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THE THERMOCHEMICAL PROPERTIES OF CAESIUM IODIDE.
I. THERMODYNAMIC FUNCTIONS OF SOLID CsI

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ABSTRACT

The enthalpy of solution of CsI(s) in water has been measured at various concentrations. From the results, and using auxiliary data, the enthalpy of formation of CsI was found to be $-\Delta H_f^0$ (298.15 K) = $-(348.14 \pm 0.18)$ kJ mol^{-1}. In addition, enthalpy increments of CsI(s) have been measured by drop calorimetry from 298 to 850.7 K. The melting temperature and the enthalpy of melting have been measured by DSC measurements; the values 630.5 ± 0.2°C, and $\Delta H_m^0 = (24.0 \pm 0.2)$ kJ mol^{-1}, respectively, have been obtained. From the results obtained, and from a selection of literature data, the thermodynamic functions of CsI(s) have been calculated in the temperature range 298–903.7 K.

INTRODUCTION

The behaviour of caesium and iodine within light-water reactor (LWR) fuel, UO_2, especially under accident conditions, has been the subject of many studies recently. From those studies it appeared that release of iodine is much less than previously anticipated when it was assumed that fission product iodine escapes from the core in the elemental form. Indeed, thermodynamic evidence indicates that the chemical form in which iodine escapes from the fuel is caesium iodide, being stable with respect to other iodides of interest, and considerably less volatile than elemental iodine [1]. Although most experimental work also provides evidence for the release of iodine as CsI, some observations are at variance herewith and this discrepancy remains to be resolved. As a contribution we present here an assessment of the thermochemical properties of solid caesium iodide based on our measurements and on literature data. In a subsequent paper we will discuss the thermochemical properties of gaseous CsI.

EXPERIMENTAL

Caesium iodide

Three different samples were used. CsI-1 (suprapur, Merck) was dried at 200°C for 2 h; CsI-2 and CsI-4 (ultrapur VENTRON) were dried in argon at

TABLE 1

High-temperature enthalpy increments of solid CsI below 550 K

T (K)	$H^0(T)-H^0(298.15)$ (J mol^{-1})		δ (%)
	Expt.	Calc.	
396.0	5236	5245	0.17
404.6	5708	5711	0.05
411.7	6105	6097	−0.13
422.5	6699	6685	−0.21
424.7	6809	6805	−0.06
434.4	7347	7334	−0.18
449.9	8150	8183	0.40
457.2	8594	8583	−0.13
457.3	8581	8589	0.09
475.3	9577	9579	0.02
486.9	10194	10220	0.26
498.9	10895	10884	−0.10
506.9	11361	11328	−0.29
514.2	11724	11733	0.08
537.6	13027	13038	0.08
540.1	13184	13178	−0.05

250°C for 4 h. In all cases the X-ray diffration patterns showed the presence of CsI only. A chemical analysis of the samples showed them to be pure within the limits of uncertainty of the analysis.

Drop calorimeter

High-temperature enthalpy increments were measured between 449.9 and 752.1 K with CsI-1, and between 396.0 and 850.7 K with CsI-4 in a diphenyl ether drop calorimeter, which was described in detail previously [2]. A 10.14067-g sample of CsI-1 was encapsulated in a silica bulb of 1.4731 g SiO_2; the enthalpy of CsI is thus about 65% of the total at room temperature. In a second series of experiments, 13.90905 g CsI-4 were encapsulated in a silica bulb of 1.33675 g SiO_2, the enthalpy of CsI thus being about 75% of the total at room temperature. The difference between the values of $[H^0(T)-H^0(T')]$ (in which T' is the temperature of the calorimeter) for the loaded and the empty silica capsule can be calculated, and is, after a correction for $(T'-298.15\text{ K})$ with the C_p-value, the values of $\{H^0(T)-H^0(298.15\text{ K})\}$ for the specimen. The results are given in Tables 1 and 2.

Enthalpy-of-solution calorimeter

Enthalpies of solution were measured in a calorimeter which has been previously described together with the calorimeteric procedure and the calibration method [3].

TABLE 2

High-temperature enthalpy increments of solid CsI above 550 K

T (K)	$H^0(T)-H^0(298.15)$ (J mol^{-1})		δ (%)
	Expt.	Calc.	
582.7	15598	15607	0.06
596.0	16405	16385	−0.12
607.5	17075	17061	−0.08
617.8	17687	17670	−0.10
631.2	18426	18466	0.22
656.0	19898	19950	0.26
663.7	20493	20414	−0.39
705.5	22941	22958	0.07
730.0	24455	24469	0.06
752.1	25836	25844	0.03
758.7	26233	26257	0.09
797.1	28687	28683	−0.01
811.0	29593	29569	−0.08
817.7	29932	29998	0.22
837.5	31255	31273	0.06
850.7	32217	32128	−0.28

DSC measurements

The melting point of CsI was determined with a Mettler DSC apparatus (type TA 13).

X-ray diffraction measurements

All samples were checked for phase purity using a Guinier-De Wolff camera (type FR 552) with Cu $K\alpha$ radiation.

RESULTS

The enthalpy of formation of CsI

The enthalpy of solution of CsI-2 in water has been measured at various concentrations; the results are listed in Table 3. Within the limits of error there appears to be hardly any dependence on concentration in this range, in agreement with an evaluation by Parker [4].

The enthalpy of solution of CsI in water has also been measured previously by several authors. The old measurements by Beketov and Beketov [5], and de Forcrand [6,7] have been evaluated by Parker [4] who selected $\Delta H^0_\infty(\text{soln}) = 33.346 \pm 0.418$ kJ mol^{-1} as the "best" value, based on these

TABLE 3

Enthalpy of solution of CsI in water at 298.15 K

Ref.	H_2O/CsI	ΔH^0(soln) (kJ mol^{-1})
Parker (1965) [4]	–	33.346 ± 0.418
Tsvetkov and Rabinovitch (1969) [8]	1500	33.280 ± 0.167
Montgomery et al. (1978) [9]	1500	33.239 ± 0.03
Thourey and Perachon (1980) [10]	–	33.361
Present work	635	33.17 ± 0.03
	1400	33.20 ± 0.10
	2800	33.30 ± 0.04
	5500	33.28 ± 0.05
	Selected value	33.35 ± 0.10

measurements. Since then other measurements by Tsvetkov and Rabinovitch [8], Montgomery et al. [9], and Thourey and Perachon [10] have been reported (Table 3). Given the apparent small dependence of ΔH^0(soln) on concentration, we select as the "best" value $\Delta H^0_\infty(\text{soln}) = 33.35 \pm 0.10$ kJ mol^{-1}.

To calculate the enthalpy of formation of CsI at 298.15 K from ΔH^0_∞(soln), the enthalpies of formation of I^-(aq) and Cs^+(aq) are required. For the latter value we take the key value from CODATA [11], $\Delta H_f^0(Cs^+, aq) = -258.04 \pm 0.13$ kJ mol^{-1}. A recent evaluation of all available data gives for $\Delta H_f^0(I^-, aq) = -56.750 \pm 0.070$ kJ mol^{-1} [12]. Combining these values we find for the enthalpy of formation of CsI(s) the value $\Delta H_f^0(298.15\ K) = -348.14 \pm 0.18$ kJ mol^{-1}. This "best" value is slightly different from the value recommended by NBS [13], -346.60 kJ mol^{-1}, mainly because a different value for $\Delta H_f^0(I^-, aq)$ has been used. The selected value is in perfect agreement with the value recommended by Glushko et al. [14].

Phase transitions

CsI has the CsCl-structure (bcc) at room temperature. At temperatures below 160 K a phase change to a tetragonal lattice has been observed [15].

Heat capacity

Two series of high-temperature enthalpy increments of solid CsI with different samples have been measured, and the results are plotted in Fig. 1, together with literature values.

Our measurements fall into two different sets of data. Up to about 560 K the data, which have a smooth connection with the low-temperature heat capacity measurements by Taylor et al. [16], can be represented by the equation

$$[H^0(T) - H^0(298.15)](\text{J mol}^{-1}) = 49.4299T + 6.00565.10^{-3}T^2 - 15271.4 \qquad (396\text{–}540\ \text{K})$$

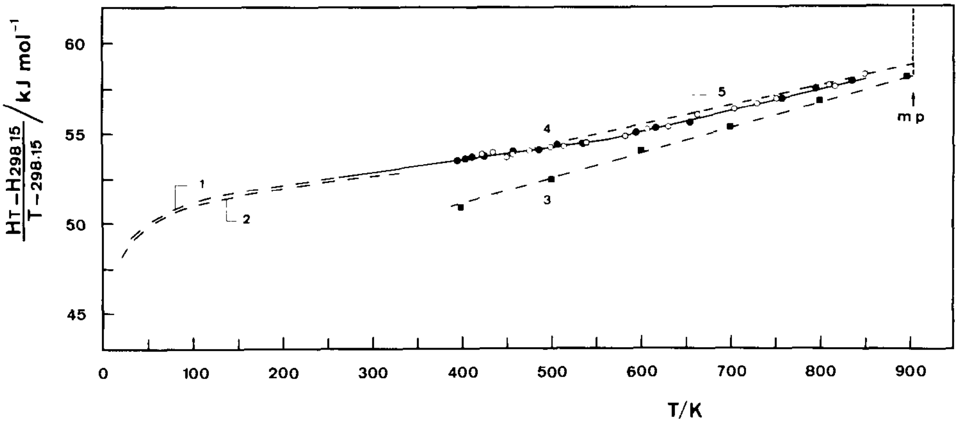

Fig. 1. The reduced enthalpy increments of CsI: (1) Taylor et al. [16]; (2) Sorai et al. [23]; (3) Kaylor et al. [17,18]; (4) ECN, present work, ○, ●; (5) Takahashi et al. [19].

Above 560 K we obtain

$$[H^0(T) - H^0(298.15)](\mathrm{J\ mol^{-1}}) = 44.0049T + 12.3085.10^{-3}T^2 - 14214.2 \qquad (583\text{–}851\ \mathrm{K})$$

High temperature enthalpy increments have also been measured by Kaylor et al. [17], and Smith et al. [18], but the measurements do not agree with either our measurements, or the low-temperature heat capacity measurements (see below). For this reason we decided to disregard these measurements.

High-temperature enthalpy increments of solid CsI have also been measured very recently by Takahashi et al. [19]. The smoothed results of their measurements differ by only 0.7% from our measurements, although the scatter in the individual measurements is rather high. The authors also observed a change in the slope of the (almost linear) enthalpy equations, however, around 400 K. The enhanced increase in the heat capacity of CsI was attributed by these authors to vacancy formation. However, their argument that the thermal expansion coefficient of CsI shows a similar behaviour above 400 K, is not based on unanimous results [20–22].

Low-temperature heat capacity measurements have been measured by Taylor et al. [16], and by Sorai et al. [23]. The latter authors claim a precision of better than 0.3%. There is a systematic deviation between the two sets of measurements, being 0.5% at 298 K, and gradually increasing to about 2% below 20 K. Low-temperature heat capacities of CsI in the temperature range 2–10 K have been measured by Marshall and Kunkler [24], but their results only agree with Sorai et al.'s data below 5 K. Above this temperature the values of both sets of measurements deviate strongly.

Entropy

The entropy of solid CsI has been derived from the low-temperature heat capacity measurements. Sorai et al.'s data [23] give the value $S^0_{298\ 15\mathrm{K}} = 121.867 \pm 0.40$ J K^{-1} mol^{-1}, Taylor et al. [16] obtained $S^0_{298\ 15\mathrm{K}} = 123.05$ J K^{-1} mol^{-1}, however, without an indication of the accuracy. In view of the fact that our high-temperature measurements fit Taylor's low-temperature data smoothly, we select for the entropy of CsI at 298.15 K the value $S^0 = 123.0 \pm 0.5$ J K^{-1} mol^{-1}.

Melting point and enthalpy of fusion

The melting point of CsI has been measured by us in the DSC apparatus, using the melting point of aluminium (660.37°C) as a reference, and a heating rate of 2° min^{-1}. A sharp, reproducible melting point has been found at 630.5 ± 0.2°C.

The measurements also yielded the enthalpy of fusion of CsI by comparing the melting peak area of CsI with that of aluminium. In this case a heating rate of 10° min^{-1} was taken, and a small correction for evaporation of CsI was applied. As a result of ten determinations the value $\Delta H^0_\mathrm{m} = 24.0 \pm 0.2$ kJ mol^{-1} has been been obtained.

In the literature, deviating values for the melting point and the enthalpy of melting of CsI have been reported (Table 4). The measurements of Kaylor et al. [17] have already been disregarded. The value, obtained by Bousquet et al. [25] seems to be rather high, whereas their value for the melting point is certainly too low, as is Jaeger's [27]. For this reason, we reject the selection given in Glushko et al.'s tabulation [14] ($\Delta H^0 = 25.65$ kJ mol^{-1} at 632°C), and recommend for CsI: $\Delta H^0_\mathrm{m} = 24.0 \pm 0.2$ kJ mol^{-1} at a melting temperature of 630.5 ± 0.2°C.

Thermodynamic functions of CsI(s)

From the data selected in this paper the thermodynamic functions of solid

TABLE 4

Melting point and enthalpy of fusion of CsI

Ref.	Melting point (°C)	Enthalpy of fusion (kJ mol^{-1})
Jaeger (1917) [27]	621	–
Bredig et al. (1955) [21]	626	–
Kaylor et al. (1960) [17]	634	25.016
Dworkin and Bredig (1960) [26]	–	23.60 ± 0.5
Bousquet et al. (1967) [25]	624	27.53 ± 0.84
Present work	630.5 ± 0.2	24.0 ± 0.2

TABLE 5

Thermodynamic functions of solid CsI

T (K)	$C_p^0(T)$ (J K^{-1} mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$H^0(T)-H^0(298.15)$ (J mol^{-1})	$\Delta H_f^0(T)$ (J mol^{-1})	$\Delta G_f^0(T)$ (J mol^{-1})
298.15	53.011	123.0	0	−348140	−342112
300	53.033	123.328	98	−348151	−342073
400	54.234	138.749	5461	−358888	−338992
500	55.436	150.980	10945	−380644	−331956
600	58.775	161.316	16620	−379949	−322275
700	61.237	170.561	22620	−378927	−312741
800	63.699	178.899	28867	−377660	−303370
900	66.160	186.544	35360	−376151	−294173
903.7	66.251	186.815	35605	−376091	−293835

CsI have been calculated. The auxiliary values for Cs and I_2 were taken from ref. 28. The results are listed in Table 5.

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