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The Enthalpy of Iron Diselenide from 300 to 853 K by Drop Calorimetry

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An adiabatic drop calorimeter has been used to measure the enthalpy of iron diselenide in the temperature range 373 to 853 K, relative to 298.15 K. The data obtained can be represented by the equation:

$$H_T^\circ - H_{298}^\circ = 0.18728 \times 10^{-9}\ T^5 - 0.41345 \times 10^{-6}\ T^4 + 0.36771 \times 10^{-3}\ T^3 - 0.15802\ T^2 + 49.957\ T - 7767.7 \text{ cal/mol}$$

Values of Cp, $H_T^\circ - H_{298}^\circ$, S° and $(G_T^\circ - H_{298}^\circ)/T$ were calculated from the experimental data.

In the course of a thermodynamic study [1] of the Fe-Se system, it was necessary to measure the heat content of $FeSe_2$ at high temperatures.

Grønvold and Westrum [2] have previously determined the heat capacity over the temperature range 5 to 350 K and obtained values for the heat content, standard entropy and free energy function.

In the present work an aneroid type drop calorimeter with adiabatic shields has been used in the determinations. The details of the construction have been described elsewhere,[3] together with measurements on a standard sample of aluminium oxide. The estimated standard deviation for a single measurement on α-Al_2O_3 has been reported as 0.21 % in the temperature interval 870 – 1270 K.

EXPERIMENTAL RESULTS

The composition of the iron diselenide employed in the present study was analysed [1] to be $FeSe_{1.973}$. Since iron diselenide has an incongruent melting point at 585°C, the enthalpy measurements were not performed at temperatures above 581°C.

Iron diselenide (7.4953 g; mol. weight 211.63) was sealed in a silica ampoule (3.1762 g) under argon at a pressure of 15 cmHg. As a precaution against breakage the ampoule was placed in a close fitting container (weight 24.518 g) made of platinum-10 % rhodium. Although the total weight of the silica and

platinum is large compared with that of the sample their overall heat capacity is small and approximately half the heat measured was due to iron diselenide. An identical ampoule without iron diselenide was sealed for empty drops. To attain temperature equilibrium the ampoules were kept in the furnace for 50 min, during which time the temperature was recorded. After each sample drop, 15 min passed before steady state conditions were reestablished in the calorimeter, whereas in comparison 10 min were needed for the empty drops.

Table 1. Enthalpies of empty ampoule.

T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 1	% dev. from eqn. 1	T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 1	% dev. from eqn. 1	T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 1	% dev. from eqn. 1
374.5	115.9	115.7	0.17	522.7	353.1	353.6	0.14	673.9	612.7	612.4	0.05
374.5	115.9	115.7	0.17	522.7	353.8	353.6	0.05	673.9	612.2	612.4	0.03
374.5	115.9	115.7	0.17	522.7	353.7	353.6	0.03	724.5	701.3	701.8	0.07
374.5	116.0	115.7	0.26	573.4	439.6	438.9	0.16	724.2	700.4	701.3	0.12
424.8	193.3	194.2	0.46	573.3	438.7	438.7	0.00	724.2	699.8	701.3	0.21
424.7	192.8	194.1	0.67	573.4	439.7	438.9	0.18	724.3	700.8	701.4	0.09
424.7	192.9	194.1	0.62	573.3	438.4	438.7	0.07	774.7	792.7	791.7	0.12
424.7	194.4	194.1	0.15	623.9	525.8	525.4	0.08	774.6	792.3	791.6	0.09
472.5	271.6	270.9	0.26	623.7	524.4	525.0	0.11	774.9	791.3	792.1	0.10
473.4	273.0	272.4	0.22	623.7	525.2	525.0	0.03	774.8	794.0	791.9	0.26
473.3	273.0	272.2	0.29	623.5	523.7	524.7	0.19	823.7	881.1	880.7	0.04
473.3	271.8	272.2	0.14	674.1	613.0	612.7	0.04	823.5	879.8	880.3	0.06
523.0	354.6	354.1	0.14	674.1	613.4	612.7	0.11	823.5	879.9	880.3	0.05
								823.6	880.5	880.5	0.00

Table 1 presents the measured enthalpies from the empty drops. The following equation with the constants determined by the method of least squares represents the empty drop data over the temperature range 373–854 K:

$$H_T - H_{298} = 1.5440\ T + 1.9076 \times 10^{-4}\ T^2 + 2.1432 \times 10^4\ T^{-1} - 546.50 \text{ cal} \quad (1)$$

The average relative deviation from the equation is 0.15 % and the standard deviation of a single measurement is 0.21 %. This equation was used when calculating the net heat by subtracting the values given by the equation from the gross values of the sample drops at the appropriate temperatures.

In order to correlate the present set of enthalpy data with the low temperature data of Grønvold and Westrum, the Shomate [4] function

$$\frac{T[(H_T - {}^1H_{298.15}) - Cp_{298.15}(T - 298.15)]}{(T-298.15)^2}$$

was applied.

This function is very sensitive to scattering in the heat content values relative to the curve, and to small variations in the $Cp_{298.15}$ value which shifts the two data sets relative to each other. A computer program was used to

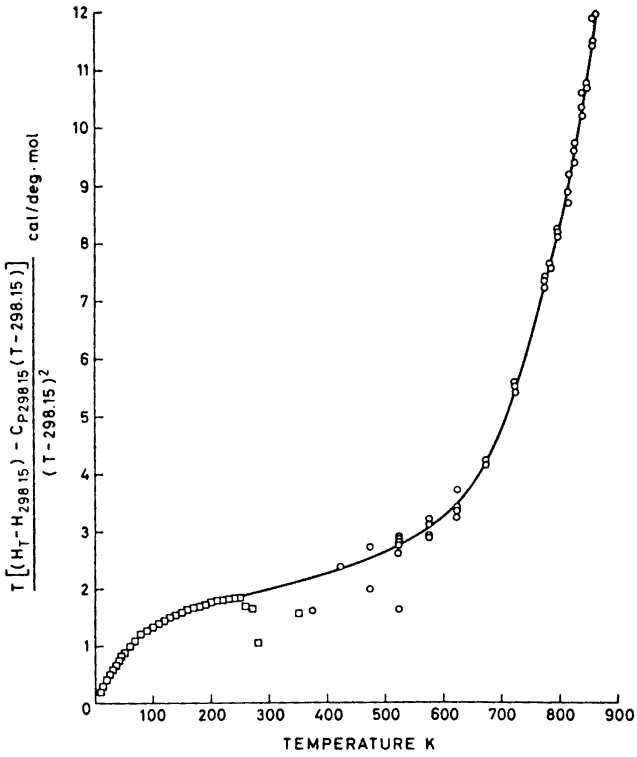

Fig. 1. Shomate function for $FeSe_{1.973}$ plotted against abs. temperature. $Cp_{298.15} = 17.36$ cal/deg.mol; □ from low temperature heat capacity data of Grønvold and Westrum, ○ present data.

find the $Cp_{298.15}$ value which gave the smoothest connection between the two sets of data. Fig. 1 presents a plot of the Shomate function against temperature with $Cp_{298.15} = 17.36$ cal/deg.mol. The $Cp_{298.15}$ value given by Grønvold and Westrum for $FeSe_2$ is 17.42 cal/deg. mol.

To provide an equation applicable from 853 K down to 298.15 K another computer program [5] was used which contained the following constraints:

$H^\circ_{298.15} - H_0^\circ = 0$, $Cp_{298.15} = 17.36$ cal/deg.mol, and $S^\circ_{298.15} = 20.76$ cal/deg.mol.

The equation giving the best fit to the experimental data is a polynomial:

$$H_T^\circ - H^\circ_{298} = 0.18728 \times 10^{-9}\, T^5 - 0.41345 \times 10^{-6}\, T^4 + 0.36771 \times 10^{-3}\, T^3 - 0.15802\, T^2 + 49.957\, T - 7767.7 \text{ cal/mol} \quad (2)$$

The average relative deviation from the equation is 0.86 %, and the standard deviation for a single measurement is 1.53 %. The overall standard deviation for a single measurement when the error in the empty drops are taken also into consideration is 1.54 %.

Table 2. Molar enthalpies of $FeSe_{1.973}$.

T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 2	% dev. from eqn. 2	T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 2	% dev. from eqn. 2	T K	$H_T-H^\circ_{298}$ obs. (cal.)	$H_T-H^\circ_{298}$ calc. from eqn. 2	% dev. from eqn. 2
376.5	1361	1375	0.98	573.8	5169	5168	0.01	793.8	11128	11107	0.19
376.5	1319	1375	4.06	622.7	6264	6223	0.67	793.8	11137	11107	0.27
376.5	1273	1375	7.42	622.7	6205	6223	0.29	813.2	11942	11895	0.39
376.6	1389	1376	0.88	622.7	6187	6223	0.58	813.0	11771	11887	0.98
423.5	2160	2229	3.08	622.7	6216	6223	0.11	812.9	11829	11883	0.45
423.6	2267	2231	1.61	674.1	7410	7434	0.33	812.9	11829	11883	0.45
423.7	2269	2232	1.65	674.1	7399	7434	0.47	823.4	12377	12341	0.29
423.6	2131	2231	4.47	674.0	7409	7431	0.30	822.9	12330	12319	0.09
474.1	3234	3180	1.67	674.0	7393	7431	0.51	822.9	12321	12319	0.01
474.1	3096	3180	2.65	724.1	8784	8776	0.09	822.8	12248	12314	0.54
474.0	3056	3178	3.84	724.1	8793	8776	0.20	835.1	12986	12882	0.81
474.0	3182	3178	0.12	724.1	8756	8776	0.22	834.9	12837	12872	0.27
524.0	4080	4154	1.78	724.2	8785	8779	0.07	834.9	12833	12872	0.31
523.9	4196	4152	1.05	774.3	10445	10384	0.58	844.4	13287	13335	0.36
524.0	4189	4154	0.85	774.3	10421	10384	0.35	844.1	13272	13320	0.37
524.3	4208	4160	1.14	774.2	10387	10380	0.06	844.0	13237	13315	0.59
524.5	4185	4164	0.51	774.2	10385	10380	0.04	844.0	13248	13315	0.50
524.3	4209	4160	1.18	783.1	10694	10702	0.08	854.5	13822	13854	0.23
575.1	5227	5195	0.61	783.8	10725	10728	0.03	854.1	13816	13833	0.13
575.3	5202	5199	0.06	793.9	11119	11111	0.07	854.2	13958	13838	0.86
575.1	5238	5195	0.82	793.9	11164	11111	0.47	854.1	13974	13833	1.02

Table 2 presents the enthalpies found for one mol $FeSe_{1.973}$ together with the calculated values from the polynomial.

The smoothed enthalpy data from the polynomial along with the derived heat capacities, entropy increments, and free energy functions at 100 K interval are given in Table 3.

Table 3. Thermodynamic functions of $FeSe_{1.973}$.

T (K)	Cp (cal/deg. mol)	$H^\circ_T-H^\circ_{298}$ (cal/mol)	S° (cal/deg. mol)	$-(G^\circ_T-H^\circ_{298})/T$ (cal/deg. mol)
298.15	17.36	0	20.76	20.76
300	17.36	32	20.87	20.76
400	18.17	1799	25.95	21.45
500	19.52	3682	30.14	22.78
600	21.60	5726	33.86	24.32
700	26.85	8106	37.52	25.94
800	39.94	11354	41.84	27.65
853	52.35	13780	44.77	28.62

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