

Physical Properties of Polonium. I. Melting Point, Electrical Resistance, Density, and Allotropy

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elements remain constant and no frequency-shift can arise from this source.

It is seen from the above results that, with the possible exception of the CH_2 bending mode, it is most unlikely that the observed frequency-shifts encountered on passing from chloride to iodide could be accounted for

by variations in small interaction constants normally assumed zero. Since we are dealing here with closely-related structures, there seems no justification for postulating the existence of small interaction constants which undergo relatively large variations in passing along the series.

Physical Properties of Polonium. I. Melting Point, Electrical Resistance, Density, and Allotropy*

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(Received May 2, 1949)

Measurements on the electrical resistance, thermal coefficient of electrical resistance, melting point and density of polonium are reported. An abrupt change in the electrical resistance near 100°C indicates that polonium exists in two allotropic forms. Observations which indicate that the temperature for crystal transformation is a function of the size and history of the specimen are reported.

SINCE its discovery in 1898, many investigations have been made into the chemical properties of polonium but the small quantities of the element available in the past made the determination of its ordinary physical properties impractical if not impossible. The larger, though still minute, amounts of polonium available today in the Manhattan Project have made possible the development of techniques by which rough measurements on some of the physical properties of polonium have been made.

The selection of a method and the accuracy of the method were influenced not only by the small amount of

material available but by the radioactivity of the element: (1) The high specific activity of polonium makes it extremely toxic if absorbed into the body, hence any method employed must keep mechanical scattering and general contamination of the laboratory at a minimum; (2) Since polonium has a half-life of 138 days,¹ the lead content of a freshly prepared sample increases at the rate of one-half percent per day. Methods requiring a long time to attain equilibrium or requiring successive measurements over an appreciable period are impractical; (3) The heat produced by the radioactivity (0.12 calorie per microgram per hour)¹ maintains polonium and its immediate surroundings at a temperature higher than the ambient temperature. The magnitude of this temperature differential varies with the size of the sample and the heat transfer characteristics of its immediate environment. This phenomenon makes the determination or reproducibility of temperature difficult.

PREPARATION AND PURITY OF POLONIUM

Metallic polonium was prepared by electro-deposition on platinum foils from dilute nitric acid solution of polonium nitrate. Earlier work by other members of the laboratory had shown that metal prepared in this manner was very pure, except, of course, for lead which is formed in the metal after deposition. A further check of the purity was made by the spectrochemical analysis of a sample used for a melting point determination. The analysis showed only the expected amount of lead and small amounts of aluminum and calcium. It is believed that these latter impurities were introduced with the acid used to dissolve the sample in preparing it for spectrochemical analysis. In the chemical process used in the recovery of the material for subsequent experiments it is possible but unlikely that other impurities

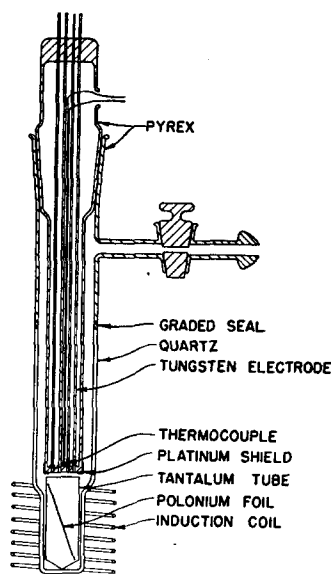


FIG. 1. Apparatus for measuring electrical resistance.

* This paper is based on a portion of thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State College, Ames, Iowa.

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¹ W. H. Beamer and W. E. Easton, *J. Chem. Phys.* **17**, 1298 (1949).

were introduced, since the electro-deposition is in itself a purification.

ELECTRICAL RESISTIVITY

The specific resistivity and the thermal coefficient of resistivity were determined on thin distilled films of polonium in the apparatus shown in Fig. 1.

After the introduction of a freshly prepared polonium coated platinum foil, the apparatus was evacuated to a pressure of from 10^{-5} to 10^{-6} mm of Hg. The polonium was then distilled onto the end of the electrode assembly by heating the tantalum tube to a dull red heat by high frequency induction. The end of the glass electrode holder and the electrodes had been ground and polished so that they formed a smooth flat surface on which the polonium condensed as a thin film and shorted the electrodes.

The apparatus was filled with approximately one-third an atmosphere of helium and placed in a vertical tube furnace where the temperature was slowly raised. The temperature of the end of the electrode assembly was measured by the thermocouple which was in contact with the glass upon which the film was deposited.

The IR drop across that portion of the polonium between the center electrodes was measured with a potentiometer while a constant current, usually 10 ma, was being passed through the film between the outer electrodes.

The amount of polonium in the film was determined after the completion of the measurements by inserting the electrode assembly into a special alpha-counter. The dimensions of the film were assumed to be those of the rectangular opening in the platinum shield fastened across the end of the electrode assembly and the thickness of the film was calculated by further assuming uniform deposition.

The validity of the last assumption was checked by D. T. Vier, who took alpha-ray photographs of several films in a special evacuated pinhole camera. The density of the photographic image thus obtained was a measure of the thickness of the polonium since the deposit was so thin that there was no complete self-absorption of alpha-particles. Visual inspection of the photographic plates showed that the edges of the polonium film were quite sharp and the deposition apparently uniform. Densitometer traces taken from end to end of two such images showed a uniform taper in the thickness of the deposit amounting to 8 percent in one case and 20 percent in the other. The assumption of uniform thickness for a film with 20 percent taper introduces an error of only 3 percent to 4 percent in the calculated specific resistance.

Microscopic examination up to 200X showed a smooth uniform film with small grain size. However, the grain size and general character of the films were found to be dependent upon rate and temperature of distillation. The optimum rate of distillation was different for polonium and each of the metals (lead, zinc, and

TABLE I. Electrical resistivity of polonium.

Determination	Heating rate °C/min.	Transition range °C	Specific resistivity, 0°C micro- ohm-cm		Thermal coefficient electrical resistivity*	
			α -P ₀	β -P ₀	α -P ₀	β -P ₀
VIA	8.0	-86	43	47	0.0045	0.0058
VIB	0.4	65-85	39	42	0.0045	0.0066
VIIA	0.5	78-110	50	43	0.0046	0.0081
VIIIB	0.5	70-105	47	46	0.0037	0.0071
VIII	0.8	100-130	33	36	0.0056	0.0071
Average			42 ± 10	44 ± 10	0.0046	0.0070

* = $(\Delta R)/(R_0 \Delta t)$.

bismuth) used as stand-ins while developing the technique.

The results of several determinations made as described above are shown graphically in Fig. 2 and are also tabulated in Table I.

It will be noted in Fig. 2 that between 65°C and 130°C there is a definite discontinuity in each curve. This was interpreted as due to a change in the crystal structure of polonium. The low temperature phase has been designated α -polonium and the high temperature phase β -polonium. This interpretation of the discontinuity has since been proven correct by the x-ray diffraction studies.²

A polonium film was held at a temperature of -64°C for 12 hours. The resistance of the film was then measured as the apparatus was slowly heated to 50°C. There was no indication of a phase change in this region.

It is estimated that all of the polonium films used in obtaining these data contained between one-half and two percent lead which was formed by radioactive decay during the electro-deposition of the metal and the preparation of the film. This could not be reduced because it was necessary for the freshly prepared film, which was deposited as β -polonium on the uncooled electrode assembly, to stand for several hours in order to form α -polonium. It was thought inadvisable to subject the glass electrode assembly with its many glass-metal seals to the thermal shock of a refrigerant during the distillation in order to deposit the alpha-phase.

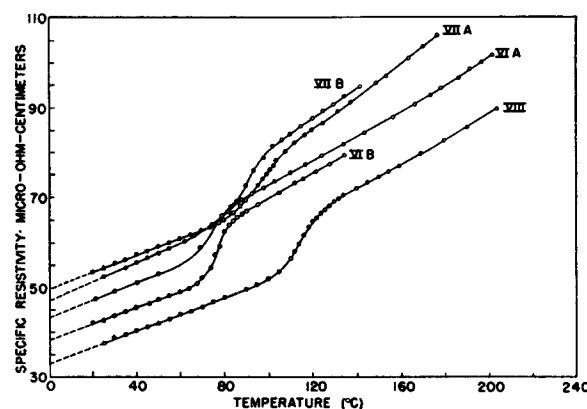


FIG. 2. Specific resistivity of polonium.

² W. H. Beamer and C. R. Maxwell, J. Chem. Phys. 17, 1293 (1949).

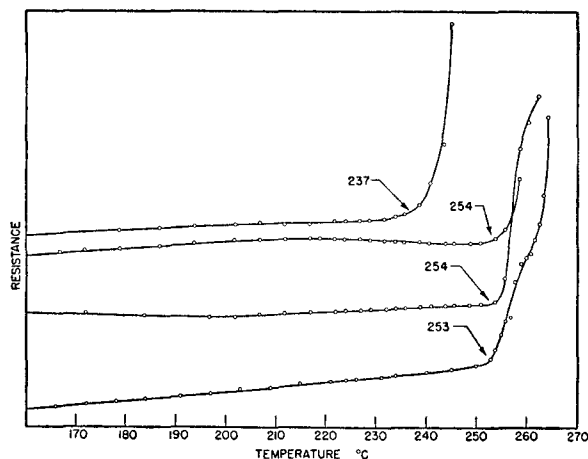


FIG. 3. Electrical resistance curves showing the melting point of polonium.

The average values of 42 ± 10 micro-ohm-centimeters for R_0 of α -polonium and 44 ± 10 micro-ohm-centimeters for R_0 of β -polonium are believed to be maximum values. All undetermined errors due to cracks, porosity or other physical defects in the polonium film add to make the specific resistivity secured with this technique larger than the true specific resistivity for massive metal. Furthermore, the presence of the unavoidable lead gives an alloy whose resistance is undoubtedly higher than that of pure polonium. It is thought that the effect of the lead is small since the resistance of a sample did not change with lapse of time and increasing lead content.

MELTING POINT

Films of polonium prepared in the same manner as described for the resistivity measurements were heated to temperatures around 250°C . Near this temperature the resistance of the films always showed a large, abrupt increase which was usually followed by the breaking of the film. Figure 3 shows the results of several melting point determinations. These curves have been displaced vertically to show clearly the change in slope. The point of abrupt change in slope was taken as the melting point.

Figure 4 is a photograph of the end of the electrical resistivity apparatus after a melting point determination. Globules of once molten metal have formed on the ends of the metal electrodes and a rectangular "fence" of tiny beads outline the edges of the film.

The melting points of several other elements (Baker's C.P. grade) were determined by J. B. Roberts using the same technique and apparatus with the following results:

Metal	Experimental	Literature
Bi	269°C	271°C
Cd	315	320.9
Zn	417	419.5.

A visual melting point was taken with a slight modification of the resistivity apparatus. Polonium was distilled from a tantalum tube with a small nozzle onto a glass surface at liquid air temperature. The sample was

transferred from the distillation apparatus to a jacket containing a window through which the polonium deposit could be observed and photographed. Figure 5 shows the sample after it had warmed up to room temperature. Note the large shrinkage cracks produced in the metal when it was "heated" from -190°C to 25°C . This shrinkage corroborates the evidence of a negative coefficient of expansion for α -polonium indicated by x-ray patterns.

The apparatus was placed in a tube furnace and the temperature slowly raised. The temperature was measured by a thermocouple placed on the other side of the glass surface. The polonium deposit was viewed through a low power microscope during the heating period. At 246°C there was a distinct change in the surface of the deposit which was interpreted as due to the melting of the sample.

DENSITY

The density of polonium was determined by measuring the length of an "ingot" of polonium which had been centrifugally cast into the end of a small capillary of pre-determined cross-sectional area. The amount of polonium in the ingot was determined calorimetrically by W. E. Easton.¹

The polonium was distilled into the capillary and sealed from the distillation apparatus by a technique of successive vacuum distillations described in detail in a companion paper.² The capillary was placed in a special centrifuge cup and heated to 450°C , which is well above the melting point of polonium. While at this temperature the massive centrifuge cup and capillary were placed in a centrifuge and whirled until cool. In this manner the molten polonium was centrifugally cast into the calibrated end of the capillary. The length of the "ingot" was then measured with a comparator and microscope.

The density of polonium was calculated to be 9.4 ± 0.5 g/cc.

The capillary and ingot were cooled overnight in an oil bath at a temperature of -50°C and then heated slowly until the ingot was observed to melt near 250°C . The measurements made of the length of the ingot over



FIG. 4. End of specific resistivity apparatus after melting point determination.

this temperature range were not sufficiently accurate to detect the allotropic change in polonium or to give a measure of the thermal coefficient of expansion.

THE ALLOTROPY OF POLONIUM

No extensive investigation of the transformation of polonium has been made. The observations presented here were incidental to other investigations and the conclusions drawn are only suggestive.

Both the x-ray data, in an accompanying paper,² and the electrical resistivity data of this investigation show that alpha- and beta-polonium co-exist for long periods of time over a considerable range of temperature and that the temperature of the transformation of beta-polonium to alpha-polonium is considerably lower than the temperature of the transformation from alpha-polonium to beta-polonium. Furthermore, the range of temperature of the α - to β -transformation was found to vary with the thickness of the sample used for the determination.

For a given film of polonium the range of temperature over which the alpha- to beta-transformation is observed to occur is independent of the rate of heating. Data for curve VIA of Fig. 2 was obtained while the sample was being heated rapidly. The sample was heated from 50°C to 98°C in six minutes. The data for curve VIB was obtained several hours later by slowly heating the same sample. The transformation began at 65°C. Eight minutes later the temperature reached 68°C and was held constant at this temperature for ten minutes. There was no change in the resistance to indicate that the transformation had proceeded during this interval. The temperature was then slowly raised until the transformation was complete. The temperature range from 50° to 98°C was covered in 103 minutes. The curves show that in both cases the transformation was complete at essentially the same temperature.

When the samples used in obtaining Fig. 2 were slowly cooled to room temperature there were no indications of a β - to α -transition. The β - to α -transition usually required 10 to 15 hours for completion at room temperature although a decided drop in resistance could be ob-

served in one or two hours. Two complete heating cycles for sample VI are recorded in Fig. 6. The numbers on the graph give the elapsed time in minutes from the start of the first cooling curve.

The possibility that this hysteresis was solely the result of a slow reaction rate was investigated by holding the sample used in obtaining curve VIIB, Fig. 2 at 60°C for four hours. Although this was 15° below the beginning of the α - to β -transition observed on heating, only one hour earlier, there was no change in resistance to show that any β - to α -transformation had occurred.

The range of temperature over which the α - to β -transformation occurred was dependent upon the size of the sample used in the determination. Curve VIB of Fig. 2 obtained with a sample approximately 4000 atoms thick shows a transition range from 65° to 85°C. Curve VIII obtained with a film only 350 atoms thick shows a range from 100° to 130°C. Curves VIIA and VIIB obtained with an intermediate thickness of approximately 3000 atoms show an intermediate range of from 75° to 105°C. Other curves with films 10,000 atoms thick show a range of 65° to 85°C.

Apparently the dependence of the transition temperature upon the thickness of the polonium is real and not the result of a systematic temperature differential between the temperature of the polonium film and the temperature observed with the thermocouple inside the electrode assembly. The temperature of a polonium film several thousand atoms thick was found to be only 3° above room temperature by the use of a special electrode assembly constructed of soft glass with three platinum and one platinum-10 percent rhodium electrodes. The transition range and melting point were observed to be 68–86°C and 254°C with this sample. It is believed that the true temperature of the polonium is measured by the (platinum)-(platinum-rhodium) thermocouple formed by the two center electrodes when they are connected by the distilled film of polonium and the polonium sample is the "bead" of the thermocouple.

The difference in transformation temperature cannot be explained by a difference in lead content since resistivity curves run on the same sample with an elapse of time sufficient to double the lead content showed no appreciable change.

An unsuccessful attempt to extend these observations to higher lead contents and to obtain a liquidus curve for lead alloys was made by R. W. Senseman. The distilled films upon which the electrical resistivity was being measured were destroyed by oxidation when they stood for long periods of time. Because of the low melting point of polonium there was no obvious way to degas the apparatus and prevent this oxidation.

The dependence of crystal transformation temperature upon grain size and heat treatment of the sample has been observed in at least one other case by Edwards and Lipson³ in their investigation on the transformation

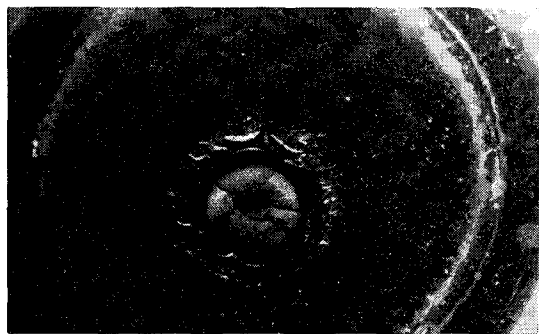


FIG. 5. Distilled polonium bead showing thermal cracks when heated from -190°C to 25°C .

³ O. S. Edwards, and H. Lipson, *J. Inst. Metals* **69**, 177 (1943).

TABLE II. Comparison of the physical properties of polonium and other elements.

Element	Atomic No.	Group in periodic table	Specific resistivity microhm-cm	Thermal coefficient of electrical resistivity $\alpha = \Delta R / \Delta T R_0$	Melting point °C	Density g/cc
S	16	VI	2×10^{23}	Large negative coefficient	113	2.07
Se	34	VIB	2×10^{11}	Large negative coefficient	220	4.80
Te	52	VIB	2×10^5	Large negative coefficient	452	6.24
Po	84	VIB	42 (α) 44 (β)	0.0046 (α) 0.0070 (β)	254	9.4
Bi	83	VB	115	0.0045	271	9.80
Pb	82	IVB	22	0.0043	327	11.34
Tl	81	IIIB	18	0.0040	303	11.85

of cobalt. The two cases are quite parallel. The β - to α -cobalt transformation and the α - to β -polonium transformation both occur over ranges of temperature, the length of the range increasing with decreasing size of specimen. The transformation begins at different temperatures for both metals and in each case the smaller specimen requires the greater thermal stress to make the reaction proceed. The reverse transformation in both metals occurs only after the specimen has been stressed considerably beyond the temperature at which the first transformation was observed to be.

According to Dehlinger⁴ the change in surface energy for small grains may become comparable with the energy of the crystal transformation, if there is a volume change accompanying the transition. In such a case the temperature of transition for a specimen would depend upon the grain size of the specimen and if there were a range in grain sizes then there would be observed a range of transition temperatures. The magnitude of the temperature change would be a function of (1) the surface energy, (2) the volume change, (3) the heat of transformation for massive metal and (4) the angle at which the free energy-temperature curves of the two phases intersect.

Dehlinger calculated that in the case of thallium, which undergoes a h.c.p. to f.c.c. transition similar to cobalt, the change in surface energy accompanying crystal transformation would be of the order of the heat of transformation for grains with a diameter of 2×10^{-5} cm. This diameter is of the order of magnitude of the thickness of the polonium samples investigated.

⁴ U. Dehlinger, Metallwirtschaft. 11, 223 (1932).

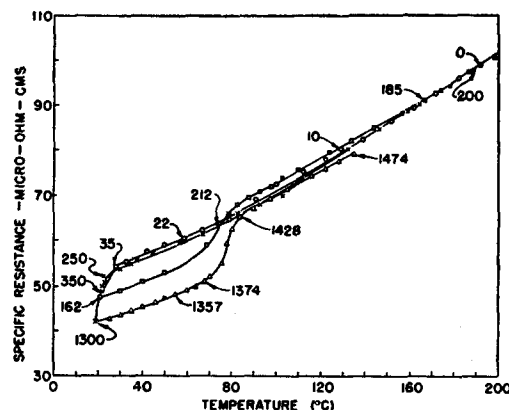


FIG. 6. The specific resistance of polonium as a function of temperature and heat treatment. O—first cooling curve, □—first heating curve, X—second cooling curve, △—second heating curve, 10, 1474, etc., elapsed time in minutes.

Dehlinger's theory seems to account for the anomalous observations on the polonium transition. There is a volume increase of 3 percent accompanying the α - to β -transition, the transition occurs over a range of temperatures and these temperatures increase with a decrease in the thickness of the samples used for the determination.

SUMMARY

Table II lists the properties of polonium as determined by this investigation and the properties of other elements as taken from the International Critical Tables.

It is apparent that polonium is quite metallic in character and resembles Tl, Pb and Bi in its physical properties more closely than it does Se and Te although these latter elements are in the same group in the periodic table.

ACKNOWLEDGMENTS

The author gratefully acknowledges his indebtedness to Dr. I. B. Johns, at whose suggestion the work was initiated, Dr. D. S. Martin and Dr. E. R. Jette for their many suggestions and helpful discussions. He also thanks Mr. Dave Durrill for the electro-deposition of most of the polonium used in the study.

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