

## Effect of Pressure on the emf of Chromel-Alumel and Platinum-Platinum 10% Rhodium Thermocouples

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A differential technique has been used to measure the absolute effect of pressure on the emf of Chromel-Alumel and Pt-Pt10Rh thermocouples. The experiments were conducted in a solid pressure medium piston-cylinder apparatus to 35 kbar and 1000°C. Extrapolation of these data shows Chromel-Alumel to read as much as 28°C high at 50 kbar and 1200°C and Pt-Pt10Rh as much as 28°C low at 50 kbar and 2000°C. Graphs are presented which show correction voltage versus temperature for various pressures.

### INTRODUCTION

The problem of temperature measurement in high-pressure studies has become more acute as the range of accessible pressures and temperatures has expanded. The high strengths required to contain tens of kilobars has led to extensive use of internally heated pressure cells. Such cells require temperature measuring techniques capable of accurately sensing interior temperatures through large temperature and pressure gradients. No such technique has yet proven to be free of problems.

By far the best technique to date is the use of thermocouples. Their small size and simplicity make them particularly well suited to high-pressure work. Although thermocouples have been studied extensively at room pressure, their behavior in typical high-pressure environments has not been well determined.

The emf of a thermocouple arises from the temperature dependence of the Fermi energies of the metals which make up the thermocouple. Because the Fermi energy of a metal is pressure sensitive, the calibration of a thermocouple changes with pressure. Insufficient progress has been made in the theoretical understanding of the thermoelectric effect to accurately predict this pressure dependence. A review of some of the effects involved here is presented by Bourassa *et al.*<sup>1</sup>

This paper presents our measurements of the absolute corrections for the effect of pressure on Pt-Pt10Rh and Chromel-Alumel thermocouples extrapolated to 50 kbar, and the maximum usable temperature of each thermocouple based on detailed measurements to 35 kbar and 1000°C.

Effects other than pressure contribute to the change in calibration of thermocouples as they are commonly used in high-pressure applications.<sup>2</sup> Among these are cold working of the thermoelements, electrical shunting, diffusion between thermoelements, and chemical contamination.

Figure 1 shows schematically a typical high-pressure thermocouple installation. The high-temperature junction and part of the wire, over which a substantial fraction of the temperature drop occurs, are subjected to pressure. The thermoelectric emf's generated in these pressurized sections of the thermocouple differ from those generated at 1 atm. Also, new junction emf's are

introduced at the pressure seal where the compressed and uncompressed segments of the thermoelement wires meet.

The voltage of a thermocouple may be thought of as being generated over a given temperature interval without specific reference to the junction (Peltier) and gradient (Thompson) emf's separately:

$$E = \int_{T_0}^{T_J} \sigma_{ab} dT, \quad (1)$$

where  $T_0$  and  $T_J$  are the reference and hot junction temperatures, respectively. The relative Seebeck coefficient  $\sigma_{ab}$  includes both the junction and gradient effects and is commonly known as the "thermoelectric power." The emf of a thermocouple is given by an integral over temperature of some coefficient  $\sigma_{ab}$  which depends both on pressure and temperature. Thus the emf is effected by the composition and/or the state of stress of the thermoelements only where there is a temperature gradient.

The effect of pressure is to modify this coefficient over the temperature interval which takes place under pressure. Thus the emf of a pressurized thermocouple is given by

$$E' = \int_{T_0}^{T_S} \sigma_{ab} dT + \int_{T_S}^{T_J} \sigma'_{ab} dT, \quad (2)$$

where  $\sigma'_{ab}$  is the pressure-modified Seebeck coefficient and  $T_S$  is the pressure seal temperature.

The effect of pressure is the amount by which the second term differs from the emf which would have been produced at 1 atm over the same temperature range:

$$\Delta E = \int_{T_S}^{T_J} (\sigma_{ab} - \sigma'_{ab}) dT. \quad (3)$$

This is the voltage we seek in preparing correction tables for thermocouples used at high pressure.

The relative Seebeck coefficient applies to a pair of thermoelements  $a$  and  $b$ . It is the difference of two absolute Seebeck coefficients, each of which applies to only one thermoelement:

$$\sigma_{ab} = \sigma_a - \sigma_b. \quad (4)$$

The voltage change introduced by pressurizing the

thermocouple is then

$$\Delta E = \int_{T_S}^{T_J} (\sigma_a - \sigma_a') dT - \int_{T_S}^{T_J} (\sigma_b - \sigma_b') dT, \quad (5)$$

where  $\sigma_a'$  and  $\sigma_b'$  are the pressure-modified absolute Seebeck coefficients. Thus we see that the change in emf of a pressurized thermocouple is just the difference of the changes in each leg separately.

Measurement of the pressure effect on each leg of a thermocouple separately is experimentally easier than measurement of the effect on the thermocouple itself.

In order to make these measurements, a homogeneous wire is subjected to a pressure and temperature distribution as shown in Fig. 2. The wire is thereby subjected to two temperature gradients, one at high pressure and the other at 1 atm. Because the temperature gradients are opposed, the observed emf is just the difference in the emf's generated in each gradient.

$$E_{SW} = \int_{T_S}^{T_J} (\sigma_a - \sigma_a') dT. \quad (6)$$

We refer to this as the single-wire voltage because it involves only one thermoelement. The difference of two single-wire voltages gives the correction for a thermocouple with a hot junction at  $T_J$  and a pressure seal at  $T_S$  as in Eq. (5).

#### PREVIOUS WORK

An experiment for directly observing the pressure effect on the emf of a thermocouple was performed by Birch.<sup>3</sup> His technique was that of holding a pressurized thermocouple at a known temperature and observing its apparent temperature. His experiments showed a decrease in the emf of Pt-Pt10Rh amounting to several degrees at 1000°C and 4 kbar. He found essentially no effect on Chromel-Alumel to 600°C and 4 kbar. Be-

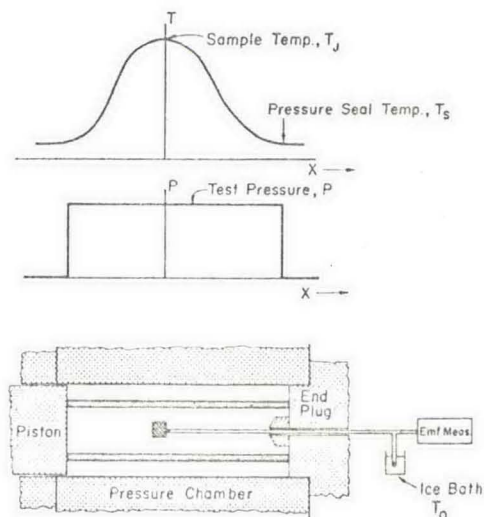


FIG. 1. Schematic view of typical high-pressure cell showing temperature and pressure distribution.

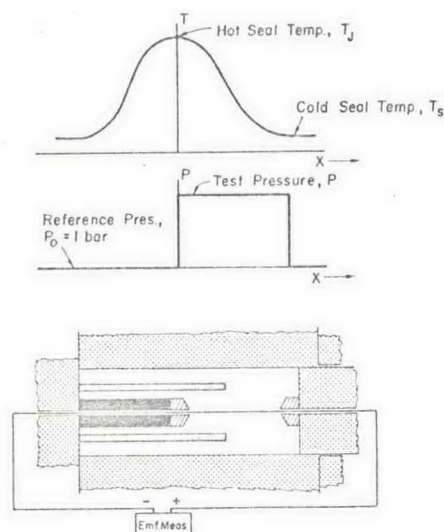


FIG. 2. Schematic view of single-wire experiment cell showing temperature and pressure distribution.

cause he failed to record seal temperatures, Birch's measurements are applicable only to his particular apparatus.

Measurements on a single wire were first made by Wagner<sup>4</sup> to 100°C and 300 kg/cm<sup>2</sup>. Bridgman<sup>5</sup> extended the experimental range to 1200 kg/cm<sup>2</sup>. Unfortunately, Bridgman's work did not include any of the more commonly used thermoelement pairs. Thus his results have not proved useful in determining the pressure corrections to be made to measurements of temperature at high pressure.

Bundy<sup>6</sup> extended the measurements to 100 kbar and 100°C. He presented data on many of the commonly used thermoelements and his results and the current results agree well within the uncertainties where the ranges investigated overlap.

Bell *et al.*<sup>7</sup> reported corrections for Pt-Pt10Rh and Chromel-Alumel to 5 kbar and 500°C. Freud and La Mori<sup>8</sup> have presented some preliminary data to 40 kbar and 400°C for the same two thermocouples. Their results are in substantial agreement with this work. They also have presented results to a few kbar at cryogenic temperatures for Chromel-Alumel and copper-constantan. Some of the data presented in this paper have been previously presented in summary fashion by Getting and Kennedy.<sup>9</sup>

Experiments designed to measure the difference in pressure effect on two different thermocouples have been carried out to considerably higher temperatures and pressures than have absolute measurements. Thus, a pair of thermocouples may be taken to the same temperature and pressure, and the apparent differences in temperature they record can be measured. This will, of course, yield the difference in the effect of pressure on the two thermocouples. Bundy<sup>6</sup> reported results of a relative pressure experiment intercomparing the

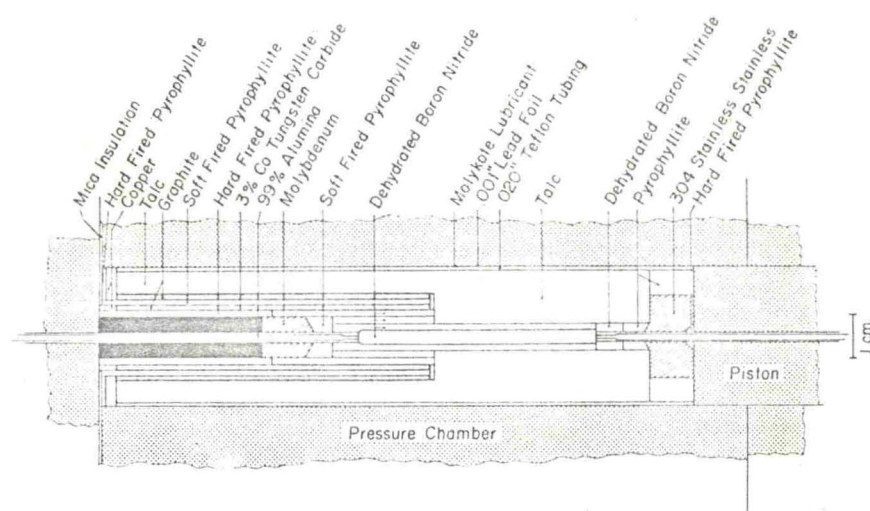


Fig. 3. Single-wire experiment pressure cell.

readings of Chromel-Alumel thermocouples and Pt-Pt10Rh thermocouples over a range of 50 kbar and to a temperature of 1200°C. However, evidence from our presently reported experiments and earlier evidence by Hanneman and Strong<sup>2</sup> suggest that the relative pressure effect which Bundy attempted to determine was masked by chemical contamination of his thermocouples and other decalibration effects at temperatures above several hundred degrees.

Hanneman and Strong<sup>10,2</sup> and Hanneman *et al.*<sup>11</sup> report results involving the intercomparison of two thermocouples. They measured the relative pressure effect for several pairs of thermocouples to 1200°C and 50 kbar. Their results are in reasonable agreement with results by Peters and Ryan,<sup>12</sup> Bell *et al.*,<sup>7</sup> and the relative effect as calculated from this work.

The difference in the effect of pressure on the emf of Chromel-Alumel thermocouples and Mo-Mo50Re has been reported by Stromberg and Stephens.<sup>13</sup>

Hanneman *et al.*<sup>10,2,11</sup> have also estimated the absolute effect of pressure on the emf of thermocouples. Their values were determined by intercomparing the temperatures of predicated phenomena at high pressure with the temperatures of the phenomena as observed by pressurized thermocouples. There are sizeable uncertainties associated with this procedure, however, and substantial disagreement exists between their estimated absolute corrections in the higher temperature-pressure regions and the directly measured values reported in this work. Wentorf<sup>14</sup> has measured absolute corrections for Pt-Pt10Rh to 50 kbar and 1100°C by the measurement of thermal noise. The results from this extremely difficult experiment are close to the estimates of Hanneman *et al.*, but show slightly larger corrections.

#### EXPERIMENTAL ASSEMBLY

Our single-wire experiment was conducted in an end-loaded piston-cylinder device. Measurements were made to 35 kbar and 1000°C. Figure 2 shows the ideal

temperature and pressure distribution required to make the desired measurements. One portion of the wire in the chamber is subjected to pressure whereas the other portion sees no pressure as it extends down an axial hole through a tungsten carbide bushing. The bushing supports the pressure outside it and provides a 1-atm environment around the wires, well into the pressure cell. An internal resistance heater was used to generate a temperature maximum at the inside end of the carbide bushing where the high-temperature seal is located. Thus the wire is subjected to one temperature gradient at high pressure and an opposed gradient at 1 atm.

Ideally, the regions of temperature gradient should be isobaric. The regions of pressure gradients should be isothermal. The length of the pressure cell was extended from our normal 5.08 cm to 15.24 cm in order to permit more uniform temperature distribution within the pressure seals. The diameter of the cell was 3.18 cm. The design and construction of this relatively large 40-kbar-pressure vessel is discussed by Au and Getting.<sup>15</sup>

The detailed configuration of the pressure cell is shown in Fig. 3. Test wires passed through the full length of the pressure chamber, entering an axial hole in the piston at one end and leaving at the other end through a hole in the carbide end-load plate. In the pressure seals and the regions where the wires were at 1 atm, they were contained in a 6-hole 99% Al<sub>2</sub>O<sub>3</sub> insulating tube. However, the Al<sub>2</sub>O<sub>3</sub> insulating tube proved much too strong to permit uniform transmission of pressure to the wires in the high-pressure environment. Here the wires were embedded in binderless boron nitride previously dried at 500°C for 5 h. Several runs were made with silver chloride substituted for the BN in order to produce more nearly hydrostatic pressure on the wires. These experiments were limited to a maximum temperature of approximately 500°C by the melting of silver chloride.

A coaxial graphite heater was used to produce a temperature maximum at the hot seal where the wires leave the 1-atm environment and enter the high-pres-

sure region. In the coaxial heater, the heating current flows in opposite directions in inner and outer sleeves. This greatly reduces inductive pickup in the test wires.

All materials subjected to high temperatures inside the pressure cell were previously fired to avoid their giving off water during the course of the experiment. Small traces of water quickly react with Chromel and Alumel at high temperatures causing contamination and decalibration. The massive talc pressure medium did not get hot enough to dewater and was not fired.

In the experimental assembly shown in Fig. 3 there are two pressure seals, one at high temperature and the other at low temperature. The temperature of each of these seals was measured with a butt-welded Chromel-Alumel thermocouple. Their location is indicated in Fig. 4. The leads of these thermocouples were taken out of the atmospheric pressure side of the seal. Thus pressure did not affect their calibration.

Substantial care was taken to avoid parasitic emf's and leakage currents in the low-level measuring circuits. The emf from each thermoelement in the test was measured with an absolute accuracy of  $\pm 2 \mu\text{V}$  on a 1-mV span strip chart recorder. Polarity is indicated in Fig. 2 and is in accordance with that of Bridgman.<sup>5</sup> At the highest furnace currents, a small amount of inductive pickup was noted. This was removed by a one-stage R-C filter.

#### EXPERIMENTAL MEASUREMENTS

Four thermoelement materials were tested simultaneously: Pt, Pt10Rh, Chromel-P, and Alumel. The noble metal thermoelements were 0.305-mm-diam reference grade thermocouple wire secured from Englehard Industries: Pt, bar number 72385 and Pt10Rh, bar number 73740. The Chromel and Alumel were supplied by Hoskins Inc. in the form of 0.320-mm-diam wire: Chromel-P coil, number 3831 and Alumel coil, number 6404. All four materials were received in the annealed condition. No further annealing was done, though care was taken to avoid undue bending of the wires during assembly of the experiment. The thermoelements were cleaned with petroleum ether before assembly and then handled only with cleaned tweezers. This was done to avoid the introduction of contaminants on the surface of the wires.

Whereas Pt and Pt10Rh seemed clean initially, Chromel and Alumel required substantial cleaning. Argon was flushed through the 1-atm high-temperature region for 1 h before the first temperature excursion. This was done to insure effective removal of oxygen. The argon flow was then continued throughout the experiment.

Pressure was first raised to a nominal value of 1 kbar. The pressure on the wires inside was probably variable and less than 1 kbar. The first temperature cycle was made at this extremely low pressure to the highest temperature to make sure there was no single-wire emf in the absence of pressure. Data was recorded on the

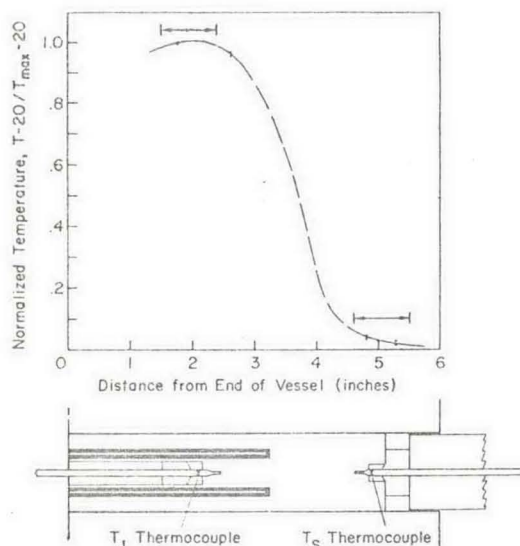


Fig. 4. Single-wire experiment temperature distribution, normalized temperature along the pressure cell as determined by five fixed thermocouples. Data was taken at maximum temperatures of 300°, 600°, and 900°C. Arrows indicate maximum extent of the pressure seals.

increasing and decreasing parts of the cycle. The pressure was then raised.

Both isobaric and isothermal excursions were made across the explored region of the pressure-temperature plane.

In the isobaric excursions the piston load was generally taken to a fixed value and maintained. This meant regulating the oil in the piston ram to counter the effects of thermal expansion and contraction. Temperature was typically cycled between room temperature and 1000°C.

At each data point the hot seal temperature was held constant for  $\frac{1}{2}$ –1 min before the single-wire voltages were recorded. During this time, one of the single-wire voltages was monitored on the strip chart recorder in order to observe any time dependency. One-half minute was typically sufficient to establish suitable stress and temperature equilibrium in the cell to terminate all short-term drift of the single-wire voltages. Occasionally the hot-seal temperature was maintained constant for 15 min to observe any longer-term changes in the voltages. This was generally done at the highest temperature of each cycle. Data were recorded on both the increasing and decreasing parts of each temperature cycle to observe any hysteresis introduced by thermal expansion induced changes in stress on the wires. Temperature excursions were made at 12, 23, and 33 kbar; and then again at 23 and 12 kbar to check reproducibility.

The values recorded at each data point were the single-wire voltage for each of the four thermoelements, hot pressure seal temperature  $T_J$ , cool seal temperature  $T_S$ , oil pressure in the piston ram, and the position of the piston as monitored with a dial gauge.

The isothermal runs were made by raising the hot seal temperature to a fixed value and maintaining it. Pressure was then cycled between several kilobars and 35 kbar. Several cycles were generally made at each temperature. During the course of these cycles the cold seal would continue to heat up slightly thus changing the magnitude of the pressurized temperature interval. This change was typically less than 2% however.

Both isobaric and isothermal excursions were made in a few runs. Most runs were limited however to one type of cycle due to mechanical failure of the wires. Runs generally lasted from 5 to 10 h. The scatter associated with cycling many times, performing both types of cycles on the same wires, holding at the extreme pressure and temperature for up to 15 min, and exposing the thermoelements to up to 10 h of cycling all appears in the final data.

Pressure was determined by monitoring the oil pressure in the piston ram with a Heise Bourdon tube gauge. In the runs where pressure excursions were made, hysteresis loops relating single-wire emf to ram oil pressure were plotted. The centers of these loops were taken as indicating the effective pressure. Corrections determined from these runs were applied to the indicated pressure of temperature cycles.

Strangely, in some cases the hysteresis loops seemed to show higher pressure on compression than that indicated by the Heise gauge and lower pressure on decompression. This is the reverse of that expected and has never been encountered in any prior measurements in this laboratory. Similar results in a solid medium single-wire experiment have been reported by Freud and La Mori.<sup>8</sup> We tentatively attribute this effect to lack of completely hydrostatic pressure on the test wires, but do not have a clear understanding of the phenomenon. The strength of the normal pressure medium was greatly reduced by replacing the talc and boron nitride with silver chloride without significant effect on the shape of the hysteresis loops nor on the magnitude of the single-wire emf. Test wire geometry was varied from the usual longitudinal orientation to a helical configuration in one silver chloride run, again with similar results.

Corrections to the pressure indicated by the Heise gauge were everywhere less than 1 kbar, positive on compression. Pressures determined in this manner differed from those calculated from the center of piston displacement hysteresis loops by as much as 3 kbar, around 10 kbar. The pressure gradient in the talc surrounding the test wire region was determined from Bi I-II transition studies. It corresponds to a maximum 3-kbar pressure drop along the wires at the highest pressures and room temperature. Guided by these quantities, the pressure uncertainty is estimated as  $\pm 3$  kbar over the entire pressure range.

It is crucial in these measurements to show that the pressure gradient at both the high-temperature seal and the low-temperature seal take place over a region

of essentially uniform temperature. Therefore, in one experiment the temperature distribution along the axis of the cell was explored by five fixed thermocouples and is shown in Fig. 4. The temperature gradient across the hot seal amounted to only 2% of the maximum temperature reached and the gradient across the cold seal amounted to no more than 4%. Accuracy in the determination of the pressurized temperature interval  $T_J - T_S$  is  $\pm 5\%$ .

## RESULTS

The experimental data are presented in Figs. 5-10. In Fig. 5 we present the data taken at 12, 23, and 33 kbar for platinum. Results are plotted in terms of the observed single-wire voltage versus temperature difference between the hot seal and the cold seal. Similar data for Pt10Rh are shown in Fig. 6; data for Chromel are shown in Fig. 7; and data for Alamel are shown in Fig. 8. Data in these four figures were taken on isobaric excursions, i.e., the pressure was held constant and the temperature was varied. In Figs. 9 and 10 we show typical data for Pt, Pt10Rh, Chromel, and Alamel with the temperature held constant and the pressure varied. Fig. 9 for Pt and Pt10Rh shows reversed hysteresis loops of the type we have discussed. Figure 10 for Chromel and Alamel illustrates data where one hysteresis loop is normal and the other reversed. Solid curves shown in these six figures do not necessarily represent the best fit to the data in each figure. There are curves taken from the smooth surface constructed to fit all our available data as discussed in a subsequent portion of this paper.

The single-wire emf for Pt varies linearly with either pressure or temperature, but for Pt10Rh it is slightly concave toward the voltage axis in both cases. The

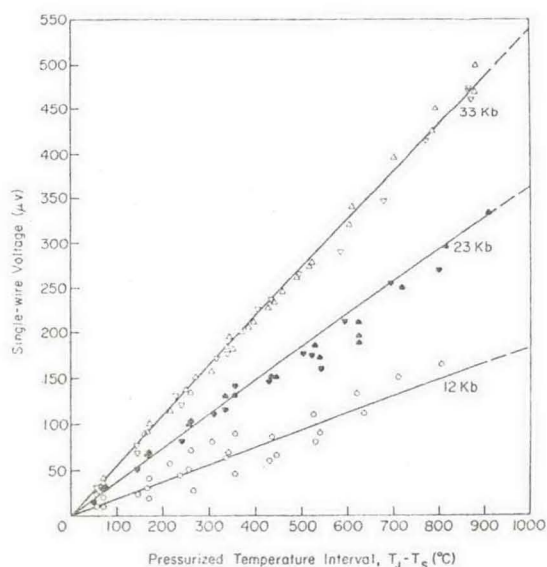


FIG. 5. Single-wire voltage for platinum.

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Single-wire Voltage ( $\mu\text{V}$ )

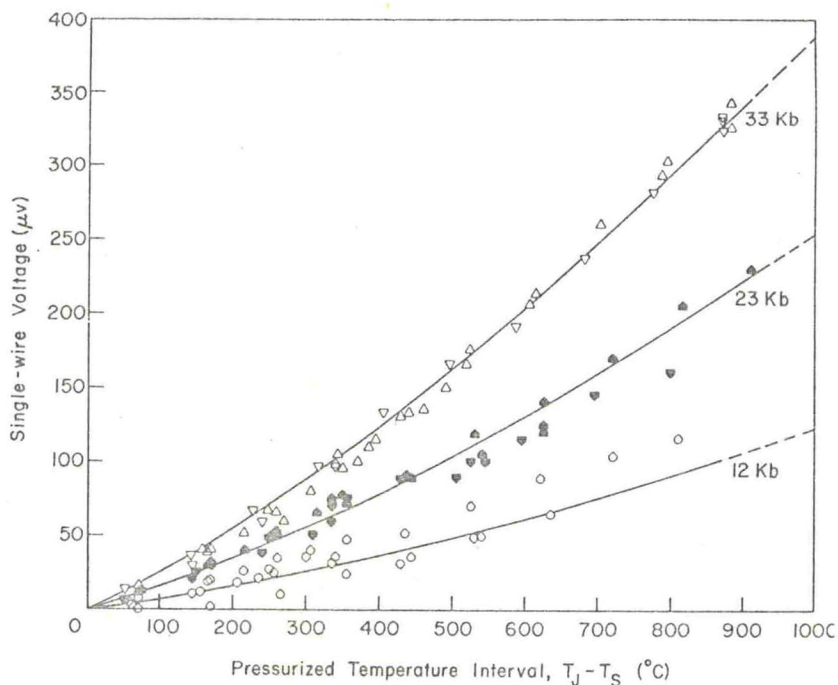


FIG. 6. Single-wire voltage for Pt10Rh.

negative thermoelement, Pt, shows a consistently larger single-wire voltage than does the positive thermoelement, Pt10Rh. Thus, a Pt-Pt10Rh thermocouple will read low under pressure. The signs of the single-wire voltages of both Pt and Pt10Rh, however, are everywhere positive. Thus the effect of pressure on each thermoelement largely compensates for the effect of pressure on the other. The difference in the single-

wire voltages for Pt and Pt10Rh is only about 30% of their mean.

The signs of a single-wire voltage for Chromel and for Alumel are also everywhere positive except for a small part of the range for Chromel where temperatures and pressures are relatively low. Both Chromel and Alumel show curvature towards the voltage axis with increasing temperature, but are nearly linear with pressure. The difference in single-wire voltages for Chromel and Alumel is not of constant sign, however. The pressure correction is positive at low temperatures but becomes negative at approximately 400°-600°C and is strongly negative at very high temperature. (See Fig. 12.)

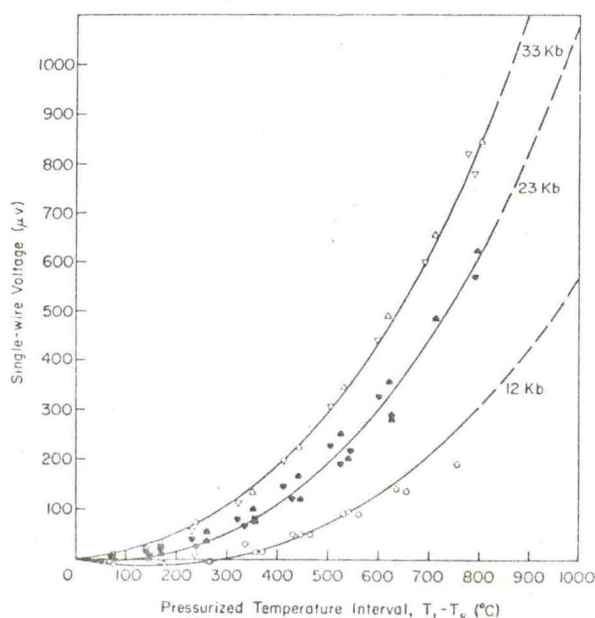


FIG. 7. Single-wire voltage for Chromel.

#### DATA REDUCTION

Mechanical and chemical failures led to the rejection of a certain amount of data. Pressure and temperature were limited by collapse of the tungsten carbide bushing during the course of the experiments. When this took place, the wires could not be pulled freely from the bushing after the run. In such cases all the data taken above the first arrival at 25 kbar were discarded.

Mechanical failure of the wires took place in the pressure-seal regions. Since these regions were essentially isothermal, the plastic deformation associated with mechanical failure should have had little effect on the thermoelectric voltages. In fact no anomalous results were associated with wires which subsequently failed at a seal. Thus data from runs terminated by

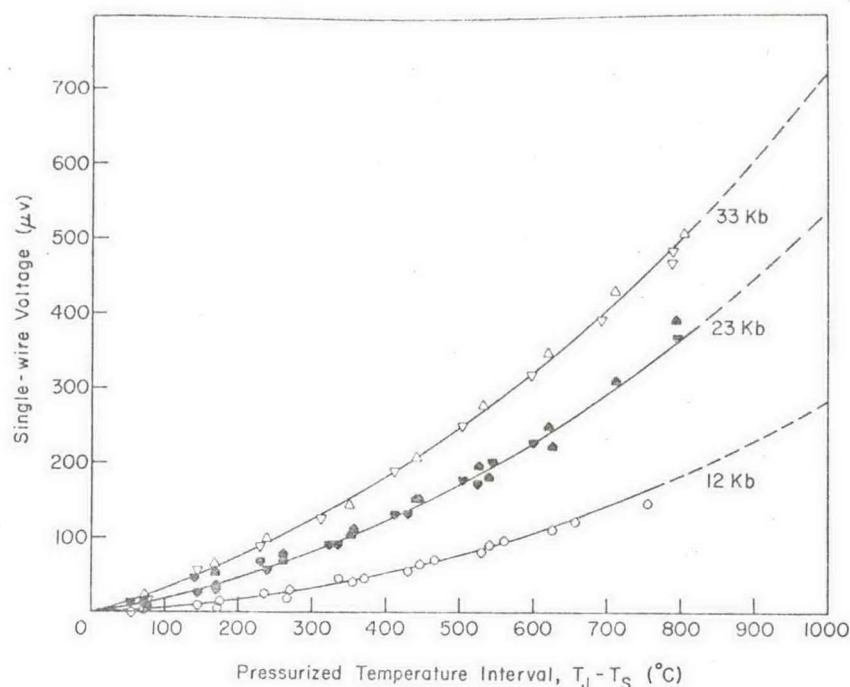


FIG. 8. Single-wire voltage for Almel.

mechanical failures of the wires were not eliminated for that reason alone.

What is presumed to be chemical deterioration of the thermoelements was a significant problem at first. Effective flushing of the 1-atm temperature gradient with an inert gas was essential to obtain reasonable reproducibility with Chromel and Almel at temperatures approaching 1000°C. On many of the runs these two wires had a darkened surface at the region of highest temperatures both in the 1-atm gradient and in the high-pressure gradient region where they were in BN. Runs whose maximum temperature was limited to 600°C did not show this effect. Since there was no apparent discrepancy in the data from the two cases, data were not eliminated from runs with slightly discolored Chromel and Almel wires.

Two runs were made with AgCl as the pressure medium immediately adjacent to the test wires. In both cases the data for Chromel and Almel were highly erratic, time dependent, and irreproducible. All the Chromel and Almel data from these two runs

TABLE I. Standard deviation of surface fits to original single-wire voltage data.

Pt10Rh	$\pm 8 \mu\text{V}$
Pt	$\pm 14 \mu\text{V}$
Pt minus Pt10Rh point by point	$\pm 10 \mu\text{V}$
Chromel	$\pm 16 \mu\text{V}$
Almel	$\pm 8 \mu\text{V}$
Almel minus chromel point by point	$\pm 13 \mu\text{V}$

were discarded. Pt and Pt10Rh were not adversely affected by the AgCl up to the maximum test temperature of 500°C.

Part of the Chromel and Almel data from several other runs was eliminated owing to a progressive change in the single-wire voltages of one or both of the wires.

In general, all data were retained which included both thermoelements for either thermocouple and were self-consistent throughout an entire run.

The retained data for Pt-Pt10Rh included 7 runs, 21 excursions across the  $P$ - $T$  plane and back, and 273 data points. There were 3 runs, 9 excursions, and 115 data points for Chromel-Almel.

The voltages for each thermoelement were fit by

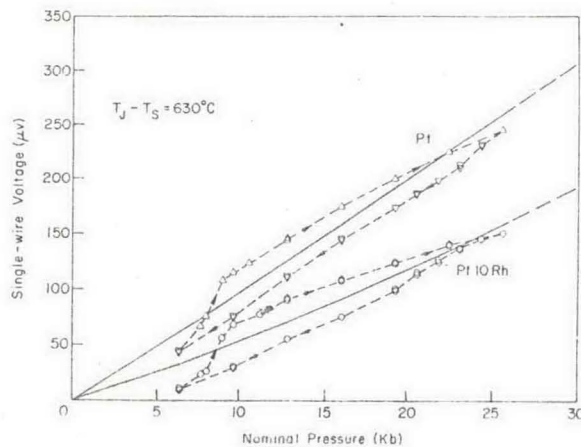


FIG. 9. Isothermal data for Pt and Pt10Rh.

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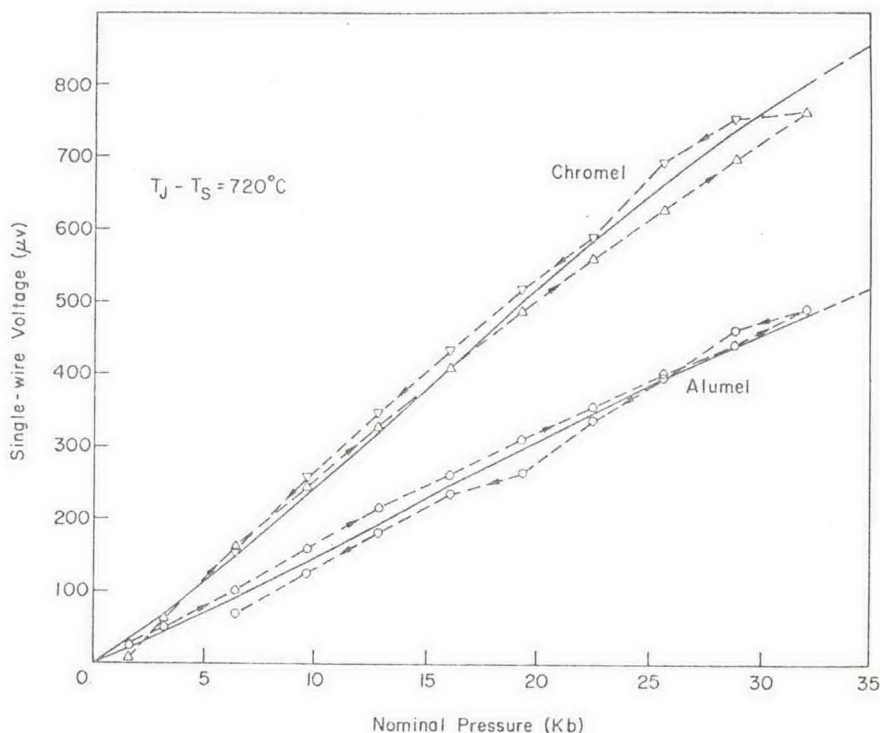


FIG. 10. Isothermal data for Chromel and Alumel.

least-squares analysis with polynomial surfaces of the form

$$E = a_1 \Delta T P + a_2 \Delta T P^2 + a_3 \Delta T^2 P + a_4 \Delta T P^3 + a_5 \Delta T^2 P^2 + a_6 \Delta T^3 P,$$

where  $P$  is the pressure as determined above and  $\Delta T = T_J - T_S$  is the pressurized temperature interval. This permits smoothing over both independent variables simultaneously as well as appropriately weighted consideration of the data from both types of excursions. The surface represented above is a general polynomial surface with only the cross-product terms retained. This constrains the surface to pass through the  $\Delta T$  and  $P$  axis assuring compliance with the boundary conditions that the single-wire voltage be zero whenever the pressure cell is isothermal or whenever the pressure is zero. Ultimately it is the differences in single-wire voltages which appear as the thermocouple corrections. These differences were calculated point by point from the data for individual thermocouples and also fit with surfaces. Table I shows the standard deviation associated with each fit.

These data include implicitly the specific relation between the two seal temperatures  $T_J$  and  $T_S$  which occurred in this particular experimental setup. In order to generalize the results, this relation must be determined explicitly and taken into account. For each of the original data points, both  $T_J$  and  $T_S$  were recorded. For conductive heat transfer to the cold seal from the hot seal region, the relation between the two seal temperatures should be linear at equilibrium. The fit by

least-squares analysis was

$$T_S - 20 = 0.0909(T_J - T_S),$$

with a standard deviation of  $\pm 12^\circ\text{C}$ . The standard deviation was essentially unchanged for polynomials of higher degree. Thus the rise above ambient of the cold seal was 9% of the pressurized temperature interval.

We would like to determine the single-wire voltages, and hence the thermocouple corrections, for the case in which the cold seal temperature remained fixed at ambient,  $20^\circ\text{C}$ . The single-wire voltages, like thermocouple voltages, are additive over adjacent temperature intervals. Thus, for example, the voltage generated between  $1000^\circ$  and  $20^\circ\text{C}$  is equal to that generated between  $1000^\circ$  and  $110^\circ\text{C}$  plus that between  $110^\circ$  and  $20^\circ\text{C}$ . This principle was applied to our data in a one step iteration to calculate generalized single-wire voltages and subsequent thermocouple corrections. This process increases the temperature uncertainty slightly to  $\pm 6\%$ .

We have also extrapolated the data from 35 kbar and  $1000^\circ\text{C}$  to 50 kbar and  $2000^\circ\text{C}$  for Pt-Pt10Rh and 50 kbar and  $1200^\circ\text{C}$  for Chromel-Alumel. Smooth graphical extrapolations on evenly spaced isobaric and isothermal profiles were made to the surface fits. No additional experimental data is included in these extrapolations, however.

The final results are shown in Figs. 11 and 12. Here the thermocouple corrections (the differences in single-wire voltages) are plotted versus a generalized temperature scale at various pressures. The voltages shown are



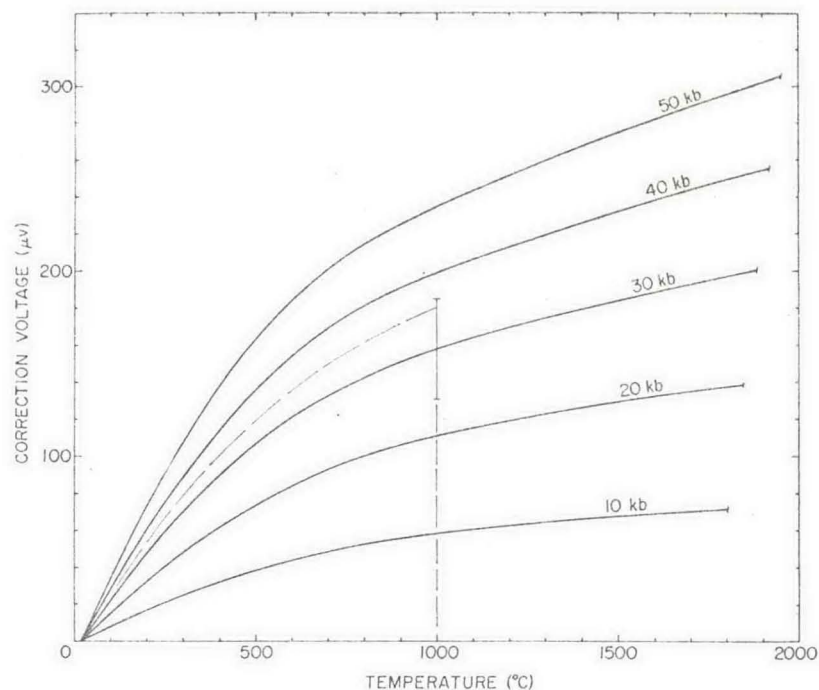


FIG. 11. Corrections for Pt-Pt10Rh thermocouples operating with a seal temperature of 20°C. The dashed lines indicate the upper limits of the experimentally explored region.

the corrections which would be appropriate if the pressure seal where the thermocouple wires exited from the high-pressure region remained at 20°C.

Estimates of the uncertainties of these thermocouple corrections were made based on: (1) the pressure and temperature uncertainties, (2) the slopes and relative magnitudes of the various fit voltage surfaces, (3) the number and distribution of data points, and (4) the

scatter in the observed voltages. The final uncertainties are  $\pm (10\% + 10 \mu\text{V})$  for Pt-Pt10Rh and  $\pm (20\% + 20 \mu\text{V})$  for Chromel-Alumel. They have been indicated by error bars in Figs. 11 and 12. They are applicable only within the experimentally explored region. Although these plotted uncertainties appear fairly large, they contribute only about  $\pm 0.2\%$  to the uncertainty of a final temperature measurement.

Surfaces of the same form as above were fit to the values shown in Figs. 11 and 12. Table II gives the coefficients of these surfaces which may be used to generate tables of thermocouple corrections. The deviations of these fits contribute negligibly to the correction uncertainty. In the experimentally explored region, up to 35 kbar and 1000°C, the maximum deviations from the values shown in Figs. 11 and 12 are  $1.7 \mu\text{V}_t$  for Pt-Pt10Rh and  $8 \mu\text{V}_t$  for Chromel-Alumel. Also included are the coefficients for the individual thermocouples.

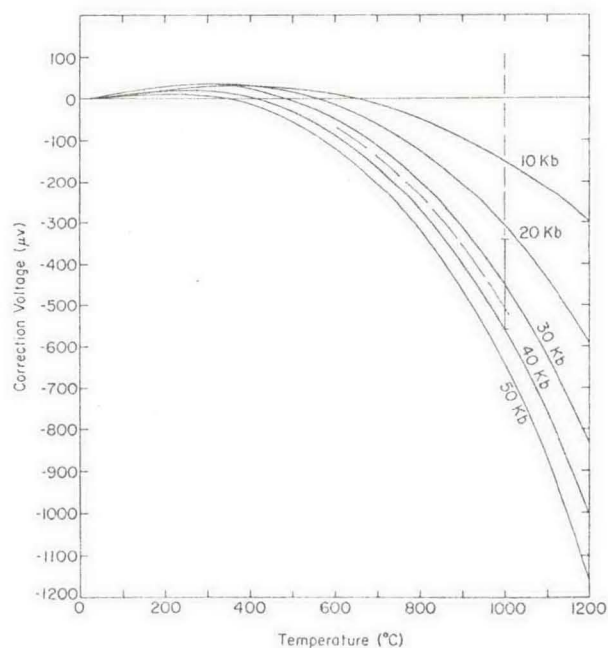


FIG. 12. Corrections for Chromel-Alumel thermocouples operating with a seal temperature of 20°C. The dashed lines indicate the upper limits of the experimentally explored region.

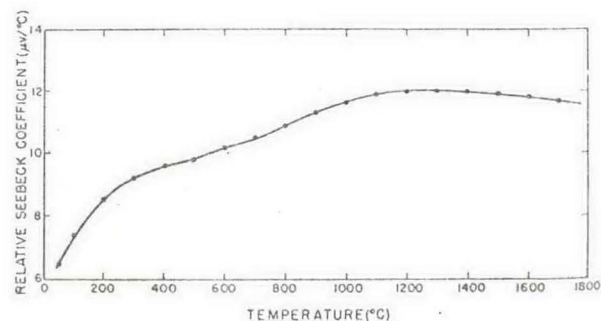


FIG. 13. Relative Seebeck coefficient of Pt-Pt10Rh at 1 atm as a function of temperature.

TABLE II. Coefficients of surface fits to single-wire and thermocouple correction data with generalized temperature axis.<sup>a</sup>

	Pt10Rh	Pt	Correction
$a_1$	$0.44187 \times 10^{-2}$	$0.15302 \times 10^{-1}$	$0.10853 \times 10^{-1}$
$a_2$	$0.85626 \times 10^{-4}$	$0.49488 \times 10^{-4}$	$-0.36139 \times 10^{-4}$
$a_3$	$0.54252 \times 10^{-5}$	$-0.60745 \times 10^{-6}$	$-0.60326 \times 10^{-6}$
$a_4$	$0.97344 \times 10^{-9}$	$-0.11452 \times 10^{-7}$	$-0.12425 \times 10^{-7}$
$a_5$	$-0.10622 \times 10^{-7}$	$-0.26313 \times 10^{-9}$	$0.10359 \times 10^{-7}$
$a_6$	$-0.12372 \times 10^{-8}$	$0.49230 \times 10^{-10}$	$0.12864 \times 10^{-8}$
Standard deviation	$\pm 2.0 \mu\text{V}$	$\pm 0.6 \mu\text{V}$	$\pm 1.7 \mu\text{V}$
	Chromel	Alumel	Correction
$a_1$	$-0.26744 \times 10^{-1}$	$-0.29198 \times 10^{-2}$	$0.23824 \times 10^{-1}$
$a_2$	$0.12950 \times 10^{-2}$	$0.71560 \times 10^{-3}$	$-0.57939 \times 10^{-3}$
$a_3$	$0.42384 \times 10^{-4}$	$0.16332 \times 10^{-4}$	$-0.26052 \times 10^{-4}$
$a_4$	$-0.11720 \times 10^{-4}$	$-0.95802 \times 10^{-5}$	$0.21401 \times 10^{-6}$
$a_5$	$-0.83299 \times 10^{-6}$	$-0.29829 \times 10^{-6}$	$0.53471 \times 10^{-6}$
$a_6$	$0.17245 \times 10^{-7}$	$0.27378 \times 10^{-8}$	$-0.14527 \times 10^{-7}$
Standard deviation	$\pm 4.4 \mu\text{V}$	$\pm 3.1 \mu\text{V}$	$\pm 6.9 \mu\text{V}$

<sup>a</sup> The values of single-wire or correction voltages may be calculated from these coefficients by use of the following equation:

$$E = a_1(tP + a_2t^2P^2 + a_3t^3P^3 + a_4t^4P^4 + a_5t^5P^5 + a_6t^6P^6)$$

where  $t = T_J - 20$ , the hot seal (for single-wire voltages) or hot junction (for thermocouple correction voltages) temperature minus 20°C; an

$P$  = pressure in kbar.

These coefficients represent our single-wire and correction voltages to 50 kbar and 2000°C for Pt and Pt10Rh and to 50 kbar and 1200°C for Chromel and Alumel. All values above 35 kbar and 1000°C are based on graphical extrapolations.

### CALCULATION OF CORRECTIONS

In most apparatus, the pressure seal does not remain fixed at ambient temperatures. It is still possible to calculate the corrections appropriate to such a case from the generalized plots in Figs. 11 and 12. First, the voltage corresponding to the junction temperature at the appropriate pressure is found from the plot. From this is subtracted the voltage corresponding to the pressure seal temperature at that same pressure. This difference is added to the observed thermocouple voltage. The temperature is then found by reference to the standard 1-atm thermocouple tables.

Alternatively, if a correction in terms of temperature rather than thermocouple voltage is desired, the voltage correction as determined above should be divided by the 1-atm relative Seebeck coefficient (thermoelectric power) of the thermocouple. For Chromel-Alumel this coefficient is essentially constant at  $41 \mu\text{V}/^\circ\text{C}$ . The value for Pt-Pt10Rh is more temperature dependent and is shown in Fig. 13. A sample calculation for Pt-Pt10Rh is given below for a thermocouple operating at 800°C and 30 kbar with a seal temperature of 150°C. The correction voltage corresponding to the junction temperature, +142  $\mu\text{V}$ . From this is subtracted the correction voltage for the seal temperature, +35  $\mu\text{V}$ , resulting in a final correction of +107  $\mu\text{V}$ . The temperature correction is found by dividing this quantity by the relative Seebeck coefficient at 800°C, 10.8  $\mu\text{V}/^\circ\text{C}$ . It is +9.9°C.

While the temperature axis in these plots is actually true temperature, using the indicated thermocouple

temperature for the hot junction temperature introduces a negligible error. The error introduced in the sample calculation above would be only 1  $\mu\text{V}$  or 0.1°C. For Pt-Pt10Rh the final correction is actually more sensitive to accurate determination of the effective seal temperature than the junction temperature because the curves have greater slopes in the seal temperature region. For Chromel-Alumel the case is just the reverse. In the seal temperature range of most apparatus, the slopes and magnitudes of the Chromel-Alumel correction curves are extremely small. This makes corrections to this thermocouple particularly insensitive to accurate seal temperature determination.

Several important factors enter into the accurate application of these observed corrections. In solid medium high-pressure applications, thermocouples are often installed inside a high-strength ceramic protection tube. The stress field on the thermoclements can be extremely nonhydrostatic in such cases. Experiments in this laboratory under such conditions have shown as much as a factor of two difference in the effective pressure on the wires at the same nominal cell pressure on compression and decompression parts of a pressure cycle. Thus the appropriate correction can differ from that for the nominal cell pressure by a major fraction of the correction as a result of stress and temperature gradients occurring simultaneously in the same region of the wires.<sup>2</sup> Some estimate of the pressure-temperature distribution along the wires should be made to account for these effects. This is usually very difficult, however.

What is thought to be chemical contamination has

frequently been a severe problem in high-pressure thermocouples use, particularly above  $\sim 700^\circ\text{C}$  for Chromel-Alumel and above  $\sim 1300^\circ\text{C}$  for Pt-Pt10Rh in this and other work in this laboratory. Hanneman *et al.*<sup>2,11</sup> report similar findings. These effects can often be larger than the pressure effect itself.

In order to apply these corrections at all, pressure seal temperatures must be measured. For previous experiments without this information, estimates would have to be made.

The corrections for Pt-Pt10Rh are considerably smaller than previous values. At the extremes of the explored region, 35 kbar and  $1000^\circ\text{C}$ , our results are just half the estimates of Hanneman *et al.*<sup>2,11</sup> This relation also holds for our extrapolated values to the extremes of their estimates, 50 kbar and  $1200^\circ\text{C}$ . The values of Wentorf<sup>14</sup> are approximately 20% greater than those of Hanneman *et al.* in this region.

The initial slopes of our correction curves for Pt-Pt10Rh are very similar to those of Hanneman *et al.*<sup>2,11</sup> The discrepancy at high pressure and temperature arises from a greater curvature in our correction curves with both pressure and temperature.

For Chromel-Alumel the corrections are particularly small and insensitive to pressure and temperature in the temperature range where Chromel-Alumel is highly reliable, below  $\sim 700^\circ\text{C}$ . Above that the correction

curves take on large negative slopes leading to quite large negative corrections. This is in contrast to the values of Hanneman *et al.*<sup>2,11</sup> which are also small at lower temperatures, but remain positive to  $1200^\circ\text{C}$ .

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## Basis for Picosecond Structure in Mode-Locked Laser Pulses

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In careful experimental measurements of mode-locked laser pulses, using nonlinear media, a number of workers have found evidence for what appear to be coexisting subpicosecond pulses, and pulses in the range of 10–40 psec. In this letter we describe a model of a light pulse in which a Gaussian random-radiation field (i.e., a thermal field) of limited spectral extent is modulated by a temporal pulse envelope, and we show that predictions based on such a model are in excellent detailed agreement with published experimental results. We also consider the case of a pulse of linearly chirped radiation, and show that a clear distinction can be made between this case and a pulse of Gaussian random radiation.

The role of coherence in determining contrast ratios in the two-photon fluorescence measurements of picosecond light pulses has been understood for some time.<sup>1–4</sup> Coherence considerations are also important in methods which use interacting orthogonal polarizations in second- or third-harmonic generating media, although in these cases the background level is absent and the question of contrast does not arise. In this paper we calculate the exposures  $\mathcal{E}(\tau)$ , resulting when a radiation field is divided into two equal portions and then recombined, with an adjustable delay  $\tau$ , in a

medium which produces a signal proportional to either the square or cube of the fundamental intensity. Three specific cases of interest are two-photon fluorescence, second-harmonic generation, and third-harmonic generation. In carrying out our calculations we will use two models for the radiation field: I, a pulse of spectrally filtered thermal radiation, and II, a coherent pulse whose frequency changes linearly with time (linear chirp). Steady-state thermal radiation and a single coherent pulse (without chirp) appear as limiting cases of I or II.