



IV. The molecular weights of radium and thorium emanations

Walter Makower B.A. B.Sc.

To cite this article: Walter Makower B.A. B.Sc. (1905) IV. The molecular weights of radium and thorium emanations , Philosophical Magazine Series 6, 9:49, 56-77, DOI: [10.1080/14786440509463255](https://doi.org/10.1080/14786440509463255)

To link to this article: <http://dx.doi.org/10.1080/14786440509463255>



Published online: 08 Jun 2010.



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certain analogy with the relation of the transfinite aggregate of type ω to the finite aggregates.

10.

I will now sum up the results of my investigations on the transfinite numbers, published in three papers in this Magazine.

The main result is that any aggregate, the cardinal number (or type) of which is not self-contradictory, can be well-ordered. A closer consideration of the proof given in my first paper led (in the present paper) to a proof of the universal validity of Cantor's third principle, and hence of the non-existence of ordinal numbers and Alephs which transcend all those defined or indicated by Cantor; and (in the first and second papers) the main theorem led to final forms that are to be given to the results of adding and multiplying any two transfinite cardinal numbers. The results on exponential numbers are not final, but one of the theorems on exponential numbers (§ 1 of the present paper) has been shown to have an important bearing on the theory of functions.

The Manor House, Broadwindsor, Dorset.
September 6th, 1904.

IV. *The Molecular Weights of Radium and Thorium Emanations.* By WALTER MAKOWER, B.A., B.Sc.*

PART I.

THE MOLECULAR WEIGHT OF RADIUM EMANATION.

1. *Introduction.*

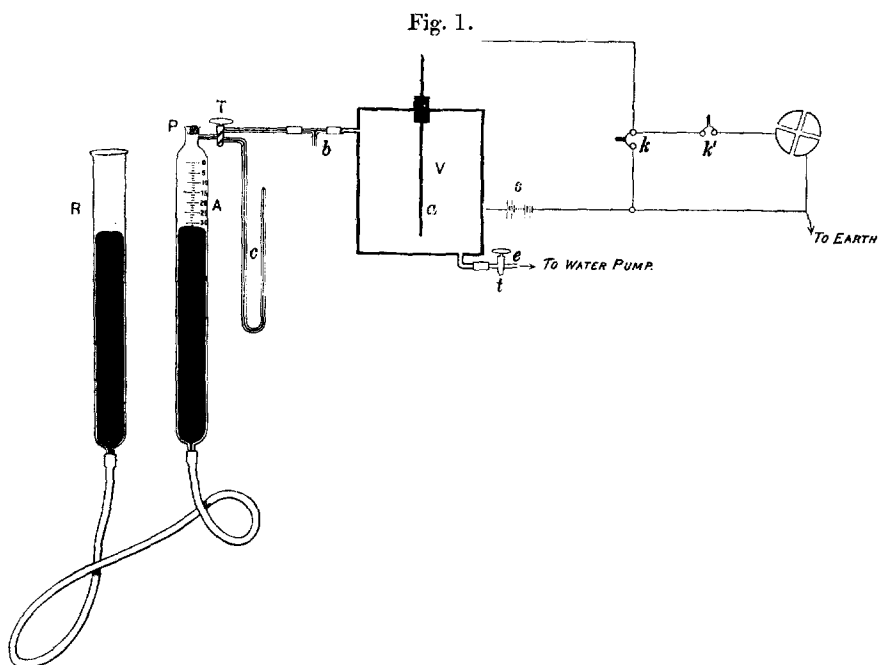
RUTHERFORD and Brooks (Trans. Roy. Soc. Canada, 1901; Chem. News, 1902) have determined the rate of diffusion of the emanation from radium into air by a method similar to that employed by Loschmidt in his investigations on the coefficient of interdiffusion of gases, and deduce that the molecular weight lies between 40 and 100. It is important to know the molecular weight with greater accuracy, and it was with the object of solving this problem that the present investigation was undertaken. During the course of the work, Curie and Danne (*C. R.* cxxxvi, p. 1314, 1903) have published some observations upon the rate of diffusion of the emanation from radium through capillary tubes of different lengths and diameters, and find for the coefficient of interdiffusion between the emanation and air

* Communicated by Prof. J. J. Thomson.

the value $\cdot 100$, which gives a molecular weight corresponding with the lower limit given by Rutherford and Brooks (*loc. cit.*). It is possible, however, that the value $\cdot 100$ is somewhat too high, since no precautions seem to have been taken to insure that temperature conditions were steady. In the experiments to be described below, the emanation was made to diffuse through porous plugs, and its rate of diffusion compared with that of other gases of known molecular weight. Assuming Graham's law, that the rate of diffusion of a gas is inversely proportional to the square root of its density, it is possible from such a comparison to calculate the molecular weight of the emanation.

2. Description of Apparatus, and Method of Experimenting with the Emanation.

The air containing the emanation, the rate of diffusion of which was to be determined, was confined over mercury in



the glass vessel A (fig. 1), which will be referred to as the "diffusion-vessel," and which was 3 centimetres in diameter and graduated downwards in cubic centimetres from 0 to 200. The volume of the "dead-space" from the tap T to the first

graduation was measured by completely filling the diffusion-vessel with mercury, and then running out the mercury to the first graduation and weighing; for the first vessel used this volume was found to be 5.0 c.c., and for the second vessel 12.4 c.c. The upper end of the diffusion-vessel was drawn off and closed by a dense porous plug of plaster-of-Paris (P), 1 cm. in diameter and .5 cm. thick, fitting tightly into the glass*. Just below the porous plug was a three-way capillary stopcock, T, provided with a syphon-pipette for collecting gases over mercury when desired. The lower extremity of the diffusion-vessel was connected by stout rubber pressure-tubing with a cylindrical mercury reservoir R of 3 cm. diameter which could be raised or lowered at will. By means of a short piece of rubber pressure-tubing the diffusion-vessel was connected to a cylindrical brass vessel V, along the axis of which ran an insulated brass wire *a* connected to earth through the key *k*, by raising which the wire *a* and its connexions could be insulated; a difference of potential of about 400 volts was maintained between *a* and the outside of the brass vessel by a battery of 200 small storage-cells S, which gave a field sufficient to saturate the air in V. All the connexions were carefully shielded from external electrostatic effects by inclosing them in earthed conductors.

The emanation was obtained from a solution of radium bromide in water. By lowering the reservoir R, a stream of air could be carried through the solution and thence through cotton-wool to remove dust, and through a small sulphuric-acid bubbler along the capillary *c* into the vessel A.

To carry out an experiment, a certain volume of air mixed with emanation was sucked into A and well mixed by raising and lowering the reservoir R several times in succession. The volume of air in A was then read to .1 c.c. and a known volume carried into V. It was important not to force any air through the porous plug during this operation, and therefore to prevent this the pressure of the air in V was reduced by means of a water-pump attached at *e*, after which the stopcock *t* was closed. The stopcock T was then turned so as to allow a certain volume of gas to pass into V, the mercury reservoir R being meanwhile raised and the level of the mercury in A and R finally adjusted to equality. Care was always taken that the pressure in V had been so far reduced, that at the end of this operation the pressure was still below atmospheric. By turning the tap *t* communication

* The plaster-of-Paris was inserted while still moist, and after it had been compressed was allowed to set in position.

was again established between the air in V and the outside, and the pressure inside thus again brought to atmospheric. After a short known interval (usually 1 minute) the conductivity of the air in V was determined thus:— At a definite instant the key k was removed so as to insulate the rod a and its connexions; after a known time (τ seconds) the key k' was removed and the key k replaced, and the deflexion of the electrometer-needle read as soon as it had come to rest, and taken as a measure of the quantity of emanation which had been carried into V. *Immediately* after disconnecting the key k' the tap t was again turned so as to connect V to the water-pump, and a rapid current of air drawn through it by opening the side tube b , which had remained closed by a rubber cap during the first part of the experiment. In this way the emanation was completely removed from V in a few minutes, after which the radioactivity “induced” on the walls of the vessel decayed according to the usual exponential law, becoming negligible before the next experiment was performed. After a known time the operations described above were repeated, and the electrometer deflexion in τ seconds again recorded. Since it was impossible to transfer exactly the same volume of air at the beginning and end of an experiment, a correction had to be applied to allow for this difference; a further small correction had to be applied for any slight change of sensitiveness of the electrometer during the experiment.

It was also necessary to allow for the natural decay of the radioactivity of the emanation in the time during which the diffusion had been proceeding. The correction to be applied on this account was always small, and in the preliminary experiments has been neglected; the method of applying it when necessary will be discussed when giving the final observations.

In most of the experiments, the scale of the electrometer was uniform; in one set of observations, however, it was found necessary to calibrate the scale and apply suitable corrections to the observations (Plug I. Table III.).

If y is the concentration of the emanation in the diffusion-vessel at any instant, then the change of concentration dy in the time dt due to diffusion is given by the equation

$$dy = -\frac{\lambda}{V}y dt, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which V is the volume of the gas diffusing, and λ is a constant depending on the nature of the porous plug.

If y_0 is the value of y at the beginning of the experiment,

i. e. when $t=0$, we obtain from equation (1), by integrating, the equation

$$\log\left(\frac{y_0}{y}\right) = \frac{\lambda}{V} t,$$

whence

$$\lambda = \frac{V}{t} \log_e\left(\frac{y_0}{y}\right) = \frac{V}{.4343 t} \log_{10}\left(\frac{y_0}{y}\right). \quad (2)$$

The value of λ thus defined is taken as a measure of the rate of diffusion of the emanation through the plug.

3. Rates of Diffusion of Gases of known Molecular Weight.

To determine the molecular weight of the emanation, its rate of diffusion was compared with that of hydrogen, oxygen, carbon dioxide, and sulphur dioxide through the same plug. A pure sample of the gas to be experimented with was sucked into the diffusion-vessel, and after a known time (t minutes) some of it was withdrawn and analysed to find out how much had escaped through the porous plug. When no statement to the contrary is made, the gas was diffusing out into the atmosphere.

In deducing the value of λ from these observations, a slight modification had to be introduced into the method of calculation given above; for, since the rates of diffusion of the gases on the two sides of the plug were different, the volume of the gas (at constant pressure) contained in the diffusion-vessel varied during an experiment. It was important to maintain the pressure equal on the two sides of the plug to prevent any gas escaping by *effusion*, and this was done by occasionally adjusting the level of the reservoir R.

As above, equation (1)

$$\frac{dy}{dt} = -\frac{\lambda}{V} y,$$

y being in this case measured volumetrically.

Here V is not constant, but varies during an experiment. Since the variation was small, it was taken as a linear function of the time, so that

$$V = V_0(1 + \alpha t)^*,$$

where V_0 is the volume at the beginning ($t=0$), and α is a constant to be determined by observing V_1 , V_0 , and t .

* This assumption is true except for the case of hydrogen; but as this gas was employed only in preliminary experiments the same assumption was taken to be sufficiently nearly correct.

Inserting this value of V in equation (1) we have

$$\log_e y = -\frac{\lambda}{V_0} \int_0^t \frac{dt}{1 + \alpha t},$$

whence

$$\log_e \frac{y_0}{y} = \frac{\lambda}{\alpha V_0} \log_e (1 + \alpha t),$$

and since $|\alpha t| < 1$,

$$\begin{aligned} \log_e \frac{y_0}{y} &= \frac{\lambda}{\alpha V_0} \left[\alpha t - \frac{\alpha^2 t^2}{2} + \frac{\alpha^3 t^3}{3} - \frac{\alpha^4 t^4}{4} + \dots \right] \\ &= \frac{\lambda}{V_0} \left[1 - \frac{\alpha t}{2} + \frac{\alpha^2 t^2}{3} - \frac{\alpha^3 t^3}{4} + \dots \right], \end{aligned}$$

whence

$$\lambda = \frac{1}{\left[1 - \frac{\alpha t}{2} + \frac{\alpha^2 t^2}{3} - \frac{\alpha^3 t^3}{4} + \dots \right]} \cdot \frac{V_0}{t} \log_e \frac{y_0}{y}. \quad (3)$$

4. Preliminary Experiments.

The earlier experiments were made to compare the rate of diffusion of the radium emanation with that of hydrogen through the plug of plaster-of-Paris which will be referred to as plug I. Although the results obtained cannot be employed to calculate the molecular weight of the emanation, a short account of them will be given since they lead to some interesting conclusions regarding the nature of the plugs used, as well as throwing light on the conditions to be attended to in performing density determinations by the present method.

As a result of the first experiments, the values of λ for hydrogen and the emanation (mixed with air) were found to be 1.77 and .138 respectively. Assuming Graham's law of diffusion, these numbers would lead to the conclusion that the molecular weight of the emanation is 328—a value which is more than three times as great as the upper limit given by Rutherford and Brooks (*loc. cit.*). Further experiments were therefore undertaken to explain the cause of this discrepancy.

It was thought possible that the density of the gas with which the emanation was mixed might influence the rate of diffusion of the emanation, and therefore to test this hypothesis experiments were made in which hydrogen was substituted for air. The emanation was carried into the diffusion-vessel by a stream of hydrogen, and in order to have this gas

on both sides of the porous plug a glass tube was attached by rubber over the plug, and a slow current of hydrogen from a Kipp maintained through it. In this case the value of λ for the emanation was found to be $\cdot 277$, *i. e.* about twice as great as when the emanation was mixed with air.

To test this point still further a series of experiments was undertaken in which the pressure of the air with which the emanation was mixed could be varied, precautions being taken to insure that the pressures on the two sides of the porous plug were always equal. The value of λ was found to vary considerably with the pressure, as will be seen from Table I.

TABLE I.—Plug I.

Emanation mixed with Air.	
Pressure in centimetres mercury.	λ .
76.0	$\cdot 138$
37.6	$\cdot 181$
36.5	$\cdot 177$
18.6	$\cdot 222$
15.8	$\cdot 246$
15.6	$\cdot 307$
9.2	$\cdot 350$
5.4	$\cdot 737$
5.3	$\cdot 577$

These results were confirmed by using another diffusion-vessel of 250 c.c. capacity and a new plug (Plug II.) of porous porcelain attached to the diffusion-vessel by sealing-wax. Similar results were also obtained when the emanation was mixed with hydrogen at different pressures.

There are two ways of explaining this change in the value of λ with the density of the gas with which the emanation is mixed. We may either suppose that the gas really exerts some influence on the apparent molecular weight of the emanation, say by condensing round its molecules; or it may be that the pores of the plugs employed are large compared with the mean free path of the gas molecules. In this case, the number of collisions of a molecule of emanation with a gas molecule while escaping through the plug would not be small compared with the number of collisions with the substance of the plug; and therefore the value of λ for the emanation would depend upon the nature of the gas with

which it is mixed, and still more upon the number of molecules of such gas present. To test which of these hypotheses is correct, experiments were made to see whether the rate of diffusion of carbon dioxide through the plugs varied with its pressure. The results of these experiments are given in Table II.

TABLE II.—CO₂.

Plug I.		Plug II.	
Pressure in centimetres mercury.	λ .	Pressure in centimetres mercury.	λ .
76.0	.234	76.0	1.58
10.0	.765	8.8	3.28
9.4	.687	7.9	2.76
		5.9	3.74

From the above table it appears that a variation of λ with the pressure, similar to that observed with the radium emanation, occurs with carbon dioxide. We are therefore led to the conclusion that the variation in the density of the emanation is only apparent, and that the pores of the plugs used were comparable in size with the mean free path of gas molecules. Subsequent experiments were all carried out at *atmospheric pressure*, the upper surface of the porous plug being in contact with air. In this way, all experiments were performed under similar conditions, and could therefore be compared.

A further point is brought out by a study of Table II. It will be noticed that the values of λ for hydrogen and carbon dioxide (at atmospheric pressure) are not in the inverse ratio of the square roots of the molecular weights of these gases. We cannot, therefore, assume this law to calculate the molecular weight of the emanation from a comparison of its rate of diffusion with that of hydrogen, a fact which gives an explanation of the very high value for the molecular weight obtained above on this assumption. The cause of the failure of Graham's law as applied to these observations is not certain but the most probable explanation is that when a gas heavier than air is diffusing *upwards* through the plug and air *downwards* into the diffusion-vessel, a layer accumulates on the

lower surface of the plug, preventing diffusion from proceeding as rapidly as theory demands. When a light gas such as hydrogen is used, the air which enters the diffusion-vessel through the plug would tend to fall through the hydrogen, and the error due to the formation of a layer of air is greatly reduced if not entirely obviated. That the failure of the ordinary law of diffusion was not due to any peculiarity of the plugs themselves was proved by testing them in the manner described by Graham (Transactions Roy. Soc. Edinburgh, vol. xii. 1834). The rubber connecting the diffusion-vessel with the adjustable mercury reservoir was detached, and the open end of the vessel placed under water contained in a tall cylinder; the diffusion-vessel was then filled with hydrogen and allowed to stand until all the hydrogen had been displaced by air, water being added from time to time to the cylinder to keep the level inside the diffusion-vessel equal to the level outside. The volume at the end of the experiment was to the original volume of hydrogen as the square root of the density of hydrogen is to the square root of the density of air, within the limits of experimental error. It was of course impossible to adopt this method for the emanation, since it depends on measurements of the volumes of gases escaping and entering through the plugs.

A series of experiments was therefore next made to find out *empirically* how the rate of diffusion of a gas through the plugs used depended on its density, and for the purpose oxygen, carbon dioxide, and sulphur dioxide were used. Unfortunately, before taking these observations the porosity of plug I. was found to have changed*, so that the results given below cannot be compared with those obtained above with the same plug. Plug II. was removed from the second diffusion-vessel and replaced by a similar but somewhat thicker one (plug III.). Some observations were, however, first taken with plug II., and these are quoted below.

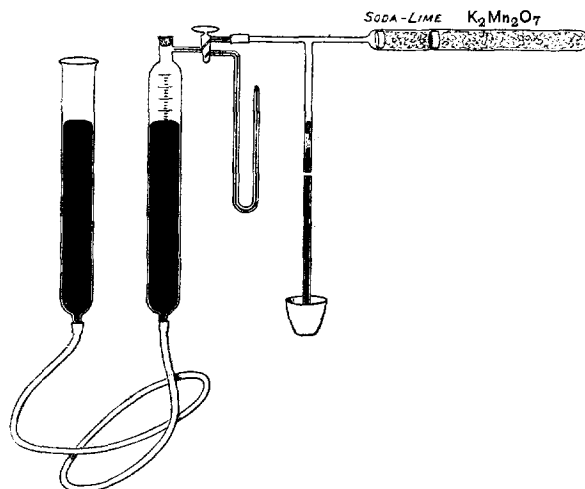
5. *Final Experiments.*

Preparation and Analysis of Gases.—Oxygen. This gas was prepared by heating pure dry potassium permanganate contained in a horizontal glass tube closed at one end and drawn off at the other, which was connected to a mercury manometer by a T-piece, the other limb of which was

* Owing to an accident the stopcock of the diffusion-vessel was broken and a new one attached. It is possible that during the operation of making the glass joint near the plug, the change mentioned may have occurred.

attached by rubber to the diffusion-vessel (fig. 2). A small quantity of soda-lime was placed near the open end of the tube, and separated from the potassium permanganate by a plug of glass-wool, so that the oxygen as it was generated had to pass over it.

Fig. 2.



Before starting an experiment, the apparatus was exhausted and filled with oxygen by heating the potassium permanganate in a Bunsen burner; this oxygen was then pumped out and the apparatus refilled with oxygen, after which the diffusion-vessel could be filled with pure oxygen whenever required.

To find the composition of the gas in the diffusion-vessel at the end of an experiment, a suitable volume was withdrawn and transferred to a gas burette, where its volume was measured. The gas was then transferred to a wide glass tube inverted over mercury, where the oxygen was removed in the usual manner by means of phosphorus vapour, and the loss of volume determined.

Carbon dioxide.—To prepare this gas, the tube containing the potassium permanganate was removed and replaced by a similar one filled with pure dry sodium bicarbonate, from which carbon dioxide is readily obtained by gently heating. As in the experiments with oxygen, the apparatus was twice exhausted and filled with carbon dioxide before starting.

The analysis of the gas left at the end of an experiment *Phil. Mag. S. 6. Vol. 9. No. 49. Jan. 1905.* F

was performed by treating a known volume of it with a concentrated solution of caustic potash and measuring the diminution in volume.

Sulphur dioxide.—This gas was obtained directly from a siphon containing the liquid, care being of course taken to remove the air from the connecting tubes. The gas left in the diffusion-vessel at the end of an experiment was analysed by treating a known volume with potassium bichromate solution and measuring the diminution of volume produced.

As already stated, the composition of the gases left at the end of the diffusion experiments was determined volumetrically. The estimation was carried out by means of a gas burette of 60 c.c. capacity of the type described by Travers ('Study of Gases,' p. 66), and graduated downwards in fifths of a cubic centimetre, so that the volume of the gas in the burette could be estimated to .1 c.c. with certainty. To avoid errors due to variations of temperature, the burette was enclosed in a water-jacket and the temperature read off on a thermometer immersed in the water. The burette was carefully calibrated by filling with water and running out by successive stages of 2 c.c. and weighing. About 20 c.c. of the gas to be analysed was usually transferred from the diffusion-vessel to the burette, so that its composition could be determined to one per cent.

6. Observations and Results.

In calculating the values of λ from the observations with oxygen, account has to be taken of the fact that the upper surface of the plug is in contact with air which contains 21 per cent. of oxygen, so that oxygen is diffusing *into* as well as *out of* the diffusion-vessel throughout the experiment. To allow for this it is necessary to slightly modify equation (3).

Since the concentration of the oxygen in the air in contact with the upper surface of the plug remains constant, the quantity dy of oxygen which, on the whole, escapes from the diffusion-vessel is given by the equation

$$dy = -\frac{\lambda}{V_0(1+at)} \left(y - \frac{21}{100} y_0 \right) dt,$$

whence

$$\lambda = \frac{1}{\left[1 - \frac{at}{2} + \frac{a^2 t^2}{3} - \dots \right]} \frac{V_0}{t} \log_e \left(\frac{\frac{79}{100} y_0}{y - \frac{21}{100} y_0} \right)$$

It is the values of $\frac{79}{100}y_0$ and $\left(y - \frac{21}{100}y_0\right)$ which are tabulated in the columns headed y_0 and y respectively (Tables III., IV., and V.).

For carbon dioxide and sulphur dioxide V_0 and y_0 are the same volumes.

In the experiments with the emanation y and y_0 were determined electrically as described above. The values of y , given in the tables, have been corrected for the natural decay of the emanation in the interval during which diffusion was taking place. From the results of Rutherford and Soddy (Phil. Mag. April 1903) the activity of the emanation falls to half its value in 3.71 days; the mean of y and y_0 was taken, and the loss of activity of this quantity in the time t calculated and added to the observed value of y . To make the method of calculation clear, one of the observations taken with plug I. is given in full :—

Time	
10.16 A.M. . .	Sensitiveness of electrometer in scale-divisions per volt, 86. Diffusion-vessel filled to 67.8 c. c.
10.27 A.M. . .	34.3 c. c. carried into testing-vessel, leaving 33.5 c. c. in the diffusion-vessel.
10.28 A.M. . .	Deflexion of electrometer-needle in 20 seconds, corrected for lack of uniformity of scale, 224.
12.33 P.M. . .	Sensitiveness of electrometer in scale-divisions per volt, 82. Volume of gas in diffusion-vessel 33.7 c. c.
12.41 P.M. . .	27.7 c. c. carried into testing-vessel.
12.42 P.M. . .	Deflexion of electrometer-needle in 20 seconds, corrected for lack of uniformity of scale, 105. Deflexion corrected to 86 scale-divisions per volt, and to volume 34.3 c. c. carried into testing-vessel

$$= 105 \times \frac{86}{82} \times \frac{34.3}{27.7} = 136.$$

Corrected for natural decay of emanation, 139.

Time during which diffusion had been proceeding, 134 minutes.

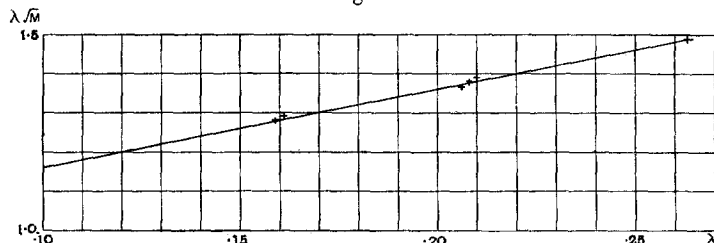
$$\lambda = \frac{33.6}{134 \times .4343} \log_{10} \frac{224}{139} = .120.$$

In the last column of Table III. are tabulated the values of $\lambda\sqrt{M}$, in which M is the molecular weight of the gas employed. In Tables IV. and V., however, the values of λ obtained are first multiplied respectively by .1362 and .312 to reduce them to equality with the corresponding quantities for plug I., and the values of $.1362\lambda\sqrt{M}$ and $.312\lambda\sqrt{M}$ respectively tabulated in the last columns. This

reduction makes a comparison of the results obtained with the three plugs less troublesome.

If Graham's law of diffusion were strictly applicable to these experiments, the value of $\lambda\sqrt{M}$ should be constant whatever gas is employed. From an inspection of the results, however, this is seen not to be the case; the value of $\lambda\sqrt{M}$ decreases as λ decreases. If, however, the values of $\lambda\sqrt{M}$ as ordinates be plotted against the values of λ as abscissæ, the points so obtained corresponding to the values of oxygen, carbon dioxide, and sulphur dioxide are found to lie on a straight line not parallel to the axis of λ (as should be the case if Graham's law were true), but inclined at a small angle to it (fig. 3). By linear extrapolation the value of $\lambda\sqrt{M}$

Fig. 3.



for the emanation is found to be 1.23 for plug I.; the value of $\cdot 1362 \lambda\sqrt{M}$ for plug II. 1.21, and the value of $\cdot 312 \lambda\sqrt{M}$ for plug III 1.205. These values are given in brackets in the tables. By dividing the values of $\lambda\sqrt{M}$ for the emanation by the corresponding values of λ and squaring, the value of the molecular weight of the emanation can be calculated. The experiments with plugs I., II., and III. lead respectively to the values 85.5, 97, and 99. On the assumption that the emanation is a monatomic gas, it probably occupies the vacancy in the periodic table in the fluorine group between Mo (96.0) and Ru (102). As this is the first vacancy in the periodic table, it is impossible to assign a place in the periodic table to the emanation on the assumption that it is polyatomic; the present experiments, therefore, confirm the view that the emanation is monatomic.

TABLE III.—Plug I.

Gas.	V ₀ in c.c.	V in c.c.	t in minutes.	y ₀ .	y.	λ.	λ mean.	λ √M.
O ₂	36.6	37.7	77	28.85	16.7	.264	.263	1.49
O ₂	35.5	36.7	88	28.05	15.0	.257		
O ₂	33.0	34.0	75	26.1	14.35	.267		
CO ₂ ...	34.3	37.0	75	34.3	21.85	.214	.206	1.37
CO ₂ ...	29.3	31.9	63	29.3	19.3	.203		
CO ₂ ...	31.9	34.6	81	31.9	19.4	.204		
CO ₂ ...	34.8	38.0	86	34.8	21.6	.202		
SO ₂ ...	34.3	39.8	90	34.3	23.4	.157	.1595	1.28
SO ₂ ...	32.0	36.2	70	32.0	23.2	.158		
SO ₂ ...	35.0	41.3	100	35.0	22.6	.166		
SO ₂ ...	36.2	42.5	95	36.2	24.75	.157		
Emana- tion	36.0	36.1	149	209	121	.132	.133	(1.23)
"	33.5	33.7	134	224	139	.119		
"	34.1	34.2	119	186	117	.133		
"	33.0	33.0	125	234	139	.137		
"	33.9	34.0	173	167	84	.135		
"	34.8	35.1	186	214	99.5	.143		

TABLE IV.—Plug II.

Gas.	V ₀ .	V.	t.	y ₀ .	y.	λ.	λ mean.	λ × .1362.	λ √M × .1362.
O ₂	85.6	89.4	40	67.7	23.5	1.89	1.93	.263	1.49
O ₂	92.3	94.5	35	72.9	35.2	1.94			
O ₂	94.3	96.4	41	74.5	32.2	1.95			
CO ₂ ...	153.2	159.8	35	153.2	106.5	1.63	1.54	.210	1.39
CO ₂ ...	153.4	164.2	50	153.4	97.5	1.44			
CO ₂ ...	111.5	118.4	32	111.5	70.7	1.64			
CO ₂ ...	129.3	136.9	30	129.3	91.5	1.54			
CO ₂ ...	122.8	131.4	40	122.8	78.5	1.43			
Emana- tion	104.9	105.4	98	255	109	.910	.906	.123	(1.21)
"	104.5	105.5	97	200	88	.884			
"	102.2	103.0	85	231	105	.943			
"	98.4	99.2	85	295	137.5	.884			
"	99.4	99.9	104	306	118	.911			

TABLE V.—Plug III.

Gas.	V ₀ .	V.	<i>t</i> .	<i>y</i> ₀ .	<i>y</i> .	λ.	λ mean.	λ × ·3120.	λ √M × ·3120.
O ₂	44·9	46·7	64	35·5	10·8	·852	·843	·263	1·49
O ₂	64·4	66·5	54	50·8	25·3	·845			
O ₂	68·3	70·3	56	54·0	27·6	·831			
CO ₂ ...	65·8	72·2	62	65·8	36·0	·670	·666	·208	1·38
CO ₂ ...	61·5	66·6	50	61·5	37·0	·650			
CO ₂ ...	63·0	69·4	60	63·0	34·3	·678			
SO ₂ ...	55·6	64·3	53	55·6	34·95	·526	·517	·161	1·29
SO ₂ ...	57·4	65·8	54	57·4	36·2	·525			
SO ₂ ...	62·4	72·6	66	62·4	38·4	·495			
SO ₂ ...	51·1	59·4	50	51·1	31·6	·529			
SO ₂ ...	50·3	57·3	43	50·3	33·5	·508			
Emana- tion	49·4	50·2	85	272	138	·395	·389	·121	(1·205)
"	53·3	53·8	91	206	107	·384			
"	52·6	53·1	88	222	117	·383			
"	48·6	49·3	98	274	123·5	·395			

PART II.

THE MOLECULAR WEIGHT OF THORIUM EMANATION.

7. Introduction and General Method.

On account of the rapid rate of decay of thorium emanation, it is not possible to measure its rate of diffusion by the method used for radium emanation and described above. Rutherford ('Radioactivity,' pp. 233, 234) has, however, described a method by which the diffusion-coefficient into air may be determined, and obtains the value $K = \cdot 09$, from which he concludes that "the two emanations do not differ much from one another in molecular weight." In the following pages an account is given of some experiments in which the rate of diffusion of thorium emanation was compared with that of radium emanation, and as a result of which the above conclusion is fully confirmed. The method used depended on maintaining, through a vessel with porous walls, a constant current of air mixed with emanation, the concentration of which was measured before and after passing through this vessel, which will be referred to as the diffusion-vessel.

To make the quantity of emanation which passed through the walls of the diffusion-vessel as great as possible, it was necessary to make the area of the porous walls great compared with the volume of the vessel, which was therefore constructed as follows:—two plates of porous porcelain

about 100 square centimetres in area (V, fig. 4) were placed parallel and attached to each other by sealing-wax round their edges at a distance of about two millimetres apart; a layer of soft wax over the sealing-wax served to make this joint air-tight. At two opposite corners, glass tubes were attached so that a current of air could be passed through the vessel. By weighing the quantity of mercury required to fill the vessel, its volume was found to be 24.6 c. c.

If t is the average time taken by a particle of gas to pass through the diffusion-vessel, then, if when a current of radium emanation is passed through, its concentrations before entering and after leaving the diffusion-vessel are y_1 and y_2 respectively,

$$y_2 = y_1 e^{-\lambda t}, \quad \dots \dots \dots (4)$$

where λ is a measure of the quantity of emanation which has escaped by diffusion in the time t .

In the case of thorium emanation, however, since the rate of decay is so much more rapid than for radium emanation, the concentration would change in the time taken to pass through the diffusion-vessel, even though none escaped by diffusion. In this case the concentration (z_2) just after emerging from the diffusion-vessel is given by the equation

$$z_2 = z_1 e^{-(K+\lambda')t} \quad \dots \dots \dots (5)$$

where λ' is a measure of the quantity of thorium emanation which has escaped by diffusion in the time t , z_1 is the concentration of the emanation just before entering the vessel, and K is a constant depending on the natural rate of decay. The air-current was so adjusted that t had the same value as in the experiment with radium emanation.

In order to determine the ratio $\frac{\lambda}{\lambda'}$, it was necessary to measure y_1 , y_2 , z_1 and z_2 . It was further necessary to determine the value of Kt ; this was done by replacing the porous vessel by a non-porous glass one of the same volume, and passing a current of thorium emanation through it. If, as before, z_1 is the concentration of the emanation on entering the glass vessel, and z_2' is its concentration on leaving it,

$$z_2' = z_1 e^{-Kt} \quad \dots \dots \dots (6)$$

From equations (4), (5), and (6)

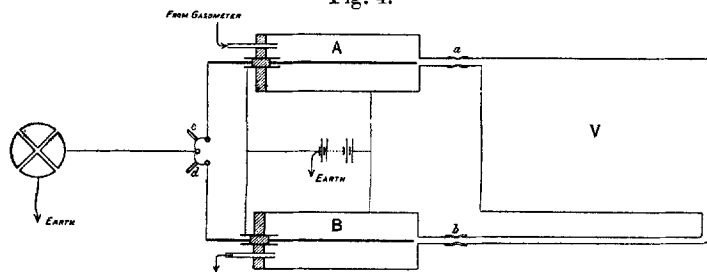
$$\frac{\lambda}{\lambda'} = \frac{\log \frac{y_1}{y_2}}{\log \frac{z_1}{z_2} - \log \frac{z_1}{z_2'}} \quad \dots \dots \dots (7)$$

The method of measuring the quantities involved will appear from the following account.

8. *Experiments with Radium Emanation.*

The general arrangement of the apparatus is shown in fig. 4. A current of air from a large gasometer was passed

Fig. 4.



through a solution of radium in water, through a drying-tube, and through a plug of glass-wool to remove dust, into the cylindrical testing-vessel A of 56.3 c. c. capacity, along the axis of which ran an insulated rod reaching nearly the whole length of the cylinder; thence the current of air passed through the porous vessel V into a second testing-vessel B, and out into the open air. The air-current could be regulated to any desired value by placing weights on the gasometer; the rate at which the gasometer fell was read on a scale and afforded a measure, in arbitrary units, of the air current passing. The vessel V was attached to the two testing-vessels by the rubber connexions *a* and *b* respectively, and could therefore be removed and replaced when necessary.

The air current was allowed to flow until the concentration of the emanation in the two testing-vessels had become constant, when the ionization currents in A and B were measured by means of an electrometer in exactly the same way as that described above for the experiments on the molecular weight of radium emanation. By means of keys *c* and *d* the central rods of A and B could be connected to or disconnected from one pair of quadrants of the electrometer, so that the saturation ionization current in either could be measured separately. There was no need to allow for the activity excited on the walls of the testing-vessels since the quantity present is proportional to the concentration of the emanation.

In spite of the fact that the ebonite plugs, used to insulate the central rods, were divided into two parts by metal guard-rings connected to earth, it was found that the rods charged up slightly on disconnecting from earth, although there was no emanation in the testing-vessels. The rate at which they acquired this charge was always measured before

starting an experiment and subtracted from the leaks subsequently obtained.

The vessels A and B were made as nearly as possible alike, so that the ionization currents through them were not very different when they contained equal quantities of emanation. Before proceeding to the diffusion experiments, however, a comparison of the leaks produced in A and B by a given ionizing agent was necessary. This was made by detaching the vessel V and replacing it by a glass tube so that no emanation could escape during its passage from A to B. A current of emanation was then allowed to pass until the leaks through the two vessels had become constant, when the series of observations given in Table VI. were taken. The numbers show considerable variations owing, probably, to irregularities in the air-current flowing. The error produced by these fluctuations is, however, greatly reduced by taking the mean of several observations extending over a long time. It will be noticed that for the same ionizing agent the leak in A is greater than the leak in B, in the ratio 100 : 96·2. In all subsequent experiments, therefore, the observed leak in B was increased in this ratio (see Table X.).

TABLE VI.—Comparison of the Two Leak Vessels.

The Current of Emanation was started at 11.11 A.M.

Time.	Leak for 30 seconds, in scale-divisions of the electrometer.			
	Vessel A.	Mean.	Vessel B.	Mean.
12.27 P.M.	169		...	
12.30 "	...		159	
12.33 "	167		...	
12.36 "	...		173	
12.39 "	177		...	
12.42 "	...		168	
12.45 "	165		...	
12.48 "	...	171	164	164·5
12.51 "	168		...	
12.54 "	...		164	
12.57 "	175		...	
1.00 "	...		165	
1.03 "	175		...	
1.06 "	...		158	
1.09 "	170		...	
1.12 "	...		165	

Experiments were next made to determine the value of λ . The porous vessel (V) was replaced and a current of about 170 c.c. per minute passed through the apparatus. The results of these experiments are given in Table VII.

TABLE VII.—Diffusion of Radium Emanation.

Gasometer fell .564 mm. per minute.

The Current of Emanation was started at 12.51 P.M.

Time.	Leak for 30 seconds, in scale-divisions of the electrometer.			
	Vessel A.	Mean.	Vessel B.	Mean.
3.03 P.M.	166	171	...	89
3.06 "	...		88	
3.09 "	168		...	
3.12 "	...		92	
3.18 "	176		...	
3.21 "	...		93	
3.24 "	180		...	
3.27 "	...		96	
3.30 "	179		...	
3.33 "	...		99	
3.36 "	168		...	
3.39 "	...		87	
3.42 "	172		...	
3.45 "	...		88	
3.51 "	176		...	
3.54 "	...		90	
3.57 "	169		...	
4.00 "	...		83	
4.03 "	170		...	
4.06 "	...		82	
4.09 "	166		...	
4.12 "	...		80	
4.15 "	164		...	
4.18 "	...		87	

9. *Experiments with Thorium Emanation to determine*

$$\log \frac{z_1}{z_2} \text{ and } \log \frac{z_1}{z_2'}.$$

The radium solution was removed and replaced by a wide lead tube containing thorium oxide wrapped in filter-paper over which a current of air could be passed into the vessel

A, through V into B, and out into the open air, as in the previous experiment. It is important to notice that in this case the ratio of the rates at which the central rods in A and B charge up is not equal to $\frac{z_1}{z_2}$. For, let the concentration in A at a point in a plane at right angles to the axis and at a distance x from the ebonite plug be z ; then, since the emanation decays according to an exponential law in passing from one end to the other of A,

$$z = z_0 e^{-Kx}$$

where z_0 is the concentration on entering A.

Now since the central rod connected to the electrometer reaches nearly the whole length of the testing-vessel, the ionization current in A is proportional to

$$S \int_0^X z dx = \frac{S z_0}{K} (1 - e^{-KX})$$

where S is the cross-sectional area of A and X is its length.

Similarly for B the ionization current is proportional to

$$\frac{S z_2}{K} (1 - e^{-KX}).$$

Hence

$$\frac{\text{The ionization current in A}}{\text{The ionization current in B}} = \frac{z_0}{z_2}.$$

To find z_1 it is necessary to measure the decrease in activity of the emanation in passing through the cylinder A. This was done by replacing the diffusion-vessel by a glass one of nearly the same volume, and measuring the ionization current in A and B as before. Knowing the volumes of A and of the glass vessel connecting A and B, it was possible to calculate the fall in concentration due to the natural decay of the thorium emanation in passing through A. It was also possible to calculate the fall in concentration in passing through the glass vessel, from which the value of $\log \frac{z_1}{z_2}$ could be found.

In these experiments the rate of flow of air was somewhat less than in the previous experiments, on which account an appropriate correction was added to the observed value of z_2' . The results of the experiments with thorium emanation are given in Tables VIII. and IX.

TABLE VIII.—Diffusion of Thorium Emanation.

Gasometer fell .562 mm. per minute.

The Current of Emanation was started at 11.58 A.M.

Time.	Leak for 30 seconds, in scale-divisions of the electrometer.			
	Vessel A.	Mean.	Vessel B.	Mean.
12.40 P.M.	268	283	...	119
12.43 "	...		115	
12.54 "	283		...	
12.57 "	...		120	
1.04 "	277		...	
1.07 "	...		128	
1.11 "	301		...	
1.14 "	...		118	
1.17 "	270		...	
1.20 "	...		118	
1.23 "	298		...	
1.26 "	...		116	

TABLE IX.—Natural Decay of Emanation.

Gasometer fell .465 mm. per minute.

Air-current started at 12.38 P.M.

Time.	Leak for 30 seconds, in scale-divisions of the electrometer.				
	Vessel A.	Mean.	Vessel B.	Mean.	Mean corrected to rate of flow .562 mm. of gasometer per min.
2.21 P.M.	265	259	...	202	211
2.24 "	...		200		
2.27 "	257		...		
2.30 "	...		203		
2.33 "	249		...		
2.36 "	...		194		
2.39 "	265		...		
2.42 "	...		201		
2.45 "	261		...		
2.48 "	...		211		

10. Calculation of $\frac{\lambda}{\lambda'}$.

In Table X. are given the mean ionization currents in A and B. For simplicity of calculation the ionization currents in A are reduced to 100.

Magnetic Change of Resistance at Various Temperatures. 77

TABLE X.

	Ionization current in A. I_A .	Ionization current in B. I_B .	$I_B \times \frac{100}{96.2}$
Radium emanation. No diffusion-vessel. }	100	96.2	100
Radium emanation. Diffusion experiment. }	100	52.1	54.2
Thorium emanation. Diffusion experiment. }	100	42.1	43.7
Thorium emanation. No diffusion-vessel. }	100	81.2	84.4

From Table X. the following values can at once be obtained:—

$$y_1=100, \quad y_2=54.2, \\ z_0=100, \quad z_1=88.8, \quad z_2=43.7, \quad z_2'=84.4.$$

Substituting in equation (7)

$$\frac{\lambda}{\lambda'} = \frac{\log \frac{100}{54.2}}{\log \frac{88.8}{43.7} - \log \frac{88.8}{84.4}} = \frac{.266}{.286} = .931.$$

It thus appears that the molecular weight of thorium emanation does not differ much from that of radium, though the former would seem to be somewhat smaller.

I am indebted to Professor J. J. Thomson for many suggestions, and I would thank him for the interest which he has taken in the progress of this investigation, which was carried out at the Cavendish Laboratory.

V. *On the Magnetic Change of Resistance in Iron, Nickel, and Nickel-Steel at Various Temperatures.* By W. E. WILLIAMS, B.Sc., Research Fellow of the University of Wales*.

THE influence of temperature on the change of resistance with magnetization in iron and nickel has been studied previously by Dr. Knott and also by the present writer.

Dr. Knott† has measured the change of resistance in nickel at various temperatures up to 400° C. for fields from

* Communicated by Professor A. Gray, F.R.S.

† Trans. R. S. Edin. xli. 1904, p. 39.