EXPERIMENTAL FUSION CURVES OF LEAD AND ZINC TO 105,000 ATMOSPHERES

Herbert E. Christensen

EXPERIMENTAL FUSION CURVES OF LEAD AND ZINC TO 105, 000 ATMOSPHERES

A Thesis

Presented to the

Department of Physics

Brigham Young University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Herbert Eugene Christensen

May, 1961

This thesis, by Herbert E. Christensen, is accepted in its present form by the Department of Physics of Brigham Young University as satisfying the thesis requirement for the degree, Master of Science.

Chairman, Advisory Committee

Member, Advisory Committee

Chairman, Major Department

Typed by Lucille Windsor

ACKNOWLEDGEMENTS

This Thesis is a report of a phase of research being conducted in the High Pressure Laboratory at Brigham Young University and has been made possible through a grant from the National Science Foundation.

The Author wishes to express sincerest appreciation and gratitude for the excellent direction and encouragement given by Dr. H. Tracy Hall. Appreciation is also expressed to Dr. J. Dean Barnett for several valuable discussions and suggestions. Thanks are extended to George Bone for his help in fitting Simon's equation to the experimental data, and to D. Clifton Carlson for his assistance in some of the experimental work.

Gratitude is also expressed to the author's wife, Elizabeth, for her encouragement and valuable assistance in composing this paper.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION

Several theories proposing to mathematically describe the melting process have been developed. The validity of these theories, additional corrective information, or evidence of their error in predicting melting curves may be obtained from experimentally obtained fusion curves of the elements. This particular thesis has been undertaken to supply additional experimental data towards obtaining more complete and accurate theories of melting.

Prominent among theories on melting is an equation due to Simon(1). He approached the problem through the methods of low-temperature physics and developed, somewhat empirically, the following equation:

$$\log (P + a) = c \log T + b$$

T is the melting temperature at the pressure P. The constants a, b, and c depend on the nature of the material. The constant b is evaluated by letting T_o be the melting temperature when P equals zero. (P equals 1 atmosphere which is approximately zero when compared to the several thousand atmospheres with which we will be dealing.) Then Simon's equation becomes:

$$P/a = (T/T_o)^c - 1$$

In this equation a is the internal pressure of the crystal due to lattice forces only (independent of the external pressure). The constant c has no particular physical significance.

Simon's equation was fitted to the experimentally obtained fusion curves to obtain values for the parameters a and c. A very complete review of all the available theories on melting can be found in the Doctoral Thesis of Dudley(2).

EXPERIMENTAL PROCEDURE (GENERAL)

All of the research reported herein has been done in the high-pressure, high-temperature laboratory on the Brigham Young University campus, under the direction of Dr. H. Tracy Hall.

Pressure Equipment:

Pressure equipment consisted of two presses. Both presses are classed "Tetrahedral Anvil Apparatus",[3] one having a larger sample volume capacity than the other. The tetrahedral anvil press consists of four independent, hydraulically-driven rams supported in such a manner as to all be converging at one point, each along lines normal to the faces of a tetrahedron. The heads (anvils) of the rams have flat, triangular faces and are machined such that when all four anvils have been driven together uniformly, they enclose a tetrahedral cavity. These anvils are constructed from cemented tungsten carbide.

Sample Holder:

The sample holder is a pyrophyllite* tetrahedron which has an edge length 25% larger than the edge of the triangular faces of each anvil. These dimensions are 15/16" and 3/4", respectively, on the small press and 1" and 1-1/4" on the large press.

As a result of the oversized tetrahedron, some of the lava (pyrophyllite) will be forced out into the narrow places between the anvils as they are all driven together on the tetrahedron. Lava has a sufficiently high coefficient of friction so that this excess lava forms a compressible

---

*Pyrophyllite - A hydrous aluminum silicate also known as grade A lava, available from American Lava Company, Chattanooga, Tennessee.

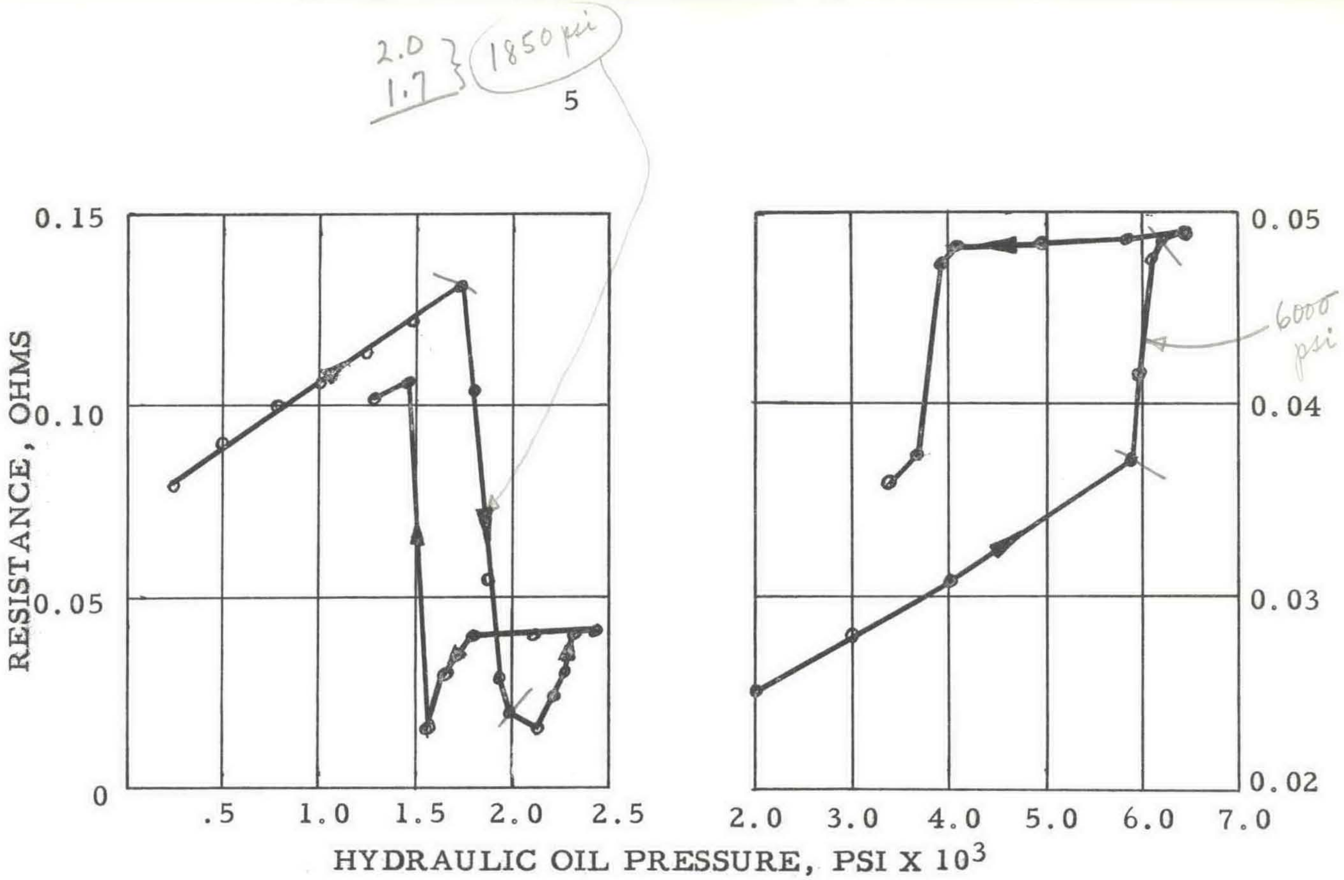
gasket. After a small amount of this has "oozed" out, a very tight gasket is formed and further travel of the anvils increases the pressure in the cavity now occupied by the lava sample holder. Figure 3, in which the gaskets mentioned can be seen, shows a tetrahedron before and after a run.

Calibration Technique:

It was necessary to calibrate the presses or, in other words, to determine how much pressure was actually transmitted to the sample inside of the lava tetrahedron with a certain oil pressure on the rams driving the anvils.

The presses were calibrated by a technique developed by Dudley(2) and a detailed description can be found in his thesis. A brief summary follows.

The known transition points of bismuth and barium which are 24,800 atmospheres for the Bi I-Bi II transition, and 77,400 atmospheres for barium, were used as calibration points. These two elements were each put inside of a tetrahedron in the same position a regular sample would occupy, then the resistance of the material was measured and recorded as a function of pressure. A typical curve, resistance vs. pressure, can be seen in Figure 1. Two or three curves like this were obtained for each of the elements, bismuth and barium. The transition point was taken as halfway between the top and bottom of the resistance drop at the point of steepest slope. These points were then plotted and a line drawn through them and the origin. This became the calibration curve for the presses. See Figure 2.



Bismuth transition

Barium transition

Fig. 1.

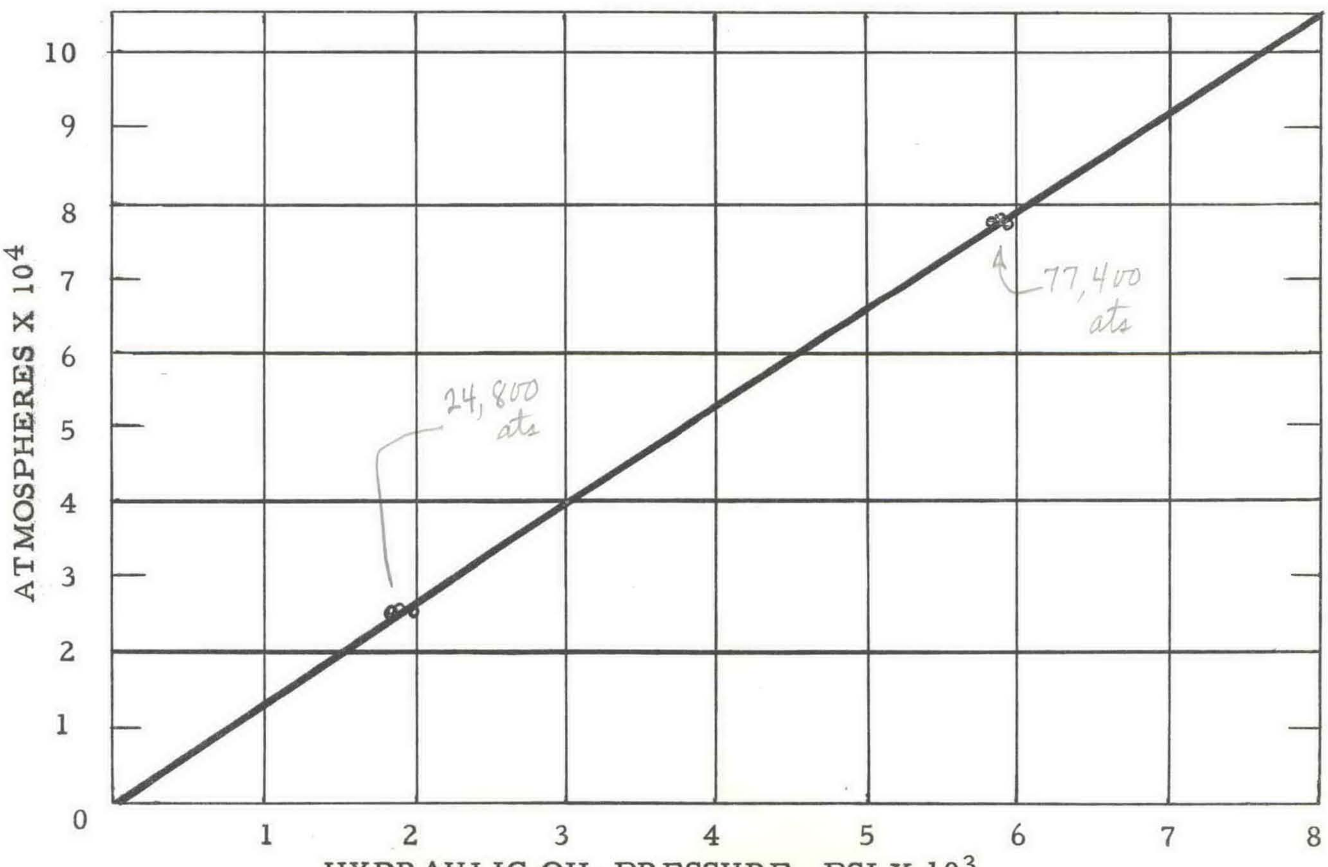


Fig. 2. - Calibration curve for large and small tetrahedral presses

Methods of Heating the Sample:

Heating of the sample has been accomplished by various, although similar, techniques. The presses have been constructed in such a way that each of the anvils is electrically insulated from the press frame itself and consequently from each other. Two anvils were then wired together and connected to one side of the power supply and the other two were wired together and connected to the other side of the power supply. When a tetrahedron is inserted into the press, having, of course, the proper internal arrangement, current can pass through one set of two anvils, through the sample or sample heaters, and back out the other set of two anvils. This heating method is basic to all the runs made. The only thing that changes is the means of getting current through the tetrahedron and the type of sample heating arrangement employed. These various arrangements will be discussed separately in the section concerned with each specific sample.

Detecting the Temperature of the Sample:

A method has been developed whereby several thermocouple wires are imbedded in the tetrahedron and run out through the gaskets to a recorder to measure the temperature of the sample, or, for that matter, the temperature at any point inside the tetrahedron.

Platinum-platinum 10% rhodium thermocouple wires were used exclusively in the runs made. Each set of runs employed various thermocouple arrangements and these will be described in the section concerning the specific runs. However, the method of bringing the thermocouple wires out of the tetrahedron through the gaskets is a technique that has been used exclusively throughout all the runs.

It was found that unless a small "protective sheath" made of lava was placed around the thermocouple wire, it would invariably break off right in the gasket area. As the gaskets were being formed by the flow of the lava tetrahedron under pressure, the thermocouple wires would be pinched apart. With these protective sheaths in place, the anvils would clamp down on these sheaths and consequently hold the thermocouple wire in place while the lava flowed around it to form the gasket. The size of these sheaths is not extremely critical. They should be .104" thick, about 3/16" wide, and 5/16" long for the large press, and .080" thick, 3/16" wide, and 3/8" long for the small press.

The above method has proven very dependable. Figure 3 shows an assembled tetrahedron with these protective sheaths around the thermocouple wires. In all cases, the thermocouple wires were run through a reference junction of zero degrees centigrade and all recording was made on a strip-chart recorder.

A. Before run

B. After run

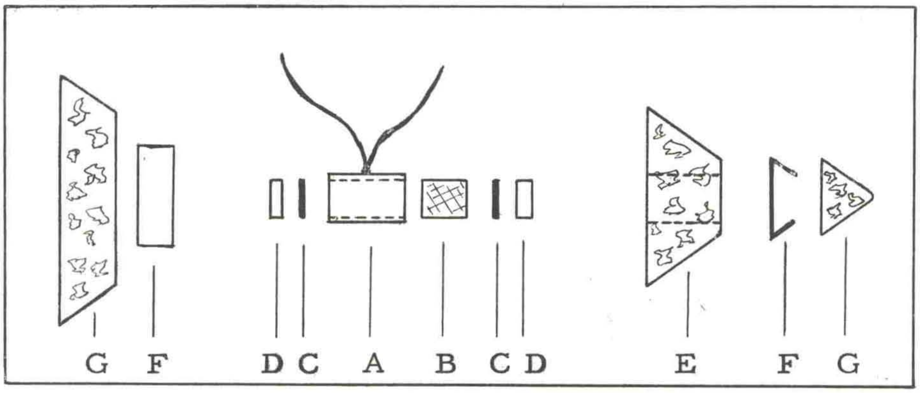
Fig. 3.--Assembled sample holder (tetrahedron).

EXPERIMENTAL PROCEDURE (SPECIFIC)

LEAD

Sample Geometry:

All of the runs on lead were made in the small press. A drawing of the tetrahedron prepared to receive a sample can be seen in Figure 4. Two opposite ends of the tetrahedron are sliced off and a hole drilled through the center of the middle piece. (See Figure 4.) This hole will contain the sample and its respective heating and temperature detection devices.



A - Tantalum tube with thermocouple wires spotwelded to side.
B - Lead sample.
C - Tantalum disk.
D - Nickel end plug.
E - Body of tetrahedron.
F - Steel end tab.
G - Sliced-off edge of tetrahedron.

Fig. 4. - Sample geometry for lead

The successful runs with lead were obtained in the following manner: The sample, lead, was encased in a tantalum tube, 0.010" wall thickness and 0.125" outside diameter. The ends of the tube were sealed with a thin tantalum disk and a nickel disk, the tantalum being next to the sample. A platinum-platinum 10% rhodium thermocouple junction was previously spot-welded to the side of the tantalum tube. This entire assembly was then inserted into the hole in the tetrahedron with the thermocouple wires running out the tetrahedron, perpendicular to the tantalum tube, through one of the edges of the tetrahedron and through the protective sheaths described previously. A steel tab (see Figure 4) was then placed over each end, and the pyrophyllite edges that were sliced off were glued back in place. Now the heating current will pass through the two anvils and the steel tab on one end, through the lead and tantalum core and out the other end through the steel tab and anvils. Since this small sample has a rather high resistance, it will serve as its own I^2R heater.

With this tetrahedron in the press and the thermocouple wires running through a cold junction to the recorder, we can measure the temperature inside the tetrahedron as the current through the sample is increased.

Melting Point Detection Method:

It was possible, with the geometry described above, to observe a very sudden rise in the temperature of the sample when it melted. This effect, which can be seen in the reproduction of the strip-chart recorder chart in the Appendix, has been explained this way: When the sample melts, the resistance rises sharply and, since the resistance of the entire heating circuit was large compared to the sample resistance, no appreciable change in the total current through the circuit was effected; however, the I^2R heating of the sample rose sharply as the resistance of the sample rose. Consequently, the temperature of the sample would rise sharply also.

It was not possible to put the thermocouple junction inside the tantalum tube in the lead itself, because lead and platinum alloy when heated, which is why the thermocouple junction was spot-welded to the outside of the tantalum tube. Since the junction would not measure the true temperature of the lead inside the tube, it was necessary to correct the temperature readings that were obtained to indicate the true melting temperature of the lead. Once again, a technique developed by my predecessor, Dr. J. Duane Dudley, was employed.

> Let t be the temperature of the sample, and t_m be the temperature measured by the thermocouple at its position on the outside of the sleeve (tantalum) containing the sample. Let t_a be the ambient temperature outside of the pyrophyllite, essentially the temperature of the anvils (taken to be the temperature to which the thermocouple immediately drops just when the power is shut off after detection of a melting point) then the heat flow (at equilibrium) from the sample out to the position of the thermocouple will be proportional to $(t-t_m)$:
>
> $$H_1 = K_1 (t-t_m),$$
>
> and the heat flow from the position of the thermocouple out to the anvils will be proportional (as a first approximation) to (t_m-t_a):
>
> $$H_2 = K_2 (t_m - t_a).$$
>
> Now if an equilibrium condition exists, these two values of heat flow must be equal in magnitude, or
>
> $$K_1 (t-t_m) = K_2 (t_m - t_a),$$
>
> from which
>
> $$t = t_m + (K_2/K_1)(t_m - t_a)$$
>
> Denoting the constant K_2/K_1 as k, the heat correction equation is obtained.[4]
>
> $$t = t_m + k(t_m - t_a)$$

The constant k is determined by correcting the extrapolated experimental curve at zero pressure (one atmosphere) to the true melting point at one atmosphere. After k has been determined at t_o and p_o, then the experimental curve can be corrected in its entirety, yielding the melting curve as a function of pressure.

Results:

Four runs have been individually corrected and then averaged together and plotted. Figure 5 is a reproduction of this plot. The melting point of lead increases from 327.3 degrees centigrade at one atmosphere to 730 degrees centigrade at 105,000 atmospheres. The curve seems to rise very smoothly. No transition points appeared.

The results obtained above compare very well with the melting point of lead obtained by Hoffman and Hudson(6) at General Electric at 30,000 kg/cm^2, and is 9.2% below the point obtained by Butuzov and Gonikberg(5) up to 30,000 kg/cm^2. Both of these points have been included in the plot of the melting curve of lead in Figure 5.

Simon's equation was fitted to this experimental curve. The constants a and c are 7,560 atmospheres and 3.38, respectively, with 5.7% maximum deviation between the two curves.

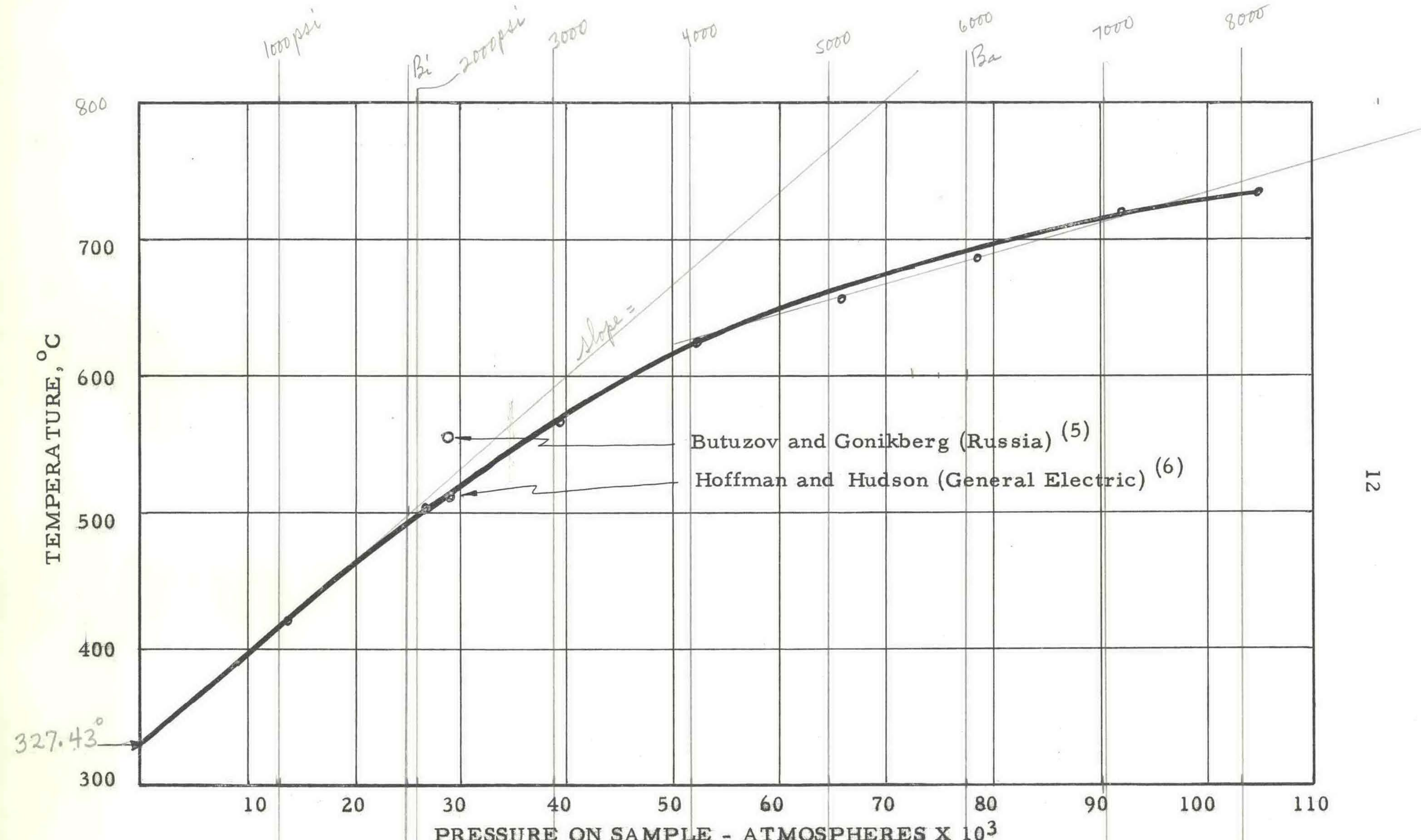


Fig. 5. - Fusion curve of lead

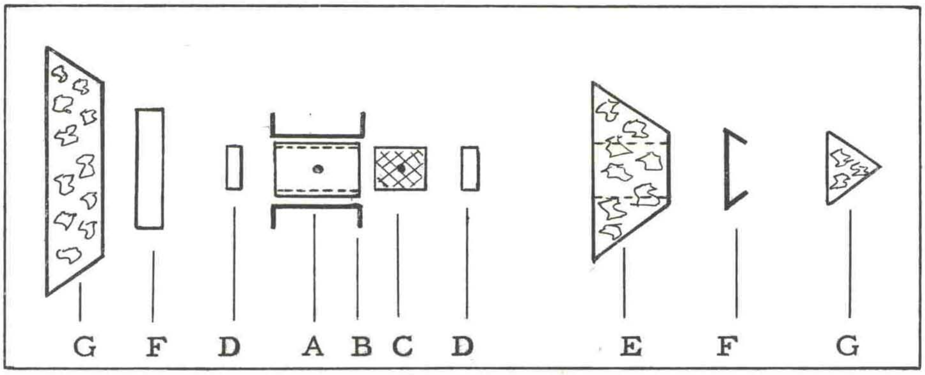
ZINC

Attempts similar to those used in the runs on lead were used in an effort to detect the melting point of zinc; however, it was found that the resistance of zinc did not change enough upon melting to cause this sudden change in I^2R heating. Consequently, no change in the temperature at melting could be seen, as was observed when using the sample geometry for lead.

Several other methods of detection and sample geometry were tried to no avail. After some time, however, a satisfactory method was found which yielded some very good and apparently accurate results; that is, no temperature correction was necessary as in lead. The thermocouple measured the exact temperature at which the sample melted, and the strip-chart recorded it.

Sample Geometry:

The above method employed detecting the latent heat of melting in the sample as it was allowed to heat and cool rather rapidly. The sample was not used as its own heater in this case but, instead, was heated indirectly. Figure 6 shows the components of the sample. In this case, the zinc was enclosed in a boron nitride (BN) tube with BN plugs in the end, so that the zinc was completely enclosed in BN. The thermocouple wires ran straight through the BN and the zinc, so the thermocouple junction was in the center of the zinc sample. This assembly was placed in the hole in the tetrahedron and heated by two tantalum strips running along the side of the BN tube. With the end pieces replaced, including the steel end tabs, the current could now pass



A - Boron nitride tube with hole through it for thermocouple wire.
B - Tantalum heating strips.
C - Zinc sample with hole for thermocouple wires.
D - Boron nitride end plug.
E - Body of tetrahedron.
F - Steel end tab.
G - Sliced-off edge of tetrahedron.

Fig. 6. - Sample geometry for zinc

from one set of anvils through the end tab, along the two tantalum strips and out the other end tab and set of anvils. The tantalum strips have enough resistance to make very good heaters. Now the zinc sample was placed inside an oven and insulated from the heating elements by the BN.

Melting Point Detection Method:

In order to detect the latent heat of melting, it is important that the sample be heated at a very constant rate. Again the thermocouple wires were connected to the strip chart recorder and temperature vs. time was recorded. As the sample was heated linearly with time, latent heat showed up as a sudden increase in the slope of the time/temperature curve. A typical chart from the recorder can be seen in the Appendix. Near linear heating was accomplished by setting the variac on the power supply (with the power off) at a large enough value that, with the power turned on, the heating would be sufficient to raise the temperature above the melting point of zinc. With the recorder operating, the power supply was turned on with the variac at this preset value. The temperature of the sample increased quite rapidly and linearly with time. As the sample melted, the latent heat showed up on this curve as a somewhat constant temperature for a short time. The sample was melted two or three times at each pressure increment in order to assure that the point observed was the true melting point, confirming it by repetition. Pressure increments of 500 psi oil pressure were taken. This corresponds to 7000 atmospheres.

It is not possible to get melting points much below 1000 psi oil pressure because the gaskets are not formed until about 600 psi and, if the sample is heated before the gaskets are fully formed, it will blow out. It was necessary in all the runs made to extrapolate the curves obtained from 1000 psi to 1 psi. In zinc the extrapolation put the melting temperature exactly on the point where it should melt at 1 atmosphere.

Results:

Three runs of zinc have been averaged together and plotted. This curve can be seen in Figure 6. The temperature increases smoothly from 419.5 degrees centigrade at 1 atmosphere to 670 degrees centigrade at 105,000 atmospheres. There were no visible transition points.

Butuzov, Ponyatovskii, and Shakhovskoi[7] have measured the melting temperature of zinc up to pressures of 30,000 kg/cm^2. In this range the melting point of zinc increased 129°C. Their point, at 30,000 kg/cm^2, is 8.0% higher than the same point obtained herein.

This point, at 30,000 kg/cm^2 has been included on the fusion curve of zinc in Figure 6.

Simon's equation was fitted to this experimental curve with the results that the constants a and c are 16,400 atmospheres and 4.19 respectively, with a maximum deviation of 0.7%.

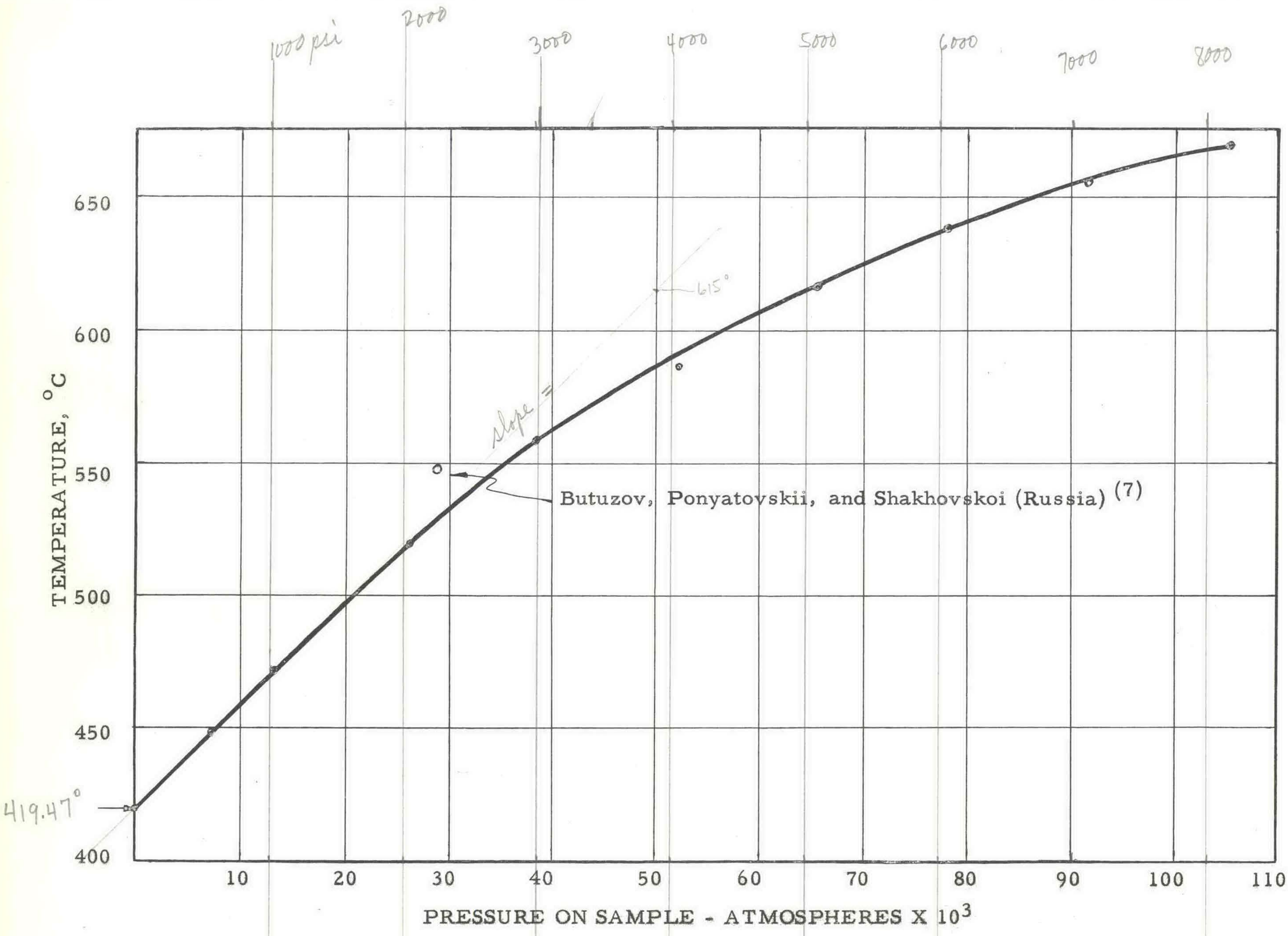


Fig. 6. - Fusion curve of zinc

APPENDIX

EXPERIMENTAL DATA

The following represents the actual data taken and the temperature corrections made from the experimental runs on lead. Although pressure increments of 200 psi (ram oil pressure) were taken in the runs, the corrections below were made only for pressure increments of 1000 psi (ram oil pressure). The detailed data taken on each of the runs on lead and zinc can be found in the journal of experimental runs in the High Pressure Laboratory at Brigham Young University.

As has been previously discussed, the runs on lead had to be temperature corrected because of the geometric location of the thermocouple junction.

Each of the runs were plotted and the curves obtained were extrapolated from 1000 psi (the lowest ram pressure at which readings were taken) to zero ram pressure. The temperature corresponding to this point was taken as t_{m_o}. The ambient temperature, t_{a_o}, was taken as the temperature to which the thermocouple junction dropped immediately after shutting the heating power off after melting was detected. Using the values for these temperatures in the heat correction equation

$$t = t_m + k(t_m - t_a)$$

along with the normal melting temperature, t, of lead, the constant k can be determined. The entire experimental curve can then be corrected, using this value of k.

The following headings will be used in listing the data:

P (psi) Oil pressure in the rams of the small presses, with 8" diameter rams.

P (atm)	Corresponding pressure on the sample with the above pressure on the rams, in atmospheres.
t_m (mv)	Thermocouple emf at the melting point, in millivolts.
t_m(°C)	The conversion of the preceding number, t_m(mv), to degrees centigrade.
t_a(°C)	Temperature to which the junction dropped when power was turned off right after melting was detected.
t (°C)	Corrected melting temperature, from the equation above.

Lead Sample #2 7/28/60

Lead in a tantalum tube, 0.010" wall thickness, 0.125" outside diameter. Thermocouple spot-welded to the outside of the tantalum tube. Two end plugs are tantalum and nickel so that the lead is completely enclosed in tantalum.

P (psi)	P (atm)	t_m(mv)	t_m(°C)	t_a(°C)	t(°C) — corrected
1000	13500	2.60	331	35	428
2000	26300	3.20	395	36	513
3000	39200	3.60	436	36	567
4000	52200	3.88	465	36	606
5000	65500	4.28	506	37	660
6000	78500	4.50	528	37	689
7000	91800	4.69	547	38	714
8000	105000	4.85	563	38	735

t_{m_o} = 255°C t_{a_o} = 35°C k= .3275

Lead Sample #1 8/5/60

Same geometry as the sample above.

P (psi)	P (atm)	t_m(mv)	t_m(°C)	t_a(°C)	t(°C) — corrected
1000	13500	2.66	337	50	404
2000	26300	3.25	400	51	481
3000	39200	3.80	457	60	549
4000	52200	4.20	498	61	600
5000	65500	4.55	533	69	641
6000	78500	4.84	562	74	675

corrected

Lead Sample #1 8/5/60 (continued)

P (psi)	P (atm)	t_m(mv)	t_m(°C)	t_a(°C)	t(°C)
7000	91800	5.08	586	72	705
8000	105000	5.30	608	80	731

$t_{m_o} = 275°C$ $t_{a_o} = 50°C$ $k = .232$

Lead Sample #2 8/12/60

Same geometry as above.

P (psi)	P (atm)	t_m(mv)	t_m(°C)	t_a(°C)	t(°C)
1000	13500	2.77	349	42	435
2000	26300	3.22	397	44	502
3000	39200	3.66	443	49	560
4000	52200	4.00	478	50	605
5000	65500	4.28	506	50	670
6000	78500	4.50	528	51	670
7000	91800	no data			
8000	105000	4.90	568	53	721

$t_{m_o} = 260°C$ $t_{a_o} = 34°C$ $k = .298$

Lead Sample #2 8/17/60

P (psi)	P (atm)	t_m(mv)	t_m(°C)	t_a(°C)	t(°C)
1000	13500	2.55	326	30	414
2000	26300	3.28	403	34	513
3000	39200	3.80	457	35	582
4000	52200	4.20	498	37	635
5000	65500	4.50	528	39	674
6000	78500	4.77	555	39	708
7000	91800	4.98	577	45	735
8000	105000	5.00	578	50	735

$t_{m_o} = 260°C$ $t_{a_o} = 34°C$ $k = .298$

All of the following runs on zinc have been made in the large Tetrahedral Press. As discussed earlier, the thermocouple junction was right in the sample and measured the true temperature at melting, so no temperature corrections were made. The following headings will be used in listing the data:

P (psi)	Oil pressure on the 12" diameter rams of the large press, in pounds per square inch.
P (atm)	Corresponding pressure on the sample with the above pressure on the rams, in atmospheres.
t(mv)	Thermocouple emf at the melting point, in millivolts.
t(^{o}C)	The conversion of the preceding number to degrees centigrade.

Zinc Sample #1 1/19/61

Zinc in a boron nitride tube, .175" outside diameter, .125" inside diameter, .210" long, with boron nitride end plugs so that the zinc sample is enclosed in boron nitride completely. The heating arrangement has been described earlier.

P (psi)	P (atm)	t(mv)	t(^{o}C) Corrected
1000	13500	4.05	483
2000	26300	4.50	528
3000	39200	4.90	568
4000	52200	5.15	593
5000	65500	5.45	622
6000	78500	5.65	642
7000	91800	5.80	656
8000	105000	5.95	670

Zinc Sample #1 1/21/61

P (psi)	P (atm)	t(mv)	t(^{o}C)
1000	13500	3.97	475
2000	26300	4.48	526
3000	39200	4.88	566
4000	52200	5.15	593
5000	65500	5.38	616
6000	78500	5.62	639

Zinc Sample #1 1/21/61 (continued)

P (psi)	P (atm)	t(mv)	t(^{o}C)
7000	91800	5.77	653
8000	105000	5.94	669

Zinc Sample #1 1/25/61

P (psi)	P (atm)	t(mv)	t(^{o}C)
1000	13500	3.85	462
2000	26300	4.32	510
3000	39200	4.70	548
4000	52200	5.00	578
5000	65500	5.40	617
6000	78500	5.62	639
7000	91800	5.83	659
8000	105000	6.00	675

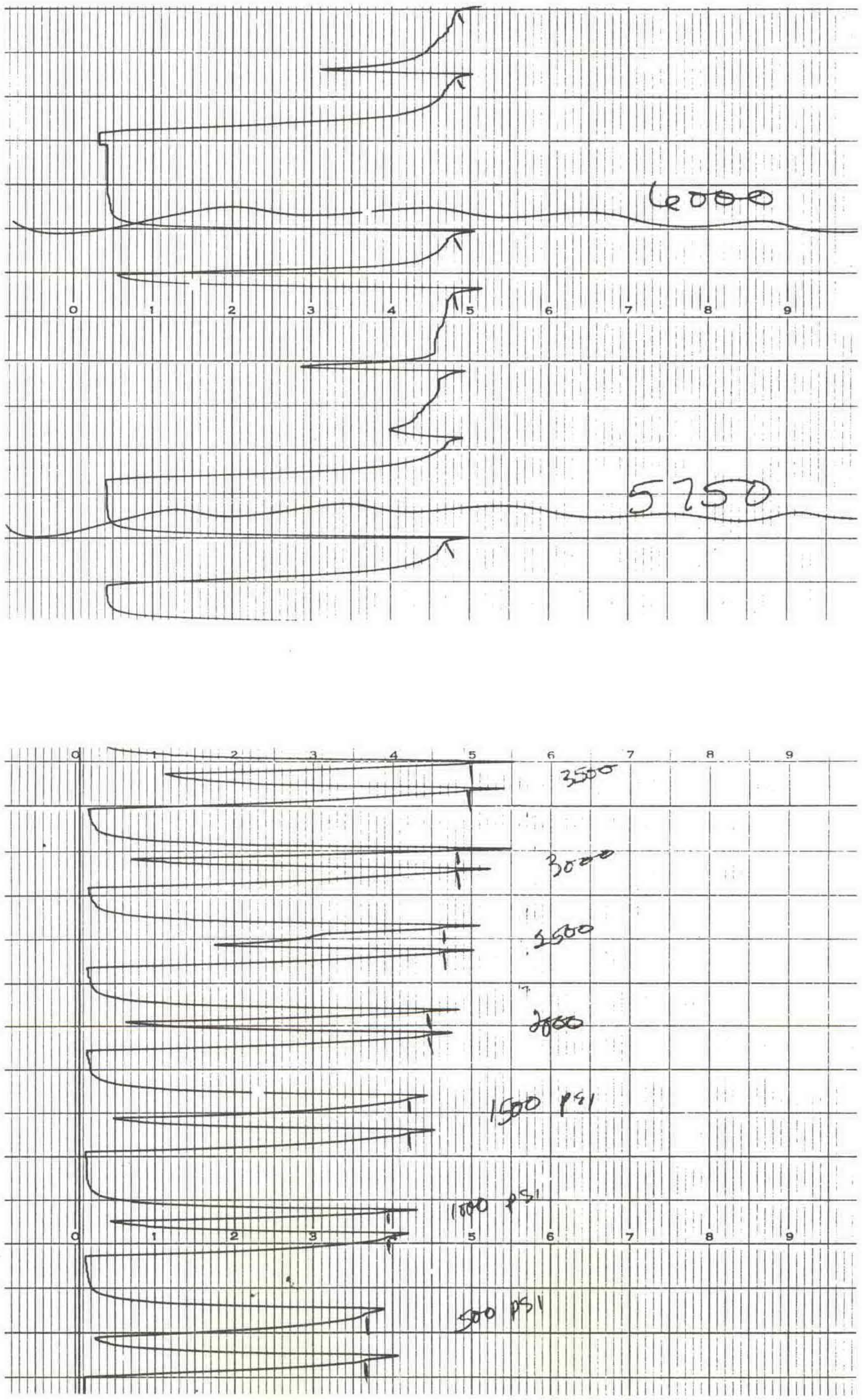


Fig. 8.--Typical Strip-chart Record of Melting for Lead (upper) and Zinc (lower).

LIST OF REFERENCES

(1) F. Simon and G. Glatzel, Z. Anorg. Allgem. Chem. 178, 309 (1929).

(2) J.D. Dudley, "Experimental Fusion Curves of Indium and Tin to 105,000 Atmospheres," Thesis, University of Utah, June, 1960.

(3) H. Tracy Hall, "Some High-Pressure, High-Temperature Apparatus Design Considerations: Equipment for Use at 100,000 Atmospheres and 3000°C.," Rev. Sci. Instr., 29, 267-275 (1958).

(4) Dudley, loc. cit.

(5) V.P. Butuzov and M.G. Gonikberg, Zhur. Neorg. Khim. 1, 1543 (1956).

(6) R.E. Hoffman, J.B. Hudson, "High Pressure Research in Metals and Ceramics," ARL Tech. Report 60-321, 13 (1960).

(7) V.P. Butuzov, M.G. Gonikberg, and S.P. Smirnov, Doklady Akademic Nauk. S.S.S.R. 89, 651 (1953). (English translation. NSF - tr- 76 Sept. 1953).

EXPERIMENTAL FUSION CURVES OF LEAD AND ZINC TO 105,000 ATMOSPHERES

An Abstract of the Thesis of

Herbert Eugene Christensen

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

in

Physics

H. Tracy Hall — Chairman, Advisory Committee
Harvey Fletcher, Jr. — Member, Advisory Committee

Brigham Young University

May, 1961

ABSTRACT

The experimental fusion curves for lead and zinc have been obtained to 105, 000 atmospheres. The fusion point in lead was detected by means of a sharp change in electrical resistance accompanied by a sharp rise in temperature, using the lead sample as its own heater. In zinc the fusion points were detected by heating the sample indirectly and observing latent heat on a temperature vs. time strip-chart recording. The melting point of lead rises smoothly from the normal value of 327.3°C to 730°C at 105, 000 atmospheres. The melting point of zinc also rises smoothly from 419.5°C to 670°C at 105, 000 atmospheres. No phase transitions were observed for lead or zinc.

Simon's equation was fitted to each of the afore mentioned fusion curves with the results that for lead a = 7,560 atmospheres and c = 3.38. For zinc a = 16, 400 atmospheres and c = 4.19.

The maximum deviation between the experimental curve and the curve from Simon's equation is 5.7% for lead and 0.7% for zinc.

APPROVED

H. Tracy Hall, Chairman
Advisory Committee

Harvey Fletcher, Jr., Member
Advisory Committee