Fusion Curves of Four Group VIII Metals to 100 000 Atmospheres

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The fusion curves of Ni, Pt, Rh, and Fe have been experimentally determined to 100 000 atmospheres. At this pressure, the melting points of the pure metals were: Ni, 1670±10°C; Pt, 2070±15°; Rh, 2400 ±15°; Fe, 1740±10°. The Pt and Rh values were extrapolated by Simon's fusion equation which fitted all of the data quite well and enabled the volume changes at the mp to be computed. $\Delta V/V_s$ for the four metals were: Ni, 0.06±0.01; Rh, 0.12±0.03; Fe, 0.03±0.005. The constants of Simon's equation differed considerably from their theoretical values but a functional relationship appears evident between Simon's exponent c and the Grüneisen constant γ.

INTRODUCTION

THE full development of the theory of solids must include an interpretation of the fusion curves of these solids. A number of attempts have been made in this direction for metals (see reference 16, 20–23) but these were hampered by total lack of data on the high-melting-point metals. As the result of recent advances in high-pressure techniques[1,2] it has become possible to measure very high melting points at pressures up to approximately 100 000 atmospheres. As a contribution to the problems in the theory of solids there are presented here data on the melting points of four group VIII metals: Ni, Pt, Rh, and Fe. The detailed data on Fe are presented elsewhere but are summarized in this paper.

It will be seen from the nature of these results that certain revisions will be required in existing theories of fusion.

EXPERIMENTAL METHODS

Under very high pressures, the melting point (mp) of metals can be determined by observing the temperatures at which one or more of the following occurs: (1) a sharp change in electrical resistance; (2) a maximum reading followed by erratic response in a thermocouple formed between the specimen and one of its higher-melting alloys; (3) a temperature step in a rising temperature-time curve due to absorption of the latent heat of fusion. All three of these means of detection were used in this work, variously adapted to the needs of the particular metal.

(a) Nickel

The methods used in determining the melting point of Ni are illustrated in Figs. 1 and 5. In the arrangement shown in Fig. 1(a), a rod of spectroscopic grade Ni (99.999% Ni)[3] was surrounded by a pure magnesium oxide sleeve. Into its center were inserted Pt-Pt+10% Rh (P-PR) and Ni-Ni+20% Co or (in a few tests)

Ni-Fe thermocouples. The Ni wire was drawn from spectroscopic grade Ni, which was also used with electrolytic cobalt to form the Ni-Co alloy. According to metallurgical charts,[4] all Ni-Co alloys have higher melting points than Ni, and Fe-Ni alloys melt higher than Ni up to about 40% Ni. This was also found to be true at all elevated pressures. The P-PR thermocouple was used to calibrate the Ni-NiCo or Ni-Fe thermocouples to within 10° or 20° of the mp. From this temperature on towards the mp, the P-PR voltage output began to drop, probably due to diffusion of Ni into the Pt. Hence the final mp temperature was measured by the extrapolated calibration of the auxiliary thermocouple.

The rod was heated by passing an electric current through it. The heating current, voltage across the specimen, P-PR voltage output, and Ni-NiCo voltage output were all recorded. At the mp the voltage increased, current decreased sharply, and both thermocouples showed a maximum reading. This behavior is illustrated in Fig. 2 for an experiment run at 60 000 atmos. A plot of Ni-NiCo voltage *vs* P-PR temperatures at different pressures is illustrated in Fig. 3.
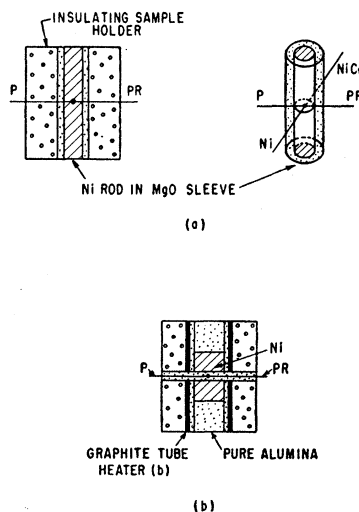

FIG. 1. Sample structures for mp of Ni: (a) by resistance change and thermocouple maximum; (b) by temperature step at mp.

[1] "Man-made Diamonds," General Electric Company Research Information Services, Schenectady, 1955 (unpublished).
[2] Bundy, Hall, Strong, and Wentorf, Jr., Nature **176**, 51 (1955).
[3] A few tests were also made on 99.85% Ni.
[4] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

The presence of a Pt wire in the Ni rod had little or no effect on the observed mp. Massive melting of the rod occurred before there was opportunity for Pt to alloy with the Ni. Further, mp's obtained as described below when Pt was not in contact with the Ni gave identical results. And finally, metallurgical charts[4] show that Ni-Pt alloys have mp's equal to or higher than Ni. In this case, fully alloyed Ni would contain <0.8% Pt and <0.04% Rh.

In the arrangement shown in Fig. 1(b), spectroscopic grade Ni was entirely inclosed in pure alumina and heating was done by a graphite sleeve surrounding the specimen. A thermocouple in an alumina tube was located in the center of the Ni to record the rising temperature and the location of the temperature step when melting occurred. As soon as the Ni melted, a little of the molten Ni invariably found its way into the graphite heater sleeve causing a sharp increase in heating current and temperature. Upon cooling a temperature step also occurred at the solidification point.
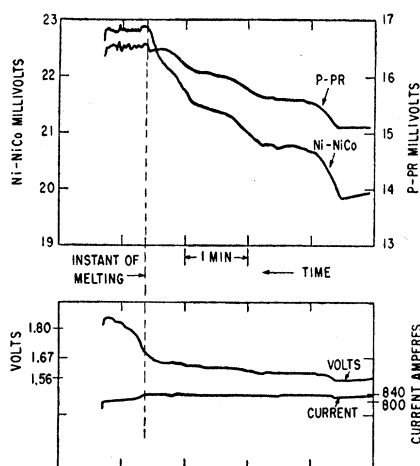

FIG. 2. Thermocouple, voltage, and current recordings at the mp for Fig. 1(a) sample at 60 000 atmos.

The freezing point usually occurred at a slightly lower temperature than the melting point, due either to supercooling or to solution of some carbon in the nickel. A thermocouple recording from the vicinity of the mp is illustrated in Fig. 4 along with heater current and voltage recordings for an experiment run at 45 000 atmos.

A third method was to heat a Ni-NiCo thermocouple by passing an ac heating current through it while simultaneously observing the thermal emf generated at the junction. Filter circuits were used to isolate the ac heating power from the dc thermocouple circuit. The sample structure and electrical circuits are illustrated in Fig. 5. The Ni-NiCo temperature calibration was taken from Fig. 3. At the mp, an abrupt maximum in thermocouple output and increase in electrical resistance were recorded. Due to a certain amount of scatter in the calibration, this method for Ni melting
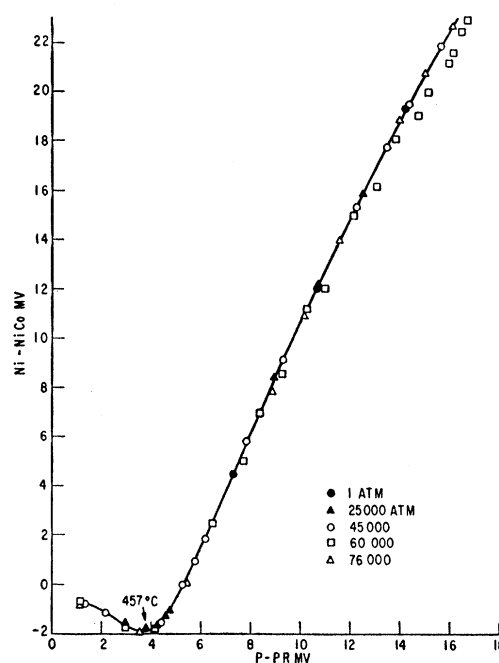

FIG. 3. Ni-NiCo and P-PR thermocouple voltage outputs compared at different pressures.

points was not so accurate as one that included a P-PR thermocouple. However it was adequate for extending the mp's to 100 000 atmos.

(b) Platinum

In melting platinum, the specimen itself was used as one branch of a P-PR thermocouple and the ac heating power was passed directly through the thermoelectric junction. According to metallographic charts,[4] PtRh melts at least as high as Pt. Two types of sample constructions were used and these are illustrated in Fig. 6. Sample (a) was handled in the same way as described for the Ni-NiCo junction (Fig. 5). Because Pt has a lower resistivity than PtRh, the Pt wire was tapered near the junction to raise its resistance and insure sufficient heat generation in the Pt to melt it ahead of the PtRh.

In the second type of Pt sample, shown in Fig. 6(b), a Pt rod was used as the heating element and a Rh wire was placed tangent to the rod at mid-span forming a thermocouple junction at the point of melting. No dc
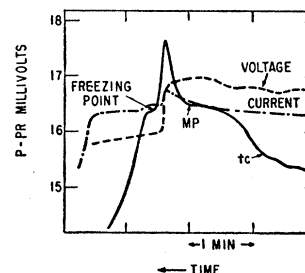
FIG. 4. Thermocouple, current, and voltage record at mp for sample as in Fig. 1(b) in experiment run at 45 000 atmos.
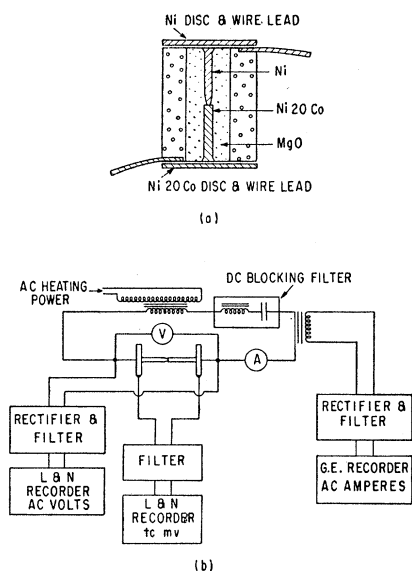
FIG. 5. Sample structure, thermocouple, and heating circuits for observing the mp of a directly heated Ni-NiCo thermocouple.

blocking was required in the ac heating circuit since there was no ac connection to the cold PtRh side of the thermocouple. However, an ac rejecting filter was necessary in the thermal emf recording circuit since half the ac heating voltage was impressed on the thermocouple circuit. Heating voltage and current were recorded to aid in locating the exact time of melting on the thermal emf record.

The method of Fig. 6(a) gave the more consistent results.

(c) Rhodium

Technically the mp of rhodium was the most difficult to obtain because there was no calibrated thermoelectric material available having a still higher mp. It was necessary to read the temperature on a Pt-Rh thermocouple as far as possible. Then a plot of temperature in terms of power input to the heated rhodium wire was used to extrapolate the sample temperature up to the mp. The mp was identified by a sudden sharp increase in voltage and decrease of the heating current through the specimen. The current and voltage were continuously recorded so that the mp could be accurately located.

The calibration of the Rh-Pt thermocouple was taken from the American Institute of Physics Handbook, 1957. As this calibration extended only to 1500°C it was extrapolated beyond this. The Pt part of the thermocouple has the lower melting point, limiting the temperature range of indication. The mp of Pt rises with pressure so that at pressures of the order of 100 000 atmos, temperatures to 2000°C could be read with fair reliability. Beyond this, the heating power was used to estimate the temperature.

The sample arrangement for melting rhodium, while similar in principle to that for melting platinum [Fig. 6(b)], had to be modified somewhat due to a peculiar behavior of rhodium at temperatures in the neighborhood of 1000 to 1400°C. When using rhodium end disks to contact the rhodium rod specimen, the rod invariably separated from the end disk in this temperature range. It was strongly indicated that a volume shrinkage had occurred. To overcome this difficulty it was necessary to use Pt end disks in place of the Rh disks; then the Pt followed the Rh in its volume shrinkage and maintained electrical contact. Both thermoelectric contacts were then made directly on the Rh rod as illustrated in Fig. 7(a). It was necessary to both wrap and spot-weld the thermocouple wires to the Rh rod to prevent loss of contact here also.

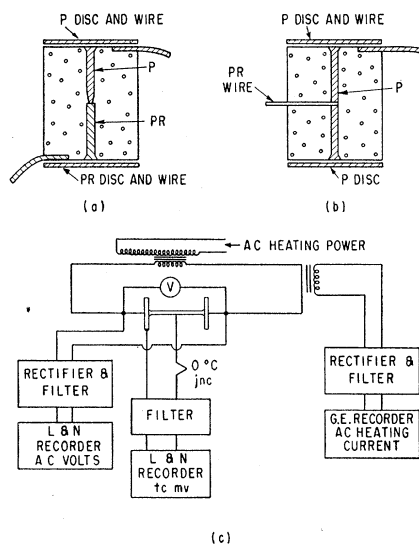If there was a phase transition in Rh under high

FIG. 6. Two arrangements for observing the mp of Pt. Sample (a) required the circuit illustrated in Fig. 5.

pressure and temperatures, it was observed only by the apparent volume decrease. The electrical resistance followed a fairly smooth curve all the way to the mp. Metallurgical handbooks give no indication of a high-temperature phase change in Rh at atmospheric pressure.

In addition to the mp's for Pt and Rh detected by a thermocouple as described above, several passes over the fusion curves of both metals were made without thermocouples by observing the heating power at which an abrupt increase in electrical resistance occurred indicating that the metal had melted. The temperature of the cell was previously found to be consistently reproducible and linearly proportional to the heating power in the experiments with thermocouples. The mp's interpreted from power input were accurately in agreement with thermocouple mp data and helped to show

that alloying of specimen with its thermocouple wire in previous experiments did not occur in such a manner as to bias the result.

The platinum and rhodium specimens used in this work were of thermocouple or cp grade.

The high-pressure apparatus of Hall's[5] general design was used in most of this work with the exception of some Ni mp's which were obtained in a modified apparatus.[6]

PRESSURE CALIBRATION

Bismuth, thallium, cesium, and barium undergo sharp electrical resistance transitions under high pressure and have so far been the only means for calibrating high-pressure apparatus. Bridgman[7] discovered these transitions and established the pressures at which they occur by containing them in silver chloride and squeezing them between flat-faced anvils, using force divided by area to compute the pressure. The bismuth transition at 24 800 atmos was also obtained in a pressure cell in which a true fluid was used for pressure transmission and so is known very accurately ($\pm$150 atmos). The
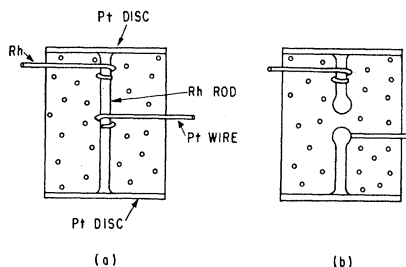

FIG. 7. Method for observing the mp of Rh: (a) Sample before melting; (b) sample after melting.

thallium (43 400 atmos), cesium (53 500), and barium (77 400) transitions were obtained between flat-faced anvils only and the accuracy at the highest pressure was estimated to be $\pm$5%.

The pressure apparatus used in this work has a linear chamber pressure vs press load characteristic over the range from 24 800 to 77 400 and possibly beyond.[8] Bundy[9] has recently used this characteristic to locate a second room-temperature Bi transition at 120 000 atmos. Because the chamber pressure proved to be linear with press load, only the Bi and Ba transitions were generally used to establish the pressure calibration. Considerably below 24 800 atmos, the pressure in terms of press load was not always linear. In this region, the mp of Bi has been used as a means of pressure calibration since the mp of Bi as a function of pressure has

been accurately measured under hydrostatic conditions by Bridgman[10] and Butuzov et al.[11]

To calibrate the chamber pressure it was necessary to substitute Bi and Ba wires, surrounded by silver chloride sleeves, for the mp specimen. The press load for which the characteristic resistance transition occurred was the press load used to establish the same pressure in a mp test. It is known that different cell geometries, the introduction of materials having differing compressibilities, and plastic yield characteristics all have some influence on the pressure calibration at room temperature. Further, the central core of the chamber was heated to temperatures exceeding 2000°C and the influence of thermal expansion of the core upon pressure has not been completely evaluated. However, certain experimental results have been helpful. The mp's of metals measured in a variety of cell geometries with the volume of the heated zone ranging between 1/6 and 1/200 of the total cell volume were the same within the experimental error of temperature measurement. Possibly because the central core is surrounded by a large cushion of a rather compressible material and because the very high temperature of the central core renders it relatively soft, pressure differences due to the factors mentioned tend to disappear. It is believed that the pressures quoted in this work are within $\pm$10% of their true absolute values, with the positive error favored on account of the high temperatures that prevail.

TEMPERATURE MEASUREMENT

Platinum, platinum-10% rhodium (P-PR) thermocouples were the primary means of temperature measurement in this work. The question was, what is the effect of pressure on the handbook values of the voltage-temperature calibration of a P-PR thermocouple. Tests on the influence of pressure on thermal emf have been made by Bridgman[12] and Birch.[13] The pressure effect was practically negligible for some thermocouple pairs, viz., chromel-alumel, but quite large for certain other metals. Both positive and negative thermal emf-pressure effects were observed. We are not aware of a theoretical approach to this problem.

In order to place some limits of reliability on the P-PR thermocouple at high pressure, the following experiments were performed. A P-PR thermocouple was subjected to pressures up to 100 000 atmos while comparing its voltage reading with an external ice junction. No variation in thermal emf due to pressure was observed to within $\pm$0.005 mv. The thermocouple pairs P-PR, P-Ni have been simultaneously compared to temperatures of 1300°C and pressures of 55 000

[5] H. T. Hall (to be published).
[6] H. M. Strong (to be published).
[7] P. W. Bridgman, Am. Acad. Arts Sci. 81, 165 (1952).
[8] H. T. Hall, J. Phys. Chem. 59, 1144 (1955).
[9] F. P. Bundy, Phys. Rev. 110, 314 (1958).

[10] P. W. Bridgman, Phys. Rev. 57, 235 (1940).
[11] Butuzov, Gonikberg, and Smirnov, Doklady Akad. Nauk. S.S.S.R. 89, 651 (1953); (translation: National Science Foundation NSF-tr-76, Sept. 1953).
[12] P. W. Bridgman, Physics of High Pressure (G. Bell and Sons, London, 1952), Chap. 10.
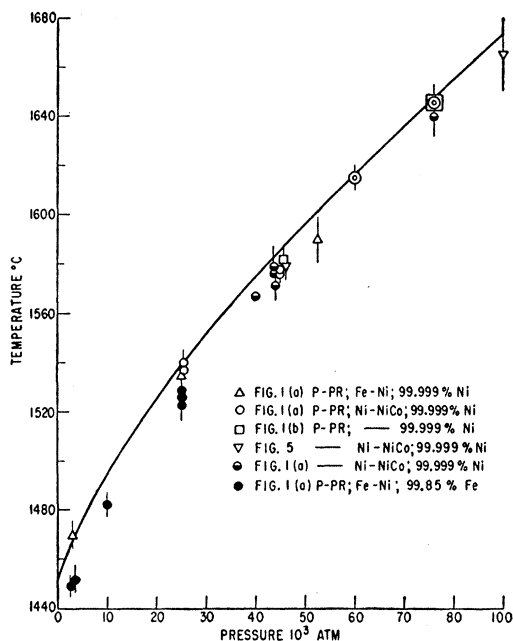[13] F. Birch, Rev. Sci. Instr. 10, 137 (1939).

FIG. 8. Fusion curve of nickel.

atmos without any significant deviations appearing when P-PR emf's were plotted against P-Ni emf's at different pressure levels. However in the same experiments, Fe-Ni emf's did deviate about 100° from P-PR at 55 000 atmos and 1300°C. P-PR and Ni-Ni20Co thermocouples have been compared to 76 000 atmos and 1600°C. Maximum deviations observed were ±20°C but were not entirely systematic with pressure. P-PR, Ni-Ni20Co and chromel-alumel (C-A) thermocouples were compared to 1000°C and 50 000 atmos in an experiment especially designed to eliminate temperature gradients. The greatest deviations found were 10° between the P-PR and C-A junctions and 20° between the P-PR and Ni-Ni20Co junctions.
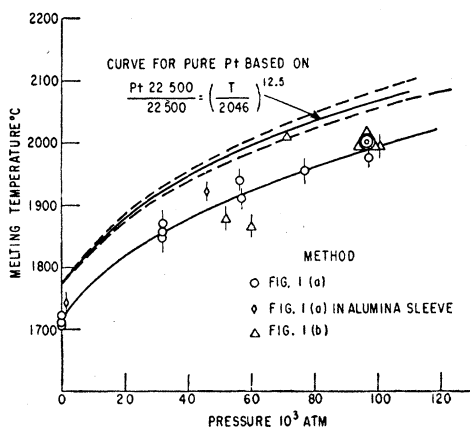

FIG. 9. Fusion curve of platinum. Lower curve: experimental data; upper curve: Simon's equation for pure Pt using constants from lower curve.

Because the thermal emf's of most of these different thermocouples differed not more than 20° from one another it was concluded that P-PR thermocouples used for measuring mp's were accurate to ±20° at least and probably to ±10°.

RESULTS

All four of the metals tested expand upon melting; hence their mp's increase with pressure. The melting temperatures measured at various pressures are plotted in Figs. 8, 9, and 10. Estimated errors in individual temperature readings are indicated in the charts but the indicated errors do not take into account possible errors due to the influence of pressure on P-PR temperature calibration.

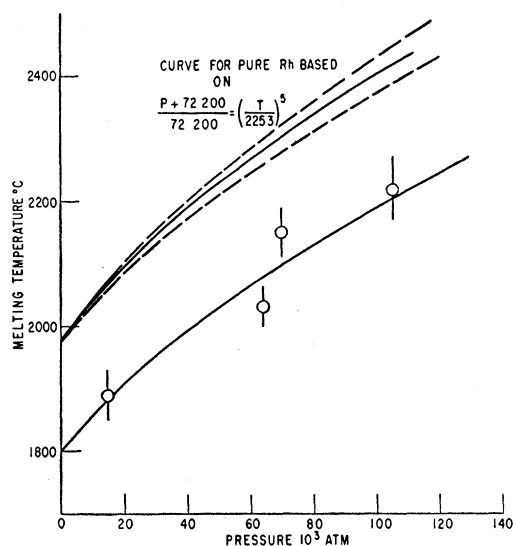The mp's were sensitive to small amounts of im-

FIG. 10. Fusion curve of rhodium. Lower curve: experimental data; upper curve: Simon's equation for pure Rh using constants from lower curve.

purities. For example, 0.15% impurity in Ni reduced its mp about 15°. Both Pt and Rh, although of thermocouple (or cp) grade, melted 60° and 170° respectively below their handbook quoted values. This was probably due to contamination picked up from the sample holders. The mp of Pt increased 30° to 1740°C at one atmosphere when the Pt wire was surrounded by a pure alumina sleeve.

Simon's fusion equation[14] could be fitted to all of the experimental melting point data. Simon's equation is

$$(P+a)/a = (T/T_0)^c, \qquad (1)$$

in which a is closely related to the "internal pressure," T_0 is the mp at the origin of the fusion curve, in this

[14] Sir Francis Simon, Z. Elektrochem. **35**, 618 (1929); Trans. Faraday Soc. **33**, 65 (1937); Sir Francis Simon and G. Glatzel, Z. anorg. u. allgem. Chem. **178**, 309 (1929).

case one atmos, and T the mp at pressure P. a and c are constants to be determined from experimental data. Differentiation of Eq. (1) gives the slope of the fusion curve at any point. At the origin, the slope so obtained can be equated to the Clausius-Clapeyron expression and this enables one to calculate the volume change associated with melting at the origin of the fusion curve. Thus, from Eq. (1) and the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{ca}{T_0} = \frac{L}{T_0 \Delta V} = \frac{\Delta S}{\Delta V},\qquad(2)$$

in which L, ΔS, and ΔV are the latent heat, entropy change, and volume increase of melting, respectively. The experimental values of c and a, along with their estimated errors due to pressure and temperature measurement and the computed values of $\Delta V/V_S$, are listed in Table I.

There are no direct measurements on the volume changes due to melting for any of the metals listed except Fe and in this case the agreement between the

TABLE I. Constants of Simon's equation and volume change at the melting point.

Element	a (atmos)	c	T_0 (°K)	(dP/dT) (atmos/ deg)	V_S[a] at mp	ΔS	$\Delta V/V_S$
Ni	40 700±5000	10±1	1726	236	7.1	2.44	0.06 ±0.01
Pt	22 500±3000	12.5±3	2046	138	9.7	2.5	0.07₇±0.01
Rh	72 200±7000	5±1	2253	160	5.4	(2.5)[b]	0.12 ±0.03
Fe[c]	75 000±5000	8±1	1805	332	7.7	2.0	0.03₂±0.005

[a] V_S =atomic volume of solid at its mp.
[b] There are no data on ΔS for Rh available in the handbooks. The value 2.5 was assumed on the basis that other similar metals have about this value.
[c] See also H. M. Strong, J. Geophys. Research 64, 653 (1959).

value in Table I and the directly measured value, $3.1\pm0.5\%$,[15] is very close.

Using the values for a and c given in the table, the fusion curves for Pt and Rh were drawn in Figs. 9 and 10 starting at the mp's for the pure metals. The experimental data for Ni seemed to fit in with the one-atmosphere mp.

The indicated volume changes occurring at the mp for Pt, Ni, and Rh were surprisingly large. Except for the fact that the ΔV obtained for iron agreed closely with the directly measured value, one would suspect that the actual pressures existing at the instant of melting were substantially larger than those indicated by the normal calibration procedure. At the present time no fully satisfactory method has been found for making an absolute pressure calibration.

Rhodium stands out in Table I as an unusual case. While difficulties were encountered in obtaining its mp, it does not seem possible that, allowing for experimental errors, its volume change could be brought into

[15] V. H. Stott and J. H. Rendall, J. Iron Steel Inst. (London) 175, 374 (1953).
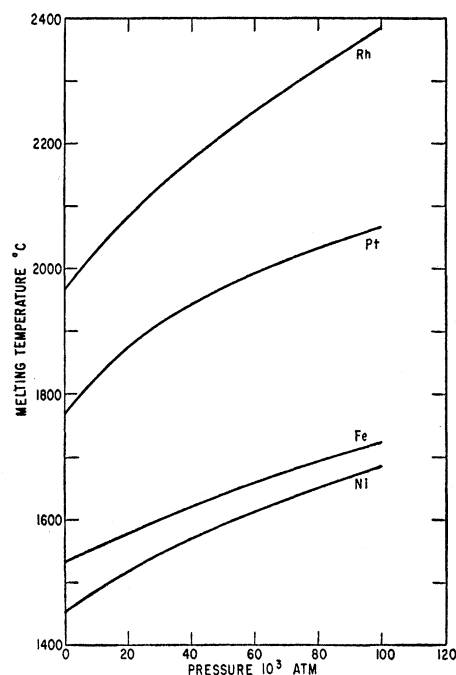

FIG. 11. Fusion curves for pure Fe, Ni, Pt, and Rh. Pt and Rh curves from Simon's equation for pure metal.

line with the other metals. Perhaps the apparent volume shrinkage at the lower temperature is recovered at the mp and to this is added the normal volume increase of melting.

A summary of the experimental fusion curves of the four metals is presented in Fig. 11 for comparison.

DISCUSSION

Simon's fusion equation has now endured a considerable amount of experimental and theoretical examination. Because it applies in so many cases, e.g., the fusion curve for solidified argon and helium,[16–18] the alkali metals,[16] and now the group VIII metals,[19] it

TABLE II. The constants a and c of Simon's equation for group VIII metals.

Element	γ reference 24	c Eq. (4)	c exptl.	a (atmos) Eq. (3)	a exptl.
Ni	1.88	1.32	10	130 000	40 700
Pt	2.54	1.22	12.5	140 000	22 500
Rh	2.2[a]	1.26	5	125 000	72 200
Fe	1.60[b]	1.39	8	110 000	75 000

[a] This value is not listed in reference 24. It was calculated from $\gamma = (\alpha/\kappa)(V/C_V)$ using P. W. Bridgman's [Am. Acad. Arts Sci. 77, 187 (1949), $\Delta V/V_0 =0.00180$ at 5000 atmos.] data on compressibility, κ. γ was also interpolated from data in Grüneisen's tables[24] for Fe, Co, Ni, Pt, and Pd. In both cases, 2.2 was obtained.
[b] Gilvarry used $\gamma =0.92$ at the mp, for which $c =1.9$.

[16] Francis Simon, Nature 172, 746 (1953).
[17] Simon, Ruhemann, and Edwards, Z. physik. Chem. B6, 62 (1929).
[18] Holland, Huggill, Jones, and Simon, Nature 165, 147 (1950).
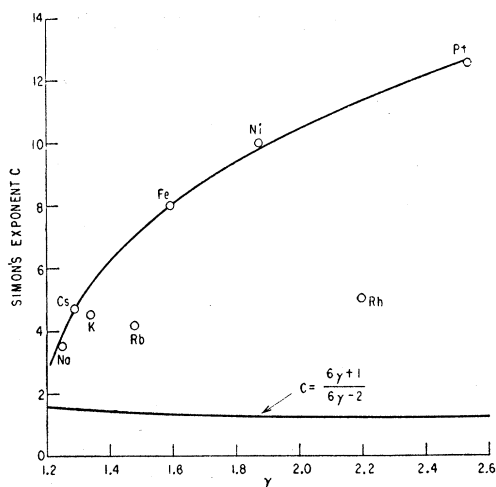[19] See also H. M. Strong, J. Geophys. Research 64, 653 (1959).

FIG. 12. Simon's exponent c in terms of the Grüneisen constant.

must contain fundamentally correct concepts concerning some of the properties of matter.

A large amount of theoretical effort[20–23] has already been applied in attempts to justify the form of the equation and to give meaning to the constants a and c. Simon[14,16] and Salter[22] interpreted a as being closely related to the internal pressure and attempted to approximate the value of a from the thermodynamic relation[24]

$$a = (\partial u / \partial V)_T = \gamma C_V T_0 / V, \qquad (3)$$

at the mp for 1 atmosphere pressure. Salter[22] and Gilvarry[23] obtained an expression for c in terms of the

Grüneisen constant[24] γ:

$$c = (6\gamma + 1)/(6\gamma - 2). \qquad (4)$$

As γ for metals is usually in the range 1 to 3, c assumes values from 1 to 2. Just how well these interpretations of the constants fit the experimental data can be seen by reference to Table II for the group VIII metals and references 16 and 22 for the alkali metals and argon. These data show that a from Eq. (3) was too low for the alkali metals and too high for the group VIII metals. The exponent c from Eq. (4) was much too low in all cases except argon where the calculated value was 1.12 and experimental values 1.16, 1.228, and 1.478 were obtained (see collected data in reference 22).

While the functional relationship between c and γ expressed by Eq. (4) seems to give the correct c in isolated cases, it does not apply to the alkali metals or the group VIII metals for which experimental data have been obtained. That a functional relationship between c and γ may exist is suggested by a plot of c and γ in Fig. 12. All except Rh fit fairly well on a smooth curve. Since rhodium has already demonstrated its unusual properties in its volume shrinkage at $\sim 1000°C$ and a large ΔV at the mp, its nonconformity on the c-γ plot is perhaps not surprising.

Apparently, the accuracy of an extrapolation of mp's to much higher pressures by Simon's equation will depend to some extent on the constancy of γ along the fusion curve. As suggested by Gilvarry,[23] it is reasonable to expect some variation of γ and this would lead to a slow drifting apart of the extrapolated and true fusion curves.

ACKNOWLEDGMENTS

[20] C. Domb, Phil. Mag. 42, 1316 (1951).
[21] J. DeBoer, Proc. Roy. Soc. (London) A215, 4 (1952).
[22] L. Salter, Phil. Mag. 45, 369 (1954).
[23] J. Gilvarry, Phys. Rev. 102, 308 (1956).
[24] E. Grüneisen, Handbuch der Physik (Verlag Julius Springer, Berlin, 1926), Vol. 10, p. 1–59. See also J. K. Roberts and A. R. Miller, Heat and Thermodynamics (Interscience Publishers, Inc., New York, 1951).