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.

Received December 30, 1918.

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.

of the α-particle emitted.[1] This velocity and corresponding kinetic energy is sufficient to impart to the "recoil atoms" ionizing properties through a limited range, which range is increased by reducing the pressure or density of the gaseous medium. "Recoil atoms" were first studied by Miss Brooks,[2] by Hahn[3] and by Russ and Makower[4] as a method of separating the "recoil atom" in a pure state. More recently the most complete investigation of "recoil atoms" hitherto undertaken has been made in the laboratory of Mme. Curie by L. Wertenstein,[5] to whose careful study we are indebted for most of our present knowledge of the subject.

The "recoil atoms" from the disintegration of Ra A have been called α-particles. Wertenstein has found they have a range in air at atmospheric pressure of 0.14 mm., and in hydrogen of 0.83 mm. This range in air is about $^1/_{350}$ of the range of an α-particle of Ra A; and since the kinetic energy of the α-particle is $^1/_{50}$ of that of the corresponding α-particle, it is evident that the expenditure of energy by the α-particle must be about 7 times greater per length of path than that of the α-particle. This does not mean that the resulting ionization is seven times as great, because the proportion of energy producing ionization is somewhat smaller in the case of α-particles, but Wertenstein finds that the ionization produced by α-particles becomes in maximum about 5 times greater than that of α-particles over the same path.

This knowledge of "recoil atoms" suffices at least for a preliminary survey of what might be expected of "recoil atoms," if they produce chemical action proportional to their ionizing power, as α-particles do. The two factors to be kept in view are the very limited range of recoil atoms, and their greater intensity of action within their limit.

Beginning in a volume and at a gas pressure at which the α-particle would have a sufficiently long path to expend a considerable fraction of its kinetic energy before striking the wall, the comparative effect of the recoil atom would be too small to be detected. On reducing the volume or pressure, the effect of the recoil atom remains constant while that of the α-particle is diminished by the shortened effective path. Therefore, the effect of the recoil atom becomes relatively more and more prominent and would reach a maximum when the pressure reaches the value at which the ionizing power of the recoil atoms would become practically constant along the path, which is the case very near its origin. If the chemical action under this condition were proportional to the ionization, the chemical effect of the recoil atoms would be about 5 times

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[1] Rutherford, "Radioactive Substances and their Radiations," 1913, pp. 174–9.

[2] Miss Brooks, *Nature*, July 21, 1904.

[3] O. Hahn, *Verh. deut. physik. Ges.*, 11, 55 (1909).

[4] Russ and Makower, *Proc. Roy. Soc.*, 82A, 205 (1909).

[5] L. Wertenstein, *Thesis*, 1913, Gauthier-Villars, Paris, Publishers.

that of the α-particles, or the total velocity would be 6 times the normal, due to α-particles alone.

With this preliminary analysis made, one is ready to proceed to the examination of the experimental data, to ascertain if they indicate the truth of the assumptions. Later the more quantitative aspects can be considered.

2. Experiments.

The experimental procedure and apparatus are the same as described in Part I, the foregoing paper, for the combination of hydrogen and oxygen by radium emanation. An electrolytic mixture of hydrogen and oxygen was employed mixed with radium emanation in a small spherical reaction bulb.

In Table I will be found the experimental data, as well as the interpolated data, and calculated results. $k\mu/\lambda$ and $(k\mu/\lambda)'$ are from Equations 1 and 2, respectively, of Part I, and have the same signification as velocity of reaction constants, or better, *factors* since they are not constant.

TABLE I.

Effect of Recoil Atoms in Producing the Combination of Hydrogen and Oxygen at Ordinary Temperature in Small Volume.

Vol. = 0.470 cc. Exact diam. = 0.9647 cm. E_0 = 0.04234 curies.

Actual data.			Calculated from actual data.				Interpolated data.	
Time.		P.			Time.			
D.	Hrs.	Mm. Hg.	$k\mu/\lambda$.	$(k\mu/\lambda)'$.	D.	Hrs.	P.	$(k\mu/\lambda)'$.
0	0	507.8	...	...	0	0	507.8	...
0	15.67	310.3	104.6	104.6	0	6	425.0	95.6
0	19.90	271.2	105.9	111.2	0	12	354.0	102.7
0	23.67	235.1	111.4	142.9	0	18	290.0	117.1
1	15.33	135.4	121.4	139.0	1	0	233.0	134.4
1	19.00	119.0	123.4	148.7	1	6	187.0	141.6
2	5.00	76.7	134.8	195.0	1	12	150.7	145.0
3	0.33	18.8	181.3	349.6	1	18	123.0	148.8
3	15.42	5.0	220.5	483.3	2	0	96.0	182.4
					2	6	73.0	210.9
					2	12	51.5	278.9
					2	18	33.0	377.6
					3	0	19.5	461.7
					3	3	14.0	594.3
					3	6	9.9	646.0
					3	9	7.5	528.5
					3	12	5.7	535.1
					3	15.42	5.0	228.3

Cols. 1 and 2 give the actual results of the measurements. In Col. 3 the values of $k\mu/\lambda$ illustrate the marked increase in the velocity. Evidently the constant should be calculated from measurement to measurement, instead of from the beginning each time. This has been done in Col. 4, where $(k\mu/\lambda)'$ brings out the increase more clearly. But even yet the intervals are rather large. Therefore, a curve has been plotted (Curve

1, Fig. 1) from the original data of Table I, from which the interpolated values of Col. 6 were taken. $(k\mu/\lambda)'$ calculated from the interpolated data brings out the rise very distinctly.

In Fig. 1, Curve 1 shows the actual course of the reaction. Curve 1 A shows the course the reaction would have under the normal action of α-particles, calculating the pressure from the equation

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

and taking $k\mu/\lambda = 90.4$ from the general relation $k\mu/\lambda = 84.1/D^2$ (Part I, Section 5). Curve 2 in Fig. 1 represents by ⊖ the values of $(k\mu/\lambda)'$ from the last column of Table I. It illustrates how the reaction velocity at high pressures has a normal value, rises slowly at first, and then very rapidly as the pressure drops.[1] After passage of the maximum, the value drops off almost perpendicularly, owing to practical exhaustion of the reaction gases. It may be remarked that for obvious reasons very pure electrolytic gas is required to avoid disturbances toward the end of the reaction.

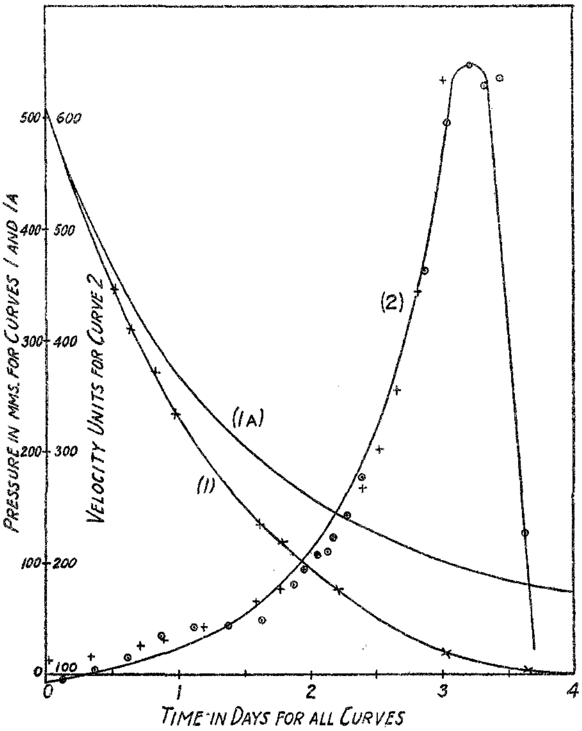

Fig. 1.

The points marked + along Curve 2 are those required by the theory to be discussed shortly; near the intersection with Curve 1 they are marked ⊕ to distinguish from the points of Curve 1.

3. Quantitative Consideration of the Results.

Having shown in a general way (Section 1) that the marked rise in the velocity constant $k\mu/\lambda$, as illustrated in Fig. 1 (Curve 2) from the data of Table I, might be accounted for by the chemical effect of the recoil

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[1] In using Curve 2, Fig 1, it is to be kept in mind that the abscissas do not refer directly to pressure, but to time. The corresponding values of pressure must be obtained through reference to Curve 1, or from Table II.

atoms, adding itself to the normal chemical effect of the α-particles, it remains to study the quantitative aspects to see if the theory seems to fit the facts.

The normal value of the velocity constant for the action of α-particles alone upon hydrogen and oxygen would be, in a bulb of the size used (Table I), *90.4*. Twice this velocity, or *180.8*, would be attained under conditions at which the chemical effect of the recoil atoms just becomes equal to that of the α-particles. As can be found from the curves of Fig. 1, this would be reached at a gaseous pressure of 118 mm. At any other pressure the proportion of chemical action being produced by each type of radiation could be estimated on the following basis:

1. That the total effect of the recoil atoms remains constant down to the pressure at which they also reach the wall before completing their paths.
2. That the total effect of the α-particle will at all pressures be proportional to the pressure. For example, at the pressure of 118 mm., the two effects are equal; and one can arbitrarily place each equal to 118. At any other pressure, 50 mm. for example, the recoil atom effect, which for convenience will be called the α-effect,[1] would still have the value 118; the α-effect will have the value 50; the combined effect will be 168, and the ratio of abnormal to normal effect will be $(a + \alpha)/\alpha = 168/50 = 3.36$. Table II shows this same calculation carried to its upper and lower limits.

By comparison of the last two columns of Table II, the general trend of the calculated and experimental values of $(k\mu/\lambda)'$ can be seen to be the same. The calculated values have been put in Fig. 1 as +, and show a satisfactory agreement between the theory and the experimental data. The maximum value found, 632, when divided by the normal α-value 90.4, shows that the maximum ratio $(a+\alpha)/\alpha$ becomes 6.99. According to Wertenstein, the maximum ionization due to α-particles is 5 times that of the α-particles over the same path, which would mean a factor of 6 times the α-effect alone. Remembering that Wertenstein's statement refers to recoil atoms of Ra A alone, it will be seen that the agreement for all three sets of recoil atoms between ionization prediction and chemical effect is perhaps as good as could be expected.

At first sight it may appear surprising that the chemical effect of the recoil atom can be observed at fairly large pressures. One must consider, however, that the radius of the reaction bulb is 4.8 mm. and that the average path within the bulb is only $^7/_{10}$ of this, or about 3.3 mm.; and,

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[1] In using the term α-particle for the recoil atoms of radium emanation, it is to be remembered that it properly refers only to recoil atoms from Ra A, but here it will be used to include also those from emanation and Ra C. The recoil atoms from the β-rays have so little energy that they can be entirely neglected.

moreover, the range of the α-particle in the electrolytic mixture will be about 0.30 mm. at standard pressure (calculated from Wertenstein's values for hydrogen and air), and would be still greater for the recoil atom of Ra C. These facts, considered together with the intensity of the energy expense by recoil atoms, make it evident that the pressure and bulb dimensions at which the effect manifests itself, are quite concordant with Wertenstein's ionization data.

TABLE II.

α-Effect = const. = 118. Calculated $k\mu/\lambda$ = 90.4 × $(\alpha + a)/\alpha$.			α-Effect = pressure (P). $(k\mu/\lambda)'$ (found) from Table I.	
P.	$\alpha + a$.	$(\alpha + a)/\alpha$.	$(k\mu/\lambda)'$ calc.	$(k\mu/\lambda)'$ found.
10	128	(12.80)	...	...
20	138	6.90	622	632
30	148	4.93	444	446
40	158	3.95	356	376
50	168	3.36	303	330
60	178	2.97	268	292
70	188	2.69	242	267
80	198	2.48	223	240
90	208	2.31	208	223
100	218	2.18	195	204
110	228	2.07	186	192
120	238	1.98	177	182
130	248	1.91	172	166
140	258	1.84	166	162
150	268	1.79	161	153
200	318	1.59	143	133
250	368	1.47	132	118
300	418	1.39	125	112
400	518	1.29	116	100
500	618	1.24	113	95
600	718	1.19	107	...

Finally it should be inquired whether the effect of recoil atoms will not also be manifested in larger bulbs at low pressures. The answer must be affirmative with certain reservations. Referring to Table I of Part I, it can be seen for the 2 cm. and 3 cm. bulbs that there is an unmistakable tendency for the velocity constant $k\mu/\lambda$ to increase slightly toward the end of the reaction, which tendency would be brought out more distinctly by calculating for $(k\mu/\lambda)'$. As already explained, however, the quantity of gas to be acted on in the larger bulbs is so much greater that before low pressures are attained the emanation is nearly exhausted and the effect on the values of $k\mu/\lambda$ is largely masked.

4. Summary.

The results of the foregoing experiments may be summarized as follows:

1. The action of radium emanation in causing the combination of electrolytic hydrogen and oxygen is abnormally high in small volume, particularly at low gas pressure.

2. Application of a suitable kinetic equation shows that in maximum the velocity becomes 6 or 7 times greater than that due to the normal α-ray effect.

3. It is shown that this can be explained by the assumption that the recoil atoms contribute to the reaction in proportion to their relative ionizing power.

4. The results appear to be in general agreement with Wertenstein's ionization data for recoil atoms.

Addendum.

In reporting the investigations of the foregoing Parts I and II, it was not desired to burden the results with a discussion of a possible mechanism of reaction. The results obtained are purely experimental and the laws governing both the rate and extent of reaction under a given set of conditions have been established, independently of the theory of the nature of the effect. Although the idea that ionization is the primary cause of the chemical actions has been the guiding hypothesis of the writer, the other possibilities are not to be lost sight of, namely, a theory of mechanical bombardment; one of thermal effect,[1] and one of electronic stress without actual ionization.

The main argument in favor of a theory of ionization as the primary agent has consisted in the statistical agreement for a number of reactions between actual number of ions and number of molecules reacting. For all reactions hitherto examined, except one, the agreement is within a multiplier of a few units in either direction. The one marked exception is the combination of hydrogen and chlorine, first pronounced exceptional by the writer,[2] to the extent of 100–1000 fold, from data of Jorrissen and Ringer[3] for β-rays. The exceptionally high ratio of chemical action to ionization has since been confirmed by Taylor[4] and Bodenstein for α-particles and computed by Taylor to be 4000 fold for a very sensitive mixture of hydrogen and chlorine (one very low in oxygen).[5] Bodenstein[6] proposed a very interesting theory in this connection not only for corpuscular radiation, but also for photochemical effect. On account of deficiency of photochemical ionization, the photochemical part of the theory was later abandoned,[7] or rather modified to a form which has not yet been available to the writer, but would probably fall under electronic stress. At any rate, it is clear that the hydrogen-chlorine reaction belongs in a class by itself, and can not be considered at present with the other

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[1] Debierne, *Loc. cit.*

[2] S. C. Lind, *J. Phys. Chem.*, 16, 610 (1912).

[3] Jorrissen and Ringer, *Ber.*, 39, 2093 (1906).

[4] H. S. Taylor, THIS JOURNAL, 37, 24–38 (1915); 38, 280–5 (1916)

[5] D. L. Chapman, *J. Chem. Soc.*, 95, I, 959–64 (1909).

[6] M. Bodenstein, *Z. physik. Chem.*, 85, 329–97 (1913).

[7] M. Bodenstein, *Z. Elektrochem.*, **22**, 53–61 (1916).

reactions conforming more closely to the statistical requirements of ionization.

The approximate statistical agreement between ionization and chemical action has been found to hold for a number of kinds of corpuscular radiation: Cathode rays,[1] β-rays,[2] α-particles,[3] and finally for recoil atoms.[4] The fact that these particles differ in mass from 1/1700 to 220 times that of the hydrogen atom is very interesting.

It remains finally to see if the excess of chemical action M over the number of ions N to the extent $M_{H_2O}/N = 3.92$ for the combination of hydrogen and oxygen can be accounted for plausibly in terms of ions and their interaction. It has been shown, Part I, Section 6, that both components are activated by the α-particles, in proportion to their specific ionizations. Therefore, we may assume either ion activated, as follows:

$$H_2 = H_2^+ + (-), \text{ or } O_2 = O_2^+ + (-).$$

The liberated electron in either case may attach itself as follows:

$$(-) + H_2 = H_2^-, \text{ or } (-) + O_2 = O_2^-$$

The resulting ions may react to form positively or negatively charged H_2O_2. For example, $H_2^+ + O_2 = H_2O_2^+$, or $O_2^+ + H_2 = H_2O_2^+$
or $H_2^- + O_2 = H_2O_2^-$, or $O_2^- + H_2 = H_2O_2^-$.

Assuming then that charged H_2O_2 reacts with H_2 to form H_2O: $H_2O_{(+ \text{ or } -)} + H_2 = 2H_2O$, and that the water formed loses its charge without further reaction, we should have 4 molecules of water resulting from one original pair of ions by a number of possible ways, all of which are quite plausible from our knowledge of gaseous ions. The experimental value of M/N was *3.92* (Part I, Section 8), or 3.7 according to Scheuer.[5] The slight deficiency below 4.0 could be accounted for by side reactions of lower efficiency, such as $H_2O_2^- + H_2^+ = 2H_2O$, and others. The reason that these less efficient reactions do not occur to a greater extent is owing to the much smaller chance of their taking place from the standpoint of concentration and mass action.

The mechanism proposed at least shows that the ratio $M/N = 4.0$ is still within the limits of ionic possibilities, without resorting to other theories. On assuming with Bodenstein that an electron can attach itself to activate a molecule, can be again detached by the reaction, and continue to act thus through a large number of cycles until consumed by some action from which it is not again liberated, there would be almost no limit to the multiplied activity of a single electron.

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[1] Krueger, *Loc. cit.*

[2] Lind, from Usher's results, *Ibid.*

[3] Several authorities.

[4] Present paper.

[5] Scheuer, *Loc. cit.*

Whether ionization is the primary step in the chemical action produced by α-particles and other corpuscular radiation or not, since it is approximately proportional to it for most reactions, it remains the most convenient means of comparative reference. The specific ionization is either known or can be calculated for most gases, and thus at least an approximate prediction may be made of the quantity of chemical action to be expected under a given set of conditions.

Golden, Colorado.

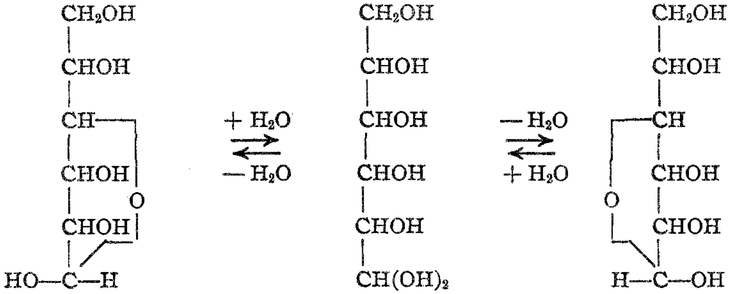
[Contribution from the Harriman Research Laboratory, Organic Chemistry, Columbia University. No. 321.]

MUTAROTATION OF GLUCOSE AND FRUCTOSE.

By J. M. Nelson and Frank M. Beegle.

Received January 2, 1919.

It is well known that a freshly prepared water solution of glucose gradually changes in optical rotatory power. This mutarotation is most commonly accounted for by considering that the dissolved sugar undergoes a transformation from one form to another, or from α- to β-glucose. The constitutions of these two forms are generally considered to be lactonic as represented in the formulas below. Various theories have been proposed for explaining the mechanism involved in this change. Among these might be mentioned that of Lowry who considers the intermediate formation of a hydrated aldehyde.



α-Glucose. Hydrated aldehyde. β-Glucose.

Since the aldehyde carbon is not asymmetric in the hydrated aldehyde, while in the other two forms it is, the disappearance and recurrence of the lactonic forms will tend to yield both the dextro and levo forms of this asymmetric group. In this way, if the dissolved glucose were originally α, part of it would go over into the intermediate and β forms until the equilibrium of the system was reached. Armstrong[1] objects to Lowry's view that the lactone bridge is opened up in the transformation, and believes that water adds to the lactone oxygen as an oxonium hydrate, instead of forming the intermediate hydrated aldehyde. When the water

[1] "The Simple Carbohydrates and Glucosides," 1912, p. 20.