Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. I. Selenium

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The heat capacity of selenium from 0 K to 1000 K is reviewed using measurements on 20 samples reported in the literature. A set of recommended data for trigonal, monoclinic, glassy, and molten selenium is derived. Ring-chain equilibrium parameters are critically evaluated. Entropy, enthalpy, and Gibbs energy functions are calculated. Selenium is a model compound for a monoatomic, linear macromolecule. This paper is first in a series which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: Calorimetry; crystal; enthalpy; entropy; floor temperature; fusion; Gibbs energy; glass transition; heat capacity; linear macromolecule; melt; selenium.

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1. Introduction

Heat capacity is the key macroscopic material property which is well enough understood to permit, when determined over a wide range of temperature, the establishment of connection to the microscopic structure and motion. Through its knowledge the other thermodynamic functions (enthalpy, entropy, and Gibbs energy) can be derived.

This is the first paper in a series of critical discussions of the heat capacity of linear macromolecules. A set of recommended data is derived for each macromolecule and entropy, enthalpy, and Gibbs energy functions are calculated. An attempt will be made to discuss heat capacities and the derived thermodynamic functions as they relate to the macroscopic and microscopic structure. At present, data on over one hundred macromolecules have been collected and are to be discussed in about 10 successive publications.

In this first paper the heat capacity of selenium has been critically analyzed. Selenium is a model compound for a monoatomic, linear macromolecule. In the second paper the heat capacity of polyethylene, the simplest organic linear macromolecule is analyzed. In the subsequent publications, the analysis of heat capacities of more complicated linear macromolecules is attempted, grouped according to their chemical structure.

In this first paper a brief general description of the heat capacity of chain structures is given, as well as a summary of experimental techniques used for heat capacity measurement. Value judgments used to set up standards for the derivation of recommended data are described. A discussion of the organization of the "Advanced Thermal Analysis (ATHAS) Data Bank" at Rensselaer Polytechnic Institute is also given. Various mathematical techniques used for curve-fitting, interpolation and critical evaluation of data are also given.

2. Heat Capacity of Chain Structures

The heat capacity represents the heat absorbed when temperature is increased, or more precisely

$$C = dQ/dT. \qquad (1)$$

Heat capacity is usually measured under the condition of constant pressure (C_p). Heat capacities at constant volume (C_v) are, however, more amenable to theoretical interpretation. They can be calculated from the constant pressure data using the thermodynamic relationship

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v \qquad (2)$$

At sufficiently low temperature the motion of linear macromolecules in the solid state can be described as coupled harmonic oscillations carried out by the atoms. The molar heat capacity is then simply the sum of the contributions of all $3N$ normal modes.

$$C_v = R \sum E\,(\Theta/T) \qquad (3)$$

Here $E(\Theta/T)$ represents the Einstein function, which is the contribution of a single mode of vibration to the heat capacity,

$$E(\Theta/T) = \frac{(\Theta/T)^2 \exp\,(\Theta/T)}{[1 - \exp\,(\Theta/T)]^2} \qquad (4)$$

and Θ represents the Einstein temperature, defined by

$$\Theta = h\nu/k = 1.4388\nu \qquad (5)$$

where ν is the wavenumber of the vibration in units of cm^{-1}. A table of the Einstein function can be found in reference [1][1]. The problem in understanding heat capacities rests with the finding of the frequency spectrum or a sufficient approximation to it.

An approximation of the vibrations in linear macromolecules is possible by separation of the normal modes into two different types: Group vibrations and skeletal vibrations. The group vibrations approximate the normal modes of the detailed structure of the chain units which are assumed to vibrate independently of each other. Their contributions can be calculated by summing over Einstein terms for the normal modes of the isolated chain units. The remaining skeletal vibrations can then be looked upon as vibrations of a chain of structureless beads of the mass of the chain units. For the vibrations of the beads the coupling can no longer be neglected. One tries to approximate these coupled vibrations by an isotropic, elastic continuum. Because the forces between macromolecules are relatively weak, the three-dimensional frequency distribution as proposed by Debye [2,3] holds only for the very lowest frequencies (long wavelengths). Tarasov [4–8] suggested the averaging of the higher frequencies (above ν_3) in the form of a constant frequency distribution

$$\rho(\nu) = 9N_3\nu^2/\nu_3^3 \qquad (0 \geqslant \nu \geqslant \nu_3) \qquad (6)$$

$$\rho(\nu) = 3N_1/(\nu_1 - \nu_3) \qquad (\nu_3 > \nu \geqslant \nu_1) \qquad (7)$$

$$3N = 3N_1 + 3N_3 \qquad (8)$$

The heat capacity of such a system of vibrators is given by the Tarasov equation:

$$C_v/(3R) = D_1(\Theta_1/T) - (\Theta_3/\Theta_1)\,[D_1(\Theta_3/T) - D_3(\Theta_3/T)] \qquad (9)$$

in which $D_1(\Theta/T)$ and $D_3(\Theta/T)$ represent the one and three dimensional Debye functions at the respective frequency limits [9,10].

The low and high temperature limits of eq (9) are

$$C_v/(3R) = D_3(\Theta_D/T) \text{ with } \Theta_D = \sqrt[3]{\Theta_3^2\,\Theta_1}, \quad \text{and } C_v/(3R) = D_1(\Theta_1/T) \qquad (10)$$

with Θ_D representing the Debye theta temperature.

The Tarasov approximation has been applied successfully to a number of linear macromolecules—selenium [11], polyethylene [9, 10, 12], fluoropolymers [13, 14, 15], and polyoxides [16, 17, 18].

The heat capacity of the melt has one additional major contribution: one associated with the creation of free volume. In its simplest form one can think of this free volume as extra holes introduced on raising the temperature. The heat capacity is then

$$C_p = C_p\,(\text{vibrations}) + C_p\,(\text{holes}). \qquad (11)$$

The vibrational contribution may be similar to that found in the solid state, except for torsional vibrations which may change to rotations and decrease their contribution to the heat capacity from R to $R/2$ over a wide temperature range. The additional contribution due to the holes can be calculated using Erying's hole theory [19, 20]. Equation (11) has been used to interpret the heat capacity of a number of molten, linear macromolecules [10, 21].

3. Heat Capacity Measurements on Linear Macromolecules

Adiabatic calorimetry is the most precise technique of heat capacity measurement with claimed accuracies of ± 0.01%.

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[1] Numbers in brackets refer to literature references in section 11.

Routinely the order of magnitude of 0.1% accuracy can be achieved in the temperature range of 10 to 600 K. Reference to calorimeters can be found in the reviews of Sturtevant [22], McCullough and Scott [23], Swietoslawski [24], White [25], Melia [26], Bartenev, Gorbatkina, and Luk'yanov [27], and Wilhoit [28]. The basic design of adiabatic calorimetry was developed by Nernst in 1911 [29]. A large number of heat capacity measurements on polymers have been made with an adiabatic calorimeter similar to that described by Scott, Meyers, Rands, Brickwedde, and Bekkedahl [30], which in turn is based on an earlier calorimeter by Southard and Brickwedde [31].

Calorimeters used for many polymer heat capacity measurements are described in references [32–34, 40–47].

The newest adiabatic calorimeter used for polymer research has been described by Sterrett, Blackburn, Bestul, Chang and Horman [36–39]. The state-of-the art instrument is fully automatic and covers the range of 2 to 375 K with an accuracy of better than 0.1%.

The adiabatic calorimeters described above can be termed classical precision calorimeters. In the polymer field it was noticed, however, that many measurements were much less precise than possible with the employed calorimeters. The main reasons were usually poor sample reproducibility and lack of thermodynamic stability. Only continuous and fast heating prevents irreversible changes of the sample during measurement. Continuously heating fast calorimeters were first devised by Hoffman [50] and Wunderlich and Dole [51]. A continuous heating rate of 1 to 2 K $\min^{-1}$ was achieved with a probable lag in temperature of less than one Kelvin. Calorimeters more adapted to a continuous heating mode have been developed by Hellwege, Knappe, and Semjonow [52]; Vol'kenshtein and Sharonov [53]; Hellwege, Knappe, and Wetzel [42]; and Tautz, Glück, Hartmann, and Leuteritz [54]. Polymer weights have been reduced in some of these instruments from typically 50 g to the order of magnitude of one gram. Heating rates could thus be increased to as much as 6 K $\min^{-1}$. The accuracy decreased to 0.5 to 5% along with the loss of strict adiabatic conditions. This far lower accuracy is often tolerable because of the change in the nature of the sample with time, which would lead to even lower accuracy on measurement with a more precise, but slower, strictly adiabatic calorimetry [51].

Heat capacity measurement at temperatures below 10 K need some specialized instrumentation. The main problems rest in this temperature range with the cryostat and thermometry [55]. Typical instruments and methods used on polymeric samples are described by Salinger and coworkers [56, 57, 61], Reese and Tucker [12, 58], Scott, et al. [59], and Zoller, Fehl and Dillinger [60]. The precision of measurements which are carried out by a transient technique or a heat pulse method may be no better than ± 10%. The low precision is tolerable, however, for the overall description of thermodynamic properties since the absolute values of the heat capacities are small in this temperature range.

Isothermal calorimeters are mostly used for higher temperatures and of less importance for polymers. The principle is to thermostat the sample at a known high temperature and measure the total enthalpy loss of the sample on transfer to a low temperature, isothermal recipient. The low temperature recipient calorimeter may be a Bunsen ice calorimeter [62]. A modern version of such arrangement has been described by Ginnings and Corruccini [63], and Opdycke, Gay, and Schmidt [64]. An isothermal aneriod calorimeter has been described by Southard [65]. The resulting data are averages over large temperature ranges. The accuracy is usually less than in the nonisothermal calorimeters, although accuracies as high as 0.2% have been reported (see Sturtevant [22]).

The recognition of metastability of many linear macromolecules and the differences that occur with thermal pretreatment has led to the application of fast differential calorimeters to heat capacity measurement. The adiabatic condition has been given up in these instruments in favor of a heat leak of identical magnitude for sample and reference. The first calorimeter of this type for the measurement of heat capacities and heats of transition of linear macromolecules was developed by Müller and Martin [66]. Significant improvement occurred more recently through the development of differential scanning calorimetry (DSC) in which the sample weights are reduced to between 1 and 100 mg. The temperature range of operation of a DSC is typically between 100 K and 1000 K, and heating rates between 0.1 and 100 K $\min^{-1}$ are possible. Measurement of heat capacity using a DSC consist of three steps: a) a baseline scan b) a standard scan and c) a sample scan. Benzoic acid (100–260 K) and sapphire (200–1000 K) are commonly used as calibrating standard [67]. Measurement of the heat capacity of linear macromolecules using (DSC) have been reported by Gray and Brenner [68], Wunderlich and coworkers [69–74], Smit [75], Simon, Beatty, and Karasz [76], Sakaguchi, Mandelkern, and Maxfield [77], Dröscher [78], Wrasidlo [79, 80], Park and Uhlman [81], Adam, Hay, Parson, and Howard [82] and Warfield and Kayser [83].

In a study of three commercial DSC instruments it was found that over the temperature of 500 to 700 K data obtained on molten selenium were within ± 3% of the literature data by adiabatic calorimetry [71]. Using a computer-interfaced DSC, accuracies of better than ± 0.5% have been achieved for zinc over the temperature range of 400–520 K on the same instrument [72]. At subambient temperatures, the error limits are somewhat larger [73] (about 3% at 100 K).

Finally, some attempts have been made in the last five years towards the determination of the heat capacity of linear macromolecules at high pressures [84–87].

In summary: adiabatic calorimeters of ± 0.1% accuracy have been built for measurement of polymer heat capacities. Their operation is somewhat slow because of the need to equilibrate after each step, usually chosen between one and twenty degrees. The data resulting from these calorimeters forms the base of most of the following discussion. Recognizing the metastability of many polymer samples, and the differences due to thermal pretreatment, has led to the recent development of the more cost effective dynamic calorimeters with an accuracy which can reach ± 1%. The loss in accuracy is often compensated for by the high heating rate which avoids changes in structure of the sample during heating. In this way, the less accurate DSC technique can in some instances lead to more precise data.

4. Literature Search, Information Retrieval, Data Storage and Handling

A first attempt to bring together all the measurements on heat capacities of linear mocromolecules was made by Wunderlich and Baur [10]. In their effort the experimental data were reviewed up to June 1968. In the present series of publications, the literature search has been extended to 1980. Section 35, 36, 37, and 38 of the Chemical Abstracts were searched in the Lockheed Dialog data based (Lockheed Information System, California) using the key phrases "Heat Capacity" and "Sp. Heat".

The following is retrieved from each publication: polymers studied, temperature range studied, thermal history and characterization of the samples, experimental technique used, claimed uncertainty, and accuracy of representation of data. The publication is then critically assessed for the quality and reliability (criteria and standards are discussed in sec. 5). Acceptable data are stored in temperature intervals of 0.1 K up to 1 K, 0.2 K to 2 K, 1 K to 10 K, 2 K to 20 K, and 5 K to 30 K. At temperatures higher than 30 K, intervals of 10 K are used. If the data are not reported in the temperature intervals desired by us, the data are interpolated. The spline function technique (discussed in sec. 5) is used to determine the interpolated heat capacity at desired temperatures.

If unsmoothed data have been reported by the authors, the data are smoothed prior to storing. Functions used for smoothing the data are discussed in sec. 6.

A detailed listing of data handling programs (high level programming language HPL) and the instructions for their operations are given in reference [88].

5. Criteria and Standards for Recommended Data

Criteria for evaluating the quality of heat capacity data are based upon the following: (a) characterization of the samples used for heat capacity measurements (b) experimental technique used and reported uncertainty (c) representation of data and (d) visual comparison of data with other investigations. The principles followed in selecting data are, briefly, as follows:

(a) Purity and morphological characterization of the samples are examined. Data on uncharacterized commercial plastics are considered unreliable. The key characterization parameter useful for our analysis, besides molecular weight and thermal history, is the crystallinity of the sample. Crystallinity calculated from density measurement is preferred over its determination from the heat of fusion, X-ray and IR spectroscopy. Crystallinity determination from enthalpy and the heat capacity change at the glass transition are considered least reliable. In cases when the two phase model on which the crystallinity concept is based is invalid, additional structure characterization parameters are needed.

(b) The experimental aspects, as discussed in section 3 are examined for each measurement. Reliability of measuring technique as determined from results on standard calibration materials is considered important. Below 200 K, adiabatic calorimetric results are, in general, considered more reliable than differential scanning calorimetric measurements. From 200 to 350 K, depending upon the sophistication of the instrument and averaging procedures used, the differential scanning calorimetry and adiabatic calorimetry data may be considered equally good. Above 350 K, in certain cases, due to metastability of the samples, differential scanning calorimetry results are preferred over adiabatic calorimetry.

(c) Heat capacity data represented only by small graphs which cannot be read accurately are not considered reliable. Tabulated data is considered more reliable than graphical data. If raw heat capacity data points are reported by investigators, their data is curve fitted and the heat capacity function obtained is preferred over the tabulated and graphical values.

(d) If any measurement shows obvious, significant deviations from other data sets of comparable samples, the data is questioned. Such discrepancies are usually several standard deviations and indicate systematic errors.

6. Data Smoothing and Interpolation

The heat capacity data are smoothed by least squares fitting with one of the following equations:

$$C_p = AT + B \qquad (12)$$

$$C_p = AT^2 + BT + C \qquad (13)$$

$$C_p = AT^{-2} + BT + C \qquad (14)$$

$$C_p = \exp\,[A(\ln T)^3 + B(\ln T)^2 + C(\ln T) + D] \qquad (15)$$

Equation (15) is used at low temperatures and eqs (13) and (14) are used at higher temperatures. Equation (12) is useful only for data on molten polymers. The Chebyshev polynomial can represent data over the entire temperature in regular temperature intervals, but a rather large number of significant figures must be carried in the coefficients.

$$C_p = \sum_{i=0}^{n} A_i T^i \qquad n < 10 \qquad (16)$$

The criterion for choosing a particular function is its deviation

$$\%\ \mathrm{RMS} = [\Sigma(C_{p,e} - C_{p,c})^2/n]^{1/2} \qquad (17)$$

where n is the number of experimental data points, $C_{p,e}$ is the experimental value at each temperature and $C_{p,c}$ is the value calculated from the function at the same temperature.

The interpolation of heat capacity data points is done by a third degree natural spline function [90].

7. Thermodynamic Properties Derived from Heat Capacity

From heat capacity, the other thermodynamic properties: enthalpy, entropy and Gibbs energy can be derived.

$$H_T - H_o = \int_0^T C_p \, dT \qquad (18)$$

$$S_T - S_o = \int_0^T \frac{C_p}{T} \, dT \qquad (19)$$

$$G_T = H_T - TS_T \qquad (20)$$

For ideal crystalline solids, the entropy at 0 K is zero ($S^c_o = 0$). Thus, the absolute entropy can be calculated directly. For crystalline linear macromolecules, the derived thermodynamic properties are reported as:

Enthalpy : $H^c_T - H^c_o$

Entropy : S^c_T

Gibbs energy: $G^c_T - H^c_o$

For amorphous solids, the residual entropy at 0 K can be calculated by equating the entropy at the equilibrium melting temperature (T_m)

$$S^c_{T_m} + \Delta S_f = S^a_{T_m} \qquad (21)$$

where ΔS_f is the equilibrium entropy of fusion of fully crystalline solid. It follows that

$$S^a_o = S^c_{T_m} + \Delta S_f - (S^a_{T_m} - S^a_o) \qquad (22)$$

With the knowledge of S^a_o we can calculate the absolute entropy of amorphous solids. The crystalline state at 0 K is chosen as a standard state for all enthalpy and Gibbs energy data. $(H^a_T - H^c_o)$ and (H^c_o) are directly related to the heat of fusion at the temperature T.

$$H^a_T - H^c_o = (H^a_T - H^a_o) + (H^a_o - H^c_o) \qquad (23)$$

$$H^a_o - H^c_o = (H^c_{T_m} - H^c_o) + \Delta H_f - (H^a_{T_m} - H^a_o) \qquad (24)$$

From the absolute entropy and $H^a_T - H^c_o$ we can calculate the Gibbs energy function $G^a_T - H^c_o$ for amorphous solids.

For amorphous linear macromolecules, the reported thermodynamic properties are

Enthalpy : $H^a_T - H^a_o$; $H^a_T - H^c_o$ (25)

Entropy : $S^a_T - S^a_o$; S^a_T (26)

Free enthalpy: $G^a_T - H^c_o$ (27)

Thermodynamic properties are determined by numerically integrating the heat capacity. The Newton-Cotes formula for equally spaced points is used for integration [91].

8. Heat Capacity of Selenium

8.1 Introduction

In the solid state, selenium is known to occur as four major allotropes: the glassy amorphous, the trigonal and two monoclinic allotropes (α and β). In the solid and liquid states, selenium exists in two chemical structures: rings and chains. The monoclinic allotropes are composed of eight-membered rings exhibiting different stacking pattern in the α- and β-forms, while the trigonal form, which is most stable, consists entirely of helical chains. The molten and glassy selenium consist of a mixture of eight membered rings and chains.

Trigonal selenium consists of helical chains (1*3/1 helix). The unit cell parameters have been redetermined by Swanson, Gilfrich and Ugrinic [92].

$$a = 0.43662 \text{ nm} \quad c = 0.49536 \text{ nm} \quad \beta = 120°$$

The density is 4.819 Mg m^{-3} at 298 K (packing density 0.85) [93]. The melting temperature of trigonal selenium is 494.2 ± 0.1 K [94]. The heat of fusion of equilibrium crystals of trigonal selenium is 6.2 kJ mol^{-1} [94, 95]. The distance between two bonded neighboring atoms in selenium chain is 0.2373 ± 0.00055 nm [96] with a bond angle of 101.0° [97]. The shortest distance between two selenium atoms of different chains is 0.346 nm [96]. This is significantly less than the combined van der Waals radii of 0.4 nm and has been attributed to the special geometry resulting from the packing of helices [98] and not to special forces between chains [96].

Both α- and β- monoclinic selenium consist purely of Se_8 rings in slightly different stacking patterns [101, 102]. Se_8 rings have a bond length of 0.234 ± 0.002 nm with a bond angle of 105.8° [100]. The density of a α-monoclinic selenium is 4.389 ± 0.015 Mg m^{-3} at 298 K [103], that of the β-monoclinic form is 4.42 Mg m^{-3} [104]. The densities of the α- and β- forms correspond to the packing densities of 0.77 and 0.78, respectively.

The melting of monoclinic selenium and its transformation to trigonal selenium has been studied by Wunderlich and coworkers [95]. Melting of the monoclinic crystals to pure Se_8-ring melt occurs at about 413 K.

Amorphous selenium may be composed of either pure rings [105] or a mixture of rings and chains. Electron spin resonance was used to verify the existence of free radicals of selenium chain ends [106]. Amorphous selenium undergoes the glass transition at 303.4 K [107] (ΔC_p = 13.29 J $mol^{-1}K^{-1}$, (see table 10).

Selenium melt is comprised of an equilibrium mixture of Se_8 rings and linear macromolecules. This ring chain equilibrium has been studied by Moynihan and Schnaus [108], Eisenberg and Tobolsky [109, 110] and by Wunderlich and coworkers [48, 71, 74, 111]. With increasing temperature this equilibrium shifts towards the linear macromolecule via a ring opening polymerization reaction, while if one goes to lower temperature, a stage is eventually reached where the concentrations of polymer chains is negligible (floor temperature).

8.2. Literature Data on Heat Capacity of Selenium

Twenty three investigations of the heat capacity of trigonal, monoclinic, amorphous and molten selenium have been reported in the literature. Heat capacity of over forty samples in various states have been measured over wide ranges of temperature.

All investigations were critically evaluated in terms of sample purity and characterization, thermal history, experimental technique used, error limits and accuracy of representation of data. It was found that only 13 of the 23 investigations met our data standards (discussed in sec. 5). These investigations are listed in table 1. These contain data on 20 samples of trigonal, monoclinic, amorphous, and molten selenium, covering a broad range of temperature from 0.1 to 1000 K. Eight investigations which did not contain acceptable data were not included in further analysis. These are listed in table 2, along with brief comments on the reasons for exclusion from this study.

Table 1 lists, chronologically, all the investigations from which data were retrieved. Each sample has been given a number which is in accordance with the file numbers of our data bank. The temperature region over which the determination of heat capacity was carried out is given in kelvin. The experimental technique used by the investigators and their claimed experimental uncertainties are listed. Sources of data (tables, graphs or fitted functions) are also listed. If the data was in tabular form, but not in temperature intervals desired by us, (0.1 K intervals below 1 K, to 10 K intervals at higher temperatures), the data was interpolated using spline functions (discussed in section 6).

The thermal history of the sample, if reported by the investigators, is also listed in table 1. Thermal history is of particular interest in the amorphous samples. Different quenching conditions used to prepare amorphous selenium may alter the ring-chain composition of the sample.

As discussed in section 3, heat capacity measurement at temperatures below 25 K require specialized instrumentation and are associated with larger error limits (as high as 15% below 1 K), for the purpose of our analysis, the low temperature data of samples 1,6,8,9–12,13,22 and 25–27 was smoothed by fitting into a logarithmic function. The results of these fittings are given in table 1a.

The heat capacity data retrieved from the literature are given in tables 3 to 8. The low temperature data for trigonal, amorphous and monoclinic selenium are given in tables 3, 4, and 5. Table 6 contains the high temperature data (30 K to melting) on trigonal selenium. High temperature data on amorphous selenium (30 K to glass transition) are given in table 7. The data on molten selenium are given in table 8.

8.3. Recommended Data on Heat Capacity of Trigonal, Monoclinic and Amorphous Selenium

The recommended heat capacity data in the solid state are discussed in three temperature regions: 0–20 K, 20–80 K and above 80 K. This division was made because fewer data sets are available in the 20 to 80 K temperature range. This also allows the use of somewhat simpler methematical functions for fitting. Data below 25 K were treated separately since they are associated with larger error limits.

The recommended heat capacity data for amorphous selenium from 0.1 to 20 K were obtained by fitting the data on samples 13, 17, 19, 26, and 27 from 0.1 to 30 K into the equation:

$$C_p = \exp[-0.118443 (\ln T)^3 + 0.183436 (\ln T)^2 + 3.13902 (\ln T) - 6.25369] \text{ J mol}^{-1}\text{K}^{-1} \quad (30)$$

The RMS deviation was 7.3% from 0.1 to 30 K and 4.1% from 0.1 to 20 K.

From 25 to 80 K, only data on samples 26 and 27 by Chang was considered reliable. Data on samples 4, 9, and 11 start at 60 K only and the initial values are somewhat lower than Chang's data. Thus, to determine the recommended data from 25 to 80 K data on samples 26 and 27 alone were fitted into the equation:

$$C_p = \exp[0.0850655 (\ln T)^3 - 1.18852 (\ln T)^2 + 6.12678 (\ln T) - 8.40205] \text{ J mol}^{-1}\text{K}^{-1} \quad (31)$$

The RMS deviation was 0.1%.

To determine the recommended heat capacity for amorphous selenium above 80 K, the data on the annealed sample (sample 27) was excluded above 210 K. The data on the annealed sample is somewhat lower. This may be due to the presence of some crystalline Se. The data on samples 4, 9, 11, 26, and 27 from 70 to 220 K were fitted into the equation

$$C_p = \exp[0.037887 (\ln T)^3 - 0.747711 (\ln T)^2 + 4.97468 (\ln T) - 7.84846] \text{ J mol}^{-1}\text{K}^{-1} \quad (32)$$

to obtain recommended data from 80 to 210 K. The RMS deviation was 0.3%. The data on samples 4, 9, 11 and 26 above 180 K were fitted into the equation

$$C_p = 85927.9\, T^{-2} + 0.047225\, T + 11.7535 \text{ J mol}^{-1}\text{K}^{-1} \quad (33)$$

to obtain the recommended heat capacity values above 210 K. The RMS deviation was 0.6% which is twice the RMS deviation for eq (32). The larger scatter in the data above 210 K is likely due to annealing of the amorphous selenium samples at temperatures close the glass transition.

The smoothed values for heat capacity of amorphous selenium from 0.1 to 20 K, obtained from eq (30), from 25 to 80 K, obtained from eq (31), from 90 to 210 K obtained from eq (32), and from 210 to 340 K, obtained from eq (33) are given in table 10. The recommended data are also plotted in figure 1.

Recommended data on the heat capacity of trigonal selenium from 0.1 to 20 K was determined by fitting the data on samples 8, 12, 18, 22, and 25 from 0.1 to 25 K into the equation

$$C_p = \exp[-0.075809(\ln T)^3 + 0.176784(\ln T)^2 + 3.10427(\ln T) - 7.6093] \text{ J mol}^{-1}\text{K}^{-1} \quad (34)$$

The RMS deviation was 10.8% from 0.2 to 30 K and 5.3% from 0.2 to 25 K.

To determine the recommended values from 25 to 80 K, the data on samples 3, 6, and 25 from 14 to 100 K were fitted into the equation

$$C_p = \exp[0.0969021(\ln T)^3 - 1.43765(\ln T)^2 + 7.68432(\ln T) - 11.5045]\ \mathrm{J\ mol^{-1}K^{-1}} \quad (35)$$

The RMS deviation was 1.3% from 14 to 100 K and 0.7% from 25 to 80 K. Data on samples 3, 6, 23, and 25 above 80 K was fitted into the equation

$$C_p = \exp[0.099608(\ln T)^3 - 1.71441(\ln T)^2 + 9.998131(\ln T) - 16.5121]\ \mathrm{J\ mol^{-1}K^{-1}} \quad (36)$$

to obtain the recommended data from 80 to 500 K. The RMS deviation was 0.3%

On comparison of the recommended heat capacities of amorphous and trigonal selenium, it is found that from 110 to 150 K the differences in heat capacity values are less than 0.1%. Thus, we can represent the data from 110 to 150 K for amorphous and trigonal selenium with the same heat capacity function. Equation (32) for amorphous selenium was arbitrarily chosen.

The smoothed values for heat capacity of trigonal selenium from 0.1 to 20 K, obtained from eq (34), from 25 to 80 K, obtained from eq (35), at 90 and 100 K, obtained from eq (36), from 110 to 150 K, obtained from eq (32) and from 150 to 500 K, obtained from eq (36) are listed in table 9. The recommended data are plotted in figure 1.

There is only one set of reliable heat capacity data on monoclinic selenium. It spans a very limited temperature range of 2 to 20 K. Recent measurements on monoclinic selenium have been made by Shu, Gaur, and Wunderlich [48] over the range of 110 to 370 K. They have established that over the temperature range of 110 to 300 K, monoclinic and trigonal heat capacities are identical within experimental error. However, above 310 K, the heat capacity of monoclinic selenium is increasingly higher than that of trigonal selenium (3.5% at 320 K to 15% at 370 K). The increase has been attributed to the start of the ring opening reaction [95]. Thus, from 110 to the melting temperature, the heat capacity of monoclinic selenium is taken to be the same as trigonal selenium. From 20 to 100 K, where no data are available, the average of the values of trigonal and amorphous heat capacity are used since at the limits of this temperature range the heat capacity of monoclinic selenium can be represented by such an average.

Heat capacity values for monoclinic selenium taken from sample 1 below 20 K and estimated values above 20 K as discussed above are listed in table 11.

For molten selenium, the data on samples 24, 28, and 30 were fitted into the equation

$$C_p = 3.2608 \cdot 10^{-5} T^2 - 4.9766 \cdot 10^{-2} T + 52.408 \quad (37)$$

Maximum percent departure at any given temperature was less than 1%. The RMS deviation was 0.4%. The heat capacity values from 303.4 to 1000 K, calculated using eq (37) are listed in table 10. The recommended data are plotted in figure 1.

The heat capacity of molten selenium shows a quadratic downward curvature, which is not typical of linear macromolecules. The heat capacity decreases from 300 to about 700 K and then increases gradually above 800 K. A semi-quantitative fitting of the heat capacity to vibrational energy contributions, free volume (hole) effects and heats of reaction from the changes in the ring-chain and depolymerization equilibria has been reported elsewhere [74]. It could be concluded that the shift in ring-chain equilibrium is not the major cause for the overall decrease in heat capacity above the glass transition. Rather, the normal decrease of the liquid heat capacity is in the case of monoatomic macromolecules not compensated by an increase in heat capacity of group vibrations excited newly at higher temperatures. The final increase in the heat capacity has been linked with the depolymerization reaction of selenium at high temperatures.

9. Thermodynamic Functions of Selenium

Thermodynamic functions for trigonal, monoclinic, and amorphous selenium have been derived from heat capacities. These are listed in tables 9, 10, and 11. H_0 and S_0 refer to zero point enthalpy and residual entropy.

Setting the trigonal entropy at absolute zero equal to zero, monoclinic selenium has at 0 K a residual entropy of 1.71 J mol^{-1} K^{-1} and the Gibbs energy of the transition of monoclinic to trigonal selenium is negative (-2.1 kJ mol^{-1}). At 0 K the residual entropy of amorphous selenium is 3.63 J mol^{-1} K^{-1} and the Gibbs energy of transition of trigonal to amorphous, glassy selenium is 3.8 kJ mol^{-1}.

From the thermodynamic functions, one can conclude that monoclinic selenium is metastable at all temperatures. The metastability of monoclinic selenium has been attributed to the exothermic heat of reaction for the Se_8 ring to chain reaction in the crystalline state [74] which is in contrast to the endothermic heat of reaction for the ring to chain reaction in the molten state.

Thermodynamic quanitities for monoclinic-to-trigonal-to-melt transitions were summarized by Murphy, Altman and Wunderlich [95] as

Monoclinic crystal → hypothetical Se_8 ring melt at 413 K,

$$\Delta H = 2.8\ \mathrm{kJ\ mol^{-1}}, \quad \Delta S = 6.8\ \mathrm{J\ mol^{-1}K^{-1}}$$

and

Monoclinic crystal → Equilibrium ring-chain melt at 413 K

$$\Delta H = 3.24\ \mathrm{kJ\ mol^{-1}}, \quad \Delta S = 7.84\ \mathrm{J\ mol^{-1}K^{-1}}$$

These quantities were checked against the improved heat capacities derived now and found to be correct. New measurements of the heat capacity and electrical conductivity of selenium [74,132] indicate that the ring-chain reaction equilibrates

Table 1. Heat capacity measurements of selenium

Investigator	Sample No. characterization	Temperature range (K)	Experimental technique (claimed uncertainity)	Source of data[b]
Anderson (1927) [112]	5. Trigonal; 0.2% Te; Vacuum distilled; melt crystallized	60-290	Unreported	Table[a]
	4. Amorphous; 0.2% Te; Vacuum distilled	60-250[c]	Unreported	Table[a]
DeSorbo (1953) [113]	6. Trigonal; 99.999% pure. Cryst. from glass at 400K for 1 week	16-300	Adiabatic (0.1%)	16-25 K : Eq 1 30-300 K: Table[a]
Fukuroi and Muto (1956) [114]	8. Trigonal; Cryst. from glass at 400 K for 1 h	1.8-4.0	Nernst-Eucken (Unreported)	Eq 2
Mamedov, et al (1966) [115]	9. Amorphous; 99.99999% pure Quench from melt at 40 K min^{-1}	60-300[d]	Adiabatic (1%)	60-230 K : Table 240-300 K : Eq 3
Tarasov, et al. (1968) [116]	11. Amorphous; cooled rapidly from 670 K	60-300	Adiabatic (0.1%)	Table
Lasjaunias (1969) [117]	12. Trigonal (single crystals)	1.5-4.0	Nernst (Unreported)	Eq 4
	13. Amorphous; 99.99% pure, quenched from melt	1.6-30.0	Nernst (Unreported)	Eq 5
Zeller and Pohl (1971) [118]	17. Amorphous; quenched from melt	0.2-1.0	Transient (15-20%)	Graph
Lasjaunias, Maynard and Thoulouze (1972) [119]	18. Trigonal; 99.999% pure. Melt cryst. at 450 K for two days	0.2-1.0	Adiabatic (25%)	Graph
	19. Amorphous; 99.999% pure. Quenched from 510 K	0.1-1.0	Adiabatic (4%)	Graph
Berton and Lasjaunias (1972) [120]	22. Trigonal 99.999% pure. Annealed at 450 K for 50 h	5-25	Adiabatic (Unreported)	Eq 6
Gronvøld (1973) [121]	23. Trigonal 99.999 % pure. Annealed at 450 K for 12 h	300-490	Adiabatic (Unreported)	Table
	24. Melt; 99.999% pure	500-1000	Adiabatic (Unreported)	Table
Chang and Bestul (1974) [122]	25. Trigonal; 99.999% pure. Annealed at 350-360 K for six days	5-360	Adiabatic (0.1%)	5-20 K: Eq 7 20-360: Table
	26. Amorphous 99.999% pure. Quenched from 320 K at 6 K min^{-1} to 300 K.	6-290	Adiabatic (0.1%)	5-20 K: Eq 8 25-290 K: Table
	27. Amorphous ; 99.999% pure. Annealed at 290-298 K for 5 h to 14 days	6-300	Adiabatic (0.1%)	5-20 K: Eq 10 25-300 K: Table
	28. Melt; 99.999% pure	310-330	Adiabatic (0.1%)	Table
Wu and Luo (1976) [123]	1. Monoclinic (α-form); 99.999% pure. Solution grown from CH_2I_2	2-20	Heat pulse (Unreported)	Eq 9
Shu, Gaur and Wunderlich (1979) [74]	30. Melt	330-530	DSC (1%)	Eq 11

[a] Data was interpolated using the spline function technique to give heat capacities at every ten degree interval.

[b] Equations cited as sources of data are tabulated separately in table 1a.

[c] Single data point also reported at 299.1 K.

[d] Data also reported over the melting range.

Table 1a. Source of data[a]

Equation 1	$C_p = \exp[1.14539 (\ln T)^3 - 11.284 (\ln T)^2 + 38.4619 \ln T - 43.5046]$ J mol^{-1} K^{-1} (RMS dev. = 1.0%)[b]
Equation 2	$C_p = \exp[9.86654 \cdot 10^{-1} (\ln T)^3 - 3.27702 (\ln T)^2 + 6.54541 \ln T - 3.25551]$ J mol^{-1} K^{-1} (RMS dev. = 6.7%)[b]
Equation 3	$C_p = \exp[-1.42968 (\ln T)^3 + 24.1188 (\ln T)^2 - 135.129 \ln T + 254.679]$ J mol^{-1} K^{-1} (RMS dev. = 1.5%)[b]
Equation 4	$C_p = 13 \cdot 10^{-5} T^3$ cal mol^{-1} K^{-1} [c]
Equation 5	$C_p = \exp[-3.24837 \cdot 10^{-2} (\ln T)^3 - 2.85710 \cdot 10^{-1} (\ln T)^2 + 3.82985 \ln T - 6.44011]$ J mol^{-1} K^{-1} (RMS dev. = 1.8%)[b]
Equation 6	$C_p = \exp[-2.7962 \cdot 10^{-1} (\ln T)^3 + 1.42744 (\ln T)^2 + 8.28024 \cdot 10^{-1} \ln T - 10.9166]$ J g^{-1} K^{-1} (RMS dev. = 1.8%)[b]
Equation 7	$C_p = \exp[-9.64909 \cdot 10^{-2} (\ln T)^3 + 4.44692 \cdot 10^{-2} (\ln T) + 4.05204 \ln T - 8.66171]$ J mol^{-1} K^{-1} (RMS dev. = 1.2%)[b]
Equation 8	$C_p = \exp[5.76883 \cdot 10^{-2} (\ln T)^3 - 8.80070 \cdot 10^{-1} (\ln T)^2 + 5.05324 \ln T - 7.21557]$ J mol^{-1} K^{-1} (RMS dev. = 1.2%)[b]
Equation 9	$C_p = \exp[-0.163359 (\ln T)^3 + 0.576771 (\ln T)^2 + 2.52528 (\ln T) + 5.03346 \cdot 10^{-3}]$ mJ mol^{-1} K^{-1} (RMS dev. = 1.8%)[c]
Equation 10	$C_p = \exp[7.27105 \cdot 10^{-2} (\ln T)^3 - 1.05351 (\ln T)^2 + 5.65446 (\ln T) - .87107]$ J mol^{-1} K^{-1} (RMS dev. = 0.7%)[b]
Equation 11	$C_p = 354814 \cdot T^{-2} - 1.16235 \cdot 10^{-2} T + 40.019$ J mol^{-1} K^{-1} (RMS dev. = 0.2%)[d]

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[a] Equation numbers correspond to the equations in table 1.

[b] Author's tabulated data fitted into the equation.

[c] Author's graphical data fitted into the equation.

[d] Equation reported by the authors.

Table 2. Investigations not included in this study

Reference	Reason(s) for exclusion
Mondain-Monval (1962) [124]	Heat capacities values reported for trigonal, monoclinic, amorphous and molten selenium from 310 to 550 K. Their values are 4-15% higher than the ones here reported.
Tammann and Gronow (1930) [125]	Data reported on amorphous selenium over a limited temperature range (280-310 K). Data is 5-10% lower than here reported.
Devries and Dobry (1932) [126]	Crystal form not reported.
Borelius and Paulson (1946) [127]	Heat capacities measured for trigonal selenium over a limited temperature range (450-490 K). Their data is 5-10% higher than here reported.
Gattow and Heinrich (1964) [49,128]	Large deviations of the order of 20-60%
Chaudhari, Beardmore and Bever (1966) [129]	Data reported for amorphous selenium in the glass transition region from 295 to 350 K only. Their values are in fair agreement with this work.
Moynihan and Schnaus (1970, 1971) [130,108]	Heat capacities measured for trigonal amorphous and molten selenium. Their values are 2-8% lower than reported here.
Krüger, Meissner, Mimkes and Tausend (1973) [131]	Heat capacities measured for trigonal and amorphous selenium from 3-300 K using heat pulse method. Data could not be read accurately from too small graphs.
Mehta, Bopp, Gaur and Wunderlich (1978) [71]	Data superceeded by later publication (Reference [74])

Table 3. Heat capacity of trigonal selenium[a] at low temperature in mJ $mol^{-1}K^{-1}$

T(K)	6	8	12	18	22	25
0.2				0.006715		
0.3				0.01570		
0.4				0.03546		
0.5				0.06781		
0.6				0.1181		
0.7				0.1892		
0.8				0.2858		
0.9				0.3950		
1.0				0.5463		
1.6			2.228			
1.8		2.978	3.172			
2.0		4.335	4.351			
3.0		15.18	14.69			
4.0		35.89	34.81			
5.0					68.34	88.28
6.0					123.7	163.0
7.0					203.6	267.3
8.0					311.1	402.1
9.0					447.9	567.0
10.0					614.7	760.5
12.0					1034.	1223.
14.0					1552.	1765.
16.0	2233.				2141.	2359.
18.0	2865.				2770.	2979.
20.0	3466.				3406.	3604.
25.0	4874.				4864.	5020.

[a] Sample numbers correspond to the samples described in table 1.

Table 4. Heat capacity of glassy, amorphous selenium[a] at low temperature in mJ mol^{-1}K^{-1}

T(K)	13	17	19	26	27
0.1			0.01749		
0.2		0.03593	0.03122		
0.3		0.05921	0.06648		
0.4		0.1203	0.1316		
0.5		0.2749	0.2515		
0.6		0.3460	0.4149		
0.7		0.5753	0.6648		
0.8		0.9566	1.009		
0.9		1.351	1.437		
1.0		2.061	2.007		
1.6	9.036				
1.8	13.65				
2.0	19.57				
3.0	72.77				
4.0	170.9				
5.0	316.1				
6.0	505.6			519.5	494.8
7.0	734.3			748.4	725.1
8.0	996.3			1006.	985.5
9.0	1285.			1285.	1269.
10.0	1595.			1581.	1570.
12.0	2257.			2208.	2204.
14.0	2945.			2861.	2859.
16.0	3632.			3523.	3517.
18.0	4299.			4182.	4166.
20.0	4932.			4833.	4799.
25.0				6320.	6292.

[a] Sample numbers correspond to the samples described in table 1.

Table 5. Heat capacity of monoclinic selenium[a] at low temperature in mJ mol^{-1} K^{-1}

T(K)	1
2.0	7.229
3.0	26.02
4.0	65.30
5.0	131.9
6.0	230.8
7.0	363.8
8.0	534.5
9.0	739.0
10.0	975.9
12.0	1533,
14.0	2173,
16.0	2860,
18.0	3561.
20.0	4249.

[a] Sample description is given in table 1.

Table 6. Heat capacity of trigonal selenium[a] in J mol^{-1} K^{-1}

T(K)	3	6	23	25
30		6.312		6.370
40		8.753		8.810
50		10.94		10.93
60	12.61	12.90		12.80
70	14.30	14.56		14.43
80	15.82	15.98		15.86
90	17.06	17.06		17.09
100	18.19	18.18		18.15
110	19.10	18.91		19.05
120	19.88	19.70		19.83
130	20.60	20.42		20.50
140	21.17	21.05		21.08
150	21.69	21.69		21.58
160	22.12	22.08		22.01
170	22.53	22.52		22.39
180	22.88	22.85		22.74
190	23.18	23.09		23.04
200	23.43	23.36		23.31
210	23.65	23.57		23.56
220	23.84	23.77		23.78
230	24.01	23.95		23.98
240	24.18	24.09		24.17
250	24.32	24.28		24.34
260	24.47	24.53		24.50
270	24.59	24.79		24.66
280	24.69	25.02		24.80
290	24.80	25.19		24.94
300		25.38	25.06	25.07
310			25.22	25.20
320			25.34	25.33
330			25.48	25.46
340			25.63	25.58
350			25.78	25.70
360			25.91	25.82
370			26.01	
380			26.18	
390			26.33	
400			26.44	
410			26.62	
420			26.70	
430			26.81	
440			26.92	
450			26.99	
460			27.11	
470			27.18	
480			27.24	
490			27.30	

[a] Sample numbers correspond to the samples described in table 1.

Table 7 Heat capacity of glassy, amorphous selenium[a] in J mol^{-1} K^{-1}

T(K)	4	9	11	26	27
30				7.660	7.640
40				9.940	9.920
50				11.83	11.81
60	13.46	13.26	13.42	13.45	13.43
70	14.78	14.66	14.86	14.87	14.26
80	16.03	16.14	16.11	16.14	16.13
90	17.17	17.34	17.23	17.27	17.25
100	18.20	18.33	18.20	18.26	18.24
110	19.10	19.15	19.09	19.12	19.11
120	19.87	19.77	19.86	19.86	19.86
130	20.54	20.40	20.51	20.52	20.50
140	21.12	20.98	21.09	21.09	21.09
150	21.63	21.45	21.62	21.62	21.59
160	22.07	21.89	22.10	22.06	22.04
170	22.46	22.29	22.51	22.47	22.44
180	22.79	22.68	22.90	22.83	22.81
190	23.10	23.02	23.23	23.17	23.13
200	23.35	23.33	23.54	23.47	23.44
210	23.60	23.65	23.82	23.76	23.71
220	23.84	23.91	24.08	24.03	23.98
230	24.05	24.24	24.33	24.31	24.23
240	24.23	24.41	24.58	24.59	24.49
250	24.39	24.85	24.83	24.88	24.74
260		25.31	25.11	25.22	25.01
270		25.79	25.41	25.57	25.29
280		26.26	25.71	25.98	25.60
290		26.72	26.06	26.53	25.93
300		27.16	27.24		26.30

[a] Sample numbers correspond to the samples described in table 1.

Table 8. Heat capacity of molten selenium[a] in J mol^{-1} K^{-1}

T(K)	24	28	30
310		40.35	
320		39.96	
330		39.61	39.44
340			39.14
350			38.85
360			38.57
370			38.31
380			38.06
390			37.82
400			37.59
410			37.36
420			37.15
430			36.94
440			36.74
450			36.54
460			36.35
470			36.16
480			35.98
490			35.80
500	35.85		35.63
510	35.69		35.46
520	35.55		35.29
530	35.41		
540	35.26		
550	35.14		
560	34.99		
570	34.85		
580	34.72		
590	34.58		
600	34.47		
610	34.37		
620	34.24		
630	34.18		
640	34.03		
650	33.95		
660	33.84		
670	33.79		
680	33.68		
690	33.61		
700	33.54		
710	33.50		
720	33.43		
730	33.39		
740	33.34		
750	33.29		
760	33.29		
770	33.25		
780	33.28		
790	33.28		
800	33.29		
810	33.31		
820	33.34		
830	33.38		
840	33.43		
850	33.49		
860	33.56		
870	33.60		
880	33.72		
890	33.80		
900	33.93		

[a]Sample numbers correspond to the samples described in table 1

Table 8. Heat capacity of molten selenium[a] in J mol^{-1} K^{-1}--Continued

T(K)	24	28	30
910	34.03		
920	34.18		
930	34.30		
940	34.47		
950	34.61		
960	34.81		
970	34.98		
980	35.19		
990	35.41		
1000	35.53		

[a]Sample numbers correspond to the samples described in table 1.

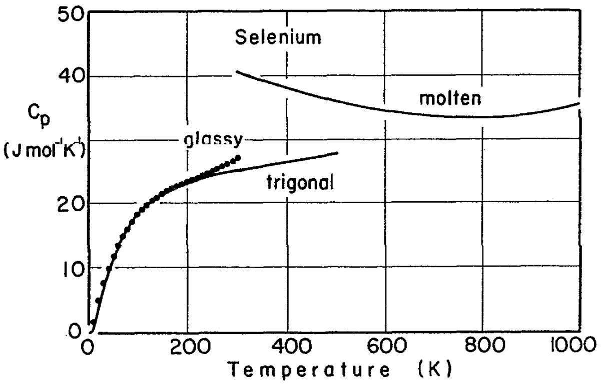

FIGURE 1. Recommended data on heat capacity of trigonal, glassy amorphous, and molten selenium.

Table 9. Recommended thermodynamic data of trigonal selenium

T(K)	C_p^t (J mol^{-1}K^{-1})	H_T^t-H_o^t (J mol^{-1})	S_T^t (J mol^{-1}K^{-1})	-(G_T^t-H_o^t) (J mol^{-1})
0.0	0.0	0.0	0.0	0.0
0.1	0.0000025	0.0000001	0.0000014	0.00000004
0.2	0.0000073	0.0000006	0.0000043	0.0000003
0.3	0.0000174	0.0000017	0.0000090	0.0000010
0.4	0.0000355	0.0000043	0.0000162	0.0000022
0.5	0.0000644	0.0000092	0.0000270	0.0000043
0.6	0.000107	0.0000176	0.0000423	0.0000077
0.7	0.000168	0.0000313	0.0000631	0.0000130
0.8	0.000250	0.0000520	0.0000907	0.0000206
0.9	0.000358	0.0000822	0.000126	0.0000314
1.0	0.000496	0.000125	0.000171	0.0000461
1.2	0.000878	0.000259	0.000293	0.0000917
1.4	0.001433	0.000487	0.000467	0.000167
1.6	0.002200	0.000847	0.000706	0.000283
1.8	0.003218	0.001384	0.001021	0.000454
2.0	0.004526	0.002154	0.001425	0.000697
3.0	0.01681	0.01193	0.005224	0.00374
4.0	0.04208	0.04010	0.01316	0.01252
5.0	0.08448	0.1018	0.02675	0.03195
6.0	0.1472	0.2159	0.04737	0.06837
7.0	0.2327	0.4039	0.07618	0.1294
8.0	0.3425	0.6894	0.1142	0.2238
9.0	0.4775	1.097	0.1620	0.3610
10.0	0.6379	1.653	0.2204	0.5514
12.0	1.034	3.308	0.3702	1.135
14.0	1.523	5.850	0.5651	2.062
16.0	2.098	9.458	0.8052	3.425
18.0	2.744	14.29	1.089	5.312
20.0	3.451	20.47	1.414	7.809
25.0	4.946	41.57	2.350	17.17
30.0	6.342	69.83	3.376	31.46
40.0	8.845	146.1	5.553	76.02

Table 9. Recommended thermodynamic data of trigonal selenium--Continued

T(K)	C_p^t (J mol^{-1}K^{-1})	H_T^t-H_o^t (J mol^{-1})	S_T^t (J mol^{-1}K^{-1})	-(G_T^t-H_o^t) (J mol^{-1})
50.0	10.98	245.5	7.762	142.6
60.0	12.80	364.6	9.928	231.1
70.0	14.39	500.7	12.02	340.9
80.0	15.80	651.8	14.04	471.3
90.0	17.10	816.6	15.98	621.5
100.0	18.19	993.2	17.84	790.6
110.0	19.10	1179.	19.62	977.9
120.0	19.84	1374.	21.31	1182.
130.0	20.49	1576.	22.92	1403.
140.0	21.07	1784.	24.46	1640.
150.0	21.58	1997.	25.93	1892.
160.0	22.03	2215.	27.34	2159.
170.0	22.41	2437.	28.69	2439.
180.0	22.75	2663.	29.98	2732.
190.0	23.05	2892	31.22	3038.
200.0	23.32	3124.	32.41	3357.
210.0	23.56	3358.	33.55	3686.
220.0	23.78	3595.	34.65	4028.
230.0	23.99	3834.	35.71	4379.
240.0	24.18	4075.	36.74	4742.
250.0	24.36	4318.	37.73	5114.
260.0	24.52	4562.	38.69	5496.
270.0	24.68	4808.	39.62	5888.
273.15	24.73	4886.	39.90	6013.
280.0	24.83	5056.	40.52	6288.
290.0	24.97	5305.	41.39	6698.
298.15	25.09	5509.	42.09	7038.
300.0	25.11	5555.	42.24	7116.
303.4 (T_g)	25.16	5641.	42.52	7260.
310.0	25.25	5807.	43.07	7543.

Table 9. Recommended thermodynamic data of trigonal selenium--Continued

T(K)	C_p^t (J mol^{-1}K^{-1})	H_T^t-H_o^t (J mol^{-1})	S_T^t (J mol^{-1}K^{-1})	-(G_T^t-H_o^t) (J mol^{-1})
320.0	25.38	6060.	43.87	7977.
330.0	25.51	6314.	44.65	8420.
340.0	25.63	6570.	45.42	8870.
350.0	25.75	6827.	46.16	9328.
360.0	25.88	7085.	46.89	9794.
370.0	26.00	7345.	47.60	10266.
380.0	26.12	7605	48.29	10746.
390.0	26.24	7867	48.97	11232.
400.0	26.36	8130.	49.64	11725.
410.0	26.48	8394.	50.29	12225.
413.0	26.51	8473.	50.48	12376.
420.0	26.60	8659.	50.93	12731.
430.0	26.72	8926.	51.56	13243.
440.0	26.84	9194.	52.17	13762.
450.0	26.96	9463.	52.78	14287.
460.0	27.08	9733.	53.37	14817.
470.0	27.20	10004.	53.96	15354.
480.0	27.33	10277.	54.53	15897.
490.0	27.45	10551.	55.09	16445.
494.2(T_m)	27.51	10666.	55.33	16677.
500.0	27.58	10826.	55.65	16998.

Table 10. Recommended thermodynamic data of amorphous selenium

T(K)	C_p^a (J mol^{-1}K^{-1})	H_T^a-H_o^a (J mol^{-1})	S_T^a-S_o^a (J mol^{-1}K^{-1})	H_T^a-H_o^t (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	-(G_T^a-H_o^t) (J mol^{-1})
0.0	0.0	0.0	0.0	3854	3.63	-3853.
0.1	0.0000156	0.0000008	0.0000111	3854.	3.63	-3853.
0.2	0.0000323	0.0000030	0.0000260	3854.	3.63	-3853.
0.3	0.0000704	0.0000080	0.0000455	3854.	3.63	-3852.
0.4	0.000138	0.0000181	0.0000742	3854.	3.63	-3852.
0.5	0.000248	0.0000370	0.000116	3854.	3.63	-3852.
0.6	0.000412	0.0000695	0.000175	3854.	3.63	-3851.
0.7	0.000646	0.000122	0.000255	3854.	3.63	-3851.
0.8	0.000965	0.000202	0.000361	3854.	3.63	-3851.
0.9	0.001385	0.000318	0.000498	3854.	3.63	-3850.
1.0	0.001923	0.000482	0.000670	3854.	3.63	-3850
1.2	0.003427	0.001007	0.001145	3854.	3.63	-3849
1.4	0.005620	0.001899	0.001828	3854.	3.63	-3848.
1.6	0.008649	0.003311	0.002766	3854.	3.63	-3848
1.8	0.01266	0.005424	0.004006	3854.	3.63	-3847.
2.0	0.01778	0.008448	0.005594	3854.	3.64	-3846.
3.0	0.06444	0.04637	0.02034	3854.	3.65	-3843.
4.0	0.1546	0.1519	0.05008	3854.	3.68	-3839.
5.0	0.2944	0.3722	0.09865	3854.	3.73	-3835.
6.0	0.4844	0.7574	0.1684	3854.	3.80	-3831.
7.0	0.7200	1.356	0.2602	3855.	3.89	-3828.
8.0	0.9976	2.213	0.3741	3856.	4.00	-3824.
9.0	1.307	3.362	0.5092	3857.	4.14	-3820

Table 10. Recommended thermodynamic data of amorphous selenium--Continued.

T(K)	C_p^a (J mol^{-1}K^{-1})	H_T^a-H_o^a (J mol^{-1})	S_T^a-S_o^a (J mol^{-1}K^{-1})	H_T^a-H_o^t (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	-(G_T^a-H_o^t) (J mol^{-1})
10.0	1.641	4.835	.6641	3858.	4.29	- 3815.
12.0	2.353	8.823	1.026	3862.	4.66	- 3806.
14.0	3.077	14.25	1.443	3868.	5.07	- 3797.
16.0	3.772	21.11	1.900	3875.	5.53	- 3786.
18.0	4.408	29.30	2.381	3883.	6.01	- 3775.
20.0	4.967	38.69	2.875	3892.	6.51	- 3762.
25.0	6.309	66.58	4.114	3920.	7.74	- 3726.
30.0	7.647	101.5	5.384	3955.	9.01	- 3685.
40.0	9.933	189.8	7.909	4043.	11.54	- 3582.
50.0	11.82	298.9	10.33	4152.	13.96	- 3454.
60.0	13.43	425.3	12.64	4279.	16.27	- 3303.
70.0	14.86	566.9	14.81	4420.	18.45	- 3129.
80.0	16.14	722.0	16.89	4575.	20.51	- 2934.
90.0	17.27	889.1	18.85	4743.	22.48	- 2719.
100.0	18.25	1066.	20.72	4920.	24.35	- 2485.
110.0	19.09	1253.	22.50	5107.	26.13	- 2233.
120.0	19.84	1448.	24.20	5302.	27.83	- 1963.
130.0	20.49	1650.	25.81	5504.	29.44	- 1676.
140.0	21.07	1857.	27.35	5711.	30.98	- 1374.
150.0	21.59	2071.	28.82	5925.	32.45	- 1057.
160.0	22.03	2289.	30.23	6143.	33.86	- 725.8

Table 10. Recommended thermodynamic data of amorphous selenium--Continued

T(K)	C_p^a (J mol^{-1}K^{-1})	H_T^a-H_o^a (J mol^{-1})	S_T^a-S_o^a (J mol^{-1}K^{-1})	H_T^a-H_o^t (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	-(G_T^a-H_o^t) (J mol^{-1})
170.0	22.44	2511.	31.58	6365.	35.21	380.4
180.0	22.81	2737.	32.87	6591.	36.50	21.86
190.0	23.14	2967.	34.11	6821.	37.74	349.4
200.0	23.44	3200.	35.31	7054.	38.94	732.8
210.0	23.70	3436.	36.46	7290.	40.09	1128.
220.0	23.92	3674.	37.56	7528.	41.19	1534.
230.0	24.24	3914.	38.63	7768.	42.26	1951.
240.0	24.58	4158.	39.67	8012.	43.30	2379.
250.0	24.93	4406.	40.68	8260.	44.31	2817.
260.0	25.30	4657.	41.67	8511.	45.30	3265.
270.0	25.68	4912.	42.63	8766.	46.26	3723.
273.5	25.80	4993.	42.93	8847.	46.56	3869.
280.0	26.07	5171.	43.57	9025.	47.20	4190.
290.0	26.47	5433.	44.49	9288.	48.12	4667.
298.15	26.80	5650.	45.23	9505.	48.86	5062.
300.0	26.88	5700.	45.40	9554.	49.03	5153.
303.4(T_g)	27.02	5792.	45.70	9646.	49.33	5320.
303.4	40.31	5792.	45.70	9646.	49.33	5320.
310.0	40.11	6057.	46.57	9911.	50.20	5649.
320.0	39.82	6457.	47.83	10311.	51.46	6157.
330.0	39.54	6853.	49.06	10707.	52.69	6678.
340.0	39.26	7247.	50.23	11101.	53.86	7211.

Table 10. Recommended thermodynamic data of amorphous selenium--Continued

T(K)	C^a_p (J mol^{-1}K^{-1})	H^a_T-H^a_o (J mol^{-1})	S^a_T-S^a_o (J mol^{-1}K^{-1})	H^a_T-H^t_o (J mol^{-1})	S^a_T (J mol^{-1}K^{-1})	-(G^a_T-H^t_o) (J mol^{-1})
350.0	38.98	7639.	51.37	11493.	55.00	7755.
360.0	38.72	8027.	52.46	11881.	56.09	8310.
370.0	38.46	8413.	53.52	12267.	57.15	8877.
380.0	38.21	8796.	54.54	12650.	58.17	9453.
390.0	37.96	9177.	55.53	13031.	59.16	10040.
400.0	37.72	9556.	56.49	13410.	60.12	10636.
410.0	37.49	9932.	57.41	13786.	61.05	11242.
413.0	37.42	10044.	57.69	13898.	61.32	11427.
420.0	37.26	10305.	58.32	14159.	61.95	11857.
430.0	37.04	10677.	59.19	14531.	62.82	12481.
440.0	36.82	11046.	60.04	14900.	63.67	13113.
450.0	36.62	11413.	60.86	15267.	64.49	13754.
460.0	36.42	11778.	61.67	15632.	65.30	14403.
470.0	36.22	12142.	62.45	15996.	66.08	15060.
480.0	36.03	12503.	63.21	16357.	66.84	15725.
490.0	35.85	12862.	63.95	16716.	67.58	16397.
494.2(T_m)	35.78	13013.	64.25	16867.	67.89	16681.
500.0	35.68	13220.	64.67	17074.	68.30	17076.
520.0	35.35	13930.	66.06	17784.	69.69	18456.
540.0	35.04	14634.	67.39	18488.	71.02	19864.
560.0	34.77	15332.	68.66	19186.	72.29	21297.
580.0	34.51	16025.	69.88	19879.	73.51	22755.

Table 10. Recommended thermodynamic data of amorphous selenium--Continued

T(K)	C^a_p (J mol^{-1}K^{-1})	H^a_T-H^a_o (J mol^{-1})	S^a_T-S^a_o (J mol^{-1}K^{-1})	H^a_T-H^t_o (J mol^{-1})	S^a_T (J mol^{-1}K^{-1})	-(G^a_T-H^t_o) (J mol^{-1})
600.0	34.29	16713.	71.04	20567.	74.67	24237.
650.0	33.84	18415.	73.77	22269.	77.40	28040.
700.0	33.55	20099.	76.27	23953.	79.90	31973.
750.0	33.43	21773.	78.57	25627.	82.21	36026.
800.0	33.46	23444.	80.73	27298.	84.36	40191.
850.0	33.67	25122.	82.77	28976.	86.40	44460.
900.0	34.03	26814.	84.70	30668.	88.33	48829.
950.0	34.56	28528.	86.55	32382.	90.18	63292.
1000.0	35.25	30272.	88.34	34126.	91.97	57846.

Table 11. Recommended thermodynamic data of monoclinic selenium

T(K)	C_p^m (J mol^{-1}K^{-1})	$H_T^m-H_o^m$ (J mol^{-1})	$S_T^m-S_o^m$ (J mol^{-1}K^{-1})	$H_T^m-H_o^t$ (J mol^{-1})	S_T^m (J mol^{-1}K^{-1})	$-(G_T^m-H_o^t)$ (J mol^{-1})
0.0	0.0	0.0	0.0	2151.	1.71	-2151.
2.0	0.007229	0.003781	0.003182	2151.	1.72	-2147.
3.0	0.02602	0.01902	0.009109	2151.	1.73	-2145.
4.0	0.06530	0.06267	0.02140	2151.	1.74	-2144.
5.0	0.1319	0.1588	0.04257	2151.	1.76	-2142.
6.0	0.2308	0.3373	0.07485	2151.	1.79	-2140.
7.0	0.3648	0.6321	0.1200	2151.	1.84	-2138.
8.0	0.5345	1.079	0.1794	2152.	1.90	-2136.
9.0	0.7390	1.713	0.2539	2152.	1.97	-2134.
10.0	0.9759	2.568	0.3437	2153.	2.06	-2132.
12.0	1.533	5.060	0.5694	2156.	2.29	-2128.
14.0	2.173	8.755	0.8529	2159.	2.57	-2123.
16.0	2.860	13.78	1.188	2164.	2.91	-2118.
18.0	3.562	20.21	1.565	2171.	3.28	-2112.
20.0	4.249	28.02	1.976	2179.	3.70	-2105.
25.0	5.628	52.71	3.070	2203.	4.79	-2083.
30.0	6.995	84.27	4.216	2235.	5.94	-2057.
40.0	9.389	166.2	6.555	2317.	8.27	-1986.
50.0	11.40	270.1	8.868	2421.	10.59	-1891.
60.0	13.12	392.7	11.10	2543.	12.82	-1774.
70.0	14.62	531.4	13.24	2682.	14.96	-1635.
80.0	15.97	684.4	15.28	2835.	17.00	-1475.

Table 11. Recommended thermodynamic data of monoclinic selenium--Continued

T(K)	C_p^m (J mol^{-1}K^{-1})	H_T^m-H_o^m (J mol^{-1})	S_T^m-S_o^m (J mol^{-1}K^{-1})	H_T^m-H_o^t (J mol^{-1})	S_T^m (J mol^{-1}K^{-1})	-(G_T^m-H_o^t) (J mol^{-1})
90.0	17.18	850.1	17.23	3001.	18.95	-1295.
100.0	18.22	1027.	19.10	3178.	20.82	-1096.
110.0	19.10	1213.	20.88	3364.	22.60	- 878.9
120.0	19.84	1408.	22.57	3559.	24.29	- 644.2
130.0	20.49	1610.	24.19	3761.	25.91	- 393.0
140.0	21.07	1817.	25.73	3968.	27.45	- 126.0
150.0	21.58	2031.	27.20	4182.	28.92	156.0
160.0	22.03	2249.	28.61	4400.	30.33	452.4
170.0	22.41	2471.	29.96	4622.	31.68	762.6
180.0	22.75	2697.	31.25	4848.	32.97	1085.
190.0	23.05	2926.	32.49	5077.	34.21	1421.
200.0	23.32	3158.	33.68	5309.	35.40	1771.
210.0	23.56	3392.	34.82	5543.	36.54	2130.
220.0	23.78	3629.	35.92	5780.	37.64	2501.
230.0	23.99	3867.	36.98	6018.	38.70	2833.
240.0	24.18	4100.	38.01	6259.	39.73	3276.
250.0	24.36	4351.	39.00	6502.	40.72	3678.
260.0	24.52	4595.	39.96	6746.	41.68	4091.
270.0	24.68	4841.	40.89	6992.	42.61	4513.
273.2	24.73	4919.	41.17	7070.	42.89	4645.
280.0	24.83	5089.	41.79	7240.	43.51	4943.

Table 11. Recommended thermodynamic data of monoclinic selenium--Continued

T(K)	C_p^m (J mol^{-1}K^{-1})	H_T^m-H_o^m (J mol^{-1})	S_T^m-S_o^m (J mol^{-1}K^{-1})	H_T^m-H_o^t (J mol^{-1})	S_T^m (J mol^{-1}K^{-1})	-(G_T^m-H_o^t) (J mol^{-1})
290.0	24.97	5338.	42.66	7489.	44.38	5381.
298.2	25.09	5542.	43.35	7693.	45.07	5745.
300.0	25.11	5588.	43.51	7739.	45.23	5830.
303.4	25.16	5674.	43.79	7825.	45.51	5983.
310.0	25.25	5840.	44.34	7991.	46.06	6288.
320.0	25.38	6093.	45.14	8244.	46.86	6751.
330.0	25.51	6348.	45.92	8499.	47.64	7222.
340.0	25.63	6604.	46.69	8755.	48.41	7704.
350.0	25.75	6860.	47.43	9011.	49.15	8192.
360.0	25.88	7119.	48.16	9270.	49.88	8687.
370.0	26.00	7378.	48.87	9529.	50.59	9189.
380.0	26.12	7639.	49.56	9790.	51.28	9696.
390.0	26.24	7900.	50.24	10051.	51.96	10213.
400.0	26.36	8163.	50.91	10314.	52.63	10738.
410.0	26.48	8428.	51.56	10579.	53.28	11266.
413.0	26.51	8507.	51.75	10658.	53.48	11429.
420.0	26.60	8693.	52.20	10844.	53.92	11802.

rather faster than originally thought and estimates of the floor temperature at 356 K seem to be in error. The heat capacity measurements place the floor temperature below the glass transition temperature.

10. Conclusions

The heat capacity of selenium from 0 to 1000 K has been reviewed using 20 measurements reported in the literature. A set of recommended heat capacity, enthalpy, entropy, and Gibbs energy data for trigonal, monoclinic, and amorphous selenium has been derived. In addition, we have arrived at the following conclusions.

1. The heat capacity of crystalline selenium is a smooth function of temperature from 0 to 490 K. The heat capacity of amorphous selenium is also a smooth function of temperature from 0 to 270 K. The upward slope above 270 K can be associated with the glass transition. The heat capacity of monoclinic selenium can be represented as an average of the heat capacities of trigonal and amorphous selenium below 100 K. Above 100 K, the heat capacities of monoclinic and trigonal selenium are identical. The heat capacity of molten selenium shows a quadratic temperature dependence from 300 to 1000 K. The heat capacity decreases from 300 to 700 K and at about 800 K a gradual upturn is observed. The decrease in heat capacity is associated mainly with free volume (hole) effects and to a smaller degree with the heat of reaction from the changes in the ring-chain equilibrium. The increase above 800 K is due to depolymerization.
2. Below 100 K the order of heat capacity is

$$\text{Amorphous} > \text{Monoclinic} > \text{Trigonal selenium}$$

From 100 K to 200 K, the differences in heat capacities are minimal. Above 200 K, the heat capacity of amorphous selenium is higher than the heat capacity of crystalline selenium.

3. At 0 K the residual entropy of amorphous, glassy selenium and monoclinic selenium are 3.63 and 1.71 J mol^{-1}K^{-1}, respectively.
4. Monoclinic selenium is metastable at all temperatures.

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