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PRESSURE DEPENDENCE OF THE emf OF THERMOCOUPLES TO 1300°C AND 50 KBAR

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Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 36, No. 2, 523-528, February, 1965
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Pressure Dependence of the emf of Thermocouples to 1300°C and 50 kbar

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(Received 6 July 1964)

The relative and absolute effects of pressure on the emf of commonly used thermocouples were measured to 1300°C and 50 kbar. The relative temperature corrections due to the effect of pressure are presented for Pt/Pt10Rh, Pt/Pt13Rh, Chromel–Alumel, and iron–constantan thermocouples as a function of temperature and pressure. The accuracy of these relative temperature corrections is approximately ±1°C and their magnitudes can exceed 40°C in some cases. The absolute corrections of these thermocouples are approximately determined by: (1) correlating experimental and theoretical results on the boundary conditions for the diamond ⇄ graphite equilibrium, (2) relating experimental and calculated results for the effects of pressure on other single-component phase transformations, and (3) evaluating theoretical and experimental results for diffusion at high pressures and high temperatures.

The absolute temperature corrections for all of the thermocouples investigated are proportional to the pressure at a given temperature. The magnitude of the absolute correction ΔT can exceed 50°C, as in the case of Pt/Pt10Rh at 50 kbar and $T>1300$°C.

I. INTRODUCTION

IN the past few years increasing effort has been devoted to numerous types of high-temperature–high-pressure studies. One of the serious limitations in many of these studies is a knowledge of the pressure dependence of the emf of thermocouples. There is, in addition, a need to know the relative effects of pressure on various types of thermocouples in order to compare the published results of various workers. The few previous studies[1,2] of the effects of pressure on thermal emf have been primarily limited to measurements up to only 100°C. The purposes of the present study are twofold: first, to determine the relative differences of thermal emf of several commonly used thermocouples up to 1300°C and over the pressure range 0 to 50 kbar; second, to approximately determine the absolute temperature corrections of commonly used thermocouples as a function of temperature and pressure.

II. DETERMINATION OF THE EFFECTS OF PRESSURE ON THE RELATIVE DIFFERENCES OF THERMAL emf OF THERMOCOUPLES

When the emf's of two different kinds of thermocouples exposed to identical temperatures and elevated pressures are referred to standard thermocouple tables, there is an apparent temperature discrepancy as long as the temperature gradient lies within the pressure zone. As the pressure approaches one atmosphere this discrepancy disappears. In order to evaluate this relative correction it was necessary to design a high-pressure cell in which two types of thermocouples could be simultaneously submitted to identical pressure and temperature conditions.

A schematic of the cells used in the present study is shown in Fig. 1. This cell was used in a GE "Belt" high-pressure apparatus.[3] The thermocouples were passed through thin boron nitride sleeves into a small center plug of the same material with their junctions just touching at the center. The center plug was surrounded by pressed sodium chloride which acted as a hydrostatic bath at temperatures above its melting point. Heating was accomplished by an internal graphite heater. Upon equilibration the emf's of both thermocouples were read simultaneously and this procedure was repeated as a function of pressure and temperature up to 50 kbar and 1300°C. Thermocouples used in this comparative procedure were: Pt/Pt10%Rh, Chromel–Alumel, iron–constantan, and Pt/Pt13%Rh. Thermocouple deterioration of Chromel–Alumel due to attack by the ambients was noted in Chromel–Alumel and iron–constantan after long times at high temperatures. Deterioration occurred much more readily at high temperatures when the Chromel–Alumel was in contact with pyrophilite instead of boron nitride. All data was rejected when any evidence of deterioration was found.

The experimental data of the differences of apparent temperature readings based on standard thermocouple emf tables are shown in Fig. 2, 3, and 4. The data are plotted as the difference in apparent readings ΔT versus the apparent reading of one of the thermocouples. Cross-comparison of any two types of thermocouples can be readily made by combination of the information on the appropriate two figures. Figure 2 shows a plot of the discrepancy between Pt/Pt10Rh and Chromel–Alumel couples up to 1300°C at 20, 40, and 50 kbar. The only previous reliable data published relating Chromel–Alumel to Pt/Pt10Rh were those of Bundy,[2] which were

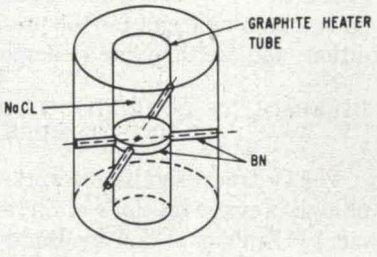


FIG. 1. Schematic of high-pressure sample holder for determination of relative thermocouple corrections.

[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **53**, 269 (1918).
[2] F. P. Bundy, J. Appl. Phys. **32**, 483 (1961).
[3] H. T. Hall, Rev. Sci. Instr. **31**, 125 (1960).

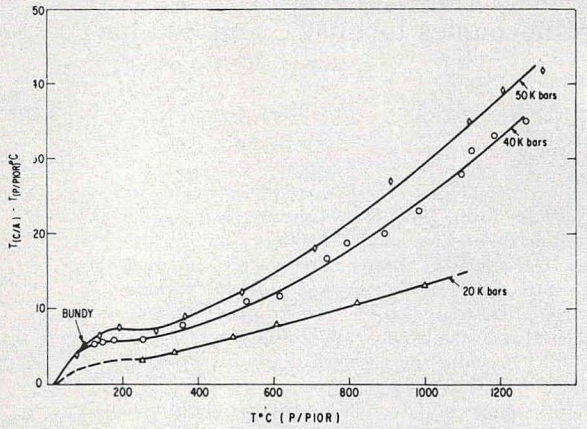


FIG. 2. Relative correction of Pt/Pt10Rh against Chromel–Alumel.

limited to a temperatue gradient of 100°C. Bundy's data are in excellent agreement with our data over the same temperature gradient and range. However, Fig. 2 shows clearly the dangers of extrapolating low-temperature thermocouple corrections to high temperature. It is also important to note that the relative thermocouple corrections become quite large and positive for Chromel–Alumel versus Pt/Pt10Rh (i.e., $\Delta T > 40$°C at 50 kbar and 1300°C).

It may be observed from the data of Fig. 2 that at a fixed temperature the correction ΔT is approximately proportional to the applied pressure. This observation is in agreement with the findings of Bundy.[2]

Figure 3 shows a plot of ΔT for Chromel–Alumel versus Pt/Pt13Rh at 40 kbar which gives a similar result except that at high temperatures the correction is even larger than for Pt/Pt10Rh. Figure 4 presents the ΔT data for iron–constantan versus Pt/Pt10Rh at 40 kbar and up to approximately 900°C. Note the sharp break in the data plotted in Fig. 4 at a corrected temperature of 685°C and 40 kbar. This point corresponds precisely with the $\alpha \rightarrow \gamma$ transformation in iron and demonstrates the immediate usefulness of thermoelectric data for rapid, accurate studies of phase transitions at high temperature and pressure.

Possible sources of errors to the present experiments which were experimentally evaluated in this work were: (1) electrical shunting due to conduction through the boron-nitride, (2) cold-working effects on thermocouple emf, (3) amount of temperature gradient outside the pressurized zone, and, (4) pressure gradients within the hot region of the cell. All of these effects were found to be less than a few percent of total true effect of pressure on thermocouple emf for the present experimental conditions and are therefore neglected.

III. ABSOLUTE CORRECTIONS OF THERMOCOUPLES AT HIGH TEMPERATURES

The two most significant works on the absolute effect of high pressure on emf's of thermocouples were carried out by Bridgman[1] and by Bundy.[2] These previous investigations have been limited to the temperature range up to ~100°C. Direct measurement of the absolute effects of pressure on thermal emf's to temperatures well above 1000°C is a formidable experimental problem. However, there are a number of indirect methods combining experimental and theoretical procedures to approximately determine the absolute thermocouple corrections under high pressure to this temperature range. Methods used in the present work include: (1) correlating the experimental and theoretical results on the boundary conditions for diamond growth, (2) relating experimental and calculated results for the effect of pressure on single-component phase transformations, and (3) using high-pressure–high-temperature diffusion data to determine the correction approximately. It will be shown in this section that all of these methods give independent, consistent results enabling an approximate determination of the temperature correction.

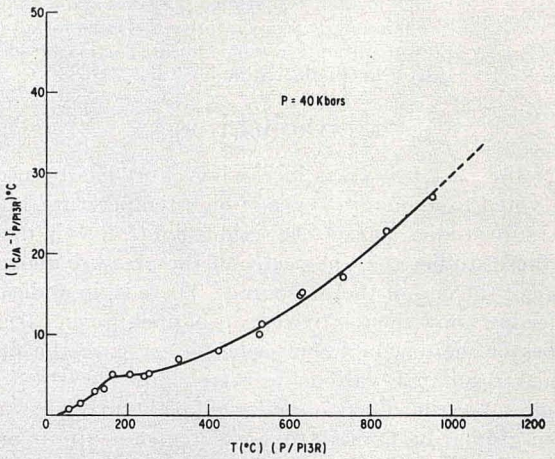


FIG. 3. Relative correction of Pt/Pt13Rh against Chromel–Alumel.

On the basis of recent measurements[4,5] it has become clear that the pressure and temperature conditions for diamond $\rightleftarrows$ graphite equilibrium presented by Berman–Simon[6] are quite accurate. From a detailed knowledge of the thermodynamic properties of carbon in the form of graphite and diamond and a knowledge of the temperature and pressure dependence of the molar volumes of each phase, they calculated that the conditions of thermodynamic stability of diamond are described by the following equation to within 5%:

$$P = 0.027T + 7.1, \qquad (1)$$

where P is in kbar and T is in °K. Experiments were carried out to define the temperature and pressure conditions at which diamonds are just barely stable to growth. In other words, the problem was to experimen-

[4] F. P. Bundy, H. P. Bovenkerk, H. M. Strong, and R. H. Wentorf, Jr., J. Chem. Phys. **35**, 383 (1961).
[5] N. L. Colburn, J. Chem. Phys. **40**, 71 (1964).
[6] R. Berman and F. Simon, Z. Elektrochem. **59**, 333 (1955).

tally determine the diamond $\rightleftarrows$ graphite equilibrium line.

Mixtures of metal catalyst and graphite with a seed diamond of known weight were exposed to numerous pressure and temperature conditions over the range 45 to 58 kbar and with apparent temperatures of 1100° to 1500°C using Pt/Pt10Rh thermocouples. The specimens were quenched under pressure and they were checked for diamond growth or dissolution by weight change in the seeds.

The internal heating of a high-pressure cell can change the pressure at fixed load with respect to the standard room-temperature pressure calibrations of Bi, Tl, Ba, and other materials. Therefore pressures were checked during diamond growth by using an internal standard of germanium, in cooler portions of the cell, whose temperature–pressure fusion curve is very well defined.[7] The experimental results of the conditions for the stable–unstable line for diamond growth (i.e., graphite $\rightleftarrows$ diamond equilibria) based on the uncorrected Pt/Pt10Rh temperatures are represented in Fig. 5 by the dotted line. The calculated Berman–Simon line which is based on true temperatures is indicated by the solid line in Fig. 5. Since diamond seeds were used during these growth experiments, no nucleation barrier

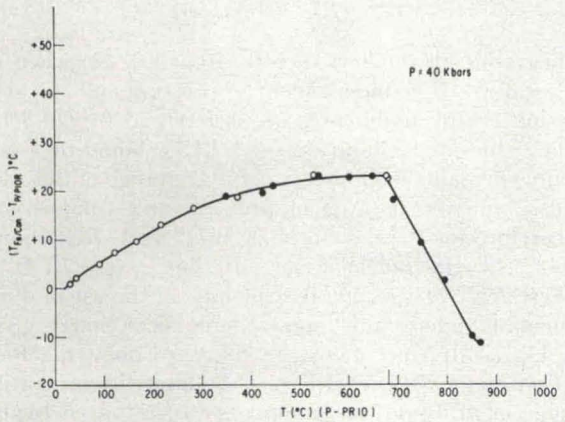


FIG. 4. Relative correction of iron–constantan against Pt/Pt10Rh.

should have existed. The lack of a nucleation barrier is also consistent with the observed $(T_{B-S}-T_{exp})$ increase with increasing temperature as is seen in Fig. 5. Thus, since the two lines should be in agreement, the discrepancy ΔT is assigned to the effect of pressure on thermocouple emf.

The second type of approach useful in independently obtaining an approximate estimate of the effect of pressure on thermocouple corrections is based upon a comparison of the experimental and calculated temperature–pressure behavior of phase transformations in single-component phase diagrams. Detailed thermodynamic calculations of the effect of high pressure on the $\alpha \rightleftarrows \gamma$ phase transformation in pure iron have been carried out by Kaufman and co-workers.[6] The detailed experimental investigations of the T vs P behavior of the $\alpha \rightleftarrows \gamma$ transformation in iron which have been made are represented in Fig. 6 up to 50 kbar with the temperatures given as uncorrected Chromel–Alumel data. The calculated diagram of Kaufman *et al.*[8] which refers to true temperatures is also plotted for comparison. It is seen that the discrepancy lies in the range 0° to +15°C for the best fit of all investigators over the range 20 to 50 kbar. The point is that this work suggests that ΔT corrections for Chromel–Alumel thermocouples in this temperature and pressure range is quite small.

The pressure dependence of the fusion curve of germanium provides another approximate check of the absolute effect of pressure on thermal emf. Probably the most accurate published experimental work on the fusion curve of germanium is that of Jayaraman *et al.*[7] which reports a slope of −3.75°K/kbar uncorrected for any thermocouple effects.

The initial slope of the fusion curve of germanium can be calculated from the Clausius–Clapeyron equation

$$dT/dP=(\Delta V/\Delta S)^{S\rightarrow L}. \tag{2}$$

Very accurate independent measurements of the volume change on melting of germanium have recently been made by Horn and Hall[9] and by Bradshaw,[10] with both workers finding $\Delta V^{S\rightarrow L}=0.99$ cm³/g-atom. The entropy of fusion is given by $\Delta S^{S\rightarrow L}=6.75$ eu,[11] giving a calculated fusion slope of $dT/dP=3.50$°K/kbar. Generally the liquid state is less dense than the solid state of a material and the liquid is expected to be more compressible than the solid which is more rigid and has less voids. However, it appears that for germanium where the density of the liquid is 7.5% greater than the den-

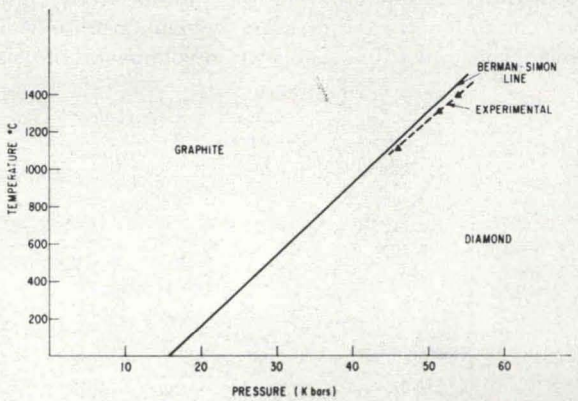


FIG. 5. Experimental and theoretical results of diamond–graphite equilibrium.

[7] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **130**, 540 (1963).

[8] L. Kaufman, E. V. Clougherty, and R. J. Weiss, Acta Met. **11**, 323 (1963).

[9] F. H. Horn and R. N. Hall, G. E. Research Laboratory (private communication).

[10] S. E. Bradshaw, Wembley Laboratories, Wembley, Middlesex, England (private communication, 1964).

[11] E. S. Greiner, J. Metals **4**, 1044 (1952).

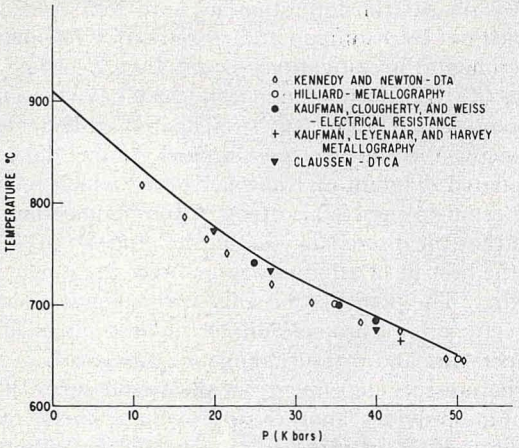


FIG. 6. Temperature–pressure behavior of $\alpha \rightleftarrows \gamma$ transformation in iron.

sity of the solid that these factors tend to compensate giving nearly equal compressibilities. The linearity of the observed fusion curve appears to support this hypothesis. Thus neglecting the effect of pressure on $\Delta S^{S\to L}$ and taking the difference of the compressibilities of solid and liquid phases as a small factor, the discrepancy between the calculated and experimental result is given by

$$\Delta T_{C-A} \approx 0.1P \text{ to } 0.2P \qquad (3)$$

along the fusion line, where P is in kilobars. Again this result would indicate that the temperature correction ΔT due to pressure for Chromel–Alumel is small and positive over the temperature and pressure conditions defined by the fusion line of germanium.

High-pressure studies of diffusion in metals and alloys are useful in two ways for estimating the absolute thermocouple correction due to the effect of pressure. One method involves determining the appropriate temperature correction at fixed pressure and composition which gives a constant value of activation volume for diffusion

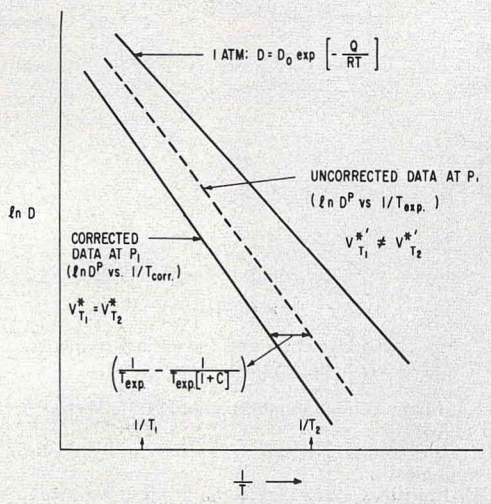


FIG. 7. Schematic plot of $\ln D$ vs $1/T$ illustrating the use of diffusion data in determination of thermocouple corrections.

over the temperature range of the experimental data while maintaining a linear $\ln D^P$ vs $1/T$ plot. The second method involves comparing experimental atmospheric and high-pressure diffusion coefficients at fixed temperatures to calculated results based on existing diffusion theories. Both methods should lead to mutually consistent results.

In single-phase systems the atmospheric diffusion coefficient D is generally found experimentally to obey a simple Arhennius equation

$$D = D_0 \exp(-Q/RT), \qquad (4)$$

where the activation energy Q and frequency factor D_0 are constants characteristic of the particular system which are temperature independent. The activation volume for diffusion has been derived from absolute reaction rate theory of diffusion by Lazarus and Nachtreib.[12] The result is

$$V^* = -RT(\partial \ln D/\partial P)|_T + RT[\partial \ln(\gamma a^2 \bar{\nu})/\partial P]|_T, \qquad (5)$$

where: $D=f(P,T)$, γ is a constant, a is the lattice parameter, and $\bar{\nu}$ is the vibration frequency. Since the second term of Eq. (5) can be shown to be small,[13] V^* can be approximated by

$$V^* = (RT/P)\ln(D/D_P). \qquad (6)$$

This result also follows directly from Eq. (4) when D_0 is assumed to be independent of pressure and the activation energy under pressure is replaced by $Q+PV^*$. The values of V^* (and thus $Q+PV^*$) should be essentially constants over the temperature range of diffusion measurements at a given pressure and composition. Therefore for these conditions, $\ln D^P$ vs $1/T_{\text{corr}}$ should obey a straight-line behavior with slope $-(Q+PV^*)/R$, where $T_{\text{corr}} = T_{\text{exp}} + \Delta T$. A schematic of the use of diffusion data to determine thermocouple corrections is given in Fig. 7. If corrections are taken to obey the form $\Delta T = cT$ at fixed pressure over the limited temperature range of diffusion measurements (as indicated by the diamond growth results), then the values of temperature in the uncorrected $\ln D^P$ vs $1/T_{\text{exp}}$ plot may be adjusted to give straight-line behavior such that V^* is a constant by selection of the suitable value for the constant c. The value of c which gives straight-line behavior is, in principle, uniquely determined at a given pressure. The resulting corrected data should be represented by

$$D^P \approx D_0 \exp[-(Q+PV^*)/R(T_{\text{exp}}+\Delta T)]. \qquad (7)$$

This method was applied to recent high-pressure interdiffusion measurements of iron–vanadium by Hanneman.[13] When the data were fitted to give linear $\ln D^P$ vs $1/T_{\text{corr}}$ behavior such that V^* is a constant for the

[12] D. Lazarus and N. Nachtreib in *Solids Under Pressure*, edited by W. Paul and D. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), Chap. III.

[13] R. Hanneman, Ph.D. thesis, MIT (1963); also R. Hanneman, H. C. Gatos, and R. E. Ogilvie, Trans. AIME (to be published).

interdiffusion coefficient $\tilde{D}$ at 40 kbar and 10 at.% vanadium for $1100°<T<1350°C$, it was found for Pt/Pt10Rh that $\Delta T \approx +0.030T$, where T is in degrees Kelvin. Analogous data at other compositions gave equivalent results.

From high-pressure binary interdiffusion studies on the iron–vanadium and iron–nickel systems[13,14] the values of V^* have been evaluated as a function of temperature at fixed concentrations and pressures in both systems. If no thermocouple correction is applied (for Pt/Pt10Rh couples) to this interdiffusion data, the following typical apparent values of (V^*/V^A) are obtained (where V^A is the atomic volume): $(V^*/V^A)^{\alpha}_{\mathrm{Fe10V}} \approx 0.4$, $(V^*/V^A)^{\gamma}_{\mathrm{Fe1V}} \approx 0.45$, and $(V^*/V^A)^{\gamma}_{\mathrm{Fe25Ni}} \approx 0.5$. On using the temperature corrections which are deduced in this section from the diamond growth data, transformation investigations under pressure and the requirement of a constant V^* at fixed *pressure and composition*, the following corrected values of (V^*/V^A) are obtained:

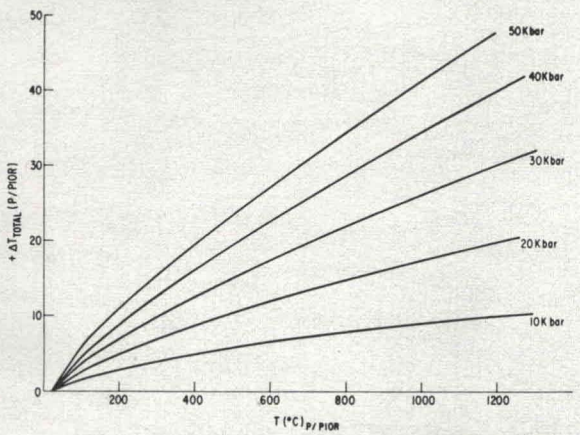


FIG. 8. ΔT_{abs} vs observed T at various isobars for Pt/Pt10Rh thermocouples. $\Delta T_{\mathrm{Total}} = \Delta T_{\mathrm{abs}} = T_{\mathrm{true}} = T_{\mathrm{exp}}$.

$(V^*/V^A)^{\alpha}_{\mathrm{Fe10V}} \approx 0.6$, $(V^*/V^A)^{\gamma}_{\mathrm{Fe1V}} \approx 0.75$, and $(V^*/V^A)^{\gamma}_{\mathrm{Fe25Ni}} \approx 0.8$. These corrected values of (V^*/V^A) are in very good agreement with previous experimental, semi-empirical and theoretical values for similar metals[12–16] and therefore the thermocouple corrections appear to be approximately right. The apparent values of V^*/V^A determined from the uncorrected temperature values are, however, far too small to be consistent with any diffusion theories or other experimental data for fcc or bcc metals.

Thus the thermocouple corrections resulting from a comparison of experimental and theoretical activation volumes are in agreement with those leading to a temperature-independent value of activation volume.

[14] J. I. Goldstein, R. E. Ogilvie, and R. E. Hanneman, Trans. AIME (to be published).

[15] R. P. Huebener and C. G. Homan, Phys. Rev. **129**, 1162 (1963).

[16] L. A. Girifalco in *Metallurgy at High Pressure and High Temperatures*, edited by K. Gschneidner (AIME, New York, 1964).

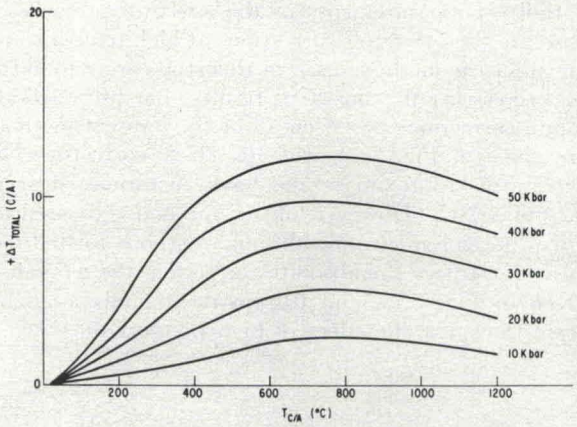


FIG. 9. ΔT_{abs} vs observed T at various isobars for Chromel–Alumel thermocouples.

IV. DISCUSSION

The curves of relative and absolute temperature corrections due to pressure implicitly include the effect of the small amount of temperature gradient outside the pressurized zone. Therefore, these corrections are directly applicable with little error to thermocouples used in any normal high-pressure cells operating in a room-temperature ambient with a 0°C cold junction. (The actual temperature gradient within the pressurized zone for the tests conducted in this work was approximately 95% of the total temperature gradient between room temperature and the hot zone.)

The relative corrections between different types of thermocouples due to the effect of pressure which were given in Sec. II of this paper are quite reproducible. The accuracy of the ΔT values given in Figs. 2, 3, and 4 is estimated to be $\sim \pm 1°C$. These corrections will permit a true comparison of high-pressure phase diagrams and other high-pressure data of any investigators using different kinds of thermocouples. It is worthwhile to emphasize that the relative differences ΔT can get quite large at high pressures and high temperatures.

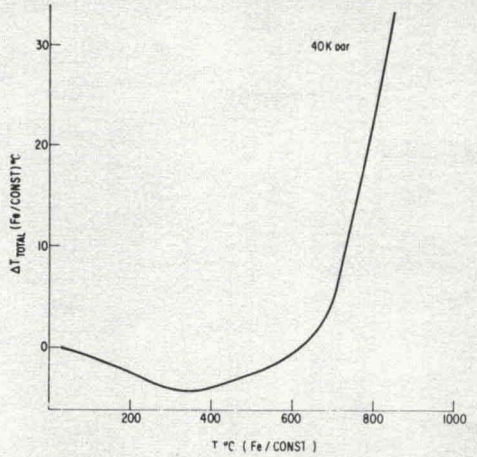


FIG. 10. ΔT_{abs} vs observed T at various isobars for iron–constantan thermocouples.

Indirect measurements of the effect of pressure on absolute thermocouple corrections at high temperatures for all of the methods used in this study were found to lead to essentially consistent results. The proposed absolute corrections based on all of the indirect methods are given in Fig. 8, 9, and 10. These corrections are necessarily approximate and have an estimated accuracy of $\pm 20\%$. However, until a method is devised for direct measurement or additional methods for indirect measurement of the absolute correction, the ΔT values given in Fig. 8, 9, and 10 provide the only available corrections for the effect of high pressure on thermocouples at high temperature. It is very important that the amount of temperature gradient lying within the pressurized zone be evaluated and reported by each worker for his experimental high-pressure cell when thermocouple measurements are made.

ACKNOWLEDGMENTS

The authors express appreciation to R. E. Tuft for assistance during some of the experiments, to F. P. Bundy for his helpful comments, and to F. H. Horn and R. N. Hall for making available their data on germanium.