

The phase diagram for tin is in excellent agreement with the work of Millet (1968), but the pressures reported by Kennedy and Newton (1963) are 2.5 kbar high even at the triple point where our pressure should be very accurate. The triple point values are given in table 2. Our measured slopes at the triple point are $(dT/dP)_{I-II} = -2.0 \text{ K kbar}^{-1}$, $(dT/dP)_{I-L} = +2.0 \text{ K kbar}^{-1}$, and $(dT/dP)_{II-L} = +6.1 \text{ K kbar}^{-1}$. Assuming the ratio of the compressibility to the thermal expansion to be independent of temperature and pressure, we can calculate the volume below the triple point in phase I using compression measurements to 30 kbar of Barnett *et al.* (1966), and from Barnett *et al.* (1963) we find the volume in phase II giving $\Delta V_{I-II} = -0.0035 \text{ cm}^3 \text{ g}^{-1}$ and $\Delta H_{I-II} = 24 \text{ cal g}^{-1}$. Taking the relative areas under the latent-heat peaks we find $\Delta H_{I-L} = 50 \text{ cal g}^{-1}$ and $\Delta H_{II-L} = 27 \text{ cal g}^{-1}$ with $\Delta V_{I-L} = +0.007 \text{ cm}^3 \text{ g}^{-1}$ and $\Delta V_{II-L} = 0.011 \text{ cm}^3 \text{ g}^{-1}$. The Sn I-II solid-solid transition is very sharp and as shown in figure 9b it takes place at the equilibrium value. The Sn II-I phase change shows supercooling, but once the transition begins the temperature rises instantaneously to the equilibrium value. This solid-solid transition should be ideal for pressure calibration. It is probably a displacive transition as suggested by Musgrave (1963) and Barnett *et al.* (1963).

The solid-solid phase changes in bismuth all showed varying amounts of hysteresis. The triple points, reported in table 1, are estimates of the equilibrium transition points judged from the shape of the DTA signals on increasing and decreasing temperatures. The hysteresis is shown in figure 6 for some of the phase lines.

The method of measuring phase changes in a liquid hydrostatic medium is very easy and gives extremely reproducible results, and, once the problem of calibration has been better refined, it will be the most accurate method of measuring phase diagrams yet used. This experimental technique allowed us to obtain all triple points in the pressure range in the same experimental cell.

The pressure increase with temperature reported here is only meaningful for a high-pressure cell of the same geometry and materials as we used. This is clearly evidenced by the much smaller value found by Mitra *et al.* (1967) in a solid pressure cell with a much smaller fraction of the volume of the cell comprising the furnace. We also have evidence that at very low pressures, before the gaskets are well formed, the pressure increase is smaller than the value we report here. In fact, heating at very low loads will often allow the sample to 'blow out'. This work might be made more universally useful by calibrating the resistance of a Manganin wire against the pressure and temperature as determined by these phase diagrams. The stability of a Manganin gauge at these temperatures, however, may be questionable.

Table 2. Triple points in the phase diagrams of tin and thallium ($^{\circ}\text{C}/\text{kbar}$).

Investigator	Sn I-II-L	Tl I-II-III
Dudley and Hall (1960)	318/31	
Kennedy and Newton (1963)	304/33	
Jayaraman <i>et al.</i> (1963)		115/38.5
Millet (1968)	308/30.1	
This work	307/29.5	106/37.3

Acknowledgements. We gratefully acknowledge helpful discussions with W. E. Evenson during this research. This work was supported in part by the National Science Foundation.

References

- Akella, J., Ganguly, J., Grover, R., Kennedy, G. C., 1973, *J. Phys. Chem. Solids*, **34**, 631-636.
- Barnett, J. D., Bean, V. E., Hall, H. T., 1966, *J. Appl. Phys.*, **37**, 875-877.
- Barnett, J. D., Bennion, R. B., Hall, H. T., 1963, *Science*, **141**, 1041-1042.
- Bogdanov, V. S., Levin, Yu. L., Sekoyan, S. S., Shimn, Yu. I., 1971, in *Accurate Characterization of the High Pressure Environment*, Ed. E. C. Lloyd, N.B.S. Special Publication 326 (US National Bureau of Standards, Washington, DC), pp.297-302.
- Bridgman, P. W., 1935, *Phys. Rev.*, **48**, 893-906.
- Butuzov, V. P., Ponyatovskii, E. G., 1956, *Sov. Phys. - Crystallogr.*, **1**, 453-455.
- Candland, C. T., Decker, D. L., Vanfleet, H. B., 1972, *Phys. Rev.*, **B5**, 2085-2094.
- Decker, D. L., 1965, *J. Appl. Phys.*, **36**, 157-161.
- Decker, D. L., 1971, *J. Appl. Phys.*, **42**, 3239-3244.
- Decker, D. L., Bassett, W. A., Merrill, L., Hall, H. T., Barnett, J. D., 1972, *J. Phys. Chem. Ref. Data*, **1**, 773-835.
- Decker, D. L., Vanfleet, H. B., 1965, *Phys. Rev.*, **A138**, 129-133.
- Dudley, J. D., Hall, H. T., 1960, *Phys. Rev.*, **118**, 1211-1216.
- Getting, I. C., Kennedy, G. C., 1970, *J. Appl. Phys.*, **41**, 4552-4562.
- Hanneman, R. E., Strong, H. M., Bundy, F. P., 1971, in *Accurate Characterization of the High Pressure Environment*, Ed. E. C. Lloyd, N.B.S. Special Publication 326 (US National Bureau of Standards, Washington, DC), pp.53-62.
- Haygarth, J. C., Luedmann, H. D., Getting, I. C., Kennedy, G. C., 1969, *J. Phys. Chem. Solids*, **30**, 1417-1424.
- Jayaraman, A., Klement, W., Newton, R. C., Kennedy, G. C., 1963, *J. Phys. Chem. Solids*, **24**, 7-18.
- Kennedy, G. C., Newton, R. C., 1963, in *Solids under Pressure*, Eds W. Paul, D. Warschauer (McGraw-Hill, New York), pp.163-178.
- Klement, W., Jayaraman, A., Kennedy, G. C., 1963a, *Phys. Rev.*, **131**, 1-6.
- Klement, W., Jayaraman, A., Kennedy, G. C., 1963b, *Phys. Rev.*, **131**, 632-637.
- Millet, L. E., 1968, "Experimental melting curves of cadmium, indium, lead, tin, and zinc and Mössbauer measurements in iron to 90 kilobars", unpublished dissertation, Brigham Young University, Provo, Utah.
- Millet, L. E., Decker, D. L., 1969, *Phys. Letters*, **29A**, 7-8.
- Mitra, N. R., Decker, D. L., Vanfleet, H. B., 1967, *Phys. Rev.*, **161**, 613-617.
- Musgrave, M. J. P., 1963, *J. Phys. Chem. Solids*, **24**, 557-558.
- Ponyatovskii, E. G., 1960, *Sov. Phys. - Crystallogr.*, **5**, 147-149.
- Tikhomirova, N. A., Tonkov, E. Yu., Stishov, S. M., 1966, *JETP Letters*, **3**, 60-62.
- Wang, C., 1967, *Rev. Sci. Instr.*, **38**, 24-26.
- Young, R. K., 1969, "Equations of state for lithium fluoride and sodium metal to very high pressures and high temperatures", unpublished dissertation, Brigham Young University, Provo, Utah.