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DENSITY OF METALLIC POLONIUM

At Interim

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INTRODUCTION

Based on resistivity measurements and crystal structure studies, Maxwell and Beamer⁽¹⁾ report that polonium exists in two allotropic forms. Observations on the transformation temperature show that the transition occurs between 65°C. and 130°C. and that the range depends upon the thickness of the sample used in the determination. X-ray diffraction studies reveal that the α form (low temperature form) has a simple cubic structure and a calculated density of 9.32 g./cc. whereas β -polonium is a simple rhombohedral crystal and has a calculated density corresponding to 9.51 g./cc. The density was also determined by measuring the volume which a known mass of metal occupied in a small capillary. The weight of polonium, 1201 ± 6 micrograms was determined calorimetrically. With this weight, a diameter of 0.258 mm. for the capillary and a length of 2.44 mm. for the "ingot", the density of polonium was calculated to be 9.38 ± 0.5 g./cc. Only one determination was made because it essentially checked with the more accurate X-ray calculation.

The X-ray pattern reported for α -polonium corresponds exactly with a pattern obtained in this laboratory for a sample of polonium metal which was permitted to remain in contact with air overnight and which changed in appearance from a metallic mirror to a white crystalline material⁽²⁾. In addition, the fact that α -polonium containing some lead is reported to have a rather large negative coefficient of thermal expansion and that there are no other metals or alloys which are reported to have this property indicated that more work would be necessary to substantiate the conclusions drawn by Maxwell and Beamer.

Gunther-Mohr and Schamp⁽³⁾ undertook the problem of measuring the density of polonium by filling a calibrated capillary with polonium metal, thus obtaining the volume of the material used. The weight was to be determined calorimetrically and the necessary calculations made. They were going to determine the exact temperature of the slug of polonium as well as the density. Several attempts were unsuccessful, due mainly to mechanical failure. Both of these men left the project before a determination was completed.

SUMMARY AND CONCLUSIONS

Two determinations of the density of polonium at 25°C. have been made.⁽⁴⁾ These values are 8.6 g./cc. and 9.2 g./cc. with a probable experimental error of 2 per cent. The reason for the disagreement between the two values is that the material used in the second determination was subjected to a preliminary purification from the more volatile constituents of production foils.

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The value of a preliminary purification is very clearly demonstrated by this pair of determinations and the desirability of knowing the exact purity of the sample used is indicated.

Apparatus suitable for directly measuring the coefficient of thermal expansion of a thread of polonium in what is called the low temperature form has been set up. If the large negative coefficient is true, the change in length with temperature of a 1 cm. thread can be easily detected from $-100^{\circ}\text{C}.$ to $0^{\circ}\text{C}.$ and from this the coefficient can be calculated.

EXPERIMENTAL

Two determinations of the density were made and of these the procedure which gave what appears to be the most reliable result will be described. The difference between the two lies in the preliminary treatment of the polonium.

About 20 curies of polonium were placed in a quartz tube which had another tube of about 4 mm. internal diameter sealed to it (Figure 1). The tube was evacuated and the portion containing the polonium was heated with an oxygen torch until the polonium collected on the cooler portions of the tube's walls. The pumps were permitted to continue the evacuating operation during this step in order to pump off any oxygen which might be formed as a decomposition product of the oxide. The tube was then sealed under high vacuum and the polonium concentrated by heating all but the very tip in a furnace at $500^{\circ}\text{C}.$ A ring of inactive material was visible toward the cooler end of the tube followed very closely by the polonium. The temperature of the furnace was then lowered to $300^{\circ}\text{C}.$ and the tube placed in the furnace with the larger portion protruding. This temperature was high enough to drive a good bit of the impurity off and low enough to leave a sufficient quantity of polonium behind to be used in the experiment.

The purity of the material finally used in the experiment was not known but it should be reasonably high in view of the treatment to which it was subjected.

The smaller tube containing the polonium was sealed off and the activity driven to one end of it. This was then broken open and placed in another tube to which a calibrated capillary was attached (Figure 2).

The new tube was evacuated and the polonium heated with an oxygen flame in a fashion similar to its preliminary treatment. After it had cooled, the pumps were turned off and the system filled to about

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— FIGURE 1 —

QUARTZ TUBE USED IN PRELIMINARY PURIFICATION OF
POLONIUM.

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FIGURE 2

QUARTZ TUBE USED IN DENSITY DETERMINATION

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100 mm. pressure with helium from which oxygen was removed by passing the gas through copper turnings at about 400°C. The tube was then sealed off from the rest of the system and placed in a furnace at 500°C. in order to move the polonium past a constriction in the direction of the capillary. This effects a separation from lead (due to decay) which has a low vapor pressure (10^{-5} mm.) compared with that of polonium (about 1 mm.)⁽⁵⁾ at 500°C. After cooling, the constriction was closed and the tube again heated at 500°C. to drive the polonium into the smaller bulb to which the capillary was sealed. This was sealed off and removed to a centrifuge cup specially designed to permit heating the sample just before centrifugation (Figure 3).

The temperature of the cup was raised to about 350°C. after the tube containing the polonium and the calibrated capillary were placed in it. This temperature is about 100°C. above the melting point of polonium. The centrifuge was permitted to spin for twenty minutes. When the tube was removed from the centrifuge, the polonium appeared in the calibrated portion of the capillary as a metallic thread. The length of the thread was measured by means of a calibrated filar micrometer eyepiece. Where bubbles were found in the thread a measurement of the base and an estimate of the height permitted a correction to be calculated.

The weight of polonium was determined by a calorimetric determination of the heat evolved in stopping the decay products.

CALIBRATION OF CAPILLARY

A heavy walled quartz capillary was drawn out by heating a piece of quartz tubing to thicken it and then exerting a fairly uniform but fast pull on either end of the hot portion. This resulted in a slightly tapered capillary which was then cut at a reasonable distance and sealed at the small end. The tube was weighed empty and with a series of small droplets of mercury. The droplets were individually forced to the bottom of the capillary by centrifugation and were subsequently measured in length by means of a calibrated filar micrometer eyepiece on a microscope. The volumes obtained in this fashion were corrected for the mercury meniscus and plotted against the length of the mercury thread. When a sufficient number of points were obtained, the tube was inverted and centrifuged in order to remove the mercury from the tip.

CALCULATIONS AND ASSUMPTIONS

It was assumed that the temperature of the thread was about 50°C. above the temperature of the surroundings on the basis of

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—= FIGURE 3 —= UNCLASSIFIED

CENTRIFUGE CUP EQUIPPED WITH FURNACE

— SCALE: FULL SIZE —

—= LEGEND —=

Brass Centrifuge Cup

Asbestos Insulation

Nichrome Wire Furnace in Thermocouple Insulators

Iron Tube and Cover

Transite Insulator

Modified Pyrex Centrifuge Cone to hold Quartz Capillary

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an observation made by R. Davis⁽⁵⁾ that the furnace temperature was only about 200°C. when a mass of polonium melted. When a thermocouple is placed directly in the metal it is observed to melt at about 254°C.⁽¹⁾ This and a value of 10×10^{-5} cm./cm./°C., for the coefficient of linear expansion, which is reasonable for a sixth group element, were used in calculating the length of the thread at 250°C., close to the observed melting point of polonium. The assumption was also made that at the melting point and during centrifugation the molten metal completely filled the end of the capillary. Also, that it acted like a normal metal in contracting when it solidified and cooled further to the temperature at which the length measurement was made.

The observed length was corrected back to the length close to the melting point, 250°C., and the volume at that temperature was read from the calibration curve for the capillary. This volume and the calorimetric determination of the weight of polonium is necessary to calculate the density at 250°C. This is then corrected to 25°C., with the aid of the following formula:

$$D_{t'} = \frac{D_t}{(1 - (3\alpha)(t - t'))}$$

where

D = density

t' = 25°C.

t = 250°C.

α = coefficient of linear expansion

Possible sources of error are considered and listed:

1. Calibration of Capillary - A straight line may be drawn through the points obtained with mercury. The mean deviation from this line may be used to assign a value for the error in determining the volume of the capillary.

2. The error in measuring the length of the thread for these experiments is determined by the sensitivity of the filar micrometer eyepiece.

3. An error may be present in making the temperature correction. If it is assumed that the correction is good to 20 per cent, this error is correspondingly reduced.

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4. The error in the calorimetric determination of the weight of polonium used is 0.2 per cent. ⁽⁶⁾

5. Correction for bubbles which were trapped in the thread. These were assumed to be spherical segments and calculations and corrections made accordingly. It appeared that all of the bubbles present were observed although the small possibility exists that some bubbles were present within the thread but could not be seen.

If the polonium sample is essentially 100 per cent pure then the overall error in such a determination should be about 2 per cent.

RESULTS

The calibration curve for the capillary used in the first determination is shown in Figure 4. The value obtained for the density was 8.6 g./cc. at 25°C. The thread which was 4.273 mm. long and contained 5.613 curies of polonium had two bubbles in it which were measured and corrected for. The picture (Figure 5) was taken two days after the measurement was made and the bubbles are not clearly visible. This value would correspond to the density for the high temperature form of polonium except, as has been pointed out, the material received no preliminary purification.

The curve for the calibration of the second capillary is shown in Figure 6. The length of the thread was 7.736 mm. and a calorimetric determination of the quantity of polonium showed 8.387 curies. This corresponds to a density of 9.2 g./cc. One bubble, for which a correction was made, appeared in this thread and can be seen in Figure 7 which is a picture taken about twelve hours after the metal was centrifuged into the capillary. The polonium used in this experiment was purified before use by separating it from the more volatile substances present in the original material. In converting curies to weight a half-life value of 138.4 days for polonium was used. This is the best value obtained to date. Assuming that this is a better run because of this preliminary purification and that the polonium was essentially 100 per cent pure the value 9.2 g./cc. should be good to ± 2 per cent.

COEFFICIENT OF EXPANSION

Maxwell and Beamer conclude that the α -phase of polonium when containing between 4 and 9 per cent lead has a negative coefficient of expansion based on a measurement of the average parameter

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Figure 4

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Figure 6

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Figure 7

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for α -polonium as recorded on their X-ray films. Calculations place a numerical value for the coefficient of thermal expansion for this alloy at $-300 \pm 100 \times 10^{-6}$ cm./cm./°C. β -polonium containing 1.5 per cent lead was assigned a value of $50 \pm 25 \times 10^{-6}$ cm./cm./°C.

If the rather large negative coefficient of expansion assigned to the alloy of α -polonium with between 4 and 9 per cent lead is true, then the expansion of a thread of this material such as that obtained in a density determination could be measured provided the sample is maintained at low temperatures to convert and keep it in the α -phase.

If the formula

$$l_t = l_o (1 + \alpha (t - t_o))$$

is used and a one centimeter thread at 25°C. is used, then its length at -100°C. should be 1.0375 cm. provided the reported coefficient of expansion is correct. This difference in length can be measured quite accurately by means of a calibrated filar micrometer eyepiece.

Apparatus for making such a measurement has been set up but it has not as yet been tested. It will be described in a report written by the person who continues the work.

The plan is to go through the same steps that were followed in making the density determinations and then maintain the sample at liquid air temperature overnight. This should convert the polonium to the α -phase. The temperature of the sample can then be noted and the length of the thread measured over a known low temperature range. From these observations the coefficient of expansion may be calculated.

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REFERENCES

1. C. R. Maxwell and W. H. Beamer, Report #LA-604, Physical Properties and Crystal Structure of Polonium, August 30, 1946.
2. T. J. LaChapelle, Final Report #31, Preliminary Work on Oxidation States of Polonium and Preparation of Some Compounds, p. 26, May 1, 1946.
3. H. Schamp and R. Gunther-Mohr, Physics Group Progress Reports, June through September, 1946.
4. B. B. Brody, Fundamental Research Group Progress Reports, January 1-15, 1947 and February 15-28, 1947.
5. R. Davis and L. Brooks, Physics Group Progress Report, November 16-30, 1946.
6. D. Anger, Calorimeter Research Group Progress Report, October 1-15, 1946.

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