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ON THE ENTROPIES OF GLASSY AND MONOCLINIC SELENIUM AT 0 K

L. Judovits and *B. Wunderlich*

DEPARTMENT OF CHEMISTRY RENSSELAER POLYTECHNIC INSTITUTE, TROY, NEW YORK 12181 U.S.A.

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The entropies of trigonal, monoclinic and glassy selenium are discussed based on the ATHAS data bank data and third law entropy considerations. Within the error limit both trigonal and monoclinic selenium have zero residual entropy at zero kelvin temperature. The residual entropy of glassy Se is similar in magnitude to other linear macromolecules.

Heat capacity, C_p, is the key thermal property. Cognizance of C_p over the whole temperature range enables derivation of the other thermodynamic quantities (enthalpy, entropy, and Gibbs energy). In recognition of the importance of obtaining reliable polymeric heat capacity data the ATHAS (Advances THermal AnalysiS) Laboratory data bank was established which contains heat capacities of linear macromolecules. Data on approximately 100 linear macromolecules have been collected [1–9] and are now being critically evaluated and expanded in a series of publications (Polytetrafluoroethylene [10], Polypropylene [11], Polyoxides [12], Polyfluoroalkanes [13], Polychloroalkanes [14], Polyesters [15], side-chain Polyalkanes [16], Polydienes [17]).

In the first paper of the data bank publications [1] the residual entropies at 0 K of monoclinic and glassy selenium were given, based strictly on empirical data, as being 1.71 and 3.63 $J K^{-1} mol Se^{-1}$, respectively [1]. This, naturally, raises the question of the error limits of the data because, as a crystal, metastable monoclinic selenium should still obey the third law and have zero entropy at 0 K. In this note we would like to investigate this question of error limits.

Data, Discussion and Calculations

The various heat capacities and the error limits for the three allotropes of selenium are listed in Table 1. The entropies are based on heat capacities recommended in functional form in reference [1].

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Table 1 Calculation of the entropy of equilibrium melt of selenium at the equilibrium melting temperature of trigonal selenium (494.2 K)

Temperature range, K	ΔS ($J K^{-1}$ mol Se^{-1})	*Deviation* (J K^{-1} mol Se^{-1})	Reference
1. Trigonal allotrope			
0 to 25	2.35	0.12	1
25 to 80	11.69	0.08	1
80 to 494.2	41.29	0.12	1
494.2 (ΔS_f)	12.46	0.01	1, 18, 20
Total:	67.79	0.33	—
2. Monoclinic allotrope			
0 to 20	1.976	0.73	1
20 to 110	18.916	0.71	1
110 to 413	30.87	0.09	1
413 (ΔS_f)[a]	7.84	1.69	19
413 to 494.2[b]	6.56	0.03	1
Total:	66.16	3.25	—
3. Glassy allotrope and melt			
0 to 25	4.114	0.30	1
25 to 80	12.776	0.01	1
80 to 210	19.57	0.06	1
210 to 303.4 (T_g)	9.24	0.06	1
303.4 to 494.2[b]	18.55	0.09	1
Total:	64.25	0.52	—

[a] Heat of transition monoclinic crystal to ring-chain equilibrium melt divided by 413, the estimated zero entropy production melting temperature. Data as estimated in Ref. 19.

[b] Entropy change in the molten state.

The errors were estimated by inspection of all measured, "acceptable" data in the standard temperature increments. The criteria of "acceptable" data are discussed in Ref. [1]. Over the whole temperature ranges used for curve fitting, errors from the recommended C_p-functions were approximately constant (random fluctuations) when expressed in per cent, i.e. on integration to entropy a similar percentage error results.

Data for monoclinic Se pose a special problem since no heat capacity measurements exist between 20 and 110 K and only one set covers the range from 0.2 to 20 K. Since, both, at 20 and 110 K the C_p of monoclinic Se is equal to the average of glassy and trigonal Se, this average was also used for the intermediate temperatures. The error in entropy from 0 to 110 K was then estimated to be no more than half of the integrals $\Delta C_p/T$.

The entropies of polymerization and the establishment of ring-chain equilibrium are included in the respective entropies of fusion; i.e. in both, trigonal and monoclinic Se, the fusion is assumed to lead to melt with fully established ring-chain equilibrium. The probably faster than usually assumed equilibrium was discussed earlier [21]. The respective differences in residual entropy of the glassy and monoclinic Se are $67.79-64.25 = 3.54 \pm 0.85$ J K^{-1} mol Se^{-1} and $67.79-66.17 = 1.63 \pm 3.58$ J K^{-1} mol Se^{-1}. The minor changes in values from the earlier data quoted above resulted from using Grønvold's heat of fusion (6.159 ± 0.004 kJ mol Se^{-1}) [18] instead of the average chosen in Ref. 1 (6.2 kJ mol Se^{-1}).

The large error for the entropy of fusion of monoclinic selenium results from the experimental difficulty of overlapping fusion of monoclinic selenium with crystallization of the trigonal selenium which is the stable phase at the melting temperature of monoclinic selenium (413 K) [19].

Possible sources of error in computation of ΔS_f of monoclinic selenium are: 1. the assumption of temperature independent heats of fusion/crystallization for the trigonal selenium, needed to separate the monoclinic fusion from the overall transition; 2. the assumption of establishment of full ring-chain equilibrium in the metastable melt at 413 K; 3. the assumption of formation of "defect" trigonal crystals during and after fusion of the monoclinic selenium; 4. the assumption in Ref. 19 that the baseline from low temperature monoclinic selenium to the melt correctly represents the heat capacity of the species present at any one temperature.

By now it is possible to recalculate heats of transition as a function of temperature using data of Ref. 1, but since the liquid heat capacity of selenium is larger than that of the crystal, its recognition would decrease the estimate of the entropy of fusion to about 7.0 J K^{-1} mol^{-1}, rather than increase it, as suggested by the third law (although the temperature corrected value would still be within the established error limit). To judge the second source of error, one finds that the total heat of reaction pure ring melt to equilibrium ring-chain melt at 494.2 is about 0.69 kJ mol Se^{-1} [19], the same order of magnitude as the integrated ΔC_p between 413 to 494.2 K. The third error source dealt with "defect" trigonal crystals which were assumed to account for the reduced heat of fusion measured for the trigonal selenium crystallized after melting of the monoclinic sample. In case we assume the monoclinic selenium to be "defect" also, the heat of fusion and entropy of the perfect crystal would increase by about 10%. Finally, baseline errors can easily contribute as much as ± 10 to 20% of the heat capacity in the 300 to 500 K range which may also amount to ±0.1 to 0.2 kJ mol^{-1} when expressed as enthalpy. The experimental error of Table 1 as suggested in Ref. [19], is thus large enough to cover also the possible error sources in the ΔS_f calculation for the metastable monoclinic selenium. In fact, it makes it likely that the best value for ΔS_f is the "third law value" 9.47 ± 1.6 J K^{-1} mol^{-1}, based on a zero entropy at zero kelvin.

The residual entropy of amorphous selenium (3.58 kJ^{-1} mol^{-1}) is somewhat larger than found per backbone chain atom for most linear macromolecules. [Amorphous polyethylene (2.59 J K^{-1} mol^{-1}) [2], polypropylene (0.94 J K^{-1} mol^{-1}) [11], polyoxyethylene (2.58 J K^{-1} mol^{-1}) [12], polyoxytrimethylene (0.98 J K^{-1} mol^{-1}) [12], polyoxymethylene (2.89 J K^{-1} mol^{-1}) [12] and polytetrafluoroethylene (3.38 J K^{-1} mol^{-1}) [13]. The difference is not sufficient to account for the extra entropy of mixing of rings and chains in the ratio expected at the glass transition (volume fraction of rings ≈ 0.67, mole fraction ≈ 1.00, $-R \ln \nu = 3.33$ J K^{-1} mol^{-1}). Similarly, the entropies of the fully macromolecular glasses do not account for full "random coil" structures of their chains which should approach a conformational entropy of $R \ln 3$. We hope to reach a better understanding of these structures by expansion of the ATHAS data bank.

Conclusions

Of the two metastable allotropes of selenium, monoclinic selenium has within the error limit a zero entropy at zero kelvin temperature, in accord with the third law of thermodynamics. Glassy selenium, in contrast, has an entropy of 3.58 J K^{-1} mol^{-1}, in accord with other typical macromolecular glasses.

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Zusammenfassung — Basierend auf Daten der ATHAS-Datenbank und auf den dritten Hauptsatz der Thermodynamik basierenden Entropiebetrachtungen werden die Entropien von trigonalem, monoklinem und glasartigem Selen diskutiert. Beim absoluten Nullpunkt haben innerhalb der Fehlergrenzen sowohl das trigonale als auch das monokline Selen eine Restentropie von Null. Die Restentropie von glasartigem Selen ist größenordnungsmäßig gleich der anderer linearer Makromoleküle.

Резюме — Энтропии тригонального, моноклинного и стеклообразного селена обсуждены, исходя из банка данных ATHAS и третьего закона энтропии. Тригональный и моноклинный селен имели, в пределах ошибки, нулевую остаточную энтропию при нулевой температуре Кельвина. Величина остаточной энтропии стеклообразного селена была подобной другим линейным макромолекулам.