

XCIH.—*The Chemical Action of Radium Emanation.* *Part III. On Water and Certain Gases.*

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THE first paper of this series (Trans., 1907, **91**, 931) contained (p. 941) a table of measurements of the rate of decomposition of water by radium emanation. The curve obtained by plotting the rate of increase of the gas volume against time was not exponential; in character it resembled the curve representing the decay of the emanation, but its period of half value was 2.53 days, that of the emanation being 3.86 days. The method of experiment caused a constant change in the ratio of the volumes of the gas and water phases; this probably explains the discrepancy observed. It appeared desirable to make further experiments in this direction.

An apparatus was devised in which both gas and water phases were kept constant, the changes in the amount of gas being read by the pressure it exerted. Under such conditions the emanation, if it obeys Henry's law, should divide itself in a definite ratio between the two phases, and, since it appears certain that the medium containing it does not affect its rate of decay (see Moore, *Proc. Roy. Soc.*, 1908, **80**, A, June), the ratio of emanation in the water phase to emanation in the gas phase should remain constant throughout the whole experiment.

The results obtained were simple. The curve showing rate of decomposition was exponential; the period representing the total action approximated more closely to that of the half decay of the emanation (3.86 days) the more exact the experimental data.

Similar results were obtained for the recombination of hydrogen and oxygen, and these were so successful that it appeared desirable to extend the observations to other gases. Great stress cannot be laid on the quantitative results in these experiments; they must be regarded as preliminary investigations. The qualitative results, however, seem to be of sufficient interest to merit immediate publication.

It was found that carbon dioxide is decomposed into carbon, oxygen, and carbon monoxide; carbon monoxide into carbon, oxygen, and carbon dioxide; ammonia is converted in considerable quantity into nitrogen and hydrogen; the component gases recombine in less amount for the same quantity of emanation present. Hydrogen chloride is decomposed into hydrogen and chlorine, and the absorption of the latter by mercury permits measurement of the rate of action. So far the only gas tested in which the action

of the emanation was not discernible is steam, this being particularly remarkable in view of the comparatively rapid decomposition of water in the same circumstances. In all, twenty experiments have to be recorded, four with water, five with hydrogen and oxygen, three with carbon dioxide, the same number with ammonia, and single experiments with carbon monoxide, hydrogen chloride, nitrogen and hydrogen, electrolytic gas at 130° , and steam at 130° .

Apparatus and Method of Experiment.

The apparatus used for most of the experiments was a modification of that described in a previous paper (Trans., 1907, **91**, 1267), and employed to measure the emanation itself. It is shown in Fig. 1. The method varied considerably with the experiment. In general, the gas to be tested was taken through the inverted siphon, *A*, into the burette, *C*, and then, by reversing the stopcock, *B*, allowed to enter the rest of the apparatus (previously pumped empty through *F*). By closing the stopcock, *H*, and allowing the mercury to rise through *J*, the amount of gas in the apparatus could be gauged, and more added, or part removed through the pump, as found desirable. Finally, the apparatus between the stopcock, *H*, and the taking-in burette was again exhausted through *F*. The electrolytic gases containing emanation, which had accumulated over a solution of radium salt during several days, were introduced through the inverted siphon, and exploded in the burette, *C*. If hydrogen was one of the products of decomposition of the tested gases (for example, with ammonia or hydrogen chloride), the residual excess of hydrogen, containing the emanation, was forced through the apparatus by raising the mercury, caused to pass through the phosphoric oxide tube, and finally added to the gases to be experimented with through the tap, *H*. *H* was then closed, and the mercury level raised to the point *N*, the pressure being given by the barometric

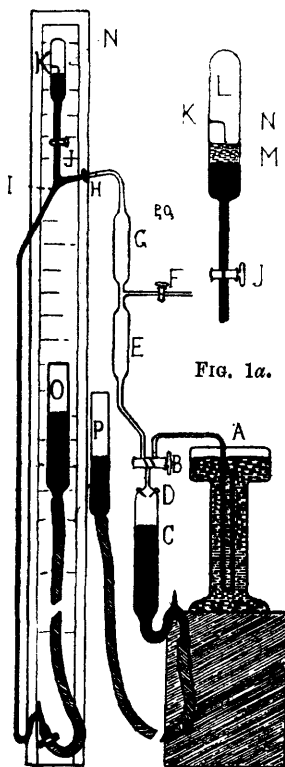


FIG. 1.

pressure less the difference of level between *N* and the mercury in the reservoir, *O*. The tap *J* was closed. Readings were taken daily, and usually extended over a period of three or four weeks.

Where not hydrogen, but oxygen, was a product of the reaction, the excess of hydrogen was exploded with about its own volume of oxygen, and the remaining oxygen and emanation added in the same way.

Where the method differed largely from that described, an account will be given under the heading of the particular experiment. That employed for the first experiment was essentially different, and may be described here. No phosphoric oxide tube was used in this case or in any similar case when water or a gas absorbable by the pentoxide was employed. The electrolytic gases containing the emanation were exploded, and a small quantity of water taken over into the burette along with the excess of hydrogen. The water and hydrogen were then introduced into the bulb *E* (by raising the mercury reservoir *P*), and water and emanation frozen by jacketing with liquid air. The excess of hydrogen was pumped off through *F*, and then water and emanation forced over through *H* and *J* into the measuring bulb (Fig. 1*a*). The point *N* was set against the lower surface of the water, and the stopcock *J* closed. In this way the gas phase, *L*, and the water phase, *M*, were definitely fixed. Daily readings were taken; the point was always set to the under surface of the water, and the pressure read. The two phases thus had always definite constant volumes, since the amount of water decomposed was never great enough to affect its volume appreciably.

Since these experiments occupied a considerable time, it was convenient to perform several simultaneously. For this purpose the measuring bulb *K* was replaced by an apparatus of the kind shown in Fig. 2. The bulbs were separately filled with different gases or water, and the taps turned. The emanation with hydrogen or oxygen, as found desirable, was allowed to rise to the level *K*, when it divided itself according to the volumes of the tubes between the taps and the horizontal bend, and each part in turn could be allowed to enter its special bulb. By calibration of the tubes afterwards, it was found possible to calculate what percentage of the total quantity of emanation was employed in any particular experiment.

In the figure, the bulb *A* was used for hydrogen chloride. Since the formation of mercury chloride seemed likely to render readings against a point difficult, a scale, *E*, was fixed to the tube, and the mercury level altered from time to time. A cup-shaped bulb was employed, the depression, *F*, containing mercury; the down-

ward flow of mercury vapour thereby produced caused much more rapid absorption of any chlorine liberated.

Tube *B* contained a point, and was packed with phosphoric oxide enclosed between plugs of glass wool. It was used for dry hydrogen and oxygen in order to measure the total recombination produced, the water being absorbed as fast as formed.

Tube *C* only contained a point, and was of the type used for ammonia, carbon dioxide, and carbon monoxide.

Tube *D* was the type employed for the final experiments with water. The water was introduced through the side-tube *H* from a weighed wash-bottle; the amount of water was ascertained by

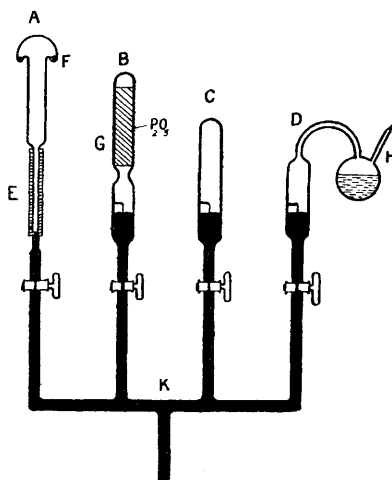


FIG. 2.

difference. The side-tube was then sealed with the blow-pipe. In this way much more exact measurements were obtained.

In order to convert the pressure readings into exact volume measurements, it was necessary to calibrate the space enclosed by the mercury surface set at the point. Where possible this was done by filling the space with mercury, which was then weighed.

For the later experiments with ammonia and with nitrogen and hydrogen, an entirely different apparatus was devised. This in some ways leads to more correct results, and it obviates the necessity of a pump.

By raising the reservoir, *K*, and lowering *G* (Fig. 3), and drawing gas from *E*, and by turning the stopcock *B* and then forcing the gas through *A*, the apparatus itself serves as a pump, and in this way it can be completely filled with mercury. The actual burette used

contained points as at *D*, the volumes to these points being accurately known. The method of using this measuring apparatus has been described by one of us previously (*Proc. Roy. Soc.*, 1905, **76**, *A*, 113; *Trans.*, 1907, **91**, 939).

The gas to be tested is taken into the burette through the inverted siphon, and accurately measured; emanation and excess of hydrogen are added, and the total volume again measured. By reversing the tap *B*, raising the reservoir *G*, and lowering *K*, the gas can be forced into *E*, and the pressure read as usual. The tap *F* is closed except when readings are being taken. Since the original volume has been determined, the space *E* to the point *H* is thereby immediately calibrated.

Errors in some of the earlier experiments are considerable, as the methods employed, especially in calculating, were only gradually perfected, particularly as regards the measurement of the water space. Whenever readings were taken with the original apparatus, bubbles passed up through the taps. These appeared to be due, not to external leakage, but to the action of a trace of emanation trapped at the taps, on the tap-grease; the gas was probably carbon dioxide. As the emanation decayed, the size of the bubble diminished. Finally, no bubble was formed; moreover, in the experiments with the apparatus in Fig. 3, where emanation did not come into contact with the tap *F*, no such phenomenon occurred. As far as possible, the pressures were measured before and after a bubble passed up, and the error thus eliminated.

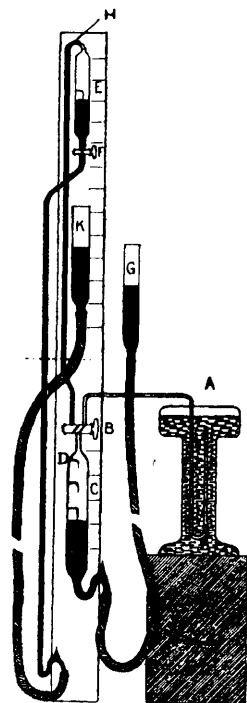


FIG. 3.

The part of the apparatus in Fig. 3 below the dotted line could also be used very simply to calibrate tubes, such as *B* and *D* (Fig. 2), the nature of which would not permit them to be filled with mercury. These were cut off below the taps, and rubbered on to the capillary tube cut at *L*. Mercury was forced up into *B*, say, and set at the point, the pressure being read as usual. Part of the gas was then drawn into *C*, the tap *B* turned, and the gas below measured, then rejected through *A*. Finally, the mercury was again set at the point in *B*, and the pressure again read. The difference of pressure ($P_0 - P$) was that

exerted by the amount of gas measured (V , say), so that the volume of B to the mercury-point surface is given by $\frac{V.760}{P_o - P}$.

In the detailed account of the experiments which follows, it has been found convenient to give the amount of the emanation used in terms of the amount produced from one gram of radium (metal) in 3.86 days.* *This quantity is called E.* In all cases the pressure readings have been corrected for expansion of mercury and gas to 0° , and, where necessary, for the vapour pressure of water.

Experiments with Water and with Hydrogen and Oxygen.

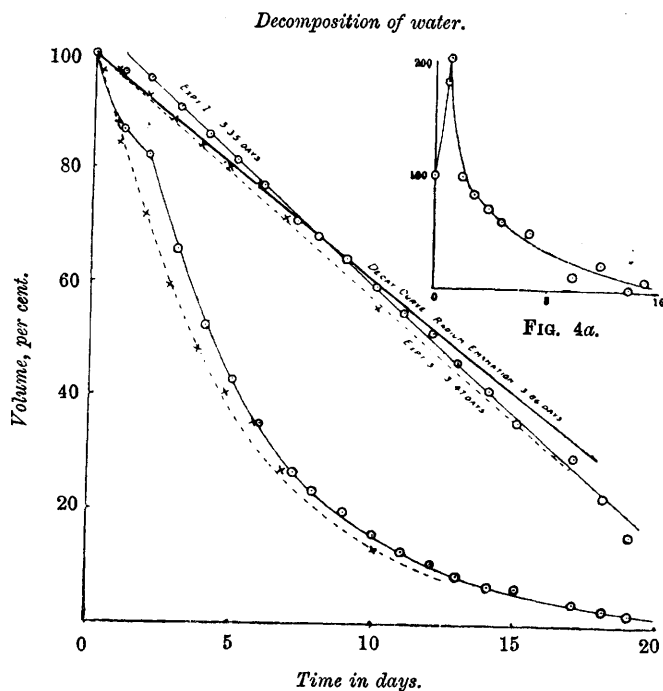
Experiment 1.—The method employed has been indicated (p. 968). The tube was calibrated by mercury, and, since the water space was not large, the error in this calibration is certainly not negligible. The result gave gas space 1.267 c.c., water space 0.291 c.c. The amount of emanation used was that collected during six days from a solution containing 101 milligrams of radium bromide and 10 milligrams of radium sulphate. This is equivalent to 0.0806 E. In the fourth and fifth columns, V_∞ is the final volume, V_o the initial volume, and V_t the volume at time t .

Time in days.	Pressure in mm.	Volume in c.c.	$V_\infty - V_t$	$100 \frac{V_\infty - V_t}{V_\infty - V_o}$	$\log \left\{ 100 \frac{V_\infty - V_t}{V_\infty - V_o} \right\}$
0	9.0	0.015	0.766	100	2.000
1.06	69.4	0.116	0.665	86.8	1.938
1.98	90.0	0.150	0.631	82.4	1.916
3.04	166.2	0.277	0.504	65.8	1.818
4.08	226.1	0.377	0.404	52.7	1.722
5.08	269.7	0.450	0.331	43.2	1.635
6.04	305.5	0.509	0.272	35.5	1.550
7.21	345.4	0.576	0.205	26.8	1.428
7.92	360.0	0.600	0.181	23.6	1.373
9.00	377.3	0.629	0.152	19.8	1.297
10.04	395.9	0.659	0.122	15.9	1.201
11.05	409.4	0.682	0.099	12.9	1.111
12.10	418.0	0.697	0.084	11.0	1.041
12.98	428.3	0.714	0.067	8.7	0.939
14.09	436.4	0.728	0.053	6.9	0.839
15.05	438.0	0.730	0.051	6.7	0.826
17.09	450.0	0.750	0.031	4.0	0.602
18.12	455.3	0.759	0.022	2.9	0.462
19.01	458.6	0.765	0.016	2.1	0.322
20.08	460.4	0.768	0.013	1.7	0.230
21.02	459.5	0.766	0.015	2.0	0.301
21.91	457.7	0.763	0.018	2.3	0.362
105.0	468.5	0.781	0.000	0.0	

* In experiments 1, 2, 5, 6, and 7, the emanation was obtained from 101 milligrams of radium bromide and 10 milligrams of radium sulphate; in the remaining experiments, from a mixture of radium bromide and carbonate, corresponding with 431 milligrams of bromide. The calculations are based on the assumptions that the formulæ $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$ and RaSO_4 are correct, that the atomic weight of radium is 226.5, and that the period of half decay of the emanation is 3.86 days.

The curve obtained by plotting the figures in the fifth column against the time, and the logarithmic curve (sixth column against time) are shown in Fig. 4. Their significance will be considered later.

Experiment 2.—The experiment was one of three conducted simultaneously. Water was introduced into the measuring bulb



⊙ Points in Experiment 1. × Points in Experiment 3.

FIG. 4.

before sealing it to the apparatus, and the height of water read and afterwards calibrated with mercury; the error in this case is possibly large. The mixed electrolytic gases containing emanation were admitted after exploding a portion of them, there being therefore a slight excess of hydrogen. The emanation used was equivalent to 0.050 E. The gas space was 3.297 c.c., the water space 0.427 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_{\infty} - V_t$	$100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$
0	632.2	2.742	0.110	100.0
0.89	653.2	2.833	0.201	182.7
1.07	658.9	2.858	0.226	205.4
1.96	632.0	2.741	0.109	99.1
2.84	627.9	2.724	0.092	83.6
3.80	624.9	2.710	0.078	70.9
4.80	622.0	2.698	0.066	60.0
6.80	619.4	2.687	0.055	50.0
9.88	609.4	2.643	0.011	10.0
11.91	612.4	2.657	0.025	22.7
13.80	607.1	2.633	0.001	0.9
15.00	609.1	2.642	0.009	8.2
15.79	604.1	2.620		
16.85	607.6	2.638	0.006	5.6
21.89	606.7	2.632	0.000	0.0

The results are irregular, and the whole volume-change small. The curve obtained by plotting the figures in column 5 against time is shown in Fig. 4a.

The gases were analysed at the conclusion of the experiment, with the following result:

Hydrogen	1.815 c.c.
Oxygen	0.634 „
Nitrogen and carbon dioxide.....	0.016 „
Total volume	2.465 „

A trace of gas not pumped off would account for the difference in volume.

Experiment 3.—The experiment was one of three conducted simultaneously. Water was pipetted into the bulb, as described previously, from a minute wash-bottle, and the amount ascertained by weighing the bottle before and after. The whole bulb was calibrated afterwards, the gas and water volumes being exactly known. (Gas space, 3.789 c.c.; water space, 2.302 c.c.) The emanation was introduced with excess of oxygen, and was equivalent to 0.062 E. At the end of ten days, considerable leakage unfortunately occurred. The real final value was accordingly determined by extrapolation.

Time in days.	Pressure in mm.	Volume in c.c.	$V_{\infty} - V_t$	$100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$	$\log 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$
0	39.9	0.200	0.390	100	2.000
0.25	42.5	0.212	0.378	96.9	1.986
0.81	49.7	0.248	0.342	87.7	1.943
0.92	52.6	0.262	0.328	84.1	1.925
1.89	62.8	0.310	0.280	71.8	1.856
2.80	71.8	0.358	0.232	59.5	1.774
3.81	80.5	0.401	0.189	48.5	1.685
4.81	86.4	0.431	0.159	40.8	1.610
5.81	90.4	0.451	0.139	35.6	1.552
6.81	97.0	0.484	0.106	27.2	1.434
10.07	107.9	0.538	0.052	13.3	1.125
∞		(0.590)	—	0.0	

The gas was analysed, and found to contain 0.272 c.c. of oxygen (after deducting the amount due to air leakage), and 0.343 c.c. of hydrogen, giving a total volume of 0.615 c.c., which agrees fairly closely with the extrapolated value.

The curves are shown in Fig. 4.

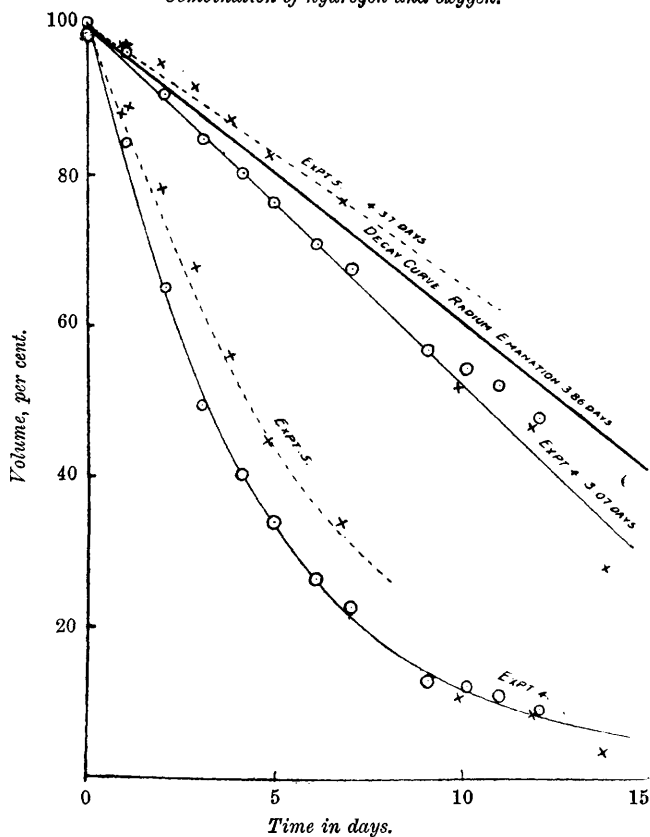
A further experiment was carried out in the same way. At the end of six days, a vacuum was created below the tap (Fig. 2, *D*), and a clear passage to the pump was left; the tap was turned for about two seconds. The gas below the tap was then pumped off, and readings continued for eleven days more. The change of volume in the second part of the experiment was much slower (0.058 c.c. in the eleven days, as compared with 0.728 c.c. in the first six days), proving that the emanation makes its escape from the water phase to a vacuum above almost instantaneously. The first curve was not exponential, but there were an insufficient number of points to determine its nature accurately.

Experiment 4 (Moist Hydrogen and Oxygen).—The electrolytic gases, with emanation, were exploded down to reasonable bulk, and introduced into the measuring bulb. They contained therefore excess of moisture throughout the experiment. The emanation corresponded with 0.093 E. The volume of the measuring tube was 2.186 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$	$Q = 100 \frac{V_t - V_\infty}{V_0 - V_\infty}$	$\log Q$
0	523.5	1.505	0.668	100	2.000
0.03	519.8	1.495	0.658	98.5	1.993
1.02	487.0	1.401	0.564	84.4	1.926
2.07	442.0	1.271	0.434	65.0	1.813
3.07	405.6	1.167	0.330	49.4	1.694
4.13	384.5	1.106	0.269	40.3	1.605
4.99	369.5	1.063	0.226	33.8	1.529
6.11	352.2	1.013	0.176	26.3	1.420
7.07	343.5	0.988	0.151	22.6	1.354
9.11	321.4	0.924	0.087	13.0	1.114
10.16	319.3	0.919	0.082	12.3	1.090
11.04	316.6	0.911	0.074	11.1	1.045
12.10	312.3	0.898	0.061	9.1	0.959
97.0	291.0	0.837	0.000	0.0	

The curves are shown in Fig. 5.

Experiment 5 (Moist Hydrogen and Oxygen).—This, exactly similar to the previous experiment, was one of three conducted simultaneously. The amount of emanation was equivalent to 0.025 E. The volume of the measuring tube was 2.79 c.c.

Combination of hydrogen and oxygen.

○ Points in Experiment 4. × Points in Experiment 5.

FIG. 5.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$	$Q = 100 \frac{V_t - V_\infty}{V_0 - V_\infty}$	$\log Q$
0	564.5	2.073	0.221	100	2.000
0.89	557.4	2.047	0.195	88.2	1.945
1.07	558.0	2.049	0.197	89.1	1.950
1.96	551.4	2.025	0.173	78.3	1.894
2.84	545.0	2.002	0.150	67.9	1.832
3.80	538.0	1.976	0.124	56.1	1.749
4.80	531.2	1.951	0.099	44.8	1.651
6.80	524.7	1.927	0.075	33.9	1.530
9.88	510.8	1.876	0.024	10.9	1.037
11.91	509.3	1.871	0.019	8.6	0.934
13.80	506.5	1.860	0.008	3.6	0.556
15.00	502.1	1.844	—	—	—
15.79	504.0	1.851	—	—	—
16.85	505.6	1.857	0.005	2.7	0.431
21.89	504.3	1.852	0.000	0.0	—

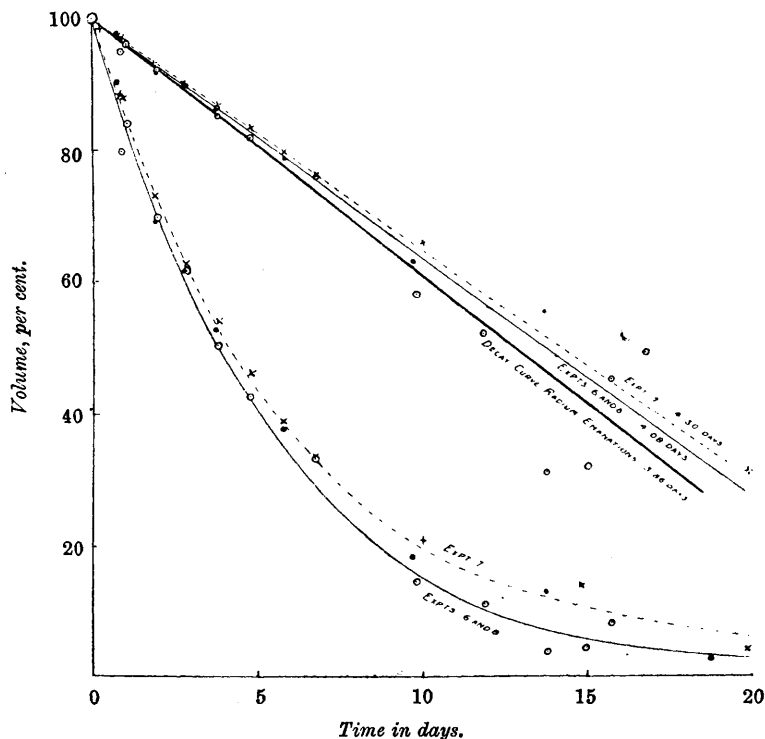
The curves are shown in Fig. 5. The gases were analysed, with the result:

Hydrogen	1.253 c.c.
Oxygen	0.579 "
Nitrogen and carbon dioxide	0.008 "
Total volume	1.840 "

The measured and final volume thus agree very closely.

Experiment 6 (Dry Hydrogen and Oxygen).—The method was that usually employed, the measuring tube containing phosphoric

Combination of hydrogen and oxygen.



- Points in Experiment 6. × Points in Experiment 7.
● Points in Experiment 8.

FIG. 6.

oxide (as in *B*, Fig. 2). The amount of emanation used was equivalent to 0.044 E. The volume of the tube was 4.996 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100 \frac{(V_t - V_\infty)}{V_o - V_\infty}$.	$\log Q$.
0	577.6	3.798	0.555	100	2.000
0.89	560.6	3.686	0.443	79.8	1.802
1.07	564.1	3.709	0.466	84.0	1.924
1.96	552.4	3.631	0.388	69.9	1.844
2.84	546.9	3.595	0.352	63.4	1.802
3.80	535.6	3.522	0.279	50.3	1.702
4.80	530.2	3.485	0.242	43.6	1.639
6.80	521.5	3.428	0.185	33.3	1.522
9.88	505.6	3.324	0.081	14.6	1.164
11.91	502.8	3.305	0.062	11.2	1.049
13.90	496.4	3.264	0.021	3.8	0.580
15.00	496.9	3.267	0.024	4.3	0.633
15.79	500.2	3.288	0.045	8.1	0.908
16.85	501.7	3.297	0.054	9.7	0.987
21.89	493.3	3.243	0.000	0.0	

The curves are shown in Fig. 6. Analysis of the gas gave the result:

Hydrogen	2.267 c.c.
Oxygen	1.004 „
Nitrogen and carbon dioxide	0.019 „
Total volume	3.290 „

Here, also, there is a close agreement between the measured and the calculated volumes.

Experiment 7 (Dry Hydrogen and Oxygen).—The experiment was one of three conducted simultaneously. The tube was filled with electrolytic gas, and oxygen, containing emanation equivalent to 0.103 E, was added. The volume of the tube was 3.432 c.c. at N.T.P.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100 \frac{V_t - V_\infty}{V_o - V_\infty}$.	$\log Q$.
0	344.2	1.551	0.526	100	2.000
0.02	343.8	1.549	0.524	99.6	
0.04	344.3	1.552	0.527	100.2	
0.06	344.8	1.557	0.532	101.1	
0.07	344.8	1.557	0.532	101.1	
0.09	343.5	1.551	0.526	100.0	
0.11	343.9	1.553	0.528	100.4	
0.21	342.0	1.545	0.520	98.8	
0.25	341.8	1.544	0.519	98.7	
0.29	340.5	1.538	0.513	97.5	
0.81	330.4	1.490	0.465	88.4	1.946
0.92	329.8	1.488	0.463	88.0	1.944
1.89	312.1	1.410	0.385	73.2	1.864
2.80	299.9	1.356	0.331	62.9	1.799
3.81	289.7	1.310	0.285	54.2	1.734
4.81	280.4	1.268	0.243	46.2	1.665
5.81	271.9	1.230	0.205	39.0	1.591
6.81	266.7	1.202	0.177	33.7	1.528
10.07	251.9	1.138	0.113	21.0	1.322
14.84	242.8	1.098	0.073	13.9	1.143
19.88	231.7	1.047	0.022	4.2	0.623
23.84	227.9	1.031	0.006	1.1	0.041
26.80	226.8	1.025	0.000	0.0	

The bubbles passed up through the tap, and measured (by difference in pressure) throughout the experiment were in all 0.026 c.c. (actual final volume, 1.051). The gas was pumped off and analysed:

Hydrogen	0.586 c.c.
Oxygen	0.415 „
Carbon dioxide.....	0.023 „
Total volume	1.024 „

The curves are shown in Fig. 6.

Experiment 8 (Dry Hydrogen and Oxygen).—This was carried out in exactly the same way as experiment 7. The tube was filled with electrolytic gas of more than 99 per cent. purity. The emanation, equivalent to 0.063 E, was added with excess of hydrogen. The volume of the tube was 1.566 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100 \frac{V_t - V_\infty}{V_o - V_\infty}$.	$\log Q$.
0	469.2	0.967	0.476	100	2.000
0.017	469.1	0.967	0.476	100	
0.73	446.8	0.921	0.430	90.3	1.956
1.93	397.8	0.820	0.329	69.1	1.839
2.73	382.8	0.789	0.298	62.6	1.797
3.75	360.2	0.743	0.252	52.9	1.723
5.80	325.4	0.671	0.180	37.8	1.577
9.77	280.7	0.579	0.088	18.5	1.267
13.78	268.0	0.553	0.062	13.0	1.114
18.76	244.1	0.503	0.012	2.5	0.398
23.86	241.4	0.494	0.003	0.6	1.778
25.76	239.6	0.491	0.000	0.0	

The gases were not analysed. The curves are shown in Fig. 6.

It is now necessary to consider the significance of the results shown by the curves in Figs. 4 to 6. The emanation decays according to the equation:

$$\frac{v_t}{v_o} = e^{-\lambda t},$$

and falls to half value, according to Sackur's determination, in 3.86 days. In experiments 4 to 8 the volume of gas has decreased continuously, hydrogen and oxygen uniting to form water. The value $(V_o - V_\infty)$ represents the whole effect of the emanation, the total quantity of gas combined. It corresponds with v_o , the total quantity of emanation acting. At any time t , the amount recombined is given by $(V_o - V_t)$. It corresponds with $(v_o - v_t)$, the amount of emanation which has decayed up to time t . The quantity $(V_t - V_\infty)$, is the amount of recombination still to take place, to be brought about by the emanation still undecayed, v_t . If the emanation produced an effect proportional to the amount present, then

$$\frac{V_t - V_\infty}{V_o - V_\infty} = \frac{v_t}{v_o},$$

from which it follows that

$$\frac{V_t - V_\infty}{V_0 - V_\infty} = e^{-\lambda t}, \quad (1)$$

where λ should have the same value, and consequently the time of half action (constant $\div \lambda$) should be 3.86 days.

Exactly the same reasoning applies to the figures in experiments 1—3. In these, the amount of gas is continually increasing; $V_\infty - V_0$ represents the total change equivalent to v_0 ; ($V_\infty - V_t$) represents the change yet to be produced after time t , corresponding with the emanation yet undecayed, v_t ; wherefore, similarly to (1),

$$\frac{V_\infty - V_t}{V_\infty - V_0} = e^{-\lambda t}. \quad (2)$$

The values in the fifth columns have all been obtained by taking the total change of volume ($V_0 - V_\infty$) as 100, the sixth column containing the corresponding logarithms. The fact that the points on the logarithmic curves in Figs. 4 to 6 lie fairly closely on straight lines, shows that the equations (1) and (2) actually hold for some constant λ .

The following table shows that the time of half action, T , approximates to 3.86 days. It has been determined graphically from the curves. P_0 is the initial pressure, and P_∞ the final pressure; their difference gives some criterion of the relative accuracy of each experiment. V_E is the volume of gas which would be decomposed or recombined by E c.c. of emanation (p. 971).

No. of experi- ment.	$(P_0 - P_\infty)$. mm.	$(V_0 - V_\infty)$. c.c.	T . days.	λ .	Gas phase. c.c.	Water phase. c.c.	Amount of emana- tion.	V_E c.c.
1	459.5	0.766	3.35	0.207	1.27	0.29	0.081E	9.46
2	—	0.110?	—	—	3.30	0.43	0.050E	(2.20)
3	84.7	0.390	3.47	—	3.79	2.30	0.062E	6.29
4	232.5	0.668	3.40	0.204	2.19	small	0.093E	7.18
5	60.2	0.221	4.37	0.159	2.79	small	0.025E	8.84
6	84.3	0.555	4.08	0.170	5.0	—	0.044E	12.61
7	117.4	0.526	4.30	0.161	3.43	—	0.103E	5.01
8	229.6	0.476	4.08	0.071	1.57	—	0.063E	7.56
		Mean	3.86					
		Theor.	3.86	0.1795				

The fact that the mean value for T exactly coincides with the theoretical value, of course, has no real significance, since the graphic determination is certainly not correct to the second decimal figure. It will be observed that experiments 2, 3, 6, and 7, where the points do not lie well on the curve, represent small changes of pressure and large experimental errors. The converse is true for the other experiments. Since the experiments give exponential curves, the constants of which approximate to those for the emanation, it would appear that in any experiment the chemical action produced by the emanation is strictly proportional to the

amount present, and, further, *that every molecule of emanation disintegrating produces a definite chemical effect.* But in experiments 6 to 8, which should be comparable, the gas in each case being dry hydrogen and oxygen, and the condition of experiment the same, the total recombination effected varies within wide limits (calculated for E between 5.01 and 12.62 c.c.). This points to some other factor than the emanation playing a part in the chemical action. Excess of one of the constituents may produce an effect. Pressure appears to be without effect. The curves remain exponential during large changes of pressure. It seems more probable that the surface is the unknown factor. It varies from experiment to experiment, but remains constant during any one experiment. The rate of change is consequently not affected, but the total change is altered. Since in these experiments the surface is large, due to the presence of phosphoric oxide, they are unsuitable for the determination of the part played by it in the reaction. In experiments 4 and 5, where the gases were moist and the surface was small, since plain measuring tubes were employed, the agreement is much closer.

We have assumed that the emanation obeys Henry's law, and divides itself in a constant ratio between the gas and water phases, as in the first three experiments. The recombination effected in the gaseous phase follows an exponential law (experiments 6 to 8). The volume changes measured in experiments 1 to 3 are the differences between decomposition in the water phase and recombination in the gas phase. They also obey the same exponential law. It follows that the decomposition in the water phase must also follow that law. The data are still insufficient to calculate the ratio in which the emanation divides itself between gas and water. It is necessary first to find some method of determining the extent to which surface plays a part in the reaction. The data of the first three experiments, however, indicate that, volume for volume, the emanation produces a far greater effect in the liquid phase than in the gas phase.

The causes underlying these changes will be discussed at the end of this paper (pp. 990, 992).

Some rough measurements have been made of the total volume of electrolytic gas obtained from the solution of radium bromide containing 0.231 gram of radium as metal. The results are tabulated:

Time of collection in hours.	Volume of gas in c.c.	Volume per gram Ra. per 100 hours.
22	7.5	148
70	20.0	123
94	26.4	122

It seems that there is gradual increase of recombination in the gas phase, as the amount of emanation in that phase increases. The corresponding figure, 60 c.c., calculated from results already published (Trans., 1907, **91**, 934: mean result, 32 c.c. per gram of radium bromide, $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$), is quite different. Here, again, it appears that surface plays a considerable part in the amount of reaction.

Experiments with the Oxides of Carbon.

These can only be regarded as preliminary and qualitative.

Experiment 1.—Four days' accumulation of electrolytic gas and emanation from 0.231 gram of radium (metal) as bromide, allowed to decay during one day, was exploded down; the residual gas was mixed with a small quantity of carbon dioxide, and cooled to -185° by means of liquid air; the hydrogen was then removed by pumping. After the temperature had risen, the carbon dioxide and emanation were forced into a small measuring tube (capacity, 0.1197 c.c.) and readings taken. It was thought probable that the dioxide would decompose into carbon monoxide and oxygen, and that the increase of volume would be measurable. On the contrary, the gas contracted very slightly in volume (from 0.0907 to 0.0870 c.c. in three days), and a black ring of carbon began to deposit immediately, just above the mercury surface. After the third day, no readings could be made, on account of this carbon deposit, and at the same time owing to the formation of an appreciable quantity of mercuric oxide at the mercury surface.

Experiment 2.—Four days' accumulation of emanation, from 0.2307 gram of radium (metal) as bromide, was separated as previously, and used to treat a much larger quantity of carbon dioxide. An exactly similar result was obtained. A ring of carbon above the mercury surface was distinctly noticeable before the end of the first day, and gradually increased in thickness. The volume slowly decreased (in three days from 0.592 to 0.581 c.c.). The gases were afterwards pumped off, pure oxygen introduced, and the tube heated to $300-400^\circ$. The carbon burned away quietly, the volume remaining unchanged. The tube was broken before the carbon dioxide could be measured.

Experiment 3.—Carbon monoxide was prepared from formic acid and sulphuric acid. It was introduced into the apparatus in the usual manner, emanation and oxygen being added (the experiment was one of three conducted simultaneously). The emanation was equivalent to 0.05 E. The gas immediately commenced to contract, and carbon was deposited. Readings were taken over a period of four weeks.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100 \frac{V_t - V_\infty}{V_0 - V_\infty}$.	$\log Q$.
0	299.2	1.046	0.177	100	2.000
0.02	300.1	1.048	0.179	101.1	
0.04	300.9	1.051	0.182	102.8	
0.06	299.7	1.047	0.178	100.6	
0.07	298.9	1.044	0.175	98.9	
0.09	298.1	1.042	0.173	97.7	
0.11	297.1	1.038	0.169	95.5	
0.21	296.2	1.035	0.166	93.8	
0.25	296.1	1.035	0.166	93.8	1.972
0.29	297.1	1.038	0.169	95.5	
0.81	290.7	1.010	0.141	79.6	1.901
0.92	289.0	1.006	0.137	77.4	1.889
1.89	281.1	0.981	0.112	63.3	1.801
2.80	275.1	0.959	0.090	50.8	1.706
3.81	272.1	0.949	0.080	45.2	1.655
4.81	266.1	0.928	0.059	33.3	1.522
5.81	262.1	0.914	0.045	25.4	1.405
6.81	260.4	0.908	0.039	22.0	1.342
10.07	258.6	0.901	0.032	18.1	1.258
14.84	252.7	0.880	0.011	6.2	0.792
19.88	253.8	0.884	0.015	8.5	0.929
23.84	250.3	0.872	0.003	1.7	0.230
26.80	249.7	0.869	0.000	0.0	

The gas was pumped off and analysed :

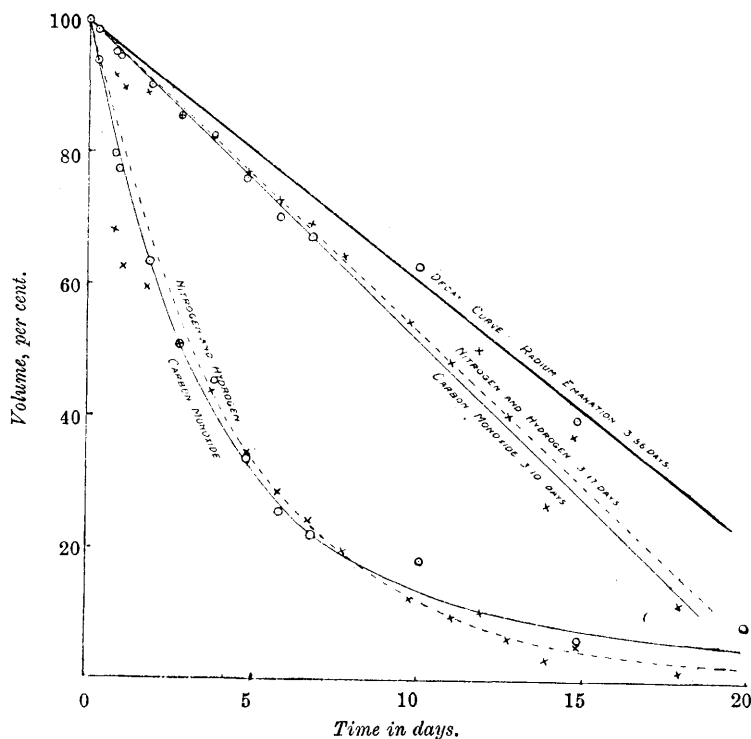
Carbon dioxide.....	0.084 c.c.
Oxygen	0.041 „
Carbon monoxide.....	0.755 „
Total volume.....	0.880 „

Apparently, therefore, the monoxide decomposed to form both carbon and oxygen, and carbon and carbon dioxide, although it is possible that the carbon dioxide was produced by the interaction of the oxygen and carbon. The curves are shown in Fig. 7; the time of half change was 3.1 days.

Experiment 4.—It was considered possible that, if yellow phosphorus were present when carbon dioxide was treated with emanation, the oxygen would be absorbed as fast as formed, and the rate of reaction thereby rendered measurable. The experiment was performed in a tube of the form *D*, Fig. 2, the tube being sealed to the apparatus, and phosphorus introduced through the side-tube, which for that purpose was made specially long and wide, and which was then sealed. Absolutely pure carbon dioxide was introduced in the customary manner, and emanation with oxygen added. The phosphorus was gently warmed, and immediately on melting, part catching fire and absorbing the oxygen present, completely changed to the red variety. Although it has been observed (Becquerel, *Compt. rend.*, 1901, **133**, 709) that β -rays change yellow into red phosphorus, such immediate action was not expected.

A series of readings was taken, and it will be observed that there was a slight increase in volume. The emanation used was equivalent to 0.125 E.

Time.	Pressure.	Volume.
0	405.6	1.828
0.75	411.0	1.894
1.66	420.3	1.937
1.75	425.8	1.963
2.66	426.7	1.968
6.0	429.4	1.980
15.71	417.6	1.925*



- Points in experiment with carbon monoxide.
 × Points in experiment with nitrogen and hydrogen.

FIG. 7.

The gas was analysed, with the following result:

Carbon dioxide.....	1.400 c.c.
Carbon monoxide.....	0.498 "
Oxygen	0.027 "
Total volume.....	1.925 "

* This reading was probably incorrect, the apparatus having been moved in the interval.

It would appear, therefore, that with carbon dioxide, also, both possible reactions take place; the non-increase of volume in the first two experiments, and the increase in the last, point to some factor, as yet unknown, which determines the nature of the change.

Experiment with Hydrogen Chloride.

The hydrogen chloride was prepared from sodium chloride and sulphuric acid, and may have contained a trace of impurity. It was introduced into the measuring tube *A*, Fig. 2, in the usual manner, and emanation (0.069 E) and hydrogen introduced. The method of reading has been indicated previously (p. 968). The measurements follow. The volume of the measuring tube was about 6.6 c.c.

Time in days.	Volume in c.c.	$V_0 - V_\infty$.	$Q = 100 \frac{V_t - V_\infty}{V_0 - V_\infty}$.	$\log Q$.
0	2.464	0.561	100	2.000
0.017	2.454	0.551	98.2	1.992
0.73	2.204	0.301	53.4	1.728
1.93	2.086	0.183	32.6	1.513
2.73	2.079	0.176	31.4	1.496
3.75	2.060	0.157	28.0	1.447
5.80	2.038	0.135	24.1	1.381
9.77	1.985	0.082	14.6	1.165
13.78	1.949	0.046	8.2	1.914
18.76	1.930	0.027	4.8	1.682
23.86	1.926	0.023	4.5	1.649
25.76	1.903	0.000	0.0	

The curves are shown in Fig. 8. The time of half change is 5.9 days.

In considering these curves, it must be remembered that the errors of observation are much larger than usual, both volume and pressure readings being taken, and that the pressure readings varied only between the limits 511.4 and 594.3. The presence of mercurous chloride was observed after the first day, and a considerable amount was deposited during the experiment on the whole surface of the tube. The gas was analysed, and found to contain 0.322 c.c. of hydrogen. This does not agree very closely with the calculated value. The actual final volume was 1.993, the difference, 0.090, was due to bubbles from the tap, added in the course of the experiment, and probably consisting of carbon dioxide.

Experiments with Ammonia and with Nitrogen and Hydrogen.

The first experiment was performed in a simple measurement tube (type *C*, Fig. 2). Ammonia, prepared from slaked lime and

ammonium chloride, was introduced as usual. Hydrogen and emanation (0.060 E) were added. The initial decrease in volume recorded below demanded attention. The remaining experiments were performed, therefore, in a specially devised apparatus, shown in Fig 3. The method of using this has been described (p. 969). In the second experiment, the presence of a trace of moisture along with the gases was observed. This was thought to account for the

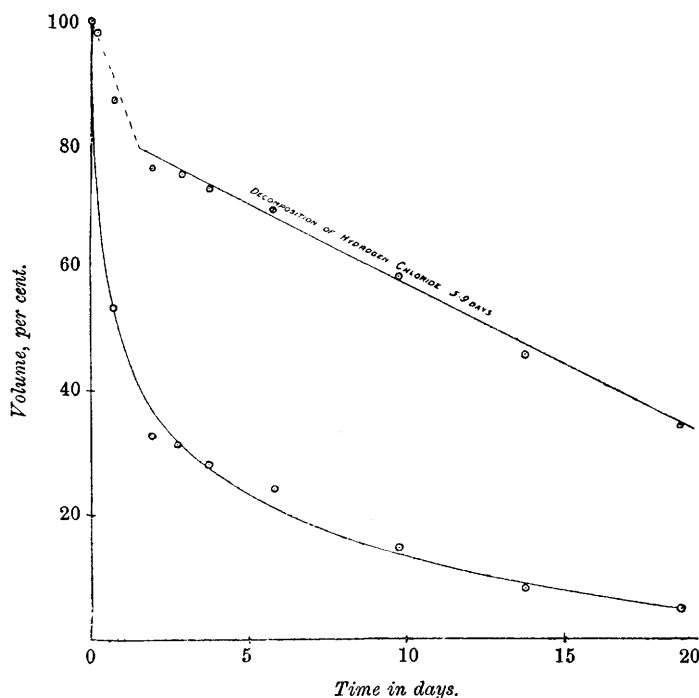


FIG. 8.

initial decrease found in that case. In the third experiment, especial precautions were taken to dry the apparatus and purify the gas. The initial decrease in volume was almost eliminated. In order to compare the results, the initial volume has been taken as zero; in all cases the corresponding numbers are shown in the fourth column. In the second and third experiments, the respective quantities of emanation employed, in each case added with hydrogen, were 0.24 E and 0.23 E.

Experiment 1.—

Time.	Pressure.	Volume.	Arbitrary scale.	$V_{\infty} - V_t$.	Q .	$\log Q$.
0	551.4	0.628	0	—	—	—
0.17	546.1	0.622	-0.006	—	—	—
0.73	485.6	0.553	-0.075	—	—	—
1.93	461.8	0.526	-0.102	0.046	100	2.00
2.73	469.7	0.535	-0.093	0.037	80	1.90
3.75	481.2	0.548	-0.080	0.024	52	1.72
5.80	491.7	0.560	-0.068	0.012	26	1.42
9.77	496.0	0.565	-0.063	0.007	15	0.82
13.78	499.6	0.569	-0.059	0.003	11	0.04
18.76	502.2	0.572	-0.056	0.000	0	—
23.86	502.0	0.572	-0.056			

Experiment 2.—

0	425.7	1.026	0
0.81	396.5	0.956	-0.070
1.74	431.7	1.040	+0.014
2.75	510.0	1.229	+0.203

Experiment 3.—

0	807.1	1.945	0			
0.18	805.3	1.941	-0.004	0.429	100	2.000
0.90	828.3	1.996	+0.051	0.374	87.2	1.940
1.90	864.7	2.084	0.139	0.286	66.7	1.824
2.18	883.0	2.128	0.183	0.242	56.4	1.751
2.92	911.0	2.195	0.250	0.175	40.8	1.610
4.90	942.4	2.271	0.326	0.099	23.1	1.363
6.91	964.4	2.224	0.379	0.046	10.7	1.030
10.05	974.2	2.348	0.403	0.022	5.1	0.710
11.90	979.0	2.360	0.415	0.010	2.3	0.367
∞		(2.370)	(0.425)	0.000	0.0	—

The curves obtained by plotting the figures in column 4 against time are shown in Fig. 9. In order to see whether those in experiments 1 and 3 are exponential (in experiment 3, the final value was found by extrapolation), the first value in column 5, showing increase in volume, was taken at 100, logarithms being obtained and plotted as usual (columns 6 and 7). The results are also shown in Fig. 9. They lie fairly closely on a straight line. The period of half action is, however, very different from 3.86 days, being 2.0 days for experiment 1 and 1.4 days for experiment 3.

The gases in experiment 2 were transferred to a tube over mercury, and allowed to stand for some weeks; they were finally analysed. Those in experiment 3 were passed back into the burette (*C*, Fig. 3), and analysed immediately. The gas in experiment 1 was also analysed.

Experiment.	Nitrogen.	Hydrogen.	Hydrogen added initially.
1	0.421 c.c.	trace	0.191 c.c.
2	0.502	0.660	0.090
3	0.249	0.846	0.222

The considerable, but decreasing, discrepancy between the measured and the calculated amounts of hydrogen corresponds with the known presence of traces of moisture. It is possible that in each case a trace of air was admitted, either as impurity in the ammonia, or with the emanation, with consequent formation of water and absorption of ammonia (giving the observed decrease). This would

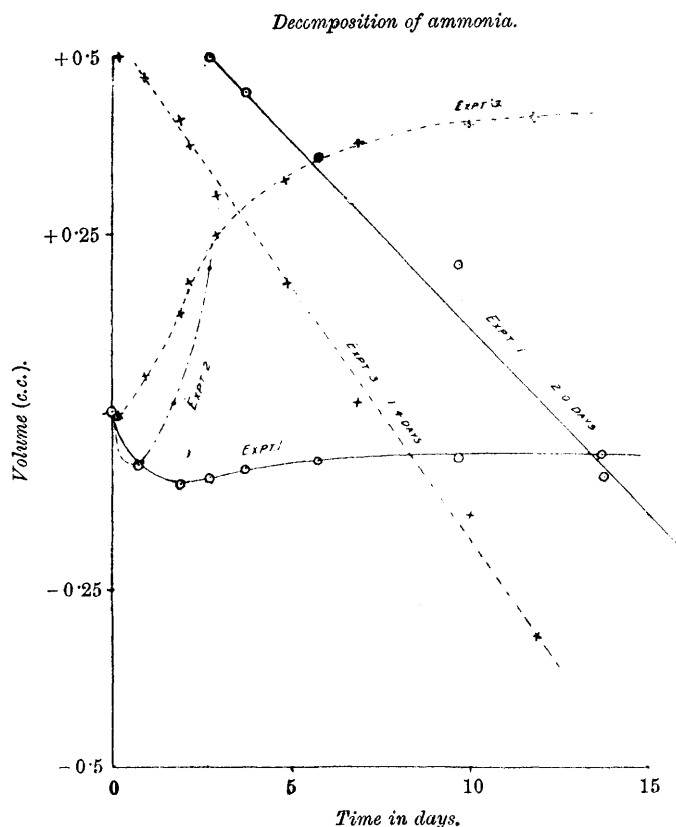


FIG. 9.

also affect the nitrogen values, and may account for the great difference between the rate of the reactions and that of the decay of the emanation.

In a similar apparatus, containing some fused calcium chloride to absorb any ammonia that might be formed, a mixture of nitrogen and hydrogen was treated with emanation (0.239 E). The gases were prepared by sparking perfectly pure ammonia, the

undecomposed ammonia being removed by dilute sulphuric acid. The emanation was added with excess of hydrogen. The results are shown below.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$	$Q = 100 \frac{V_t - V_\infty}{V_o - V_\infty}$	$\log Q$
0	745.6	2.256	0.236	100	2.000
0.005	743.8	2.250	0.230	97.4	
0.019	745.3	2.255	0.235	99.6	
0.08	751.5	2.273	0.253	108.0	
0.79	720.8	2.180	0.160	67.8	1.831
1.06	716.3	2.167	0.147	62.3	1.794
1.76	714.1	2.160	0.140	59.3	1.773
2.77	707.6	2.140	0.120	50.8	1.706
3.77	701.6	2.123	0.103	43.6	1.640
4.85	694.3	2.101	0.081	34.3	1.536
5.77	690.1	2.087	0.067	28.4	1.453
6.76	686.6	2.077	0.057	24.4	1.383
7.76	683.1	2.066	0.046	19.5	1.290
9.76	677.1	2.049	0.029	12.3	1.089
11.01	675.0	2.042	0.022	9.6	0.969
11.86	675.6	2.044	0.024	10.2	1.007
12.77	672.4	2.035	0.015	6.4	0.803
13.86	670.0	2.023	0.008	3.4	0.530
14.77	671.9	2.033	0.013	5.5	0.741
17.93	669.1	2.024	0.004	1.7	0.229
		(2.020)	0.000	0.0	

The curves are shown in Fig. 7; the time of half change was 3.17 days. Considering the small changes in pressure, and, in consequence, the larger percentage error, the approximation to an exponential curve is very good.

Experiments at 130°.

*Experiment 1 (Hydrogen and Oxygen).—*The electrolytic gases from the radium bromide solution, containing emanation corresponding with 0.263 E, were exploded, the emanation frozen at -185° , and the excess of hydrogen pumped off. Very pure electrolytic gas was then passed up over the frozen emanation, and, after the temperature had risen to air temperature, the gases and emanation were pumped off; carbon dioxide was removed by introducing a trace of potash. The gases were then introduced into an apparatus of the type shown in Fig. 1, and forced up into a small measuring tube, containing a point (volume at N.T.P., 0.1197 c.c.), and jacketed with chlorobenzene vapour. A series of readings were taken for nearly six hours. (The pressure has been corrected to 0° ; the volume to N.T.P.)

Time in hours.	Pressure in mm.	Volume in c.c.	Time in hours.	Pressure in mm.	Volume in c.c.
0.12	556.5	0.0877	2.52	551.4	0.0869
0.28	557.6	0.0878	2.77	549.9	0.0866
0.45	558.0	0.0879	3.08	547.7	0.0863
0.62	556.1	0.0876	3.52	544.4	0.0857
0.78	558.2	0.0879	3.83	542.6	0.0855
0.95	560.4	0.0883	4.08	541.6	0.0853
1.13	558.2	0.0879	4.35	540.2	0.0851
1.27	558.1	0.0879	4.65	538.9	0.0849
1.43	556.9	0.0877	4.92	535.6	0.0844
1.60	554.9	0.0874	5.25	535.0	0.0843
1.78	554.5	0.0873	5.58	533.1	0.0840
2.05	553.5	0.0872	5.73	532.6	0.0839
2.28	552.4	0.0870			

The curve is shown in Fig. 10.

Experiment 2 (Steam).—A similar apparatus was used; the

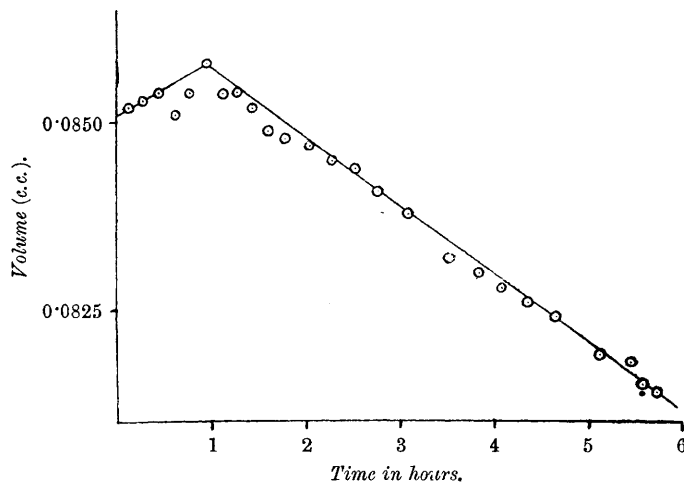


FIG. 10.

measuring tube was much larger (capacity, 1.287 c.c.). Platinum wires were fused through to act as a spark gap. The gases containing emanation (0.14 E) were sparked down to small volume, the remaining gas forced through a phosphoric oxide tube into the measuring apparatus, and, finally, a spark passed there, the flame being visible and proving the formation of steam. The mixture of steam and hydrogen was jacketed as usual, and readings were taken over a period of six hours. No expansion, such as would result from the formation of hydrogen and oxygen, was observed. On the contrary, a slight contraction took place. It was irregular, amounting in all to 3 per cent. of the total volume

(0.425 to 0.414 c.c.), and may be perhaps accounted for by irregularity in the heating. The gas was allowed to stand at constant volume and air temperature overnight; on re-heating next day, it again varied in volume from 0.412 to 0.420 c.c. These measurements were repeated over several days, with similar results. The tube glowed brilliantly in the dark, and gradually became coloured, proving undoubtedly that emanation was present.

It must be concluded that the decomposition of steam by emanation is extremely small in amount, if any, and that the accuracy of measurement, certainly correct to 0.001 c.c., was not great enough to detect a change.

Neglecting, therefore, the decomposition of steam by emanation, it is possible to calculate the amount of recombination of electrolytic gas under the conditions of the first experiment. In 5.73 hours, $(0.0883 - 0.0839) \times 3 \text{ c.c.} = 0.0132 \text{ c.c.}$ had become converted into steam. The amount of emanation used was 0.252 E. If we presume that each particle of emanation in decomposing causes a certain definite volume of hydrogen and oxygen to combine, then 0.011 E has effected the combination of 0.0132 c.c. of gas, whence it follows that E will cause 1.2 c.c. of gas to combine. This is of a less order of magnitude than the figures obtained at ordinary air temperatures (compare experiments 6 to 8).

The Nature of the Chemical Change brought about by Radium Emanation.

We have already shown that whenever exact measurements have been obtained for water, hydrogen, and oxygen, the results give an exponential curve of half time approximating to 3.86 days, the period of half decay of radium emanation. We have pointed out that it would appear that each particle of emanation in disintegrating produces a definite quantitative chemical effect, since the amount changing at any time is proportional to the change of gas volume in that time. The rate of reaction of nitrogen and hydrogen, and of carbon monoxide, confirms these statements, although, in the latter, apparently several changes take place simultaneously. The question remains, in what manner are these chemical actions brought about? Many observers have studied the chemical phenomena produced by electrical energy applied in various ways. Thus a great number of chemical actions have been brought about by the silent electrical discharge, described in numerous papers by Berthelot and others. These treat chiefly of the production of organic compounds. Collie (*Trans.*, 1901, **79**, 1063) has shown that a current at low pressure decomposes carbon

dioxide very rapidly; under its influence oxygen and carbon monoxide recombine slowly.

Numerous researches have also shown that various chemical actions, such as the formation of ozone, the decomposition of ammonia, of nitrous oxide, and of carbon monoxide, take place under the action of ultra-violet light. In this connexion, the work of Chapman, Chadwick, and Ramsbottom (*Trans.*, 1907, **91**, 942) may be consulted.

Strictly comparable with such phenomena are the numerous chemical changes produced by radium preparations enclosed in glass bulbs, and allowed to act by means of the rays penetrating the glass envelope, that is, the β -rays or electrons.

These have been found to have no action on water, or on mixtures of hydrogen and oxygen (Ramsay, *Meddel. K. Vet. Akad. Nobelinst.*, 1905, **1**, 909; Jorissen and Ringer, *Ber.*, 1906, **39**, 2093). They cause combination between hydrogen and chlorine (Jorissen and Ringer, *ibid.*), convert yellow into red phosphorus (Berthelot, *loc cit.*), and liberate iodine from hydriodic acid (Creighton and Mackenzie, *Amer. Chem. J.*, 1908, **39**, 474). The changes described in this paper are of the same nature, but the degree of action is far greater. This is explicable on the assumption that the actions are brought about by α -particles. Their energy, as shown by their ionising power, is enormously greater than that of β -particles. The ionisation produced in gases by α -particles, or by cathode or X-rays, is supposed to be due to the gas particles obtaining an electric charge by collision, or by some other method. If we suppose that a mixture of hydrogen and oxygen is bombarded with α -particles, so that charged ions of both gases are produced, partial combination of hydrogen and oxygen is rendered certain. The effect of liberation of particles in water might be expected to be much greater; compare the effect of a charge of gun cotton exploded in a confined and in an open space. The collision disrupts innumerable molecules of water, producing charged atoms of hydrogen and oxygen. Some of these recombine. The part that escapes recombination produces the changes in volume which are actually measured.

The experiments carried out at 130° do not altogether support this view. In the first place, it is well known that radium emanation itself gives off α -particles only, disintegrating into successive products, radium *A*, *B*, and *C*, of which the first and third give α -particles, and the second and third β -particles. The half life of these products is less than half an hour. During the first four hours after which emanation has been confined in any known space, the α -activity increases to almost three times the initial value. The amount of recombination of hydrogen and oxygen should increase

similarly, if every α -particle produces a definite effect. But the curve in Fig. 10 is practically a straight line, and does not bear out that supposition. (The initial increase in the volume, reaching a maximum at the end of the first hour, seen in this experiment, and in those with electrolytic gas at air temperature, p. 977, with carbon monoxide, p. 982, and with a mixture of nitrogen and hydrogen, p. 988, seems to be due to the local increase in temperature set up by the emanation, which, even at 130° , imparts sufficient heat to the gas containing it to raise its pressure appreciably.)

Again, the action on steam should be analogous to that on hydrogen chloride, in which case decomposition was observed. But no action was noted. The only explanation which will bring this observation into line with the remainder, is the supposition that at the temperature of the experiment the reverse action is sufficiently rapid to cause any hydrogen and oxygen formed immediately to recombine. It must be remembered that the gas contained free hydrogen, the presence of which would increase the chances of recombination.

This paper has been wholly concerned with atomic changes. Whether, when the emanation produces these, some part of the energy is utilised in disintegrating the atoms of, say, carbon, or chlorine, according to the gas under observation, is a very different problem. For the present, we content ourselves with reiterating the chief conclusion reached in this paper, that *whenever radium emanation produces chemical action, then, other conditions being unaltered, each particle of emanation as it disintegrates produces the same amount of change.*

In conclusion, we desire to thank Professor A. W. Porter for his kindness in assisting us with the mathematical interpretation of these results.

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