be due to partial decomposition. Some of the results obtained by us are as follows:

Table V.—Purity of Silver Nitrite.

Composition of solution.	0.1 N $KMnO_4$ solution. Cc.		
	Calculated.	Required.	Error.
0.3847 g. $AgNO_2$ + 15.00 cc. 0.1 N $Na_2C_2O_4$	65.00	63.95	—1.05
		62.87	—2.13
		62.66	—2.34

These results show clearly that silver nitrite is not reliable as a standard in nitrite determinations.

Summary and Conclusions.

1. The volumetric methods described in the literature for the determination of nitrous acid or nitrites are not satisfactory.

2. A method has been devised for determining nitrites which is, briefly stated, oxidation in acid solution with excess permanganate, reduction of the excess permanganate with excess ferrous sulfate, sodium oxalate or hydrogen peroxide and titration of the excess of reducing agent with permanganate. The titration is not interfered with by moderate amounts of chloride, or small amounts of bromide.

3. Silver nitrite is not a satisfactory material for use as a standard in nitrite determinations. A satisfactory standard solution may be made by titrating sodium nitrite solution with potassium permanganate according to the method described above; or sodium nitrite solution may be standardized gravimetrically by the reduction of silver bromate to silver bromide according to the method of Busvold.

University of Michigan.

CHEMICAL ACTION PRODUCED BY RADIUM EMANATION. I. THE COMBINATION OF HYDROGEN AND OXYGEN.[1]

By S. C. Lind.

Received December 30, 1918.

1. Introduction.

In 1903 Ramsay and Soddy[2] reported quantitative data on the decomposition of water in a solution of radium salt. In 1907, Bragg[3] used their data to make the first comparison between the chemical and ionizing effects of α-particles. Although Bragg calculated that the number of molecules of water decomposed was almost exactly equal to the number of ions that would have been produced in air by the emanation employed, he was apparently not impressed by the equality he found, and referred to it as a "curious parallelism in numbers." In 1910 Bergwitz[4] gave the results of

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[1] Published with permission of the Director of the U. S. Bureau of Mines.

[2] Ramsay and Soddy, *Proc. Roy. Soc.*, 72, 204 (1903).

[3] W. H. Bragg, *Phil. Mag.*, [6] 13, 356 (1907).

[4] Bergwitz, *Physik. Z.*, 11, 273–5 (1910).

the decomposition of water by α-rays from polonium deposited on copper foil, but failed to make any comparison of the chemical and electrical relationships. In a brief notice in the fifth edition of his *Lehrbuch der Elektrochemie*, Le Blanc[1] called attention to this omission, and stated that the α-ray effect closely approached the requirements of Faraday's law. Later Le Blanc[2] published in full his calculations from Bergwitz's data on which his statement was based.

In 1911 the writer[3] determined chemically the amount of ozone formed in oxygen by α-rays, and calculated that one molecule of ozone was formed per two pairs of gaseous ions. This was the first comparison between ionization and chemical action in a gaseous system, and hence the first instance where ionization and chemical reaction referred to the same medium in each case.

A little later Krueger and Moeller[4] devised an ultraviolet absorption method for the determination of ozone in very minute quantities, which Krueger[5] employed to determine the amount of ozone formed by the passage of electrons of high velocity through gaseous oxygen. Krueger arrived at a conclusion similar to that of the writer, that one pair of ions is involved in the formation of each molecule of ozone.

In 1912 the writer[6] collected all the available data on the chemical action of α-particles, and drew from his calculations based on them the general conclusion that ionization by α-particles and the resulting chemical action are always of the same statistical order (ion for molecule) and may be treated as illustrative of a modified form of Faraday's law. The results and applications of this theory were discussed in a number of papers.[7] The experimental data employed by the writer in the comparison of ionization and chemical action were largely those of Cameron and Ramsay[8] obtained by mixing radium emanation with various gases and following the course of the reaction manometrically. In order to calculate the ionization from their results, a method of calculating the average path of all the α-particles in a given volume was devised[9] and applied to the data of Cameron and Ramsay, with the result stated in the preceding paragraph.

[1] M. Le Blanc, *Lehrbuch der Elektrochemie*, Ed. V, p. 317.

[2] M. Le Blanc, *Z. physik. Chem.*, **85**, 511–12 (1913).

[3] S. C. Lind, *Sitzb. Akad. Wiss., Wien*, **120**, 1709–24 (1911); *Monatshefte*, **32**, 295–310 (1911); *Am. Chem. J.*, **47**, 397–415 (1911); *Le Radium*, **9**, 104–6 (1911).

[4] F. Krueger and M. Moeller, *Physik. Z.*, **13**, 729 (1912).

[5] F. Krueger, *Nernst Festschrift*, pp. 240–51; *Physik. Z.*, **13**, 1040–3 (1912).

[6] S. C. Lind, *J. Phys. Chem.*, **16**, 564–613 (1912).

[7] S. C. Lind, *Am. Electrochem. Soc.*, **24**, 339–49 (1913); *Le Radium*, **11**, 108–111 (1914); *Z. physik. Chem.*, **84**, 759–61 (1913).

[8] Cameron and Ramsay, *J. Chem. Soc.*, **93**, 966–92 (1908).

[9] S. C. Lind, *Loc. cit.*

More recently several chemical reactions under the influence of α-particles have been very carefully studied in the laboratory of Mme. Curie. The decomposition of water, measured by Duane and Scheuer[1] employing emanation in an α-ray capillary tube, showed a close equivalence between ionization and chemical effect. The combination of hydrogen and oxygen was studied by Scheuer[2] in a mixture of emanation and electrolytic gases in glass spheres, by determining the diminution in pressure in a single measurement after decay of most of the emanation. Scheuer calculated the ionization from the Duane and Laborde[3] empirical formula, and found, with a good agreement among all his experiments, that about 5.5 molecules of gas recombined for each pair of ions. A small proportion of the molecules recombined to form H_2O_2, according to Scheuer's analysis; but approximately, we may express his result as 3.6 molecules of water formed for one pair of ions. This is a much higher value than 1.0, the average earlier calculated by the writer from the data of Cameron and Ramsay.

The decomposition of hydrogen sulfide was also measured in the Curie laboratory by Wourtzel[4] who found 3.3 molecules decomposed per pair of ions (in air), and calculated the decomposition to be 4.7 times greater than Duane and Scheuer found for water. Wourtzel[5] later reported briefly the results of other reactions, namely, decomposition of ammonia, of nitrous oxide, and of carbon dioxide. In all these reactions Wourtzel finds the amount of reaction to be in excess of the ionization.

A. Debierne[6] has been led by the statistical disagreement found by Scheuer and by Wourtzel between ionization and chemical action to reject the theory of ionization put forward by the writer as the primary cause, and to substitute one based on the hypothesis that the passage of an α-particle through a gas may thermally decompose molecules lying outside the path of its ionizing effect. This view of thermal decomposition is not favored by Wourtzel[7] because in some cases he found reactions actually having negative temperature coefficients.

The difference between the conclusions drawn by the writer in regard to the rôle played by ionization and those of Debierne, Scheuer, and Wourtzel, based on the Paris measurements, demonstrate the desirability of further experimental work to determine first, whether the discrepancy lies in the data themselves, or in their treatment; and second, whether the higher chemical values, if correct, are too great to be brought into accord with ionization. In order to settle the first point, it appeared advisable

[1] Duane and Scheuer, *Le Radium,* **10,** 33–46 (1913).

[2] Scheuer, *Compt. rend.,* **159,** 423–6 (1914).

[3] Duane and Laborde, *Ibid.,* **150,** 1421 (1910).

[4] E. Wourtzel, *Ibid.,* **157,** 929–31 (1913).

[5] E. Wourtzel, *J. Russ. Phys. Chem. Soc. Proc.,* **47,** 210–11, 493–4, 494–5 (1915).

[6] A. Debierne, *Ann. phys.,* [9] **2,** 97–127 (1914).

[7] E. Wourtzel, *Loc. cit.*

to make an exhaustive experimental study of the simplest possible case, such as the combination of hydrogen and oxygen gases in order to establish thoroughly the laws governing the reaction under various conditions as regards volume of the reacting vessel, pressure of the gases, concentration of emanation, temperature, and variation of the proportions of hydrogen and oxygen. The results of this study are reported in the present paper. In the main, the experimental method of Cameron and Ramsay has been used and found well suited for the purpose. The writer was able to profit by the experience of Cameron and Ramsay to improve the manipulative details somewhat, to which attention will be called later. Following the course of the reaction manometrically enables one to study the kinetics of the reaction thoroughly. The reaction between hydrogen and oxygen has been chosen because the products of reaction are continually removed and the system maintains itself in a constant condition with respect to the composition of the gases being acted upon.

The kinetic equation earlier deduced by the writer[1] for the data of Cameron and Ramsay has been confirmed over a much wider range than was formerly possible. By varying the size of the spherical reaction bulbs, experimental confirmation has also been obtained of the law of the average path of α-particles as applied to their chemical effect in such vessels. Briefly expressed, all the assumptions previously made by the writer in treating the Cameron and Ramsay data have now been verified by direct experiment and show that the treatment was in every way justified. The disagreement, however, between the data of Cameron and Ramsay and of Scheuer has been found to be real and must be decided in favor of Scheuer through a good agreement between his and the new results. The explanation of the discrepancy lies in the quantities of emanation reported by Cameron and Ramsay, which were not measured *in loco*, but calculated from the amount of radium employed and the time of accumulation, which apparently led to a considerable error through incomplete evolution or collection of the radium emanation.

2. Source of the Radium Emanation.

The radium employed as a source of emanation was part of that produced in the coöperative work[2] of the U. S. Bureau of Mines and the National Radium Institute. 297.8 mg. of radium element in the form of bromide, protected by a ninefold excess of barium bromide, was dissolved in water containing 20% of hydrobromic acid; the high percentage of the latter has proved somewhat disadvantageous on account of the liberation by the α-rays of so much free bromine. In later work, the salt will be

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[1] S. C. Lind, *Loc. cit.*

[2] U. S. Bureau of Mines, *Bull.* 104 (1915), by C. L. Parsons, R. B. Moore, S. C. Lind and O. C. Schaefer.

converted into chloride and only 5% of hydrochloric acid employed in the solution.

The Duane[1] apparatus for the purification of radium emanation without the use of liquid air has been employed and given very satisfactory results. The pumps employed for the apparatus were the Gaede mercury pump and the Gaede preliminary oil pump. The latter was used not only to start the mercury pump, but in handling the mercury in the three reservoirs of the Duane apparatus, and also the mercury in the McLeod gage.

3. Apparatus and Manipulation.

A simple modified form of the Cameron and Ramsay[2] apparatus has been used (Fig. 1). The glass reaction bulb *c* was made spherical to simplify the calculation of the average path of the α-particles, and was provided with a fine blue-glass pointer, *d*, to define sharply the setting of the mercury at *e*. By means of a capillary tube, *b*, connection was made at *a* with the Duane apparatus. After thorough exhaustion through *a*, *b* and *c* to *e* by means of the Gaede mercury pump, the purified emanation was introduced into *c* and sealed off at *b*.

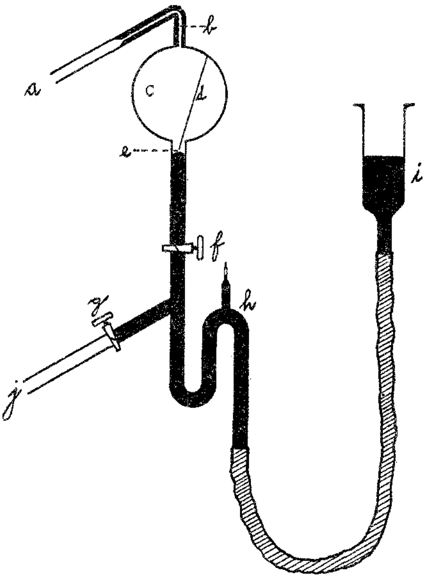

Fig. 1.

Electrolytically prepared hydrogen and oxygen were collected over mercury in a Ramsay gas pipet,[3] sealed on at *j*, from which the gas could be passed through *g* and later through *f* to *c* where it mixed with the emanation. This arrangement avoids bringing the emanation into contact with any stopcock grease, which caused Cameron and Ramsay much trouble in their early experiments through the continued generation around the stopcock *f* of foreign gases which would rise into *c* and vitiate the manometric results. The gas mixture can be collected below *f*, either before or after the collection of emanation in *c*. Only the latter procedure, however, permits of the measurement of the initial pressure (usually negligible) of gas collected with the emanation. The mercury leveling bulb *i* is connected by means of rubber tubing to the glass apparatus which is provided with a gas trap at *h*.

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[1] W. Duane, *Phys. Rev.*, [2] 5, 311–14 (1915).

[2] Cameron and Ramsay, *Loc. cit.*

[3] Ramsay, *Proc. Roy. Soc.*, 76A, 113 (1905); *Trans.*, 91, 939 (1907).

The reaction can be begun immediately after collecting emanation, or after equilibrium with induced activity. The stopcock *f* was open only while taking readings. A water-jacket (not shown) was brought about the bulb *c* to prevent temperature fluctuations while reading.

When a drying agent was desirable, a mixture of equal weights of fused sodium and potassium oxides was introduced into *c* before assembling the apparatus and fused to the wall with a weak flame. Owing to the low melting point of the mixture, it could be melted in a very thin layer at two or three spots on the inner wall without deformation of the bulb, or materially affecting the spherical volume. The volume was determined by calibration with mercury after the mixture was in place.

The quantity of emanation actually employed in each experiment was determined by the γ-ray method of measurement at any time (usually the next day) after the introduction of the emanation. For this comparison three of the Bureau of Mines standards were employed containing 10.56, 59.26 and 157.3 mg. of radium element, respectively, all of which had been compared with the U. S. Bureau of Standards international standard.[1] This measurement was greatly facilitated by the fact that the whole apparatus was mounted on a single iron stand and could be readily transported and the bulb brought into any desired position with reference to the electroscope. A correction of 0.8% is applied to the γ-ray indication on account of the lag of radium C.[2]

The course of the reaction was followed by determining the pressure at suitable intervals. The difference in mercury level between *e* and *i* was determined by mounting the whole apparatus close before a vertical mirrored millimeter glass scale. The difference thus determined was added (algebraically) to barometric pressure after all necessary corrections had been made to reduce the results to standard conditions.

4. The Course of the Reaction.

A kinetic equation was previously deduced by the writer[3] for gaseous reactions being produced by radium emanation in fixed volume when accompanied by change in pressure. It was assumed that for a given gaseous mixture maintaining constant composition during reaction, the rate of action would depend on two variables only, the pressure and the quantity of emanation present. The integrated form of the kinetic equation was

$$k\mu/\lambda = \text{constant} = (\log P/P_0)/(E_0(e^{-\lambda t} - 1)). \qquad (1)$$

The constancy of the first term $k\mu/\lambda$ holds only for a gaseous mixture in which the specific ionization remains constant during the reaction. The

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[1] The writer wishes to take this opportunity of expressing his indebtedness to Dr. N. E. Dorsey for making these comparisons.

[2] E. E. Rutherford, "Radioactive Substances and their Radiations," Sec. 197, also p. 659.

[3] S. C. Lind, *J. Phys. Chem.*, 16, 592 (1912).

numerical value of $k\mu/\lambda$ also depends on the volume of the reaction bulb. The definition of the terms of $k\mu/\lambda$ will be given later; for the present purposes it may be regarded only as a velocity of reaction *constant.* P_0 and P are, respectively, the initial pressure and that at any time t expressed in millimeters of mercury. E_0 is the initial emanation expressed in curies, which is decaying proportionally to the factor $e^{-\lambda t}$ to be found in the Kolowrat[1] table for radium emanation.

The actual course of the reaction in spherical bulbs of several different sizes can be seen in Table I, in which the application of Equation 1 is to be found in the last column.

TABLE I.

Velocity of Reaction $2H_2 + O_2 = (2H_2O)$ at Constant Volume in Bulbs of Various Diameters, and Values of Velocity Constant $k\mu/\lambda$. (Equation 1.)

2 cm. Sphere.

Vol. = 3.738 cm.^{3}. Exact diam. = 1.925 cm. E_0 = 0.1464 curies.

Time. Days.	Time. Hrs.	P. Mm. Hg.	Volume decrease. Cc.	% reaction completed.	% Em. decayed.	$k\mu/\lambda$ (constant).
0.....	0	436.6	0	0	0	..
0.....	4.83	387.8	0.2400	11.18	3.56	22.8
0.....	8.58	358.0	0.3866	18.00	6.23	21.8
1.....	0.75	248.0	0.9276	43.30	16.94	22.8
1.....	7.67	216.8	1.081	50.34	21.14	23.1
2.....	0.00	155.2	1.384	64.45	30.23	23.3
2.....	7.67	141.2	1.453	67.66	34.13	22.6
3.....	0.25	111.9	1.597	74.35	41.83	22.2
4.....	0.58	69.7	1.805	84.05	51.53	24.3
6.....	0.08	42.6	1.937	90.24	66.06	24.0
8.....	6.00	30.4	1.997	93.03	77.35	23.5
						Av., 23.04
3 cm. Sphere.						
Vol. = 13.272 cc. Exact diam. = 2.924 cm. E_0 = 0.1682 curies.						
0.....	0	584.6	0	0	0	...
0.....	20.17	466.6	2.043	24.52	14.04	9.54
1.....	4.67	424.1	2.802	33.63	19.35	9.86
1.....	20.25	371.8	3.715	44.60	28.24	9.51
2.....	3.75	341.7	4.241	50.91	32.17	9.93
2.....	20.00	296.6	5.029	60.37	39.95	10.10
3.....	9.50	272.6	5.449	65.40	45.73	9.93
3.....	23.42	249.8	5.845	70.17	51.11	9.89
5.....	21.17	197.1	6.767	81.23	65.31	9.90
8.....	0.75	161.7	7.384	88.63	76.44	10.00
11.....	0.00	142.0	7.729	92.76	86.19	9.77
14.....	23.50	115.4	8.194	98.35	93.25	10.35
22.....	3.17	111.4	8.264	99.19	98.14	10.06
30.....	2.75	107.5	8.332	100.00	99.56	10.19
						Av., 9.92

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[1] Kolowrat, Léon, *Le Radium*, 6, 195–6 (1910); Mme. Curie, *Traité de Radioactivité*, 2, 361–2; *Chemiker Kalendar*, 2, 361–2 (1914); Rutherford, "Radioactive Substances and their Radiation," **1913**, p. 665.

4 cm. Sphere.

Vol. = 32.58 cc. Exact diam. = 3.963 cm. E_0 = 0.1396 curies.

Time. Days.	Hrs.	P. Mm. Hg.	Volume decrease. Cc.	% reaction completed.	% Em. decayed.	$k\mu/\lambda$ (constant).
0.....	0	437.1	0	0	0	..
0.....	20.67	391.1	1.972	20.29	14.36	(5.55)
1.....	20.50	353.8	3.572	36.73	28.65	5.29
2.....	20.75	324.7	4.818	49.56	40.29	5.29
4.....	0.0	297.3	5.995	61.66	51.33	5.38
5.....	20.33	268.9	7.211	74.16	65.87	5.28
6.....	23.75	247.6	8.127	83.58	76.96	5.29
9.....	22.58	235.8	8.630	88.76	83.29	5.31
12.....	20.50	222.6	9.196	94.58	90.11	5.37
15.....	3.50	220.5	9.287	95.52	93.45	5.25
20.....	2.50	214.5	9.545	98.17	97.32	5.24
31.....	1.00	210.3	9.723	100.00	99.62	5.26
						Av., 5.30

5 cm. Sphere.

Vol. = 61.321 cc. Exact diam. = 4.893 cm. E_0 = 0.1640 curies.

0.....	0	557.7	0	0	0	..
0.....	18.13	518.8	3.138	17.36	12.71	3.47
1.....	1.50	506.7	4.115	22.76	17.41	3.36
1.....	18.50	478.9	6.357	35.17	27.29	3.40
2.....	2.25	467.0	7.318	40.48	31.40	3.45
2.....	18.08	445.3	9.067	50.16	37.08	3.51
3.....	1.67	437.9	9.668	53.47	42.45	3.47
3.....	20.92	416.1	11.42	63.19	50.19	3.56
5.....	18.17	386.4	13.82	76.43	59.52	3.76
7.....	18.25	362.6	15.74	87.06	70.26	3.73
12.....	22.50	333.6	18.08	100.00	90.26	3.47
						Av., 3.52

$5^1/_2$ cm. Sphere.

Vol. = 92.604 cc. Exact diam. = 5.613 cm. E_0 = 0.2078 curies.

0.....	0	504.4	0	0	0	..
0.....	21.08	465.6	4.728	18.77	14.63	2.64
1.....	15.58	433.9	8.590	34.10	25.68	2.82
1.....	23.50	425.2	9.215	36.59	29.97	2.74
2.....	15.33	407.1	11.85	47.07	37.81	2.73
2.....	23.25	397.7	13.00	51.62	41.39	2.76
3.....	15.58	384.8	14.57	57.86	48.15	2.71
4.....	16.83	365.6	16.91	67.16	57.10	2.72
6.....	0.33	350.2	18.79	74.59	66.12	2.62
6.....	15.17	344.5	19.48	77.36	69.61	2.64
7.....	20.42	334.0	20.76	82.41	75.66	2.62
9.....	19.58	321.5	22.28	88.47	92.91	2.62
14.....	15.33	305.2	24.28	96.36	92.79	2.61
22.....	21.25	297.7	25.19	100.00	98.37	2.58
						Av., 2.68

Cylinder 4 cm. long, 1.8 cm. diam.

Vol. = 6.787 cc. Diam of equiv. sphere = 2.375 cm. E_0 = 0.01219 curies.

Time. Days.	Hrs.	P. Mm. Hg.	Volume decrease. Cc.	% reaction completed.	% Em. decayed.	$k\mu/\lambda$ (constant).
0.....	0	578.1	0	0	0	..
0.....	23.00	562.6	0.1385	15.88	15.84	14.1
2.....	0.00	549.5	0.2555	29.31	30.23	14.1
3.....	22.00	527.9	0.4480	51.44	50.58	14.7
5.....	4.00	517.7	0.5394	61.89	60.54	14.9
7.....	22.75	505.1	0.6519	74.80	76.08	14.6
12.....	1.00	491.5	0.7734	88.74	88.55	15.4
18.....	22.00	484.0	0.8405	96.42	96.37	15.1
30.....	2.00	480.5	0.8716	100.00	99.54	15.2
						Av., 14.8

The degree of constancy is satisfactory and proves that the velocity of reaction in a given volume depends only on the two variables mentioned above, the quantity of emanation and the pressure of the gas. This test of Equation 1 is far more rigid than the one earlier obtained[1] with the data of Cameron and Ramsay, in whose experiments the total change of pressure was frequently quite limited, owing to the small quantities of emanation employed.

It will be observed by comparing Cols. 4 and 5 that the percentage of reaction completed runs well ahead of the percentage of emanation decayed, but it approaches it as the quantity of gas to be acted on is increased and the quantity of emanation decreases. Notice that in the case of very fast reactions where the quantity of gas is small and the quantity of emanation high, half of the chemical reaction is completed in $1^1/_3$ days, or less; and only in reactions where the quantity of gas to be acted on is relatively large and the quantity of emanation small, and hence the total change in pressure very slight, would the limiting case be approached that would agree with the rate claimed by Cameron and Ramsay, proportional to the decay of emanation with a half period of three days and 21 hours. This case is illustrated by the cylinder with very low emanation, chosen purposely to parallel Cameron and Ramsay's conditions and shows how the limiting case can be attained within the limits of experimental precision.

The reaction can come to an end by approximate exhaustion of either the emanation or the reacting gases; the former takes place in small bulbs with high emanation, the latter in larger bulbs. The actual final pressure after decay of all the emanation, may be calculated from Equation 1 for any given case.

While the ratio of emanation to gas affects greatly the actual velocity of the reaction, it does not influence the constancy of $k\mu/\lambda$, thus proving

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[1] S. C. Lind, *Loc. cit.*

that the kinetic equation applies in all cases. The ratio of radium emanation to reacting gases may rise continuously as in small bulbs, may pass through a maximum as in 3 cm. bulbs, or may fall continuously as in larger bulbs without affecting the constancy. However, for reasons to be brought out in Part II, the following paper, the gas pressure may not fall too low in a small (1–2 cm.) bulb without affecting the velocity constant, due to action of the "recoil atoms."

Experiments with and without drying agent show, in agreement with Cameron and Ramsay, that the presence of moisture does not influence the velocity of the reaction. However, in larger bulbs starting with dry gases and no drying agent, some time would be required to saturate the gases with water vapor, which would lead to unnecessary complications in applying the kinetic equation during this period, which are best avoided by having drying agent present in the reaction bulb.

The question of chemical equilibrium in the reaction between hydrogen and oxygen has recently been considered by the writer in another paper,[1] where it was shown that the equilibrium in some cases can attain 99% of the total combination of the hydrogen and oxygen. This is mentioned here to show that it is not necessary to consider the possibility that either hydrogen or oxygen is removed by side reactions permanently from the main reaction. Although Scheuer[2] has reported the formation of some hydrogen peroxide, it is evident that its formation must be of somewhat temporary nature and that the reaction later proceeds to the practically complete formation of water.

5. Influence of the Size of the Reaction Bulb. (Law of the Inverse Square of the Diameter.)

Increasing the size of the reaction bulb influences the velocity constant of the chemical reaction in two oppositely directed ways: first, with the pressure remaining constant, the effective path of the α-particle is lengthened directly by 0.7 of the radius of the spherical bulb[3] and hence, other things being equal, the velocity of reaction is directly proportional to the diameter of the bulb, provided that the diameter does not exceed the range of any of the α-particles. Second, a given amount of chemical action, or volume change, will produce a change of pressure dependent on the volume of the reaction bulb. The smaller the bulb, the larger the change of pressure produced, in proportion to the cube of the diameter. Combination of these two opposite effects shows that the velocity constant expressed with reference to pressure, as in Equation 1, must vary inversely with the square of the diameter of the reaction bulb. The data from Table I are summarized in Table II so as to show that this is actually

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[1] S. C. Lind, *Amer. Electrochem. Soc.*, 34th General Meeting, Advance Copy No. 5.

[2] Scheuer, *Loc. cit.*

[3] S. C. Lind, *Ibid.*

the case to a high degree of precision for bulbs varying in diameter from 1 to 5.5 cm. and in volume over almost 200-fold.

TABLE II.

Effect on the Velocity Constant ($k\mu/\lambda$) of Varying the Volume of Reaction Bulb.

Approx. diam. of sphere. Cm.	True diam. D. Cm.	Vol. of sphere. Cc.	$k\mu/\lambda$ (const. found).	$(k\mu/\lambda)/D^2$.
1	0.9647	0.4701	(89.6)[1]	83.4
2	1.925	3.738	23.04	85.3
$2^3/_8$ (cylinder)[2]	2.375	6.787	14.76	83.3
3	2.924	13.272	9.92	84.8
4	3.963	32.58	5.30	83.2
5	4.893	61.32	3.52	84.3
$5^1/_2$	5.613	92.60	2.68	84.1
				Av., 84.1

This appears to establish thoroughly the nature of the law governing the influence of the size of the sphere on the velocity of the reaction. There appear to be no reasons why it should not apply to any other gaseous reaction as well as to the one under consideration. It appears to the writer to confirm his earlier theory of the average path of α-particles in spherical volumes with reference to their chemical effect.

On passing to volumes other than spherical, it has not been possible as yet to give a mathematical treatment of the average path. A graphical treatment for cylinders such as will be represented by glass tubes of moderate dimensions showed that the average path would have the same numerical value as in a sphere of the same volume. In the present work, it was not only possible to test this conclusion experimentally, but it was also of great service in comparing the present results with those of Cameron and Ramsay, who used for this reaction glass tubes instead of spherical bulbs. Accordingly, one spherical reaction chamber was used, 1.8 cm. in diameter, 4 cm. long, having an actual volume of 6.787 cc., equal to the volume of a sphere 2.375 cm. in diameter. In Table II, the data for this cylindrical vessel have been reported together with the spheres, and it is found that the cylindrical volume furnishes a value of 83.3 for $(k\mu/\lambda)/D^2$, agreeing with the other values for true spheres. This is of considerable interest in that it enables a direct comparison between most of Cameron and Ramsay's results and the present ones. (See Section 9 for a later discussion.)

It may be of interest to inquire how great the diameter of the reaction bulb may become before the validity of the formula $(k\mu/\lambda) = (84.1/D^2)$ is affected. Evidently it still holds for the largest bulbs used in these experiments and, as will be seen in Section 9, it still holds within 2% for Scheuer's results in a bulb of 7.18 cm. diameter at a pressure of 1580 mm.

[1] Extrapolated value. See following paper on "recoil atoms."

[2] Vessel cylindrical for sake of comparison with spherical ones.

Even on considering that the stopping power of the electrolytic mixture is only about one-half that of air and that the average path is about 0.7 of the radius, it is evident that many α-particles are being completely absorbed before reaching the wall, while many others reach the end of their range where the ionization is no longer proportional to the path traveled. These two effects tend to compensate each other, but when the diameter of Scheuer's bulb reaches 8.94 cm. at a pressure of 1680 mm., the value of $k\mu/\lambda$ drops 6.7% below the theory for uniform path, and continues to fall for larger sizes. The limit of the applicability of the formula appears to be at about 7 cm. for 1580 mm. of $2H_2 - O_2$, which would be a diameter of 10 cm. at 760 mm., corresponding to an average path in air of about 3.7 cm.

It was the writer's earlier view[1] that the general law would hold only over the first 2 or 3 cm. of path of the α-particle where ionization remains constant. This would doubtless be true for a single type of α-particle, for example, from Ra C alone, but comparison of Bragg's[2] combined ionization curves indicates that ionization per length of path in emanation in equilibrium would remain almost constant up to 4 cm. of air, agreeing very well with the results of the foregoing paragraph.

6. Influence of Changing the Proportions of Hydrogen and Oxygen.

All reactions discussed in the foregoing sections have been carried out using electrolytic hydrogen and oxygen in exact proportions of 2 to 1 by volume. The effect of an excess of either gas can be predicted on the assumption that the change thus produced in the specific ionization of the gas mixture will change the reaction velocity correspondingly. The specific (molecular) ionization compared with air is, according to Bragg[3] 1.09 for oxygen and 0.24 for hydrogen. Consequently, an initial excess of oxygen should increase the relative reaction velocity. The velocity constant calculated by Equation 1 should be initially higher than the normal, and should continue to rise as the mixture became relatively richer in oxygen with the progress of the reaction. With initial excess of hydrogen, the case should be exactly the opposite; the velocity constant should start abnormally low and show a further fall as the mixture enriched in hydrogen.

Both cases have been experimentally investigated and the predictions found to be fully confirmed. Since the specific ionization, however, is variable in these reactions, Equation 1 is not strictly applicable. The development of a new equation taking into account the changing ionization is so complicated that the simpler method has been adopted of using Equation 1 to show that the change in velocity is proportional to the

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[1] S. C. Lind, *Loc. cit.*

[2] Bragg, "Studies in Radioactivity," 1912, p. 21; *Phil. Mag.*, [VI] 10, 323 (1905).

[3] W. H. Bragg, "Studies in Radioactivity," Macmillan and Co., 1912, p. 65.

change in specific ionization. Since $k\mu/\lambda$ now becomes a variable, it should be calculated over short intervals to avoid undue masking of its variability. To accomplish this, the value of $k\mu/\lambda$ is calculated not from the beginning in each case, but from each measurement to the next, a procedure quite common in chemical kinetics.[1]

In this form the equation may be written

$$((k\mu/\lambda)' = \text{Log } P_2/P_1)/(E_o(e^{-\lambda t_1} - e^{-\lambda t_2})). \qquad (2)$$

Table III gives the data for the initial mixture $4H_2 - 1O_2$, and in Col. 4 the application of Equation 2 shows that $(k\mu/\lambda)'$ is not constant, but falls approximately as required by the change of specific ionization (cf. Col. 5). Col. 5 has been calculated from the normal value of $(k\mu/\lambda)$ for a bulb of this size and the changing specific ionization.

TABLE III.

Effect of Excess of H_2 on the Velocity Constant.

Init. Mixt. $4H_2 - 1O_2$. Vol. = 11.64 cc. Diam. = 2.812 cm. E_o = 0.1169 curies.

Time.		Total P. Mm. Hg.	Partial P. O_2.	$(k\mu/\lambda)'$ (found).	$(k\mu/\lambda)'$ calc. from spec. ionization.	$(k\mu/\lambda)'$ for P.Pr.O_2.
Days.	Hrs.					
0	0	682.8	136.6	..	..	...
0	19.25	605.9	110.9	7.92	7.93	13.20
1	3.25	580.3	102.4	7.30	7.50	13.50
1	23.00	528.2	85.0	7.17	7.38	14.20
2	23.67	480.6	69.2	6.80	7.17	14.90
4	19.33	425.2	50.7	6.42	6.89	16.30
6	3.75	397.9	41.6	6.24	6.62	18.61
7	19.67	375.8	34.2	5.74	6.46	19.50
8	23.75	363.9	30.2	5.89	6.30	22.71
11	19.33	346.7	24.5	5.24	6.10	22.71
13	22.33	338.4	21.8	5.50	5.97	27.91
15	22.50	332.9	19.9	5.65	5.90	30.24

NOTE.—10.65 is the value of $k\mu/\lambda$ for a normal mixture ($2H_2 - 1O_2$) in a bulb of this size.

Another question of importance can be considered in this connection, whether it is only one component, or both, that are effectively activated by the α-particle; or, in terms of ionization, are both the hydrogen and oxygen ions capable of taking part in the chemical reaction? In having shown the reaction to be proportional to the specific ionization of the mixture, this question has already been answered in favor of the supposition that both ions are active. But it may receive a more definite answer still by calculating $(k\mu/\lambda)'$ for partial pressures of the components. In the last column of Table IV will be found values using partial pressure of oxygen. As will be seen, the constant rises, which can be interpreted only as meaning that the partial pressure of oxygen alone does not con-

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[1] Mellor, "Chemical Statics and Dynamics, Longmans, Green and Co., 1904, pp. 31, 36, 37.

trol the reaction, since there is no interpretation to be put on a rising velocity constant.

In Table IV will be found results for mixtures of oxygen in chemical excess of hydrogen in the proportions 1 to 1, 2 to 1, and 4 to 1.

TABLE IV.

Effect of Excess of O_2 on the Velocity Constant.

Time. Days.	Hrs.	P. Mm. Hg.	Pt. P. H_2. Mm. Hg.	$(k\mu/\lambda)'$ found.
Orig. mixt. $1O_2$ to $1H_2$. Vol. = 13.517 cc. Diam. = 2.955 cm. E_o = 0.1401 curies.				
0	0	510.4	255.2	..[1]
0	16.00	422.0	196.3	12.0
0	23.75	386.8	172.8	12.4
1	23.75	300.7	115.4	13.0
2	17.17	254.8	84.8	13.9
3	20.00	203.9	50.8	14.2
4	20.00	172.3	29.8	14.6
5	20.00	150.1	15.0	14.3
6	16.00	130.6	2.0	20.4
7	0.42	127.6	0.0	9.1
Orig. mixt. $2O_2$ to $1H_2$. Vol. = 13.849 cc. Diam. = 2.983 cm. E_o = 0.1542 curies.				
0	0	553.5	184.5	..[2]
0	16.25	446.6	113.2	12.13
0	20.58	421.0	96.1	13.66
1	16.25	327.5	33.9	13.86
1	20.58	310.5	22.5	14.69
2	0.08	297.2	13.7	15.43
2	16.25	253.3	0	13.02
2	23.75	249.1	0	3.19
5	0.17	245.9	0	0.47
8	17.08	242.0	0	0.52
Orig. mixt. $4O_2$ to $1H_2$. Vol. = 12.609 cc. Diam. = 2.887 cm. E_o = 0.1093 curies.				
0	0	660.3	132.1	..[3]
0	6.16	611.6	99.7	15.46
0	11.58	573.5	74.2	15.47
0	21.92	509.4	31.5	16.68
1	2.00	487.2	16.7	16.33
1	6.42	464.7	1.7	15.54
1	22.67	451.8	0	2.87
4	21.83	448.6	0	0.22
12	5.58	444.1	0	0.31
18	22.00	443.3	0	0.26

The comparison with the theoretical values is not made since the change in specific ionization would not be so great as in the mixture $4H_2 — 1O_2$;

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[1] Normal constant $(k\mu/\lambda)$ for $2H_2 — 1O_2$ in bulb of 2.955 cm. diam. is $84.1/D^2$ = 9.63.

[2] Normal constant $(k\mu/\lambda)$ for $2H_2 — 1O_2$ in bulb of 2.983 cm. diam. is $84.1/D^2$ = 9.45.

[3] Normal constant $(k\mu/\lambda)$ for $2H_2 — 1O_2$ in bulb of 2.887 cm. diam. is $84.1/D^2$ = 10.09.

but it can be seen that the constants show a tendency to rise in all cases and start abnormally high when compared with the electrolytic mixture, as required by theory.

From the data for the 2 to 1 and 4 to 1 mixtures (Table IV) can also be noticed that when the hydrogen is exhausted the reaction does not stop entirely, but the velocity drops at once to one of an entirely lower order. This is due to some reaction that the oxygen alone undergoes when acted on by α-rays, which is more fully discussed in the following section (7).

7. Action of Alpha Rays on the Pure Components.

The limit of changing the proportion of the two gases will be pure oxygen or pure hydrogen. According to the earlier results of the writer,[1] under different experimental conditions, ozone is formed by the action of α-particles on pure oxygen; and in the present case a secondary reaction between this ozone and the mercury of the manometer might be expected, and is indicated by the results near the end of reactions in Table IV for the second and third experiments. Scheuer[2] found that emanation mixed with oxygen led to very little pressure reduction, but it was not stated whether his reaction took place in the presence of mercury.

Direct experiments with pure oxygen, using the apparatus of Fig. 1, have shown that a decided diminution in pressure does take place, but that the velocity is dependent upon the surface of mercury exposed. If the surface is only that exposed by the mercury ordinarily in the stem of the reaction bulb at *e*, the reaction is relatively slow; but if the mercury is allowed to rise in the bulb and spread out, the action increases many fold. This probably means that primary ozonization takes place in all cases, but that deozonization also takes place unless the opportunity for ready combination with mercury is favorable. The surface of the mercury becomes black, loses its coherence, clings to the glass and is covered finally with a black powder, apparently mercurous oxide. The actual experimental data for the diminution of oxygen pressure will not be presented here, as the work must be regarded as preliminary only.

In the case of pure hydrogen, a smaller diminution in pressure was also found to result, accompanied by a darkening of the mercury and loss of coherence, though no powder becomes visible on the surface as in the case with oxygen. The diminution of pressure ceases after a time and could not be made to proceed further by exposing a greater mercury surface. To explain reduction of pressure in the case of hydrogen, several possibilities present themselves. Usher[3] found, in trying to cause hydrogen and nitrogen to unite, that the reduction in pressure was mainly due to

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[1] S. C. Lind, *Loc. cit.*

[2] Scheuer, *Ibid.*

[3] F. L. Usher, *J. Chem. Soc.*, 97, I, 389–405 (1910).

driving hydrogen into the glass wall by the α-particle. Duane and Wendt[1] have discovered the existence of an active modification of hydrogen produced by radium emanation, which may be H_3, or possibly H found by Langmuir.[2] The loss of hydrogen in the present case may then be mechanical, in which connection it may be pointed out that when the reduction in pressure had ceased, heating the bulb with free flame liberated part of the hydrogen again, either from the glass or the darkened mercury clinging to it. Most of the liberated hydrogen again disappeared overnight. That the effect can not be wholly on the glass walls is proved by the change in the property of the mercury, which suggests that the active hydrogen can react, either with mercury or possibly with some more basic impurity present in the mercury in small amount, to form an hydride.

Neither in the case of pure oxygen nor pure hydrogen can these results be considered as anything more than preliminary. The experiments will be repeated under more exact conditions. They were undertaken to show whether side reactions with the separate components might possibly disturb the main course of the reaction. While the possibility is apparent, it is not believed that such disturbances are serious for the following reasons: First, the active forms of hydrogen or oxygen appear to react more readily with each other than to enter into side reactions. This is evident from the fact that reaction sometimes proceeds to 99% of completion, which would hardly be the case if either component had been permanently removed. Also the mercury never shows these marked changes in property in the presence of equivalent quantities of hydrogen and oxygen. Finally when either component is exhausted the reaction velocity sinks to a low order not possible to confuse with the main reaction (see Table IV, 2nd and 3rd reactions).

8. Ratio of Chemical Action to Ionization.

Having established a general law for the reaction between hydrogen and oxygen and shown that it holds for all spherical volumes up to the largest diameter investigated (5.6 cm.) and also for a cylinder (4 × 1.8 cm.), the way is open to evaluate the statistical ratio of the actual number of molecules reacting (M) to the number of pairs of ions (N) produced by the α-radiation. In Section 5 it was shown that $k\mu/\lambda = 84.1/D^2$.

For a sphere with $D = 1$, $k\mu/\lambda = 84.1$.

λ = transformation constant of Ra emanation = 2.085×10^{-6} sec^{-1}. μ = efficiency factor for the chemical effect of the ion[3] and may be expressed as $\mu = (M/N).(760/V.2.75 \times 10^{19})$. k = ionization coefficient = number of α-particles per second for 1 curie of emanation in equilibrium

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[1] Duane and Wendt, *Phys. Rev.*, 10, 116–128 (1917).

[2] I. Langmuir, THIS JOURNAL, 34, 1310–25 (1912).

[3] S. C. Lind, *J. Phys. Chem.*, 16, 592 (1912).

with Ra A, B and C ($= 3 \times 3.57 \times 10^{10}$)[1] × number of ions for 1 α-particle per 1 cm. of path (2.2×10^4) × specific ionization of gas mixture (for $2H_2 - 1O_2$: $^1/_3[2 \times 0.24 + 1.09] = 0.523$) × average path (for sphere of 1 cm. diam. = 0.348) × 1/760 (to refer to 1 mm. of pressure).

Therefore, $k = 4.29 \times 10^{14}.1/760.$

Substituting in $k\mu/\lambda = 84.1$ and solving for M/N

$$M/N = 5.87, \text{ or } M_{H_2O}/N = {}^2/_3 M/N = 3.92.$$

That is to say, for each pair of ions produced in the gaseous mixture $2H_2 + 1O_2$, *3.92 molecules of water are formed.*

Before discussing this result some consideration of the method of determining the average path of the α-particles is necessary. The theory has already been developed by the writer[2] and the earlier value of the average path from all points within a spherical volume (0.798 × radius) was obtained by calculating from 10 concentric spheres dividing the whole into 10 equal volumes. By using 100 instead of 10 spheres, a more exact value has now been obtained, $0.8138 \times r$. Making the same assumption as before that practically all Ra A and Ra C diffuse to the wall before decaying, the effective average of all paths is

$$r/3(0.8138 + 2 \times 0.6366) = 0.6957\,r.$$

The assumption that Ra A and Ra C have time to diffuse to the wall before emitting their α-radiation is one requiring consideration. No data having a very direct bearing on the subject have been found in the literature. A. Debierne[3] has made the most complete examination of the diffusion of the radioactive deposit by using parallel plates at different distances apart exposed to emanation. His results showed that the practical limit of diffusion is much less than the theoretical, indicating a particle 140 times as heavy as the atom of the decay products. Debierne also found that increase of concentration of the emanation diminishes the diffusion limit. Since the present experimental conditions were so different from those of Debierne as regards volume and concentration of emanation, it appeared advisable to make a few direct experiments by allowing the emanation to reach equilibrium in a vessel and gas mixture exactly the same as employed in the velocity measurements, and then suddenly displace the gas by mercury into a new vessel in which the rise of the α-radiation would disclose the quantity of Ra C transferred. The result showed that in a bulb of 2 cm. diameter filled with $2H_2 + O_2$ at atmospheric pressure and containing 126.5 millicuries of emanation, 93.3% of the Ra C is deposited on the wall of the original vessel, since only 6.7% passed into the new one. For a 6 cm. bulb 88.4% remains on the wall of

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[1] Rutherford, *Phil. Mag.*, [VI] **28**, 320–7 (1914).

[2] S. C. Lind, *Loc. cit.*

[3] Debierne, *Le Radium*, **6**, 97–108 (1909).

the original vessel. This result, not to be expected from Debierne's data, is probably due to convection arising from the much higher concentration of emanation. At any rate, it is evident that even in a 6 cm. bulb a large part of the Ra C reaches the wall before decaying. This would not necessarily be true for Ra A in large bulbs, owing to its much shorter life, but one must not lose sight of the fact that the velocity constants (cf. Table II) do not indicate any difference between large and small bulbs as to the effectiveness of the emanation (plus decay products). Therefore, whatever assumption as to position of decay products is made for one size must be made for all. The most plausible assumption is then that about the same portion of Ra A and Ra C reaches the wall in all sizes used, and the writer has, therefore, kept the original assumption that practically all α-particles from Ra A and Ra C originate at the wall. However, to assume that only part of the Ra A, even a small part, reaches the wall would not greatly change the value of the average path.

9. Discussion of Results.

From the kinetic standpoint, the reaction between hydrogen and oxygen when brought about at ordinary temperature by radium emanation proceeds with great regularity. This is in decided contrast with the thermal action of the same gases at higher temperatures, which has hitherto baffled all investigators in attempting to study the kinetics, on account of the extreme irregularity of the reaction.

Although the action of radium emanation is frequently referred to as *catalytic* in nature, it can no more be properly termed so than can the effect of the electric current in producing chemical action. Each produces a definite amount of action having a definite relation to the electrical quantities concerned.

The effect on the velocity of varying the proportions of hydrogen and oxygen is of importance expecially as it shows more strikingly the parallelism to ionization. The greater the proportion of oxygen the faster the reaction, because the greater its ionization, compared with hydrogen.

Since the temperature coefficient of ionization is zero through quite wide limits, one would expect a chemical reaction resulting from ionization also to have a temperature coefficient equal to zero. Through two parallel experiments, one at 25° and the other at 0°, this has been shown to be the case over this range. This, of course, has no bearing on what the temperature effect might be outside this limited range, but is mentioned to show that the neglect of constant temperature conditions does not introduce error in carrying out the velocity measurements at room temperature. This is very fortunate as it would be much more inconvenient to make the measurements in a thermostat.

In order to compare these results with those of Scheuer,[1] Equation 1

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[1] Scheuer, *Loc. cit.*

was applied to his data, obtaining an experimental value of $k\mu/\lambda$ which can be compared with one calculated from the size of his bulb, using the general relation $k\mu/\lambda = 84.1/D^2$. From Scheuer's Expt. II ($D = 7.18$ cm.; $P_0 = 1580$ mm.; $P_{\text{final}} = 1433.8$ mm.), $k\mu/\lambda$ (found) = *1.601*, calc'd *1.633*. For his Expt. III ($D = 8.94$ cm.; $P_0 = 1680$ mm.; $P_{\text{final}} = 1518$ mm.), $k\mu/\lambda$ (found) = *0.987*, calc'd *1.054*. For II the agreement within 2% with the writer's results may be regarded as very satisfactory. In III the value from Scheuer's data begins to drop below theoretical, owing to the effective diameter of Scheuer's large bulb with high gas pressure exceeding the range of some of the α-rays, thus making the prediction higher than the actual. This effect becomes predominant for Scheuer's Expt. IV ($D = 6.0$; $P_0 = 11445$ mm.), where $k\mu/\lambda$ (found) is only *0.3278*, compared with the calculated value *2.278*. For some reason not apparent, the agreement with Scheuer's Expt. I is not good; the reaction is higher than theory, but should be considerably lower owing to the size of the bulb (13.78 cm. diam.). It is of great interest, however, that two of Scheuer's experiments agree with the writer's as to the amount of reaction for the quantity of emanation and size of bulb employed; and a third, which is outside the range to which the writer's theory is applicable, varies in the right direction.

The agreement for the value M/N between Scheuer and the writer may also be regarded as satisfactory, when it is considered that the methods of calculating N, the ionization, were quite different. The average of Scheuer's 4 values with emanation mixt. with the gases is 5.51 and the writer's 5.87. Scheuer states he used the Duane and Laborde formula for calculating ionization, but not enough details are given for the writer to be able to follow the calculation; and unfortunately the promised full report of Scheuer's work did not appear before he fell, early in the war.

Comparison of the present results with those of Cameron and Ramsay can not be fairly made without recalling the fact that Cameron and Ramsay's pioneer work was regarded by them only as preliminary in nature. It was carried out when the proper conditions for handling radium in solution and for collecting and measuring the emanation were not thoroughly understood. Their kinetic equation has been shown to be (Section 3) a special limiting case of the more general form. They made no calculations as to ionization. The quantity of reaction which they found in a tube of given size is several times below that found by Scheuer or the writer, doubtless due to the inefficiency of the collection of their emanation. This can be readily understood from the fact that their radium was not guarded in solution by protective acid; and from a foot note (*loc. cit.* p. 97) it appears that part of their radium was in the form of sulfate and carbonate, salts very insoluble in neutral solution, which would, therefore, liberate much less than the theoretical quantity of emanation. To illustrate the above statements, their Expt. IV in a volume of 2.186 cc. gives a value of 12.7 for $k\mu/\lambda$, which should be for that volume 32.43. For their Expt. VI in a volume of 4.996 cc. $k\mu/\lambda = 6.9$, but should be 16.03.

Further values for M/N for other gas reactions calculated from the data of Cameron and Ramsay are probably in error by a similar amount, but it would hardly be safe to assume and use a correction factor. The experiments themselves should be repeated, which the writer hopes to be able to undertake in the near future.

Any discussion of the possibility of giving theoretical significance to the M/N value of 3.92 will be reserved for the conclusion of the following paper, Part II.

10. Summary.

The foregoing experiments on the combination of hydrogen and oxygen gases at ordinary temperatures under the influence of radium emanation mixed with the gases in spherical vessels of different diameters show:

1. The velocity of reaction in a given volume is dependent on two variables only, the quantity of emanation E and the gas pressure P. The velocity constant obtained by integration of the equation arising from this assumption has been verified. Its form is

$$\text{const.} = (\log P/P_0)/E_0(e^{-\lambda t} - 1)).$$

2. The effect of increasing the spherical volume is to diminish the velocity constant (expressed in terms of pressure) according to the equation: const. $= 84.1/D^2$, where D is the diameter in cm. This is to be expected from the increase of the average path of the α-particle proportional to D, while the pressure effect diminishes proportional to D^3. This formula is applicable only to spheres in which the size of the shortest α-ray is not exceeded by the diameter.

3. Varying proportions of hydrogen and oxygen changes the velocity as would be expected from the change produced in the specific ionizations ($H_2 = 0.24$, $O_2 = 1.09$ referred to air $= 1$). Excess of oxygen gives a velocity higher than normal and which increases as the proportion of oxygen increases. Excess of hydrogen produces the opposite effect.

4. From No. 3 it follows that the emanation activates both of the pure components.

5. The temperature coefficient of the reaction between 0° and 25° is zero, as would be expected from ionization.

6. Calculation of the ionization by the method of average path of the α-particles shows that for each pair of ions produced in the gaseous mixture, about 3.9 molecules of water are formed. (Scheuer found 3.7.) Theoretical interpretation of this is deferred to the following paper.

7. Reaction in cylindrical volumes obeys the same law as in spherical

ones, appearing to confirm the writer's earlier claim that the average path in the cylinder is the same as in sphere of equal volume.

The writer desires to thank Dr. R. B. Moore, Dr. Herman Schlundt and Mr. J. E. Underwood for their advice and assistance in carrying out the foregoing experiments.

GOLDEN, COLORADO.

CHEMICAL ACTION PRODUCED BY RADIUM EMANATION. II. THE CHEMICAL EFFECT OF RECOIL ATOMS.[1]

BY S. C. LIND.

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1. Introduction.

In Part I, the preceding paper, it was shown that the velocity of combination of hydrogen and oxygen gases at ordinary temperature, under the influence of radium emanation mixed with them, can be conveniently measured by following the reduction in pressure at constant volume. An apparatus suitable for this purpose was described, and data were given proving the applicability of a kinetic equation based on the assumption that in a given limited volume the reaction velocity is proportional to the amount of emanation E present at any time and the gas pressure P, both variables, the latter varying as a function of the former.

The change of pressure produced is also dependent on the volume of the containing vessel as well as on the quantity of emanation. In small vessels, say a sphere of one cm. diameter, owing to the limited quantity of gas, the pressure falls very rapidly (unless the quantity of emanation be extremely small) so that a condition is soon reached in which the layer of gas traversed by an α-particle becomes very thin, the order of a few millimeters. Of course, the same condition can be attained in larger chambers but is not reached, starting from normal pressure, without much larger quantities of emanation, owing to the greater volume of gases to be acted on before the pressure sinks to low values.

On attempting to apply the same kinetic equation to the velocity observed in a one cm. sphere, as had been found applicable for larger spheres, no constant was obtained but a value which rose rapidly as the pressure diminished. This puzzling discovery could not be explained by the action of α-rays alone, but an analysis of the results suggested that it could be explained on the assumption that the "recoil atoms" produce chemical action proportional to their ionization, just as the α-particles do.

It may be profitable to consider briefly something of the properties of "recoil atoms." When an atom, like Ra A or Ra C, emits an α-particle, the residual atom recoils with a velocity that may be calculated from the principle of conservation of momentum to be about $^1/_{50}$ of the velocity

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[1] Published with permission of the Director of the U. S. Bureau of Mines.