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Determination of the Vapor Pressures of Lithium Iodide and Potassium Chloride by Molecular Beam Surface Ionization

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Combined techniques of molecular beam effusion from a Knudsen cell and of positive surface ionization on a heated polycrystalline rhenium filament were employed to determine the vapor pressures P (in atm) of LiI and KCl as a function of cell temperature T (in K), thereby yielding the equations:

$$\log_{10} P(\mathrm{LiI})=(7.498\pm0.046)-(9254\pm30)/T \text{ for } 583\text{—}717 \text{ K},$$

$$\log_{10} P(\mathrm{KCl})=(7.210\pm0.058)-(11135\pm45)/T \text{ for } 687\text{—}877 \text{ K}.$$

The present data on the pressure and on both entropy and enthalpy of sublimation are compared with others in literature.

In the research fields of thermochemistry and molecular beam chemistry, it is one of the important problems to know the accurate value of vapor pressure at a given temperature. From this point of view, we have been trying to determine the vapor pressures of alkali-metal halides after having developed a technique of molecular beam surface ionization, and we have already published some of the results thus obtained with CsF and CsCl[1] and with LiCl and NaBr.[2] In this paper we describe the experimental results obtained with LiI and KCl.

Experimental

In the same manner as in the previous works,[1,2] a molecular beam of an alkali-metal halide (MX) effusing from a Knudsen cell heated to a temperature (T) was directed onto a polycrystalline rhenium filament (F) kept at a high temperature (T_F) in the residual gas pressue of about 3×10^{-5} Pa. The total ion current ($I^+(M^+)$) of an alkali-metal ion (M^+) emitted from F was measured as a function of T or T_F. The samples of LiI and KCl used in this work were obtained from Aldrich Chem. Co., Inc. and Wako Pure Chem. Ind., Ltd., respectively.

Results and Discussion

In order to find a filament temperature suitable for producing M^+ from MX under study, $I^+(M^+)$ was measured as a function of T_F while the Knudsen cell was kept at a constant temperature such as T=766, 761, 686, or 627 K for LiI or as T=877, 874, or 763 K for KCl. Two examples of the results thus obtained are illustrated in Fig. 1. The reason why the two are quite different in emission pattern may be explained reasonably[3] by our previous theory[4] that the degrees of both dissociation of MX and ionization of M depend upon the effective work function for positive surface ionization. As may be seen in Fig. 1, $I^+(Li^+)$ and $I^+(K^+)$ are virtually constant at 3.10 ± 0.08 and 13.1 ± 0.4 nA in the ranges $T_F\simeq1280$—1390 and $\gtrsim1050$ K, respectively. These results indicate that the ionization efficiencies of LiI and KCl incident upon F are virtually unity in the respective ranges. Consequently, F was kept at a constant temperature in either of the above ranges, and $I^+(M^+)$ was measured as a function of T. The vapor pressure is given by[1]

$$P(\mathrm{MX}) = 0.0144\, S_C^{-1}[M(\mathrm{MX})\; T]^{1/2}\, I^+(\mathrm{M}^+), \qquad (1)$$

where P(MX) and $I^+(M^+)$ are expressed in atm and ampere, respectively, and M(MX) is the molecular weight of MX. The values of the effusing slit area S_C were 1.13×10^{-2} and 1.46×10^{-2} cm^2 in the experiments with LiI and KCl, respectively.

The data on P(MX) determined in this work are summarized in Table 1, and they are illustrated in Figs. 2 and 3, leading to a general expression:

$$\log_{10} P(\mathrm{MX}) = A - B/T. \qquad (2)$$

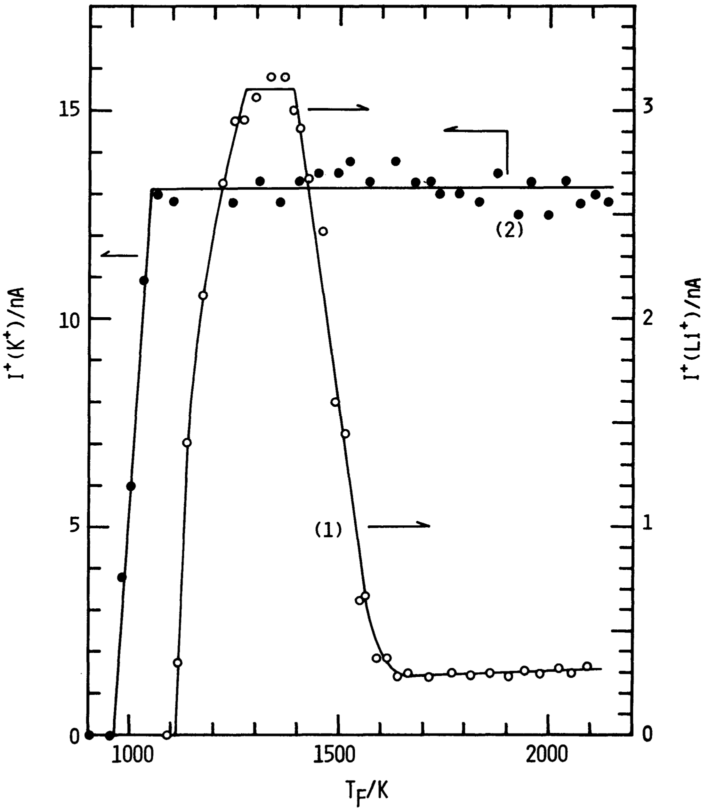

Fig. 1. Dependence of the total ion current ($I^+(M^+)$) upon the filament temperature (T_F) at a constant cell-temperature (T).
(1): Li^+ from LiI at T=686 K, (2): K^+ from KCl at T=874 K.

TABLE 1. VAPOR PRESSURES DETERMINED IN THIS WORK

Sample	T_F/K	T/K	P(MX)/atm	T_F/K	T/K	P(MX)/atm
LiI	1309	717	3.73×10^{-6}	1299	706	2.47×10^{-6}
		701	1.95×10^{-6}		688	1.11×10^{-6}
		681	8.43×10^{-7}		674	5.81×10^{-7}
		669	4.86×10^{-7}		662	3.36×10^{-7}
		650	1.76×10^{-7}		640	1.09×10^{-7}
		634	8.08×10^{-8}		621	4.07×10^{-8}
		611	2.27×10^{-8}		603	1.40×10^{-8}
		596	9.13×10^{-9}		583	4.17×10^{-9}
KCl	2113	877	3.15×10^{-6}	1588	874	3.19×10^{-6}
		860	1.64×10^{-6}		855	1.58×10^{-6}
		841	8.49×10^{-7}		836	7.72×10^{-7}
		818	3.58×10^{-7}		824	4.83×10^{-7}
		796	1.60×10^{-7}		804	2.36×10^{-7}
		777	7.30×10^{-8}		786	1.08×10^{-7}
		753	2.64×10^{-8}		764	4.20×10^{-8}
		738	1.28×10^{-8}		742	1.69×10^{-8}
		723	6.35×10^{-9}		729	8.32×10^{-9}
		704	2.36×10^{-9}		715	4.22×10^{-9}
		687	1.11×10^{-9}		692	1.26×10^{-9}
	1193	866	2.38×10^{-6}	1193	765	4.66×10^{-8}
		847	1.23×10^{-6}		744	1.80×10^{-8}
		827	6.22×10^{-7}		729	8.88×10^{-9}
		807	2.75×10^{-7}		714	4.01×10^{-9}
		787	1.21×10^{-7}		696	1.68×10^{-9}

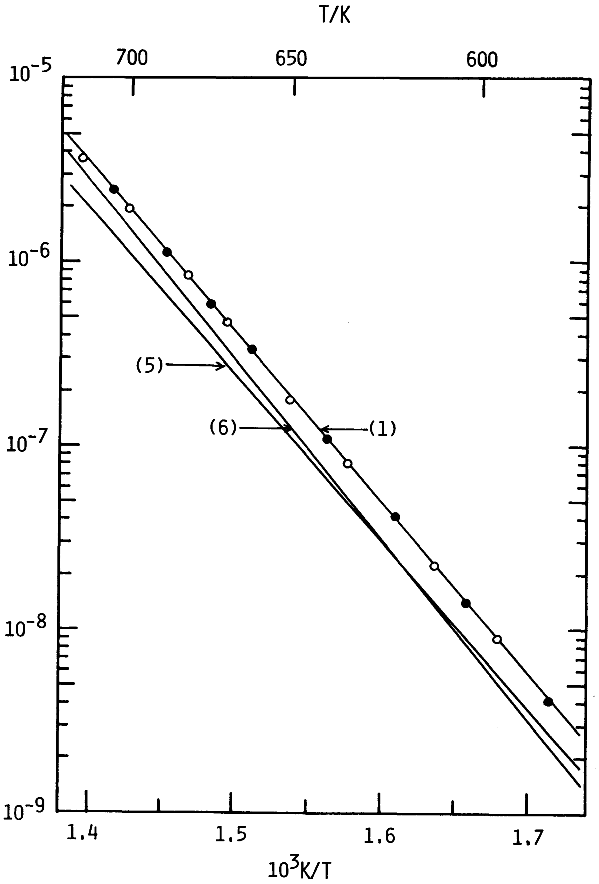

Fig. 2. Temperature dependence of the vapor pressure of LiI.

(1): This work at T_F=1309 K (open circle) or 1299 K (solid circle), (5): Ref. 5, (6): Ref. 6.

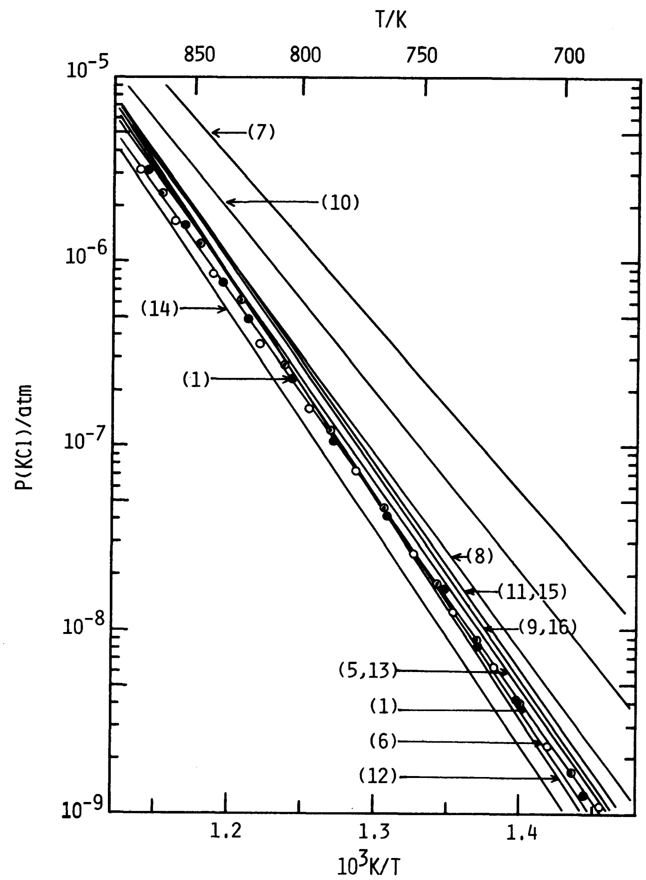

Fig. 3. Temperature dependence of the vapor pressure of KCl.

(1): This work at T_F=2113 K (open circle), 1588 K (solid circle), or 1193 K (double circle), (5, 13): Refs. 5 and 13, (6): Ref. 6, (7): Ref. 7, (8): Ref. 8, (9, 16): Refs. 9 and 16, (10): Refs. 10, (11, 15): Refs. 11 and 15, (12): Ref. 12, (14): Ref. 14.

TABLE 2. SUMMARY OF THE EXPERIMENTAL DATA OBTAINED BY THE PRESENT AND OTHER WORKERS

Sample	T_{R} / K	$\bar{T}$ / K	A	B / K	P(MX)/μatm			$\Delta S(\bar{T})$ / cal* mol^{-1} K^{-1}	$\Delta S(300)$ / cal mol^{-1} K^{-1}	$\Delta H(\bar{T})$ / kcal mol^{-1}	$\Delta H(300)$ / kcal mol^{-1}	Ref.
					600 K	700 K	800 K					
LiI	500-700	600	7.000±0.057	9081±33	0.00733	1.06	—	32.0±0.3	35.3±0.3	41.6±0.2	43.0±0.2	5
	574-697	636	8.094±0.156	9752±98	0.00693	1.45	—	37.0±0.7	40.5±0.8	44.6±0.4	46.2±0.5	6
	596-717	657	7.486±0.093	9247±61	0.0119	1.89	—	34.3±0.4	37.9±0.5	42.3±0.3	44.0±0.3	(a)
	583-706	645	7.513±0.040	9263±26	0.0119	1.91	—	34.4±0.2	37.9±0.2	42.4±0.1	44.0±0.1	(b)
	583-717	650	7.498±0.046	9254±30	0.0119	1.90	—	34.3±0.2	37.9±0.2	42.3±0.1	44.0±0.1	(A)
KCl	600-900	750	7.360±0.047	11207±34	—	0.00224	0.225	33.7±0.2	37.8±0.2	51.3±0.2	53.3±0.2	5
	693-989	841	7.936±0.089	11682±98	—	0.00177	0.216	36.3±0.4	41.0±0.5	53.4±0.4	55.9±0.5	6
	821-1407	1114	5.389	9027	—	0.0311	1.27	24.7	30.6	41.3	45.0	7
	853-955	904	6.837±0.035	10685±45	—	0.00374	0.303	31.3±0.2	36.3±0.2	48.9±0.2	51.6±0.2	8
	819-945	882	7.574	11324	—	0.00249	0.262	34.7	39.5	51.8	54.4	9
	818-1118	968	6.016	9788	—	0.0108	0.604	27.5	32.8	44.8	47.8	10
	859-1024	942	7.318±0.040	11116±37	—	0.00274	0.265	33.5±0.2	38.7±0.2	50.9±0.2	53.8±0.2	11
	899-935	917	8.289±0.329	11981±409	—	0.00149	0.206	37.9±1.5	43.0±1.7	54.8±1.9	57.6±2.0	12
	847-936	892	7.352±0.067	11207±109	—	0.00220	0.220	33.6±0.3	38.6±0.4	51.3±0.5	54.0±0.5	13
	898-959	929	7.695±0.170	11658±281	—	0.00110	0.133	35.2±0.8	40.3±0.9	53.3±1.3	56.2±1.4	14
	624-945	785	7.395±0.053	11154±56	—	0.00289	0.283	33.8±0.2	38.2±0.3	51.0±0.3	53.2±0.3	15
	711-870	791	7.570	11310	—	0.00259	0.271	34.6	39.1	51.7	54.0	16
	687-877	782	6.976±0.071	10966±54	—	0.00204	0.186	31.9±0.3	36.3±0.4	50.2±0.2	52.4±0.3	(c)
	692-874	783	7.337±0.065	11234±50	—	0.00194	0.197	33.6±0.3	37.9±0.3	51.4±0.2	53.6±0.2	(d)
	696-866	781	7.376±0.050	11249±39	—	0.00202	0.206	33.8±0.2	38.1±0.3	51.5±0.2	53.6±0.2	(e)
	687-877	782	7.210±0.058	11135±45	—	0.00201	0.196	33.0±0.3	37.3±0.3	50.9±0.2	53.1±0.2	(B)

*1 cal=4.184 J.

The values of A and B determined by the present and other workers are summarized in Table 2. The entropy and enthalpy changes due to sublimation at the mean temperature ($\bar{T}$) in the range (T_{R}) covered in each measurement and also those at 300 K were evaluated from Eqs. 3—6, respectively, in order to compare the latter with literature values at the same temperature (see Table 2).

$$\Delta S(\bar{T}) = 4.575\,A \text{ cal mol}^{-1}\text{ K}^{-1}, \tag{3}$$

$$\Delta H(\bar{T}) = 4.575\times 10^{-3}\,B \text{ kcal mol}^{-1}, \tag{4}$$

$$\begin{aligned}\Delta S(300) &= \Delta S(\bar{T}) + \int_{300}^{\bar{T}}\left[\frac{C_{\mathrm{p}}(\mathrm{c})-C_{\mathrm{p}}(\mathrm{g})}{T}\right]\mathrm{d}T \\ &\simeq \Delta S(\bar{T}) + aR[\ln \bar{T} - \ln 300],\end{aligned} \tag{5}$$

$$\begin{aligned}\Delta H(300) &= \Delta H(\bar{T}) + \int_{300}^{\bar{T}}[C_{\mathrm{p}}(\mathrm{c})-C_{\mathrm{p}}(\mathrm{g})]\mathrm{d}T \\ &\simeq \Delta H(\bar{T}) + aR[\bar{T}-300].\end{aligned} \tag{6}$$

Here, 1 cal is equal to 4.184 J, and $C_{\mathrm{p}}(\mathrm{c})$ and $C_{\mathrm{p}}(\mathrm{g})$ are the specific heats of MX at crystalline and gaseous states at 1 atm, respectively. On the basis of data on the heats,[5] the values of a in the ranges 300—650 and 300—850 K may be taken as 2.35 and 2.28 for LiI and KCl, respectively.

The values of T_{F} in the present works indicated as (a)—(e) in the last column in Table 2 were 1309, 1299, 2113, 1588, and 1193 K, respectively. The present works (A) and (B) indicate the mean values of those (a) and (b) and those (c)—(e), respectively.

To the best of our knowledge, it is from Refs. 5 and 6 alone that the data on P(LiI) below a melting point (719 K) are available today. As may be seen in Fig. 2 and Table 2, the data on P(LiI) do not agree well with each other among the three, suggesting the necessity of further measurements by many workers using various experimental methods. Both Fig. 3 and Table 2 show that the values of P(KCl) measured in this work are very close to those in Refs. 5, 6, and 13, and also suggest that the data in Refs. 7 and 10 are very poor in reliability probably because of systematic errors.

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