Determination of the Vapor Pressures of Lithium Chloride and Sodium Bromide by a Molecular Effusion-Surface Ionization Method

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Synopsis. By means of molecular effusion from a Knudsen cell and of thermal positive ionization on a glowing polycrystalline rhenium filament, the vapor pressure P (in atm) of LiCl or NaBr was measured as a function of cell temperature T (in K). The following equations were established empirically.

$$\log_{10} P(\text{LiCl}) = (7.948 \pm 0.102) - (10954 \pm 76)/T \quad \text{for } 662\text{—}848\ \text{K},$$

$$\log_{10} P(\text{NaBr}) = (7.716 \pm 0.072) - (11138 \pm 55)/T \quad \text{for } 669\text{—}882\ \text{K}.$$

In order to study the chemical reactions in the gas phase or on solid surfaces, many workers have recently employed a molecular beam technique, where the beam intensity of molecules (MX) effusing from a Knudsen cell is usually evaluated thermodynamically from published data on the vapor pressure (P(MX)) of MX. Literature values of P(MX), however, scatter widely in general, thereby suggesting that reliable data on P(MX) should be obtained by precise measurements of both effusion rate and cell temperature.

From the above point of view, the present authors already tried a precise determination of the vapor pressures of CsF and CsCl, and obtained fruitful results in a previous work.[1] Therefore, the same method of thermal positive ionization was employed in this work, too, in order to detect a molecular beam of LiCl or NaBr.

In this paper the experimental data on the vapor pressure and on the entropy and enthalpy changes due to sublimation are summarized briefly and also compared with data published to date.

Experimental

Experimental apparatus and method employed in this work were the same as in the previous work.[1] A molecular beam of MX (LiCl or NaBr) 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), and the total ion current ($I^+(M^+)$) of M^+ (Li^+ or Na^+) emitted from F was measured as a function of T or T_F. The samples (LiCl and NaBr) of optical grade were obtained from Wako Pure Chem. Ind., Ltd.

Results and Discussion

At first, the Knudsen cell was kept at a constant temperature higher than 800 K, and $I^+(M^+)$ was measured as a function of T_F in order to find a filament temperature suitable for detecting a beam of MX. In consequence, $I^+(Li^+)$ and $I^+(Na^+)$ corresponding to the cell temperatures T=840 and 885 K, for example, were constant at 38.4±1.8 and 35.6±0.6 nA in the ranges $T_F \simeq$1430—1520 and 1100—1500 K, respectively, indicating that the ionization efficiencies of LiCl and NaBr incident upon F were essentially unity in the respective ranges.

Next, $I^+(M^+)$ was measured as a function of T at T_F=constant in either of the above ranges.

Finally, the vapor pressure was evaluated from

$$P(\text{MX}) = 1.27[M(\text{MX}) \cdot T]^{1/2}\, I^+(\text{M}^+), \tag{1}$$

where P(MX) and $I^+(M^+)$ are expressed in atm and ampere, respectively, and M(MX) is the molecular weight of MX. This equation is the same as Eq. 3 in the previous paper.[1]

Temperature dependence of P(MX) determined by the present and other workers is illustrated in Figs. 1 and 2, which indicate that the following equation holds in general.

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

The values of A and B determined empirically and of P(MX) evaluated from Eq. 2 for three selected temperatures are shown together with literature values in Table 1. The entropy and enthalpy changes ($\Delta S(\bar{T})$ and $\Delta H(\bar{T})$) due to sublimation at the mean temperature ($\bar{T}$) in the range (T_R) covered in each measurement were calculated from Eqs. 3 and 4, respectively.

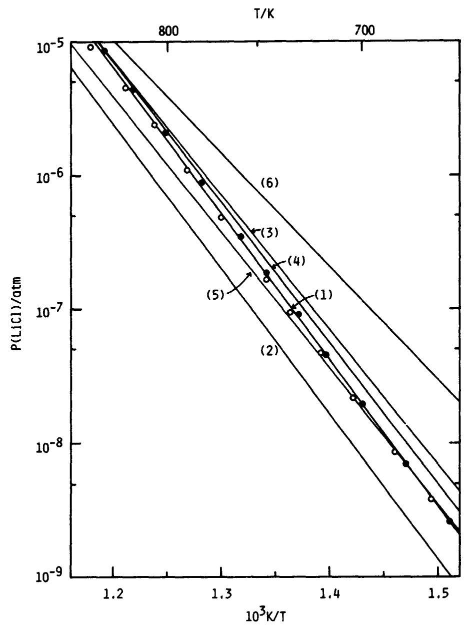

Fig. 1. Temperature dependence of the vapor pressure of LiCl.
(1): This work at T_F=1480 K (open circle) or 1510 K (solid circle), (2): Ref. 2, (3): Ref. 3, (4): Ref. 4, (5): Ref. 5, and (6): Ref. 6.

TABLE 1. EXPERIMENTAL DATA OBTAINED WITH LiCl AND NaBr BY THE PRESENT AND OTHER WORKERS

Sample	T_R/K	$\overline{T}$/K	A	B/K	P(MX)/μatm 700 K	800 K	900 K	$\Delta S(\overline{T})$ cal† mol^{-1} K^{-1}	$\Delta H(\overline{T})$ kcal mol^{-1}	$\Delta H(300)$ kcal mol^{-1}	Ref.
LiCl	500—800	650	7.356±0.051	10816±32	0.0080	0.69	21.8	33.7±0.2	49.5±0.1	51.1±0.1	2
	798—877	838	6.872±0.099	10020±83	0.0361	2.22	54.8	31.4±0.5	45.8±0.4	48.2±0.4	3
	644—855	750	7.419±0.173	10483±126	0.0278	2.07	59.1	33.9±0.8	48.0±0.6	50.0±0.6	4
	783—823	803	6.829±0.124	10199±103	0.0182	1.20	31.4	31.2±0.6	46.7±0.5	49.0±0.5	5
	783-1382	1083	5.116	8430	0.118	3.79	56.2	23.4	38.6	42.1	6
	670—848	759	7.790±0.060	10858±45	0.0190	1.65	53.2	35.7±0.3	49.7±0.2	51.8±0.2	This work (a)
	662—838	750	8.148±0.042	11081±31	0.0208	1.98	68.5	37.3±0.2	50.7±0.1	52.7±0.1	This work (b)
	662—848	755	7.948±0.102	10954±76	0.0199	1.80	59.8	36.4±0.5	50.1±0.3	52.2±0.3	This work (A)
NaBr	600—900	750	7.267±0.132	11001±98	0.00356	0.328	11.1	33.3±0.6	50.3±0.4	52.2±0.4	2
	687—991	839	6.942±0.081	10748±65	0.00387	0.321	10.0	31.8±0.4	49.2±0.3	51.5±0.3	4
	833—933	883	7.275±0.054	10748±48	0.00833	0.692	21.5	33.3±0.2	49.2±0.2	51.7±0.2	5
	806-1392	1099	5.332	8842	0.0502	1.90	32.2	24.4	40.5	43.9	6
	758—911	835	7.570±0.100	11093±80	0.00528	0.506	17.6	34.6±0.5	50.8±0.4	53.1±0.4	7
	673—875	774	7.825±0.083	11206±63	0.00655	0.657	23.7	35.8±0.4	51.3±0.3	53.3±0.3	This work (c)
	669—882	776	7.625±0.066	11082±51	0.00622	0.592	20.5	34.9±0.3	50.7±0.2	52.7±0.2	This work (d)
	669—882	776	7.716±0.072	11138±55	0.00638	0.622	21.9	35.3±0.3	51.0±0.3	53.0±0.3	This work (B)

† 1 cal=4.184 J.

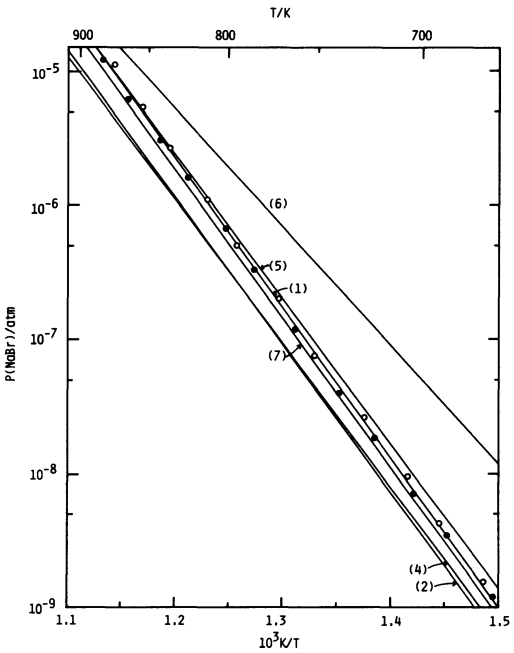

Fig. 2. Temperature depenednce of the vapor pressure of NaBr.
(1): This work at T_F=1360 K (open circle) or 1400 K (solid circle), (2): Ref. 2, (4): Ref. 4, (5): Ref. 5, (6): Ref. 6, and (7): Ref. 7.

$$\Delta S(\overline{T}) = (\ln 10)RA \equiv 4.575\,A \text{ cal mol}^{-1}\text{ K}^{-1}, \quad (3)$$

$$\Delta H(\overline{T}) = (\ln 10)RB \equiv 4.575\times 10^{-3}\,B \text{ kcal mol}^{-1}, \quad (4)$$

where 1 cal is equal to 4.184 J. In a similar way as in the previous work,[1] the heat of sublimation at 300 K was calculated from

$$\Delta H(300) \simeq \Delta H(\overline{T}) + aR(\overline{T}-300). \quad (5)$$

According to the data on specific heats of MX,[2] the values of a in the range 300—800 K were taken as 2.27 and 2.16 for LiCl and NaBr, respectively, in this work.

The values of T_F in the present works (a)—(d) given in the last column in Table 1 were 1480, 1510, 1360, and 1400 K, respectively. The present works (A) and (B) indicate the average values of those (a) and (b) and those (c) and (d), respectively. As may be seen in Fig. 1 and Table 1, the values of P(LiCl) cited from Refs. 3, 4, and 5 and from Refs. 2 and 6 are close to and apart from those determined in this work, respectively. Figure 2 and Table 1 indicate that the data on P(NaBr) obtained in this work lie in the region between those quoted from Ref. 5 and those from Ref. 7, and also that the data in Ref. 6 have the largest deviation from the other data cited therein.

The above results may lead to the conclusions that the data on LiCl in Refs. 3, 4, and 5 are more reliable than those in Refs. 2 and 6, and that the data on NaBr in Refs. 5 and 7 are more accurate than those in Refs. 2, 4, and 6, and also that the data in Ref. 6 are not available for a precise evaluation of P(LiCl) or P(NaBr) in the temperature range lower than the melting point (887 K for LiCl or 1028 K for NaBr).

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