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ART. XIV.—*On the Ratio of Radium to Uranium in some Minerals;* by BERTRAM B. BOLTWOOD.

THE experiments which will be described in this paper were undertaken with the object of determining the relative proportions of radium and uranium present in certain mineral substances.*

The method which has been used for the quantitative estimation of the radium depends upon the electrical measurement of the radium emanation which is given off when a known quantity of the mineral is dissolved or decomposed by suitable chemical reagents and this solution is allowed to stand for several days in direct communication with a closed glass vessel. Another plan which has also been tried is to decompose the mineral completely in an open vessel and to heat the solution to boiling in order to expel all of the accumulated emanation. The solution was then sealed up in a closed glass vessel and the emanation allowed to accumulate for a given period, at the end of which it was removed and measured†.

The testing of the emanation was carried out in an air-tight electroscope (fig. 1) similar in principle and design to that described by C. T. R. Wilson. It consisted of a rectangular brass case *A*, 15^{cm} high, 10^{cm} wide and $4{\cdot}5^{cm}$ deep. The

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*A preliminary notice in which some of the results were given has already appeared in the Engineering and Mining Journal, lxxvii, p. 756, and in the London Nature, lxx, p. 80.

† In a paper by Strutt (Proc. Royal Soc., lxxiii) some measurements of the amounts of radium emanation given off by certain minerals on heating are described. Some experiments which I have made show that samarskite, on heating to low redness, gives off only 10 per cent, and on heating to bright redness only 20 per cent, of the emanation set free when this mineral is completely decomposed with hot sulphuric acid.

walls of this case were 6^{mm} in thickness and were grooved on the edge to a depth and width of 3^{mm}. Two plates of plate-glass 3^{mm} thick fitted closely into the grooves of the case and the joint was made air-tight by the use of hot sealing-wax. The glass plates formed the front and back of the electroscope case. The case was provided with two brass stopcocks, *G*, and carried on the top a glass tube *T*, $2{\cdot}5^{cm}$ in diameter and $7{\cdot}5^{cm}$ in length. The gold-leaf, *l*, was attached to the brass plate *p*, which was 5^{cm} long and 1^{cm} wide, and was soldered to a brass rod $1{\cdot}5^{cm}$ long and 3^{mm} in diameter. The rod *s* of cast sulphur, 4^{cm} long and 1^{cm} in diameter, served as an insulating support for the gold-leaf and was attached at the top to a brass rod 12^{cm} in length and 3^{mm} in diameter. The brass rods were connected firmly to the sulphur support by warming the rods to above the melting point of sulphur and pushing them a short distance into the ends of the sulphur rod. Fitted to the top of the tube *T* was a brass ring, *C*, into which screwed the cap *B*, also of brass. Through the latter passed a short glass tube 1^{cm} in diameter and contracted somewhat at the top. This glass tube was filled with melted sulphur, which was then allowed to solidify. The end of the rod *t* was then warmed and pushed through the sulphur plug until it extended about 5^{mm} beyond

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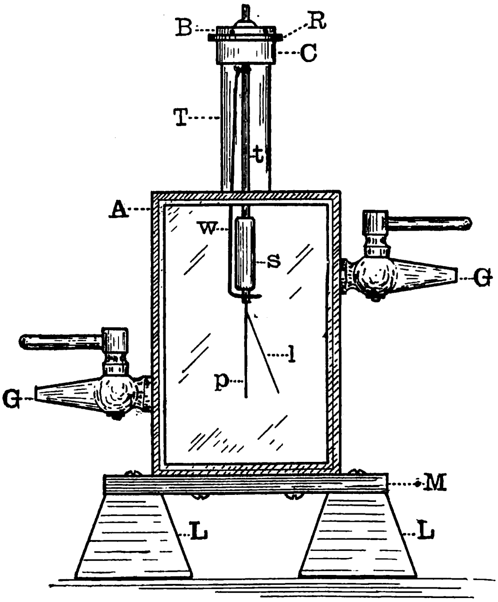

it, and the joint was made still tighter by the application of a small quantity of melted sealing-wax. Suspended by a small hook near the top of the rod *t* was a soft iron wire *w*, which extended to below the sulphur rod and terminated in a loop which surrounded the rod supporting the plate *p*. When hanging in its normal position this wire did not touch the lower rod, but on bringing a small magnet near the tube *T* the wire was deflected and established a metallic circuit between the upper rod and the gold leaf. The plate *p* and the metal portions of its supports were heavily gold-plated to prevent tarnishing. All of the joints and crevices were filled with sealing wax except that between *B* and *C*, which was closed air-tight by a rubber washer, *R*, between them. By unscrewing the cap *B* the gold-leaf and its supports could be removed from the case.

The electroscope was attached by screws to an iron plate, *M*, which in turn was fastened to two lead ingots, *L*, *L*, weighing about seven pounds each. The whole apparatus was therefore very steady and connections could be made at the cocks without fear of altering the adjustment.

For charging the gold-leaf a large stick of sealing-wax was used. This was rubbed lightly on the clothing and approached to the top of the rod *t*, the wire *w* being brought at the same time into contact with the plate *p* by means of a small magnet. On rubbing the rod gently with the sealing-wax a sufficient charge was imparted to the gold leaf to produce the desired deflection. After removing the sealing-wax stick and the magnet, the top of the rod and cap were touched with the finger. This method of charging worked very well during the dry weather of winter and early spring but became troublesome when the air of the laboratory grew moister, and has therefore been superseded by the use of a battery of small storage cells giving a potential of from 300 to 400 volts.

The fall of the gold-leaf due to leak of the electric charge was observed by means of a microscope mounted on a separate support in front of the electroscope. This microscope consisted of a Bausch and Lomb combination of a 2-inch eye-piece and a 1½-inch objective mounted in an ordinary draw-tube. The diameter of the field was about 4^{mm} and the eye-piece contained a glass scale divided into nine divisions, which were further subdivided into tenths; each tenth of a division therefore corresponded to about $0{\cdot}044^{\mathrm{mm}}$.

The radium emanation given off by a known weight of mineral substance was collected in the apparatus shown in fig. 2. This was made entirely of glass and consisted of an elongated bulb, *A*, connected by a tube with the smaller bulb *B*, which in turn was connected with the still smaller bulb *C*. A weighed quantity of the very finely powdered mineral was introduced from a long, thin weighing-tube into the bulb *B*, and, except where the reagent afterwards employed was concentrated sulphuric acid, enough water to cover the mineral was then introduced into *B* from a small pipette. *C* was then filled with the acid used to decompose or dissolve the mineral and, the capillary tubes at *f* and *g* having been already closed, the tube *CD* was drawn out into a short capillary and sealed off in the flame of a blast-lamp. At the moment of sealing off, a slight negative pressure was created in the interior of the apparatus by drawing out a small portion of the air through a rubber tube attached at *D*.

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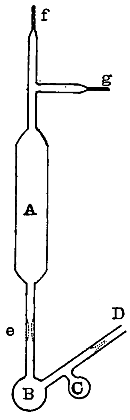

The apparatus was tipped until the acid in *C* ran over into *B*, and *B* was then warmed gently until the mineral contained in it had been entirely decomposed. The apparatus was then allowed to stand undisturbed for several days to come into equilibrium and the tube connecting *A* and *B* was then drawn out into a short capillary and sealed off at *e*. The bulb *A*, separated in this manner from the rest of the apparatus, was then allowed to stand for about two hours in order that any rapidly decaying emanation (thorium or actinium) might be entirely removed. The air and radium emanation contained in *A* were then transferred to the electroscope in the following manner: The capillary tube at *e* was first notched with a file and then broken off under the surface of a strong sodium hydroxide solution. Because of the diminished pressure in *A*, several cubic centimeters of the sodium hydroxide solution would be drawn into the bulb. A short rubber tube filled with water was then slipped over *e*. The other end of this rubber tube dipped into a vessel of water. A closed screw pinchcock was then attached to the rubber tube near *e* and the bulb *A* was tilted so that its interior walls were completely wetted with the sodium hydroxide solution. This served to dry the gas somewhat and to remove any acid fumes which might be present. The pressure on the interior of the electroscope was now exhausted to about one-half atmosphere and the stopcocks closed. The capillary tubes at *f* and *g* were notched with a file and *f* was connected with one of the stopcocks of the electroscope by a short section of rubber tubing. The pinchcock at *e* was then opened, the tip of the capillary tube *f* was broken off inside the rubber tube, the stopcock of the electroscope was opened slightly and the air in *A* was drawn over into the electroscope. When the water had risen in *A* until it had reached the junction of the side-tube *g*, the pinchcock at *e* was closed, the tip of *g* was broken off and the external air was allowed to sweep through the system of tubes until the pressure within and without the electroscope was the same. The stopcock of the electroscope was then closed and the other apparatus disconnected.

For determining the rate of leak or discharge of the gold-leaf, measurements were made of the time required for the gold-leaf to fall through a distance equal to eight divisions of the scale in the eye-piece in the microscope. The time required was recorded by means of a stop-watch divided to fifths of a second. Because of the initial rise in the activity, due to the formation of induced activity within the electroscope, the rate of leak at the end of three hours was chosen in comparing the results obtained with different minerals.

In order to determine the quantity of uranium present in the mineral under examination, the solution in the bulb B was washed out into a beaker and the quantity of uranium determined by one of the ordinary methods of analysis.

The capacities of the two final sections of the apparatus were determined by filling them with water and weighing them, and then weighing them when empty. The average capacity of *A* in the different experiments was about 48^{cc} and the average capacity of the rest of the apparatus was about 9^{cc}. In comparing the results obtained with different minerals it was in general assumed that the distribution of the emanation throughout the different parts of the apparatus was uniform and the volume occupied by the solution was neglected. Since the capacities of the different pieces of apparatus used were in all cases approximately the same and the volumes of the different solutions were all approximately equal, this possibly doubtful assumption would cause no serious error in the results when used for purposes of comparison.

The results obtained with eight different samples of uranium minerals are given in a table below. For decomposing the uraninites strong hydrochloric acid containing a little nitric acid was used, the gummite and uranophane were treated with strong hydrochloric acid and the carnotite was dissolved in dilute (1:1) nitric acid. The sample of samarskite used was obtained in a very finely divided condition by suspension in water and decantation from the coarser material. In this form it could be readily decomposed with concentrated sulphuric acid.

The samples No. 1, 2, 3 and 4 were from North Carolina, No. 5 from Branchville, Conn., Nos. 6 and 7 from Colorado and No. 8 from Saxony.

Between experiments 5 and 6 the adjustment of the electroscope became slightly altered from an accidental movement of the microscope support. A re-determination of the constant for sample No. 1 under these conditions gave the value of the ratio as 263.

No.	Substance.	Per cent uranium in mineral.	Grams uranium taken.	Leak divisions per min.	Ratio leak to uranium.
1	Uraninite	82·5	0·1067	22·5	211
2	Gummite	66·1	0·0982	20·8	212
3	Uranophane	46·6	0·0671	12·1	181
4	Samarskite	9·8	0·0299	6·4	214
5	Uraninite	83·9	0·0994	20·6	207
6	Carnotite	18·0	0·0258	6·9	267
7	Uraninite	54·6	0·0783	19·8	253
8	Uraninite	48·5	0·0699	16·5	231

The low value of the ratio in the experiment with No. 3 was at first attributed to the fact that this material appeared to give off in the cold a greater proportion of its emanation than the other minerals of the series and that it had, therefore, not reached a state of equilibrium at the time when the emanation was measured. A more careful measurement of the proportion of emanation lost by the cold pulverized samples was made and no differences sufficiently great to explain the low value in No. 3 were obtained. Since the solution of the uranophane had gelatinized on standing in the solution apparatus, owing to the relatively high proportion of silica which the mineral contains, it was thought that this might have been the cause of the low result. Small samples of Nos. 1, 2 and 3 were, therefore, completely decomposed with acids and the resulting solutions evaporated to dryness on the water-bath. The residues were treated with dilute hydrochloric acid and the solutions thus obtained were introduced into apparatus similar to the solution tubes (fig. 2) already described, except that the lower part consisted of a single bulb only. The solutions were then sealed up and allowed to stand for thirty days. At the end of this period the bulb *A* was sealed off and the accumulated emanation transferred to the electroscope. The results thus obtained are given in the following table:

No.	Substance.	Per cent uranium in mineral.	Grams uranium taken.	Leak divisions per min.	Ratio.
1	Uraninite	82·5	0·1227	16·6	135
2	Gummite	66·1	0·0964	13·3	138
3	Uranophane	46·6	0·0686	9·8	143

It is therefore probable that the low value obtained in the first experiment with the uranophane was due to the formation of gelatinous silica. The value of the ratio stands in no direct relation to that obtained in the other series, since the adjustment of the electroscope was again different.

The chief sources of error in the method as described are due to two causes. One of these lies in the fact that the heating of the tube connecting the bulb *A* with the bulb *B* naturally warms the gases contained within them and causes a slight alteration in their relative capacities. This difficulty was avoided as much as possible by wrapping both bulbs in wet filter paper before the tube connecting them was heated. The other possible error lies in the fact that some of the minerals tested, particularly Nos. 7 and 8, contained a considerable per cent of sulphides. On treating these minerals with the aqua regia necessary to decompose them, the sulphur of the sulphides was in part oxidized to sulphuric acid and a noticeable quantity of lead sulphate separated from the solution. Although radium sulphate is quite soluble in the strong aqua regia used, it is not impossible that slight traces of this compound were carried down by the precipitated lead sulphate. This would explain the lower values of the ratios obtained with 7 and 8.

I am particularly indebted to Prof. H. A. Bumstead of Yale University for valuable assistance and advice given in connection with this research, and to Prof. S. L. Penfield of Yale University and Dr. Joseph Hyde Pratt of Chapel Hill, N. C. for most generously supplying me with the minerals used in these experiments.

Conclusions.

The quantities of radium present in the uranium minerals which have been examined are apparently directly proportional to the quantities of uranium contained in the minerals.

Since it has been suggested by J. J. Thomson and Rutherford* as very probable that radium is formed by the breaking down of the uranium atom, and if such were the case a final state of equilibrium and a definite proportion between the uranium and radium present in minerals would be expected, these results seem to be of value in furnishing experimental evidence of the actual existence of this fixed relation. It is planned to extend the work to other minerals containing a smaller per cent of uranium and to introduce certain modifications in the method which will considerably increase its accuracy.

New Haven, Conn., June 29, 1904.

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* Radio-activity, Cambridge University Press, 1904.