\Delta_s H^\infty$  (LiCl, 25 °C) =  $-(37.11 \pm 0.35)$  kJ mol<sup>-1</sup> LiCl. The published values of  $\Delta_s H^\infty$  for both compounds were critically assessed and their reliability discussed. The comparison of measurements of previous authors reveals unidentified calorimetric errors.

### INTRODUCTION

Apelblat et al. [1] summarized some data of enthalpy of solution for the LiCl–H<sub>2</sub>O system and presented the results of their measurements for the anhydrous salt as well as for the monohydrate. Their finding of  $\Delta_s H^\infty = -36.65 \pm 0.12$  kJ mol<sup>-1</sup> for anhydrous LiCl agrees with those given by Lange and Dürr [2]; however, the values are close to the lower limit of a set of all data published, which range from  $\Delta_s H^\infty = -36.65$  to  $-37.63$  kJ mol<sup>-1</sup> LiCl (except the very low value  $-35.99$  [3] and a value of  $-36.36$  [4] which is based on a single measurement only). A comprehensive critical assessment of the thermochemical data for a wide range of temperatures (25–250 °C) was published by Holmes and Messmer [5] and their value for  $\Delta_s H^\infty$  (LiCl, 25 °C) =  $-36.94 \pm 0.36$  kJ mol<sup>-1</sup> LiCl represents a nearly precise arithmetic mean of a set given in Table 1 ( $\sim 37.0$  kJ mol<sup>-1</sup>). Values of  $\Delta_s H^\infty$  compiled from the literature were corrected to 25 °C using the equation

$$\Delta_s H^\infty(\vartheta) = -34.10 - 0.11343\vartheta \text{ (kJ mol}^{-1} \text{ LiCl)} \quad (1)$$

TABLE 1

Literature data for enthalpy of dissolution of anhydrous lithium chloride in water at 25 °C for an infinite dilution

Authors	Year	$-\Delta_s H^\infty$ (kJ mol <sup>-1</sup> LiCl)
Lange, Dürr [2]	1926	36.67 ± 0.10
Wassermann [6]	1930	37.17 ± 0.13
Askew, Bullock, Smith, Tinkler, Gatty, Wolfenden [4]	1934	36.36
Bichowsky, Rossini [7]	1936	37.24
Lange, Martin [8]	1937	37.50
Slansky [9]	1940	37.24
Rossini, Wagman, Evans, Levine, Jaffe [10] <sup>a</sup>	1952	37.14
Samoilov, Buslaeva [11]	1960	36.78 ± 0.42
Parker [12]	1965	37.05 ± 0.20
Somsen [14]	1966	37.20
Rodewald, Mahendran, Bear, Fuchs [15]	1968	37.03
Drakin, Yu-min [16]	1969	37.01 ± 0.1
Joly, Thourey, Perachon [3]	1973	35.99 ± 0.40
Tsvetkov, Tsvetkov [18]	1973	37.11 ± 0.20
Vorob'ev, Umiarova, Urusov [17]	1974	37.23 ± 0.10
Vorob'ev, Monajenkova, Padunova [19]	1977	37.05 ± 0.25
Vorob'ev, Privalova, Smirnova [20]	1977	36.89
Krestov, Egorova, Lyakushin, Korolyev [21]	1979	37.29 ± 0.1
Wagman, Evans, Parker, Schumm, Nuttall [22]	1981	36.97
Holmes, Mesmer [5]	1983	36.94 ± 0.36
Apelblat, Weintraub, Tamir [1]	1984	36.67 ± 0.10

<sup>a</sup> Cited according to Feakins, Smith and Thakur [13].

which for  $15 \leq \vartheta \leq 30$  °C approximately describes the temperature dependence given by Holmes and Mesmer [5] with a maximum difference of less than 0.01.

It should be noted that for similar simple alkali halides also the published data of  $\Delta_s H^\infty$  scatter more than LiCl, with few exceptions. For example, for KCl and NaCl, which are easily preparable with high purity and defined composition the difference between maximum and minimum values of the set of the data published amounts to  $\pm 0.27$  and  $\pm 0.40$  kJ mol<sup>-1</sup>, respectively [12]. Similarly, data for KBr and KI measured very carefully—by the National Bureau of Standards among others [23]—also show a surprisingly high uncertainty of  $\pm 0.35$  and  $\pm 0.85$  kJ mol<sup>-1</sup>, respectively. These unexplained discrepancies between the results from different sources are several times higher than experimental error estimated in individual laboratories.

The strongly hygroscopic nature of lithium chloride causes difficulties in handling this salt as well as problems connected with inexact stoichiometric water content in the monohydrate. Apelblat et al. [1] assumed that the amount of water in the salt exceeding its stoichiometric content is present in  $\text{LiCl} \cdot \text{H}_2\text{O}$  as a saturated aqueous solution. The scatter of the data published could be partly ascribed to these reasons. However, in our previous study [24], it was shown for three levels of water content in lithium chloride monohydrate that excess of water up to 1.07 mol  $\text{H}_2\text{O}$ /mol  $\text{LiCl}$  does not practically influence the enthalpy of dissolution within the given experimental error.

Since the differences in  $\Delta_s H^\infty$  of  $\text{LiCl}$  and  $\text{LiCl} \cdot \text{H}_2\text{O}$  between recent data (see Table 1), those of Apelblat et al. [1], and those measured by us [24] were not negligible, we decided to check their reliability by means of more careful measurements of the dissolution enthalpy of both salts in very dilute solutions.

## EXPERIMENTAL

The procedure for filling or closing ampoules and preparing the samples for analysis was carried out in a glove box. The box was filled with air and dried by means of a cold trap with liquid nitrogen. The vapour pressure of water corresponding to the value of  $\text{LiCl} \cdot \text{H}_2\text{O}$  was then fixed in the box by means of a saturated aqueous solution of  $\text{LiCl}$  in equilibrium with solid  $\text{LiCl} \cdot \text{H}_2\text{O}$ . For handling anhydrous  $\text{LiCl}$  the box was air-dried with  $\text{P}_4\text{O}_{10}$ . Lithium chloride (analytical grade, Merck) was used for preparation of samples.  $\text{LiCl} \cdot \text{H}_2\text{O}$  was prepared by dissolving  $\text{LiCl}$  in bidistilled water at  $65 \pm 5^\circ\text{C}$  and by crystallizing at  $25^\circ\text{C}$ . The crystalline material was then dried for two days at  $50^\circ\text{C}$ . Anhydrous  $\text{LiCl}$  was dried with  $\text{P}_4\text{O}_{10}$  at a lower pressure of  $\sim 10^3$  Pa at  $\sim 150^\circ\text{C}$  before measuring.

The water content in the prepared samples was determined by different methods: (i) by the Karl-Fischer titration method; (ii) indirectly by determination of the  $\text{Cl}^-$  anion concentration; and (iii) from analysing the TG curves. The sensitivity of the methods used was  $\pm 10^{-2}$  mol  $\text{H}_2\text{O}$ /mol  $\text{LiCl}$  in the case of the monohydrate, and  $\pm 10^{-4}$  mol  $\text{H}_2\text{O}$ /mol  $\text{LiCl}$  for the anhydrous salt.

In anhydrous salt a water content within experimental uncertainty was not detected. The content of water in the monohydrate ranged within the limit of  $1.00 \pm 0.01$  mol  $\text{H}_2\text{O}$ /mol  $\text{LiCl}$ .

The dissolution enthalpy was measured using a modified LKB 8700 calorimeter [25] with 100 ml reaction vessels. The NBS 724a standard reference material was used for calibration. All measurements were carried out at  $25^\circ\text{C}$ . The relative molar mass of  $M(\text{LiCl}) = 42.393$  and  $M(\text{LiCl} \cdot \text{H}_2\text{O}) = 60.408$  and the conversion factor  $1 \text{ cal} = 4.184 \text{ J}$  were used.

## RESULTS AND DISCUSSION

The results of our measurements on the anhydrous salt are summarized in Table 2 and shown in Fig. 1 together with results given previously by Apelblat et al. [1] and by us [24]. Results of studies on the monohydrate are similarly shown in Table 3 and in Fig. 2. For an extrapolation of the  $\Delta_s H$ -values to zero concentration a concentration dependence of relative apparent molal enthalpy of the solution is necessary. Older relative apparent molal enthalpy values were reviewed by Parker [12]. Apelblat et al. [1] used for this purpose a concentration dependence given by Fortier et al. [26], which does not differ significantly from that given by Parker [12] (Fig. 3). Integral enthalpy of dissolution of LiCl in water was approximately described by the equation

$$\Delta_s H^{\text{in}}(\text{LiCl}, 25^\circ \text{C}) = \Delta_s H^\infty + \phi_L(\sqrt{m}) \quad (2)$$

TABLE 2

Enthalpy of dissolution of lithium chloride in water at 25°C

$m \times 10^2$ (mol LiCl/1 kg H <sub>2</sub> O)	$-\Delta_s H$ (kJ mol <sup>-1</sup> LiCl)	$-\Delta_s H^\infty$ (kJ mol <sup>-1</sup> LiCl)	$-\Delta_s \bar{H}^\infty$ (kJ mol <sup>-1</sup> LiCl)
This work			
6.93	36.44	36.87	
6.93	36.37	36.80	
6.93	37.05	37.48	37.11 ± 0.35
6.93	36.85	37.28	
6.93	36.71	37.14	
Ref. 1 (operator Luna Wajsbrodt)			
6.705	36.243	36.664	
6.998	36.280	36.708	
7.738	36.177	36.624	
7.851	36.283	36.735	36.65 ± 0.12
8.278	36.279	36.739	
10.290	36.945	36.447	
Ref. 1. (operator Alexander Lorber) 36.67 ± 0.13			
3.768	36.669	36.992	
4.554	36.663	37.020	
4.597	35.449	36.808	
4.621	36.491	36.851	
4.688	36.023	36.385	36.67 ± 0.22
4.796	36.392	36.757	
4.876	36.151	36.519	
5.125	35.760	36.136	
5.679	36.213	36.606	
Ref. 24			
6.93	37.07	37.50	
6.93	37.05	37.48	
6.93	36.85	37.28	37.38 ± 0.21
6.93	36.82	37.25	

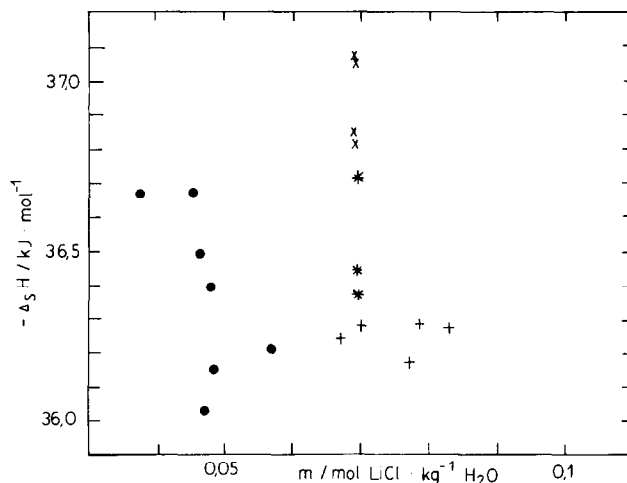


Fig. 1. Concentration dependence of enthalpy of dissolution of lithium chloride in water at 25°C.  $\Delta_s H$ , molar dissolution enthalpy in  $\text{kJ mol}^{-1}$  LiCl;  $m$ , molality in mol LiCl/1 kg  $\text{H}_2\text{O}$ ; \*, this work; ×, Wolf et al. [24]; ●, Apelblat et al. [1], operator Alexander Lorber; +, Apelblat et al. [1], operator Luna Wajsbrodt.

where  $m$  is molality in mol LiCl/1 kg  $\text{H}_2\text{O}$  and  $\phi_L$  is relative molal enthalpy of the solution defined as

$$\phi_L = \sum_{i=1}^5 a_i (\sqrt{m})^i \quad (3)$$

( $a_1 = -0.29955$ ,  $a_2 = -1.408417$ ,  $a_3 = 0.97913$ ,  $a_4 = -0.35007$ , and  $a_5 = 0.036087$ ) which fits experimental data given by Lange and Dürr [2] in the concentration range  $0.14 < m < 19.9$ . In the region  $m < 0.1$  the concentration dependence of  $\phi_L$  ( $m$ ) represented by eqn. (3) is distinctly inconsistent with those given by other authors [12,26], as is shown in Fig. 3. Since the concentration dependencies given by Fortier et al. [26] and Parker [12] are mutually consistent, we have preferred to use their data for calculating the  $\Delta_s H^\infty$  values.

In our previous paper [24] we neglected corrections of dilution enthalpy owing to the relatively small values of  $\phi_L$  for  $m < 0.1$  given by Lange and Dürr [2]. Therefore, we recalculated all our data by using the same source [26] for correction as did Apelblat et al. [1], and the resulting values of  $\Delta_s H^\infty$  are summarized in Tables 2 and 3.

Since there are few data for each quantity given by various authors, a 95% interval of reliability of the arithmetic mean  $\bar{x}$  of  $n$  selected individual values  $x_i$  was estimated as

$$\left\langle \bar{x} - t_\alpha^+ \left( \frac{s_x}{\sqrt{n}} \right); \bar{x} + t_\alpha^+ \left( \frac{s_x}{\sqrt{n}} \right) \right\rangle$$

TABLE 3

Enthalpy of dissolution of lithium chloride monohydrate in water at 25°C

$m \times 10^2$ (mol LiCl/1 kg H <sub>2</sub> O)	$-\Delta_s H$ (kJ mol <sup>-1</sup> LiCl)	$-\Delta_s H^\infty$ (kJ mol <sup>-1</sup> LiCl)	$-\Delta_s \bar{H}^\infty$ (kJ mol <sup>-1</sup> LiCl)
This work			
2.24	17.98	18.20	
2.78	18.04	18.30	
3.27	18.08	18.37	
4.27	17.94	18.28	
5.48	17.99	18.38	
5.55	17.89	18.28	18.29 ± 0.05
6.93	17.89	18.32	
6.93	17.88	18.31	
6.93	17.85	18.28	
6.93	17.75	18.18	
Ref. 1			
5.45	18.118	18.504	
5.51	18.154	18.542	
5.79	18.174	18.570	18.56 ± 0.09
5.83	18.235	18.632	
Ref. 24			
6.93	17.55	17.98	
6.93	17.65	18.08	
6.93	17.54	17.97	
6.93	17.64	18.07	18.00 ± 0.07
6.93	17.47	17.90	
6.93	17.60	18.03	

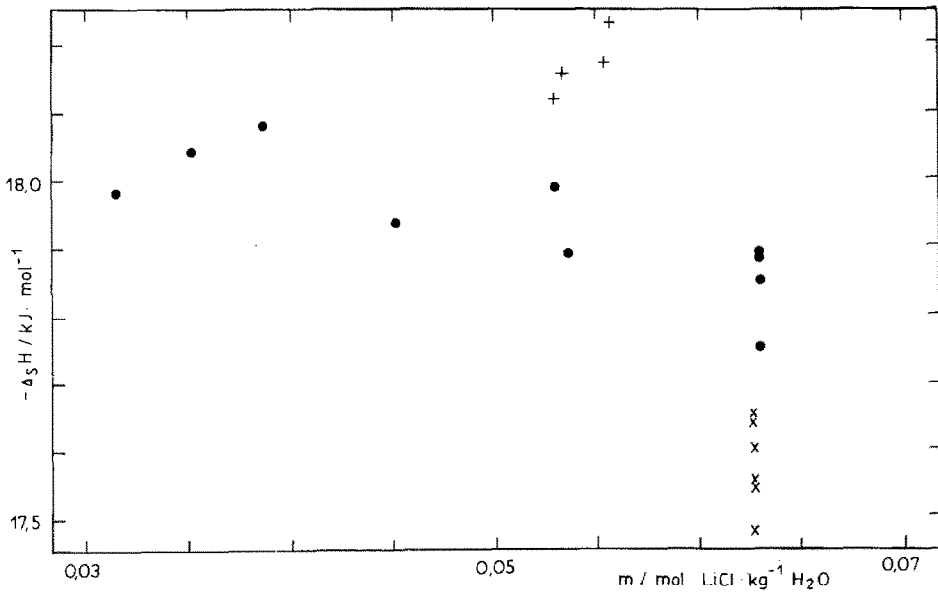


Fig. 2. Concentration dependence of enthalpy of dissolution of lithium chloride monohydrate in water at 25°C.  $\Delta_s H$ , molar dissolution enthalpy in kJ mol<sup>-1</sup>;  $m$ , molality in mol LiCl/1 kg H<sub>2</sub>O; ●, this work; ×, Wolf et al. [24]; +, Apelblat et al. [1].

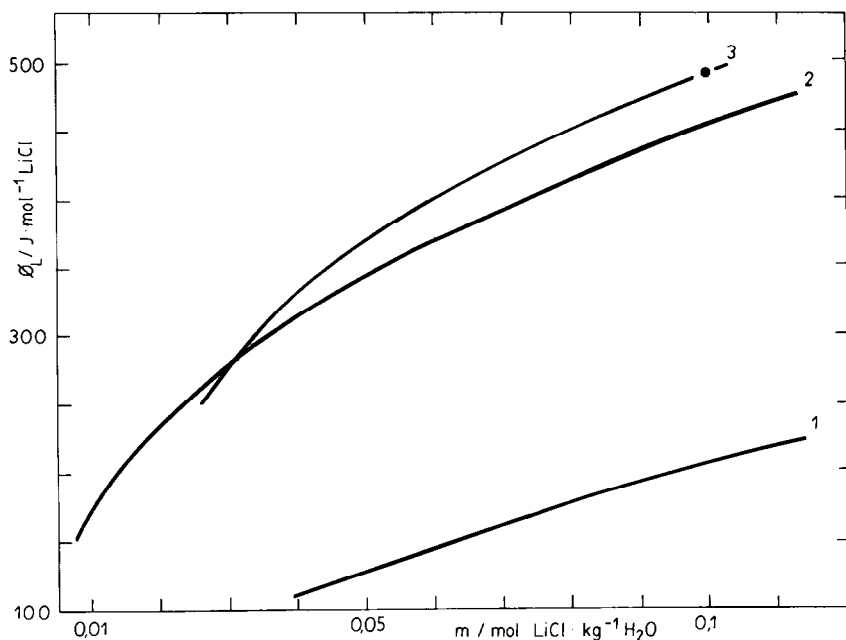


Fig. 3. Concentration dependence of relative apparent molal enthalpy for the LiCl-H<sub>2</sub>O system at 25 °C.  $\phi_L$ , relative apparent molal enthalpy in J mol<sup>-1</sup> LiCl;  $m$ , molality in mol LiCl/1 kg H<sub>2</sub>O; curve 1, calculated from eqn. (3) which approximates the data of Lange and Dürr [2]; curve 2, data given by Parker [12]; curve 3, data given by Fortier et al. [26]; ●, value given by Gibbard et al. [27].

where  $t_\alpha^+$  is a critical value of Student's distribution for  $n - 1$  degree of freedom for  $(1 - \alpha)$  probability level ( $\alpha = 0.05$ ),  $n$  is the number of values  $x_i$ ,  $\bar{x}$  is the arithmetic mean  $\Sigma x_i/n$ , and  $s_x$  is the standard deviation  $[(\Sigma x_i^2 - n\bar{x}^2)/(n - 1)]^{-1/2}$ . For each set of results these characteristics of  $\pm t_\alpha^+ s_x / \sqrt{n}$  were evaluated and are presented in Tables 2 and 3.

Our resulting value of  $-\Delta_s H^\infty$  (LiCl, 25 °C) =  $(37.11 \pm 0.35)$  kJ mol<sup>-1</sup> for the anhydrous salt represents a set of values published recently (see Table 1) quite well. However these values have not so far been assessed critically. From Table 1 it follows that only four sources of data [1-4] are outside the experimental uncertainty of  $\pm 0.35$  kJ mol<sup>-1</sup>.

For lithium chloride monohydrate only few data are available which differ from that in Table 3. From two values presented by Parker [12],  $\Delta_s H^\infty$  (LiCl · H<sub>2</sub>O, 18-23 °C) =  $-18.99$  kJ mol<sup>-1</sup> LiCl (based on 4 measurements in the range 0.28 to 0.40 mol LiCl/1 kg H<sub>2</sub>O) and  $\Delta_s H^\infty$  (LiCl · H<sub>2</sub>O, 19.5 °C) =  $-19.20$  kJ mol<sup>-1</sup> LiCl (based on a single measurement at  $m = 0.17$ ), he recommended the value of  $\Delta_s H^\infty$  (LiCl · H<sub>2</sub>O, 25 °C) =  $-19.08 \pm 0.40$  kJ mol<sup>-1</sup> LiCl [12]. A similar value is given by Slonim [28] with  $\Delta_s H^\infty$  (LiCl · H<sub>2</sub>O, 25 °C) =  $-18.90$  kJ mol<sup>-1</sup> LiCl (after correction according to eqn. (1) from 19.5 °C to 25 °C).

Values measured by Apelblat et al. [1] ( $-18.56 \pm 0.09$  kJ mol<sup>-1</sup>) and by us ( $-18.29 \pm 0.05$  and  $-18.00 \pm 0.07$  kJ mol<sup>-1</sup> LiCl [24]) are lower, but are based on more extensive experimental work. From comparison of Tables 2 and 3 it is evident that the experimental data obtained for each set of measurements are less scattered for the monohydrate than for the anhydrous salt. The difference between maximum and minimum values of different samples measured is, however, practically the same for both salts. The higher scatter in each set of measurements on the anhydrous salt can be explained by the strong hygroscopic behaviour of the anhydrous substance.

In measuring two different sample preparations of LiCl · H<sub>2</sub>O, the difference measured was greater than the sum of their standard deviations, although experimental apparatus and method was the same. We therefore suppose that the enthalpy of dissolution of LiCl · H<sub>2</sub>O is sensitive to the actual composition and nature of the compound studied. If it is assumed that an excess of water in the sample forms an equivalent amount of saturated solution, and this is corrected by means of enthalpy of dilution, the results do not agree with our value of  $\Delta_s H^\infty$  (LiCl · H<sub>2</sub>O) obtained for a salt of stoichiometric composition. Another source of discrepancy seems to be the temperature correction of the experimental data [12,29] to 25 °C.

The molar hydration enthalpy  $\Delta_H H$  of the hydration reaction LiCl(s) + H<sub>2</sub>O(l) → LiCl · H<sub>2</sub>O(s) is equal to the difference between both enthalpies of dissolution

$$\Delta_H H = \Delta_s H^\infty(\text{LiCl}) - \Delta_s H^\infty(\text{LiCl} \cdot \text{H}_2\text{O})$$

Using our values of  $\Delta_s H^\infty$  for both salts a value of  $\Delta_H H = -18.8 \pm 0.4$  kJ mol<sup>-1</sup> is obtained. The values published earlier are  $\Delta_H H = -18.09 \pm 0.14$  kJ mol<sup>-1</sup> [1];  $-17.95 \pm 0.63$  kJ mol<sup>-1</sup> [12]; and  $-17.57 \pm 0.42$  kJ mol<sup>-1</sup> [29].

The less exothermic values of  $\Delta_H H$  are caused by the more exothermic values of  $\Delta_s H^\infty(\text{LiCl} \cdot \text{H}_2\text{O})$  discussed above. Comparing the values of Apelblat et al. [1] with our values of  $\Delta_H H$ , it may be seen that the lower value given in ref. 1 is a consequence of the deviation of the value of  $\Delta_s H^\infty$  (LiCl) [1] from an average of all data published (Tables 2 and 3).

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