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HEAT CAPACITIES OF LINEAR MACROMOLECULES

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The heat capacity of liquid selenium was measured from 500 K to 700 K. Three commercial dynamic differential calorimeters were used for the evaluation (du Pont, Mettler, Perkin—Elmer). Comparison with limited literature data by adiabatic calorimetry shows that all three instruments give data of better than ±3% accuracy. Differences among the instruments are thus mainly in the convenience of sample handling and calibration. The heat capacity measured shows a decreasing trend with increasing temperature, opposite to synthetic linear macromolecules.

The heat capacity of a linear macromolecule [1] is the key thermal property, providing basic information for the thermodynamic description. Through its knowledge, the enthalpy, entropy and free enthalpy (Gibbs free energy) of the system can be calculated and used to advantage in discussions of interactions, degrees of disorder and stability, respectively. Despite this importance, determinations of heat capacity have not kept pace with advances in other areas of macromolecular science. The main reason must be the experimental difficulties initially encountered.

The majority of all early heat capacity determinations were made using adiabatic calorimetry [1, 2]. In the adiabatic method of calorimetry heat exchange between the calorimeter and its environment is kept at a minimum by maintaining the calorimeter and its jacket at almost the same temperature. Detailed descriptions of the technique and variations used for polymers can be found in references 1 and 2. Adiabatic calorimetry is capable of a high degree of precision and accuracy, but is a rigorous, protracted operation, requiring considerable operational skill. Each adiabatic calorimeter represents a substantial investment of time and money since, more often than not, the instruments are custom designed and built. Additionally, the analysis of the data from adiabatic calorimetry [1] has revealed that although intrinsically the instruments are capable of a ±0.1% precision or better, the sample variation and the essential metastability of polymer samples during the discontinuous, long periods of measurement result often in overall accuracies of only ±3%.

This recognition of metastability of many macromolecular samples and of the differences that occur with thermal pretreatment has in recent years led to experimentation with dynamic differential calorimeters [1, 3, 4]. A continuous and fast heating mode minimizes irreversible changes of the sample during measurement and makes for more effortless generation of experimental data. Results [5] on a variety of polymer samples of sufficient stability has indicated possible accuracies of measurement within $\pm 3\%$. This loss in intrinsic accuracy of dynamic differential calorimetry when compared to adiabatic calorimetry, is compensated for by the higher heating rates possible which avoid changes in sample structure during heating.

In this paper we describe the measurement of the heat capacity of molten liquid selenium using three commercially widely available dynamic differential calorimeters. In each case it was attempted to determine the quality of the heat capacity measurements. Selenium was chosen for the study since from a recently completed survey of the existing literature [6], it appeared that heat capacity data of sufficient accuracy on liquid selenium are limited. Such data can be used to advantage in the understanding of selenium, which in the liquid consists of a mixture of eight membered rings and polymeric chains in a state of dynamic equilibrium [7]. Measurements on the three instruments were made to obtain a comparison of the accuracy and convenience of the experiment.

Experimental

Heat capacity measurements were made using each of the following commercial calorimeters,

a) du Pont 900* (DSC cell) [8]
b) Mettler TA 2000 [9]
c) Perkin-Elmer DSC-2 [10]

Complete details about each instrument and the measuring technique for determining the heat capacity are provided in the respective instrument manuals available from each manufacturer [8-10]. The amplitude method of heat capacity determination was employed. Initially a value for isothermal power input or temperature difference was established, the temperature then being raised a preset amount at a constant heating rate. The recorded amplitudes at the different temperatures which are proportional to the rate of heat flow, were used for direct heat capacity determination by comparison with a calibration standard. We used crystallized, pure alumina (sapphire) as a standard, whose heat capacity is accurately known over a wide temperature range [11]. Full details of the method are provided in reference 4.

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* A du Pont model 900, in operation in our laboratory since 1967, was used in this study. Since that time, du Pont has introduced a Model 990 Thermal Analysis system. The manufacturer claims significant performance specification improvements, including higher sensitivity, constant calorimetric response, and resultant inprovements in accuracy and precision. Specifically, they claim a twenty-fold increase in sensitivity to 0.01 mcal/s/inch, and simultaneous derivative display to a sensitivity of 0.01 mcal/s/min/inch.

The starting material used in the experiments was selenium shot of 99.999% purity. The samples were hermetically sealed in aluminum pans. The crimping of the covers was done in a nitrogen atmosphere to avoid any oxidation at the elevated temperatures. The measurements on liquid selenium covered the temperature range 500 K to about 700 K. To ensure an equilibrium liquid state prior to measurement, a thermal pretreatment was performed. The sample was initially heated in the calorimeter from room temperature to 493 K at 10 deg/min and then to 503 K at 2 deg/min. After a few minutes at this temperature, the sample was cooled to 496 K at 5 deg/min. The melting point of the trigonal form of selenium has been observed to be 494.33 K [12]. Repeat weighings after completion of the measurement assured no weight loss by evaporation. The heating rates, sample weights, operation mode, averaging procedure (number of runs), and sensitivity of recording are given in the footnotes to the table for each instrument.

Results and discussion

The heat capacity results obtained are shown in the figure as average values in 10 degree intervals and as smooth curves of the data, tabulations of the results and error values are presented in the table. Also shown in the table are the data by Gronvold [13], who used adiabatic calorimetry for the measurement.

The three sets of heat capacity results obtained, measured on the different instruments, are seen to match each other within ±3% over the entire temperature range studied. Additionally, the results obtained on dynamic differential calorimetry agree with the independent measurement of Gronvold using adiabatic calorimetry [13], the agreement being better than ±2% (see table).

The experimental trend of the heat capacity data of liquid selenium presented above is seen to be a gradual decrease in heat capacity with increasing temperature. This behavior in the liquid state contrasts markedly the behavior of the synthetic organic linear macromolecules measured to date [polyethylene, polystyrene, poly(methyl methacrylate), polybutene], which all exhibit a nearly linear increase in heat capacity with increasing temperature over a wide temperature range [5]. An explanation of this behavior of selenium has been offered by Moynihan and Schnaus [14] in terms of the equilibrium structure of the liquid state. Currently the liquid is thought to be comprised of an equilibrium mixture of Se_8 rings and long polymeric chains. With increasing temperature this equilibrium shifts towards the linear macromolecule via a ring-opening polymerization reaction, while if one goes to lower and lower temperatures, a stage is eventually reached where the concentration of polymer chains is negligible (floor temperature). A calculation of the heat capacity of liquid selenium by Moynihan and Schnaus [14] considering the contribution arising from the ring/chain equilibrium affords a semiquantitative match with the experimental data. Additional details on the chemical reactions found when heating and cooling liquid selenium can be found in references [7, 14, 15].

Table 1

Heat capacity of liquid selenium over the temperature range 500K—700K (J mol^{-1} K^{-1})[a]

Temp. K	Data from adiabatic calorimetry[b]	Data from duPont 900[c]	Data from Mettler TA2000[d]	Data from Perkin-Elmer DSC—2[e]
500	35.85		36.30	36.50
510	35.69		36.11	36.35
520	35.55	36.69	35.92	36.20
530	35.41	36.13	35.74	36.05
540	35.26	35.62	35.57	35.90
550	35.14	35.16	35.40	35.76
560	34.99	34.76	35.24	35.62
570	34.85	34.41	35.09	35.48
580	34.72	34.11	34.94	35.34
590	34.58	33.87	34.80	35.21
600	34.47	33.67	34.67	35.08
610	34.37	33.54	34.54	34.95
620	34.24	33.45	34.41	34.83
630	34.18	33.42	34.30	34.70
640	34.03	33.44	34.19	34.59
650	33.95		34.09	34.47
660	33.84		33.99	34.36
670	33.79		33.90	34.24
680	33.68		33.82	34.14
690	33.61		33.74	34.03
700	33.54		33.67	33.93

[a] Heat capacities have been smoothed by curve fitting into the polynomial $C_p = AT^2+BT+C$

[b] Heat capacities reported by Gronvold [13]. Interpolated from author's table of points generated by a least square curve which fits his experimental data

[c] Calculated from the equation

$$C_p = 2.634 \cdot 10^{-4}T^2 - 0.3337\,T + 138.7$$

Experimental values agree with the calculated values within 0.2% (standard deviation 0.039)

Heating rate 20 K/min

Sample weights about 28 mg

[d] Experimental values were obtained from mean values of 4 different determinations. Heating rate of 10 K/min was used. Data calculated from the equation

$$C_p = 3.175 \cdot 10^{-5}T^2 - 0.005128T + 54.00$$

Deviation of experimental values from calculated values is as high as 1.3% (standard deviation 0.25). Sample weights about 84 mg

[e] Experimental values were obtained by taking an average of two measurements at range sensitivities of 2 mcal/s and 5 mcal/s. Heating rate was 10 K/min. Data calculated from the equation

$$C_p = 1.342 \cdot 10^{-5}T^2 - 0.02889T + 47.64$$

Calculated and experimental values agree within 0.2% (standard deviation 0.043). Sample weights about 30 mg

Comparing the three dynamic differential calorimeters one finds only small differences in internal reproducibility; and on an absolute basis, sufficiently careful calibration gives similar match with the adiabatic calorimetry data. It remains to comment on specific features of importance to the measurement.

The du Pont 900 instrument needed greatest attention in the establishment of initial and final isotherm conditions for baseline, calibration, and sample runs when not using time base recording (as in our case). We feel that here lies the greatest error source in our measurements. The whole temperature range was best run in one heating cycle because of the isotherm uncertainty. Calibration had to be done point by point which eliminates effects due to non-linearity of the temperature scale. Slope compensation should naturally remain identical for calibration and sample run. Sample loading is easy, but careful placement is required and checks of no slip during measurement are necessary, particularly on purging at higher velocity of inert atmosphere.

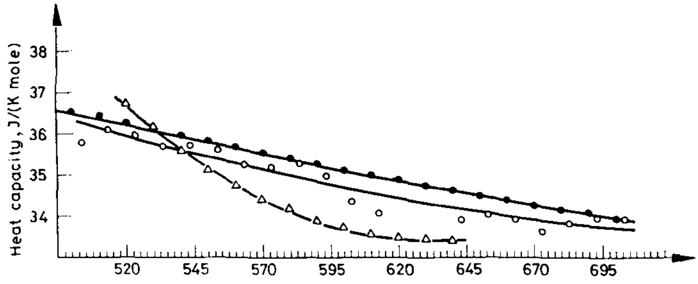

Fig. 1. Heat capacity of liquid selenium as measured by three dynamic differential calorimeters: △ du Pont 900, ○ Mettler TA2000, ● Perkin—Elmer DSC 2

The Mettler TA 2000 does achieve easy isothermal baseline constancy, but was slowest in reaching steady state at constant heating rate (it took 15—20° in our case) and time was needed to establish isothermal conditions again. Baseline shifts were quite linear over the whole temperature range so that single runs could cover the whole temperature range. Placement of the sample pans was secure and reproducible, but the pans suffered from buckling at high temperature when hermetically sealed. The furnace design seemed to give the most reproducible environments.

The Perkin-Elmer DSC 2 suffered from none of these minor difficulties mentioned above. Steady state was reached in about 1/2 to 1 minute (5° at 10°/min heating rate). The instrument appears initially more complex, and it takes a longer time to optimize baseline controls.

The time required for all measurements after initial calibration was comparable for all three instruments. The most time consuming part is the point by point numerical analysis of the data, so that presently all three manufacturers offer computer or calculator-coupled options.

Conclusions

The data generated here underscores the observation that several high quality dynamic differential calorimeters of sufficient speed, accuracy, and precision exist today on which heat capacity determinations can be performed routinely. The accuracy and reproducibility of such measurements are within a factor of 10 of those obtained via adiabatic calorimetry which is sufficient for many problems in thermal properties of linear macromolecules. The development of such equipment has furthermore reached the stage where the thermal analysis data is available also in digital form for computer-coupled evaluation. Such an automated system has been programmed in our laboratories at Rensselaer for fast heat capacity determination [16]. This system allows for the complete evaluation of the heat capacity of a sample over an extended temperature range in a period of one to two days; a similar undertaking by adiabatic calorimetry would involve many times as much effort.

With the growing availability of dynamic differential calorimeters it is hoped that a large amount of heat capacity data will become available in the near future. We are in the process of collecting all measured data to establish at Rensselaer a data bank of heat capacities of linear macromolecules. Such data compilations will help in the eventual goal of the development of a suitable addition scheme [17] for the prediction of the heat capacities of macromolecules. Any help, in the form of reprints of tables of newly measured data with experimental information, will be appreciated.

The decrease in heat capacity of selenium confirmed in these measurements is an indication of complicating processes in the selenium melt. It is hoped by extending the measurements into the metastable region below the melting temperature to gain quantitative information on the ring-chain equilibrium of selenium.

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Résumé — On a mesuré la chaleur spécifique du sélénium liquide entre 500 et 700 K, à l'aide de trois analyseurs calorimétriques différentiels commerciaux *(Du Pont, Mettler, Perkin-Elmer)*. La comparaison avec les données restreintes de la littérature, obtenues par calorimétrie adiabatique, a montré que les trois instruments donnent des résultats dont l'exactitude est meilleure que ±3 %. Ainsi, les différences entre les instruments résident surtout dans la commodité de manipulation des échantillons et d'étalonnage. La chaleur spécifique ainsi mesurée tend à dimineur quand la température augmente, contrairement aux macromolécules synthétiques linéaires.

Zusammenfassung — Die Wärmekapazität von flüssigem Selen wurde zwischen 500 und 700 K gemessen. Drei handelsübliche dynamische Differentialkalorimeter wurden zur Bewertung eingesetzt (du Pont, Mettler, Perkin-Elmer). Der Vergleich mit einigen Literaturangaben bezüglich adiabatischer Kalorimetrie zeigt für alle drei Instrumente eine höhere Genauigkeit als ± 3 %. Der Unterschied zwischen den Instrumenten besteht demnach hauptsächlich in der Leichtigkeit der Probenbehandlung und der Eichung. Die gemessene Wärmekapazität zeigt eine Abnahme mit steigender Temperatur, im Gegensatz zu synthetischen linearen Makromolekülen.

Резюме — Была измерена теплоемкость жидкого селена в области температур 500—700 К. Для оценки были использованы три промышленных динамических калориметра — Дюпон, Меттлер и Перкин—Эльмер. Сопоставление с ограниченными литературными данными по адиабатической калориметрии, показывает, что все три прибора дают данные с точностью лучше чем ±3%. Таким образом, различия среди приборов обусловлены главным образом удобством приготовления образца и калиброванием. Измеренная теплоемкость показала тенденцию к уменьшению с увеличением температуры, противоположно синтетическим линейным макромолекулам.