

NICKEL TRIHYDROXYGLUTARATE.			COBALT HYDROXYGLUTARATE.		
Mol. wt. = 237.			Mol. wt. = 237.		
0.6050	0.080°	140	0.5625	0.072°	145
0.3025	0.042	317	0.2813	0.037	141
0.1513	0.025	112	0.1407	0.021	124
MAGNESIUM TRIHYDROXYGLUTARATE.					
Mol. wt. = 202.					
1.9087	0.293°	121			
0.9544	0.154	115			
0.4772	0.092	96			

When we compare the apparent molecular weight with the molecular weight calculated on the basis of the simple formula in the above table there appears to be but little evidence of polymerization. In the case of the tartrates of nickel and cobalt, apparent molecular weights were obtained which exceeded the calculated molecular weights, and this was the reason for postulating polymerization in those cases. Since, however, the trihydroxyglutarates yield somewhat higher apparent molecular weights than the other glutarates and also molecular conductivities, it can be said that, if there is any tendency toward polymerization of these salts, it is strongest when the maximum number of hydroxyl groups are present in the molecule.

It may, however, be stated that the tendency toward polymerization shown by the cobalt and nickel salts of malates and tartrates apparently grows no stronger with similar salts of the higher hydroxy-acids of this series.

WESTERN RESERVE UNIVERSITY,
January, 1905.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

RADIOACTIVITY AS AN ATOMIC PROPERTY.

BY HERBERT N. MCCOY.

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It is now generally considered that the radioactivity of any element is independent of its form of chemical combination, that, in fact, radioactivity is a property of the atom rather than of the molecule. There is already much evidence in favor of this view. Thus it is well established that the rate of decay of activity of temporarily radioactive products is wholly independent of all

chemical as well as physical conditions.¹ Further, all compounds of radium and uranium are active, as are also, probably, all those of thorium.² The radioactivity of pure uranium compounds is roughly proportional to the percentage of uranium.³

Table I shows the results obtained by Mme. Curie for the activities of a number of uranium compounds, in terms of the saturation current, i , in amperes. It is apparent that the greatest activity is shown by those compounds richest in uranium. I have calculated the ratio of the current to the percentage, P, of uranium. The ratio is of the same order for all compounds, but it is by no means constant.

TABLE I.

	P.	$10^{11}i$.	$\frac{10^{13}i}{P}$.
Metallic uranium.....	100	2.3	2.3
Uranium oxide black.....	86	2.6	3.0
" " green.....	85	1.8	2.1
Uranic acid.....	72	0.6	0.8
Sodium uranate.....	75	1.2	1.6
Potassium ".....	72	1.2	1.7
Ammonium uranate.....	76	1.3	1.7
Urano sulphate.....	48	0.7	1.5
Uranyl ".....	56	1.2	2.1
" nitrate.....	47	0.7	1.5

In connection with a study of the relative activities of uranium ores and pure compounds of uranium,⁴ I have also made some measurements of a similar nature, the results of which are reproduced in Table II. Here θ is the time of discharge of the electro-scope through a certain number of divisions of the scale of the micrometer microscope. The radioactivity is inversely proportional to θ . P is the percentage of uranium and $K = \frac{10^5}{P \times \theta}$.

TABLE II.

	Formula.	θ .	P.	K.
1	U_3O_8	259	85	4.55
2	$U_3O_8^5$	270	85	4.37
3	$UO_2(OH)_2$	303	72	4.59
4	$UO_2(NO_3)_2 \cdot 6H_2O$	650	47	3.27
5	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	492	56	3.62
6	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	545	56	3.28

Mean, 3.86

¹ P. Curie: *Soc. Phys.*, 1900, p. 20; *Compt. Rend.*, **136**, 225 (1903). Becquerel: *Ibid.*, **133**, 199 (1901); Rutherford and Soddy: *Phil. Mag.* [6], **4**, 385 (1902).

² Inactive thorium has been reported by Hofmann and Zerban, *Ber. d. chem. Ges.*, **36**, 3093 (1903) and by Baskerville and Zerban, *This Journal*, **26**, 1642 (1904).

³ Mme. Curie: *Thèse*, Paris (1903); also *Chem. News*, **88**, 98 (1903); McCoy: *Ber. d. chem. Ges.*, **37**, 2641 (1904).

⁴ McCoy: *Loc. cit.*; Boltwood: *Am. J. Sci.*, **18**, 97 (1904).

⁵ Two different samples of each the oxide and acetate were studied.

It was found that the ratio of the activity to the percentage of uranium was more nearly constant for the ores than for the pure compounds. But the activity constant, K , was approximately 5.7 times as great for the ores as for the pure substances. This excess of activity of the ores is due to radium. It would follow that imperfect purification in the process of preparation might give products containing more or less radium, and therefore abnormally active. The question whether the radioactivity of all pure uranium compounds is directly proportional to the percentage of uranium and whether radioactivity is really an atomic property was so important that further study was devoted to the problem, with the results here reported.

The following experiment showed conclusively that the above-mentioned suggestion is inadequate to explain the variability of K , for which a constant value might be expected. Five grams of pure uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (C. A. F. Kahlbaum's best grade) gave upon ignition 2.802 grams of U_3O_8 ; calculated, 2.797 grams. The ratio of the activities of 0.5-gram portions of the oxide, so obtained, and of the original nitrate were as 356 to 115. The measurements were made with an electroscope in the manner previously described.¹ The percentages of uranium are 85 and 47 respectively, from which K equals 4.2 and 2.5. In this experiment the two compounds must have contained the same proportion of radioactive impurity (radium), if any at all were present. The non-agreement of the two values of K is due to an entirely different cause.

Mme. Curie had shown² that the effective activity, as measured by the conductivity method, of any uranium compound, spread uniformly upon a given area, is nearly independent of the thickness of the layer, for layers between 0.5 and 3 mm. thick. This result was confirmed by Rutherford and McClung³ who found that in the case of uranium oxide the maximum activity was practically reached for a weight of 0.035 gram per square centimeter. Taking the density of U_3O_8 as 7.2, such a layer would be about 0.05 mm. thick. This effect is due to the great absorption of the α -rays, which are the chief cause of ionization, by the uranium compound itself. The absorption of the Becquerel and cathode rays by screens of inert matter has been extensively

¹ McCoy: *Loc. cit.*

² *Loc. cit.*

³ *Phil. Trans. A*, 1901, p. 25.

studied. The intensity, I , of the rays after passing through a thickness, x , of the screen is expressed by $I = I_0 e^{-\lambda x}$, where I_0 is the initial intensity and λ the absorption constant for unit thickness. It has been shown by Strutt¹ that the coefficient of absorption of the β -rays of radium by various forms of matter is nearly proportional to the density of the absorbing screen. Leonard² had found a similar result for cathode rays.

It has been shown³ that the α -rays of all compounds of the same radioactive element have the same power of penetration for screens of inert material. Experiments of Rutherford and Miss Brooks⁴ show that the coefficients of absorption of the α -rays of thorium, radium and uranium by aluminium and by air are approximately proportional to the densities of these two substances. Considering these facts, it seemed possible that the coefficients of absorption of the α -rays by the uranium compounds themselves might be proportional to their densities; and therefore that for equal weights of all uranium compounds spread uniformly upon equal areas the observed activities, as measured electrically, should be proportional to the percentages of uranium. The results shown in Tables I and II indicated that either such a simple absorption law did not apply in the case of the radiations of uranium, or that radioactivity is not strictly an atomic property. As will be shown subsequently, the former of these alternative suggestions is the true explanation of the facts.

If a thin layer, of weight w , of a radioactive substance is spread uniformly upon a metal plate of area s , and if A is the observed activity, as measured electrically, it is readily shown that

$$\frac{dA}{dw} = \frac{1}{2} \left(k_1 - \frac{k_2 A}{s} \right) \quad (1)$$

where k_1 is the total activity of unit mass for no absorption of the rays, and k_2 is the constant of absorption for unit mass of substance upon unit area.⁵ The factor $\frac{1}{2}$ is used, since half of the rays are directed downward, and are absorbed by the metal plate. Integration of (1) gives⁶

¹ *Nature*, **61**, 539 (1900).

² *Wied. Ann.*, **56**, 255 (1895).

³ *Mme. Curie: Loc. cit.*; Rutherford: *Phil. Mag.*, [5], **47**, 117 (1879); Owens: *Ibid.*, **48**, 360 (1899).

⁴ *Phil. Mag.* [6], **4**, 6 (1902).

⁵ If λ is the coefficient of absorption for unit thickness; $k_2 = \frac{\lambda}{\text{density}}$.

⁶ Cf. Rutherford and Grier: *Phil. Mag.* [6], **4**, 327 (1902).

$$A = \frac{k_1 s}{2k_2} \left(1 - e^{-\frac{k_2 w}{s}} \right). \quad (2)$$

For all but small values of w , $e^{-\frac{k_2 w}{s}}$ is practically zero, and

$$A = \frac{k_1 s}{2k_2} = A_1 \quad (3)$$

where A_1 is the maximum value of the function. Therefore

$$A = A_1 \left(1 - e^{-\frac{k_2 w}{s}} \right). \quad (4)$$

By means of the last equation it is possible to determine k_2 and k_1 from the observed activities of layers of different weights.

$$\text{If } \frac{A}{A_1} = x,$$

then

$$k_2 = \frac{2.303 s}{w} \log \frac{1}{1-x}. \quad (5)$$

I have found that when finely powdered uranium oxide is sifted on a plate, so as to obtain a fairly uniform distribution, the maximum activity is practically reached for about 0.02 gram per sq. cm. The thickness of such a layer is about 0.03 mm. This result agrees well with that obtained by Rutherford and McClung¹ by the same method. It was found to be almost impossible by the method of sifting to get perfectly uniform layers much thinner than 0.03 mm. This is not remarkable, since the finest bolting-cloth obtainable had meshes of 0.1 mm. The desired result was accomplished by grinding the uranium compound in an agate mortar with a volatile liquid in which the compound was insoluble and then pouring the liquid, containing the suspended substance, into a shallow flat-bottomed metal dish. This was covered with a cover-glass until the sediment had settled. When the liquid had evaporated the solid was left in the form of a thin, exceedingly uniform film. In some cases this was not more than 0.0005 mm. in thickness. Chloroform and ethyl and methyl alcohols were used as the suspending liquids.

The measurements of radioactivity were made with an electro-scope as previously described.² The sensitiveness of the electro-scope varied somewhat from day to day. The maximum change was about 3 per cent., as shown by measurements of the activity of a certain portion of uranium oxide used as a standard. Usually five determinations of the activity of each film were

¹ *Loc. cit.*

² McCoy: *Rev. d. chem. Ges.*, **37**, 2648 (1904).

made, and the average taken. For the same film successive averages so found did not differ by as much as $\frac{1}{2}$ per cent. In order to detect any possible change in the sensibility of the electroscope, determinations with the standard sample were made immediately before and after every set of measurements made with each film. The ratio of the activity of the standard to that of any film remained quite constant from day to day as the following results obtained on different days show: 2.152, 2.158, 2.157, 2.164; also in another case: 0.9916, 0.9917, 0.9934, 0.9933, 0.9966, 0.9917. The variations in the sensitiveness of the instrument did not, therefore, cause appreciable errors in the determinations of relative activity.

Thus far, three pure compounds of uranium have been systematically examined. These are the oxide, U_3O_8 ; the oxalate, $UO_2 \cdot C_2O_4 \cdot 3H_2O$; and ammonium uranate, $(NH_4)_2U_2O_7$. Good films of the nitrate could not be obtained because no volatile liquid could be found in which the finely powdered nitrate would remain suspended. The oxalate is obtained as a yellow crystalline meal upon mixing solutions of the nitrate and oxalic acid.¹ Kahlbaum's purest uranium nitrate was used as the starting material in all cases. Analysis of the hydrated salt: 1.6108 grams at 105° lost 0.1432 gram of H_2O ; 0.5783 gram gave upon ignition 0.3925 gram of U_3O_8 .

	Calculated for $UO_2C_2O_4 \cdot 3H_2O$.	Found.
$3H_2O$	8.70	8.89
U.....	57.82	57.59

The dried salt, from the above determination of water of crystallization, took up moisture rapidly when exposed at ordinary temperature to the air of the laboratory.² The gain in forty minutes was one-fourth of the total water lost. After twenty-four hours the gain was 0.1414 gram. This represents 8.69 per cent of the weight of the hydrated salt. The oxalate is not very soluble in water, and is not deliquescent. Since it was possible that a trace of radium might be present in the original nitrate, the activity of a quantity of oxide obtained by direct ignition of the nitrate was compared with that of the oxide resulting from the oxalate. There was no detectable difference in activity. In transformations of uranium compounds radioactive impurities usually concentrate in either the precipi-

¹ Peligot: *Ann. Chem. (Liebig)*, **43**, 282 (1842); Ebelmen: *Ibid.*, **43**, 287 (1842).

² This was in December, when the outside air was very dry.

tate or in the mother-liquor. It, therefore, seemed probable that no appreciable amount of such impurities was present. Table III gives the results obtained with uranium oxalate. Ethyl or methyl alcohol was used as the suspending liquid.

TABLE III.

	w .	x .	$\frac{w}{x}$.	k_2 .
1	0.0558	0.505	0.1105	507
2	0.0654	0.558	0.1172	501
3	0.0763	0.616	0.1239	504
4	0.0766	0.621	0.1233	509
5	0.0870	0.669	0.1301	510
6	0.1035	0.730	0.1418	508
7	0.1095	0.752	0.1456	511
8	0.2771	0.99	0.280
9	0.4235	1.00	0.424
10	0.6491	1.00	0.649
				—
			Mean,	507

The circular metal dishes used all measured 7.15 cm. in diameter. Therefore, the area, s , was 40.15 sq. cm. for each film; w is the weight of substance spread upon the area s ; x is the ratio of the activity of any film to that of No. 10, which had the maximum activity. The results given in Table III are shown graphically in Fig. 1. For Curve I the ordinates are proportional to $x = \frac{A}{A_1}$; for Curve II to $\frac{w}{x}$; the abscissas are proportional to w in both cases.

Uranouranic oxide, U_3O_8 , was obtained by igniting the oxalate.¹ The best films were obtained by the use of chloroform. Table IV gives the results for the oxide.

TABLE IV.

	w .	x .	$\frac{w}{x}$.	k_2 .
1	0.0084	0.0663	0.127	328
2	0.0206	0.1521	0.136	321
3	0.0339	0.2495	0.136	340
4	0.0433	0.3001	0.144	331
5	0.0471	0.3220	0.146	331
6	0.0526	0.3535	0.149	333
7	0.0609	0.3817	0.160	317
8	0.0716	0.4520	0.159	337
9	0.1725	0.7755	0.222	348
10	0.2342	0.8774	0.267	360
11	0.3281	0.98	0.335
12	0.5617	1.00	0.562
				—
			Mean,	335

¹ Zimmermann: *Ann. Chem.* (Liebig), **232**, 276 (1885).

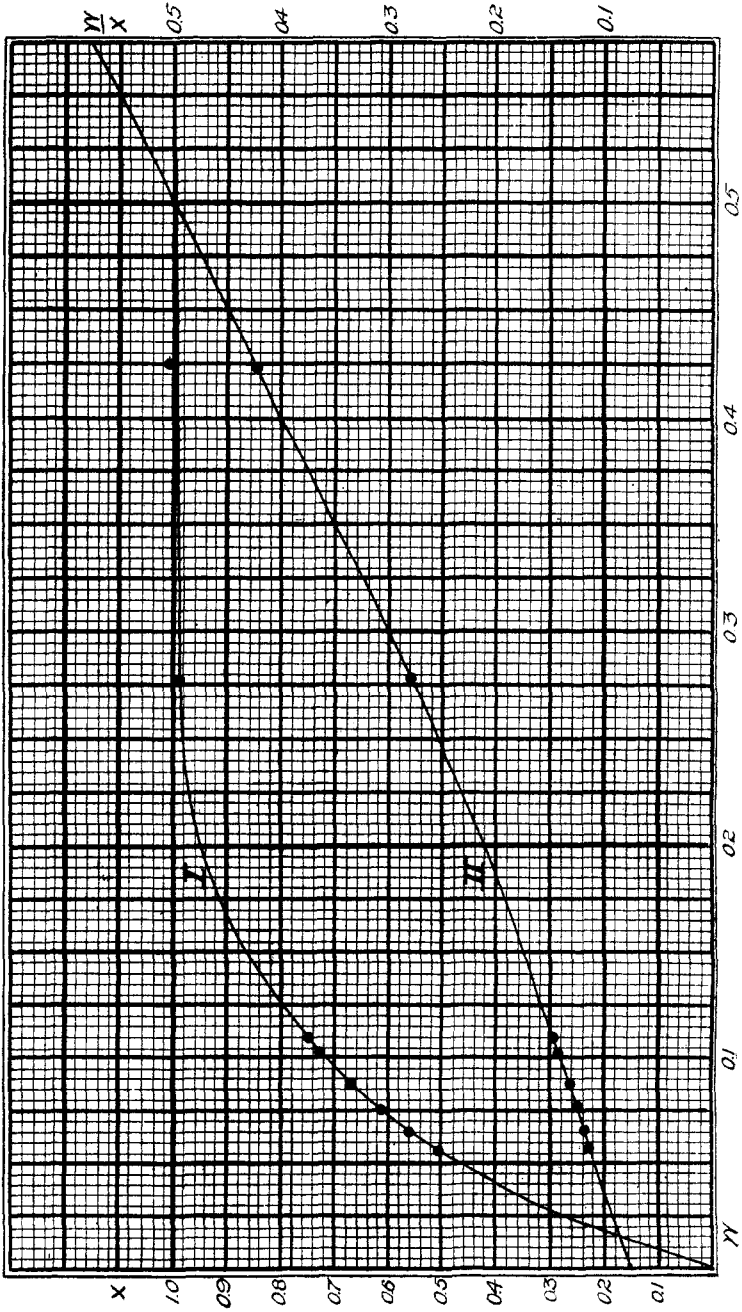


Fig. 1. Uranium oxalate.

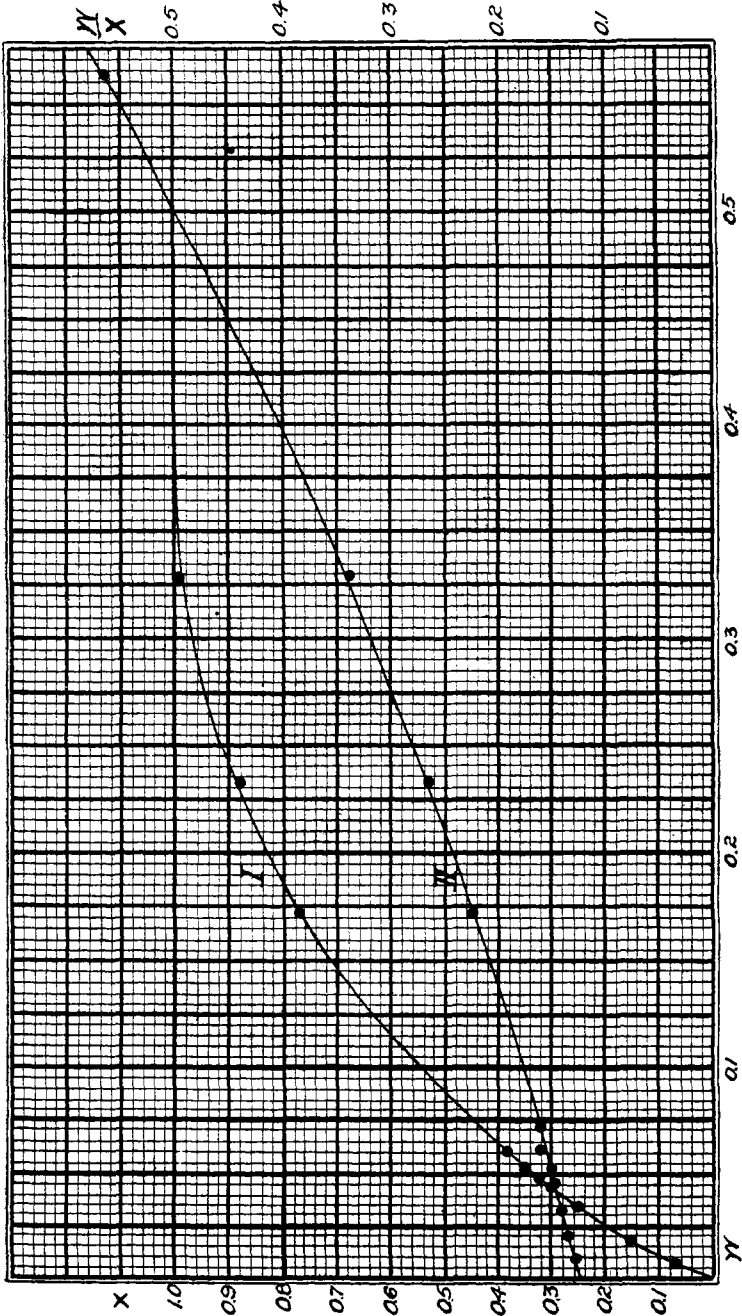


Fig. 2. Uranium oxide.

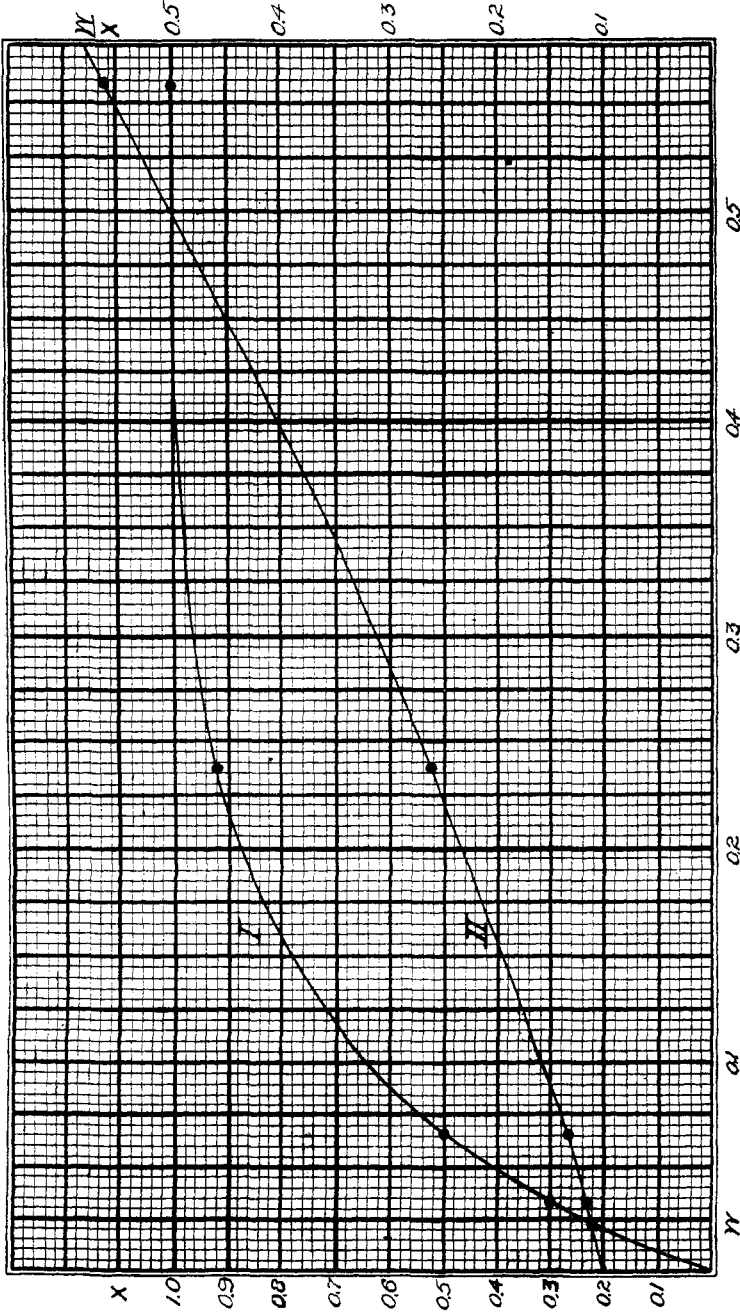


Fig. 3. Ammonium uranate.

The curves for the oxide are given in Fig. 2.

Similar, but less complete measurements were made with ammonium uranate. This substance was obtained by precipitating uranium nitrate with ammonium hydroxide. The precipitate was carefully washed and dried, finally at 140°. Analysis: 0.2274 gram of the substance gave upon ignition 0.1992 gram U₃O₈, equal to 74.4 per cent. uranium, calculated for (NH₄)₂U₂O₇, 76.4 per cent. It is probable that the substance prepared as above does not have a perfectly definite composition. Table V gives the results obtained with ammonium uranate, the films of which were deposited from alcohol.

TABLE V.

	<i>w.</i>	<i>x.</i>	$\frac{w}{x}$.	<i>k</i> ₂ .
1	0.0238	0.2185	0.109	420
2	0.0338	0.2983	0.114	415
3	0.066 ¹	0.5 ¹	0.132	416
4	0.2367	0.914	0.259	416
5	0.5620	1.00	0.562
				—
			Mean,	417

Fig. 3 shows the curves for ammonium uranate.

The values of *k*₂ are nearly constant for a given substance, but differ greatly for different substances. These results may now be used to calculate the *total* activities of unit weights of each of the uranium compounds. From (3)

$$k_1 = \frac{2k_2A_1}{s} \tag{6}$$

The relative values of A₁ for the three compounds are given in the first column of Table VI. These figures represent the relative values of the reciprocals of the times of discharge of the electro-scope for layers of maximum activity. The area, *s*, was the same in all cases and equal to 40.15 sq. cm. The values of *k*₁ are calculated on the basis of A₁, equal to unity for the oxide. P is the proportion of uranium in each substance.

TABLE VI.

	A ₁ .	<i>k</i> ₂ .	<i>k</i> ₁ .	P.	$\frac{k_1}{P}$.
Oxide	1.000	335	16.69	0.849	19.7
Oxalate.....	0.459	507	11.59	0.576	20.1
Uranate.....	0.720	417	14.95	0.744	20.1
					—
				Mean,	20.0

¹ By graphic interpolation.

If radioactivity is an atomic property $\frac{k_1}{P}$ should be a constant.

The results seem to justify this conclusion.

There is still another way to determine the value of k_1 . The curves for $\frac{w}{x}$ may be continued until they cut the axis of ordinates. The point of intersection of any curve represents the theoretical value of w for an infinitely thin film. Since for such a film there would be no absorption $A = \frac{1}{2}k_1w$ and $k_1 = \frac{2A}{w} = \frac{2A_1x}{w}$. The values of w as found by such graphical extrapolation are given in column one, Table VII. The fourth column gives for comparison the values of (k_1) as found by the first method.

TABLE VII.

	$\frac{w}{x}$.	A_1 .	k_1 .	(k_1) .	P.	$\frac{k_1}{P}$.
Oxide.....	0.123	1.000	16.26	16.69	0.849	19.2
Oxalate	0.0825	0.459	11.13	11.59	0.576	19.3
Uranate	0.0995	0.720	14.47	14.95	0.744	19.5
					Mean,	19.3

The average value of $\frac{k_1}{P}$ is 19.7. This represents the total activity of the α -rays of unit weight of metallic uranium when the maximum activity of a layer of uranium oxide 40.15 sq. cm. in area is taken as unity. Instead of employing arbitrary units, k_1/P may be expressed in terms of the saturation current which would be due to the ionization caused by the α -rays of one gram of the element uranium, providing there was no absorption of the rays. Rutherford and McClung¹ have found the maximum saturation current due to the α -rays of a layer of uranium oxide to be about 4.5×10^{-13} amperes per square centimeter. Therefore, $A_1 = s \times 4.5 \times 10^{-13}$ amperes, and $\frac{k_1}{P} = 19.7A_1 = 3.6 \times 10^{-10}$ amp.

Summary.—1. These experiments show that the effective (or directly observed) activity of the layers of uranium compounds sufficiently thick to show the maximum α -ray activity depends not only on the uranium content but also on the coefficient of absorption of the rays by the radioactive substance itself. 2. A method of determining such absorption coefficients has been worked out. 3. It is further shown that, when absorption is taken

¹ *Loc. cit.*

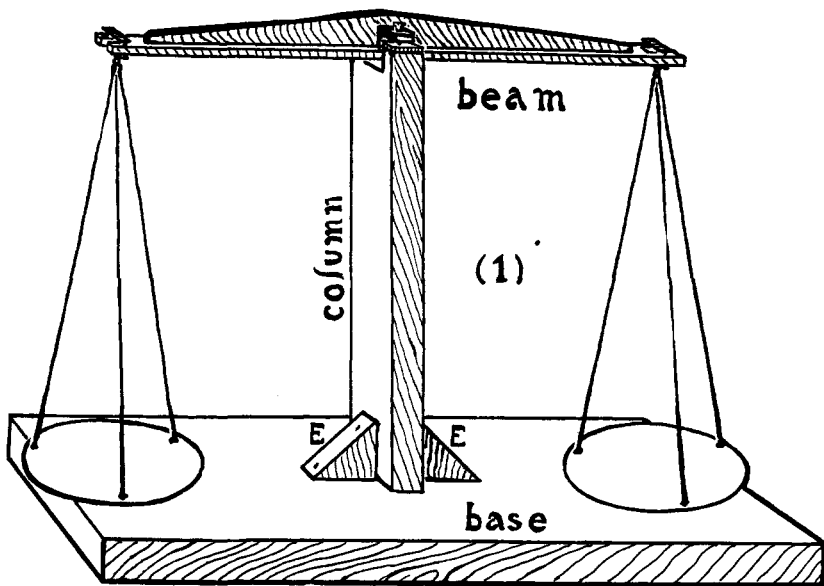
into account, the *total* α -ray activity of any uranium compound is strictly proportional to its percentage of uranium. This is a direct confirmation of the theory that radioactivity is an atomic property.

February 8, 1905.

NOTE.

A Home-made balance.—It is thought that the balance figured below may prove useful in schools to illustrate the law of conservation of mass, and for other chemical and physical experiments. It can be made for less than a dollar; and when carrying a kilogram on each arm, half a gram additional is enough to move the pans through three inches.

In the figure (i) shows the balance in perspective, (ii) is a trans-



verse section through the beam, column and screws which serve as "knife edges," (iii) is the stiffening piece, (iv) is a view of the beam from above, and (v) is a section through the beam near the end, to show how the pans are supported.

The base is a piece of board 8 x 30 inches. The column is of