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Heat capacity and thermodynamic properties of equilibrium sulfur to the temperature 388.36 K, and the heat capacity of Calorimetry Conference copper[a]

by

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[a] This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards

Abstract

The heat capacity of specially prepared orthorhombic sulfur has been measured in a low-temperature adiabatic calorimeter. Measurements from $T \approx 6$ K to near the melting temperature transition at $T_{fus} = 388.36$ K are reported for equilibrium sulfur: for the orthorhombic modification from $T \approx 6$ K to the temperature of the orthorhombic-to-monoclinic transition $T_{trs} = 368.3$ K, and for the monoclinic modification from T_{trs} to T_{fus}. The molar entropy $\Delta_0^T S_m^\circ/R$ and molar enthalpy function $\Delta_{T'}^T H_m^\circ/RT$ for orthorhombic sulfur calculated from this data set are (3.843 ± 0.010) and (1.776 ± 0.005), respectively, where $T = 298.15$ K, $T' \rightarrow 0$, and $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Four measurements of the enthalpy of the orthorhombic to monoclinic phase transition were made with three samples. At T_{trs}, the average value for the enthalpy of transition $\Delta_{trs}H_m^\circ$ is $(401.3 \pm 0.8 \text{ J}\cdot\text{mol}^{-1})$. The heat capacity of the orthorhombic phase is given by the equation: $C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 15.830 + 0.023036\cdot(T/\text{K})$ for the temperature interval (290 to 368.3) K, and that of the monoclinic phase by $C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 11.8498 + 0.035197\cdot(T/\text{K})$ for the temperature interval (368.3 to 388.36) K. Previous determinations of the heat capacity of sulfur are discussed in the text.

1. Introduction

The reliability of thermodynamic property measurements can be jeopardized by the presence of undetected impurities in experimental materials. Accordingly, in the most careful calorimetric investigations, great efforts are often expended on the purification and analysis of substances to be studied.

Almost 40 years ago, Murphy et al.(1) devised a method for the preparation of high-purity sulfur to be employed in measurements of its boiling temperature, a fixed point on the International Temperature Scale. A portion of this material was used by West(2) in a determination, by adiabatic calorimetry, of the heat capacity of sulfur at room and superambient temperatures. Samples of sulfur prepared by the same technique and at about the same time were used by Montgomery(3) in low-temperature heat-capacity calorimetry (it is not clear from Montgomery's thesis whether his specimen was from the same batch as West's), and as a secondary standard (designation, USBM-P1b) in combustion calorimetry of organo-sulfur compounds.(4)

Seven years ago, Susman et al.(5) pointed out that previous measurements of the physical properties of sulfur had been "seriously compromised" by the unsuspected presence in research specimens of such impurities as carbon, hydrocarbons, H_2S, H_2S_x, sulfone, sulfoxide, and sulfonic and sulfinic acids. As preamble to their successful efforts to prepare sulfur with a targeted mass fraction of impurity close to 10^{-6}, they analyzed other specimens of putative high purity. They found, *inter alia*, that the USBM-P1b secondary standard contained mass fraction $3.1\cdot10^{-4}$ of contaminants and, in harmony with that observation, later calorimetric measurements(6) showed a statistically significant difference between the massic energies of combustion in fluorine of USBM-P1b and sulfur with mass fraction impurity of $5\cdot10^{-6}$ from Susman et al. It may be inferred that other specimens prepared by the method of Murphy et al. could have had levels of contaminant similar to that of USBM-P1b, and that the mole fractions of liquid-soluble, solid-insoluble impurity, $1.3\cdot10^{-5}$ and $7\cdot10^{-5}$, claimed by West(2) and Montgomery(3) on the basis of the "freezing-point depression", may be too low. It is impossible to deduce the molar mass of impurity and, thus, the corresponding mass fraction for comparison with the other samples. Contamination of West's and Montgomery's specimens solely by H_2SO_4, for example, would imply a mass-fraction impurity of $\approx 4\cdot10^{-3}$.

An earlier investigation by Eastman and McGavock(7) described the purification of commercial sulfur by recrystallization from CS_2, which was then removed by pumping. Although residual CS_2 was stated to be less than mass fraction 10^{-5}, we do not believe, in light of the elaborateness of subsequently developed efforts for the removal of organic matter from sulfur, that Eastman and McGavock's procedure could have yielded material of acceptable quality. Those authors gave no additional analytical details.

Berezovskii and Paukov(8) took care to acquire high-purity sulfur for use in their low-temperature calorimetric studies. It appears, however, that their specimen may have contained mass fraction $1.1\cdot10^{-3}$ of SiO_2; other (nonmetallic) contaminants could also have been present, but no analytical results are given for C, H, O, or N.

In light of the preceding observations, and the key role played by the thermodynamics of sulfur in many areas of science and technology, we thought it advisable to remeasure the low-temperature heat capacity of equilibrium sulfur, using the very pure, fully characterized material provided by Susman et al., which contains a factor of 10, perhaps even 100, less impurity than the other specimens described in the preceding paragraphs. (This work was done in cooperation with Malcolm W. Chase, and P. A. G. O'Hare, National Institute of Standards and Technology (NIST), Physical and Chemical Properties Division, Gaithersburg, MD 20899, U.S.A., who arranged for the transfer of the sulfur sample to the U.S. Geological Survey, requested this study, received copies of the data base, and reviewed this report. This report contains a description and analysis of the heat capacities measured in the Thermodynamic Properties Laboratory of the U.S. Geological Survey and transferred to NIST.)

2. Material

Prior to the present work, Susman et al.'s(5) sample had been protected from exposure to the atmosphere at all times since it was prepared and analyzed. Its composition and chemical analyses have been presented in detail;(6) total impurities amounted to mass fraction $5\cdot10^{-6}$. The unit-cell dimensions were calculated from 41 diffraction lines using a Guinier-Hägg[†] X-ray camera with a copper target and standard reference material Si (SRM 640) as an internal standard. The unit cell parameters and volume were: $a = (1.0454 \pm 0.0002)$ nm; $b = (1.2870 \pm 0.0003)$ nm; $c = (2.4472 \pm 0.0005)$ nm; and $V = (3.2927 \pm 0.0009)$ nm^3.

Within the normal temperature range of low-temperature calorimetry, sulfur undergoes two transitions: from orthorhombic to monoclinic modifications at $T \approx 368$ K, and from monoclinic to liquid at $T \approx 388$ K, both of which are presumably influenced by impurities.

[†] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the U.S. Geological Survey or the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

3. Calorimetric methods

Measurements of the standard molar heat capacities at low temperature employed the intermittent heating technique with the adiabatically shielded calorimeter and methods described by Robie and Hemingway(9) and Robie.(10) A calorimeter with an internal volume of about 30 cm^3 was used. Calorimetric temperatures were determined with a Minco model S1059-1 platinum-resistance thermometer. This thermometer ($R_0 = 100.014997\ \Omega$) was calibrated by the Temperature Measurements Section of the U.S. National Institute of Standards and Technology on IPTS-68 between $T = 13.8$ K and $T = 505$ K, and between 4.2 K and 13.8 K on a provisional temperature scale used in the laboratory.(11) The calorimeter contained a mass of 27.2366 g of sulfur.

The calorimeter was calibrated with Calorimetry Conference reference material copper; the results obtained for the heat capacity of copper agreed with those published earlier[12]. In 1965, the Calorimetry Conference made available a high purity copper sample to be used for interlaboratory comparisons of heat-capacity measurements[13]. The sample received by the U.S. Geological Survey bore the designation T7.2, was in the form of a right-circular cylinder 3.18 cm in diameter, 5.34 cm in length, and was 376.2 g in mass. Sample preparation and an earlier set of heat-capacity measurements were presented in an earlier study[11]. For this study, the copper mass was 242.5746 g (in vacuo).

In 1987, Martin[12] published a reference equation for the heat capacity of copper from $T = 20$ to 320 K that was based upon measurements from his laboratory. This equation superceded an earlier reference equation developed by Martin that used the copper data given in reference [11] and earlier data from Martin's laboratory. We believe that Martin's revised equation for copper when combined with the equation for copper for temperatures at and below $T = 20$ K given by Osborne and others[13] provides the best reference heat capacities for copper. Between $T = 30$ and 320 K, our observed heat capacities differ from the reference values by less than 0.1% (generally less than 0.05%), except at about $T = 60$ K where one value differs by 0.25%. Between $T = 13.5$ and 30 K, our values differ from the reference values by about 0.5% or less. At lower temperatures, deviations of 1 to 5% occur and reflect the rapid decrease in sensitivity of the platinum resistance thermometer as the absolute 0 of temperature is approached. Accordingly, the calorimeter was deemed to be functioning properly.

Our heat capacity measurements for copper are listed in table 1, in the chronological order of measurement. The heat capacities of series 1 and 2 were smoothed separately using an 11th order polynomial. The smoothed results were integrated to obtain the entropy difference for the temperature interval of $T =$ 60 to 320 K yielding 31.137 and 31.139 $J\ mol^{-1}\ K^{-1}$, respectively for series 1 and 2. Smoothed values from Martin's reference equation were similarly integrated yielding 31.136 $J\ mol^{-1}\ K^{-1}$. For the temperature interval $T = 6$ to 60 K, the entropy calculated from our smoothed heat capacities is 3.713 $J\ mol^{-1}\ K^{-1}$ and is compared to the value calculated from the reference equations of Martin and Osborne and others of 3.718 $J\ mol^{-1}\ K^{-1}$, a difference of -0.13%. For the temperature interval $T = 6$ to 320 K, the entropies calculated from our data differ from that calculated from the reference equations by 0.01%.

4. Results for orthorhombic sulfur

Low-temperature heat-capacity results for orthorhombic sulfur are listed in chronological order in table 2. The values were smoothed by means of a cubic spline: $C^\circ_{p,m}(T) = a + b\cdot T + c\cdot T^2 + d\cdot T^3$. Because of scatter, the experimental heat capacities at $T < 10$ K could not be fitted as a smooth function of T. This may reflect the effects of partial adsorption of some of the He exchange gas at the lowest temperatures. Accordingly, for temperatures between $T \to 0$ and 10 K, values of $C^\circ_{p,m}$ were calculated at 1 K intervals based on the assumption that sulfur, a non-metal, obeyed the relation: $C^\circ_{p,m} = A\cdot T^3$. The corresponding $C^\circ_{p,m}$ against T curve merged smoothly with the cubic spline fit at $T \approx 10$ K. A deviation plot in figure 1 compares the experimental and smoothed results; the latter are also shown in figure 2, as a function of temperature.

Values of the thermodynamic functions of orthorhombic sulfur from $T \to 0$ to $T = 368$ K, calculated from the smoothed $C^\circ_{p,m}$s, are listed in table 3. The entropy $\Delta_0^T S^\circ_m/R = (3.843 \pm 0.010)$ and enthalpy function $\Delta_{T'}^T H^\circ_m/RT = (1.776 \pm 0.005)$, where $T = 298.15$ K and $T' \to 0$. Smoothed heat capacities for temperatures between 290 K and 368.3 K were fit with the equation:

$$C_{p,m}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 15.830 + 0.023036\cdot(T/\mathrm{K}), \qquad (1)$$

with an average absolute deviation of $\pm 7\cdot 10^{-4}\cdot C^\circ_{p,m}$.

5. Results for monoclinic sulfur

Conversion of orthorhombic to monoclinic sulfur proceeds slowly near the transition temperature, as noted in earlier studies.(2,3,7) Therefore, for the Series 2 and 4 (table 4) experiments, our sample was heated to $T \approx 380$ K (where conversion is facile) and then cooled rapidly (to the starting temperature of the measurements) in order to freeze in the monoclinic modification.

Experimental heat capacities for monoclinic sulfur are listed in table 4 in the chronological order of measurement. The results were fit with the equation:

$$C_{p,m}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 11.8498 + 0.035197\cdot(T/\mathrm{K}), \qquad (2)$$

with an average absolute deviation of $\pm 7\cdot 10^{-4}\cdot C^\circ_{p,m}$. This equation is valid for the temperature interval 368.3 K to 388.36 K, and smoothed heat capacities derived from it were used to compute the thermodynamic quantities for monoclinic sulfur listed in table 3. Deviations of the smoothed heat capacities from the experimental results are shown in figure 1. The smoothed data are also shown in figure 2 as a function of temperature.

6. Enthalpy of transition: orthorhombic to monoclinic sulfur

Four measurements of the enthalpy of transition were made with three samples of sulfur. Experimental details are given in table 5. Because of the slow equilibration of the monoclinic phase at temperatures below 375 K, measurements were made of the enthalpy from $T < 368.3$ K to $T > 375$ K. These values were corrected for the heat capacity of the orthorhombic phase at $T < 368.3$ K and the monoclinic phase at $T > 368.3$ K, on the basis of equations (1) and (2).

7. Discussion

No evidence has been found in our measurements of the heat capacity of β-sulfur for the transition in the temperature region between 368.3 K and 374 K suggested by West.(2) Our conclusion is in agreement with that of Montgomery.(3) West indicated that his sample was converted to the monoclinic form at a temperatures greater than 374 K, from which he cooled it to lower temperatures, where measurements were begun. Identical procedures were followed in the present study. The first measurement of series 5 is significantly higher than measurements at similar temperatures in series 4. However, this measurement was followed by measurements that are consistent with the earlier series without indication of a transition.

Difference in sample response could mean that an intermediate structure develops on heating. At $T < 375$ K, change from orthorhombic to monoclinic sulfur proceeds slowly. At $T > 375$ K, transition is complete in a few minutes or less. West's observations suggest that the transformation from the orthorhombic to the unknown monoclinic form requires substantial time, which may vary with the purity of the sample. Currell and Williams[14] reported a double peak in differential scanning calorimetric heat capacities for flowers of sulfur that occur in the temperature interval identified by West. These authors attribute the first peak to the α-β transition in sulfur, and the second peak to the melting of chain structure sulfur. West was aware of the possible formation of chains of sulfur instead of the ring structure of monoclinic sulfur and took precautions to avoid development of sulfur having the chain structure.

Four studies have presented structural data for β-sulfur, two provide unit cell information[15,16] and two provide x-ray diffraction data.[17,18] The unit cells differ in both axial length and in the size of the β-angle. The space groups were given as $P2_1/c$[15] and $P2_1/a$[16]. The x-ray diffraction patterns of Taylor and Rummery[17] and Pinkus et al.[18] were based on the unit cells of Templeton et al.[15] and Burwell[16], respectively. The calculated d-spacings differ and led Taylor and Rummery to conclude that the data of Pinkus et al. were in error.

Sample preparation for the materials used in the structural determinations differed and may provide some insight into the question of a possible transition in the stability field of monoclinic sulfur. Burwell crystallized sulfur from the melt and held the sample at $T = 376$ K during the x-ray analysis. Pinkus et al. used a heating stage that melted a pure orthorhombic sulfur sample and the diffraction pattern was "determined immediately on solidification." Taylor and Rummery heated their sample in a heating camera through the α-β sulfur transition to about $T = 373$ K and determined the diffraction pattern. Taylor and Rummery observed anomalous intensities that they attributed to recrystallization of the sample. Thus Burwell and Pinkus et al. synthesized β-sulfur in the temperature interval where heat-capacity measurements demonstrate rapid conversion to the monoclinic structure. Taylor and Rummery synthesized β-sulfur in the temperature region where conversion is anomalously slower as compared to conversion at the higher temperatures. Templeton et al. synthesized their sample as a by-product of a reaction in which they were attempting to make a substituted diethietene complex of uranium. Other details of the sample preparation are not given. Because the disparate data sets were derived from samples having different synthesis histories, some support is given to the idea that a second monoclinic form of sulfur may exist in the narrow temperature interval of $T = 368.3$ to 374 ± 1 K. Final resolution of this dichotomy must await a more detailed structural analysis of sulfur in this region of temperature.

The average of the four values for the enthalpy of transition from orthorhombic to monoclinic sulfur, $\Delta_{trs}H^{\circ}_{m} = (401.2 \pm 1)\ \mathrm{J\cdot mol^{-1}}$, is in good agreement with the results of West,(2) $(401.7 \pm 2)\ \mathrm{J\cdot mol^{-1}}$, and Montgomery,(3) $(400.4 \pm 2.9)\ \mathrm{J\cdot mol^{-1}}$. It should be noted here that if a second monoclinic form does exist, the procedure used in this study captures any enthalpic effect in the value reported for the enthalpy of the α-β transition.

For completeness, we compare our results with those from five previous experimental studies, and with three sets of earlier recommendations. Although measurements to be contrasted here were made on the basis of different temperature scales, adjustment of each set to ITS-90 would not bring about any significant difference in the $C^\circ_{p,m}$s within the experimental uncertainties.

The standard molar entropy obtained in this study for orthorhombic sulfur at $T = 298.15$ K, (31.953 ± 0.083) $J \cdot K^{-1} \cdot mol^{-1}$, is in good agreement with the values recommended by CODATA,(19) (32.045 ± 0.050) $J \cdot K^{-1} \cdot mol^{-1}$; Gurvich et al.,(20) (32.070 ± 0.080) $J \cdot K^{-1} \cdot mol^{-1}$; and the JANAF Thermochemical Tables (32.056 ± 0.050) $J \cdot K^{-1} \cdot mol^{-1}$.(21) The CODATA selection was calculated from the heat capacities reported by Berezovskii and Paukov(8) $\{5 \leq (T/K) \leq 306\}$, Eastman and McGavock(7) $\{15 \leq (T/K) \leq 361\}$, and Montgomery(3) $\{12.3 \leq (T/K) \leq 361\}$; Gurvich et al. used the data of Berezovskii and Paukov and Montgomery; and the JANAF table is based on Montgomery's results alone. Measurements by Mal'tsev and Demidenko(22) were performed over the limited temperature interval between 53 K and 305 K and, therefore, were not used in these evaluations.

Figure 3 compares the smoothed values in table 3 with those obtained by previous authors for orthorhombic sulfur. Despite the large differences in impurity contents of the various samples, there is remarkable agreement among the different studies except at low temperatures and in the transition to fusion region. It is interesting that, with each study treated independently, the values of $\Delta_0^T S^\circ_m$ at $T = 298.15$ K agree within the assigned uncertainties.

The recommended value of $C^\circ_{p,m}(T \approx 6 \text{ K})$ from Berezovskii and Paukov is about 2% larger than ours, which is assumed to be due to the influence of contaminants. These authors gave some details of the purity of their sample, prepared by a method devised by Kiseleva and Smykova.(23) It contained as major impurity mass fraction $5 \cdot 10^{-4}$ of Si which, arguably, came from the silica apparatus in which the sulfur was prepared. In that case, the corresponding mass fraction of SiO_2 impurity would be $\approx 10^{-3}$. Berezovskii and Paukov made no mention of C, H, O, or N contaminants. It is not unlikely that their sample had a mass fraction of impurity that exceeded ours by almost three powers of ten.

The heat capacities reported here increasingly diverge from those reported by Montgomery(3) and West(2) for orthorhombic sulfur in the temperature range from 298.15 K to 368.3 K, and for the monoclinic phase as well. There is good accord between the results at $T = 368.3$ K for the monoclinic phase, but they also deviate with increasing temperature. The values of $dC^\circ_{p,m}/dT$ from West are similar to those found in this study, but the $C^\circ_{p,m}$s lie about 1 per cent below those listed in table 3. The smoothed $C^\circ_{p,m}$s from Montgomery deviate from ours by several per cent at $T = 388.36$ K. Experimental heat capacities for the temperature interval 364 K to 370 K given by Montgomery are not shown, but are in good agreement, with respect to both value and $dC^\circ_{p,m}/dT$, with the measurements reported here. At $T > 370$ K, the $C^\circ_{p,m}$ against T curve obtained by Montgomery becomes horizontal and then breaks sharply downward at $T \approx 384$ K. We attribute this to the rupture of the sample container in the calorimeter, to which Montgomery referred in his thesis.

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Table 1. Experimental heat capacities of copper corrected for curvature

$\{M = 63.546\ \mathrm{g{\cdot}mol^{-1}};\ p = 100.000\ \mathrm{kPa};\ R = 8.31451\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}\}$

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series 1		Series 2		Series 3	
58.13	0.9859	56.86	0.9491	5.863	0.001728
61.88	1.093	60.66	1.058	6.761	0.002303
66.30	1.214	65.06	1.180	7.981	0.003499
70.92	1.334	69.67	1.302	8.267	0.003992
76.13	1.461	74.89	1.432		
81.34	1.579	80.12	1.552	Series 4	
86.55	1.687	85.32	1.663		
91.71	1.786	90.48	1.763	6.997	0.002592
96.81	1.875	95.58	1.854		
101.86	1.955	100.61	1.936	Series 5	
106.86	2.028	105.60	2.010		
111.82	2.095	110.55	2.079	6.633	0.002223
116.73	2.156	115.45	2.140	8.023	0.003553
121.62	2.212	120.30	2.197	9.627	0.005876
126.49	2.264	125.13	2.250	12.25	0.01162
131.33	2.311	129.95	2.298		
136.13	2.354	134.73	2.342	Series 6	
140.93	2.394	139.49	2.382		
145.73	2.431	144.24	2.420	11.28	0.009105
150.50	2.464	148.98	2.454	12.67	0.01294
155.25	2.496	153.71	2.486	13.42	0.01549
159.99	2.525	158.42	2.516	14.31	0.01909
164.70	2.554	163.11	2.544		
169.43	2.579	167.78	2.571	Series 7	
174.16	2.604	172.45	2.595		
178.89	2.627	177.12	2.618	13.09	0.01437
183.62	2.650	181.81	2.641	13.80	0.01701
188.34	2.670	186.48	2.662	14.93	0.02185
193.06	2.688	191.16	2.681	15.71	0.02575
197.78	2.707	195.85	2.700	16.69	0.03108
202.53	2.724	200.54	2.717	17.86	0.03849
207.30	2.739	205.25	2.733	19.24	0.04896
212.09	2.754	209.99	2.748	20.85	0.06362
216.91	2.769	214.76	2.763	22.70	0.08388
221.77	2.783	219.57	2.776	24.81	0.1120
226.72	2.796	224.44	2.790	27.20	0.1501
231.75	2.810	229.42	2.804	29.88	0.2003
236.86	2.823	234.50	2.816	32.90	0.2655
242.01	2.835	239.65	2.828	36.30	0.3482
247.19	2.847	244.83	2.842	40.10	0.4506
252.38	2.858	250.03	2.854	44.31	0.5720
257.58	2.869	255.23	2.865	49.00	0.7128
262.77	2.879	260.43	2.874	54.29	0.8700
267.96	2.888	265.62	2.883	59.85	1.032
273.15	2.897	270.81	2.893	65.42	1.189
278.34	2.908	276.00	2.901	71.01	1.338
283.52	2.915	281.19	2.910	76.49	1.470
288.68	2.924	286.35	2.919	81.88	1.592
293.84	2.933	291.51	2.928	87.15	1.700
298.98	2.939	296.66	2.936	92.32	1.797
304.12	2.946	301.80	2.944	97.44	1.885
309.23	2.955	306.92	2.951	102.46	1.964
314.34	2.962	312.04	2.958	107.42	2.036
319.44	2.968	317.14	2.965	112.34	2.102
				117.22	2.162
				122.07	2.217

Table 2. **Experimental heat capacities of orthorhombic sulfur corrected for curvature**
{M = 32.066 g·mol^{-1}; p = 100.000 kPa; R = 8.31451 J·mol^{-1}·K^{-1}}

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series 1		Series 3		Series 3	
6.009	0.01859	48.20	0.8682	231.18	2.478
6.717	0.02377	53.16	0.9349	235.89	2.499
7.614	0.03217	58.45	1.004	240.65	2.522
8.514	0.04188	63.90	1.087	245.43	2.543
9.926	0.05964	69.40	1.177	250.23	2.563
11.212	0.08299	74.83	1.250	255.04	2.582
		80.16	1.315	259.85	2.600
Series 2		85.40	1.370	264.70	2.617
		90.61	1.434	269.58	2.635
6.635	0.02322	95.78	1.489	274.46	2.651
7.263	0.02856	100.88	1.553	279.32	2.665
8.015	0.03620	105.94	1.595	284.17	2.683
9.084	0.04859	110.96	1.643	289.03	2.704
9.874	0.06149	115.89	1.692	293.83	2.721
11.022	0.07891	120.77	1.739	298.64	2.733
12.096	0.09977	125.60	1.786		
13.274	0.1274	130.40	1.829	Series 4	
		135.16	1.870		
Series 3		139.89	1.910	294.63	2.717
		144.58	1.948	299.23	2.734
9.676	0.05775	149.25	1.984	303.87	2.748
10.40	0.06855	153.89	2.021	308.50	2.761
11.69	0.09127	158.50	2.055	313.22	2.777
12.62	0.1120	163.09	2.089	317.93	2.789
14.06	0.1471	167.66	2.123	322.63	2.800
15.01	0.1719	172.22	2.155	327.31	2.811
16.13	0.2015	176.76	2.185	331.98	2.824
17.45	0.2365	181.29	2.214	336.65	2.838
18.93	0.2765	185.81	2.244	341.30	2.849
20.63	0.3215	190.32	2.272	345.96	2.865
22.56	0.3706	194.82	2.298	350.64	2.879
24.73	0.4246	199.33	2.322	355.31	2.890
27.15	0.4818	203.83	2.347	359.97	2.900
29.85	0.5409	208.34	2.369	364.61	2.909
32.84	0.6018	212.85	2.392		
36.15	0.6643	217.38	2.413	Series 5	
39.82	0.7307	221.92	2.436		
43.81	0.8034	226.52	2.456	364.66	2.910

Table 3. Standard molar thermodynamic properties of reference state sulfur {$M = 32.066\ \mathrm{g{\cdot}mol^{-1}}$; $p = 100.000$ kPa; $R = 8.31451\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$; $\Phi_m = (-\Delta_0^T H_m/T + \Delta_0^T S_m)$}

$\frac{T}{\mathrm{K}}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m/T}{R\cdot \mathrm{K}}$	$\frac{\Phi_m}{R}$
5	0.0078	0.0025	0.0017	0.0008
10	0.062	0.0207	0.0091	0.0116
15	0.172	0.0646	0.0434	0.0212
20	0.304	0.1321	0.0919	0.0402
25	0.431	0.2137	0.1472	0.0665
30	0.544	0.3025	0.2041	0.0984
35	0.644	0.3939	0.2599	0.1340
40	0.735	0.4859	0.3137	0.1722
45	0.818	0.5774	0.3651	0.2123
50	0.892	0.6675	0.4142	0.2533
60	1.033	0.8425	0.5056	0.3369
70	1.179	1.013	0.5914	0.4216
80	1.311	1.179	0.6734	0.5056
90	1.428	1.340	0.7507	0.5893
100	1.536	1.496	0.8240	0.6720
110	1.636	1.648	0.8933	0.7547
120	1.732	1.794	0.9593	0.8347
130	1.825	1.936	1.022	0.9137
140	1.911	2.075	1.083	0.9923
150	1.990	2.209	1.141	1.068
160	2.067	2.340	1.196	1.144
170	2.140	2.468	1.250	1.218
180	2.207	2.592	1.301	1.291
190	2.270	2.713	1.351	1.362
200	2.326	2.831	1.398	1.433
210	2.378	2.945	1.443	1.502
220	2.426	3.057	1.487	1.570
230	2.473	3.167	1.529	1.638
240	2.518	3.273	1.568	1.705
250	2.562	3.376	1.608	1.768
260	2.600	3.477	1.645	1.832
270	2.636	3.577	1.681	1.896
273.15	2.647	3.610	1.692	1.918
280	2.670	3.673	1.716	1.957
290	2.705	3.767	1.750	2.017
298.15	2.730	3.843	1.776	2.067
	±0.008	±0.010	±0.005	±0.010
300	2.736	3.860	1.781	2.079
310	2.766	3.950	1.812	2.138
320	2.794	4.038	1.844	2.194
330	2.820	4.124	1.873	2.251
340	2.848	4.208	1.900	2.308
350	2.874	4.291	1.928	2.363
360	2.900	4.373	1.954	2.419
365	2.915	4.414	1.968	2.445
368.3	2.924	4.439	1.976	2.463
368.3	2.984	4.570	2.107	2.463
370	2.991	4.585	2.111	2.474
380	3.034	4.665	2.135	2.530
388.36	3.069	4.731	2.155	2.576

Table 4. Experimental heat capacities of monoclinic sulfur corrected for curvature $\{M = 32.066\ \mathrm{g{\cdot}mol^{-1}}$; $p = 100.000$ kPa; $R = 8.31451\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}\}$

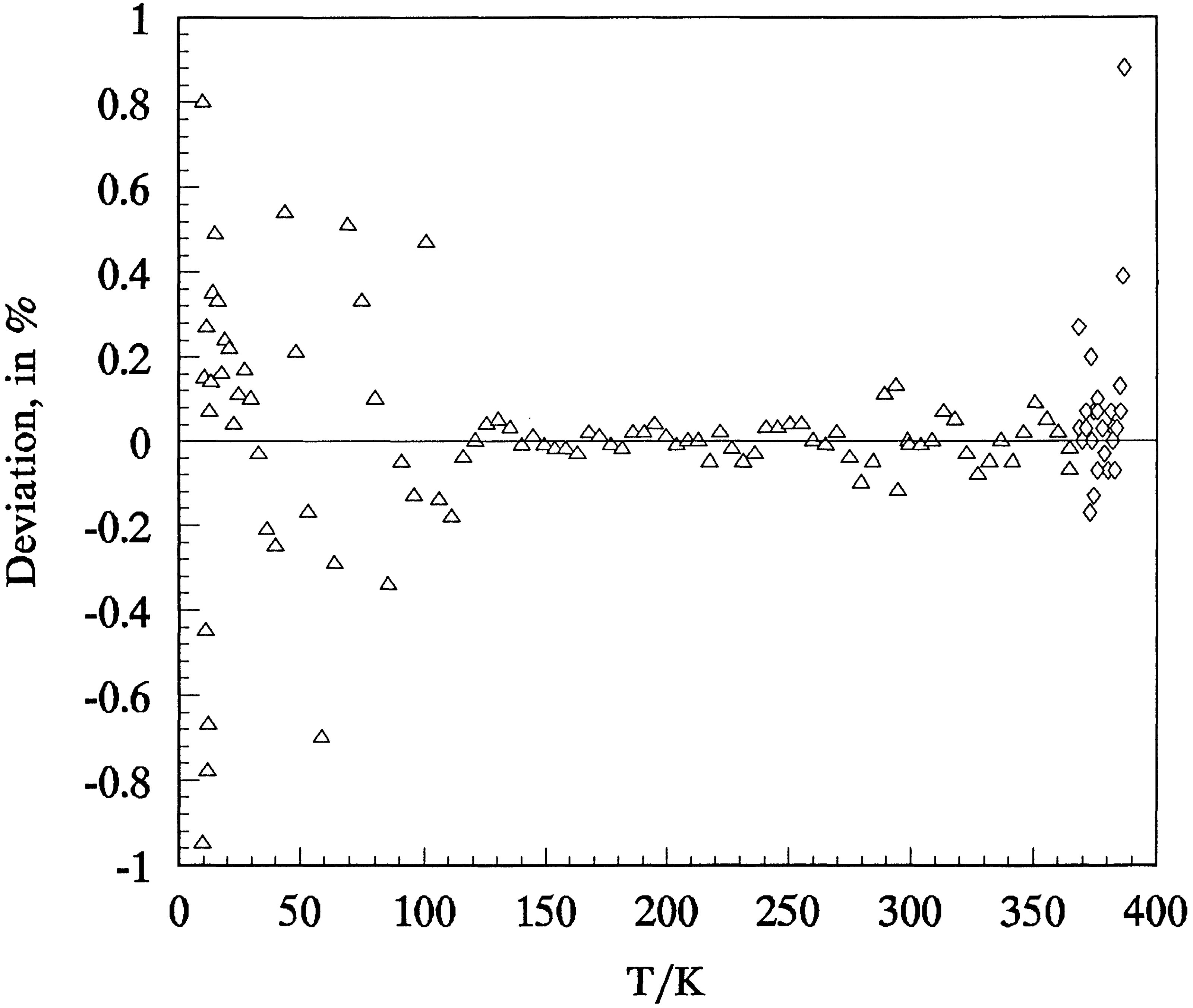
T/K	$C_{p,m}/R$
Series 1	
382.25	3.044
383.84	3.051
Series 2	
373.19	3.011
374.30	3.012
375.77	3.019
377.76	3.025
380.19	3.033
Series 3	
380.20	3.033
381.30	3.037
382.88	3.044
384.73	3.058
386.02	3.071
386.83	3.090
Series 4	
368.58	2.986
369.71	2.990
371.19	2.998
372.77	2.998
374.36	3.006
375.94	3.015
Series 5	
368.26	2.992
371.10	2.998
373.49	3.006
375.89	3.018
378.75	3.028
382.03	3.042
385.30	3.058

Table 5. Enthalpy of the transformation, $\Delta H_{p,m}$, of orthorhombic to monoclinic sulfur at 368.3 K $\{M = 32.066\ \mathrm{g{\cdot}mol^{-1}};\ p = 100.000\ \mathrm{kPa}\}$

Sample mass g	Initial Temperature T/K	Final Temperature T/K	Energy J·mol^{-1}	Enthalpy of Transition J·mol^{-1}
29.4592	363.554	376.588	724.45	402.5
29.4592	366.661	381.774	777.82	400.6
27.3389	366.014	381.126	777.10	400.5
27.2366	366.594	375.633	625.68	401.3
		Average value		401.3 ±0.8
		West (1959)		401.7 ±2.0
		Montgomery (1975)		400.5

List of Figures

Figure 1.



Deviation, in %
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
50
100
150
200
250
300
350
400
T/K

Figure 2.

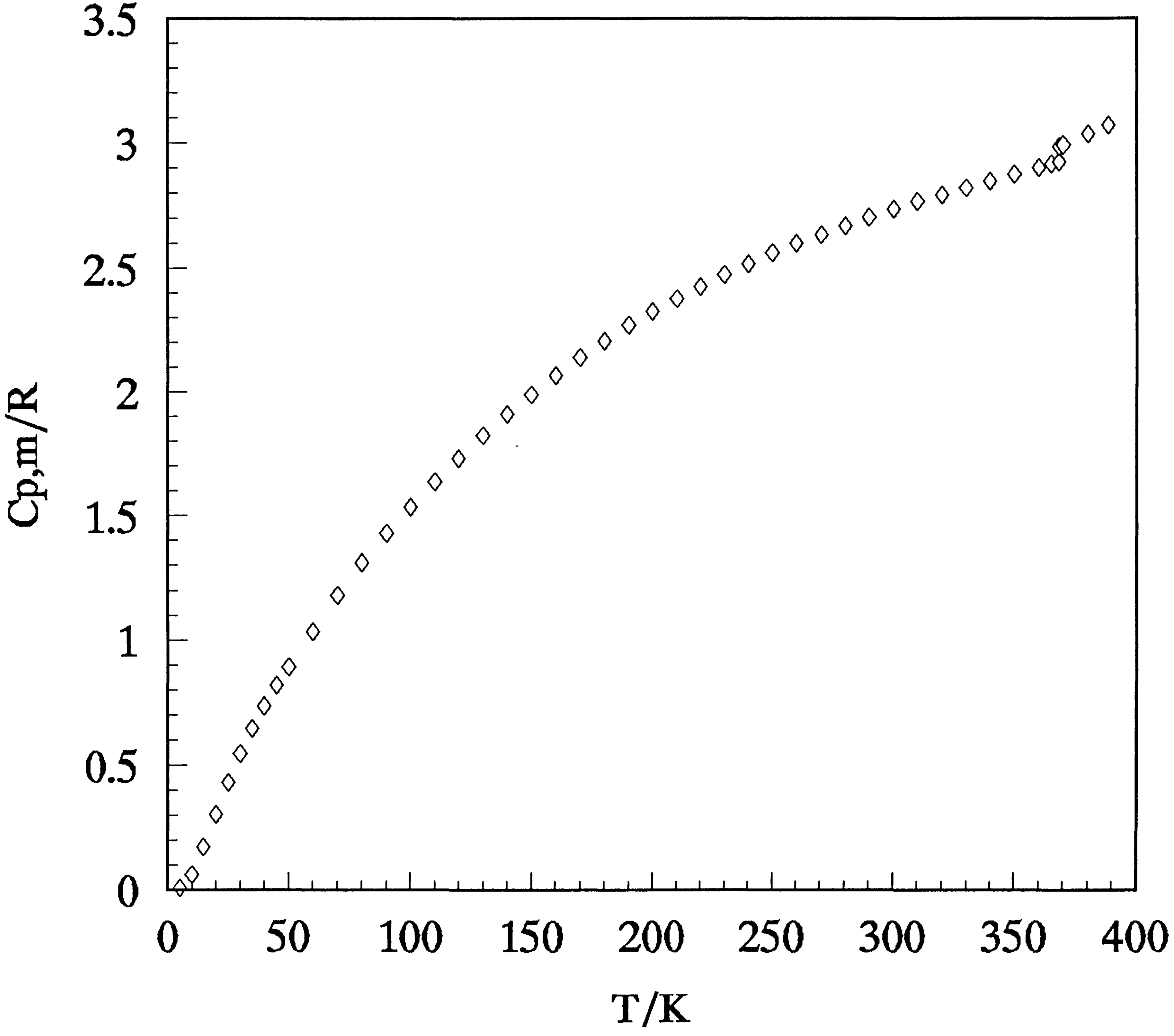
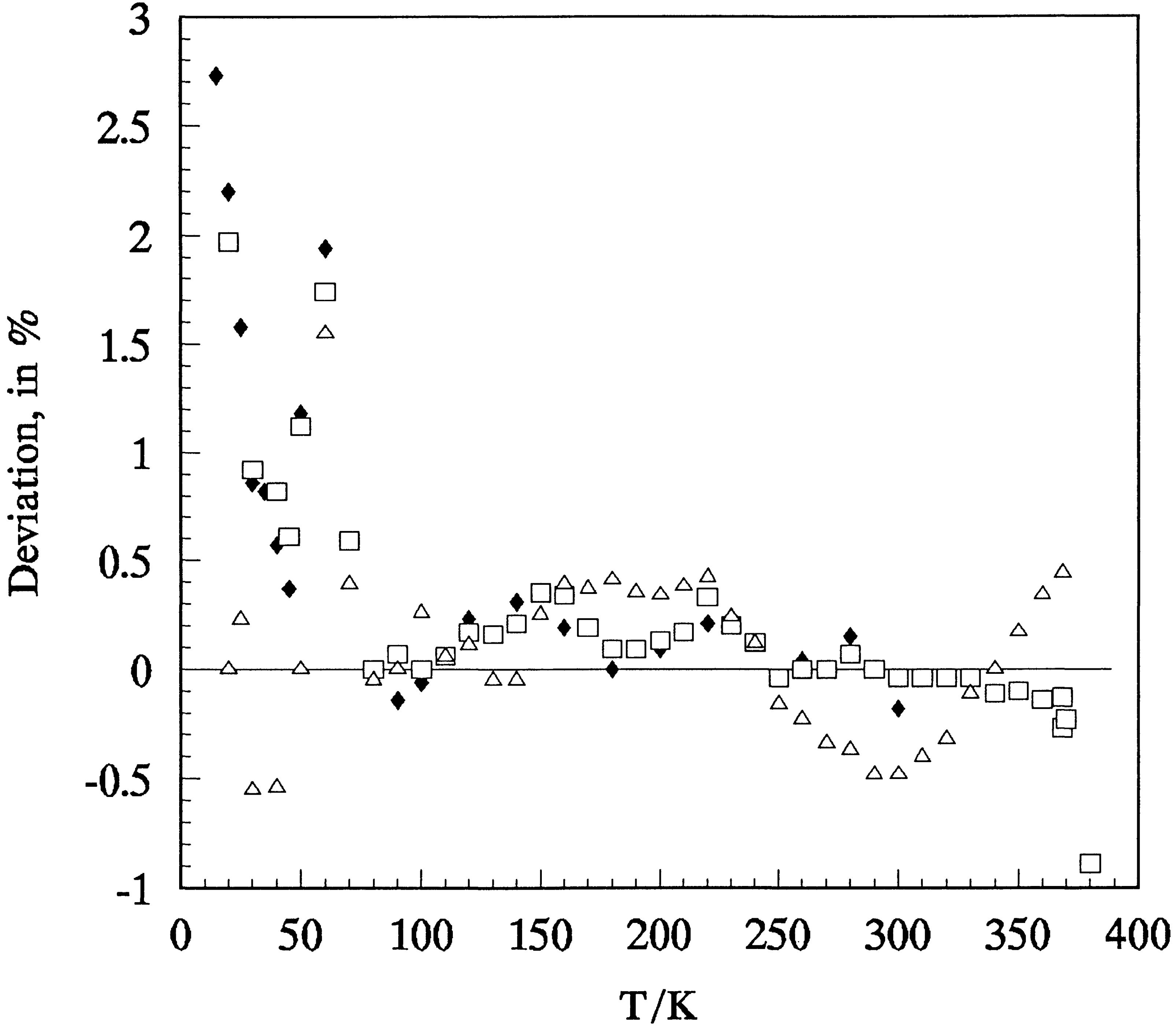


Figure 3.



Deviation, in %
3
2.5
2
1.5
1
0.5
0
-0.5
-1
0
50
100
150
200
250
300
350
400
T/K