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Melting Curves of Five Metals under High Pressure*

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Techniques have been developed for the determination of the melting curves of metals under pressure and are applied to five metals. These data are used to evaluate the constants appearing in the Simon equation, with and without approximate values of the corrections to be applied to the thermocouples. These corrections can make as much as 20% difference. The values of these constants are compared with the theoretical expressions of Gilvarry, and agreement is close.

INTRODUCTION

A CONSIDERABLE body of literature exists on the almost classical problem of the melting curve. The success of the Simon equation[1] in representing the data has aroused considerable theoretical interest[2-4] from which it has become clear that the metals, as a group, have less agreement with theoretical expressions for the Simon equation constants than for other elements, or compounds. Unfortunately, except for the work of Bridgman[5] on the alkali metals, bismuth, gallium, and mercury, very little work of high precision has been done, due to the difficulties of accurately measuring the melting curves under simultaneous application of high temperatures and pressures. This paper reports the developments of a method of measuring the melting curves of metals with a precision on the order of 0.1°C, and its application to five metals.

APPARATUS AND PROCEDURE

The pressure equipment is standard enough to need little comment. The pressures were provided by a 35:1 intensifier actuated by a hand oil pump. The system was primed by a free piston pump, which was in turn driven by an air-operated oil pump. Thus the system was raised to about 2000 bar before the high-pressure piston was advanced. The pressure transmitting medium was argon in all of the experiments reported in this paper. The cell in which the furnace was located has an inside diameter of $1\frac{1}{16}$ in., and a length of 7 in. Due to the large volume of the pressure cell and the relatively small displacement of the intensifier, a single stroke of the intensifier would yield but 5000 bar pressure in the cell. In order to raise the pressure to our normal working range of 10 000 bar, it was necessary to incorporate a valve between the pressure cell and intensifier so the cell could be isolated during the recycling of the intensifier. Failure of this valve limited

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[1] F. Simon and G. Glatzel, Z. anorg. u. allgem. Chem. **178**, 309 (1929).

[2] C. Domb, Phil. Mag. **42**, 1316 (1951).

[3] L. Salter, Phil. Mag. **45**, 369 (1954).

[4] J. J. Gilvarry, Phys. Rev. **102**, 317 (1956).

[5] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, England, 1952), Chap. VII.

the range of these experiments to one stroke of the intensifier or about 5000 bar.

Pressures were determined with a manganin manometer, calibrated at the freezing pressure of mercury at 0°C. This pressure was taken as 7574 bar (7723 kg/cm²).[6] The coil was recalibrated during the course of this work.

The furnace will be the subject of a separate paper.[7] Briefly, it consists of a slip-cast ceramic body, in which were cast the windings and the tubes through which the thermocouple wires were later drawn. After firing, this results in a small, rugged, easily handled furnace. The furnace used for these measurements (only one such furnace was used for all of the measurements reported herein) was wound with 22-gauge Chromel-A, and ordinary white ceramic slip was used, fired to 900°C. The inner bore of the furnace was $\frac{5}{16}$ in., and its length 2.5 in. Power for the furnace was supplied by a Variac, the maximum power required for these experiments being about 400 W. To reduce convection, and more sharply define the melting plateaus it was necessary to cap the furnace with a loosely fitting cap of lava.

The experiment required a plug with thermocouple leads and a power lead. This plug has been described,[8] as have the seals.[9]

The samples were cast into outgassed ceramic crucibles *in vacuo*. The crucibles were prepared from two pieces of ceramic tubing, the body being $\frac{5}{16}$ in. o.d. and 2 in. long. A piece of $\frac{1}{16}$-in.-o.d. tubing $2\frac{1}{4}$ in. long was placed inside and coaxially with the body of the crucible. The two tubes were then sealed together at one end, the smaller tube protruding slightly, with Astroceram type A cement. The small tube thus formed a thermocouple well extending completely through the crucible. At the temperatures encountered here no trace of contamination of the samples from the crucible materials was detected.

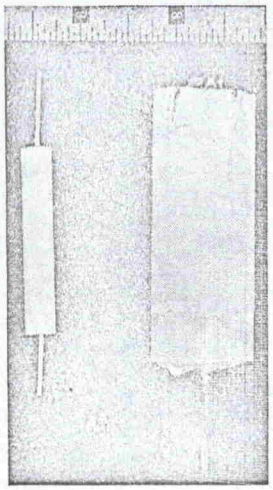


FIG. 1. Furnace and sample holder.

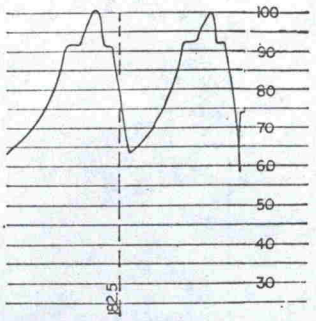


FIG. 2. Melting plateaus of an indium sample as a function of time. Increasing time runs to the left, and the width of the melting plateaus is about 35 sec.

A photograph of a typical furnace and a crucible is shown in Fig. 1. For clarity, the axial tube in the crucible is shown longer than usual.

The thermocouples were of Chromel P and Alumel, 0.010 in. in diameter, and butt welded. The necessary connections which were made inside the pressure vessel between like legs of the thermocouple were welded. Great care was taken, since earlier techniques of soft and silver soldering gave rise to parasitic emf's at these points. The data in the literature[10,11] are contradictory as to the corrections which must be applied to such a thermocouple due to the effects of pressure. Accordingly, no correction was made. This will be the subject of a separate investigation. The maximum error due to this cause will be less than 1°C for the temperatures and pressures encountered here, and will be discussed below.

The axial placement of the thermocouple tube in the sample allowed the melting and freezing of the sample to be measured directly. The temperatures were determined with a Leeds and Northrup K–2 potentiometer, the duration of the plateaus being sufficient to set the instrument carefully. Figure 2 shows a graphic recording of the temperature of an indium sample as a function of time made with a Varian model 22 recorder connected directly to the thermocouple. On the run which was thus recorded, the power to the furnace was cut a few seconds before the end of melting, giving a plateau of 35-sec duration. The apparent discrepancy between melting and freezing temperatures, as shown on the recording, was pen tracking error. When freezing was detected, its temperature coincided with that of melting to within the accuracy of the setting, about 1–3 μV.

The procedure was to load the furnace and contents into the pressure cell, evacuate, and flush once or twice with argon, and then commence a pressure run. Each point is the result of several determinations of the temperature (and pressure). Three determinations were always made, and usually four to six. The ex-

[6] R. S. Dadson and R. G. P. Greig (private communication). This value is still provisional, but the best currently available.
[7] G. J. Scott (to be published).
[8] G. J. Scott and S. E. Babb, Jr., Rev. Sci. Instr. **32**, 868 (1961).
[9] S. E. Babb, Jr., Rev. Sci. Instr. **31**, 219 (1960).
[10] F. Birch, Rev. Sci. Instr. **10**, 137 (1939).
[11] W. E. Deming, *Statistical Adjustment of Data* (John Wiley & Sons, Inc., New York, 1943), p. 167.

TABLE I. Values for the Simon constant.

Substance	Type of data[a]	a (kbar)	$\sigma(a)$ (kbar)	c	$\sigma(c)$	Fit[b] (bar)	Fit[c] °C
Indium	uncorr.	43.5	14.9	1.96	0.61	135	0.6_6
Indium	with TC	35.8	4.0	2.30	0.23	51	0.2_5
Tin	uncorr.	32.1	18.3	4.76	2.57	71	0.2_3
Tin	with TC	34.2	20.3	4.30	2.40	69	0.2_3
Bismuth	uncorr.	−14.0	5.9	11.36	5.67	103	0.3_5
Bismuth	with TC	−13.5	5.8	12.3	6.32	113	0.3_6
Thallium	uncorr.		average slope 6.78°±0.04°/kbar			16	0.1_1
Thallium	with TC		average slope 6.93°±0.04°/kbar			14	0.1_1
Lead	uncorr.		average slope 7.4° ±0.2°/kbar			37	0.2_2
Lead	with TC		average slope 7.8° ±0.2°/kbar			25	0.2_1

[a] Uncorr.=data without any correction for the effects of pressure on the thermocouple; with TC=data with 0.05°/100°C/1000 bar correction added.
[b] The quantity in this column is: $[(P-P_{calc}P)^2/N-1]^{\frac{1}{2}}$.
[c] The quantity in this column is that of the last multiplied by the slope.

treme spread of the readings was on the order of a few microvolts (1 μV=0.025°C). Accordingly, the precision of each point determination is on the order of 0.1°C or better. The rise of pressure upon heating was followed on the manganin gauge, and the pressure taken at the moment melting started. The change during the plateau was small, usually about 1 bar. The precision of the pressure measurement was about 1–3 bar. The error of the determination of temperature outweighs any pressure errors.

For sharp definition of the melting point, it was found advantageous to use fairly fast heating rates, on the order of 3°–5°/sec. Higher rates resulted in insufficient time to set the potentiometer, and lower rates resulted in poorer definition of the melting point and higher spread of measured values.

It was found impractical to take points under vacuum in the setup used for the pressure experiments. Attempts to measure the atmospheric melting points resulted in a temperature which decreased with time, and the samples became progressively more contaminated. This has been tentatively ascribed to an imperfect vacuum tightness of the pressure seals. None of these effects occurred under high pressures. Consequently, it was most convenient to extrapolate the curves back to 1 atm. This extrapolation was short, on the order of a degree or so. This point was then used to correct the thermocouple readings. For the particular batch of wire on hand, the thermocouples always read slightly low, by a variable amount (1°–4°C). Thus the thermocouple reading which would correspond to the melting point at atmospheric pressure was obtained by extrapolation, and the difference between this value and that which it should have was added to all thermocouple readings. There was never any evidence of the emf of the thermocouple varying with time.

This extrapolation was done graphically, at first, and then the data fitted to the Simon equation

$$P_{calc}=a[(T/T_0)^c-1]$$

by a least-squares technique which minimized the quantity $(P-P_{calc})^2$. Then the correction factor which had been applied was varied until the best fit was obtained. This variation was on the order of a few tenths of a degree, and represents the uncertainty in graphical estimation of the extrapolation. This corresponds to expansion of the thermocouple error into a series: $E=A+BT+\ldots$, and neglecting all terms other than A. To assume the other extreme, i.e., set $A=0$, and use B alone, results in a difference of but 0.05° at the maximum temperature for the worst case herein reported, thanks to the force fit at 1 atm, and the short range of measurement.

The use of the Simon equation, fitted to the uncorrected data, as a means of checking the graphical extrapolation is open to slight question. Presumably the equation fits the actual melting curve, not the melting curve modified by the presence of the pressure effects on the thermocouple. The difference is probably negligible, but will be reinvestigated when accurate values for this correction are available (see also Table I).

The standard deviations of the constants in the Simon equation were calculated by applying the procedure given in Deming.[12]

RESULTS

Indium

The source of the indium used was some old lab stock from Fisher Company, purity not stated. This was one of the first substances which was run and several runs were taken with it. The results shown in Fig. 3 are from two runs. One of these was the last run

[12] F. P. Bundy, J. Appl. Phys. **32**, 483 (1961).

used for the development of techniques and shows somewhat larger scatter than usual. This was also the last run before the aforementioned valve failed, and the only substance in this paper for which data are presented for over 6000 bar. An idea of the consistency of these experiments may be gained from the fact that these two runs taken on the same sample with different thermocouples agree very well after each has been independently corrected. The second run is amazingly good, showing a standard deviation of but 0.02°C. After corrections, the two runs diverge by but 0.1°C at the maximum pressure of the second run. The Simon constants are shown in Table I. The melting curve of indium has been determined before[13–15] at greater pressure ranges in all investigations than were used here. The details of the methods of Kennedy have not yet been published, but Butuzov and Ponyatovskii claim an accuracy of about 1.5° at each measured point, and 100 bar, while Dudley and Hall claim about 7°–10°, and 5% in pressure. Butuzov *et al.* barely detected the curvature to 30 000 bar, while it is quite clear in our measurements to 9000 bar. The agreement between these observations is satisfactory, as the data lie within the combined experimental errors.

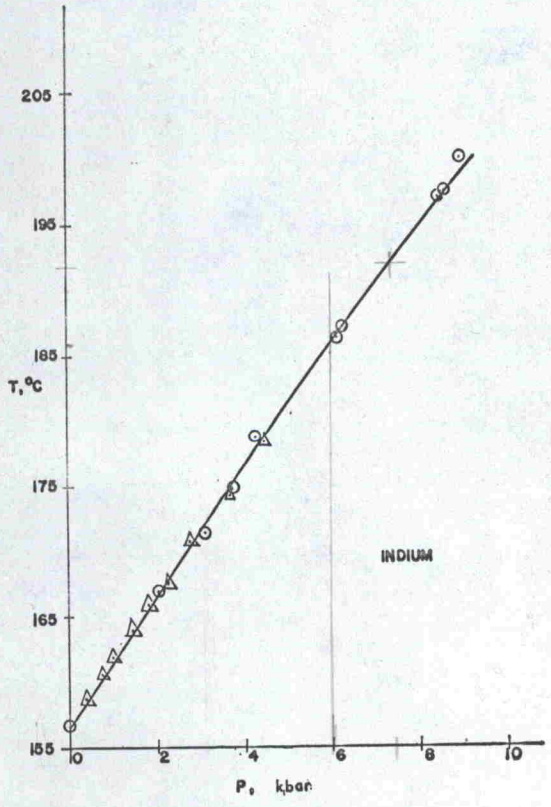


FIG. 3. Melting curve of indium.

[13] J. D. Dudley and H. T. Hall, Phys. Rev. **118**, 1211 (1960).
[14] G. C. Kennedy (private communication).
[15] V. P. Butuzov and E. G. Ponyatovskii, Kristallografiya **1**, 746 (1956).

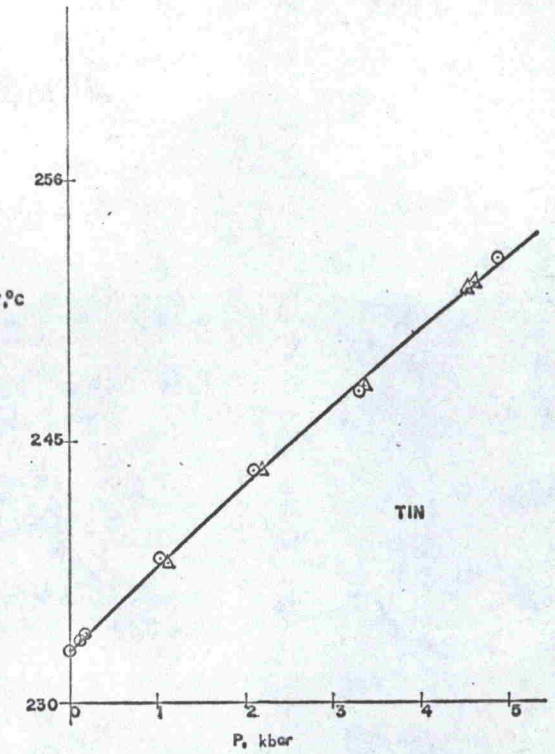


FIG. 4. Melting curve of tin.

Tin

Tin was the substance used for most of the trouble shooting, and consequently samples of all descriptions were run. The data reported here were taken on Baker analyzed-reagent tin, of 99.9+% purity. The data shown in Fig. 4 are the results of two runs. These two runs are completely independent, being made on different samples, from different batches of tin from the same source, using different thermocouples, and two weeks separation in time. The agreement between the two runs is excellent, after the thermocouple corrections are applied, the disagreement being less than 0.1°C at the maximum pressure. This is eminently satisfactory. The values for the Simon constants are shown in Table I. The melting curve of tin has been measured before.[13–18] Once again the agreement is satisfactory. Tin is one of the two substances for which we can check the errors arising from the effects of pressure on the thermocouple. The data of Babb[18] are roughly accurate to 0.5°C, and permit a comparison of melting curves taken with the thermocouple inside and outside the pressure vessel, and all other conditions being the same. The curve taken with the pressurized thermocouple lies consistently under the other curve, with the disagreement increasing with increasing pressure (and temperature). From Bundy's[12] data, one may arrive at a figure for the correction which

[16] V. P. Butuzov and M. G. Gonikberg, Doklady Akad. Nauk. S.S.S.R. **91**, 1083 (1953).
[17] J. Johnson and L. H. Adams, Am. J. Sci. **31**, 501 (1911).
[18] S. E. Babb, Jr., J. Chem. Phys. (to be published).

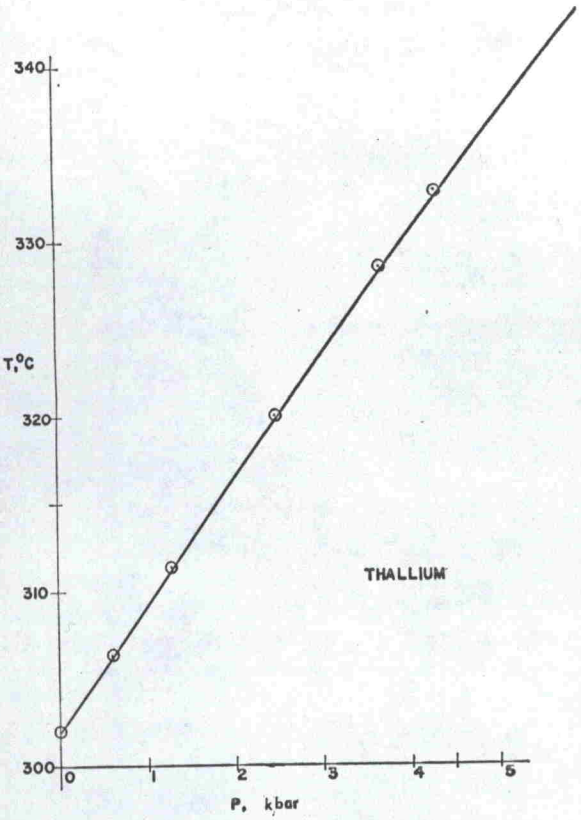


FIG. 5. Melting curve of thallium.

should be applied, on the order of 0.05°C/100°C/1000 bar; i.e., to the base temperature of the thermocouple, 0.05°C must be added for each 100°C temperature difference between junctions, and for each 1000 bar pressure applied. The application of this correction to the data makes the curves coincide. The difference is on the order of 0.05°C at the highest pressures reached with these experiments. This is strong presumptive evidence for the correctness of Bundy's values for the thermocouple correction. Unfortunately, this correction is certainly nonlinear with pressure, and probably so with temperature and thus is too uncertain to be applied.

Thallium

The thallium was from the American Smelting and Refining Company, of 99.999+% purity. The impurities detected by standard spectrographic analysis were for Mg, <0.0001%; for Pb, <0.0001%; for Fe, <0.0001%; and for Cu, <0.001%. Thallium oxidized quickly in contact with air and special precautions were found necessary to get a sample of sufficient purity into the pressure cell. The melting curve, as shown in Fig. 5, is practically straight, as has been obtained by other investigators.[14,19] Thallium has a transition between room temperature and the melting point. This transition was detected, but the latent heat is small, and the arrest was not of sufficient duration to allow measurement.

Bismuth

The melting curve of bismuth was run as a check by comparison with the excellent data of Bridgman. The characteristic expansion of bismuth on freezing caused considerable difficulty in the investigation of this metal. The breaking of crucibles and thermocouple tubes with a resultant shorting of the thermocouple was corrected by using a folded thermocouple and wrapping the crucible with aluminum foil to contain the cracked pieces. The bismuth used was from the American Smelting and Refining Company, and of 99.999+% purity. Spectrographic analysis was furnished with this particular sample.

Bismuth is another substance for which a comparison between melting curves taken with internal and external temperature measurements may be made. If the aforementioned correction is applied to our data, then the disagreement between it and that of Bridgman is less than 0.07°C at the maximum pressures of our experiments. Bismuth has also been run by other investigators,[16,17,20] and the uncorrected curve

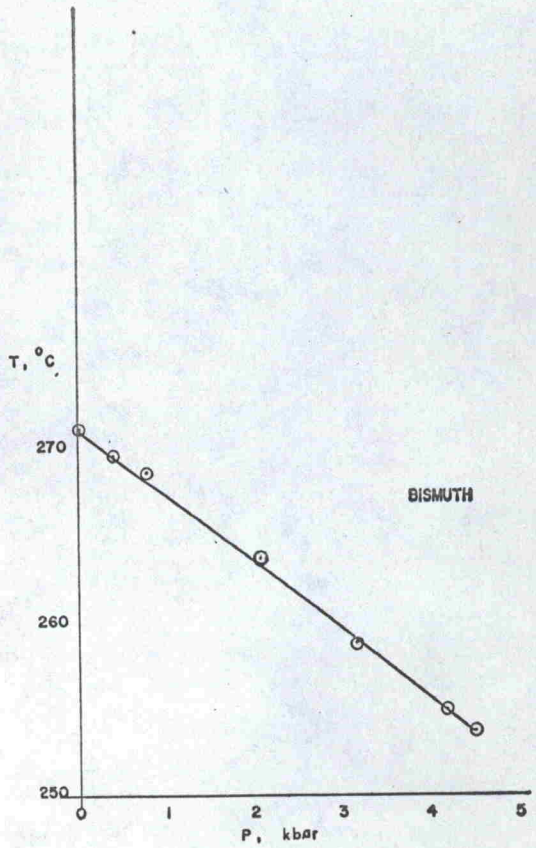


FIG. 6. Melting curve of bismuth.

[19] V. P. Butuzov, E. G. Ponyatovskii, and G. P. Shakhovskoi, Doklady Akad. Nauk. S.S.S.R. **109**, 519 (1956).

[20] V. P. Butuzov, M. G. Gonikberg, and S. P. Smirnov, Doklady Akad. Nauk. S.S.S.R. **89**, 651 (1953).

is shown in Fig. 6. The Simon constants are shown in Table I.[21]

Lead

The lead was from the American Smelting and Refining Company and was of 99.999+% purity. As shown in Fig. 7, the melting curve of lead is almost straight in agreement with Butuzov.[16]

The previous work of Johnson and Adams, to 2000 bar, is the only very precise work done on lead. Their value for the slope, 0.007921°C/bar, is somewhat higher than our value of 0.00770°C/bar. Their precision is higher than ours, being about 0.02°C, and their thermocouple corrections are known fairly well. When their data are corrected for the pressure effect on the thermocouples, a value of 8.0±0.3°C/kbar is obtained, as compared with our corrected value of 7.8±0.2. Their value may be somewhat high, for their melting point of the lead at 1 atm indicates some impurities, and their effect would decrease with increasing pressure.

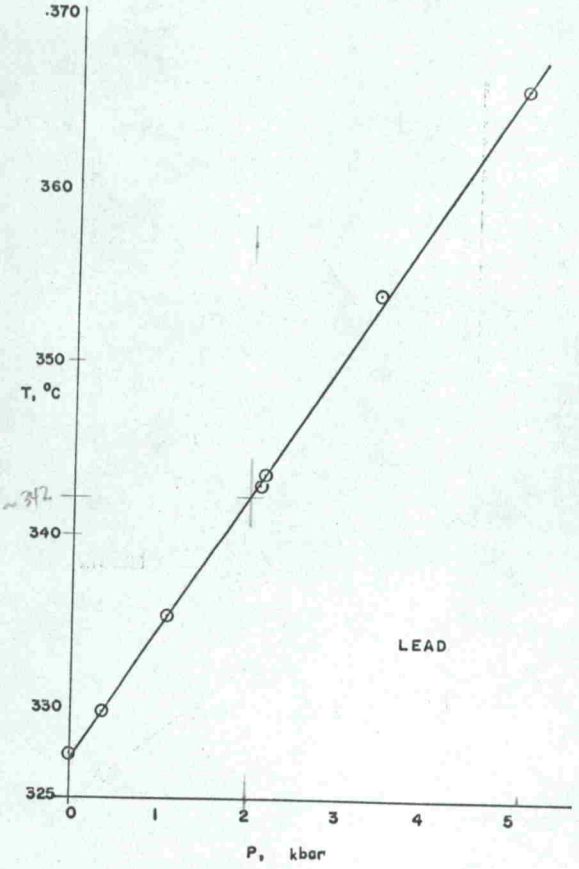


FIG. 7. Melting curve of lead.

[21] The use of a Simon equation for falling melting curves has no theoretical basis and is apparently novel. We have found that the fits with this equation are as good as those for a normal substance, but the spread between the values obtained from various investigations is somewhat larger than normal.

TABLE II. Comparison with theoretical expressions.[a]

Substance	Thallium	Lead	Tin	Indium
a_{th}, kbar	64	37	38	43
a_{exp}, kbar	61	32	39	36
c_{th}	1.44	3.06	4.87	2.98
c_{exp}	1.38	2.40	4.30	2.3

[a] Bulk modulus data: P. W. Bridgman, Pb: Proc. Am. Acad. Arts Sci. **76**, 1–7 (1945); In and Tl, 9–24; Sn, **77**, 129–146 (1949); Grüneisen constant; Tl, Pb, Sn, from O. E. Grüneisen, *Handbuch der Physik*, Vol. X, edited by F. Hennig (Verlag Julius Springer, Berlin, Germany, 1926), pp. 1–59; In, from data in *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1926).

DISCUSSION

The errors of these curves is a matter of some concern. The error at the atmospheric pressure end of the curve is essentially zero, since the data were force-fitted to the considerably more accurate values of the melting points at this pressure. The maximum error at the other end of the curve may arise from several causes. The first error would be that of the error of the thermocouples. The fit is extraordinarily sensitive to small changes in the correction, so this is determined to better than 0.05°C. The error involved in the assumption of a constant correction to be applied is, as indicated earlier, believed to be less than 0.05°C. The other sources of error are in the pressure measurement, one due to the precision of setting, and the other due to the precision of the calibration of the manganin monometer. The metals have slopes of the melting curves such that the error of setting results in an error of 0.01°–0.02°C maximum. The error of calibration should be small, usual experiments showing a precision of about 2 parts in 7800 or better. Therefore, the error in this would be on the order of 0.02°–0.03°C. All in all, the maximum absolute error of the temperatures could hardly exceed 0.15° to 0.2°C, plus the standard deviation of the measurements, and then only at the highest pressures and temperatures. The internal precision is materially higher than this.

In the values of the Simon constants there is another source of error, that of ignoring the thermocouple corrections. This is a serious effect, and the application of the rough correction mentioned earlier gives rise to the changes shown in Table I. It should be noticed that including the corrections improves the fit. This is as expected, for presumably the Simon equation fits the true melting curve, not that modified by thermocouple corrections. When better values of the thermocouple corrections are available, then more confidence in the Simon constants will result.

The rather high values of the standard deviations of the constants in the Simon equation are misleading at first sight. For tin, for example, the standard deviation of c is about 55% of its value. However the difference in the melting temperatures predicted by the two equations using extremal values of a and c is only

0.4°C at 5000 atm. This is essentially one standard deviation on each side of the curve. The pressure range of these measurements is large enough to show that there is definite curvature in the melting curve, but not large enough to determine the constants accurately.

The values of the constants appearing in the Simon equation, as given in the literature, are not as well known as generally supposed. Dudley and Hall, for instance, state that for indium, c is known to about 2%, as their summarized data show. This figure is misleading, for if their data are corrected for the presumed nonlinearity of their pressure scale,[22] then the new value of c is known to but 10%, (2.7 ± 0.23) or to the same accuracy as ours. The variation between individual runs, however, is more than twice the standard deviation of the summarized data.

CONCLUSIONS

A method has been developed for the determination of the melting curves of substances which utilizes internal heating in the pressure vessels, and achieves an accuracy on the order of 0.1°C. It has been applied to five metals. These data may be used to evaluate the constants in the Simon equation and thus provide a means of checking theoretical predictions.

Though insufficient data are available to directly check Gilvarry's theoretical expressions, one may assume his relationship between the Grüneisen constant and the Murnaghan parameter; using this assumption, one may then obtain the comparison shown in Table II, where the data for the Simon equation fits has been taken from the work of Butuzov *et al.* for thallium and lead.

This table shows that the disparity between theoretical and experimental values is not as great as has been usually reported. It also shows that, while earlier theories tended to predict values of c which were too low, the expressions of Gilvarry give values which are too high.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge a generous grant from the Alumni Development Foundation of the University of Oklahoma, which furnished the gas handling and priming system, as well as much of the low-pressure piping.

[22] G. C. Kennedy and P. N. La Mori, J. Geophys. Research 67, 851 (1962).