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Standard Gibbs energy of formation of Cs_2CdI_4

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Abstract

The vapor pressures of CdI_2 and Cs_2CdI_4 were measured below and above their melting points, employing the transpiration technique. The standard Gibbs energy of formation $\Delta_f G°$ of Cs_2CdI_4, derived from the partial pressure of CdI_2 in the vapor phase above and below the melting point of the compound could be represented by the equations $\Delta_f G°\langle Cs_2CdI_4\rangle$ (± 6.7) kJ mol^{-1} $= -1026.9 + 0.270\ T$ $(643\ K \leq T \leq 693\ K)$ and $\Delta_f G°\{Cs_2CdI_4\}$ (± 6.6) kJ mol^{-1} $= -1001.8 + 0.233\ T$ $(713\ K \leq T \leq 749\ K)$ respectively. The enthalpy of fusion of the title compound derived from these equations was found to be 25.1 ± 10.0 kJ mol^{-1} compared to 36.7 kJ mol^{-1} reported in the literature from differential scanning calorimetry (DSC). The standard enthalpy of formation $\Delta_f H°_{298.15}$ for $\langle Cs_2CdI_4\rangle$ evaluated from these measurements was found to be -918.0 ± 11.7 kJ mol^{-1}, in good agreement with the values -920.3 ± 1.4 and -917.7 ± 1.5 kJ mol^{-1} reported in the literature from two independent calorimetric studies.

1. Introduction

The thermochemistry of compounds of iodine provides some of the vital information needed for the safe operation of nuclear reactors and in the prediction of the extent of iodine release into the environment in the event of nuclear reactor accidents. In the case of catastrophic accidents involving overheating of the core, the iodine released from the hot irradiated fuel can come in contact with several other components of the reactor assembly such as the control rods. The reactions of iodine with control-rod components such as silver, cadmium and indium would influence the release of iodine significantly by forming various compounds such as CdI_2, AgI and InI_3. In addition to the binary compounds such as cadmium iodide, the formation of ternary caesium–cadmium–iodine compounds, like Cs_2CdI_4 in the primary circuit has been postulated to occur as a result of reaction of caesium iodide with cadmium or cadmium iodide aerosol [1] according to the reaction

$$2CsI_{(g)} + CdI_{2(s,l)} = Cs_2CdI_{4(s,l)}. \tag{1}$$

Such reaction can reduce the volatility of fission product iodine and caesium. The knowledge of the thermodynamic stability of Cs_2CdI_4 in this context is therefore important. In this paper we present our data on the vapor pressure measurements of CdI_2 and Cs_2CdI_4 and the derivation of the Gibbs energy of formation of Cs_2CdI_4 from these measurements.

2. Experimental

The compound Cs_2CdI_4 was prepared by dissolving stoichiometric amounts of CsI (99.995% pure, Sisco Research Lab. Chem.) and CdI_2 (BDH AnalaR) in distilled water and heating the solution to dryness. The material so obtained was then dried in an air oven at 350 K for 24 h.

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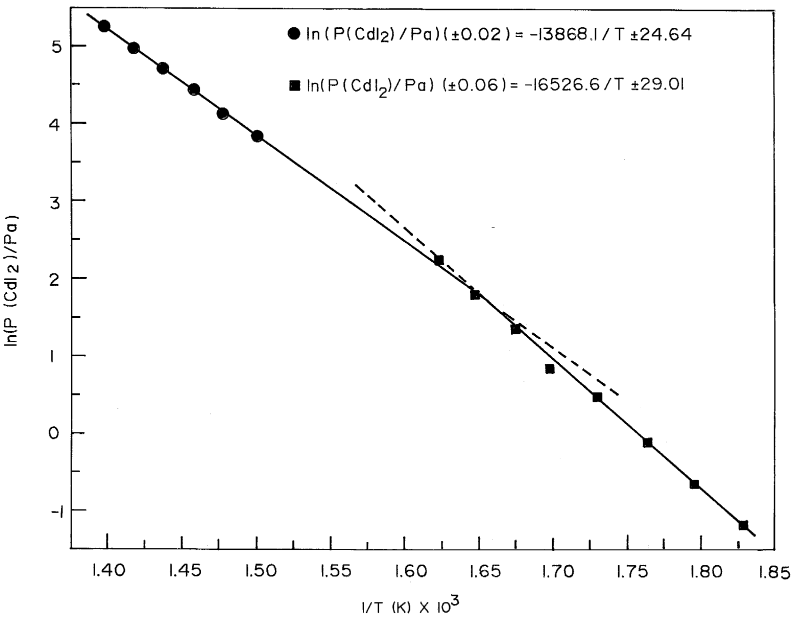

Fig. 1. ln $p(CdI_2)/Pa$ versus $1/T$ for pure CdI_2 in the solid and liquid range.

The product was confirmed as Cs_2CdI_4 from the X-ray powder diffraction pattern recorded on a Philips automatic recording X-ray diffractometer (model PW 1729/40) using CuKα radiation. The stoichiometry of the compound was also independently established by chemical analysis. The differential scanning calorimeter curve recorded for Cs_2CdI_4 using a power compensated DSC (Sinku–Rico (model DSC-1500 M/L)) showed the melting point to be 705 K, in close agreement with that reported in reference [2]. An automatic recording transpiration apparatus described elsewhere [3] was used for following the isothermal mass loss of the sample in flowing purified argon. During the vapor pressure measurement above the melting point of Cs_2CdI_4, sufficient care was taken to limit the total mass loss to a minimum, such that the composition change of the melt was virtually insignificant and remained around the stoichiometry of the solid compound. The temperature of the sample was measured with a chromel–alumel thermocouple calibrated at the melting points of pure metals (In, Bi, Cd, Al, Ag) [4], with ice junction as reference.

The mass loss per unit volume of the carrier gas swept over the sample maintained at a constant temperature of 689 K was monitored as a function of flow rate in the range 3.15 to 4.15 $dm^3\ h^{-1}$. It was observed that the mass loss per unit volume was almost independent of flow rate in the range 3.39 and 3.53 $dm^3\ h^{-1}$ establishing thereby the equilibrium condition for the vapor transport. The equilibrium vapor pressure at different temperatures was measured at the mean flow rate of 3.46 $dm^3\ h^{-1}$.

The vapor pressure of pure CdI_2 was measured with the same apparatus before the vapor pressure measurement of the compound was carried out. It was observed that the mass loss per unit volume of carrier in this case, was independent of flow rate in the range 3.09 to 3.36 $dm^3\ h^{-1}$

Table 1
Vapor pressure data for $CdI_2(s)$ and $CdI_2(l)$

Temperature (K)	Mass loss (mg dm^{-3})	Observed pressure (Pa)	Third law $\Delta H^\circ_{298.15\ K}$ (kJ/mol)
547.0	0.045	0.303	147.88
557.0	0.076	0.512	148.07
567.0	0.130	0.877	148.11
578.0	0.236	1.591	147.16
589.0	0.337	2.272	148.00
597.0	0.564	3.803	148.39
607.0	0.875	5.900	148.57
616.0	1.372	9.252	148.38
666.0	6.818	46.972	150.23
676.5	9.114	61.453	150.48
685.5	12.376	83.448	150.33
695.5	16.330	110.108	150.46
705.0	21.232	143.161	150.55
715.0	28.219	190.272	150.54

Table 2
Thermodynamic properties of cadmium iodide

Enthalpy of sublimation at 298.15 K		Enthalpy of fusion $\Delta_{fus}H°$ (kJ mol^{-1})	Method employed to obtain $\Delta_{fus}H°$	Reference
Second law (kJ mol^{-1})	Third law (kJ mol^{-1})			
142.76 ± 7.6 [a]	148.2 ± 0.2 [a]	22.1 ± 3.3 [b]	vapor pressure	this work
142.5 ± 6.7 [a]	146.8 ± 0.2 [a]			[5]
		20.103	drop calorimetry	[6]
		20.71 ± 0.54	drop calorimetry	[8]
143.7 ± 6.4 [c]	150.4 ± 0.1 [c]			this work

[a] Measured over solid.
[b] From Eqs. (3) and (4).
[c] Measured over liquid.

at 593 K. The equilibrium vapor pressures were measured at different temperatures at the flow rate of 3.21 dm^3 h^{-1}.

3. Results and discussion

3.1. Vaporization of pure CdI_2

The measurement involved monitoring of mass loss due to congruent vaporization of CdI_2. The vapor pressure of CdI_2(g) in equilibrium with CdI_2(s) or CdI_2(l) was calculated from mass loss of the sample per unit volume of the carrier gas swept over it from the relation

$$p^0(CdI_2) = W/V_c \times RT_c/M, \quad (2)$$

where W is the mass transported, V_c is the total volume of the carrier gas passed over the sample, T_c is the ambient temperature (in the present case 297.0 ± 0.5 K) at which the volume of the carrier gas was measured and M is the molecular weight of the vapor species. The Knudsen effusion mass spectrometry measurement [5] showed (CdI_2) to be the most abundant species in the vapor phase in the temperature range of the present investigation. The vapor pressures of $\langle CdI_2 \rangle$ and $\{CdI_2\}$ could be expressed by the equations

$$\ln p^0(CdI_2)/Pa\langle CdI_2\rangle\ (\pm 0.06)$$
$$= -16526.6/T + 29.01 \quad (547\,K \le T \le 616\,K), \quad (3)$$

$$\ln p^0(CdI_2)/Pa\{CdI_2\}\ (\pm 0.02)$$
$$= -13868.1/T + 24.64 \quad (666\,K \le T \le 715\,K). \quad (4)$$

The results of vaporization of solid and liquid CdI_2 are presented in Fig. 1 and Tables 1 and 2. The third-law enthalpies presented in Table 1 were calculated from each measured point using the heat capacity values from Kon-

Table 3
Gibbs energy of formation of $\langle Cs_2CdI_4 \rangle$ in the solid range

Temperature (K)	Mass loss (mg dm^{-3})	$p(CdI_2)$ (Pa)	$p°(CdI_2)$ (Pa)	$\Delta_f G_T$ (kJ mol^{-1}) [a]
643.0	0.009	0.061	21.589	−853.3
651.0	0.011	0.075	28.141	−851.1
658.0	0.019	0.129	35.299	−849.2
661.0	0.021	0.143	38.843	−848.4
669.5	0.029	0.197	50.698	−846.1
671.0	0.032	0.217	53.101	−845.7
678.0	0.041	0.278	65.731	−843.8
683.0	0.054	0.367	76.349	−842.5
692.5	0.095	0.645	100.873	−839.9
Enthalpy of fusion = 25.1 ± 10.0 kJ mol^{-1} at 705 K				
713.0	0.166	1.127	179.406	−835.7
723.0	0.235	1.595	234.785	−833.3
732.0	0.320	2.172	297.231	−831.2
742.0	0.431	2.926	383.691	−828.9
749.0	0.564	3.828	456.922	−827.3

[a] $\Delta_f G_T$ obtained from Eqs. (12) and (13).

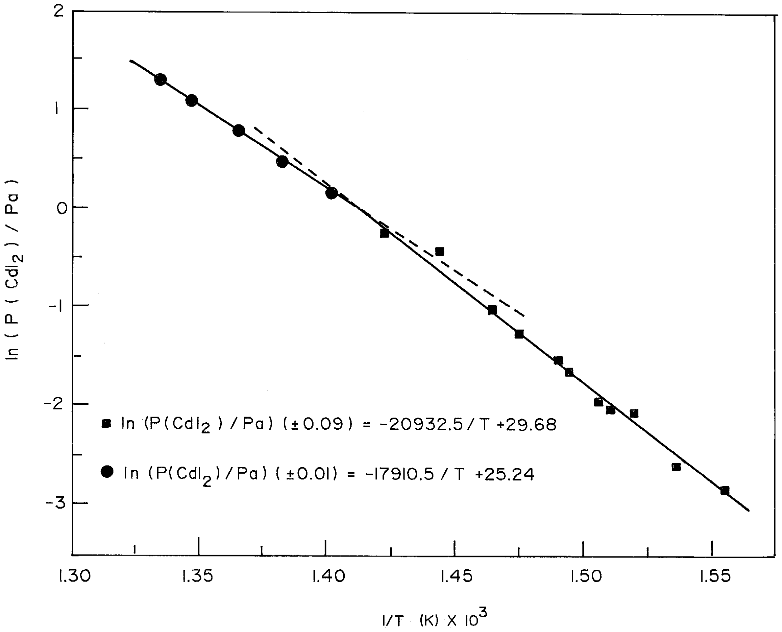

Fig. 2. ln $p(\mathrm{CdI_2})/\mathrm{Pa}$ versus $1/T$ for $\mathrm{Cs_2CdI_4}$ in the solid and liquid range.

ings et al. [6] for solid and liquid $\mathrm{CdI_2}$ and Kubaschewski et al. [7] for $\mathrm{CdI_2(g)}$. Second-law enthalpies were calculated from the least squares fitted Eqs. (3) and (4) and using the same heat capacity values as in the case of third-law calculations. In Table 2, the second-law and the third-law enthalpies of sublimation of $\mathrm{CdI_2}$ obtained from this work are compared with those of [5]. There is excellent agreement between the second-law and the third-law values of this work with literature values. The enthalpy of fusion of $\mathrm{CdI_2(s)}$ derived from Eqs. (3) and (4) is also in good agreement with literature values (Table 2). Thus, having established the credibility of the vapor pressure measurement of $\mathrm{CdI_2}$, vaporization measurements were carried out on the compound $\mathrm{Cs_2CdI_4}$.

3.2. Vaporization of Cs_2CdI_4

The compound $\mathrm{Cs_2CdI_4}$ was found to vaporize incongruently above 640 K in inert atmosphere giving $\langle\mathrm{CsI}\rangle$ and $(\mathrm{CdI_2})$ according to the reaction

$$\langle\mathrm{Cs_2CdI_4}\rangle = 2\langle\mathrm{CsI}\rangle + (\mathrm{CdI_2}). \qquad (5)$$

As mentioned in the previous section, the Knudsen effusion mass spectrometry measurement [5] showed $(\mathrm{CdI_2})$ to be the most abundant species in the vapor phase in the temperature range of the present investigation. The X-ray pattern of the partially vaporized compound showed the lines of CsI in addition to that of the parent compound. The product condensed in the colder part of the reaction tube gave the X-ray pattern matching with pure $\mathrm{CdI_2}$ in support of our assumption.

The determination of vapor pressure of $\mathrm{Cs_2CdI_4}$ mainly involved monitoring of mass loss due to incongruent vaporization of $\mathrm{Cs_2CdI_4}$ according to reaction Eq. (5). The vapor pressure of $\mathrm{CdI_2}$ in equilibrium with $\mathrm{Cs_2CdI_4}$ was calculated from mass loss of the sample per unit volume of the carrier gas swept over it using Eq. (2). In the present case the ambient temperature is 299.0 ± 0.5 K.

The values of vapor pressure of $\mathrm{CdI_2}$ over the mixture of $\langle\mathrm{Cs_2CdI_4} + \mathrm{CsI}\rangle$ and its melt close to the composition of $\{\mathrm{Cs_2CdI_4}\}$ at different temperatures are listed in Table 3 and plotted in Fig. 2. The corresponding linear least squares fitted equations are given by

$$\ln p(\mathrm{CdI_2})/\mathrm{Pa}\langle\mathrm{Cs_2CdI_4}\rangle\ (\pm 0.08)$$
$$= -20932.5/T + 29.68 \quad (643\,\mathrm{K} \le T \le 693\,\mathrm{K}), \qquad (6)$$

$$\ln p(\mathrm{CdI_2})/\mathrm{Pa}\{\mathrm{Cs_2CdI_4}\}\ (\pm 0.02)$$
$$= -17910.5/T + 25.24 \quad (713\,\mathrm{K} \le T \le 749\,\mathrm{K}). \qquad (7)$$

The standard Gibbs energy change for Eq. (5) could be expressed by the equation

$$\Delta_r G^\circ = 2\Delta_f G^\circ\langle\mathrm{CsI}\rangle + \Delta_f G^\circ(\mathrm{CdI_2}) - \Delta_f G^\circ\langle\mathrm{Cs_2CdI_4}\rangle. \qquad (8)$$

Substituting $-RT \ln p(\mathrm{CdI_2})$ for $\Delta_r G^\circ$ and rearranging the above equation we have

$$\Delta_f G^\circ\langle\mathrm{Cs_2CdI_4}\rangle = 2\Delta_f G^\circ\langle\mathrm{CsI}\rangle + \Delta_f G^\circ(\mathrm{CdI_2})$$
$$+ RT \ln p(\mathrm{CdI_2}). \qquad (9)$$

Since in the present case the vapor pressure of the compound is measured in the temperature range above the melting point of $\langle CdI_2 \rangle$, the value of $\Delta_f G^\circ (CdI_2)$ was obtained from the equilibrium between $\{CdI_2\}$ and (CdI_2).

The above equation can then be rewritten as

$$\begin{aligned}\Delta_f G^\circ \langle Cs_2CdI_4 \rangle &= 2\Delta_f G^\circ \langle CsI \rangle + \Delta_f G^\circ \{CdI_2\} \\ &\quad + RT \ln p(CdI_2)/p^0(CdI_2),\end{aligned} \tag{10}$$

where $p(CdI_2)$ is the partial pressure of CdI_2 in equilibrium with the mixture $\langle Cs_2CdI_4 + CsI \rangle$ and given by Eq. (6) and $p^0(CdI_2)$ is the partial pressure of (CdI_2) over pure liquid CdI_2 which is given by Eq. (4).

Similar equation can be derived for Gibbs energy of formation of $\{Cs_2CdI_4\}$ which is represented as

$$\begin{aligned}\Delta_f G^\circ \{Cs_2CdI_4\} &= 2\Delta_f G^\circ \langle CsI \rangle + \Delta_f G^\circ \{CdI_2\} \\ &\quad + RT \ln p(CdI_2)/p^0(CdI_2).\end{aligned} \tag{11}$$

In this case, $p(CdI_2)$ is the partial pressure of (CdI_2) in equilibrium with nearly stoichiometric $\{Cs_2CdI_4\}$, given by Eq. (7) and $p^0(CdI_2)$ is given by Eq. (4). The Gibbs energy of formation of $\langle Cs_2CdI_4 \rangle$ and $\{Cs_2CdI_4\}$ was derived from Eqs. (10) and (11) using $\Delta_f G^\circ \langle CsI \rangle$ and $\Delta_f G^\circ \{CdI_2\}$from [9,6] and by substituting for $\ln p(CdI_2)$ and $\ln p^0(CdI_2)$ from Eq. (6) or Eqs. (7) and (4), respectively. These are represented as

$$\begin{aligned}\Delta_f G^\circ \langle Cs_2CdI_4 \rangle\ (\pm 6.7)\ \mathrm{kJ\,mol^{-1}} \\ = -1026.9 + 0.270T \quad (643\,\mathrm{K} \le T \le 693\,\mathrm{K}),\end{aligned} \tag{12}$$

and

$$\begin{aligned}\Delta_f G^\circ \{Cs_2CdI_4\}\ (\pm 6.6)\ \mathrm{kJ\,mol^{-1}} \\ = -1001.8 + 0.233T \quad (713\,\mathrm{K} \le T \le 749\,\mathrm{K}).\end{aligned} \tag{13}$$

4. Conclusion

The standard Gibbs energy of formation of Cs_2CdI_4 derived from its vapor pressure above and below melting could be expressed as a function of temperature by Eqs. (12) and (13), respectively. The standard enthalpy of formation at 298.15 K evaluated from the ΔH° term in Eq. (12), which represents the enthalpy of formation at the mean temperature of measurement, namely 668 K, using the heat capacity and enthalpy of transition data for Cs_2CdI_4 given in reference [2], was found to be -918.0 ± 11.7 kJ mol^{-1}, in good agreement with the measured calorimetric values of -920.3 ± 1.4 and -917 ± 1.5 kJ mol^{-1} reported in references [10,11], respectively. The enthalpy of fusion of Cs_2CdI_4 derived from Eqs. (12) and (13) was found to be 25.1 ± 10.0 kJ mol^{-1} against 36.7 kJ mol^{-1} reported in the literature [2].

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