Determination of the Vapor Pressures of Cesium Fluoride and Cesium Chloride by Means of Surface Ionization

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Synopsis. A molecular beam of CsF or CsCl effusing from a Knudsen cell was detected with a heated rhenium filament, and the vapor pressure P (in atm) of each halide at a temperature T (in K) was found to be expressed by $\log_{10}P(\mathrm{CsF})=(7.239\pm0.072)-(9883\pm72)/T$ for 630—830 K, $\log_{10}P(\mathrm{CsCl})=(7.269\pm0.064)-(10054\pm66)/T$ for 640—820 K.

When a beam intensity of molecules (MX) effusing from a Knudsen cell at a given temperature is evaluated thermodynamically, it is necessary to know the accurate value of the vapor pressure (P(MX)) at the temperature. Literature values of P(MX), however, are generally in poor agreement with each other. For example, P(CsF) changes from literature to literature by up to ≈6 times. This fact suggests that further investigations should be made with many samples in order to obtain reliable data on the pressure.

From the viewpoint mentioned above, the present authors have tried to measure accurately the pressures of CsF and CsCl using a positive surface ionization technique developed in their laboratory and also to determine the entropy and enthalpy changes due to molecular sublimation. The results thus obtained are summarized together with literature values, thereby indicating that the present method is quite useful for pressure measurements.

Experimental

Sectional views of the present instrument are shown in Fig. 1, where F is the ionizing filament (0.013 cm in diameter) made of rhenium; B the stainless steel box; R the rotatable shutter; P the shield plate; K the Knudsen cell made of stainless steel; H the molybdenum wire heater; W the pipe for cooling water; A_1 and A_2 the calibrated alumel–chromel thermocouples; and C the Faraday cup. A molecular beam of cesium halide (CsX) effusing from the exit slit S_1 (0.12 cm in diameter) impinged upon F after passing through the inlet slit S_2 (0.17 cm in diameter). The ion-extraction voltage applied to F was usually 50 V. A part of the positive ions (Cs^+) emitted from F was collected with C, and the ion current ($i^+(\mathrm{Cs}^+)$) was measured with a vibrating reed electrometer. The collection efficiency of the ions was 1.45±0.03%, which was determined in a separate experiment by simultaneous measurement of the ion currents collected by B and C. Accordingly, the total ion current ($I^+(\mathrm{Cs}^+)$) is equal to $i^+(\mathrm{Cs}^+)/0.0145$. The residual gas pressure inside the vacuum vessel containing the above system was usually $\approx 2\times10^{-7}$ Torr (1 Torr≈133.322 Pa). The temperatures (T and T_F) of the cell and the filament were determined with A_1 and an optical pyrometer, respectively. The temperature measured with A_1 was always higher by up to ≈3K than that with A_2. The samples (CsF and CsCl) of optical grade were obtained from Aldrich Chem. Co., Inc., and Wako Pure Chem. Ind., Ltd., respectively.

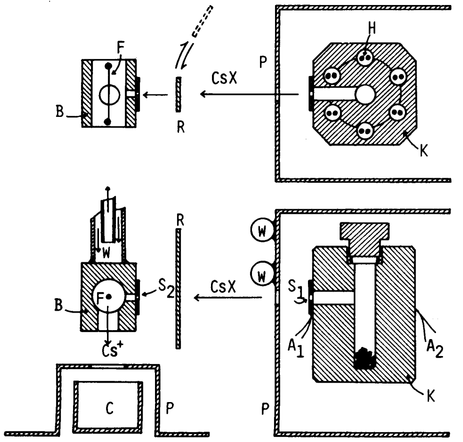

Fig. 1. Horizontal and vertical sectional views of the instrument employed in this work.

Results and Discussion

When the cell containing CsF was heated to 824 K, for example, $I^+(\mathrm{Cs}^+)$ was constant at $(4.50\pm0.21)\times10^{-8}$ A without depending upon the filament temperature so long as T_F was higher than ≈1300 K. In this range, therefore, the ionization efficiency of the molecules incident upon F may be concluded to be essentially 100%. A similar result was obtained with CsCl, too. These results may be natural because the first ionization energy (≈3.9 eV) of Cs is much smaller than the effective work function (≈5.4 eV) of Re for positive ion production.[1]

Consideration of the present experimental method and of gas kinetics[2] leads to the following equations:

$$P(\mathrm{CsX}) = \frac{\pi L^2[2\pi M(\mathrm{CsX})RT]^{1/2}}{1.013\times10^6\, N_A S_C} N(\mathrm{CsX}), \qquad (1)$$

$$N(\mathrm{CsX}) = \frac{I^+(\mathrm{Cs}^+)}{e\, S_F}. \qquad (2)$$

Here, P(CsX) is the vapor pressure (in atm) in the cell; L the distance (6.5 cm) between the cell orifice and the ionizing filament; M(CsX) the molecular weight of CsX; R the gas constant; N_A the Avogadro's number; S_C the effusing slit area (1.13×10^{-2} cm^2) of the cell; N(CsX) the flux of sample molecules (in cm^{-2} s^{-1}) at L; e the elementary electric charge; and S_F the sectional area (2.16×10^{-3} cm^2) of the filament intercepting the molecular beam. Consequently, we obtain the relation:

$$P(\mathrm{CsX}) = 1.27[M(\mathrm{CsX})\,T]^{1/2}\, I^+(\mathrm{Cs}^+), \qquad (3)$$

where $I^+(\mathrm{Cs}^+)$ is expressed in ampere.

A typical result obtained by the present authors is shown, together with results by other workers,[3–5] in Fig. 2, which leads to a general expression as follows:

$$\log_{10} P(\mathrm{CsX}) = A - B/T. \qquad (4)$$

The values of both A and B determined in this work and also cited from literatures[3–8] are summarized in Table 1, where the pressures at three selected tempera-

Table 1. Summary of the experimental data obtained by the present and other workers

Sample	T_R/K	$\bar{T}$/K	A	B/K	P(CsX)/μatm			$\Delta S(\bar{T})$	$\Delta H(\bar{T})$	$\Delta H(300)$	Ref.
					700 K	800 K	900 K	cal[a] mol^{-1} K^{-1}	kcal mol^{-1}	kcal mol^{-1}	
CsF	677—878	778	7.708	10140	0.167	10.8	276	35.3	46.4	48.6	3
	753—856	805	7.556	10208	0.0940	6.25	164	34.6	46.7	49.1	4
	838—919	879	6.458±0.037	9783±47	0.0304	1.70	38.7	29.6±0.2	44.8±0.2	47.5±0.2	5
	644—821	733	7.419±0.079	9989±78	0.141	8.58	209	33.9±0.4	45.7±0.4	47.7±0.4	This work (a)
	685—834	760	7.229±0.079	9878±85	0.131	7.61	179	33.1±0.4	45.2±0.4	47.3±0.4	This work (b)
	634—823	729	7.050±0.117	9767±117	0.125	6.93	157	32.3±0.5	44.7±0.5	46.7±0.6	This work (c)
	634—834	734	7.239±0.072	9883±72	0.132	7.68	181	33.1±0.3	45.2±0.3	47.2±0.3	This work (A)
CsCl	720—892	806	7.534	10198	0.0923	6.11	160	34.5	46.7	49.1	3
	793—893	843	6.424	9670	0.0408	2.17	47.9	29.4	44.2	46.9	6
	784—905	845	6.854±0.041	9806±50	0.0701	3.95	90.8	31.4±0.2	44.9±0.2	47.5±0.2	7
	690—891	791	7.649±0.058	10230±59	0.108	7.29	192	35.0±0.3	46.8±0.3	49.2±0.3	8
	638—819	729	7.329±0.093	10109±95	0.0772	4.93	125	33.5±0.4	46.3±0.4	48.4±0.5	This work (d)
	639—820	730	7.229±0.057	10013±57	0.0841	5.16	127	33.1±0.3	45.8±0.3	47.9±0.3	This work (e)
	638—820	729	7.269±0.064	10054±66	0.0806	5.03	125	33.3±0.3	46.0±0.3	48.1±0.3	This work (B)

a) 1 cal=4.184 J.

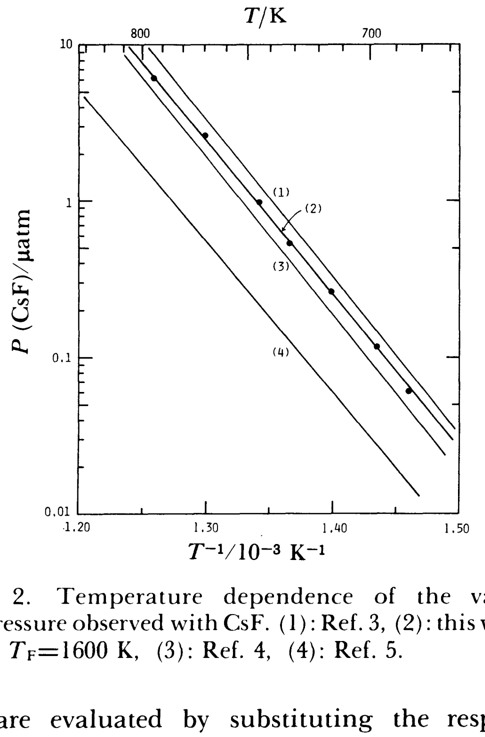

Fig. 2. Temperature dependence of the vapor pressure observed with CsF. (1): Ref. 3, (2): this work at T_F=1600 K, (3): Ref. 4, (4): Ref. 5.

tures are evaluated by substituting the respective values of A and B in Eq. 4. The entropy change due to sublimation ($\Delta S(\bar{T})$) and the heat of sublimation ($\Delta H(\bar{T})$) at the mean temperature ($\bar{T}$) in the range (T_R) covered in each measurement are evaluated from Eqs. 5 and 6, respectively, where 1 cal is equal to 4.184 J.

$$\Delta S(\bar{T}) = (\ln 10)\,R\,A \equiv 4.575\,A \quad \text{cal mol}^{-1}\,\text{K}^{-1}. \tag{5}$$

$$\Delta H(\bar{T}) = (\ln 10)\,R\,B \equiv 4.575\times 10^{-3}\,B \quad \text{kcal mol}^{-1}. \tag{6}$$

The heat of sublimation at 300 K is given by

$$\Delta H(300) = \Delta H(\bar{T}) + \int_{300}^{\bar{T}} [C_P(\text{c}) - C_P(\text{g})]\text{d}T, \tag{7}$$

$$\simeq \Delta H(\bar{T}) + a\,R\,(\bar{T} - 300). \tag{8}$$

Here, C_P(c) and C_P(g) are the specific heats of CsX at crystalline and gaseous states, respectively. According to data compiled in Ref. 9, Eq. 7 may be approximated by Eq. 8, where the values of a in the range 300—800 K are taken as 2.34 and 2.47 for CsF and CsCl, respectively.

The temperatures of the ionizing filament in the cases (a)—(e) indicated in the last column in Table 1 were 1910, 1600, 1450, 2108, and 2215 K, respectively. The data (A) and (B) are the mean values of those (a)—(c) and those (d)—(e), respectively. In the case of CsF, the values in Refs. 3 and 4 and Ref. 5 are close to and apart from those in this work, respectively, as may be seen in Fig. 2 and Table 1. Our data on CsCl fall between those in Ref. 3 and those in Ref. 7, and most deviate from those in Ref. 6. Consequently, the data in Refs. 5 and 6 seem to be less accurate probably because of a systematic error.

Conclusion

The positive surface ionization method is quite useful for determining the vapor pressure of cesium halide without citing any thermochemical value from literatures, and hence for checking the accuracy of published data on the pressure. Since the effective work function of an oxygenated tungsten wire for positive ion production is ≈6.7 eV,[1] the ionization efficiency of element having the ionization energy less than ≈6 eV is generally expected to be essentially unity when the wire at a suitable temperature is employed as a beam detector. Therefore, the present method may also be applicable to those salts which include a readily ionized element[1] such as alkali metal, alkaline earth, actinoid, or lanthanoid.

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