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THERMODYNAMIC PROPERTIES OF CsI. II. VAPOUR PRESSURES AND THERMOCHEMICAL PROPERTIES OF CsI(g) AND Cs_2I_2(g)

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ABSTRACT

The vapour pressure of caesium iodide has been measured in the vicinity of the melting point (903.5 K). Below the melting point dimerization in the vapour is negligible. The vapour pressure can be expressed as:

$$\log p/\text{atm} = (-9550 \pm 79)/T + (6.945 \pm 0.093)$$

and for the enthalpy of sublimation, according to the "third law method", the value $\Delta H^0_{298.15} = 193.1 \pm 0.1$ kJ mol^{-1} has been found. Above the melting point a sudden increase in the fraction of dimers has been observed until a value (18.6 ± 1.8)% was reached at ~ 912 K.

The vapour pressure of Cs_2I_2(g) can be expressed as

$$\log p/\text{atm} = (-7587 \pm 530)/T + (4.19 \pm 0.54)$$

and for its enthalpy of sublimation the value $\Delta H^0_{298.15} = 229.9 \pm 1.0$ kJ mol^{-1} has been found. From the enthalpies of sublimation it has been found that

$$\Delta_f H^0(\text{CsI, g, 298.15 K}) = -155.0 \pm 0.2 \text{ kJ mol}^{-1}$$

$$\Delta_f H^0(\text{Cs}_2\text{I}_2\text{, g, 298.15 K}) = -466.4 \pm 1.1 \text{ kJ mol}^{-1}$$

A discussion of the literature is given.

INTRODUCTION

The vapour pressure of caesium iodide over solid and liquid CsI has been measured by many authors. Different methods have been used to obtain the vapour pressures: Knudsen effusion, transpiration experiments, mass spectrometry, and boiling point experiments. Notwithstanding the vast amount of experimental material now available, there is not a consistent picture of the vaporization behaviour of CsI and, consequently, it is hardly possible to derive reliable thermodynamic data for the vapour. For instance, it is now generally accepted that the vapour contains a substantial amount of dimers — as is the case with the other alkali halides — but there is no general agreement on the amount of dimers present at a given temperature (range). Even in recent mass spectrometric studies the amount of dimers differs widely. Whereas Emons et al. [1] observed an increase in the dimer fraction

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with increasing temperature from 2% at 683 K to 20% at 958 K, Venugopal et al. [2] concluded recently that the contribution of dimers to the vapour pressure is negligible below 873 K. Near the melting point (903 K) they observed a sudden increase in the dimer fraction which afterwards decreased from 22% at 1240 K to 18% at 1400 K. However, Topor [3], who measured the vapour pressure of caesium iodide in the temperature range 1156–1376 K, found a constant amount of dimers (29%) over the whole temperature range.

Because of the disturbing discrepancies in the literature we have decided to measure the vapour pressure of caesium iodide in the vicinity of the melting temperature of CsI in an attempt to connect the various measurements published. These results, together with an evaluation of the literature, will be given in this paper.

EXPERIMENTAL

The vapour pressures were measured using a transportation method, as described before [4], in which the saturated vapour, in equilibrium with the solid or liquid, is condensed and determined after transportation with a known volume of an inert carrier gas (in the present case argon). The velocity of the carrier gas has to be chosen such that it is saturated with CsI vapour at each temperature of the measurements; this has to be determined experimentally (plateau curve). A velocity of about 40 ml min^{-1} was taken.

After each experiment the amount of carrier gas (which was collected over water in a bottle of known volume) was determined after corrections for temperature and pressure.

The amount of CsI vapour, carried by a known amount of gas, and condensed in the tube, was determined by dissolving it in water and analysing both caesium and iodine in the solution. Small amounts of caesium were measured by atomic absorption spectrometry (AAS), larger amounts by potentiometric acid–base titration with standard solutions. Iodine was titrated with a standard silver nitrate solution.

RESULTS

Two series of experiments have been done, one below the melting point of caesium iodide (903.5 K) [5], the other above the melting temperature.

The vapour pressure in equilibrium with solid CsI

Equilibrium vapour pressures of CsI have been calculated from the data in Table 1, taking CsI(g) as the only gaseous species. From these data the

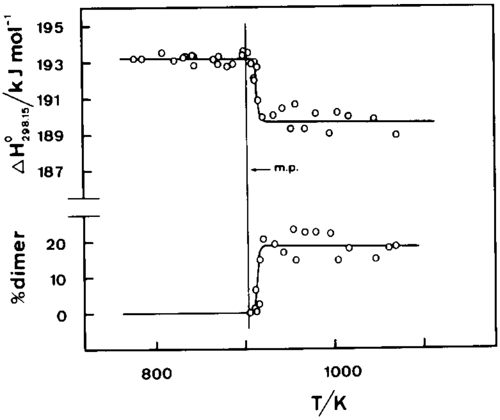

Fig. 1. The sublimation enthalpy at 298.15 K and the percentage of dimer as a function of temperature.

enthalpy of sublimation of monomeric CsI at 298.15 K has been calculated by the "third law method". For this purpose the free energy function of CsI(g), as calculated by Glushko et al. from spectroscopic data [6], has been combined with the free energy function of CsI(s) obtained from our measurements [5], and based on new determinations of the enthalpy increment values ($H^0_T - H^0_{298.15}$) for CsI(s). As a result we obtain the value $\Delta_{\text{sub}} H^0_{298.15} = +193.17 \pm 0.12$ kJ mol^{-1}. This value is independent of the temperature of the measurements, and we conclude therefore that a negligible amount of dimers is present in the caesium iodide vapour below the melting point.

The vapour pressures of the equilibrium CsI(s) = CsI(g) as a function of the temperature can now be expressed as:

$$\log p/\text{atm} = (-9550 \pm 79)/T + (6.945 \pm 0.093)$$

and

$$\Delta_{\text{sub}} G^0/\text{J mol}^{-1} = (182828 \pm 1512) - (132.96 \pm 1.78)T$$

The vapour pressure in equilibrium with liquid CsI

When the vapour pressures of caesium iodide, above the melting point, calculated as if the vapour consists of only monomers, are used to calculate the sublimation enthalpy at 298.15 K using the "third law method", the $\Delta_{\text{sub}} H^0$ values gradually change between 910 and 920 K until a new constant value has been obtained (Table 2). This can be ascribed to the formation of dimers in the vapour. In order to calculate the amount of

TABLE 1

Numerical results of the transportation measurements of the equilibrium $CsI(s) = CsI(g)$

No.	Furnace temp. (K)	Bottle volume (10^{-6} m^3)	Temperature (K)		Pressure (mm Hg)		Condensate (mg)		p_{CsI} (mm)	ΔH^0_{298} (kJ mol^{-1})
			lab.	water in bottle	environment	Δp (manometer)	caesium	iodine		
31	843.8	13.376	295.6	295.6	756.1	0.1	3.04	2.88	0.0314	193.37
32	873.0	8.620	295.6	295.6	754.9	2.8	4.70	–	0.0759	193.28
33	834.0	13.979	295.6	295.6	758.7	2.9	2.37	–	0.0236	193.25
34	809.4	16.708	295.7	295.7	764.7	0.1	1.23	–	0.0102	193.48
35	881.6	6.967	296.6	296.6	764.2	1.9	5.20	–	0.1041	192.73
36	836.6	55.841	297.5	297.5	764.1	0.2	10.20	9.53	0.0253	193.34
37	867.4	13.758	297.7	297.7	767.3	0.1	–	6.20	0.0659	193.11
39	899.8	6.1943	301.0	301.0	760.2	3.1	6.50	6.90	0.1571	193.36
58	787.8	90.506	294.8	294.8	764.9	1.3	3.31	–	0.0051	193.15
80	872.4	38.191	293.5	293.5	732.4	0.6	21.93	–	0.0791	192.84
81	822.8	45.827	294.3	294.3	746.4	0.5	5.60	–	0.0169	193.06
82	845.0	33.637	294.5	294.5	758.5	0.6	8.06	–	0.0331	193.28
83	855.2	45.798	292.0	292.0	754.9	0.6	16.17	–	0.0484	192.78
89	779.0	145.063	292.7	292.7	747.6	0.5	3.86	–	0.0037	193.17
92	899.6	33.056	295.3	295.3	774.4	0.6	36.20	–	0.1518	193.59
98	889.2	53.810	296.2	296.2	762.9	0.5	48.72	–	0.1259	192.88
									$\Delta H^0_{298.15} =$	$+\overline{193.17 \pm 0.12}$

66	916.6	6.1943	296.3	294.6	763.2	2.4	14.62	13.98	0.3283	190.82
91	911.6	13.801	294.5	294.5	760.1	0.51	24.66	–	0.2470	192.13
93	905.8	35.104	296.0	296.0	775.1	0.57	45.50	–	0.1801	193.51
94	910.4	41.373	296.3	296.3	776.8	0.54	64.52	–	0.2169	192.90
95	916.1	35.690	296.5	296.5	779.1	0.63	64.65	–	0.2521	192.75
96	913.2	35.546	296.3	296.3	767.8	0.51	58.07	–	0.2272	193.04
97	912.1	34.632	296.7	296.7	760.9	0.51	62.67	–	0.2520	192.06
60	1005.4	4.2829	295.3	293.9	766.9	3.0	62.70	59.34	2.0665	190.18
61	1070.4	0.9981	295.6	294.1	765.7	2.0	49.89	48.16	7.0784	188.90
62	1017.4	1.9951	292.4	298.7	775.1	1.8	40.42	37.32	2.7685	189.51
63	997.0	1.9951	293.1	290.7	760.0	1.8	29.56	27.76	2.0530	188.99
64	980.8	4.2829	293.9	291.6	759.5	2.5	45.98	43.80	1.5068	189.10
65	934.6	6.1943	294.9	292.8	759.0	2.6	23.36	22.52	0.5363	190.05
67	958.2	6.1943	295.9	273.2	766.2	2.2	34.42	34.48	0.8084	190.62
68	1046.0	1.9951	296.3	294.1	765.9	1.8	60.33	59.39	4.3450	189.80
70	953.4	6.1943	294.6	292.1	768.0	2.1	38.02	37.01	0.8741	189.24
71	943.8	6.1943	294.7	292.0	765.8	2.1	27.31	26.07	0.6222	190.38
72	1062.6	0.9981	295.1	292.9	764.4	1.8	40.88	40.14	5.8334	189.54
73	968.2	6.1943	295.6	293.6	757.9	2.1	50.27	49.45	1.1687	189.24
74	921.2	6.1943	295.2	292.9	749.0	2.4	17.61	17.47	0.4107	189.88
									$\Delta H^0_{298.15} =$	$+\overline{189.65}$

TABLE 2

The vapour pressures of CsI(g) and Cs_2I_2(g), and sublimation enthalpies

No.	T (K)	$\Sigma\, p_{CsI}$ (mm) (from Table 1)	p_{CsI} (mm) calc. from eqn. (II)	$p_{Cs_2I_2}$ (mm)	% dimer	ΔH_1^0 (298.15) (kJ mol^{-1})	ΔH_2^0 (298.15) (kJ mol^{-1})
66	916.6	0.3283	0.2437	0.0423	14.8		
91	911.6	0.2470	0.2177	0.01465	6.3		
93	905.8	0.1801	0.1904	–	–		
94	910.4	0.2169	0.2118	0.00255	1.2		
95	916.1	0.2521	0.2413	0.0054	2.2		
96	913.2	0.2272	0.2259	0.00065	0.3		
97	912.1	0.2520	0.2202	0.0159	6.7		
60	1005.4	2.0665	1.5380	0.2643	14.7	192.65	232.06
61	1070.4	7.0784	4.8759	1.1013	18.4	192.22	229.46
62	1017.4	2.7685	1.9244	0.42205	18.0	192.59	230.01
63	997.0	2.0530	1.3105	0.37125	22.1	192.69	227.92
64	980.8	1.5068	0.9550	0.2759	22.4	192.81	227.93
65	934.6	0.5363	0.3646	0.08585	19.1	193.04	229.66
67	958.2	0.8084	0.6032	0.1026	14.5	192.95	232.95
68	1046.0	4.3450	3.2155	0.56475	14.9	192.42	231.84
70	953.4	0.8741	0.5456	0.16425	23.1	192.97	227.72
71	943.8	0.6222	0.4450	0.0886	16.6	193.01	230.99
72	1062.8	5.8334	4.2772	0.7781	15.4	192.28	231.44
73	968.2	1.1687	0.7412	0.21375	22.4	192.89	228.00
74	921.2	0.4107	0.2708	0.06995	20.5	193.07	228.92
					$\overline{18.6 \pm 1.8}$	$\overline{192.74 \pm 0.2}$	$\overline{229.9 \pm 1.0}$

dimers, we consider the following equilibria:

$$\mathrm{CsI(s) = CsI(g)} \quad (1)$$

$$\mathrm{CsI(s) = CsI(l)} \quad (2)$$

$$\mathrm{CsI(l) = CsI(g)} \quad (3)$$

$$\mathrm{2CsI(l) = Cs_2I_2(g)} \quad (4)$$

Since for the enthalpy of melting the value $\Delta H^0 = 24000$ J mol^{-1} has been selected [5], we obtain

$$\Delta G_2^0/\mathrm{J\ mol^{-1}} = (24000 \pm 200) - (26.56 \pm 0.22)T$$

and by combination of ΔG_1^0 and ΔG_2^0:

$$\Delta G_3^0/\mathrm{J\ mol^{-1}} = (15828 \pm 1500) - (106.4 \pm 1.8)T \quad \mathrm{(I)}$$

The vapour pressure of the monomeric species can thus be calculated from eqn. (I) to give:

$$\log p/\mathrm{atm} = -(8296 \pm 80)/T + (5.56 \pm 0.10) \quad \mathrm{(II)}$$

and, because $\Sigma p = p_{\mathrm{mono}} + 2p_{\mathrm{di}}$ (where Σp is the total caesium iodide pressure in Table 1, calculated as monomeric vapour) we obtain p_2, the vapour pressure of the dimer, by difference. In Table 2 the results of the calculations are listed.

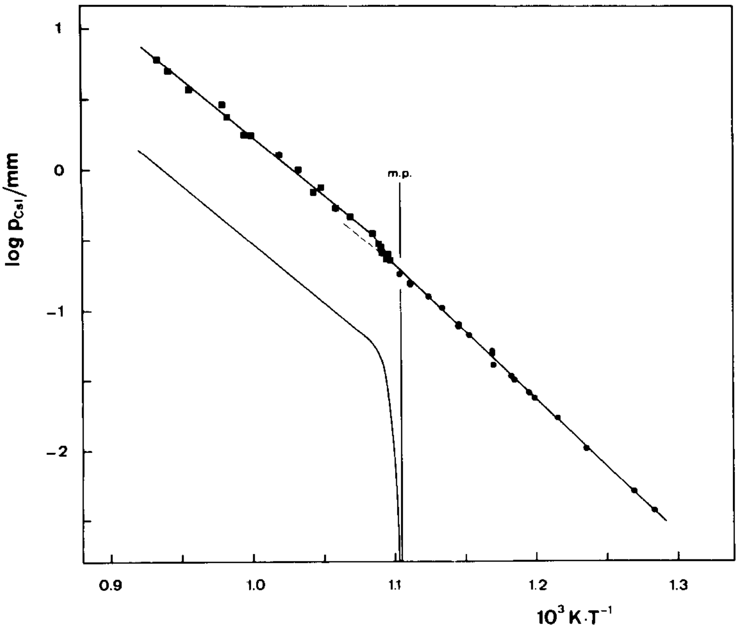

Fig. 2. The total vapour pressure of caesium iodide, and the vapour pressure of Cs_2I_2, as a function of temperature.

For the vapour pressure of the dimer in equilibrium with CsI(l) we find:

$$\log p_{Cs_2I_2}/\text{atm} = -(7587 \pm 530)/T + (4.19 \pm 0.54)$$

and for the percentage of dimers 18.6 ± 1.8.

In Table 2 the enthalpies of sublimation for the monomeric and dimeric species have also been listed. Again, the free energy functions of CsI(g) and Cs_2I_2(g), calculated by Glushko et al. [6], have been used to calculate these values.

With the selected value for the enthalpy of formation of CsI(s) given in part I of this paper, the enthalpies of formation of CsI(g) and Cs_2I_2(g) can be calculated. Since the enthalpy of sublimation of CsI(g) obtained from the (l → g) equilibrium has a larger uncertainty than the value obtained from the (s → g) equilibrium, we take the latter. We thus obtain:

$$\Delta_f H^0_{298.15}(\text{CsI, g}) = -155.0 \pm 0.2 \text{ kJ mol}^{-1}$$

$$\Delta_f H^0_{298.15}(\text{Cs}_2\text{I}_2\text{, g}) = -466.4 \pm 1.1 \text{ kJ mol}^{-1}$$

These values are slightly more negative than the values assessed by Glushko et al. [6] (-152.320 and -454.033 kJ mol^{-1}, respectively). The differences arise mainly from the different free energy function of the solid adopted here, resulting in more positive values for the enthalpies of sublimation of monomer and dimer.

DISCUSSION

Dimerization in the vapour of caesium chloride was observed for the first time in 1958 by Milne et al. [7], and by Berkowitz and Chupka [8]. Shortly thereafter, Akishin et al. [9] demonstrated that dimerization also occurred in the vapour of the other caesium halides. For CsI they found a ratio between the dimeric and the monomeric species of 0.03 at 787 K and 0.04 at 820 K. Since that time a number of other mass spectrometric studies have appeared confirming the presence of dimers in the vapour of CsI; however, without any agreement on the equilibrium composition as a function of temperature. For instance, whereas recent measurements by Venugopal et al. [2] indicated that the amount of dimers below 883 K is much less than 5%, Matsumoto et al. [10] observed the presence of dimers even at 673 K. The latter authors, however, did not indicate the amount of dimers. Viswanathan and Hilpert [11] could detect the presence of dimers in the vapour over solid CsI even at 604 K, but up to the melting point the amount of dimers observed by them was low: the p_2/p_1 ratio increased from 0.05 at 820 K to 0.08 at the melting point.

Since most of the recent experimental determinations agree that the amount of dimers in equilibrium with the solid phase is less than 5%, the

TABLE 3

Enthalpies of sublimation of CsI(g) and Cs_2I_2(g)

Ref.	$\Delta_{\text{subl.}}H^0$(298.15 K) (kJ mol^{-1}) monomer (recalculated values)	dimer
Deitz [12]	195.5 ± 0.3	–
Cogin and Kimball [14]	195.4 ± 0.7 190.7 ± 0.8	– –
Scheer and Fine [13]	191.5 ± 0.4	–
Murgulesco and Topor [17]	196.1 ± 0.1	226.6 ± 0.4
Emons et al. [1]	165.0 ± 2.1	–
Viswanathan and Hilpert [11]	$[191.2 \pm 2.0]$ [a]	237.7 ± 0.7
Venugopal et al. [2]	–	–
Present investigation	193.17 ± 0.12	229.9 ± 1.0

[a] Not recalculated.

experimental studies of Deitz [12], Scheer and Fine [13], and Cogin and Kimball [14] can be treated as if the vapour consists of monomers only. The gradual change in $\Delta_{\text{sub}}H^0$(298.15 K) found in the extensive series of measurements of the last authors indicates, however, that this is probably not the case over the entire range of the measurements. Moreover, the two series of measurements of these authors do not agree with each other. The results have been summarized in Table 3.

Above the melting point the percentage of dimers rapidly increases. It can easily be derived that

$$\frac{\partial(\ln p_2/p_1)}{\partial T} = \frac{\Delta H_2^0 - \Delta H_1^0}{RT^2}$$

in which p_1, p_2, and ΔH_1^0, ΔH_2^0 are the vapour pressures and sublimation enthalpies of monomer and dimer, respectively. At the melting point the value of $(\Delta H_2^0 - \Delta H_1^0)$ changes. This results in a rapid increase in the p_2/p_1 ratio above the melting point. In the interpretation of the measurements, done before 1960, no account has been made for dimerization in the vapour. Thus, Ruff and Mugdan [15] and von Wartenberg and Schultz [16] observed a boiling point of CsI at 1553 K, being the temperature at which the CsI vapour pressure $(= p_1 + 2p_2)$ reaches the value of 1 atm, but the amount of dimers at the boiling point cannot be derived solely from these experiments.

The measurements by Murgulescu and Topor [17] could be evaluated completely due to the fact that various techniques have been applied. Thus, the authors combined the results of the transportation method with those obtained by the quasi-static Rodebush–Dixon method [18], and obtained in this way average molecular masses of the vapour, yielding for CsI 29% of dimers in the vapour between 1276 and 1376 K. This enables us to calculate the vapour pressures of monomer and dimer, and their enthalpies of sublimation. For a recalculation of these measurements we used the free energy function of CsI(l), as calculated from our $[H^0(T) - H^0(298.15)]$ measurements [5], and for the vapour species the free energy functions given by Glushko et al. [6]. The results are listed in Table 3.

Venugopal et al. [2] combined the transpiration method (916–1125 K) with the Rodebush–Dixon method (977–1430 K), and found a sharp increase in the dimer fraction near the melting point, and a decrease thereafter from 22% at 1240 K to 18% at 1400 K. However, a recalculation of their original data appeared to give not only lower values for the dimer fraction, but at higher temperatures even mole masses lower than that of the monomer.

Much of the scatter in the experimental determination of the fraction of dimers in the present investigation arises from the fact that this fraction is obtained by difference of two large numbers. A direct determination of the dimer fraction by mass spectrometry can give more accurate results. Thus, recent mass spectrometric measurements by Emons et al. [1] over solid and liquid caesium iodide indicated a dimer fraction of 2% at 683 K and 20% at 958 K, in good agreement with our own measurements.

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