

the hysteresis loop. Because the length of the AgCl column was not known in this case the transition pressure was estimated by averaging the transition pressures on the increasing and decreasing pressure strokes. These points are shown as solid circles in Fig. 5 and can be compared with the open circles obtained by applying Eq. (3) to another run where there was no extrusion. The agreement is very good. Further evidence supporting our analysis of the sample pressure is the fact that the bismuth II-III transition at room temperature agrees very well with extrapolations of the data of Tikhomirova *et al.*⁷ However, it should be noted that there seems to be some disagreement between various authors regarding the pressure for the bismuth II-III transition.

It is important to point out that the data for the bismuth II-III transition pressures below about 225°K are very uncertain and are included in the phase diagram only to indicate that the bismuth II-III transition was actually observed at these temperatures. The uncertainty is due to the fact that the separation in pressure between the I-II and II-III transitions is approaching zero. When this separation in pressure becomes smaller than the pressure difference across the sample, a condition arises wherein phases I, II, and III are present in the sample simultaneously. This gives rise to a decreasing contribution to the total resistance by the II phase as pressure is increased beyond this point. This effect tends to obscure the bismuth II-III transition because the total resistance is the quantity determined in the experiment. As a result the triple point could only be obtained by an extrapolation from higher temperatures. If this is done the triple point is found to be in approximate agreement with Bridgman's¹ extrapolated result as shown in Fig. 5. The data also seems to indicate that the slope dT/dP , along the phase boundary becomes infinite at $T=0^\circ\text{K}$ as required by Clausius-Clapyron equation for a first-order phase transition.

No evidence was found of the new phase of bismuth reported by Il'ina and Itskevich.⁹ This is surprising in view of the similarity of the apparatus; their system as well as ours employed AgCl as a pressure transmitting medium in a piston-cylinder device. Direct comparison of isothermal tests can be made. They associated the existence of a new phase with a dip in the R - P curve (see Fig. 1 in Ref. 9) which we did not observe. The only resistance changes we observed were those normally attributed to the familiar phase transitions of bismuth as shown in Fig. 4. The disagreement could possibly be attributed to differences in pressurization rates. This author used pressurization rates of 1 to 2 kbar/min; the pressurization rates used by Il'ina and Itskevich were not reported. Furthermore there appear to be some inconsistencies between Il'ina and Itskevich's⁹ data and their interpretation of their results. For ex-

ample, in one isobaric run at 28 kbar they did not observe resistance discontinuities associated with the "new phase"-II and II-III transitions as they raised the temperature to about 275°K. (See Fig. 4, Ref. 9.) These transitions should have been observed according to their phase diagram (see Fig. 2, Ref. 9). Also they show a large resistance discontinuity in an isobaric run at 28 kbar (see Figs. 3 and 4, Ref. 9) as temperature is raised, which they associate with the I-"new phase" transition and a small resistance discontinuity which they associate with the "new phase"-II transition. This appears to contradict runs at 77° and 200°K as pressure is increased, wherein small resistance discontinuities are attributed to the I-"new phase" transition and large resistance discontinuities are attributed to the "new phase"-II transition. (See Fig. 1, Ref. 9.) These apparent inconsistencies in the work of Il'ina and Itskevich⁹ and our failure to obtain evidence of a new phase of bismuth suggests that another more conclusive experiment be done. The experiment would require a hydrostatic system, slow pressurization rates, temperatures below 289°K and pressure between 25 and 30 kbar. These temperatures and pressures are implied by extrapolating Il'ina and Itskevich's⁹ data to find the I-"new phase"-II triple point at 25 kbar, 298°K.

In summary the phase diagram of bismuth at low temperatures was determined and compared with previously published phase diagrams. The question of a new phase of bismuth was answered tentatively in the negative. Further experimentation to conclusively determine the existence of the new phase was suggested.

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