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The Bi I–II Transition Pressure Measured with a Dead-Weight Piston Gauge

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A dead-weight piston gauge was used to determine the bismuth I–II transition pressure and the volume change at the transition. The transition pressure at 25°C for one sample, believed to contain less than 0.001% impurities, was found to be 25 306 bar, with an estimated uncertainty of 60 bar. With another sample, of substantially less purity and of larger grain size, a transition pressure of 25 500±60 bar was measured. The average relative volume change was 0.035. See erratum sheet.

I. INTRODUCTION

The importance of the Bi I–II transition—also called the α, β transition—as a fixed point on the pressure scale is amply demonstrated by the many references made to this point in literature and by the number of recent attempts to determine the transformation pressure more accurately[1] (summarized in Ref. 2). These determinations have been made with simple piston-cylinder equipment. The bismuth sample may thus be subjected to a stress field with strong nonhydrostatic components. The transition is usually detected by the accompanying volume change. Internal as well as external friction produces an hysteresis loop in compression and decompression, the size of which can be reduced but not easily eliminated. The mean between critical pressures observed in compression and decompression is usually assumed to be close to the thermodynamic transition pressure. The width of the hysteresis loop adds to the over-all uncertainty of the measurement.

II. 26-kbar PISTON GAUGE

In the investigation reported here, a dead-weight piston gauge with a freely rotating piston (and load) was used for the first time in an attempt to determine the Bi I–II transition pressure with samples subjected to hydrostatic pressure. The idea for this piston gauge was conceived by Johnson, Hutton, and Newhall. It was designed and constructed by Newhall of Harwood Engineering. Since the gauge will be described elsewhere in detail, only a short explanation of the apparatus is given here.

Figure 1 shows a cross section through the gauge. The tungsten carbide gauge piston P and the tapered cylinder C with jacket J are shown in the center of the apparatus. Jacket pressure is applied at the port JP. Samples are placed in the cylinder and the rest of the space is filled with amyl alcohol as a confining liquid. Pressure is built up by advancing the ram R with the mushroom head seal S into the cylinder. Endload is applied to the cylinder through the ram E. Pressure produced on the tapered surface of the cylinder by means of the endload supports the cylinder and controls the clearance between gauge piston and cylinder. Also the jacket pressure affects the clearance.

The gauge piston pushes against a pivot carrying the weight hanger and an oil pan. In operation piston, weight hanger, weights and oil pan rotate as one unit to relieve friction between piston and cylinder. Oil pumped into or withdrawn from the oil pan serves to change the load, and hence the pressure in the cylinder, continuously at rates between about 2 and 14 bar/min [1 bar$=10^5$ N/m^2] over a range of up to 1% of the internal pressure.

In operation the gauge piston was kept floating at about constant level while the ram R was continuously advanced to make up for leakage and compression of oil and sample. The leakage around the mushroom seal is believed to be negligible. The position of the ram is read from a sight column connected to the volume above the large ram piston, giving an almost two-hundredfold magnification. The change of the sight column reading is proportional to the change of volume in the cylinder as caused by compression, transition and leakage. Another sight column indicates the amount of oil pumped into or withdrawn from the oil pan. Both sight columns are read at 1-min intervals.

III. SAMPLES

Two different samples were used. Sample A was cast from granules supplied by Allied Chemical and Dye Corporation, General Chemical Division. It was claimed to be 99.8% pure with the following maximum impurities:

As	0.0001%
Sb	0.01%
Fe	0.002%
Cu	0.002%.

Sample B was cast from granules supplied by the American Smelting and Refining Company. The stated purity was 99.999%. Both samples were machined to cylinders of about 0.9 cm diameter, 0.9 cm long. The volume of sample A was 0.556 cm^3, that of B 0.607 cm^3. Before use in the piston gauge, sample B was exposed to several runs through the I–II and II–III transitions in a simple piston and cylinder assembly. This resulted in an average grain size of about 0.03 cm as compared

[1] G. C. Kennedy and P. N. Lamori, *Progress in Very High Pressure Research* (J. Wiley & Sons, New York, 1961), p. 304.
[2] G. C. Kennedy, and P. N. Lamori, J. Geophys. Res. **67**, 851 (1962).

to about 0.15 cm in sample A. Care was taken to avoid contamination of the samples.

IV. EXPERIMENTAL RESULTS

A typical curve obtained from a successful run on 11–16–65 is shown in Fig. 2. The ram sight column reading is plotted versus the applied mass. At a given rate of change of load the slope of the straight lines is determined by the leak rate; their vertical separation gives the volume change of the sample. For very small load rates the transition would appear as an almost vertical straight line connecting the two inclined lines. At higher rates the effect of latent heat and, possibly, a finite transition rate and inhomogeneities in the sample cause the transition to be spread out over a certain range of pressure as shown in Fig. 2. The effect of the latent heat of transition is treated in greater detail in Sec. VI of this report.

Eight such curves were obtained from successful runs. They permit determination of the following significant information: (a) the apparent transition pressure P_a; (b) the transition pressure P_{tr} corrected for the effect of latent heat; and (c) the volume change at the transition ΔV.

V. THE APPARENT TRANSITION PRESSURE P_a

The apparent transition pressure is defined as that pressure at which the beginning of the transition is first observed. At this point, due to the limited sensitivity of the apparatus, a small amount of material has already been converted and the actual transition

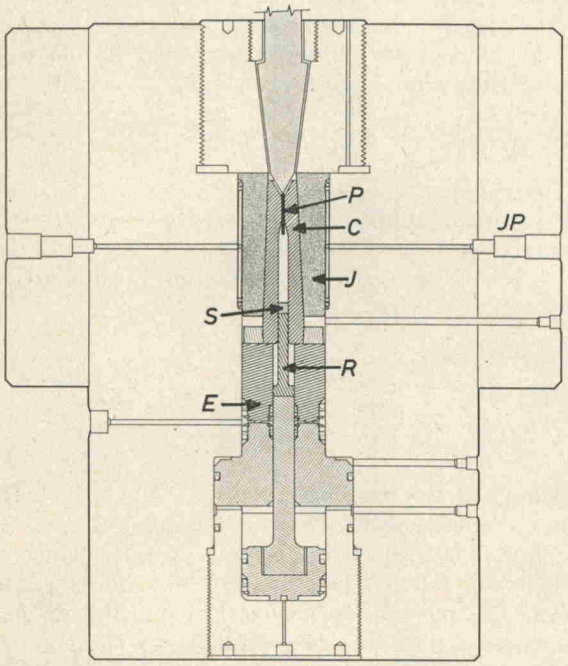


FIG. 1. 26-kbar piston gauge, schematic: P, carboloy gauge piston; C, cylinder, J, jacket; JP, connection for jacket pressure; S, seal; R, pressure generator ram; E, end load ram.

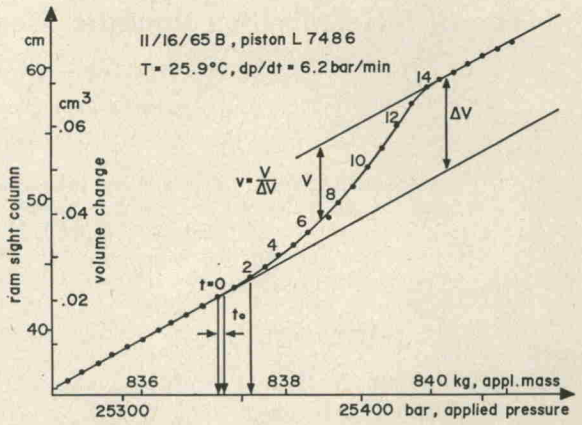


FIG. 2. Ram position as indicated by sight column vs applied load (uncorrected) and applied pressure. t(min) is a time scale with arbitrary starting point assigned to the run.

pressure is slightly lower or higher, depending on the direction from which the transition is approached. In Fig. 2 this point ($t=2$) is marked. The data from this and the other runs are collected in Table I and apparent transition pressures P_a are calculated.

The piston diameters (row 2, Table I) were obtained from calibration by the NBS Engineering Metrology Section prior to their use. Except for run 12–6–65 all successful runs were preceded by one or more runs causing wear of the piston. The uncertainty connected with this is probably very small compared to the uncertainty ascribed to the clearance. The same holds for taper of the pistons. Since the clearance can not be reset to a predetermined value, the jacket pressure-clearance relation can not be determined and the clearance can only be estimated (row 4). An upper limit for the clearance is obtained by extrapolating low pressure data to the present conditions. The lower limit is set by zero clearance. The uncertainty then is half the difference between the two limiting values. This extrapolation was made for the lowest fall rate (dh/dt). Clearance values C for larger fall rates were then computed from $C=\text{constant}\times(dh/dt)^{1/3}$. The fall rates (row 19) are determined from the leak rates (row 18) assuming that there is no leak around the mushroom seal. A correction factor of 0.999278 is applied to the piston diameter for elastic distortion.[3] The elastic constants for the cemented carbide were determined by ultrasonic measurements at atmospheric pressure.

The mass of the stainless steel weights on the weight hanger (row 10) was obtained from calibrations by the NBS Mass Section. The mass of the weight hanger of 173.841 kg was determined in substitution weighing on a hydraulic load cell. The mass of oil in the load pan (row 9) was obtained from sight column readings on the oil reservoirs. The density of the oil is well-

[3] D. P. Johnson *et al.*, Ind. Eng. Chem. **49**, 2046 (1957).

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Erratum: The Bi I–II Transition Pressure Measured with a Dead-Weight Piston Gauge

[38, 2640 (1967)]

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Due to an arithmetical mistake rows 13 to 15 in Table I are partly in error. They should read:

row 13
25.472 25.489 25.488 25.500 25.515 25.547 25.491 25.439
row 14
25.447 25.490 25.486 25.501 25.515 25.548 25.491 25.443
row 15
25.481 25.499

The pressures given in lines 3 and 5 of the abstract should read 25499 bar and 25481 bar, respectively. The pressure given in line 18 of Sec. VIII should read 25499 bar.

TABLE I. Computation of transition pressure.

1. Run and sample	5/7-A	I 5/14-A	II 5/14-A	III 5/14-A	11/15-B	11/16-B	12/6-B	12/7-B	Estimated uncertainty
2. Piston diameter (cm)	0.202758		0.202758		0.202758		0.202778		6×10^{-5}
3. Calibration rep.			*L* 7342		*L* 7486		*L* 7485		
4. Estimated clearance (μm)	2.00	2.09	2.03	2.03	2.06	1.91	1.53	1.63	±2 μm
5. Effective area (cm^2)	0.032305	0.032308	0.032306	0.032306	0.032307	0.032303	0.032297	0.032300	$\pm2\times10^{-3}$
6. Temperature (°C)	24.3	25.0	25.0	25.0	26.8	26.9	26.7	26.4	±0.1°C
7. Change of res. level (cm)	103.5	46.0	45.0	49.5 decomp	19.5	129.0	60.0	48.0 decomp	±0.1 cm
8. Corrected oil density (g/cm^3)	0.8777	0.8772	0.8772	0.8772	0.8759	0.8768	0.8763	0.8763	
9. Mass of oil[a] (kg)	9.289	4.126	4.037	4.441	1.750	11.567	5.377	4.307	±10 g
10. Constant mass[b] (kg)	831.557	836.093	836.093	836.093	836.088	827.016	831.552	831.552	
11. Total applied mass[c] (kg)	840.846	840.219	840.130	840.534	837.838	838.583	836.929	835.859	$\pm10^{-4}$
12. Pressure at onset of observable transition P_a (kbar)	25.510	25.489	25.488	25.500	25.417	25.443	25.398	25.363	
See erratum sheet 13. Pressure red. to 25°C[d] (kbar)	25.548	25.489	25.488	25.500	25.318	25.340	25.305	25.287	
See erratum sheet 14. Pressure corrected for latent heat effect.	25.523	25.490	25.486	25.501	25.318	25.341	25.305	25.291	
See erratum sheet. 15. Transition pressure P_{tr} (kbar)			25.500			25.306			±0.06 kbar
16. Load rate (kg/min)	0.460	0.224	0.158	−0.24	0.123	0.206	0.089	−0.215	
17. Rate of change of pressure (bar/min)	13.9	6.8	4.77	7.26	3.72	6.23	2.71	−6.50	
18. Leak rate (cm^3/min)	0.00217	0.00251	0.00227	0.00227	0.00244	0.00193	0.00098	0.00118	
19. Fall rate (cm/min)	0.069	0.080	0.072	0.072	0.078	0.062	0.031	0.038	

[a] Air buoyancy correction for oil 0.99867. [b] Air buoyancy correction for steel 0.99986. [c] $g=980.10$ cm/sec.^{2} [d] -54.5 bar/°C.

known; a temperature correction was applied. Air buoyancy correction was applied to all parts of the load. A temperature correction of −54.5 bar/°C was applied to the apparent transition pressures. The apparent transition pressures reduced to 25°C are entered in row 13 of Table I. Row 14 contains the transition pressures corrected for the latent heat effect discussed in the next paragraph. The mean values for the samples A and B respectively are given in row 15.

The last column of Table I contains the estimated uncertainties for the data going into the computation.

Whether the difference of the transition pressures for samples A and B is due to difference in purity, grain size, etc., can only be decided on the basis of more experiments. The difference is beyond the estimated range of uncertainty.

VI. CORRECTION FOR THERMAL EFFECTS

The transition of bismuth I to II and vice versa is accompanied by absorption and release of heat. According to Butuzov's[4] recent measurement the latent heat Q for this transition is −1.78 cal/g. This causes a change of sample temperature at the interface between the rare and the dense phases, which due to the negative slope of the phase boundary in the phase diagram has a retarding effect on the transition. To estimate the magnitude of the time constants involved, first the time constant for heat flow from the sample into the surrounding apparatus is calculated.

The thermal conductivity of the sample and the surrounding steel cylinder are assumed to be very large compared to that of the confining fluid.

Let the sample be surrounded by a cylindrical layer of amyl alcohol with d_o and d_i being the outer and inner diameter, L its length. The flow of heat through this cylinder is

$$\frac{dE}{dt} = -\frac{2\pi L\lambda(T_0-T_i)}{\ln d_o/d_i}, \tag{1}$$

with λ thermal conductivity, T_0 temperature of the steel vessel, and T_i temperature of the sample.

The temperature difference is determined by the thermal energy released or absorbed during the transformation, and the heat capacity of the sample. The maximum value for T_0-T_i follows for instant release of the heat of transformation Q

$$T_0-T_i=Q/c=-60°\text{C}, \tag{2}$$

where c is the specific heat of the sample.

Whence, with $E=Qm$,

$$E^{-1}\frac{dE}{dt} = -\frac{2\pi L\lambda}{mc\ \ln d_o/d_i} \tag{3}$$

and

$$E=\exp-\frac{2\pi L\lambda t}{mc\ \ln d_o/d_i}. \tag{4}$$

Heat is removed from the sample with the time constant

$$\tau=\frac{mc\ \ln d_o/d_i}{2\pi L\lambda}=-mc/\sigma=5\text{ sec}, \tag{5}$$

where $m=5.9$ g; $c=0.0295$ cal/g·deg; $d_o=0.94$ cm; $d_i=0.88$ cm; $\lambda=0.0235$ cal/cm·min·deg; $L=0.9$ cm. σ in Eq. (5) is the heat flow in cal/min·deg.

According to equations developed by D. P. Johnson in connection with the determination of the freezing point of mercury the relative amount v of bismuth I decreases as the pressure is increased as

$$v=1-\frac{dp}{dt}\left[\left(\frac{\alpha V p_0}{Q}+\frac{c}{QB}\right)t+\frac{\sigma}{2QBm}t^2\right], \tag{6}$$

where α compressibility of bismuth at the transition pressure p_{tr}; V specific volume of bismuth I at p_{tr}; p_0 reference pressure close to p_{tr}; B slope of the phase boundary $=-54.5$ bar/°C.

In order to determine the time $(t-t_0)$ at which during a measurement the transition pressure was reached, the experimental data for v up to about 0.5 were fitted to curves of the type

$$v-1=a(t-t_0)+b(t-t_0)^2. \tag{7}$$

The best fit in the least-squares sense then determines a, b, and t_0. The load at t_0 is used to compute the transition pressure corrected for the effect of latent heat. This pressure is generally found to be a few bars below the apparent transition pressure. The corrected pressure is entered in row 14 of Table I.

The constant b, as determined from the curve-fitting operation, is in fair agreement with calculated values. The term at cannot satisfactorily be determined from the experimental data since it is rather small compared to bt^2. The mean value of the corrected pressures obtained from compression runs with sample A does not differ from the pressure obtained from the decompression run. With sample B this difference is 34 bar. This indicates a very small zone of indifference; probably less than our uncertainty of 60 bar and also less than the value of 60 bar reported by Bridgman as an upper limit.[5] Butuzov's value of 1000 bar is much in contrast to our own observation.

VII. VOLUME CHANGE ΔV AT THE TRANSITION

The experiment is not designed for a precise determination of ΔV. However, in four runs the leak rate was sufficiently constant to permit the determination of the volume change at the transition. Table II

[4] V. P. Butuzov *et al.*, Kristallografia **VI (A56)**, 572 (1956).

[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 1 (1940).

TABLE II. Volume change at the Bi I–II transition.

	5–7–65	I 5–14–65	II 5–14–65	11–16–65
ΔV	0.021	0.020	0.018	0.021 cm³
V_0	0.556	0.556	0.556	0.607 cm³
M	5.421	5.421	5.421	5.915 g
$\Delta V/M$	0.0039	0.0037	0.0033	0.0035 cm³/g
$\Delta V/V_0$	0.038	0.036	0.032	0.035
	$\Delta V/V_0$ average: 0.035			

lists the results for these runs. The average relative volume change of 0.035 with an estimated uncertainty of ± 0.01 is less than Bridgman's value of 0.046 (7) or Butuzov's value of 0.055.

VIII. CONCLUSIONS

The present study demonstrated the feasibility of dead-weight piston gages for the generation of precisely known pressures up to at least 25 kbar. The piston gage may be used to determine transition pressures for polymorphic phase transitions accompanied by volume changes with an estimated uncertainty of about ± 60 bars at 25 kbar.

Because of leakage of the pressure transmitting fluid past the gauge piston, volume transitions cannot be observed at constant pressure. Rather the pressure has to be increased or decreased continuously. The latent heat of transformation absorbed or released during the transformation causes the transition to be spread out over a certain pressure range. A simplified thermodynamic treatment adequately describes the shape of the experimental transition curve and permits the determination of the transition pressure. A value of 25 306 bar with an uncertainty of 60 bar is ascribed to the transition pressure of a bismuth sample of high purity (99.999%) at 25°C.

One of the earliest determinations of this pressure under hydrostatic conditions was made by Bridgman[6] in 1937 using the change of the electrical resistance as an indicator for the transition. Bridgman's value, extrapolated to 25°C, was 24.5 kbar. If, as we in fact assume, detection of the transition by electrical resistance measurements is equivalent to volumetric methods, this value now appears rather low. Another determination is that by Butuzov,[4] using differential thermal analysis. His data extrapolate to 25 350 bar at 25°C. Butuzov's value is within our range of uncertainty.

Bridgman determined the bismuth transition pressure also under nonhydrostatic conditions. With a piston cylinder device[7] using volumetric methods of detecting the transition, his results give 25 150 bar (extrapolated to 25°C) and with electrical resistance measurements in anvils[8] he obtained the same value.

None of the quoted reports gives a detailed analysis of the uncertainty of the end result. The major source of uncertainty in all these cases is the width of the hysteresis loop, which in the case of Bridgman's work of 1940 was 1500 bar.

Using their oscillating piston and cylinder device, Kennedy and Lamori[1] reported the reduction of the hysteresis loop (or friction band) to about 200 bars. When a temperature correction of 55 bar/°C—a mean value of the coefficients quoted in Refs. 7 and 9—is applied to Kennedy's data, his mean value becomes 25 400 bar. This compares very favorably with our value and the close agreement might be an indication that the presence of the high shear stresses in Kennedy's apparatus does not greatly affect the transition pressure.

Kennedy's paper, however, does not contain a statement of the uncertainties systematic to the measurement. We will therefore have to assume that the estimated uncertainty of a measurement with Kennedy's apparatus is the same as with our own piston and cylinder assembly of the same type. Such an assembly has been used in this laboratory for a variety of transition pressure measurements, but the results are as yet unpublished. In this work the estimated uncertainty includes the mean value for half the friction and hysteresis (about 100 bar), the uncertainty in ram pressure (25 bar), the uncertainty in the computation of the cylinder distortion (50 bar) and a number of other, smaller effects. Our total uncertainty of a measurement in a piston and cylinder assembly of this type then exceeds 175 bar.

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 157 (1937).

[7] P. W. Bridgman, Phys. Rev. **48**, 893 (1935).

[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 165 (1952).

[9] F. P. Bundy, Phys. Rev. **110**, 314 (1958).