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An investigation of the thermodynamic properties of cadmium sulphide

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Abstract

The free energy of formation of cadmium sulphide has been determined by an electrochemical technique using a molten salt electrolyte (LiCl–KCl + 5 wt.% $CdCl_2$) galvanic cell. From the open circuit e.m.f. of the galvanic cell measured at different temperatures the $\Delta G^{\ominus}$ versus T relationship for the reaction Cd(l) + S(l) = CdS(s) has been established: $\Delta G^{\ominus} = (-164.295 + 31.37T) \pm 310$ J mol^{-1} ($640 < T < 690$ K). The enthalpy of formation was measured directly in a differential thermal analysis calorimeter. For these investigations, the values of $\Delta G^{\ominus}_{298}$, $\Delta H^{\ominus}_{298}$, $\Delta S^{\ominus}_{298}$ and $S^{\ominus}_{298}$ were calculated as -149.8 ± 2.0 kJ mol^{-1}, -153.3 ± 2.8 kJ mol^{-1}, -11.7 J K^{-1} mol^{-1} and 72.0 J K^{-1} mol^{-1}, respectively. The estimated values of the lattice constants (based on the covalent, rationalised and ionic radii of cadmium and sulphur), the enthalpy of formation (based on Pauling's and Phillips' methods) and the standard entropy (based on Latimer's method) are compared with the experimental values and discussed with reference to the structure and bonding.

INTRODUCTION

In the system Cd–S [1], there is only one compound, CdS, with wurtzite structure. It has a very narrow range of homogeneity. Normally it sublimes above 1253 K and melts under a pressure of 100 atm [2]. Cadmium sulphide has gained prominence as a semiconductor compound for several electronic applications [3,4], such as heterojunction solar cells (e.g., n-CdS/p-Cu_2S, n-CdS/p-CdTe, n-CdS/p-Si, etc.), window materials, non-linear optical devices, etc.

The thermodynamic properties of CdS have been determined by various investigators using vapour pressure [5–9] and electrochemical [10] techniques. Because these techniques do not yield accurate values for the enthalpy and entropy of formation and because no reliable calorimetric measurement has been reported so far, the present investigation was

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carried out in order to determine the free energy of formation of CdS by an electrochemical technique and the enthalpy of formation by differential thermal analysis calorimetry. The entropy of formation was obtained by combination of these experimentally determined values.

EXPERIMENTAL

Materials

High purity (99.999%) cadmium, sulphur and tellurium obtained from Johnson Matthey (UK) were used in this investigation. The following Analar grade salts were used for preparation of the electrolyte: cadmium chloride (Thomas Baker, UK), lithium chloride (Sisco, India) and potassium chloride (Qualigens, India).

Electrochemical measurements

The free energy of formation of CdS was determined in the range 640–690 K by measuring the open circuit e.m.f. of the following galvanic cell

$$\mathrm{Cd(l)/LiCl{-}KCl + 5\ wt.\%\ CdCl_2/CdS(s) + S(l)}$$

The virtual cell reaction is

$$\mathrm{Cd(l) + S(l) = CdS(s)} \qquad (1)$$

The free energy of formation of CdS is calculated from the relation

$$\Delta G^{\ominus} = -nFE \qquad (2)$$

where n is the number of electrons transferred during reaction (1), E the open circuit e.m.f. of the cell and F the Faraday constant.

A cell assembly made of borosil glass containing two lower limbs (8 mm internal diameter) below a tubular electrolyte compartment (35 mm internal diameter) was used in this investigation. A tungsten lead wire 0.4 mm in diameter and 20 cm in length was sealed at the bottom of each limb. Cadmium sulphide CdS with 20 at.% excess S was formed in one limb by heating an intimate mixture of CdS and S powders under argon. In the other limb, 6 g of pure Cd was melted under argon. The details of the experimental technique and cell assembly have been described elsewhere [11,12].

The cell temperature and e.m.f. were both measured by a digital electrometer (Keithley, USA; Model 617) at an input impedance of greater than 2×10^{12} Ω. The cell attained equilibrium after 20 h and thereafter e.m.f. values remained stable for over 35 h. The e.m.f. measurements were made during heating as well as cooling cycles and were reproducible within

± 1.5 mV. Three independent runs were performed to check the reproducibility of the results.

Differential thermal analysis calorimetry

The standard enthalpy of formation of CdS was measured directly in a quantitative differential thermal analysis (DTA) calorimeter using a stainless steel block as a reference surrounding. The calorimeter has been successfully employed for the study of a number of chalcogenides, namely CdSe [13], CdTe [12], ZnSe [14] and ZnTe [15]. The construction and operation of the calorimeter were similar to those described by Shamsuddin and coworkers [12,16].

An intimate mixture (8.01255 g) of fresh powders of cadmium (150 μm) and sulphur (100 μm) in stoichiometric proportion corresponding to the composition CdS was placed in the graphite sample container of the calorimeter, which after evacuation and insertion of argon (with oxygen impurity less than 2 ppm) was heated at a constant and reproducible rate of 3 K min^{-1} by a thermal program controller (ULVAC, Sinku–Riku, Japan; Model HPC-7000). The temperature of the sample and the differential temperature ΔT between the sample and the reference block were recorded with a four-pen recorder (BBC, Austria; Model SE-460). During the exothermic pyrosynthesis of CdS, the values of ΔT showed a pronounced upward peak, from the area of which the enthalpy of formation was calculated. The calorimeter was calibrated by studying the fusion of pure Cd, Te and $CdCl_2$, under conditions identical to those of the runs with the powder mixture of Cd and S. Three independent runs were performed to check the reproducibility of the results.

RESULTS AND DISCUSSION

Free energy of formation

Figure 1 shows a plot of e.m.f. against temperature for the galvanic cell. From least-squares analysis of the variation of e.m.f. with temperature, the following E versus T equation was obtained

$$E = (851.2 - 0.1625T) \pm 1.6 \text{ mV} \qquad (640 < T < 690 \text{ K}) \tag{3}$$

Using this, a $\Delta G^{\ominus}$ versus T relationship for reaction (1) was established

$$\Delta G^{\ominus} = (-164\,295 + 31.37T) \pm 310 \text{ J mol}^{-1} \qquad (640 < T < 690 \text{ K}) \tag{4}$$

The intercept and slope of eqn. (4) represent the average values of enthalpy and entropy of formation of CdS, respectively, in the temperature range 640–690 K. Making use of the available thermodynamic and phase equilibria data and the associated solution model for the liquid phase in

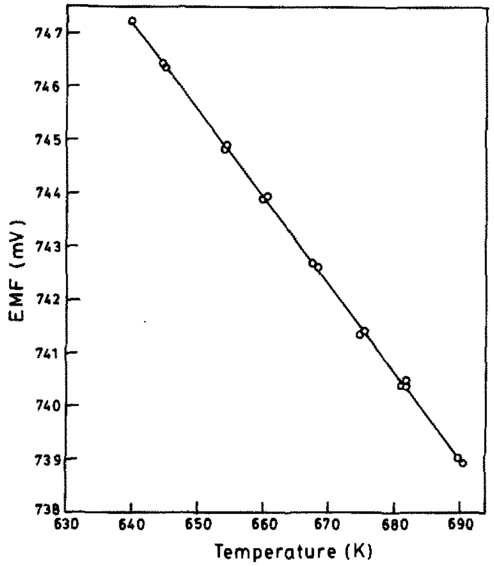

Fig. 1. E.m.f. vs. temperature plot of the galvanic cell.

the system Cd–S, Sharma and Chang [17] have optimised the following $\Delta G^{\ominus}$ versus T relationship for reaction (1)

$$\Delta G^{\ominus} = -162760 + 40.1786T \text{ J mol}^{-1} \qquad (5)$$

Our eqn. (4) is in good agreement with the above eqn. (5).

The $\Delta G^{\ominus}_{298}$ value calculated from eqn. (4), taking into account the enthalpies of fusion of cadmium and sulphur and Kirchhoff's law correction [1,18], is -149.8 ± 2.0 kJ mol^{-1}. This value for the free energy of formation is comparable with the value of -153.1 kJ mol^{-1} reported by Hartmann et al. [3]. The value of $\Delta G^{\ominus}_{298} = -140.6$ kJ mol^{-1} obtained by Makolkin [10] is less exothermic.

Enthalpy of formation

The enthalpy of formation of CdS at 687 K from liquid cadmium and liquid sulphur obtained by DTA calorimetry is -165.3 ± 2.0 kJ mol^{-1}. This value for the enthalpy of formation is in excellent agreement with the average value of -164.3 ± 2.2 kJ mol^{-1} obtained by electrochemical measurements (eqn. (4)) in the temperature range of 640–690 K. The standard enthalpy of formation of CdS at 298 K is calculated by taking into account the enthalpies of fusion of cadmium and sulphur and Kirchhoff's law correction [1,18]. The resulting value, $\Delta H^{\ominus}_{298} = -153.3 \pm 2.8$ kJ mol^{-1}, is in satisfactory agreement with the values reported by Munir [9] and Hartmann et al. [3] and also with that calculated from our eqn. (4).

TABLE 1

Thermodynamic properties [a] of CdS at 298 K

Investigators	Experimental technique/ temperature range (K)	$-\Delta G^{\ominus}$ (kJ mol^{-1})	$-\Delta H^{\ominus}$ (kJ mol^{-1})	$-\Delta S^{\ominus}$ (J K^{-1} mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})
Boev et al. [5]	Transpiration 1173–1553	–	125.9	–	–
Goldfinger and Jeunehomme [7]	Knudsen effusion 902–1062	–	159.0	–	–
Isakova and Nesterov [8]	Transpiration 1173–1473	–	158.2±2.1 [b]	–	–
Munir [9]	Torsion effusion 882–1107	–	149.4±2.1 [b]	–	–
Makolkin [10]	Electrochemical	140.6	–	–	–
Mills [1]	Compilation	–	149.4±2.1	–	69.0±2.1
Hartmann et al. [3]	Compilation	153.1	156.9	–	71.1
This investigation	Electrochemical 640–690	149.8±2.0	152.3	8.4	75.3
	DTA calorimetry	–	153.3±2.8	–	–
Proposed values		149.8±2.0	153.3±2.8	11.7	72.0

[a] The error limit and temperature range of measurements are specified wherever available.
[b] Values estimated at 298 K from the reported data.

Entropy of formation

The best value for the entropy of formation of CdS may be calculated from the experimental values of free energy of formation determined directly by electrochemical measurement and the enthalpy of formation obtained by calorimetry, using the relation

$$\Delta S_{\mathrm{T}}^{\ominus}=\frac{\Delta H_{\mathrm{T}}^{\ominus}-\Delta G_{\mathrm{T}}^{\ominus}}{T} \tag{6}$$

The value of $\Delta S_{298}^{\ominus}$ thus obtained is -11.7 J K^{-1} mol^{-1}. The large negative value of the entropy of formation suggests that the vibrational entropy term plays a predominant role in formation of the compound. Moreover the negative value of the entropy of formation is consistent with the well ordered structure of CdS and the presence of a strong Cd–S bond.

The standard entropy $S_{298}^{\ominus}$ of CdS obtained from the value of the entropy of formation is in reasonable agreement with the values reported in the literature (Table 1).

The thermodynamic properties of CdS at 298 K are summarised in Table 1.

Enthalpy and entropy of fusion

The attempt to measure the enthalpy of fusion of CdS by DTA calorimeter was unsuccessful due to sublimation of the compound before melting. At 1255 K, ΔT values started decreasing continuously and did not return to the normal background value. The sublimation of CdS was observed at the top of the reaction tube where the vapours condensed, the cooler end being at room temperature. In the absence of an experimental value for the enthalpy of fusion of CdS, we have used $\Delta H^{\mathrm{f}}_{\mathrm{CdS}} = 50.6$ kJ mol^{-1} as estimated by Sharma and Chang [17], for the analysis. The corresponding value of the entropy of fusion ($\Delta S^{\mathrm{f}}_{\mathrm{CdS}} = \Delta H^{\mathrm{f}}_{\mathrm{CdS}}/T^{\mathrm{f}}_{\mathrm{CdS}}$) is 30.2 J K^{-1} mol^{-1}. A theoretical value for the entropy of fusion of CdS may be estimated according to the procedure outlined by Kubaschewski and Alcock [18] by adding the entropies of fusion of the component elements to their entropy of mixing. Because the experimental value of the entropy of mixing of cadmium and sulphur is not available, complete order in the solid state and complete disorder in the liquid state may be assumed. The theoretical value of the entropy of fusion of CdS is thus given by

$$\Delta S^{\mathrm{f}}_{\mathrm{CdS}} = \Delta S^{\mathrm{f}}_{\mathrm{Cd}} + \Delta S^{\mathrm{f}}_{\mathrm{S}} - 4R(0.5 \ln 0.5)\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{7}$$

This yields a value of 26.7 J K^{-1} mol^{-1} which is smaller than that calculated from the data reported by Sharma and Chang [17]. This discrepancy may be due to the error involved in the thermodynamic and phase equilibria data used by Sharma and Chang [17] in their calculation.

Structure and bonding

The experimental values of the hexagonal lattice parameters (c and a) and bond length (l) of CdS, determined in this investigation by X-ray diffractometry, are listed in Table 2 which also includes the theoretical

TABLE 2

Lattice constants (Å) of CdS

Lattice constant	Experimental	Calculated [a]		
		Covalent radii	Rationalised radii	Ionic radii
c	6.711	6.720	6.752	7.067
a	4.134	4.115	4.135	4.327
l	2.52	2.52	2.53	2.65

[a] Values calculated for ideal wurtzite structure, i.e. $c/a = 1.633$.

values of the lattice constants based on the tetrahedral covalent [19], ionic [20] and rationalised (after Phillips [21]) radii of cadmium and sulphur, as estimated by the relation (for ideal wurtzite hexagonal structure, i.e. $c/a = 1.633$ and $u = 3/8$)

$$r_{\mathrm{Cd}} + r_{\mathrm{S}} = l_{\mathrm{CdS}} = uc = \left[\tfrac{1}{3}a^2 + c^2\left(\tfrac{1}{2} - u\right)^2\right]^{1/2} \tag{8}$$

Table 2 clearly indicates that the experimental values of the lattice constants are in good agreement with those calculated from the covalent and rationalised component radii of the compound. The wide disagreement between the estimated lattice constants based on the ionic radii and the experimental values reflects the non-ionic nature of the compound CdS.

Pauling [19] has presented the following empirical equation for calculation of the standard enthalpy of formation of an ionic compound AB

$$\Delta H^{\ominus}_{\mathrm{AB}} = -193.016(X_{\mathrm{A}} - X_{\mathrm{B}})^2 \ \mathrm{J\ mol^{-1}} \tag{9}$$

where X refers to the value of the electronegativity. The enthalpy of formation of CdS obtained by substituting the electronegativity values from the scale due to Pauling [19] is -123.5 kJ mol^{-1}, which is smaller than the experimental value of -153.3 kJ mol^{-1}. This discrepancy indicates that the bonding in CdS is only partly ionic. Phillips [21] has improved the empirical formula for the calculation of enthalpy of formation, by considering both ionicity and metallisation terms based on spectroscopic data. A value of $\Delta H^{\ominus}_{\mathrm{CdS}} = -149.8$ kJ mol^{-1}, as predicted by Phillips' spectroscopic formula [21], is in remarkably good agreement with that measured experimentally.

Latimer [22] has proposed a method for calculation of the standard entropy of an ionic compound by adding the entropies of the cationic and anionic constituent elements. The value of $S^{\ominus}_{298} = 74.9$ J K^{-1} mol^{-1} for CdS, estimated by assuming the presence of cadmium as a bivalent cation and of sulphur as a bivalent anion, is in close agreement with the experimental value of 72.0 J K^{-1} mol^{-1}. This suggests the ionic nature of the Cd–S bond in the compound.

The ionicity of the Cd–S bond, as estimated quantitatively from Pauling's equation [19]

$$\text{ionicity} = \left[1 - e^{-\frac{1}{4}(X_{\mathrm{A}} - X_{\mathrm{B}})^2}\right] \tag{10}$$

is only 0.15. The value of ionicity based on the band theory of Phillips [21] is much larger, 0.685.

Consequently, in the light of the above discussion, we can say that bonding in CdS is neither substantially ionic nor covalent.

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