SOLID–GAS EQUILIBRIUM IN THE BINARY SYSTEM LITHIUM IODIDE–WATER*

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An investigation has been made of the equilibria of hydration in the system solid lithium iodide–water vapour in the temperature interval covering the range of existence of the solid hydrates, using a dynamic method in a flow apparatus. From measured equilibrium pressures, the changes of the thermodynamic functions accompanying these reactions were determined and the values of the heats of formation, of the Gibbs energies of formation and of the absolute entropies of the solid mono-, di- and trihydrate of lithium iodide at 298·15 K were calculated.

Some of the heterogeneous reactions of the lithium salts appeared recently as a part of reaction sequences which might constitute a basis for the production of hydrogen by a thermochemical method in a closed cycle of chemical reactions[1]. In connection with the investigation of these reactions, the necessity of the knowledge of the equilibria of hydration of lithium iodide arose, *i.e.* of the equilibria between water vapour and the solid phases, formed by lithium iodide and by its hydrates, respectively.

In the current literature, we have found only one paper dealing directly with an experimental determination of the vapour pressure in this system[2]; the method used there was a static one and the experiments were performed with solid phases at four temperatures. For the temperatures above 64°C, there are no direct experimental results available; such data are especially interesting when considering the above-mentioned connection of the hydration equilibria with other reactions of the lithium iodide. Some older papers[3,4], which were devoted to the study of aqueous solutions of lithium iodide and the results of which could – under certain assumptions – yield partial informations about the values of the saturated vapour pressure above the supposed solid phase, do not lead to mutually consistent results.

We decided, therefore, to investigate the above-mentioned hydration equilibria. The temperature and pressure interval were chosen in such a way that they were accessible with the normal arrangement of the dynamic equilibrium method. From experimental data obtained in this way, the changes of the thermodynamic functions

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accompanying these hydration reactions were calculated, and by combining them with the respective functions for the solid anhydrous lithium iodide and for the water vapour, the thermodynamic functions of the individual hydrates of lithium iodide were lastly determined.

According to the literature[5], the binary system LiI–H_2O can form several stable hydrates. The existence of the mono-, di- and trihydrate is confirmed by all the authors; some of them[3] even report the occurrence of the hemihydrate, while other authors[2] argue against it. Already now we can state that even in our experiments the existence of the hemihydrate has not been observed. Therefore, our experimental study of the heterogeneous hydration reactions covered the measurement of equilibrium conditions in the following systems of the type gas (g) – two solid phases (s):

$$\text{LiI (s)} + \text{H}_2\text{O (g)} = \text{LiI.H}_2\text{O (s)} \qquad (A)$$

$$\text{LiI.H}_2\text{O (s)} + \text{H}_2\text{O (g)} = \text{LiI.2 H}_2\text{O (s)} \qquad (B)$$

$$\text{LiI.2 H}_2\text{O (s)} + \text{H}_2\text{O (g)} = \text{LiI.3 H}_2\text{O (s)} \qquad (C)$$

The equilibrium constants of these reactions in terms of activities are given by the same formula:

$$K = 1{\cdot}013 \,.\, 10^5 \,(\mathrm{P}_{\mathrm{H_2O}})^{-1}\,, \qquad (1)$$

where $P_{\mathrm{H_2O}}$ denotes the equilibrium value of the vapour pressure of water in Pa in the system under investigation – *i.e.* (*A*), (*B*) or (*C*) – at the given temperature. The standard state for water vapour was chosen as the ideal gas with the fugacity equal to $1{\cdot}013 \,.\, 10^5$ Pa and at the temperature of the system. Because of the low values of pressure, its effect on the unit activities of pure solids could be neglected. Under these circumstances, the equilibrium constants of the reactions (*A*), (*B*) and (*C*) are therefore functions of temperature only. The values of $P_{\mathrm{H_2O}}$ represent the equilibrium vapour pressures over the two solid phases in reaction (*A*), (*B*) or (*C*) for the temperatures in question.

The dynamic method and the experimental arrangement used here were esentially the same as in some of the previous investigations[6,7]. In contrast with the previous studies, however, the orientation experiments already have shown[8] that these systems manifest relatively easily metastable values of vapour pressures, even at temperatures beyond the range of equilibrium existence of individual hydrates, supposed on the basis of solubility measurements[9]. To get reliable equilibrium values of the vapour pressures, it was therefore necessary to check very carefully the attainment of equilibrium at every point; this proved to be a time-consuming task especially in the case of reaction (*A*), namely at lower temperatures.

EXPERIMENTAL

Substances Used

Lithium iodide — a reagent grade product (BDH Chemicals) has been used after recrystallization from redistilled water under reduced pressure. The analysis of the original product led to the following result (in per cent by weight): 89·4% of LiI, the remainder being H_2O (the manufacturer gives these amounts of impurities in per cent by weight: As 0·0002; Fe 0·001; Pb 0·002; SO_4 0·03). The recrystallization led to a product which was practically the dihydrate of this salt, the content of water being 23·0% by wt. The content of carbonate was determined by titration with hydrochlorid acid; its amount did not pass over 0·2% by wt. The content of iodide was determined by argentometry and the content of water by titration using the method of K. Fischer.

Nitrogen from a cylinder has been used as the carrier gas; it was the purest commercially obtainable nitrogen, declared as "nitrogen for bulbs". The remaining reagents used for analyses were altogether of analytical purity and redistilled water was used throughout the experiments.

Apparatus and Experimental Procedure

The flow apparatus with the absorbers for the measurement of equilibrium pressures of water vapour over the respective pairs of hydrates was essentially the same as in one of the previous parts in this series[6]; when compared with the original arrangement, some minor changes were introduced, *i.e.*: the tower for drying the carrier gas was prolonged and filled with anhydrous magnesium perchlorate; the preheater of the carrier gas entering the reactor was also prolonged; the bed thickness in the reactor was increased by about a quarter of the original value, and the ratio between the inert part and the reactive solids in the reactor was also increased, in order to enlarge the surface of the solid phases freely accessible to the flowing gas.

As far as the characterization of the solid phase in the reactor was concerned, it was even with these systems impossible — similarly as in the previous study[7] — to supplement the equilibrium measurements with a reliable X-ray analysis of the equilibrium solid mixture. The opening of the reactor and the following handling of the samples led immediately to such a deliquescence that the corresponding diffractograms were distorted; therefore the X-ray analysis allowed only to check the starting solid substance inserted into the reactor at the ambient temperature.

RESULTS AND DISCUSSION

Because of the relatively low values of the equilibrium pressures of water vapour in all the three reactions (A), (B) and (C), it was possible in all these three systems to check the attainment of equilibrium from both sides, *i.e.* by increasing or decreasing the temperature in the reactor and by changing the water content in the carrier gas entering the reactor from values substantially lower than was the expected equilibrium value, to values substantially higher.

The results of the equilibrium measurements, fulfilling in all the instances the criterion of a long-term stability of the measured tensions of water vapour leaving the reactor, are given in Table I. As was stated earlier, we did not observe in all our experiments even after an extremely long time and after a most intensive drying any decrease of the water tension to a time-independent value that would correspond to

TABLE I

Equilibrium vapour pressures

t, °C	P, Pa
	system LiI–LiI.H_2O
63·8	11
63·9	11, 11, 9
64·0	11, 11, 11, 9, 11, 11, 9, 12, 13
64·1	12, 9, 12, 9
70·9	17
71·0	19, 19, 17, 21
74·0	24, 24
75·0	27, 24, 28, 23, 28, 32, 27, 31, 27, 27, 29, 29, 31, 24, 24, 25
80·0	39, 43, 36, 41, 41, 39, 39, 41
82·7	48, 48, 48, 52
82·8	53, 48, 48
90·0	81, 91, 81, 88, 87, 85, 81, 72, 83, 81, 87, 80
100·0	157, 157, 164, 164, 155, 164
104·0	200, 200, 193, 201, 200
109·9	285
110·0	281, 284, 279, 277, 283, 277, 283, 283, 277, 284, 289
110·1	283, 285, 281
110·2	280
120·0	455, 477, 477, 497, 451, 463, 461, 460, 445
	system LiI.H_2O–LiI.2 H_2O
53·5	53, 57, 61, 56, 59, 55
64·0	124
70·0	185, 205, 199, 183, 209, 199, 197, 188, 192, 189, 191
71·0	220, 233
71·1	220, 220, 217
75·0	301, 261, 261, 288, 273, 285, 263, 260, 249, 292, 300, 279, 303, 228, 244, 276, 260, 279, 245, 255, 248
77·0	337, 331, 336
77·1	331
	system LiI.2 H_2O–LiI.3 H_2O
43·1	135, 140, 144, 133, 137, 128, 139, 152, 132, 139, 140, 140
50·0	228, 224
53·5	265, 268
60·0	463, 479, 453, 456

an intermediary phase between the monohydrate and the anhydrous lithium iodide. Therefore, we do not confirm the existence of the hemihydrate, allegedly observed by some authors, and the data given in the tables consequently correspond to the reactions (*A*), (*B*) and (*C*). The accuracy of the results obtained in individual cases is obvious from the small scattering of the respective data.

The values of equilibrium tensions obtained at various temperatures yielded linear dependencies of $\log P_{H_2O}$ on $1/T$ which were treated by the method of the least squares. The analytic expression of these dependencies is given by the following equations for the individual systems:

$$(A) \qquad \log P_{H_2O} = -\frac{3\,934}{T} + 12{\cdot}72 \qquad (2)$$

$$(B) \qquad \log P_{H_2O} = -\frac{3\,605}{T} + 12{\cdot}79 \qquad (3)$$

$$(C) \qquad \log P_{H_2O} = -\frac{3\,179}{T} + 12{\cdot}19\,. \qquad (4)$$

The unit of pressure is Pa, the temperature is given in K. From the least-squares adjustment it follows that the average value of the relative error of the constants in these equations amounts to ±3 per cent.

Our results can, at least partially, be compared with some data found in the literature. Such a comparison is summarized in the following tables. It has been carried out both for the experimental results and for the data derived from them, in order to emphasize the consistency of our results with the results obtained by other experimental techniques, and to accentuate some questionable points.

For the sake of information, we give in Table II the values of vapour pressure from the literature[2,4] at 18°C. These data were also obtained by measuring the vapour pressure over the solid phases, although by a quite different method. To allow the comparison, it was necessary to extrapolate our relations (*2*), (*3*) and (*4*) to this temperature. Further, we give in Table II some data from the literature[9,5] for conditions described as eutectic points of the systems containing the hydrates of lithium iodide and water. If we accept the description of the solubility conditions in the system $LiI-H_2O$ according to the literature[3,5,9] with the congruent melting points of the respective hydrates, it is possible to compare the values of the vapour pressures in the eutectic points of the respective phase diagram[9] with the values obtained from our equations (*2*) to (*4*) which are valid even for these points. All the pressure values have been recalculated and are given in Pa.

Because the paper cited above[9] guarantees an approximate value of vapour pressure only, the agreement of the results is relatively very good. The exceptionally good agreement of the results for the last compared system convinces us that in the paper cited[9], the case of the eutectic with the highest temperature also corresponds to the system monohydrate–anhydrous iodide, and not to the system monohydrate–hemihydrate as is given there[9].

Combining relations (*2*) to (*4*) with the equation (*1*), we get the following expressions for the temperature dependency of the equilibrium constants of the respective reactions:

$$(A) \qquad \log K = \frac{3\,934}{T} - 7{\cdot}72 \qquad (5)$$

$$(B) \qquad \log K = \frac{3\,605}{T} - 7{\cdot}79 \qquad (6)$$

$$(C) \qquad \log K = \frac{3\,179}{T} - 7{\cdot}19\,. \qquad (7)$$

The temperature intervals in which the relations (*5*) to (*7*) are experimentally verified are the same as for the equations (*2*) to (*4*), *i.e.* 64–110°C for the system (*A*), 53 to 77°C for (*B*) and 43–60°C for (*C*). Because of a very good linearity of the relations (*2*) to (*4*), it is of course possible to make reliable extrapolations of the equations (*2*) to (*7*) beyond these intervals, especially to lower temperatures, where the very low values of the vapour pressure would make the experimental determination by our method rather difficult. The upper limits for extrapolation are represented by the melting points of the individual hydrates.

TABLE II

Comparison of vapour pressure data for the systems (*A*)–(*C*)

Reference[a]	(*A*) *t*, °C	*P*, Pa		(*B*) *t*, °C	*P*, Pa		(*C*) *t*, °C	*P*, Pa	
4	18	0·02	(0·16)	18	1·2	(2·6)	18	18·7	(18·7)
2	18·2	0·4	(0·16)	18·2	5·1	(2·6)	18·2	37·1	(19·0)
9	130	866[b]	(916)	77	600	(312)	70·5	933	(869)
5	129	866[b]	(866)	78·2	600	(338)	70·5	933	(869)

[a] Data in parentheses: this paper. [b] In the original paper (see[5,9]) assumed to be valid for the system monohydrate–hemihydrate, not monohydrate–anhydrous salt.

For the changes of thermodynamic functions accompanying the reactions (*A*), (*B*) and (*C*) and valid in the respective temperature intervals, we get from equations (*5*) to (*7*) the data summarized in Table III, together with the enthalpy changes calculated from other experimental data; as can be seen, these heats of reaction taken from the literature do not show a good mutual agreement. The enthalpy changes accompanying the dissociation of the hydrates[2] are given in Table III with opposite signs to comply with the course of the respective reactions (*A*), (*B*) and (*C*). The deviations of these values from our data can be explained by the fact that the linear dependence of $\log K$ on $1/T$ has in all cases a steep slope; a small number of experimental data used for the construction of such a dependence – as in the case of ref.[2] – can lead to large differences in the calculated values of enthalpy changes. We have observed this also in our orientation experiments[8]. The heats of hydration calculated from the solubilities using an approximative method[3] can be considered to be in a satisfactory agreement with our values when taking into account the method of calculation used. The last column in Table III contains the values of the standard reaction enthalpy changes calculated from the standard enthalpies of formation of

TABLE III

Changes of thermodynamic properties accompanying reactions (*A*)—(*C*)

System	Property	Value		
		this paper		
(*A*)	ΔG°	$-(75\cdot3 \pm 2\cdot2) + (147\cdot8 \pm 4\cdot4) \,.\, 10^{-3}\,T$ kJ.mol^{-1}		
	ΔH°	$-(75\cdot3 \pm 2\cdot2)$ kJ.mol^{-1}		
	ΔS°	$-(147\cdot8 \pm 4\cdot4) \,.\, 10^{-3}$ kJ.K^{-1} mol^{-1}		
(*B*)	ΔG°	$-(69\cdot0 \pm 2\cdot1) + (149\cdot1 \pm 4\cdot4) \,.\, 10^{-3}\,T$ kJ.mol^{-1}		
	ΔH°	$-(69\cdot0 \pm 2\cdot1)$ kJ.mol^{-1}		
	ΔS°	$-(149\cdot1 \pm 4\cdot4) \,.\, 10^{-3}$ kJ.K^{-1} mol^{-1}		
(*C*)	ΔG°	$-(60\cdot9 \pm 1\cdot8) + (137\cdot6 \pm 4\cdot1) \,.\, 10^{-3}\,T$ kJ.mol^{-1}		
	ΔH°	$-(60\cdot9 \pm 1\cdot8)$ kJ.mol^{-1}		
	ΔS°	$-(137\cdot6 \pm 4\cdot1) \,.\, 10^{-3}$ kJ.K^{-1} mol^{-1}		
		calculated from literature data		
		ref.[2]	ref.[3]	ref.[11,12]
(*A*)	ΔH°	$-62\cdot8 \pm 6\cdot3$	$-81\cdot1$	$-77\cdot70_5$
(*B*)	kJ.mol^{-1}	$-54\cdot4 \pm 6\cdot3$	$-68\cdot6$	$-58\cdot87_7$
(*C*)		$-46\cdot0 \pm 6\cdot3$	$-66\cdot9$	$-59\cdot38_0$

the substances involved at 298·15 K. As far as the latter values are concerned, the data in the literature are likewise not in a good mutual agreement, especially in the case of higher hydrates[10,11]. The values of reaction enthalpy changes given in Table III have been derived from the standard enthalpies of formation of water vapour and of anhydrous iodide[12] and of the respective hydrates[11].

As a criterion of the consistency of our results, we can use the values of entropy changes accompanying the reactions (*A*) to (*C*). We have found no data in the literature enabling us to compare them with our values; yet nearly the same entropy changes for the reactions (*A*) and (*B*) and only a slightly different entropy change for (*C*) are in a very good agreement with the rule according to which the entropy increment caused by the addition of one mole of the hydrate water to a solid substance is costant[13].

Therefore, the values of the changes of thermodynamic properties obtained here can be considered as sufficiently accurate and precise. Both this fact and the possibility of a reliable extrapolation of all the temperature dependencies found here to lower temperatures allow the combination of the values of the changes of thermodynamic properties accompanying the rections (*A*), (*B*) and (*C*) with the published values of these quantities for solid anhydrous lithium iodide and for water vapour for the calculation of the respective properties for the individual hydrates of lithium iodide. For this calculation, the following values of the thermodynamic properties, all at 298·15 K, have been used[12]: LiI (s) $\Delta H_f^0 = -271{\cdot}081$ kJ . mol^{-1}, $\Delta G_f^0 = -266{\cdot}92$ kJ . mol^{-1}, $S^0 = 73{\cdot}22$ J . K^{-1} mol^{-1}; H_2O (g) $\Delta H_f^0 = -241{\cdot}83$ kJ . mol^{-1}, $\Delta G_f^0 = -228{\cdot}60$ kJ . mol^{-1}, $S^0 = 188{\cdot}72$ J . K^{-1} mol^{-1}.

From these data and from our results given in Table III, the enthalpies of formation, the Gibbs energies of formation and the absolute entropies of solid lithium iodide hydrates have been calculated at 298·15 K. The calculated values are given in Table

TABLE IV

Thermodynamic properties of solid lithium iodide hydrates at 298·15 K

Property	$LiI.H_2O$	$LiI.2\,H_2O$	$LiI.3\,H_2O$
ΔH_f^0 kJ.mol^{-1}	—588·2	—899·0	—1 201·8
ΔG_f^0 kJ.mol^{-1}	—526·7	—779·9	—1 028·4
S^0 J.K^{-1} mol^{-1}	114·1	153·7	204·8
ΔH_f^0 kJ.mol^{-1} [a]	—590·6	—891·3	—1 192·5

[a] Taken from ref.[11].

IV; their preciseness corresponds to that of the data given in Table III. For the sake of comparison, the values of the enthalpy of formation of the hydrates at 298·15 K taken from the literature[11] are also given; these values seem to us the most reliale ones from the collection of several published and mutually contradicting data, as stated above. It was impossible to make a similar comparison in the case of the remaining thermodynamic functions because these data are lacking in the literature. We can only state that the values of the absolute entropies of the anhydrous lithium iodide and of its hydrates yield for the contribution of one mol of the hydrate water to the value of the absolute entropy of a solid substance 41, 40 and 51 $J . K^{-1} mol^{-1}$, respectively. These experimental values – especially the first and the second one – are consistent with the estimated constant value of this increment which according to the literature[13] should be approximately 39 $J . K^{-1} mol^{-1}$.

The analysis of the experimental data obtained in this paper and their treatment as given above leads to the conclusion that our experimental results yield reliable information on the chemical equilibria in the system LiI–H_2O and on the thermodynamic quantities of the lithium iodide hydrates.

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