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HEAT CAPACITY AND STABILITY OF MONOCLINIC SELENIUM

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ABSTRACT

Heat capacities of monoclinic selenium have been measured by computer interfaced differential scanning calorimetry from 100 to 379 K. Using literature data for low temperature heat capacities, enthalpies, entropies, and free enthalpies are calculated up to the zero entropy production melting temperature of 413 K. A comparison with trigonal selenium shows that there is no floor temperature for the stability of trigonal selenium. Monoclinic selenium is metastable relative to trigonal selenium at all temperatures.

INTRODUCTION

Crystalline selenium exists in three allotropes. Two monoclinic crystal forms, called α and β with space groups $P2_1/n$ and $P2_1/a$, respectively, differ only slightly in packing [1]. Both consist of Se_8 rings. Slow evaporation of the solvent carbon disulfide yields α crystals [2] whilst fast evaporation yields β crystals [3]. At higher temperatures, these crystals are metastable relative to the macromolecular, trigonal selenium. Slow partial transformation has already been observed at room temperature [4]. We studied earlier the thermodynamics and the kinetics of this transition [5]. The overall heat of transition from the monoclinic crystal form to somewhat defective trigonal crystals was found to be —2.1 kJ (mole Se)$^{-1}$. In the liquid state, the same ring—chain reaction has a heat of reaction [6] of +1.19 kJ (mole Se)$^{-1}$. In order to correlate the respective crystal stabilities and for calculation of entropies, it is necessary to know the heat capacities of all species as a function of temperature. While heat capacities of trigonal selenium are well established [7], we could find only rather poor data on monoclinic selenium [8,9] with the exception of data by Wu and Luo [10]. The latter covers, however, only the temperature range from 2 to 20 K.

In this paper, measurements of the heat capacity of monoclinic selenium in the temperature range from 100 to 370 K are reported. These are used in conjunction with data on trigonal and liquid selenium [7] to establish thermodynamic data for monoclinic selenium.

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EXPERIMENTAL

The selenium utilized as starting material was of 99.999% purity supplied by the Materials Research Corp. Orangeburg, N.Y. The selenium was first heated to 523 K to produce melt which contains a ring and chain mixture. These samples were quenched to glassy selenium of similar ring composition (~35%). The ring fraction was then extracted by heating ground, vitreous material in boiling carbon disulfide under reflux. The solution was filtered and, on cooling, a mixture of red α and β monoclinic selenium crystals was grown which showed predominant (001) faces in a platy crystal habit.

A Perkin-Elmer DSC-2 scanning calorimeter connected to a digital data converter was used for the heat capacity measurements. The digital output range is 0—10 000 for full scale deflection. Data sampling was done every 0.6 sec. Calculation of heat capacities from reference measurements (on Al_2O_3), baseline measurements, and sample measurements were done by feeding the digital data on paper tape into a Hewlett-Packard 9821A calculator. The details of equipment, calibration and programming can be found in ref. 11. The small crystals were packed and measured in a nitrogen atmosphere in hermetically sealed aluminium sample pans. Typically, sample weights of 25 mg were used. From 100 to 260 K, measurements were made using the liquid nitrogen bath for the calorimeter. Overlapping measurements from 230 to 370 K were done with outside calorimeter temperatures regulated by a mechanical refrigerator. All measurements were done on heating at 10 K min^{-1}.

RESULTS

The results are shown in Fig. 1. Also shown in Fig. 1 is the best curve for macromolecular, trigonal selenium. Up to 310 K, the measured heat capacities are within 5% of the trigonal selenium, which is close to the accuracy of

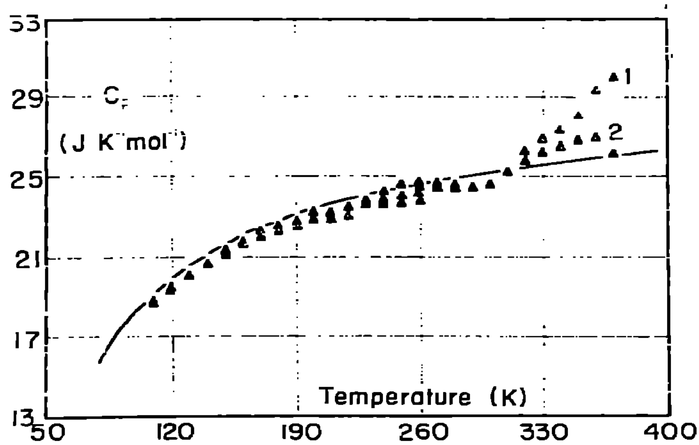

Fig. 1. Heat capacity of monoclinic selenium as measured from 100 to 370 K. The curve drawn represents the best data for trigonal selenium [7].

TABLE 1

Thermodynamic properties of monoclinic selenium in J, K and mole. Superscripts m and t denote monoclinic and trigonal selenium, respectively. Subscript T denotes temperature in K and subscript 0 denotes 0 K.

T (K)	C_p^m	$H_T^m - H_0^t$	S_T^m	$-(G_T^m - H_0^t)$
2.0	0.007229	2 151	1.72	—2 147
3.0	0.02602	2 151	1.73	—2 145
4.0	0.06530	2 151	1.74	—2 144
5.0	0.1319	2 151	1.76	—2 142
6.0	0.2308	2 151	1.79	—2 140
7.0	0.3648	2 151	1.84	—2 138
8.0	0.5345	2 152	1.90	—2 136
9.0	0.7390	2 152	1.97	—2 134
10.0	0.9759	2 153	2.06	—2 132
12.0	1.533	2 156	2.29	—2 128
14.0	2.173	2 159	2.57	—2 123
16.0	2.860	2 164	2.91	—2 118
18.0	3.562	2 171	3.28	—2 112
20.0	4.249	2 179	3.70	—2 105
25.0	5.623	2 203	4.79	—2 083
30.0	6.995	2 235	5.94	—2 057
40.0	9.389	2 317	8.27	—1 986
50.0	11.40	2 421	10.59	—1 891
60.0	13.12	2 543	12.82	—1 774
70.0	14.62	2 682	14.96	—1 635
80.0	15.97	2 835	17.00	—1 475
90.0	17.18	3 001	18.95	—1 295
100.0	18.22	3 178	20.82	—1 096
110.0	19.10	3 364	22.60	—878.9
120.0	19.84	3 559	24.29	—644.2
130.0	20.49	3 761	25.91	—393.0
140.0	21.07	3 968	27.45	—126.0
150.0	21.58	4 182	28.92	156.0
160.0	22.03	4 400	30.33	452.4
170.0	22.41	4 622	31.68	762.6
180.0	22.75	4 848	32.97	1 085
190.0	23.05	5 077	34.21	1 421
200.0	23.32	5 309	35.40	1 771
210.0	23.56	5 543	35.54	2 130
220.0	23.78	5 780	37.64	2 501
230.0	23.99	6 018	38.70	2 833
240.0	24.10	6 259	39.73	3 276
250.0	24.36	6 502	40.72	3 678
260.0	24.52	6 746	41.68	4 091
270.0	24.68	6 992	42.61	4 513
273.2	24.73	7 070	42.89	4 645
280.0	24.83	7 240	43.51	4 943
290.0	24.97	7 489	44.38	5 381
298.2	25.09	7 693	45.07	5 745
300.0	25.11	7 739	45.23	5 830
303.4	25.16	7 825	45.51	5 983
310.0	25.25	7 991	46.06	6 288
320.0	25.38	8 244	46.86	6 751
330.0	25.51	8 499	47.64	7 222

TABLE 1 (continued)

T (K)	C_p^m	$H_T^m - H_0^t$	S_T^m	$-(G_T^m - H_0^t)$
340.0	25.63	8755	48.41	7704
350.0	25.75	9011	49.15	8921
360.0	25.88	9270	49.88	8687
370.0	26.00	9529	50.59	9189
380.0	26.12	9790	51.28	9696
390.0	26.24	10051	51.96	10213
400.0	26.36	10314	52.63	10738
410.0	26.48	10579	53.28	11266
413.0	26.51	10658	53.48	11429
420.0	26.60	10844	53.92	11802

the scanning calorimeter at the lowest temperatures. At higher temperatures, the accuracy of the calorimeter increases to ±1% (ref. 11). One can see that at about 300 K the heat capacity of both the trigonal and the monoclinic forms have practically reached the vibrational limit of 3 R. Above 310 K, the monoclinic selenium shows irreproducible increases in the heat capacity which indicate the beginning of the monoclinic—trigonal transition. It is interesting that this initial indication of the transition is endothermic despite the fact that the overall transition is exothermic. The initial effect at a heating rate of 10 K min^{-1} observed here is only a few per cent of the heat capacity. At a higher heating rate, the endotherm develops into the melting peak of monoclinic selenium which is estimated [5] to be at 413 K. The beginning endotherm may be due to initial ring-opening reactions on the surface, which would be an indication that the floor temperature of amorphous selenium is lower than 320 K, and perhaps even below the glass transition temperature of liquid selenium since there is no indication of pure Se_8 ring melt as deduced from electrical conductivity measurements [12] and heat capacity measurements on liquid selenium [13].

For the overall discussion of the thermodynamic properties, our data were combined with those of Wu and Luo [10] in the range 2—20 K. These heat capacities are intermediate between glassy and trigonal selenium. Since glassy selenium heat capacities also approach trigonal heat capacities at about 100 K, we estimated the heat capacity in the 20—100 K range to be intermediate between glassy and trigonal also. The best presently available heat capacities of monoclinic selenium are listed in Table 1 together with the derived thermodynamic functions.

DISCUSSION

The heat capacity of monoclinic selenium does not deviate sufficiently from trigonal selenium to change the relative stability of the two phases. Setting the trigonal selenium entropy at absolute zero equal to zero, monoclinic selenium has, at 0 K, a residual entropy of about 1.7 J (K mole Se)$^{-1}$ and the free enthalpy of the transition of monoclinic to trigonal selenium remains negative [—2.1 kJ (mole Se)$^{-1}$]. Intermediate values can be seen from the table.

The thermodynamic functions were calculated using the equilibrium data for trigonal selenium as evaluated earlier [7]. At 494.2 K, trigonal selenium melts to an equilibrium melt with a heat of fusion of 6.20 kJ (mole Se)$^{-1}$ and an entropy of fusion of 12.55 J (K mole Se)$^{-1}$. The heat capacity of liquid selenium [13] was then used to calculate the thermodynamic functions for the equilibrium melt above 494.2 K and the metastable melt below 494.2 K to absolute zero [at 0 K, the residual entropy is 3.63 J (K mole Se)$^{-1}$ and the free enthalpy of transition of trigonal to amorphous, glassy selenium is +3.8 kJ (mole Se)$^{-1}$]. The zero entropy production melting of monoclinic selenium, i.e. the transition from metastable monoclinic selenium to metastable melt without change in stability (equal free enthalpies) occurred [5] at 413 K. The heat of fusion [5] at this temperature is 3.24 kJ (mole Se)$^{-1}$, a figure checked in this research. This leads to an entropy of fusion of 7.84 J (K mole Se)$^{-1}$. With these values and the heat capacities measured here, which, above 310 K, were taken as being identical to trigonal selenium, the thermodynamic functions listed in Table 1 were arrived at.

One can conclude from these data that, due to the considerably higher heat of fusion of trigonal selenium, the slightly positive heat of reaction for the ring-to-chain reaction in the melt (which leads to a floor temperature for chain stability) is changed to a negative heat of reaction for the ring—chain reaction in the crystalline state and makes the Se_8 ring metastable at all temperatures. A ceiling temperature for the chain should exist, but melting intercedes before it can be reached. Since bond length, bond angles, and dihedral angles of monoclinic and trigonal selenium are similar (0.234 nm, 105.8°, 102° and 0.236 nm, 103.6° and 101°, respectively) [1], the main reason for the stability of trigonal selenium must be its much higher packing density. The crystalline density of monoclinic selenium at room temperature is 4.4 Mg m^{-3}, while that of trigonal selenium is 4.8 Mg m^{-3}. The density of liquid selenium extrapolates to about 3.9 Mg m^{-3}, almost in proportion to the heats of fusion.

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