

Heat Capacity and Thermodynamic Properties of Bismuth in the Range 300 to 950 K. Fusion Characteristics

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The heat capacity of nominally 99.9999 mass per cent pure bismuth has been studied by adiabatic shield calorimetry in the region 300 to 950 K. Values of enthalpy and entropy increments have been derived and tabulated for selected temperatures. The enthalpy and entropy of fusion at 544.60 K are (11131 ± 11) J mol⁻¹ and 20.44 ± 0.02 J K⁻¹ mol⁻¹, respectively. The premelting excess heat capacity corresponds to the presence of about 1×10^{-5} M of liquid-soluble/solid-insoluble impurities in the sample. The postmelting (or prefreezing) excess heat capacity is of comparable magnitude and is apparently not caused by impurities. The derived constant volume heat capacity shows excess over the harmonic value for solid bismuth which is attributed to a beginning higher-order transformation. For liquid bismuth C_V decreases from about 26 to 22.6 J K⁻¹ mol⁻¹ over the region 550 to 900 K.

1. INTRODUCTION

The heat capacity behavior of solid metals in the region just below melting has not yet been thoroughly explored and diverging opinions and results exist with regard to premelting. Thus, in the case of tin, which we have recently studied,¹ the premelting anomaly does not exceed the effect of 3×10^{-6} M of liquid-soluble/solid-insoluble impurities. The anomaly is thus of the order 300 times smaller than indicated by earlier results^{2,3} which accordingly had been incorrectly related to heterophase fluctuation premelting.

In order to gain further insight in the premelting phenomenon we have also been studying bismuth, another low-melting element with melting temperature suitably located for exploration under close to equilibrium conditions in our adiabatic shield type calorimeter.

In addition to the many heat capacity results for solid bismuth above room temperature, derived from enthalpy measurements over large temperature intervals,⁴⁻¹¹ data have also been obtained over smaller intervals with a semi-adiabatic technique by Carpenter and Harle.¹² They interpreted the rapidly increasing rise in heat capacity of solid bismuth near the melting point as due to the presence of about 2×10^{-4} M of impurity. According to Hultgren *et al.*¹³ both the results by Kubaschewski and Schrag¹¹ and a single measurement by Umino¹⁰ just below the melting point show an increase in heat capacity which might be preparatory to melting. The cited measurements were performed on samples of unstated or low purity, however, and more accurate measurements on high purity bismuth were therefore desirable.

Both Carpenter and Harle,¹² Bronson and MacHattie,¹⁴ Franzosini and Clusius¹⁵ and others have deduced constant volume heat capacities from their experimental results and concluded that the excess over the harmonic value could not be ascribed to conduction electron contributions, but rather to peculiarities of the lattice vibrations.

The heat capacity determinations on liquid bismuth have been largely diverging.^{7,8,10,16} Smoothly decreasing heat capacity values in the molten region were first observed by Carpenter and Harle,¹² and more recently by Bell and Hultgren¹⁷ in the range 545 to 800 K. Preliminary measurements by Brooks¹⁸ showed a similar decrease, but the values were 2 to 3 % higher.

The absence of a pronounced decrease in heat capacity just after melting was seen by Bell

and Hultgren¹⁷ as a disproof of the usual interpretation of the diffraction patterns of liquid bismuth in terms of aggregates of atoms with solid-like structure. Such aggregates should finish breaking up only a few kelvin above the melting point, and the process should thus give much higher heat capacity values in the vicinity of fusion than those observed. The available data seemed more in accord with the theory by Kincaid and Eyring¹⁸ in which the bonding is considered to change into that of a monoatomic gas, with C_p decreasing toward $5R/2$ at high temperatures. Decreasing heat capacities above the melting temperature are common to many metallic liquids, and in a statistical mechanical treatment Chapman²⁰ showed that this can be related to the pair correlation function behavior. The increase in C_p on further rise in temperature was ascribed mainly to the increasing dilational heat capacity.

The early enthalpy of fusion determinations on bismuth^{7-11,21-23} offered a wide choice between 8.95 and 12.3 kJ mol⁻¹. The three most recent sets of determinations³⁰⁻³² have narrowed the band to 11.3 ± 0.2 kJ mol⁻¹. This is still discomfotingly wide compared to the presently attainable accuracy, and the results are only partly overlapping within their stated limits from about 0.5 to 1.0 %. Thus, an improved determination of the enthalpy of fusion of bismuth seemed of interest.

2. EXPERIMENTAL

Sample. The zone-refined 99.9999 mass per cent pure bismuth was obtained from Koch-Light Laboratories, Ltd. England. Typical analyses of the impurities present were (in ppm by mass): Ag(0.1), Ca(0.1), Mg(0.1), Pb(0.1), Si(0.1). Of the crushed 12 mm diameter rod 261.124 g was sealed in the calorimetric container together with about 1 m of 3 mm diameter silica cord. The silica cord was coiled spirally in the sample space and its purpose was to prevent breakage of the container on fusion and thermal cycling of the sample.

A mass spectrometric analysis was carried out after the completion of the measurements. It showed the presence of the following impurities (in ppm by atoms): C(4), N(0.6), O(16), F(0.4), Na(17), Mg(1), Al(0.6), Si(3), P(0.1), S(1), Cl(6), K(7), Ca(5), Ti(≤ 0.1), Cr(≤ 0.1), Fe(5), Cu(7), Zn(0.4), Ga(0.7), As(≤ 0.1), Y(≤ 0.1), Ag(≤ 0.2), W(≤ 0.2).

Calorimetric technique. The calorimetric apparatus and measurement technique have been

described in detail³³ along with results obtained for the heat capacity of a standard sample of α -Al₂O₃. The calorimeter is operated with adiabatic shields and intermittent energy inputs with temperature equilibration between each input. The 50 cm³ sample container of silica glass has a well for the heater and platinum resistance thermometer, axially located in the cylindrical silver calorimeter. The calorimeter-sample assembly is suspended inside a double-walled silver shield system with enclosed heaters. Outside the shields is a heated guard system, also of silver. The whole assembly is placed in a vertical tube furnace.

The temperature differences between corresponding parts of calorimeter and shield are measured by means of Pt-to-(Pt + 10 mass per cent Rh)thermopiles. The amplified signals are recorded and also used for automatic control of the shield heaters to maintain quasi-adiabatic conditions during input and drift periods. The temperature of the guard body is kept automatically 0.4 K below that of the shield, while the temperature of the furnace core is kept 10 K lower to secure satisfactory operation of the control units.

Heat-capacity measurements of the empty calorimeter were carried out in a separate series of experiments. They represented from 67 to 72 per cent of the total outside the fusion region. Small corrections were applied for differences in mass of the empty and full containers and for "zero" drift of the calorimeter. The temperature excursions of the shields from the calorimeter temperature were of negligible importance. The thermometer resistance was measured with a Mueller bridge (Leeds & Northrup Model 8072), automated locally with stepping motors and a gated null-detector, operated by a computer (Hewlett-Packard Model 2114 B) in the more recent series of experiments. The derived temperatures are judged to correspond with the IPTS-68 to within 0.01 at 500 K and 0.1 K at 1000 K. Precision is considerably better, and the temperature increments are measured to 0.0003 K. The computer-operated energy inputs from a constant-current supply (John Fluke Current Calibrator Model 382 A in most of the experiments) were measured with an integrating voltmeter (Hewlett-Packard Model 2401 C). The accuracy of the energy inputs is about 0.025 %. Both Mueller-bridge and (potential) \times (time) readings are automatically transferred to punch cards (IBM 545) together with time and other relevant information and then processed by a digital computer.

3. RESULTS AND DISCUSSION

Thermodynamic properties. Results of the determinations of the molar heat capacity of bismuth are presented in Table I in chronological order. The approximate temperature

Table 1. Heat capacity of bismuth. $M(\text{Bi}) = 208.98 \text{ g mol}^{-1}$.

$\frac{\langle T \rangle}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\langle T \rangle}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{ mol}^{-1}}$
Series I		Series VIII	
302.72	26.04	529.93	28.89
317.55	26.08	539.69	32.56
332.38	26.33	544.55	4424.1
347.11	26.52	546.19	3373.9
		550.25	29.89
Series II		555.23	29.80
360.48	26.59	560.22	29.96
375.29	26.77	565.23	29.88
390.06	27.04	570.25	29.80
404.82	27.19	575.38	29.75
419.59	27.38	580.72	29.71
434.37	27.52		
449.16	27.70	Series IX	
464.00	27.85	541.91	1887.9
478.88	28.12	544.60	301 000
		544.60	219 000
Series III		544.60	96 300
489.89	28.40	544.62	12 610
504.76	28.40	545.14	165.30
		547.41	29.96
Series IV		549.92	29.96
516.28	28.88	Series X	
521.21	28.94	311.44	26.11
527.79	28.99	320.44	26.08
534.37	29.03	328.23	26.14
538.76	29.17	337.25	26.40
540.93	29.36	346.25	26.38
542.57	29.68		
543.57	46.94	Series XI	
544.26	170.22	616.87	29.45
544.52	1367.0	630.89	29.38
		644.98	29.47
Series V		659.13	29.37
534.56	28.94	673.38	29.21
537.03	29.02	687.73	29.04
539.49	29.29	702.17	28.90
541.94	30.51	716.72	28.69
543.85	91.85	731.36	28.72
544.57	5633	746.11	28.56
544.59	170 400		
544.60	574 000	Series XII	
544.60	9 700 000	756.98	28.42
544.60	1 320 000	771.95	28.22
548.70	109.13	787.01	28.17
560.25	29.80	802.16	28.17
		817.38	28.30
Series VI		832.67	28.35
591.35	29.54	847.99	28.41
606.51	29.60	863.34	28.55
621.75	29.38	878.78	28.57
637.10	29.17	894.35	28.38
		909.99	28.58
Series VII		925.75	28.65
457.68	27.62	941.66	28.67
472.53	27.98	950.08	28.88
487.41	28.36		
502.32	28.50		
517.27	28.75		

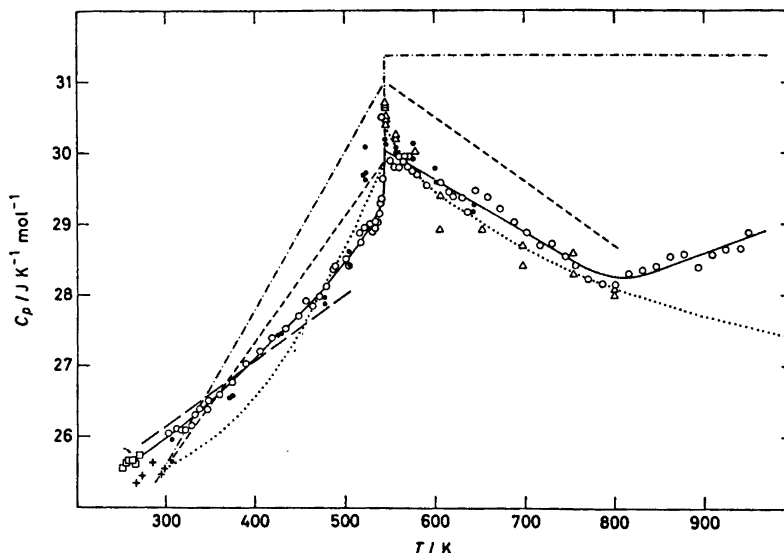


Fig. 1. Heat capacity of bismuth. —○— represents present results, — — — assessment by Kelley,³⁴ ··· assessment by Hultgren *et al.*³⁵, □ results by Franzosini and Clusius,¹⁵ + results by Anderson,³⁶ ● results by Carpenter and Harle,¹² — results by Bronson and MacHattie,¹⁴ △ results by Bell and Hultgren,¹⁷ - - - results by Brooks.¹⁸

increments in the determinations can usually be inferred from the adjacent mean temperatures in the table.

The curve of heat capacity against temperature is shown in Fig. 1 together with the assessed values by Kelley³⁴ and Hultgren *et al.*³⁵ and some of the earlier heat capacity determinations. The spread between the assessments is indicative of the divergencies in the earlier multitude of data which will not be discussed in detail here. In the lower temperature region the present results join well with those by Franzosini and Clusius,¹⁵ which are about 1 % higher than those by Anderson³⁶ in the region 250 to 280 K and 5 % lower than the result by Mikryukov and Tyapunina³⁷ at 293 K. Excellent agreement with the results by Bronson and MacHattie¹⁴ was obtained over the common region (300 to 400 K), while the observations by Carpenter and Harle¹² are slightly lower than the present below 450 K and rise considerably above as the melting point is approached. The excessive rise was ascribed to impurity premelting by the authors. Recent measurements by Brooks¹⁸ on solid and liquid bismuth coincide with the present ones around 350 K, but diverge negatively below and

positively above. At 500 K they are about 2 % higher and likewise at 800 K for liquid bismuth. The results were considered as preliminary, however, due to the larger than usual spread. The results by Carpenter and Harle¹² for liquid bismuth are practically equal to the present ones over the common region (550 to 650 K), while those by Bell and Hultgren¹⁷ are about 0.5 % lower in the region 600 to 800 K.

A steady increase from 29 to 36 J K⁻¹ mol⁻¹ over the region 550 to 1200 K was claimed by Wüst *et al.*⁷ while almost constant values (31 to 33 J K⁻¹ mol⁻¹) over the region 550 to 1000 K were reported by Iitaka,⁸ Umino,¹⁰ and Förster and Tschentke.¹⁶

Results of the fractional enthalpy of fusion determinations are found in Table 2. Slight pre- and postmelting contributions above the smoothly extrapolated heat capacities of the solid and liquid phases are included in the enthalpy and entropy of fusion values:

$$\Delta H_f = (11131 \pm 11) \text{ J mol}^{-1}, \quad \Delta S_f = (20.44 \pm 0.02) \text{ J K}^{-1} \text{ mol}^{-1}$$

The observed temperature of fusion for about 95 % of the sample fused is at zero pressure $T_f = (544.60 \pm 0.01) \text{ K}$ from calibrations of the

Table 2. Fractional enthalpy of fusion determinations on bismuth. $M(\text{Bi}) = 208.98 \text{ g mol}^{-1}$.

$\langle T \rangle$ K	C_p $\text{J K}^{-1} \text{ mol}^{-1}$	ΔT K	Δt min	$\sum \Delta H$ J mol^{-1}	T_{fin} K	$\frac{1}{F}$
Series IV, run 7–10						
542.480	29.68	1.097	15	0	543.108	
543.573	46.94	0.9286	26	16.3	544.037	683
544.261	170.22	0.4476	44	79.3	544.485	140.4
544.522	1 367.0	0.0742	27	178.5	544.559	62.35
Series V, run 3–12						
539.480	29.29	2.4746	45	0	540.718	
541.942	30.51	2.4465	49	2.7	543.165	4 126
543.855	91.85	1.3790	30	88.7	544.544	125.6
544.565	5 633	0.0422	29	325.2	544.586	34.25
544.590	170 400	0.0085	66	1 773	544.594	6.283
544.598	574 000	0.0076	82	6 134	544.602	1.816
544.602	9 700 000	0.0003	120	9 038	544.602	1.232
544.602	1 320 000	0.0011	44	10 490	544.603	1.062
548.701	109.13	8.1972	60	11 139	552.800	1.000
560.245	29.80	14.891	48	11 139	567.691	1.000
Series VIII, run 1–5						
529.930	28.89	9.9340	85	0	534.895	
539.693	32.56	9.5958	68	31.5	544.491	353.1
544.545	4 424.1	0.1075	21	503.9	544.599 ^a	22.07
546.186	3 373.9	3.1751	158	11 123	547.774	1.000
550.252	29.89	4.9069	30	11 123	552.735	1.000
Series IX, run 1–7						
541.905	1 887.9	5.3956	136	10 028	544.601	1.110
544.602	301 000	0.0008	38	10 269	544.602	1.084
544.603	219 000	0.0011	52	10 510	544.603	1.059
544.604	96 300	0.0025	53	10 751	544.605	1.035
544.615	12 610	0.0191	46	10 991	544.624	1.013
545.141	165.30	1.0336	153	11 131	545.657	1.000
547.413	29.96	2.5021	34	11 131	548.159	1.000
$\Delta H_f = (11131 \pm 11) \text{ J mol}^{-1}$; $\Delta S_f = (20.44 \pm 0.02) \text{ J K}^{-1} \text{ mol}^{-1}$; $T_f = 544.60 \text{ K}$.						

^a No wait for complete equilibration.

platinum resistance thermometer at the triple point of water and the melting points of tin and zinc on the International Practical Temperature Scale of 1968.³⁸ The fusion temperature is in good agreement with the results by McLaren and Murdock³⁹ [$T_f = 544.525 \text{ K}$ (ITPS 48)] allowing for change to ITPS 68 (+0.067 K) and reduction to zero pressure (+0.004 K).

Earlier determinations of the enthalpy of fusion of bismuth are collected in Table 3. The agreement between the present value and that by Castanet *et al.*³¹ is very good. Among the earlier values none is closer than that by

Person²² of 1848; his determination of the enthalpy of fusion of tin was also remarkably good.¹ The estimate by Kelley²⁴ (10.88 kJ mol⁻¹) and the most recent one by Hultgren *et al.*³⁵ (11.30 kJ mol⁻¹) are 2.3 % lower, and 1.5 % higher than the present result, respectively.

Values of C_p , [$H^\circ(T) - H^\circ(298.15 \text{ K})$], and [$S^\circ(T) - S^\circ(298.15 \text{ K})$] are listed in Table 4 for selected temperatures. The results for solid bismuth up to 542.60 K have been least squares fitted by a polynomial expression, with a standard deviation of 0.32 % for a single

Table 3. Enthalpy of fusion determinations on bismuth.

Authors	Year	$\Delta H_f/\text{kJ mol}^{-1}$
Person ²¹	1846	10.8
Person ²²	1848	11.05
Mazzotto ²³	1886	10.84
Roos ²⁴	1916	10.9
Wüst <i>et al.</i> ⁷	1918	8.95
Iitaka ⁸	1919	10.70
Awbery and Griffiths ⁹	1926	11.37
Umino ¹⁰	1926	12.33
Kubaschewski and Schrag ¹¹	1940	11.00
Cavallaro ²⁵	1944	11.77
Nagasaki and Fujita ²⁶	1952	11.92
Oelsen <i>et al.</i> ²⁶	1955	11.38
Oelsen ²⁷	1957	{ 11.21 11.46
Schürmann and Träger ²⁸	1961	11.42
Chiotti <i>et al.</i> ³⁰	1966	11.527 ± 0.075
Castanet <i>et al.</i> ³¹	1968	11.125 ± 0.063
Malaspina <i>et al.</i> ³²	1971	11.247 ± 0.113
Grønvold	1975	11.131 ± 0.011

measurement. For the liquid region from 547.44 K a similarly fitted expression resulted in a standard deviation of 0.31 %. The accuracy of the integrated thermodynamic function values is estimated to be 0.3 % and of the fusion properties 0.1 %. The present enthalpy values are 0.94 % higher than the assessed values by Hultgren *et al.*³⁶ for solid bismuth at the melting temperature, 0.57 % lower for liquid bismuth at the same temperature, and only 0.10 % lower at 900 K. The older assessment by Kelley ³⁴ differs considerably more, from +0.8 to +2.7 % in the enthalpy of solid bismuth, and from -0.4 to +2.8 % for liquid bismuth. It reflects the large inaccuracy in many of the earlier determinations.

Pre- and postmelting. The heat capacity of solid bismuth shows a considerable upwards trend already around 500 K, but the measurement at 543.57 K (Ser. IV, run 8) is the first which deviates markedly from the polynomial curve which reaches 29.49 J K⁻¹ mol⁻¹ at the temperature of fusion. The excess above this curve is provisionally ascribed to premelting. The observed heat capacity values in the fusion region—uncorrected for curvature—are shown in Fig. 2 on a semi-logarithmic scale. They compare surprisingly well with the excess heat capacity calculated for 1 × 10⁻⁵ M of liquid-

soluble/solid-insoluble impurities according to the equation:⁴⁰

$$C_i(\text{prem}) = x_2^+ RT_f^2 / [(T_f - T_i)^2 - (\Delta T/2)^2]$$

Here x_2^+ is the total mol fraction of impurities, T_i the temperature, and ΔT the temperature interval to which $C(\text{prem})$ refers.

For comparison the results of Carpenter and Harle ¹² in this region are also shown in Fig. 2. They indicate that the presence of 3 × 10⁻⁴ M of liquid-soluble/solid-insoluble impurities might explain the high heat capacities observed. Even such a moderate amount of impurity is seen to have an enormous influence on the observed heat capacities as melting is approached, and causes 2 % of the bismuth to be in the molten state 3 K below the ideal fusion temperature. In the present case only 0.1 % of the bismuth is molten 1 K below the ideal fusion temperature.

According to the mass spectrometric analysis several elements are present in the sample in amounts sufficient to cause the observed excess heat capacity below the fusion temperature provided they are less soluble in solid bismuth than in liquid. This is no doubt the case with oxygen, which presumably is present in form of oxides in the grain boundaries of solid bismuth. Based upon the results by Griffith and Mallett ⁴¹

Table 4. Thermodynamic properties of bismuth. $M(\text{Bi}) = 208.92 \text{ g mol}^{-1}$.

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{H^\circ(T) - H^\circ(298.15 \text{ K})}{\text{J mol}^{-1}}$	$\frac{S^\circ(T) - S^\circ(298.15 \text{ K})}{\text{J K}^{-1} \text{ mol}^{-1}}$
298.15	25.90	0	0
300	25.92	47.9	0.160
320	26.15	568.9	1.840
340	26.39	1094	3.431
360	26.63	1624	4.947
380	26.86	2159	6.393
400	27.09	2698	7.777
420	27.33	3242	9.104
440	27.60	3792	10.381
460	27.89	4346	11.614
480	28.18	4907	12.807
500	28.47	5474	13.964
520	28.77	6046	15.085
540	29.30	6626	16.180
544.60(s)	(29.49)	6761	16.429
544.60(l)	(30.06)	17892	36.867
560	29.83	18353	37.702
580	29.67	18947	38.745
600	29.58	19540	39.750
620	29.50	20131	40.718
640	29.39	20720	41.653
660	29.24	21306	42.555
680	29.07	21889	43.426
700	28.88	22469	44.266
720	28.70	23045	45.077
740	28.54	23617	45.861
760	28.41	24186	46.620
780	28.32	24754	47.357
800	28.28	25320	48.074
820	28.28	25885	48.772
840	28.32	26451	49.454
860	28.39	27018	50.121
880	28.47	27587	50.774
900	28.56	28157	51.415
920	28.65	28729	52.044
940	28.74	29303	52.661

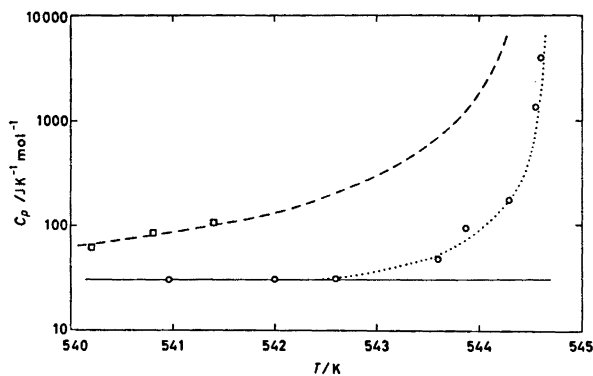


Fig. 2. Premelting heat capacity of bismuth. \circ represents present results, \square results by Carpenter and Harle,¹² \cdots and $- - -$ calculated values for $1 \times 10^{-5} \text{ M}$ and $3 \times 10^{-4} \text{ M}$ of liquid-soluble/solid-insoluble impurities.

in the region 400 to 750 °C the oxygen equilibrium concentration is only 3×10^{-6} M in liquid at the temperature of fusion. The observed oxygen content is therefore mainly assumed to be due to oxides of sodium, potassium, calcium, iron, and copper. If part of these oxides go into solution, sufficient impurities are at hand. In the case of sodium, the bismuth-rich binary eutectic temperature is 491 K,⁴² and of potassium it is 538 K.⁴³ These two elements are thus suspected as responsible for the premelting behavior. While iron is known for its insolubility in solid and liquid bismuth, both calcium and copper show binary eutectics close to pure bismuth at 543 K.⁴³ Thus, the premelting seems to have been caused by the solid-insoluble/liquid-soluble impurities present in the sample, and the study of even purer samples and also of samples with addition of suitably controlled impurities is desirable in order that a more definite answer to the question be provided.

Solid-soluble/liquid-soluble impurities will in general cause interval melting. Under equilibrium conditions the heat capacity will then rise rather sharply, but not become infinite, and fall rapidly again at a higher temperature. From Series V it appears that 89 % of the enthalpy of fusion occurs within 0.017 K, but again it is not possible to relate this interval unambiguously to the impurities present, even though calcium and copper are likely candidates. The width is evidently not caused by temperature gradients in the calorimeter, since 26 % of the enthalpy of fusion falls within a

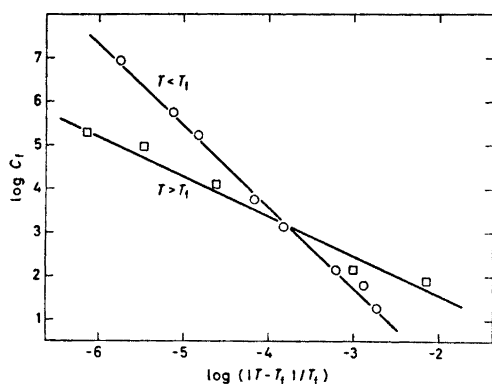


Fig. 3. Log-log plot of estimated pre- and postmelting heat capacity of bismuth against $(T - T_f)/T_f$ where T_f is the fusion temperature. Circles for $T < T_f$, squares for $T > T_f$.

temperature interval of 0.0003 K (Series V, run 9).

As can be seen from the runs of Series V and IX, the postmelting heat capacity is of considerable magnitude. About 3.5 % of the fusion enthalpy remains to be acquired 0.002 K above the temperature at which the heat capacity starts to decrease, and 1.3 % still remains at a temperature 0.021 K higher.

In order to compare the pre- and postmelting behavior of the bismuth sample the logarithm of the excess heat capacity is plotted against the logarithm of $(|T - T_f|/T_f)$, see Fig. 3. A constant slope indicates that the results can be described in terms of a critical index α according to the equation:

$$C_f = a(|T - T_f|/T_f)^{-\alpha} + b$$

Below the temperature of the maximum – taken as the fusion temperature – the critical exponent $\alpha \approx 1.9$, or close to the value expected for a liquid-soluble/solid-insoluble impurity. Above the maximum $\alpha \approx 0.6$. This change is not unexpected, since the behavior above the liquidus line is principally different from that in the solidus/liquidus region. The presence of an exponent value of the same magnitude as for other critical phenomena is therefore pleasing. The problem of delayed equilibration, especially with regard to solution of impurities and its influence on the derived critical exponent, has not yet been explored in detail.

Heat capacity of bismuth at constant volume. The molar heat capacity of bismuth at constant volume can be derived from that at constant pressure by the thermodynamic relationship:

$$C_V = C_p - (\alpha^2/\kappa)VT$$

where α is the volume expansion coefficient, κ the isothermal compressibility and V the molar volume.

The thermal expansivity of solid bismuth has been measured in the low-temperature region and up to temperatures approaching the melting point by several authors.⁴³ The discontinuities reported in the range 250 to 350 K by Jay and Jacobs⁴⁴ and Goetz⁴⁵ were not supported by more recent work of Cave and Holroyd⁴⁶ and others. Over the region 150 to 540 K the expansion coefficient of the hexagonal a -axis increases from 11.5 to 11.8×10^{-6} K⁻¹, and of the

c-axis from 17.3 to $17.6 \times 10^{-6} \text{ K}^{-1}$. These results agree with those by White⁴⁷ at 283 K ($\alpha_a = 11.63 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 17.05 \times 10^{-6} \text{ K}^{-1}$) and are taken as representative. The molar volume of the solid is calculated from the lattice constant data, while that for liquid bismuth and also the expansivity of the liquid, are taken from the extensive investigation by Lucas.⁴⁸

The isothermal compressibility (κ_T) is $2.9 \times 10^{-12} \text{ Pa}^{-1}$ at room temperature.⁴³ Its value for solid bismuth at the fusion temperature ($\kappa_T = 3.7 \times 10^{-12} \text{ Pa}^{-1}$) is derived from the value for liquid bismuth at the same temperature ($4.25 \times 10^{-12} \text{ Pa}^{-1}$ by Kleppa⁴⁹ and $4.38 \times 10^{-12} \text{ Pa}^{-1}$ by Filippov *et al.*⁵⁰) and the difference in compressibility between liquid and solid bismuth ($\kappa_T = 0.58 \times 10^{-12} \text{ Pa}^{-1}$ according to Bridgman.⁵¹ From the increase in the adiabatic compressibility (κ_S) of liquid bismuth with temperature, as derived by Filippov *et al.*⁵⁰ from ultrasonic velocity measurements, the isothermal compressibility ($\kappa_T = \kappa_S + \alpha^2 VT/C_B$) rises to $5.2 \times 10^{-12} \text{ Pa}^{-1}$ at 900 K .

The derived dilation contribution and heat capacity at constant volume are given in Table 5 for selected temperatures. The unusually small dilation contribution for solid bismuth compared to the liquid is mainly caused by the small thermal expansivity of the solid. This results in a notable rise in the constant volume heat capacity of solid bismuth above the classical limit $3R$ or $24.76 \text{ J K}^{-1} \text{ mol}^{-1}$, see Fig. 4. Such a large increase in C_V over the harmonic value in the solid state does not seem to be a general prerequisite to fusion, and was not observed in our related study of the fusion of tin.¹ For

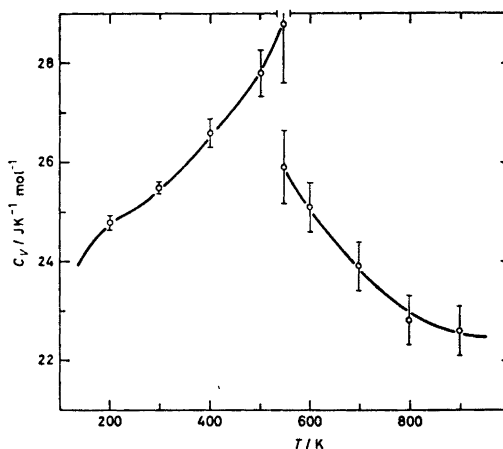


Fig. 4. Estimated constant volume heat capacity of solid and liquid bismuth.

liquid bismuth a pronounced decrease in C_V to $22.6 \text{ J K}^{-1} \text{ mol}^{-1}$ at 900 K is noted.

Earlier authors^{12,14,15} who have deduced constant volume heat capacities of solid bismuth, have generally attributed the observed excess over the harmonic value to peculiarities of the lattice vibrations. There are presently no firm indications, however, that the excess is due to further anharmonic contributions. In view of the low temperature of fusion, the excess heat capacity from structural disorder in the solid is presumably small. It seems therefore more tempting to attribute the excess heat capacity mainly to a beginning higher-order transformation into a more metallic phase with a smaller molar volume. Thereby the small expansivity

Table 5. Tentative resolution of the heat capacity of bismuth into components. $M(\text{Bi}) = 208.98 \text{ g mol}^{-1}$.

T K	$C_p(\text{obs})$ $\text{J K}^{-1} \text{ mol}^{-1}$	$C(\text{d})$ $\text{J K}^{-1} \text{ mol}^{-1}$	C_V $\text{J K}^{-1} \text{ mol}^{-1}$
200	(25.0)	0.2	(24.8)
300	25.92	0.4	25.5
400	27.09	0.5	26.6
500	28.47	0.6 ⁵	27.8
544.60(s)	(29.5)	0.7	(28.8)
544.60(l)	(30.1)	4.2	(25.9)
600	29.58	4.5	25.1
700	28.88	5.0	23.9
800	28.28	5.5	22.8
900	28.56	6.0	22.6

might be accounted for, and the possible presence of such a phase finds further support in the actual existence of four allotropic modifications of solid bismuth⁴³ at pressures below 40 000 atm.

Inferences about the structure of liquid bismuth have been derived from many diffraction studies.⁴³ According to Danilova *et al.*⁴³ the structure is close-packed with some face-centered character. The same conclusion was arrived at by Sharrah and Smith.⁵³ The face-centered component is reported to decrease with increasing temperature by Richter *et al.*⁵⁴ Further X-ray diffraction evidence for the existence of two types of structures in liquid bismuth have recently been presented by Richter.⁵⁵ The spherical close-packing (structure I) and the other structure (II) both show up as straight chains with shortest neighbour distances of 3.17 and 3.35 Å, respectively. (These results have not been correlated with the previously reported changes in structure with temperature and thermal data.)

The statistical theory of fluids which allows for high mobility of the short-range ordered particles and is utilizing the radial distribution function behavior^{50,56,57} seems appropriate for deriving the thermal properties. Very precise diffraction data are required, however, in order that the radial distribution function might show further structural effects than those associated with the repulsive part of the interatomic potential. The considerable drop in C_V for liquid bismuth signals important changes in the radial distribution over the region 545 to 800 K which might ultimately be detected.

The heat capacity at constant volume at 900 K is far above the value $3R/2$, which supposedly is the high-temperature limit in the usual statistical approach, and is equally far below the values derived in the collective moment approach by Eisenschitz and Wilford⁵⁸ and by Bratby *et al.*⁵⁹ An intermediate limiting value for $C_V = 2R$ was derived by Brillouin⁶⁰ who assumed that the two transverse wave motions for a monoatomic liquid degenerate into a whirl system for which there is no potential energy. The estimated C_V for liquid bismuth at 900 K is closest to the latter value.

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