JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 74A, No. 1, January–February 1970

Temperature Coefficient of the Bismuth I–II Transition Pressure

James C. Houck

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

(September 24, 1969)

A rotatable piston in a supported cylinder was used to determine the temperature coefficient of the bismuth I–II transition pressure for the temperature range of 20 to 50 °C. The temperature coefficient of the transition pressure is −40.6 bar/°C.

Key words: Bismuth transition; calibration point; high pressure; pressure measurement; temperature coefficient.

1. Introduction

The importance of the Bi I–II transition, also called the α, β transition, as a fixed point on the pressure scale is well established and warrants continuing efforts to improve the determination of the pressure at which it occurs. P. W. Bridgman [1, 2][1] reported the pressures for the Bi I–II transition over the temperature range −50 to 183 °C. His values show a constant temperature coefficient of −50 bar/°C for the Bi I–II transition over the range of −50 to 150 °C. A later determination by Bridgman [3] for use in calibration of a manganin gage gave a temperature coefficient of −45 bar/°C between 30 and 75 °C. V. P. Butuzov and Ye. G. Ponyatovsky [4, 5] give a temperature coefficient of −38 bar/°C from 65.5 to 125 °C, −56 bar/°C from 125 to 163.5 °C, and −96 bar/°C from 163.5 to 184 °C.

P. L. M. Heydemann [6, 7] ascribes a best value for the bismuth I–II transition pressure of 25499 bar [2] with an uncertainty of 60 bar at 25 °C. In his work a value of the temperature coefficient of the transition pressure of −54.5 bar/°C, chosen as an average of various values computed from the literature, was used but not presented as a correction for use of the transition at other temperatures.

It was desired to obtain a value of the temperature coefficient of the transition pressure both to present as an aid in the use of the transition as a reference value in pressure calibrations and for our use in the future redetermination of the bismuth transition pressure in a planned improved version of the dead-weight piston gage. Because of the difficulties and expense encountered in operation of a dead-weight piston gage to these pressures a rotatable piston and supported cylinder device which is readily operated at these pressures was used for these measurements.

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] 1 bar = 10^5 N/m^2

2. Rotatable Piston and Supported Cylinder Apparatus

The rotatable piston and supported cylinder device used for these measurements has been described previously [8]. It had been used several years ago for the determination of transition pressures of solid to solid transitions in bismuth and thallium similarly to the method of Kennedy and LaMori [9]. The pressure then obtained for the bismuth I–II transition at 25 °C from a mean value of transition in both directions was 25212 bar with a standard deviation of 18 bar, a half-friction of 15 bar, and an estimated systematic uncertainty of 100 bar. These results agree with the value of 25154 bar extrapolated from Bridgman [3], but they disagree with the value of 25405 bar reported by Kennedy and LaMori [9] and with the value of 25499 bar established by Heydemann [6, 7] in the dead-weight piston gage by more than the combined uncertainties. However for the purpose of determining the temperature coefficient of the transition pressure the uncertainties due to the ratio of the area of the ram to that of the piston, the ratio of the effective area of the piston and cylinder at elevated pressure to the measured area of the cylinder, the location of the transition within the half-friction band, and corrections to the bourdon tube gage are greatly reduced by performing as nearly identical experiments as possible at the different temperatures.

3. Determination of the Temperature Coefficient

Bismuth with a purity of 99.999 percent was obtained from the American Smelting and Refining Company. It was cast in vacuum and machined. The finished sample was 0.882 cm long, the edges were bevelled at 45° to receive steel anti-extrusion rings, and the diameter was a close fit to the cylinder which was 1.263 cm I.D. The short 1 cm cylinders were used for these experiments.

The transition was detected by observing the volume change accompanying the transition. The volume of the sample was indirectly observed by following the piston advance with dial indicators mounted to bear on arms fixed to one of the intermediate pieces between the 15.25 cm diameter low pressure ram and the 1.263 cm high pressure piston. The motion of the dial gage indicators is due to the sum of the compression of the bismuth sample, the compression of the parts of the piston stack between the arms and the sample end of the high pressure piston, the cylinder expansion, and the distortion of a bridge plate. The method of determining the transition pressures is shown in figure 1. One psi oil pressure on the ram causes approximately 10 bar pressure on the sample. With all of the bismuth in phase I the pressure was increased to point A approximately 500 bar below the transition pressure. After a 10 min interval the piston stack was rotated approximately 2° and then rotated back 2° to its original position. This reduced the friction and permitted the piston to advance causing the pressure on the ram to decrease to point B. The ram pressure was then increased to 20 psi above the pressure at A. This was followed by a similar interval, rotation and pressure increase routine. Then the pressure increments were reduced to 10 psi. These routines were continued until at point D it was observed that the pressure decrease due to the piston advance on rotation was greater than the preceding ones. The pressure was then increased to E, equaling that at C rather than exceeding it. This was followed by a series of five 10-min intervals and piston rotations which ended at point F. The pressure was increased to point G and six more 10-min intervals and piston rotations established point H. The average of the pressure at points F and H, suitably corrected, was taken as one determination of the bismuth I to II transition pressure. At this point approximately 2 percent of the bismuth had been transformed to phase II. It is important that the phase conversion occurs in the immediate vicinity of the piston so that friction can be effectively reduced. An additional 2 percent (point J) was transformed by increasing the pressure to point I and then relieving friction by waiting and rotating the piston twice. Pressure was then released by valving to point K. A series of 10-min intervals, rotations and pressure releases then led to point L. From previous experience and from the details of the trace shown in figure 1 we expected that at this point the piston had retracted enough, so that after further relief of friction by rotation bismuth would convert from II to I. As the bismuth sample converted, the piston was pushed out and the ram pressure was further increased. A series of five 10-min intervals and rotations led to point M. A repetition through point N to point O verified point M. The average of the pressure at points M and O, suitably corrected, was taken as one determination of the bismuth II to I transition.

The equilibrium transition pressure is taken as the mean of the two pressures obtained for different directions of the transition. For a discussion of the characterization of the bismuth I–II transition see R. J. Zeto et al. [10].

The temperatures 24.8 °C and above were obtained by use of an air bath. All the equipment including the

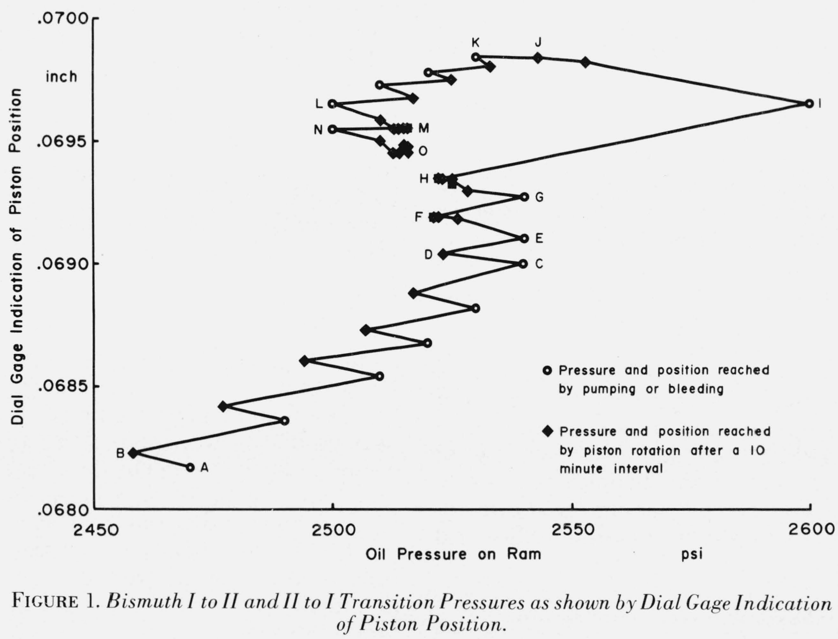

FIGURE 1. *Bismuth I to II and II to I Transition Pressures as shown by Dial Gage Indication of Piston Position.*

clamping press which held the low pressure piston and cylinder assembly with bridge plates and the high pressure piston and cylinder was in the bath. A long lever for the rotation of the piston stack was brought out through a cloth covered slit. Thermometers and the dial gage were read through a plastic window. Two to four days were required for the equipment to reach equilibrium. The temperatures 22.5 °C and below were obtained through control of the room temperature.

Table 1 shows the transition pressures for both directions, the temperatures, the average pressures, the difference between the pressures, and the average temperature. The transition pressures were calculated from the observed ram pressures with corrections for ram weight, difference in height, gage correction, ratio of area of low pressure cylinder to high pressure cylinder, and cylinder expansions due to pressure and temperature. Figure 2 shows the transition pressures for both directions of the transition plotted versus temperature. The straight line is drawn to a least squares fit of the average pressures.

Omnitab POLYFIT least squares solutions for first degree equations were obtained for the set of pressures and temperatures for Bi I to II, for the set of pressures for Bi II to I, and for the set of average pressures of each pair of determinations. The fits were obtained from data taken over the temperature range 20 to 50 °C. For convenient use of the statistics available from the POLYFIT program the straight line was fitted to:

$$P_T = P_{25°} + (T - 25\ °C) dP/dT$$

TABLE 1. *Temperature dependence of the transition pressure of the bismuth I–II transition*

P_{I-II}	T	P_{II-I}	T	P_{av}	$P_{I-II} - P_{II-I}$	T
Bar	*°C*	*Bar*	*°C*	*Bar*	*Bar*	*°C*
25366.	20.8	25276.	20.8	25321.	90	20.8
25356.	20.9	25256.	21.0	25306.	100	20.95
25336.	21.0	25216.	21.1	25276.	120	21.05
25256.	21.9	25187.	22.0	25222.	69	21.95
25267.	22.1	25217.	22.0	25242.	50	22.05
25306.	22.1	25187.	22.1	25247.	119	22.1
25237.	22.4	25177.	22.4	25207.	60	22.4
25267.	22.5	25177.	22.4	25222.	90	22.45
25138.	24.8	25098.	24.8	25118.	40	24.8
25148.	24.8	25093.	24.8	25120.	55	24.8
25143.	25.0	25088.	25.0	25115.	55	25.0
24731.	34.0	24711.	34.0	24721.	20	34.0
24751.	34.0	24701.	34.0	24726.	50	34.0
24771.	34.1	24716.	34.1	24744.	55	34.1
24424.	42.7	24374.	42.7	24399.	50	42.7
24444.	42.7	24394.	42.7	24419.	50	42.7
24419.	42.7	24384.	42.7	24402.	35	42.7
24117.	49.9	24067.	49.9	24092.	50	49.9
24102.	50.1	24057.	50.1	24080.	45	50.1
24092.	50.1	24057.	50.1	24075.	35	50.1
25202.	22.5	25147.	22.6	25174.	55	22.55
25157.	23.1	25107.	23.1	25132.	50	23.1
25157.	23.0	25077.	23.0	25117.	80	23.0

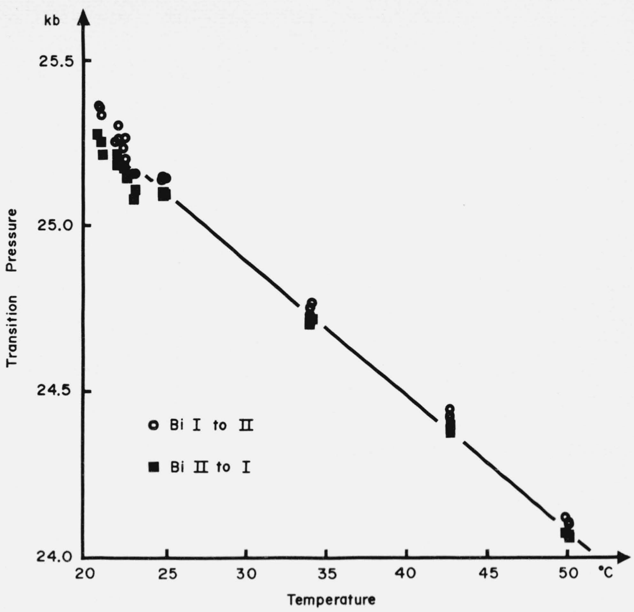

FIGURE 2. *Temperature Dependence of the Bismuth I–II Transition Pressure.*

where

T = temperature in degrees celsius (IPTS 1948)
P_T = transition pressure in bar at temperature T
$P_{25°C}$ = transition pressure in bar at 25 °C
$\frac{dP}{dT}$ = derivative of transition pressure with respect to temperature in bar per °C.

Table 2 shows the results of the three POLYFITs. The temperature coefficient of the transition pressure from the averaged points is −40.6 bar/°C with a standard deviation of 0.5 bar/°C. The systematic uncertainties due to the area of the pistons and cylinders, the effective area at elevated pressure, and the gage calibration do not influence this temperature coefficient. The uncertainty in thermal expansions of the tungsten carbide high pressure cylinder and of the steel ram cylinder are systematic in this measurement but are less than 0.1 bar/°C. The estimated systematic uncertainty of the temperature is 0.2° at 20 °C and 0.4 °C at 50 °C resulting in an estimated systematic uncertainty of 0.8 bar/°C. The maximum uncertainty due to friction is the difference between the tempera-

TABLE 2

Omnitab POLYFIT least squares fit of $P = P_{25} + (T - 25\ °C)\ dP/dT$

Transition	Standard deviation of the fit	Transition pressure at 25 °C	Standard deviation of transition pressure	dP/dT	Standard deviation of dP/dT
	Bar	*Bar*	*Bar*	*Bar/°C*	*Bar/°C*
I to II	33	25140	8	−41.3	0.6
II to I	25	25072	6	−39.9	.5
Average	27	25106	6	−40.6	.5

ture coefficient of the averaged pressures and that of the I to II or II to I which is 0.7 bar/°C.

The transition pressure was 25106 bar at 25 °C with a standard deviation of 6 bar and a half-friction of 34 bar. The estimated systematic uncertainty is 200 bar (150 bar cylinder expansion correction, 20 bar high-pressure cylinder measurement, 10 bar low-pressure cylinder measurement, 10 bar ram weight and oil head correction, 10 bar gage calibration).

The high estimated systematic uncertainty in the cylinder expansion correction arises from bismuth having extruded past the anti-extrusion ring and therefore the effective area lies between that of the corrected piston area and the corrected cylinder area. The value of 25106 bar differs from the present best value 25499 bar [6, 7] by more than the sum of the estimated uncertainties.

4. Conclusion

A value of −40.6 bar/°C with a standard deviation of 0.5 bar/°C, an estimated systematic uncertainty due to temperature of 0.8 bar/°C, and an estimated uncertainty due to friction of 0.7 bar/°C was found for the temperature coefficient of the bismuth I–II transition over the range of 20 to 50 °C. This value may be used for temperature correction within the range 20 to 50 °C of the present best value of 25499 bar at 25 °C for the pressure of the bismuth I–II transition.

5. References

[1] Bridgman, P. W., Phys. Rev. **47,** 427 (1935).
[2] Bridgman, P. W., Phys. Rev. **48,** 893 (1935).
[3] Bridgman, P. W., Proc. Am. Acad. Arts. Sci. **74,** No. 1, 1–10 (1940).
[4] Butuzov, V. P., and Ponyatovsky, Ye. G., Crystallography **1,** No. 5, 572–576 (1956).
[5] Butuzov, V. P., Soviet Physics-Crystallography **2,** 533, (1957).
[6] Heydemann, P. L. M., J. Appl. Phys. **38,** No. 6, 2640–2644 (1967).
[7] Heydemann, P. L. M., J. Appl. Phys. **38,** No. 8, 3424 (1967).
[8] Heydemann, P. L. M., and Houck, J. C., J. Res. Nat. Bur. Stand. (U.S.), **71C** (Eng. and Instr.) No. 1, 11–17 (Jan-Feb. 1967).
[9] Kennedy, G. C., and LaMori, P. N., Geophysical Research **67,** No. 2, 851–856 (1962).
[10] Zeto, R. J., and others, Characterization of the Bismuth I–II and Barium I–II Points under Hydrostatic Pressure, to be published in proceedings of the Symposium on the Accurate Characterization of the High-Pressure Environment, Oct. 14–18, 1968 at National Bureau of Standards.

(Paper 74A1–584)