ORNL/TM-4975

Preparation of ^{147}Pm Metal and the Determination of the Melting Point and Phase Transformation Temperatures

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OAK RIDGE NATIONAL LABORATORY
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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy $4.00; Microfiche $2.25

ORNL/TM-4975

Contract No. W-7405-eng-26

PREPARATION OF ^{147}Pm METAL AND THE DETERMINATION OF THE MELTING POINT AND PHASE TRANSFORMATION TEMPERATURES

Part I of a Thesis presented for the
Master of Science Degree, The University of Tennessee

P. Angelini and H. L. Adair

Operations Division

JULY 1976

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PREPARATION OF ^{147}Pm METAL AND THE DETERMINATION OF THE MELTING POINT AND PHASE TRANSFORMATION TEMPERATURES

P. Angelini and H. L. Adair***

ABSTRACT

The promethium metal used in the determination of the melting point and phase transformation temperatures was prepared by reduction of promethium oxide with thorium metal at 1600°C and distilling the promethium metal into a quartz dome. The melting point and phase transformation temperatures of promethium metal were found to be 1042 ± 5°C and 890 ± 5°C, respectively. The ratio for the heat of the high-temperature transformation to the heat of fusion was determined to be 0.415.

INTRODUCTION

Promethium metal has been prepared by Weigel[1] on a milligram scale by reduction of PmF_3 with lithium in a tantalum crucible system. The melting point reported for promethium metal was 1080 ± 10°C. In additional work, the melting point was later revised by Weigel[2] to be 865 ± 40°C.

Wheelwright[3] has also reported the preparation of kilogram quantities of promethium metal. In this case, the promethium was prepared by calcium reduction of anhydrous $PmCl_3$. Additional purification was obtained by vacuum distillation of calcium and magnesium impurities. The melting point of promethium metal was reported by Wheelwright[3] to be 1168 ± 6°C.

In the present report the determination of the melting point and phase transformation temperatures of promethium metal are reported to be 1042 ± 5°C and 890 ± 5°C, respectively.

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*Formerly with Isotopes Division, now with Metals and Ceramics Division.

**Formerly with Isotopes Division, now with Solid State Division.

MATERIAL

Preparation of Promethium-147 Metal

Approximately 6 g of high-purity ^{147}Pm metal was prepared for use in neutron scattering studies and for ^{147}Pm melting point measurements. The basic metal preparation technique is as described in articles by Kobisk and Grisham[4] and by H. L. Adair.[5] Also, since ^{147}Pm is highly radioactive, a glove box system[6] was used and is briefly described.

The reduction-distillation process to obtain promethium metal was performed in a 10-cm-diam oil diffusion pumped vacuum system; a liquid nitrogen baffle was used to reduce oil backstreaming into the vacuum chamber. The entire vacuum system was contained in a glove box; this enclosure was maintained at a negative pressure of $\sim$12 mm of water with respect to the atmosphere. Use of an argon purge system assured that the atmosphere in the glove box was chemically inert.

Eight grams of ^{147}Pm as Pm_2O_3 were mixed with approximately a 5% stoichiometric excess of thorium metal powder. After these components were thoroughly mixed, several 4.8-mm-diam pellets were pressed and placed in a tantalum metal reactor and distillation assembly as shown in Fig. 1. The vacuum system was evacuated to less than 1×10^{-5} torr, and radiofrequency heating of the reactor vessel was used to slowly heat the reaction mixture to approximately 1300°C for 30 min. A thermal gradient was established up the distillation column as shown in Fig. 2. The ^{147}Sm daughter of ^{147}Pm was reduced to metal and distilled from the reaction mixture;

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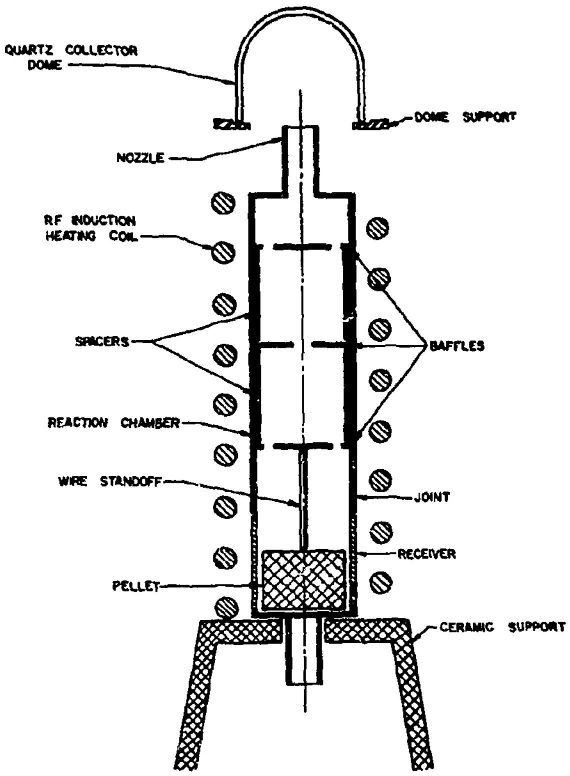

Fig. 1. Reduction Still for Quantities of Material Greater than 200 mg.

this product was collected in a quartz hemishell. After weighing the quartz dome, a determination was made that most of the ^{147}Sm had been removed. A new quartz dome was installed and the system evacuated again.

The temperature of the tantalum crucible was slowly raised to approxmately 1600°C, as determined by an optical pyrometer, and the ^{147}Pm was reduced and distilled into the quartz dome. This procedure was used to prepare 7 g of high-purity ^{147}Pm metal which was easily dislodged from the quartz dome after it was cooled to room temperature.

A small amount of the metal was used in the present experiment. The major part of the metal was arc-melted and drop-cast into a cylinder 0.635 cm in diameter and 2.54 cm long, weighing 6 g. The cylindrical rod was used by Koehler and Moon[7] in neutron scattering experiments to determine nuclear magnetic properties of the isotope.

Fig. 2. Thermal Gradient Established up the Distillation Column.

Purity of Promethium-147 Metal

Approximately 10 mg of promethium metal was sent for spark-source mass spectrometric analysis to the Mass and Emission Spectrometry Section of the Analytical Chemistry Division of ORNL. The results of the analysis are presented in Table 1.

Table 1. Spark-Source Mass Spectrometric Analysis of the Resulting Promethium-147 Metal

Element	Weight (ppm)	Element	Weight (ppm)
Al	10	S	0.3
Ba	0.2	Sc	<1
Ca	200	Y	<1
Co	<0.1	La	<1
Cr	7	Ce	<1
Cu	4	Pr	<1
Fe	100	Nd	20
K	20	Sm	2
Mn	0.7	Eu	<1
Ni	4	Gd	<1
P	<0.1	Tb	<1
Pb	50	Dy	<1
Li	20	Ho	<1
Ta	0.7	Er	<1
Th	9	Tm	<1
Ti	<0.2	Yb	<1
V	<0.1	Lu	<1
Zn	3	Pm	Major
Cl	700		

The concentration of tantalum in the final ^{147}Pm metal product was <1 wt (ppm). The concentration of thorium metal in the product was ~10 wt (ppm). Thus, there occurred little sublimation of tantalum or thorium metal during the promethium distillation process. There also occurred little if any vaporization of other lanthanides. The low concentration of samarium in the product indicated that the vast majority of the samarium had been reduced and vaporized during the samarium distillation procedure. The analysis indicated that very pure promethium metal may be obtained by the reduction-distillation process.

Melting Point Standards

The silver and gold reference materials used for melting point calibration experiments were NBS Standard Reference Material 748 and 745, respectively.

APPARATUS

Glove Box

The promethium metal was transferred to an argon atmosphere glove box capable of handling radioactive materials such as ^{147}Pm (see Fig. 3). The glove box was a modified high-level, alpha-handling, hot cell. The front of the hot cell served as the main access area. The front access plate contained a plate glass viewing window having four glove ports, a 14-in. bag-in and bag-out entry port, two vacuum line feedthroughs, three electrical feedthroughs, eight BNC-type connector on coaxial cable (BNC cable) feedthroughs, and two filtered gas inlet lines. An additional access area was located on the top of the glove box. The top access area contained a plate glass viewing window having two glove ports.

Two other glove-box-associated instruments were the gas inlet manifold, which automatically controls the glove box negative pressure, and a Beckman G2 oxygen analyzer. Two standardized compressed gases were used to calibrate the oxygen analyzer. These were a pure argon gas and a 700-ppm oxygen remainder argon-compressed gas cylinder.

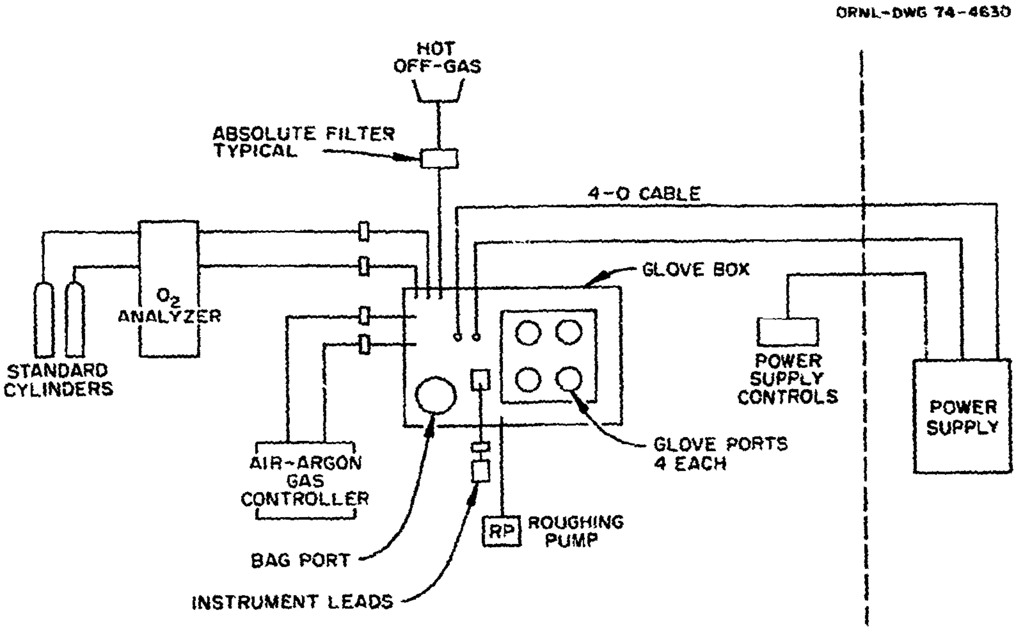

Fig. 3. Argon Atmosphere Glove Box.

High-Temperature Vacuum Furnace

The high-temperature vacuum furnace used was designed by various Isotopes Division personnel and fabricated by personnel of the Plant and Equipment Division at ORNL. Figure 4 is a diagram of the furnace. The octal base ports permit access within the furnace. On these ports were located a main vacuum line, a thermocouple vacuum gage, an ionization gage, a backfill valve, and an octal instrument feedthrough with the remainder of the ports sealed with blank flanges. Viton O-ring seals were used on all vacuum ports.

The furnace bonnet, the base plate, the bonnet access unit, the power posts, and the main power leads were water-cooled by means of a closed-loop recirculating chilled-water supply. The bonnet and base plate were made of aluminum metal. The water-cooled power posts were made of copper. The heat shields were made from five sheets of 20-mil molybdenum metal, and the heating element was made from 15-mil tantalum metal.

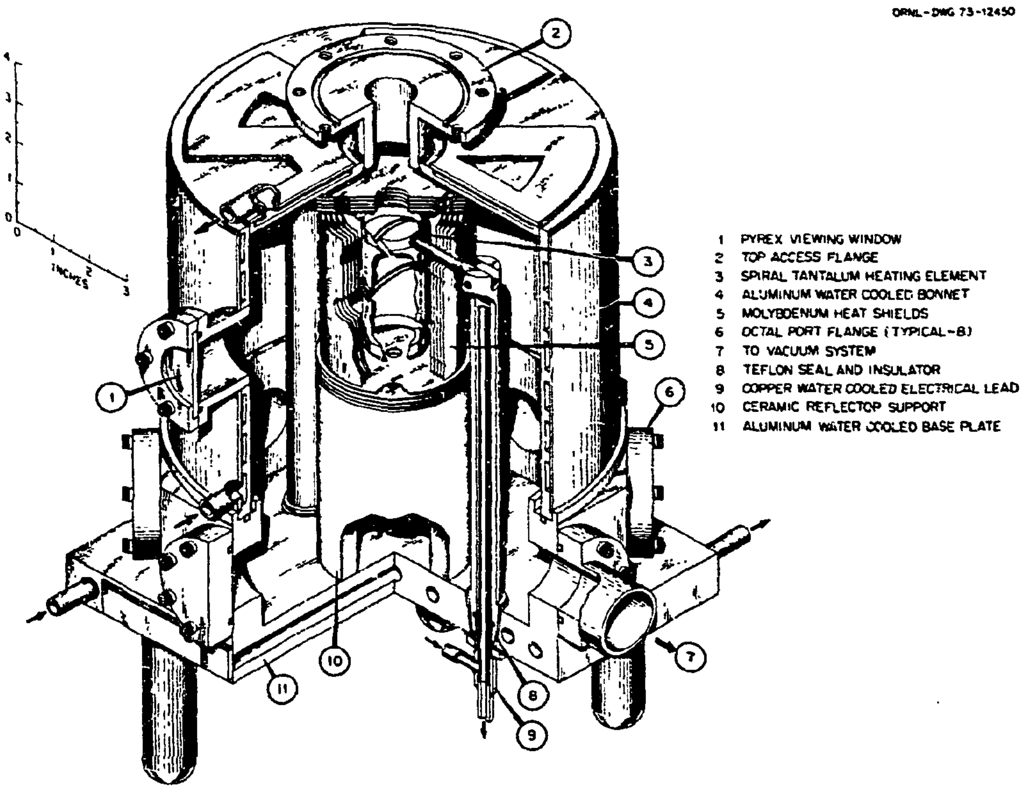

Fig. 4. High-Temperature Vacuum Furnace.

The heating element was of the double-spiral type and was 1-1/2-in. wide and 4-in. long. The interior of the heat zone could be seen through a 1/4-in. hole punched in the heating element and through a 1/2-in. hole in the molybdenum heat shield. The furnace could obtain a maximum temperature of 2100°C in a two-minute period from an ambient condition.

The furnace DC power supply was a modified 600-amp welder. The unit was located in a separate room, and power was supplied to the furnace by two 4-0 flexible copper cables. The output power could be ramped either up or down and held at prescribed power levels. The controls for ramping the supply, the safety on-off switch, and the output current and voltage meters were located in the operating area near the glove box.

The furnace vacuum system included a Welch 2.1-cfm mechanical roughing pump, an air-cooled 2-in. Varian oil diffusion pump, a water-cooled oil vapor baffle, and an absolute filter. The mechanical pump and absolute filter were located outside the glove box, and the diffusion pump and baffle were in the glove box. A flexible vacuum line was used to connect the two vacuum pumps.

The experimental equipment was safety interlocked. A furnace thermocouple vacuum gage and set point controller would turn off both the furnace cooling water supply and the furnace power supply if the pressure increased above the set point. A fire alarm probe on the glove box would alarm and turn off all power and water to the furnace if a heated condition existed. A water-pressure switch on the furnace outlet water line would turn off both the furnace water supply and the furnace power supply if the outlet water pressure decreased below a set value. The system would have to be manually reset if a failure condition had shut down the equipment.

Pyrometer

A pyrometer was used to measure temperature and observe the sample area. The unit, Model No. 95 fabricated by The Pyrometer Instrument Company, was of the brightness measuring, disappearing filament type.

Instruments

Various instruments were used to measure the output of the thermocouples. These were a Tektronik Model 5031 dual beam storage oscilloscope, a Keithly Model 151 nullmeter microvoltmeter, a Hewlett Packard Model 3440-A digital voltmeter with 3444-ADC multifunction unit, and a constant voltage supply. The instruments had been calibrated prior to use.

EXPERIMENTAL

Method of Melting Point Measurement

MgO Crucible Method

The rare-earth elements are very reactive when in the metallic form. The rare-earth oxides are some of the most stable oxides known.[8] The metals also alloy very easily and form solid solutions, eutectics, and compounds with each other and nearly every other element.[9] Such processes occur at ambient temperatures and pressures, but also to a greater extent at high temperature. A material with which promethium metal would not react or with which a minimum of reaction would occur needed to be found in order to obtain a meaningful melting point temperature. Magnesium oxide (MgO) was chosen as the container material[10] for promethium metal. The free energy of formation of MgO is more negative than that of Pm_2O_3 to temperatures greater than 1200°C. Thus, thermodynamically speaking, promethium metal should not react with MgO. Above 1200°C, MgO is quite volatile in vacuum; however, the maximum temperature at which the sample and crucible would be in contact was not expected to exceed 1200°C. Other oxides more stable than MgO exist; however, their fabrication qualities are not as

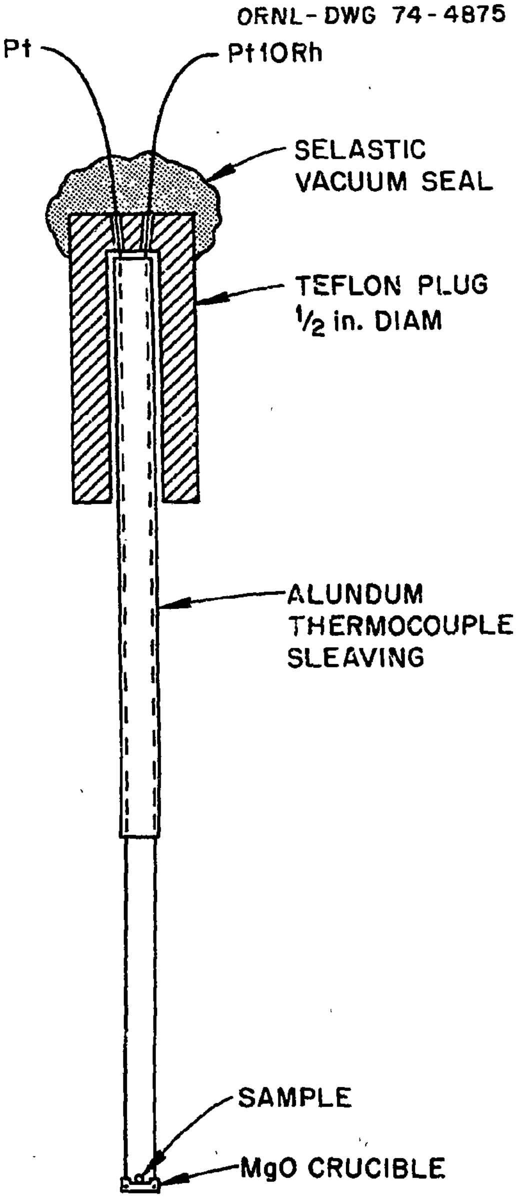

Fig. 5. MgO Crucible Assembly.

good as those of MgO. Thus, MgO crucibles were fabricated and an assembly as shown in Fig. 5 was made. The unit used one Pt-Pt10Rh thermocouple with the thermocouple junction being in a hole drilled into the bottom of the MgO crucible.

During an experiment ∿70 mg of promethium metal was placed in the MgO crucible and the thermocouple assembly placed in the furnace. Insulated copper wire with clips was used to connect the thermocouple wires to the BNC cables. On the outside of the glove box the same type of insulated copper wire was used to connect the signal leads of the BNC cable to the measuring instrument. The daca obtained in using silver and gold as melting point temperature standards were used for calibrating the promethium metal data. Corrected temperature readings were then obtained by linearly interpolating these data. This same type of wiring procedure was used in the modified MgO crucible method described below. The sample temperature was then increased and equilibrated at 900°C. At this level, the furnace temperature was ramped at a rate of 20°C/min until the melting point was indicated in the electromotive force (EMF) output of the thermocouple. The sample which was located in the center of the heat zone was observed with the pyrometer during the temperature increase.

Modified MgO Crucible Method

In this method the MgO crucible was made much smaller, and a second Pt-Pt10Rh thermocouple was placed alongside the crucible but not in contact with it. The walls of the MgO crucible were made thinner and lower such that a sample placed in it could be observed with a pyrometer. Calibration experiments using gold and silver were performed. During these experiments, it was determined that both thermocouples produced the same output within experimental error at an equilibrated temperature or during a temperature ramp of 20°C/min. During an experiment the sample was observed by using the optical pyrometer. The output of one of the thermocouples was recorded to be the melting point when the sample was seen to melt. In each case, upon the first melt the irregular-shaped metal pieces became spherical. A distinctive change in the appearance of the sample's surface occurred as the sample was taken through additional melts and freezes. The thermocouple measurements were taken to be the sample's melting point when this surface change was observed. The measurements for promethium metal were obtained using the same procedure as with gold and silver. The gold and silver data were linearly interpolated in order to obtain corrected temperature measurements for promethium.

W5Re-W26Re Differential Thermocouple Method

Another method used to identify not only the melting point but also a high-temperature phase transformation of promethium metal was differential thermal analysis. The thermocouple assembly is shown in Fig. 6. Three thermocouples were used in this unit. The two W5Re-W26Re thermocouples used 10-mil-diam calibrated wire and were connected such that they formed a difference thermocouple. One of those forming the difference thermocouple was fabricated such that the thermocouple bead region was demountable. The third, temperature measuring, thermocouple was made from 10-mil Pt-Pt10Rh wire with the thermocouple bead located near the difference thermocouple. Inside the glove box the thermocouples were connected to the leads of the BNC cables by using the insulated

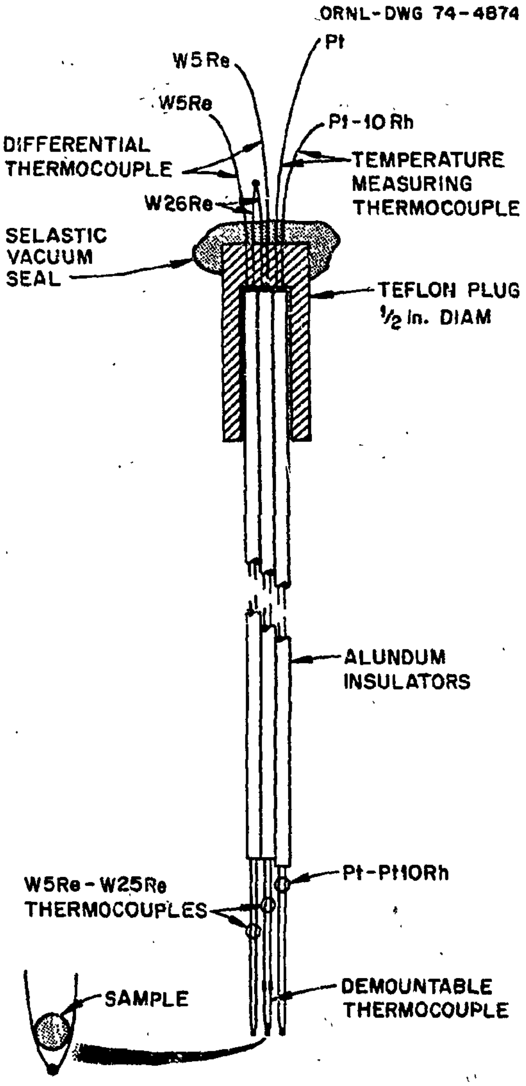

Fig. 6. W5Re-W26Re Differential Thermocouple Assembly.

copper wire cables. Outside the glove box the insulated copper cables were used to connect the BNC cable leads of the difference thermocouple directly to the oscilloscope. The output of the Pt-Pt10Rh thermocouple was connected to a 0°C reference junction prior to wiring the signal to the digital voltmeter. During the experiments the sample and thermocouple zone of the assembly was observed through the viewing port of the furnace by using an optical pyrometer.

Calibration of the unit was performed by melting gold standards. A small piece of metal was placed on the demountable W5Re-W26Re thermocouple and the assembly loaded into the furnace. The output of the difference thermocouple was recorded on the oscilloscope as a function of time. The temperature of the metal sample was increased and equilibrated at a value below its melting point. The temperature was then ramped at ∿10°C per minute through the melting point of the sample. The output of the Pt-Pt10Rh temperature-measuring thermocouple was recorded to be the melting point when the melting began to affect the output of the difference thermocouple.

In the promethium experiments the glove box was first placed under an inert argon atmosphere. After the oxygen reached a level of <500 ppm, the promethium metal was unloaded and lodged in the demountable W5Re-W26Re thermocouple. The assembly was then placed in the vacuum furnace. During the experiment the sample and thermocouple zone of the assembly was observed through the viewing port of the furnace by using an optical pyrometer.

Pt-Pt10Rh Thermocouple Method

Another thermocouple assembly was fabricated having one Pt-Pt10Rh thermocouple. A sample of promethium metal was lodged in the thermocouple bead area.[11] A constant voltage supply was used to null the output of the thermocouple such that the EMF measuring instrument (an oscilloscope) could be operated at a more sensitive range.

RESULTS

MgO Crucible Method

Approximately 70 mg of promethium metal was placed in the MgO crucible and the unit loaded in the furnace. No EMF change was measured in a temperature range where the promethium metal was observed to melt. This indicated that a larger sample mass would be required if this method was to yield satisfactory results. It is believed that the relatively low thermal diffusivity and high heat content of the MgO crucible in conjunction with the small amount of promethium metal placed in the crucible prevented the successful use of this method. This result led to the modified MgO crucible method.

Modified MgO Crucible Method

The results for the silver and gold calibration experiments are presented in Table 2. The data are on four samples of melting point standards. The samples were each melted and frozen a number of times. In each case, the observed EMF varied only ±0.2 mv.

Table 2. Modified MgO Crucible Calibration Results

Sample	Observed EMF (mv)	Observed Melting Point (°C)	Standard Melting Point (°C)	Observed-Standard EMF (mv)	Observed-Standard Temperature (°C)
Ag	9.41	989	961	0.29	28
Ag	9.44	986	961	0.32	25
Au	10.64	1092	1063	0.33	29
Au	10.57	1085	1063	0.26	22

Two promethium metal samples were used with two melting and freezing experiments performed on each sample. In each case the temperature was taken to 950°C and the system equilibrated. The temperature was then ramped at 20°C/min to above the melting point. After the sample had melted, the temperature was decreased at 20°C/min and the freezing point was measured. No measurable difference between the freezing and melting point was observed. The results of the promethium metal experiments are presented in Table 3.

Table 3. Modified MgO Crucible Promethium Metal Melting Point Results

Sample	Observed EMF (mv)	Corrected Melting Point (°C)
Pm-1	10.25	1037
	10.23	1035
Pm-2	10.26	1037
	10.29	1039

An additional promethium metal sample was unloaded from its closed container while the glove box was under an inert atmosphere. The glove box atmosphere was then replaced with air and the promethium sample exposed to this condition for ∿18 hr. The sample was then placed in the MgO container and a melting point experiment performed. The melting point was measured to occur at 1063°C. This temperature is significantly higher than the previous melting points measured using pure promethium metal. These results indicate that the partial oxidation of promethium metal will result in an increased melting point temperature.

W5Re-W26Re Differential Thermocouple Method

In these experiments the thermographs were recorded as EMF versus time. Figure 7 is a typical thermograph of a gold melting point experiment. Table 4 presents the numerical data associated with a gold melting point experiment. The freeze occurred within experimental error of the melt in the gold melting point experiment. Also the measurements did not change when the melt and freeze experiments were performed up to four times. The sample was evaporating at a significant rate at these temperatures. This was observed by noting the condensate on the furnace viewing window.

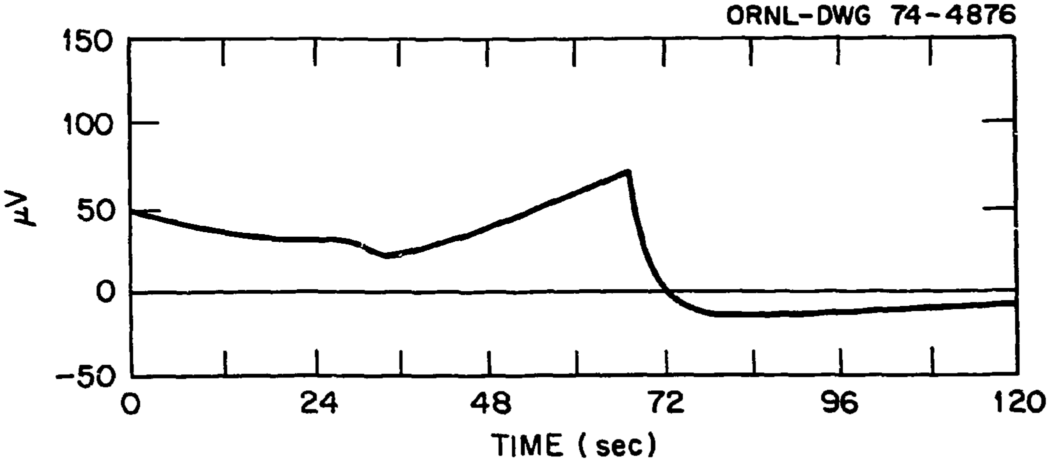

Fig. 7. Thermograph of a Gold Melting Point Experiment.

Table 4. W5Re-W26Re Gold Melting Point Calibration

Sample	Gold
Beginning of Melt EMF (mv)	10.23
End of Melt EMF (mv)	10.51
Observed Melting Point (°C)	1057
Standard Melting Point (°C)	1063
Observed-Standard EMF (mv)	−0.07
Observed-Standard Temperature (°C)	−6

In the promethium metal experiment, ∿10 mg of sample was lodged in the demountable thermocouple. Both melting and freezing thermographs were obtained. After the initial melt, the promethium sample had become spherical and completely surrounded the thermocouple bead. The later thermographs were much sharper than the initial one due to better thermal contact between the thermocouple bead and the promethium metal sample. Figure 8 presents one of the promethium metal thermographs on the sample's second melt.

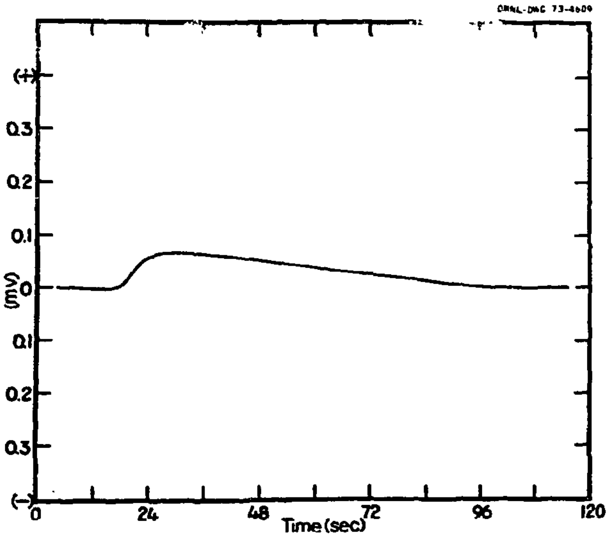

Fig. 8. Promethium Metal Thermograph of the Sample's Second Melt.

A second transformation was observed to occur at a lower temperature than the melting point. A thermograph of the high-temperature phase transformation upon heating is presented in Fig. 9. This figure can be directly related to Fig. 8, for it was obtained immediately prior to the melt shown in Fig. 8.

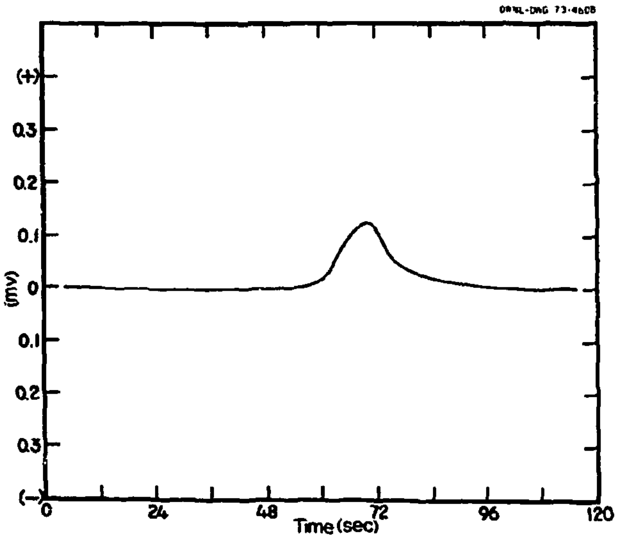

Fig. 9. Promethium Metal Thermograph of the High-Temperature Phase Transformation.

The temperature at which the high-temperature phase transformation occurred did not vary with the number of times it was measured or with the number of melts the sample had undergone. Also no difference in the temperature was observed when the temperature was increasing or decreasing through the phase transformation temperature.

The numerical data for the melting point and phase transformation temperature experiments are presented in Table 5. Corrections obtained from the gold calibration experiment were applied to the temperature values.

Table 5. W5Re-W26Re Promethium Melting Point and Phase Transformation Temperature Results

Phase Transformation	Melting Point	Observed EMF (mv)	Corrected Temperature (°C)
T↓		8.25	890
T↑		8.25	890
	T↓	10.06	1048
T↓		8.25	890
T↑		8.25	890
	T↑	10.09	1051
	T↓	10.01	1044
	T↑	10.04	1046
	T↓	9.99	1042

Note: T↑ = temperature increasing
T↓ = temperature decreasing

Pt-Pt10Rh Thermocouple Method

The high-temperature phase transformation for promethium was clearly evident and the temperature at which it commenced was measured to be 893°C. The signal from the thermocouple became increasingly noisy as the temperature was increased. At the temperature at which the promethium metal should have melted, the peak-to-peak noise level had increased from its ambient temperature value of <30 μV to a value of 3 V peak-to-peak. The melt was completely obscured. Immediately above this temperature range the thermocouple separated; the promethium metal had reacted with the Pt-Pt10Rh thermocouple. Using the thermocouple noise level as an indication of extent of interaction, the reaction was first observed at a temperature slightly lower than the phase transformation temperature.

DTA Area Measurements

Additional experiments were performed to better understand the problem of relating the DTA areas of the two transformations. Table 6 presents data obtained with silver and gold samples using a similar W5Re-W26Re thermocouple assembly as used in the promethium work. In each of the four cases listed in Table 6 a separate demountable thermocouple was used. One may observe that the areas of the DTA curves decrease for each experiment as to the number of melts or freezes the sample has undergone. This occurs because of vaporization of the sample from the W5Re-W26Re thermocouple. As mass is lost the total heat content affecting the thermocouple decreases, thus the area of the DTA curve diminishes. This effect was noted with silver and gold; it also occurred to some extent in the promethium work. The two thermographs in the ^{147}Pm experiment whose areas were compared were obtained in succession, with the temperature increasing through both transformations and in a time period of less than ten minutes such that the vaporization effect would be minimal.

Table 6. Silver and Gold Melting Point Area Determinations

Experiment Number	Melt	Freeze	DTA Area
	Gold, 41.64 mg		
A-1		X	34.10
A-2	X		34.03
A-3		X	32.78
A-4	X		31.61
A-5		X	31.24

Table 6. (Continued)

Experiment Number	Melt	Freeze	DTA Area
	Gold, 80.27 mg		
B-1	X		44.83
B-2		X	41.74
B-3	X		40.32
	Silver, 19.36 mg		
C-1		X	24.64
C-2	X		23.12
C-3		X	28.58
C-4	X		24.38
C-5		X	25.89
	Silver, 59.14 mg		
D-1		X	46.63
D-2	X		38.16
D-3		X	43.51
D-4	X		35.45
D-5		X	41.42
D-6	X		35.21
D-7 (slow)	X		31.00
D-8 (slow)		X	25.65

Another effect is that of the heating or cooling rate through a transformation on the measured DTA area. Noting the results in Table 6, A-1 freeze was performed over a 1-min period. In A-3 and A-5, the temperature was quenched with the cooling rate being at least a factor of 10 greater than in freeze A-1. The values for the DTA areas are not significantly different due to the cooling rates. The differences in areas are due to the vaporization of the sample. Thus, heating or cooling rate with respect to promethium should not effect the DTA areas significantly. Thus the measured ratio of $\Delta HT/\Delta HF$ for promethium as obtained in these experiments should be an accurate one.

It was thought that by performing experiments on silver and gold absolute values could be obtained for the heat of fusion and heat of transformation for promethium metal. However, the data in Table 6 show that this method was not useful in determining absolute values of such quantities. A problem encountered was that, in using different demountable thermocouples, different DTA areas would be measured using samples of equal mass for an element. This occurs because of the differences in mass and size of the demountable thermocouple. Such an effect should diminish with a sample of larger mass. Also only those thermographs where the temperature is either increasing or decreasing should be compared, for there was a difference in the areas determined under these two conditions. These are the major problems affecting this method using the present experimental equipment where absolute values for the heat of fusion and the heat of transformation are required.

DISCUSSION

Promethium Melting Point Temperature

Four determinations of the melting point for ^{147}Pm metal were performed using the modified MgO crucible method. Assigning an accuracy of ±5°C to each temperature measurement, the average melting point temperature within a 95% confidence limit is 1037 ± 3°C.

In the W5Re-W26Re differential thermocouple method, five melting point determinations were performed. Assigning an accuracy of ±5°C to each temperature measurement, the average melting point temperature within a 95% confidence limit is 1046 ± 4°C.

The average melting point temperature as determined by one method does not fall within the 95% confidence band of the other method. There is a possibility that the two techniques yield different results. This difference, however, was not explored further through experimentation with additional samples. Thus equal weight was given to each temperature measurement irrespective of method. Using all of the results for two methods, the average melting point temperature for ^{147}Pm metal is 1042 ± 5°C.

Promethium melting point determinations have been performed by other workers. The results of Weigel[1] of 1080 ± 10°C and Wheelwright[3] of 1168 ± 6°C for the melting point of promethium metal may have been caused by the partial oxidation of the promethium metal sample. In later experiments Weigel[2] revised the melting point of promethium metal from 1080 ± 10°C to 865 ± 40°C. The latter temperature was obtained by using McWhan's "solder rupture" method. This latter temperature is in the range of the high-temperature phase transformation temperature of 890°C as determined by the differential thermocouple method used in the present study. Perhaps the bead in Weigel's[2] latter result ruptured at this polymorphic phase transformation temperature. Also various intermetallic compounds exist between the precious metals and the rare-earth metals.[12-14] It is evident that such an intermetallic interaction occurred between promethium metal and the Pt-Pt10Rh thermocouples when the metals came in direct contact at high temperature. This occurred in the Pt-Pt10Rh thermocouple method of the present work and in the thermocouple arrest method used unsuccessfully by Wheelwright.[3]

Solid-Solid Phase Transformation

A high-temperature solid-solid phase transformation was found to occur for promethium metal by using the W5Re-W26Re differential thermocouple method. The phase transformation temperature was determined to be 890 ± 5°C. This is in the range of values for elements close to promethium.[15] The high-temperature crystal structure of promethium metal is not known; however, from the knowledge of the transformations of the other rare-earth elements,[16,17] the high-temperature phase for promethium should be bcc. The low-temperature phase is reported to be the double hexagonal close-packed structure.[18] In Fig. 10 are presented the data for the melting point and high-temperature phase transformation temperatures of the rare-earth elements.

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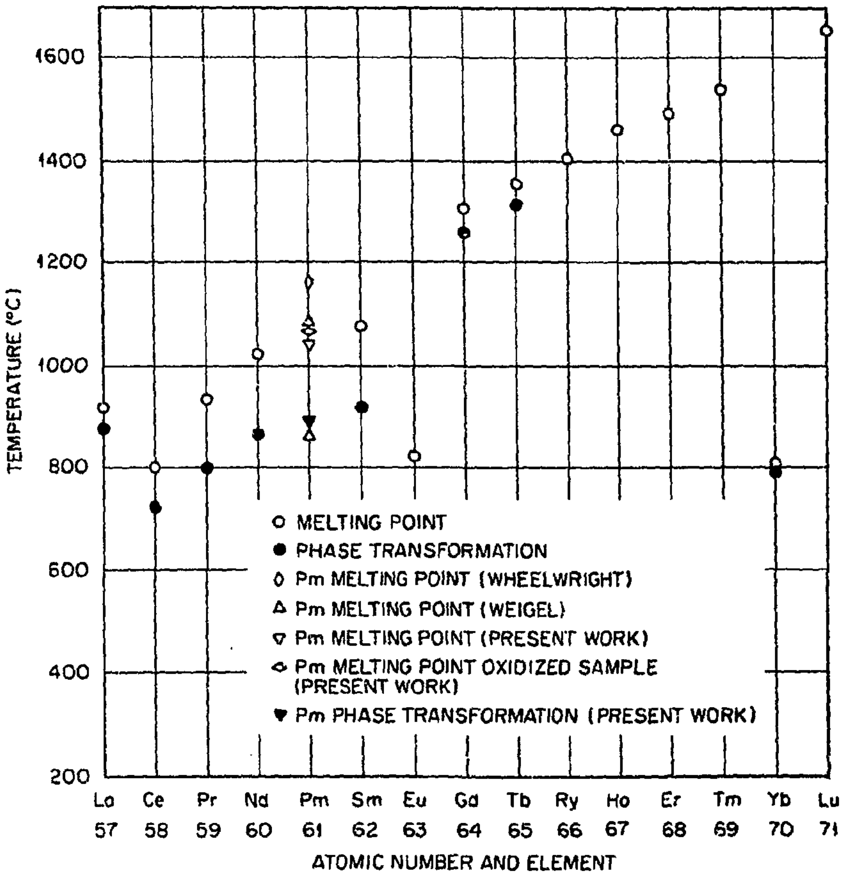

Fig. 10. Melting Point and High-Temperature Phase Transformation Data for the Rare-Earth Metals.

The areas of the DTA curves for the phase transition and the melting point were measured. The area of such curves is proportional to the heat of the transformation, all other factors being constant. The ratio of the two areas from the thermographs yields $\Delta HT/\Delta HF = 0.415$. This value together with other such values where the heat of fusion and heat of transformation[15] have been determined experimentally for other rare-earth elements are presented in Table 7.

Table 7. Heat of Fusion and Heat of High-Temperature Phase Transformation for the Rare-Earth Metals

Element	Heat of Fusion ΔHF (kcal/mole)	Heat of Transformation ΔHT (kcal/mole)	Ratio
Pr	1.650	0.760	0.461
Nd	1.705	0.713	0.417
Pm			0.415[a]
Sm	2.061	0.744	0.360
Gd	2.10	1.03	0.490
Tb	2.20	1.06	0.482

[a] This work.

The value of the ratio for promethium compares very favorably with those for praseodymium and neodymium. It is significantly different than the ratio for samarium. Samarium has a rhombohedral low temperature crystal structure, while praseodymium and neodymium have a double hexagonal close-packed low-temperature crystal structure.

ACKNOWLEDGMENT

The authors are grateful to R. E. McHenry of Oak Ridge National Laboratory for his interest and direction in the experiments; Dr. P. G. Huray of the University of Tennessee who served as faculty advisor for the thesis program; T. R. Rice of Oak Ridge National Laboratory for his assistance in the performance of the promethium experiment; and W. B. Grisham of Oak Ridge National Laboratory for his aid in producing the promethium metal.

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