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Heat Capacity and Thermodynamic Properties of Bismuth in the Range 333 to 923 K

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Calorimetric studies on the behavior of the heat capacity of bismuth have been carried out in the range 333 to 923 K. Values of the enthalpy and entropy have been determined for selected temperatures. The enthalpy and entropy of fusion at 544.54 K are 11.360±0.014 kJ mol^{-1} and 20.86±0.03 JK^{-1}mol^{-1}, respectively. Appropriate polynomial temperature functions of the C_p for solid and liquid bismuth are given. Earlier reported increasing C_p at temperatures above 800 K proved not to be reliable. The heat capacity at constant volume decreased from 25.80 to 21.14 JK^{-1} mol^{-1} over the region 544.54 to 873 K. Due to beginning of higher-order transformation, the C_v of solid bismuth showed an excess over the harmonic value (3R).

Studies on the heat capacity and thermodynamic properties of solid and liquid bismuth have been undertaken with the views to obtain more accurate values of the C_p and of enthalpy and entropy of fusion since earlier ones showed discrepancies.[1-4]

Earlier works[4] on liquid bismuth showed increasing heat capacity at temperatures above 800 K. This was a somewhat surprising observation since decreasing C_p behavior is common for liquid metals. In order to understand this unusual behavior, we have been studying bismuth in the range 333 to 923 K.

The most recent study on solid bismuth[3] showed an excess of the C_v over the harmonic value ($3R$). This behavior was attributed to beginning of higher-order transformation. On the other hand, the curve of the C_v against temperature has not indicated any signal (such as a bend) which points to beginning transformation. This phenomenon has attracted our interest to investigate the C_v behavior in the solid region using adiabatic calorimeter for the C_p measurements.

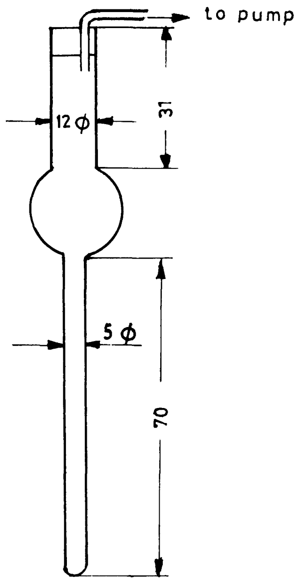

Fig. 1. Zintl funnel.

Experimental

Metal. Bismuth of extra purity grade procured from E. Merck Company was further purified by means of a melting device (similar to a Zintl funnel: Fig. 1). By this melting device, while the clean metal flows down into the lower tube of silica glass, the oxide layer remains apart in the first one. Analysis of the metal showed the presence of the following impurities in ppm by mass: Na: 0.1, Be: 0.1, Zn: 0.1, Pb: 0.1, Ag: 0.1.

Sample. The cylindrical metallic sample (ϕ=5 mm, h=20 mm) weighing 65.288 g was sealed in the sample container of Pyrex glass. Since bismuth expands on solidification after completion of the measurements, a cord of Pyrex glass was coiled spirally in the space of the sample to prevent breakage of the container. The external dimensions of the sample container were similar to the internal ones of the calorimeter (small corrections for small C_p).

Procedure and Calorimetric Technique. The measurement technique and calorimeter were described before.[5] The procedure employed depended on the method of primary indirect provision of energy under adiabatic conditions. The slightly modified calorimeter was tested by measurements on the heat capacity of a standard α-Al_2O_3 sample. The accuracy was estimated to 0.3%. The heating of the calorimeter occured with a speed of 0.6 K min^{-1} while that of the adiabatic shield was regulated to a speed of 0.5 K min^{-1}.

The sample container with a cover possessing holes for heater and thermopile was sealed in a calorimeter of silver which was suspended inside the shield of Cu-Al alloy (90 at-% Cu) with enclosed heater. Both calorimeter and shield were placed in a vertical tube furnace which in turn was protected by another larger one (principle of double shielding).

The temperature differences between the calorimeter and the shield were measured by means of a set of twelve differential Pt-to-(Pt+10 pass per cent Rh) thermopiles. These were connected in series and calibrated as follows: On comparing the thermal potential of these thermopiles with that of a standard Pt-Pt/Rh, we obtain a calibration curve giving the values of temperature with an accuracy of ±0.1 K. The measurement of the thermal potential of the thermopiles was made by means of a digital millivoltmeter (Hewlett-Packard Model 2401 C). The temperature drifts of the shield from the calorimeter temperature were of negligible importance. The observed short-term fluctuation of the null-point was mea-

Table 1. Experimentally Determined Constant Pressure Heat Capacity of Bismuth
M(Bi) = 208.96 g mol^{-1}

T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}
Series 1		Series 4 (continued)		Series 7		Series 9 (continued)		Series 11 (continued)	
332.98	27.14	542.26	29.35	462.97	28.19	544.54	134500	733.09	28.12
343.02	27.19	543.567	46.61	473.01	28.29	544.57	13278	743.21	28.07
353.01	27.22	544.256	145.96	483.11	28.41	545.10	130.8	Series 12	
362.81	27.27	544.516	1462.40	493.21	28.62	547.35	29.95	752.81	27.94
373.02	27.30	Series 5		502.92	28.57	553.17	29.93	763.13	27.85
383.11	27.40	532.17	28.85	513.31	28.73	Series 10		773.07	27.75
Series 2		539.48	29.28	Series 8		332.89	27.14	782.90	27.69
382.94	27.50	541.94	30.50	533.44	28.92	343.21	27.20	793.41	27.67
402.97	27.60	543.85	57.43	539.69	32.55	353.19	27.23	803.22	27.56
413.01	27.70	544.60	5488	544.69	5042.10	Series 11		813.11	27.50
423.12	27.80	544.54	161111	546.18	3405	613.13	29.45	823.39	27.47
432.97	27.90	544.55	62286	550.24	29.95	623.09	29.33	832.96	27.38
443.03	28.00	544.55	9673333	553.01	29.93	633.01	29.22	843.21	27.29
453.11	28.10	544.56	1453000	558.23	29.92	643.09	29.00	853.32	27.20
462.95	28.20	548.68	105.42	563.01	29.90	653.17	28.85	863.04	27.08
483.01	28.40	560.255	29.91	568.31	29.85	663.54	28.73	872.83	27.01
Series 3		Series 6		573.02	29.81	672.91	28.70	883.32	26.83
492.96	28.50	593.01	29.58	578.24	29.75	683.15	28.60	893.11	26.81
503.01	28.60	602.98	29.54	583.21	29.75	692.93	28.51	903.07	26.71
Series 4		613.02	29.45	Series 9		702.77	28.37	913.35	26.63
513.02	28.70	623.10	29.34	541.93	1897	712.86	28.29	923.04	26.51
523.11	28.80	633.02	29.23	544.54	364429	723.31	28.19		
533.09	28.90			544.54	253333				

sured to 2.5×10^{-4} K min^{-1}. The time needed to reach the adiabatic state was registered to 20 min. Excellent regulation of the temperature was obtained by means of a p-regulator.[6] A constant current supply (John Fluke Calibrator Model 382 A) was used in the measurement processes. The mueller bridge (Leeds & Northrup Model 8072, used in the current circuit) and other instruments were controlled by a digital computer. The thermometer resistance was measured with a Mueller bridge automated with stepping motors and a gated null-detector, operated by a computer of the type Hewlett-Packard 2224 B. Calibration of the platinum resistance thermometer used for determination of the fusion temperature of bismuth was made at the triple point of water and the melting points of tin and zinc on IPTS-68.[7] The derived temperatures were judged to correspond to the IPTS-68 to within 0.01 at 500 K and 0.1 at 1000 K. In fact the temperature increments were precisely measured to 0.0002 K.

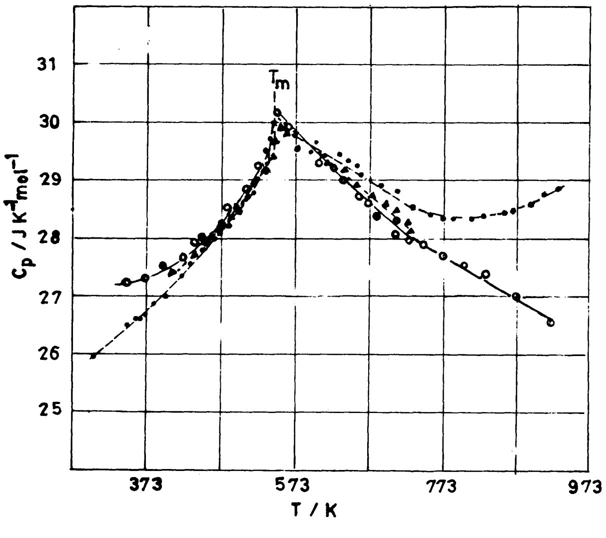

Fig. 2. Heat capacity of bismuth, —O— represents present results, —●— results by Grønvold,[4] —▲— results by Okhotin.[3]

The heat capacity of the empty calorimeter which represented 10 to 15% of the total heat capacity was indirectly measured: From measurements of the heat capacity for samples of silver of different masses and comparing these results with each other, the C_p of the empty calorimeter was calculated at the temperature of measurement. Neglect of this C_p value in the calculation of the total C_p would cause an error of about 0.10 to 0.15%. For this reason small corrections were derived to obtain accurate values of the C_p of bismuth.

From the calibration of the calorimeter on the exactly measured enthalpy of a standard sample of tin (Ref. 5), the "Interchange of heat constant" of the calorimeter has been determined in the whole region of temperature.

Results and Discussion

Heat Capacity of Bismuth. In Table 1 are listed the values of the heat capacity of bismuth in chronological order as determined in the present study. The reader can infer the approximate temperature increments in the determinations from the adjacent mean temperature in the table.

Figure 2 shows the curves of the C_p of solid and liquid bismuth, versus temperature. From curve-fitting calculations of the C_p values illustrated in Table 1, the appropriate temperature functions for solid and liquid bismuth were derived, respectively as

$$C_p=24.081+9.023\times10^{-3}\,T-3.1\times10^{-7}\,T^2 \quad \text{J K mol}^{-1},$$

$$C_p=35.000-9.023\times10^{-3}\,T-3.1\times10^{-7}\,T^2 \quad \text{J K mol}^{-1}.$$

The deviations ranged from 0 to 0.36% for solid bismuth and from 0.2 to 0.365% for liquid bismuth.

The most recently reported heat capacity measurements by Okhotin[3] carried out in the region 417 to 733 K, are in agreement with the present ones.

In the region 333 to 400 K, the values of the heat capacity of bismuth reported by Grønvold[4] differ from our values, although comparable results are obtained in the melting point region and in the liquid state from 545 to 634 K. The differences in the two results could not have been caused by temperature gradients in the calorimeter used in the present study since the temperature excursions of the shield from calorimeter in the null-point period were found to be negligible. Another area of differing results in the region 840 to 923 K, where the present studies show decreasing heat capacity while increasing C_p is reported by others.[4,8] To decide the dependency of the C_p on temperature and to shed light on the factors determining the behavior of the C_p in this striking region of temperature, we redetermined the measurements of the heat capacity in the whole range of temperature. It was found that the deviations of the comparable C_p values in both series of experiments which ranged from 0 to 0.05% are of negligible importance. Furthermore, C_p measurements were carried out in a wider range of temperature (333 to 960 K). The C_p value at 940, 950, and 960 K were measured to 26.20, 26.10, and 26.00 $JK^{-1} mol^{-1}$, respectively. This means that the C_p of liquid bismuth does not show the tendency to increase at high temperatures. Such behavior of the C_p is common to many metallic liquids. The decreasing heat capacity at high temperatures can be related to the pair correlation behavior. In the case of bismuth, the bonding changes into that of a mono-atomic gas with heat capacity decreasing toward $5R/2$ (20.35 $JK^{-1} mol^{-1}$). Taking this theory by Kincaid and Eyring[9] into consideration, the present C_p data at temperatures above 800 K seemed to be more reliable. It is also noteworthy that the existence of mono-atomic liquid bismuth was decided by other authors.[10] Also the present study could confirm the existence of mono-atomic liquid bismuth through X-ray diffraction study (to be published). It was observed that the neighbour distances of the straight chains in the structure decreased regularly with increasing temperature as follows: 850 K: 3.43 Å, 900 K: 3.60 Å, 950 K: 3.81Å. This means that the potential energy of the system decreased with increasing temperature to reach the value of zero for a mono-atomic gas. As a result of this the C_p must decrease with increasing temperature to reach a certain value at $E_{pot}=0$. On the basis of the above discussion, earlier reported[4,8] increasing heat capacity at temperatures above 800 K proved not to be reliable.

Thermodynamic properties of bismuth. The values of C_p, $H°(T)-H°$ (298.15 K), and $S°(T)-S°$ (298.15 K) are collected in Table 2 for selected temperatures. For the solid region up to 542.52 K, the results have been least squares fitted by a polynomial expression, with a standard deviation of 0.29% for a single measurement. Similarly fitted expression with a standard deviation of 0.28% has been derived for liquid bismuth in the region beginning from 646.98 K. The accuracy of the obtained thermodynamic functions values was estimated to 0.2%. The present results of the enthalpy and entropy vary between 1 and 3% from those reported by other workers[1,2] and are in reasonable agreement with the values obtained by some researchers.[3,4]

In Table 3 are presented the results of the fractional enthalpy of fusion determination on bismuth. The values of the enthalpy and entropy of fusion are found to be

$$\Delta H^{\circ}_{fus} = 11.360 \pm 0.14 \text{ kJ mol}^{-1},$$

$$\Delta S^{\circ}_{fus} = 20.86 \pm 0.03 \text{ J mol}^{-1}.$$

As reported by Westrum,[11] the pre-melting excess heat capacity can be calculated through the following equation:

Table 2. Thermodynamic Properties of Bismuth

T/K	C_p/$JK^{-1} mol^{-1}$	$H°(T)-H°$(298.15 K)	$S°(T)-S°$(298.15 K)
298.15	26.80[a]	0	0
333	27.15	(0.93)	(3.00)
383	27.40	2.28	6.84
433	27.90	3.62	10.33
483	28.40	5.09	13.66
533	28.90	6.53	15.83
544.54(s)	29.40	6.77	16.46
544.54(l)	30.00	17.90	36.87
583	29.69	19.04	38.90
633	29.23	20.50	41.43
683	28.60	21.77	43.10
733	28.12	23.01	45.06
783	27.70	24.41	46.37
833	27.38	25.67	48.10
883	26.90	26.87	49.39
923	26.50	27.79	50.37

a) Extrapolated value. The values in brackets depend on the extrapolated C_p value at 298.15 K.

Table 3. Fractional Enthalpy of Fusion Determinations on Bismuth

T/K	$(\Delta T/2)$/K	C_p/JK^{-1}mol^{-1}	Δt/min	$\sum\Delta H$/J mol^{-1}	T_{fin}/K	$\Delta H_{\mathrm{fus}}/\sum\Delta H$
Series 4, run 4—7						
542.255	0.547	29.35	14	0	543.102	
543.567	0.464	46.61	25	16.7	544.031	679
544.256	0.223	145.96	45	81.8	544.479	138.9
544.516	0.0366	1462.4	26	188.7	544.553	60.19
Series 5, run 2—11						
539.475	1.2375	29.28	46	0	540.712	
541.936	1.2235	30.5	50	30	543.159	4111
543.848	0.69	57.43	33	109	544.538	124.98
544.559	0.0215	5488	30	345	544.580	33.99
544.543	0.0045	161111	70	1795	544.588	6.279
544.553	0.0041	622857	79	6155	544.556	1.81
544.553	0.0002	9673333	117	9057	544.556	1.229
544.557	0.0005	1453000	39	10510	544.557	1.519
548.676	4.098	105.42	57	11374	552.774	1.000
560.255	7.43	29.91	52	11374	567.685	1.000
Sries 8, run 1—5						
533.443	0.723	28.92	91	0	534.889	
539.687	4.798	32.55	73	32.23	544.485	351.998
544.49	0.054	5042.1	26	539.5	544.544	21.099
546.181	1.587	3405	137	11346	547.768	1.000
550.235	2.454	29.94	28	11346	552.689	1.000
Sries 9, run 1—7						
541.934	2.697	1897	151	10234	544.541	1.110
544.542	0.0004	364429	35	10489	544.54	1.083
544.543	0.0005	253333	49	10717	544.543	1.060
544.544	0.001	134500	48	10986	544.545	1.034
544.565	0.009	13278	39	11225	544.574	1.012
545.101	0.516	130.8	147	11360	545.617	1.000
547.353	0.7465	29.95	27	11360	548.099	1.000

$\Delta H_{\mathrm{fus}}=11360\pm14$ J mol^{-1}; $\Delta S_{\mathrm{fus}}=20.86\pm0.03$ JK^{-1}mol^{-1}; $T_f=544.54$ K.

Table 4. Constant Volume Heat Capacity of Bismuth

T/K	C_p/JK^{-1}mol^{-1}	$(\alpha^2/x)vT$ / JK^{-1}mol^{-1}	C_v/JK^{-1}mol^{-1}
373	27.30	0.47	26.83
473	28.30	0.57	27.73
544.54(s)	29.40	0.70	28.70
544.54(l)	30.00	4.20	25.80
573	29.80	4.30	25.50
673	28.70	4.86	23.84
773	27.75	5.37	22.38
873	27.00	5.86	21.14

$$C_i(\mathrm{prem}) = x'RT_f^2/[(T_f - T_i)^2 - (\Delta T/2)^2],$$

where x' is the total mole fraction of impurities, T_i the temperature and ΔT the temperature interval to which C_i (prem) refers. It was found that the pre-melting excess heat capacity is caused by impurities of about 1×10^{-4} M (1 M=1 mol dm^{-3}). These liquid-soluble and solid-insoluble impurities in the sample constrain 0.1 of bismuth to melt 1.1 K below the ideal melting point. This was taken into consideration to include slight pre- and post-melting contributions above the extrapolated heat capacities of solid and liquid bismuth in the above given enthalpy and entropy of fusion values. These values differ 2% from those obtained in earlier studies. On the basis of fractional melting experiments (Table 3), about 96% of the bismuth sample fused at 544.54 K and zero pressure. The calibration of the platinum resistance thermometer used for the determination of the T_f occured as described before. The observed melting point of bismuth is in good agreement with that one reported earlier.[3)]

Constant volume heat capacity of bismuth. Table 4 represents the values of the heat capacity at constant volume for selected temperatures, calculated according to the following equation:

$$C_v = C_p - (\alpha^2/x)vT,$$

where α is the thermal coefficient, x the compressibility, and v the molar volume. The curve of the C_v against temperature is shown in Fig. 3.

The molar volume of solid and liquid bismuth was computed from the lattice data, while the study by Lucas[12)] provided the data for liquid bismuth and for the thermal coefficient values. The compressibility values were derived from many sources.[13—19)]

An excess over the harmonic value $3R$ is shown in the present estimate of the C_v of solid bismuth. This behavior is not common for all metals. In the case of bismuth, the expansion on solidification would cause a considerable dilation contribution in the C_v value due to lattice vibrations. On the other hand, the anharmonic contributions are small if compared with

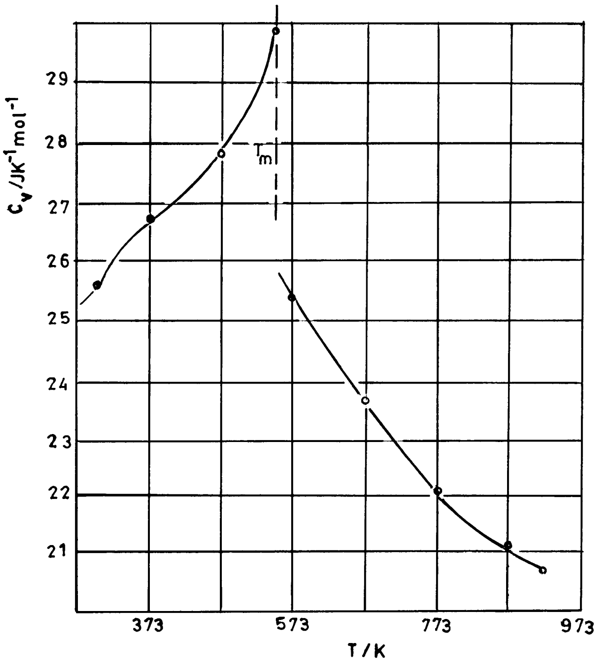

Fig. 3. Constant volume heat capacity of bismuth.

the dilation contributions observed in our study. This is due to the fact that the excess heat capacity from the disorder in the structure of the low-melting bismuth is small. Therefore, the excess over the harmonic value could be attributed to a beginning higher-order transformation. It is also noteworthy that the transformation to a new metallic phase was reported earlier.[10]

For liquid bismuth, the present C_v value is as low as 21.14 JK^{-1}mol^{-1} at 873 K, calculated on decreasing C_p value over the region 840 to 900 K as compared to a value of 22.6 JK^{-1}mol^{-1} at 900 K by Grønvold[4] who based his calculations on values of increasing C_p over the same region of temperature. The present value of C_v at 900 K seemed to be close to that limiting value given by Brillouin.[10] The observed drop in the C_v value over the region 540 to 900 K points to eventual radial distribution in this range of temperature.

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