

CXXII.—*Some Physical Properties of Radium Emanation.*

By ROBERT WHYTLAW GRAY and SIR WILLIAM RAMSAY, K.C.B.

THAT radium emanation can be condensed by cold was discovered by Rutherford and Soddy in 1903 (*Phil. Mag.*, [vi], 5, 561); Ramsay and Soddy, in the same year, proved that it obeyed Boyle's law; a preliminary measurement of the wave-lengths of its spectrum was carried out by Collie and Ramsay; Rutherford and Soddy, in 1902, and Ramsay and Soddy, in 1903, made experiments demonstrating the inactivity of the gas, which may therefore be taken as one of the argon series.

Two other radioactive elements also evolve inactive gases, namely, thorium and actinium. The emanation from thorium was shown by Rutherford and Soddy to resist the attack of the most powerful oxidising and reducing agents (*Phil. Mag.*, 1902, [vi], 4, 581; 1903, [vi], 5, 457); and it is practically certain that actinium emanation is also inactive. Attempts to determine the molecular weights of these gases by means of diffusion have yielded approximate results only in the case of radium emanation; the most trustworthy experiments appear to be those of Perkins (*Amer. J. Sci.*, 1908, [iv], 25, 461), in which he compared the rates of diffusion of emanation and mercury vapour at 250° and 275°, and deduced the numbers 235 and 234 for the molecular and for the atomic weight of the emanation. On the other hand, P. Curie and Danne found 176; Bumstead and Wheeler, 180; and Makower, and Rutherford and Miss Brooks obtained similar results.

An excerpt from the periodic table shows the probable atomic weights of the higher members of the series, of which helium is the first member.

	N.	P.	As.	Sb.	?	Bi.	?, ⁷
	14 (17)	31 (44)	75 (45)	120 (44)	164 (44)	208 (44)	252
	O.	S.	Se.	Te.	?	?	?
	16 (16)	32 (47)	79 (48)	127 (42)	169 (43)	212 (45)	257
H.	F.	Cl.	Br.	I.	?	?	?
1 (18)	19 (16·5)	35·5 (44·5)	80 (47)	127 (44)	171 (44)	215 (44)	259
He.	Ne.	A.	Kr.	Xe.	?	?	?
4 (16)	20 (20)	40 (43)	83 (48)	131 (44)	175 (44)	219 (44)	263
Li.	Na.	K.	Rb.	Cs.	?	?	?
7 (16)	23 (16)	39 (46)	85 (48)	133 (44)	177 (44)	221 (44)	265
Gl.	Mg.	Ca.	Sr.	Ba.	?	Rd.	?
9 (15)	24 (16)	40 (47)	87 (50)	137 (45)	182 (44)	226 (45)	271

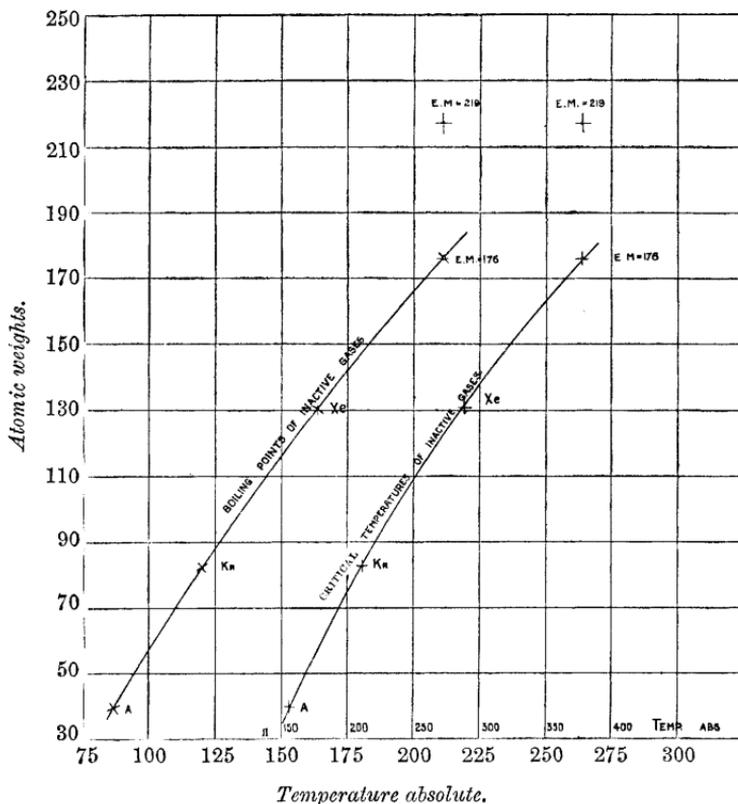
(The figures in brackets give the differences between consecutive atomic weights.)

It is obviously possible to decide which of the inactive gases occupies the position of the elements with atomic weights 175, 219, and 263, by determining their vapour-pressures. This has been now experimentally accomplished for radium emanation; the boiling point under atmospheric pressure is -62° or 211° absolute. The critical temperature has also been observed; it is $104\cdot5^{\circ}$, or $377\cdot5^{\circ}$ abs. In Fig. 1 are shown the boiling points and critical points of argon, krypton, and xenon plotted against molecular weights. The lines lie on the arc of a circle; and this arc, if prolonged, cuts the ordinate on which the boiling point lies at the point representing the atomic weight 176. The critical point also lies on a similar arc, and gives the same value for the atomic weight of the emanation. If, on the other hand, the atomic weight be taken as 219, that of the second element after xenon, the boiling point would be 260° abs., 49 degrees higher; and the critical temperature, instead of $377\cdot5^{\circ}$, would be 430° abs., no less than 53 degrees higher. Looking at the question from another point of view, the boiling and critical temperatures have been mapped on the assumption that the atomic weight is 219; it is evident that in no case could curves be drawn which with any probability would pass through these points.

Lastly, as seen in Fig. 2, the critical pressures of argon, krypton, and xenon also lie on the arc of a circle with much smaller radius than circles passing through the boiling and critical temperatures; this makes it more doubtful whether the position assigned to the emanation on the arc of this circle is justified; but, if it be placed on the circle, the atomic weight is again indicated as approximately

176. The volume of gas obtainable from unit volume of liquid has also been measured; but it is impossible to draw any useful deduction from this ratio; for, if the density of the gas be taken as $176/2$, the liquid has a density which places it on a point on the almost straight line joining the densities of liquid argon, krypton, and xenon mapped against their atomic weights nearly on the 176 ordinate; if, however, the liquid be assumed to be derived from

FIG. 1.



a gas of density $219/2$, its density is proportionately higher, and it fits the curve at a point where the 219 ordinate intersects it.

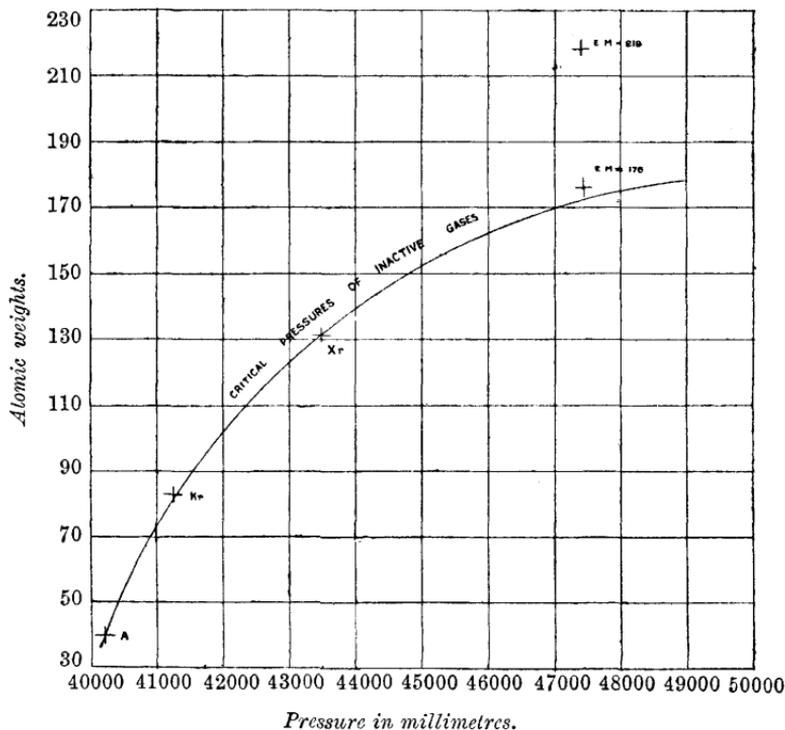
EXPERIMENTAL.

After a number of preliminary trials (of one of which an account has appeared: Proc., 1909, **25**, 82), three completely successful experiments were made, in which different quantities of emanation yielded by a solution of radium bromide containing 0.2111 gram of metallic radium were accurately measured, and then compressed

in a modified Andrews' apparatus and their vapour pressures measured at different temperatures. The volume of the liquid was also determined.

(1) *Quantity of Radium Employed.*—The quantity of radium consisted of two lots of 50 milligrams each, bought from Buchner and Co., and tested not only against each other, but also against three different lots of bromide from the same source, all of which showed uniform γ -ray discharging power. This, of course, is no guarantee of purity; but, as Professor Giesel informed us that they were all

FIG. 2.



extracted at different times, the fact of uniformity is in itself a strong presumption that the specimens were of high purity. This evidence, it may be remarked, is the same in nature as that of the purity of any chemical compound. The fact that a specimen of sodium chloride is considered to be pure depends on the quantitative agreement of one or more of its properties with those of other specimens prepared under different conditions. The remainder of the radium bromide was the sample kindly lent by the Vienna Academy (for data regarding its quantity, see *Sitzungsber. K. Akad. Wiss. Wien*, 1908, 117, July). The total quantity of radium

bromide used in these experiments was 0.3942 gram of $\text{RdBr}_2 \cdot 2\text{H}_2\text{O}$, and the content of all in metallic radium (atomic weight = 226) was 0.2111 gram.

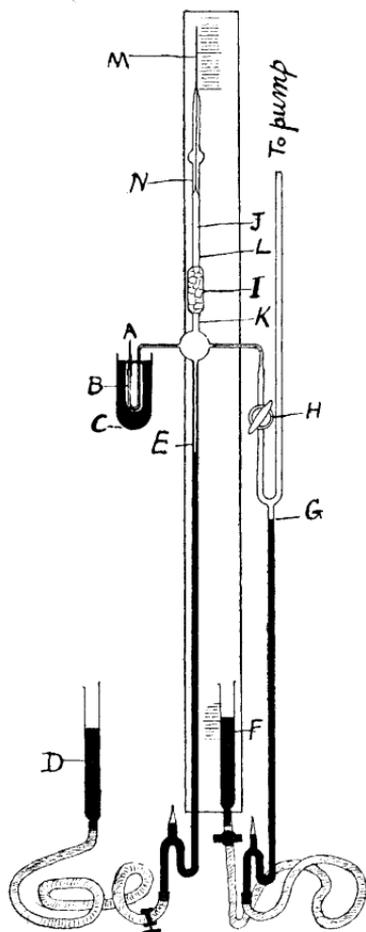
(2) *Method of Collection.*—The radium bromide contained in three bulbs in solution in water was in communication with a pump, by means of which the mixture of explosive gases could be withdrawn when required. After the curious change of rate of production of the explosive gases, described in a letter to *Nature* (December, 1908), of which a short account is given in the appendix to this paper, had ceased, the rate of evolution has remained quite constant at 25 c.c. every seven days, measured at atmospheric temperature and pressure.

This gas was stored for about an hour in the collecting-tube, the interior of which was coated with fused potassium hydroxide. It was then transferred in portions to an explosion burette, previously washed out with pure hydrogen, prepared from palladium-hydrogen; before each explosion, care was taken to draw the mercury past the stopcock, so that no contact was possible between the exploding gas and the grease of the tap. This residue always consisted of hydrogen, and varied in amount; we are unable to ascribe any cause to this variation. The residue, which was usually about 0.2 c.c. in volume, was transferred to a small tube, also previously washed out with hydrogen, the interior of which was coated with potassium hydroxide; the burette was washed out with about 1 c.c. of pure hydrogen into this tube, and the small amount of gas was left standing for an hour or more, to guard against the possible presence of carbon dioxide.

If the emanation comes into contact with grease, it apparently dissolves, and pure hydrogen is continuously generated; this renders it impossible to evacuate the apparatus perfectly; and it will be seen that the secret of success is due to the practical absence of "uncondensable" gas. To avoid contact with grease, the apparatus shown in Fig. 3 was employed. The cap *A*, ground to fit the constricted end of the inverted siphon *B*, was kept covered with mercury in the trough *C*; no grease was used, for the mercury itself made the joint a tight one. The reservoir *D* was lowered, so that the mercury stood at the level *E* in the vertical tube. Similarly, the reservoir *F* was lowered until the mercury stood at *G*, thus forming connection with the pump, when the tap *H* was opened. The tube *I* contained small lumps of quicklime freshly made from calc-spar. After evacuation, the apparatus was heated several times with a Bunsen flame until no further trace of gas could be extracted with the pump. In this way complete absence of absorbed gas on the interior walls of the tube was ensured, as well as on the lime in

tube *I*. Hydrogen was then admitted through the inverted siphon *B*, by quickly removing the cap *A*, and at once depressing a small tube containing pure hydrogen over the inverted siphon. In a moment, the hydrogen enters, the tube is removed, and the cap replaced. This hydrogen was left in the apparatus overnight. Next morning, the apparatus was again pumped empty, and again

FIG. 3.



heated until no trace of gas appeared in the fall-tube of the pump. Next, by raising the reservoir *F*, mercury passed the tap *H*, which was then closed. The emanation, mixed with hydrogen, was then admitted to the apparatus through the inverted siphon, and the cap replaced. The reservoir *D* was then raised until the mercury attained the level *K*; the gas was left in contact with the lime for about an hour; it is absolutely necessary that it should be dry, else moisture is continuously decomposed, and it is impossible afterwards to evacuate the apparatus. At this stage, the lime was heated. The tube *J* was then cooled with liquid air, contained in a moist paper cone, so as to condense the emanation; this was complete in twenty minutes. Both reservoirs were then lowered; the tap *H* was opened, and the hydrogen was pumped off until no trace of gas was visible in the capillary fall-tube of the pump. This fall-tube had a capacity of 2.3 cub. mm. per centimetre length, so that less than 0.0006 cub. mm. of gas could easily be detected at the top of the fall-tube. The mercury was then run up to *L*,

and the liquid air in the paper cone, which needed constant renewal during these operations, was allowed to evaporate; the cone was then removed. After the emanation had volatilised, the mercury was run up, and the emanation was driven into the fine capillary tube *M*. Its volume was at once measured against the scale shown in the figure, at atmospheric, and also under diminished, pressure.

The tube was then cut at *N*, after raising the mercury in the reservoir to that level; and the tube was transferred to the compression apparatus, and compressed until liquid appeared. It was then jacketed at various temperatures, and the corresponding pressures were read.

(3) *Properties of the Liquid Emanation.*—The liquid emanation is colourless, and transparent, like water, when seen by transmitted light; it itself is, however, phosphorescent, and shines with a colour varying with the nature of the glass forming the tube in which it is confined; it might be more correct to say that it causes the glass to phosphoresce. The colour varies from blue to lilac; in silica, it is blue; in lead-potash glass, bluish-green; and in soda-glass, lilac; when compressed strongly in soda-glass, the colour reminds one of the cyanogen flame, at once blue and pink. On cooling further, the liquid solidifies, and ceases to transmit light; on warming, it again becomes transparent. This gave a means of determining its melting point, using a pentane thermometer, which registered correctly at the ordinary temperature and at the temperature of a pasty mixture of carbon dioxide and alcohol (-78.3° : Travers, *Experimental Study of Gases*). The actual temperature at which the emanation melts is -71° .

(4) *Properties of the Solid Emanation.*—On cooling further with alcohol cooled with liquid air, the colour of the phosphorescence changes. The solid glows with great brilliancy, like a small, steel-blue arc-light. Further reduction of temperature changes the colour to yellow, and in liquid air it is brilliant orange-red; the colour change takes place in inverse order on warming. The red phosphorescence disappears pretty sharply at -118° .

All these phenomena were observed with a microscope the objective of which was about one inch focal length.

(5) *Vapour Pressures of Radium Emanation.*—The tube containing the liquid was calibrated in the following manner: It was drawn from thermometer-tubing of regular bore; its diameter was about $1/20$ th mm. As it would have been impossible to weigh accurately the mercury, which formed a short thread in the tube, the somewhat varying capacity of the narrow capillary was found by comparing the length of a thread at a number of points by means of a travelling microscope. This thread was then sucked into the wider capillary of the thermometer-tube, and its length again determined. The volume of a known length of the thermometer-tube was determined by weighing the mercury which filled it.

The pressure was found to vary with the volume, even although liquid was present; this, as usual, was due to uncondensable gas.

To estimate its volume, pressure readings were taken with different quantities of liquid in the tube, at a series of constant temperatures; and, at the same time, measurements of the total volume of the gas and vapour were made. From these data, the pressure exerted by the uncondensable helium and hydrogen was calculated and subtracted in each case from the observed vapour pressure.

The ratio between the absolute temperature observed at any pressure and that of methyl alcohol at the same pressure was calculated for all the observations, varying between -10° and $+104.5^{\circ}$, the latter being the critical temperature. These ratios were then mapped against the absolute temperatures of methyl alcohol, and gave a series of points through which a straight line could be drawn with small risk of error. From these observations, the vapour-pressure curve was calculated, and the divergence of each observation from the calculated temperature is given in the following table:

First Series.

Pressure in mm.	Ratio found.	Ratio smoothed.	Temperature found, ° abs.	Temperature smoothed, ° abs.
6224	1.478	1.492	273.0°	270.4°
6303	1.479	1.488	273.2	271.5
6553	1.474	1.486	275.5	273.2
9524	1.444	1.461	291.3	287.9
14055	1.439	1.439	303.0	303.0
14458	1.437	1.431	304.4	305.7
17345	1.416	1.418	314.9	314.5
17480	1.417	1.417	315.6	315.5
17779	1.414	1.415	316.1	316.3
17961	1.412	1.414	316.8	318.2
18713	1.409	1.411	318.7	318.4
13826	1.406	1.411	319.6	318.4
19937	1.402	1.403	322.5	322.3
21056	1.396	1.401	325.9	324.6
23572	1.383	1.392	332.9	330.7
24392	1.380	1.389	334.7	332.6
24865	1.379	1.387	336.0	334.0
26074	1.371	1.385	340.0	336.5
28295	1.365	1.375	344.0	341.9
28739	1.361	1.373	346.0	343.0
33618	1.355	1.359	354.0	352.8
36561	1.347	1.349	359.2	360.8
38065	1.340	1.347	362.6	362.9
38607	1.341	1.345	363.0	361.9
39215	1.339	1.341	364.2	363.8
41084	1.335	1.339	367.5	366.4
46051	1.330	1.325	374.0	375.4
47053	1.329	1.324	375.0	376.5

Second Series.

Pressure in mm.	Ratio found.	Ratio smoothed.	Temperature found, ° abs.	Temperature smoothed, ° abs.
5031	1·504	1·505	263·0°	262·9°
5528	1·495	1·496	266·8	266·7
6078	1·497	1·491	269·0	270·2
6654	1·499	1·486	271·0	273·3
11671	1·461	1·444	293·8	297·3
11703	1·462	1·444	293·7	297·3
14123	1·440	1·433	303·0	304·4
15132	1·437	1·422	308·0	311·2
17263	1·424	1·417	313·0	314·5
20024	1·399	1·405	323·0	322·4
22460	1·396	1·396	328·0	328·0
23709	1·384	1·391	333·0	331·3
27164	1·381	1·378	339·0	339·6
42026	1·303	1·336	377·5	368·3

In drawing the straight lines from which the smoothed ratios and smoothed temperatures are deduced, equal weight has been given to each observation; thus, in each series, if the algebraic sum of the minus and plus quantities be divided by the number of observations, it will be found that the quotients cancel out. Thus, although individual observations show considerable divergence from the smoothed values in many cases, the calculated temperatures may be taken as accurate. The vapour pressures of the emanation, calculated from the smoothed ratios, are given in the table which follows:

Vapour Pressures of Radium Emanation.

Pressure in mm.	Temp. ° abs.	Pressure in mm.	Temp. ° abs.	Pressure in mm.	Temp. ° abs.
500	202·6°	5000	262·8°	30000	346·0°
800	212·4	10000	290·3	35000	356·0
1000	217·2	15000	307·6	40000	364·4
2000	234·5	20000	321·7	45000	372·9
4000	255·3	25000	334·5	47450	377·5 (crit.)

Below 500 mm. pressure, the emanation is solid.

(6) *Volume of the Emanation.*—Three successful experiments were made; in the first of these, measurements made at atmospheric temperature and pressure gave for the emanation collected from 0·2111 gram of radium as bromide, during seven days, 0·0986 cub. mm., corrected to 0° and 760 mm. Measurements at 111·2 mm. and 16° gave 0·0882 cub. mm., corrected to 0° and 760 mm. The mean of these, 0·0934 cub. mm., was diminished by subtracting the volume of hydrogen and helium which it contained, namely, 0·0054 cub. mm.; the remainder is 0·0880. To that has to be added the volume of emanation pumped off, the quantity of

which was estimated by the relative γ -ray activity of the two quantities; this was 0.0032 cub. mm.; the total is 0.0912 cub. mm.

The second experiment gave at atmospheric temperature and pressure a volume 0.1060 cub. mm.; at 135.4 mm., the volume was 0.1106 cub. mm.; the mean is 0.1083 cub. mm. Subtracting the volume of the uncondensable gas, 0.0054, the remainder is 0.1029 cub. mm.; and adding the volume pumped off, 0.0037, the total volume is 0.1066 cub. mm. at 0° and 760 mm. This was obtained from the same quantity of radium in ten days.

In the third experiment, at atmospheric temperature and pressure, the corrected volume was 0.1271 cub. mm.; at 275 mm., the corrected volume was 0.1237 cub. mm., giving a mean volume of 0.1254 cub. mm., at 0° and 760 mm. The volume of impurity was 0.0083, and that of the emanation pumped off was 0.0064, making a final volume of 0.1235 cub. mm. This emanation had accumulated from the same quantity of radium in twenty-three days.

These results, calculated for the equilibrium quantity obtainable from 1 gram of radium metal, are as follows:

I.	0.604	cub. mm.	at 0°	and 760	mm.
II.	0.606	"	"	"	"
III.	0.594	"	"	"	"
	0.601	"	"	"	"
Mean =	0.601	"	"	"	"

This gives a half-life period for radium, on the two assumptions that the half-life period of the emanation is 3.86 days, and that the atom of radium, as well as that of the emanation is monatomic, of 1258 years.

Previous experiments by Cameron and Ramsay have shown larger volumes for the emanation; this is explainable by the fact that foreign gas remained mixed with the emanation; its presence has, as mentioned, been allowed for in the present research. The volume does not differ materially from the first observations of Ramsay and Soddy; but they, as well as Rutherford, neglected the original volume measured, in which foreign gas was undoubtedly present. It would appear that hydrogen and helium, in presence of the emanation, enter the walls of the tube; Mr. Usher, in this laboratory, has made quantitative observations on the point, which will be recorded later. The initial contraction of the gas, observed by Cameron and Ramsay, as well as by Ramsay and Soddy, and also by Rutherford, is undoubtedly due to this circumstance.

(7) *Volume of the Liquid Emanation.*—The gaseous emanation, confined in the narrow capillary tube connected with the pressure apparatus, was liquefied in each experiment, and the volume of the liquid was measured at atmospheric temperature; one

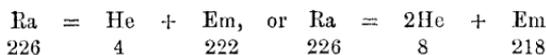
observation only was made at about the boiling point of the emanation; this is a difficult matter, owing to the freezing of the mercury at the low temperature. The length of column of the capillary tube occupied by liquid was measured with a reading microscope to the 500th of a millimetre, the volume of the conical end of the tube being estimated on the assumption that it was a perfect cone; little error is introduced by this assumption, as most of the liquid was in the cylindrical part of the tube. The results are stated in cubic millimetres of gas at 0° and 760 mm., yielded by 1 cubic millimetre of liquid:

(1) 461; (2) 686; (3) 535; (4) 623; (5) 447; (6) 581 (near boiling point of emanation).

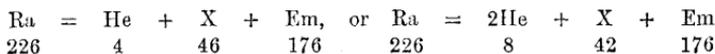
The mean is 555. The actual volume measured was about 0·00025 cub. mm., and occupied about 0·24 mm. length of the tube. Of course, it varied in different experiments; these figures are given only to show the magnitude of the quantities measured.

The density of the liquid can be calculated only by assuming the density of the gas. If it be assumed that the atomic weight of the gas is 176, and the density 88, the density of the liquid becomes 4·6; the curve indicates that 4·8 would have been a more probable number. On the other hand, taking the atomic weight as 219, implying the density 109·5, the value would be 5·7; this number would equally well fit the curve. Until the actual density of the gas has been determined by weighing, it must be left doubtful which of these numbers is correct. But the strong presumption is in favour of the lower number.

We are well aware that the deduction drawn from these results, namely, that the emanation has the atomic weight 176, does not agree with the theory advanced by Rutherford regarding the progressive degradation of radium. Perhaps a non-radioactive substance is simultaneously produced when the emanation escapes from radium. It is possible to speculate that, instead of the equation:



the change actually occurring should be:



Appendix.

In November, 1907, the Imperial Academy of Science of Vienna was so kind as to lend one of us a relatively large quantity of what professed to be radium bromide of approximate purity. This

sample, as well as two others, was dissolved in water in three bulbs, all of which were sealed to a Töpler pump, and use was made continuously of the emanation mixed with the decomposition products of water. The total amount of radium, as metal, was 0.2111 gram, and it produced about 25 c.c. of mixed oxygen and hydrogen every week. Much of the specimen from Vienna was insoluble in water; and it was found to consist largely of carbonate. On December 20th, 1907, some hydrobromic acid was introduced into the bulb containing the large quantity of radium; the insoluble matter all dissolved, with effervescence. For some months after this, bromine was evolved, and attacked the mercury of the pump; it ceased to appear in April, 1908. After that, the evolution of explosive gas was regular, until November, 1908. On November 11th, the normal amount of gas was produced; on that day, an apparatus, constructed of lead and paraffin, containing a mixture of mercuric chloride and ammonium oxalate, was placed by Dr. Flaschner close to the "Vienna bulb." On November 18th, there was "remarkably little gas; about 10 c.c." On November 25th, there were "only a few c.c." Suspecting a stoppage in the tap, air was introduced into the pump, the tap and tubes were cleaned, but there was no sign of a stoppage. The apparatus was again pumped to a vacuum, and left. On November 30th, only half a cubic centimetre was collected; on December 7th, about the same quantity; and on the 14th and the 18th, no greater amount was collected. On that date, Dr. Flaschner removed his apparatus, and after some hours replaced it, refilled. The emanation was not drawn, after this, until January 11th—three weeks later. Eight c.c. of explosive gas were collected. On that date, Dr. Flaschner finally removed his apparatus. On January 18th, 1909, 25 c.c. of gas, the old amount, were pumped off, and since then that volume has been collected weekly.

Experiments have, however, been made to try to reproduce the inhibiting conditions. First, the bulbs were surrounded by beakers containing the actinometric mixture employed by Dr. Flaschner; next, each bulb was placed in a lead cup, more than one-eighth inch thick; third, the lead cups were paraffined in their interior, and filled with the solution already referred to; and last, the identical apparatus used by Dr. Flaschner, charged as in his experiments, was placed as nearly as possible as he had placed it. But all to no purpose; 25 c.c. of explosive gas can be pumped off each week. We have failed to reproduce the conditions.

We are absolutely certain as regards the facts, and we are convinced that there has been no mistake. *Something* inhibited the action of the radium on water for a month and a half. Whatever

that was, it was coincident in time with the presence of an apparatus placed outside the bulbs; when that apparatus was removed, the inhibition ceased. It may be remarked that the whole apparatus is in a locked room, and had not been disturbed.

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