[CONTRIBUTION FROM THE DEPARTMENT OF THE INTERIOR, BUREAU OF MINES]

CHEMICAL ACTION PRODUCED BY RADON
V. REVISION OF THE CHEMICAL EFFECT OF RECOIL ATOMS[1]

BY S. C. LIND AND D. C. BARDWELL

RECEIVED JUNE 4, 1924 PUBLISHED SEPTEMBER 5, 1924

It was previously shown by one of us[2] that the recoil atoms from alpha-radiation of radon (and of its decay products) produce chemical action in general agreement with their ionization. The reaction studied was the combination of electrolytic gas. In more recent work[3] radon was employed when confined in an α-ray bulb,[4] which does not allow recoil atoms to pass. In making comparison of the amount of reaction produced under these conditions with that when radon is mixed with the gases being acted on, it was necessary to correct for the recoil atom effect. A reëxamination of this effect was therefore undertaken with the following objects: (1) to confirm its reality by directly proving that when recoil atoms are absent, the chemical effects attributed to them are also absent; (2) to remove a certain discrepancy between the recoil-atom effect and the "average path" law; (3) to redetermine the quantity of the recoil-atom effect at various pressures and to attempt to extend the measurements to lower pressures than previously attained.

1. Reaction under Alpha Radiation in the Absence of Recoil Atoms

This experimental condition is readily met by the introduction of radon into an α-ray bulb, which is thin enough to transmit α-rays, while stopping all recoil atoms. It should be recalled that the recoil-atom effect was first discovered and measured by means of the abnormally high velocity of combination of hydrogen and oxygen at low pressures when mixed with radon in a small (1 cm. diameter) glass sphere. With pressure diminishing as the reaction proceeded, the velocity became higher, owing to the increasing relative importance of the recoil-atom effect, reaching five or six times the normal rate. Therefore, if an α-ray bulb be mounted at the center of such a sphere filled with hydrogen and oxygen, no enhancement in rate would be expected in the absence of recoil atoms, and the velocity constant should remain really constant down to low pressures of the gases reacting under the influence of alpha particles alone.

With a few minor changes the apparatus and manipulation were the same as described in Part III.[3] Table I contains the data and velocity

[1] Published by permission of the Director of the Bureau of Mines, Department of the Interior.

[2] Lind, (a) THIS JOURNAL, 41, 551 (1919). (b) American Chemical Society Monograph No. 2, Chemical Catalog Co., 1921, pp. 154–161.

[3] Lind and Bardwell, THIS JOURNAL, 45, 2585 (1923).

[4] Ref. 2 b, p. 76.

constants calculated from equations previously given. Col. 4 shows the constancy of the rate of reaction when carried out in a small sphere by alpha-radiation alone. Col. 5 ("stepwise calculation") is a still severer test, and while showing correspondingly larger individual deviations, as would be expected, no trend is disclosed. Cols. 6 and 7 are explained in footnotes.

TABLE I

VELOCITY OF COMBINATION OF HYDROGEN AND OXYGEN BY ALPHA-RAYS

Radon confined in an α-ray bulb at the center of a small sphere
Vol. = 0.6885 cc. Diam. = 1.095 E_0 = 0.0395 curies

Experimental data			Calculated velocity constants			
			Direct calculation α-Rays only		Corrected α-Rays only	Corrected α-Rays + recoil
Days	Time Hrs.	Pressure Mm. Hg	Whole periods t_0-t_n	Stepwise $t_{n-1}-t_n$	$t_{n-1}-t_n$	
0	0.00	356.3	..	..	..[a]	...[b]
0	12.75	291.5	55.8	55.8	65.4	87
0	*17.25*	*273.6*	*55.2*	*53.2*	*62.4*	*90*
1	13.00	211.5	54.5	50.5	59.2	95
2	0.50	185.7	54.1	52.8	62.0	100
2	13.00	162.4	54.2	54.7	63.2	105
3	3.08	143.0	53.7	50.6	59.3	114
4	14.25	109.5	53.1	51.2	60.0	121
5	20.00	90.44	53.4	55.4	65.0	135
7	13.25	75.36	52.9	49.7	58.2	153
10	15.75	57.69	54.0	61.5	72.0	173

[a] The factor 1.172 used to convert the experimental velocity constants in Col. 5 to the values in Col. 6 includes all corrections discussed in Part IV (Ref. 6, p. 2593). The constants in Col. 6 are those which would result if we could radiate in mixtures with α-rays only.

[b] These constants show what those in Col. 6 would have been in a mixture with both α-rays and recoil atoms acting.

The results of Table I, Col. 6, show that when recoil atoms are screened out by an α-ray bulb, there is no rise in velocity as one goes to lower pressures, whereas the last column shows what the increase is when no such screening occurs.

2. Inverse Square of the Diameter Relation for Alpha-Ray Effect

In Part I[5] it was reported that the product of the velocity constant (expressed in terms of millimeters of pressure change per curie of radon) by the square of the diameter of the reaction sphere in centimeters is a constant, namely, 84.1 for electrolytic gas. This means that the velocity of reaction is proportional to the average path of alpha particles in the gas phase or to the diameter of the spherical reaction vessel. It was realized that there is a certain secondary discrepancy between this and the recoil effect, in that the velocity of reaction in mixtures includes that due to recoil atoms, which is a constant effect not dependent on the diameter or average free

[5] Lind, THIS JOURNAL, 41, 541 (1919).

path. The fact that the law of the inverse square of the diameter seemed to hold quite accurately, in spite of the apparent discrepancy just mentioned, was attributed to an assumed compensation between the relatively diminished recoil effect in larger volumes and the enhancement of ionization (and of its chemical effect) owing to the increase of intensity of ionization toward the end of the range which would be more completely attained in larger volumes at higher pressures. However, the subsequent considerations of intensity of ionization reported in Part IV[6] showed that the latter effect could not wholly compensate the recoil-atom effect, and hence a reëxamination of the law of the inverse square of the diameter was undertaken.

The following graphical method was found useful in examining data for trends, especially in small bulbs as treated later in Section 3. Differentiating the velocity equation[7] $\frac{k\mu}{\lambda} = ln(P/P_0)/(E_0(e^{-\lambda t}-1))$, with respect to the decay factor $(e^{-\lambda t})$ we have: $\frac{d\,ln\,P}{d\,(e^{-\lambda t})} = E_0 \cdot \frac{k\mu}{\lambda}$ or $\frac{d\log P}{d\,(e^{-\lambda t})} = \frac{E_0}{2.3026} \cdot \frac{k\mu}{\lambda}$.

Since E_0, the initial radon, is a constant for a given experiment, a plot of the common logarithm of the pressure against the decay factor should be a straight line, if there is no trend in the value of $\frac{k\mu}{\lambda}$. If there is curvature, the slope of the curve at any point is the instantaneous value of $\frac{E_0}{2.3026} \cdot \frac{k\mu}{\lambda}$ for the corresponding pressure. Velocity constants obtained by this method will be designated as $\left(\frac{k\mu}{\lambda}\right)''$. For bulbs from 1 to 3 cm. in diameter, such a graph gave curves with increasing slope at low pressures.

Table II contains a summary of the results thus calculated from previous data. The value of $\frac{\alpha + R}{\alpha}$ (the abnormality factor) is calculated by

TABLE II

INVERSE SQUARE LAW CORRECTED FOR RECOIL ATOMS

Diam.	Bulb Press.	$\frac{\alpha+R}{\alpha}$	$\left(\frac{k\mu}{\lambda}\right)'' \times D^2$	$\frac{\left(\frac{k\mu}{\lambda}\right)'' \times D^2}{\frac{\alpha+R}{\alpha}}$
1.932	248	1.245	97.6	78.4
2.924	400	1.100	85.1	77.4
3.960	350	1.084	84.2	77.7
1.932	820	1.074	84.6	78.8
4.893	539	1.044	82.6	79.1
5.613	471	1.044	82.3	78.8
				Av. 78.4

[6] Bardwell and Doerner, THIS JOURNAL, **45**, 2597 (1923).

[7] Ref. 5, p. 536.

taking 117 mm. (see Section 3) as the pressure at which the recoil-atom effect (R) is equal to the α-ray effect (α) in a bulb 1 cm. in diameter.

The fourth column contains the new values for the observed velocity constant times the square of the diameter of the reaction sphere, which will be seen not to be entirely constant as shown in Part I[8] but to have a downward trend for larger volumes or higher pressures, as would be expected. Dividing this product by the abnormality factor eliminates the recoil-atom effect and gives the values recorded in Col. 5. From a comparison of the last two columns, it is clear that the inverse square law applies more exactly to the α-ray effect alone, and the discrepancy referred to is thus removed.

3. Recoil-Atom Effect at Various Pressures

In repeating the experiment[9] on recoil-atom effect in a small bulb, changes were made which it was hoped would improve the results. Measurement of low pressures was facilitated by having an evacuated, closed manometer tube of the same bore as the constant-volume setting tube, thus measuring the pressure directly instead of by barometric difference and also eliminating corrections for capillarity. The experiment previously reported (Part II) was carried out with moist gases at room temperature. The presence of water vapor or of any other gases except the reactants is undesirable because of their stopping power for recoil atoms. The presence of liquid water in droplets on the wall makes uncertain the extent of back reaction in the region of very low pressures. Removal of water vapor by fused alkali was found to be unsatisfactory, due to back reaction by decomposition of water in the alkali. In Expt. I, reported in Table III, the reaction sphere was immersed in a bath of sodium chloride and ice at a temperature of approximately —3.0° where the water-vapor pressure is about 3.5 mm. and the possibility of back reaction should be greatly diminished, as ice is only very slightly decomposed by radon.[10] The velocity of reaction is the same at 0° as at room temperature.[11] In Expt. II the reaction bulb was immersed in a bath of carbon dioxide and alcohol at about —75°, to render the pressure of water vapor negligible. In a separate experiment which will be reported later it was shown that the reaction velocity (in larger bulbs and at higher pressures which do not involve the abnormal velocity arising from recoil-atom effect) is the same at —75° as at +25°.

The velocity constants in the last column of Table IV were obtained by the graphical method described in Section 2. The value 78.4 was obtained in Section 2, for the product of pure α-ray velocity constant and the square of the diameter of the reaction sphere. For the bulbs used in Experiments 1

[8] Ref. 5, p. 541.

[9] Ref. 2, p. 553.

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

[11] Ref. 5, p. 548.

TABLE III

RECOIL-ATOM EFFECT ON $2H_2 + O_2$ AT LOW TEMPERATURES, TO REDUCE THE VAPOR PRESSURE OF WATER

Expt. I Temp., about —3° Diameter of bulb, 0.9645 cm. E_0 = 0.0382 curie			Expt. II Temp., about —75° Diameter of bulb, 0.9804 cm. E_0 = 0.0866 curie	
D.	Time Hrs.	P_0[a] (0°) Mm. Hg	Time hrs.	P_0[a] (0°) Mm. Hg
0	0.00	265.5	0.0	95.28
0	3.00	241.0	0.5	89.02
0	9.00	195.6	1.0	83.47
0	19.00	140.0	1.5	78.07
0	22.00	126.9	2.5	68.11
1	1.00	114.0	4.0	54.26
1	3.25	104.5	5.0	45.86
1	9.00	82.12	6.0	38.92
1	18.67	46.50	7.0	31.86
	Final	2.05	Final	3.55

[a] P_0 values in Expt. I are partial pressures after deducting water vapor (4.0 mm.) and foreign gas (2.5 mm.). In Expt. 2, no water vapor correction is necessary: foreign gas pressure is 0.7 mm. at 0°.

TABLE IV

CALCULATIONS USING EXPERIMENTAL DATA OF TABLE III

P	R	$R + \alpha$	$\frac{R+\alpha}{\alpha}$	$\left(\frac{k\mu}{\lambda}\right)''_{\text{calcd.}}$	$\left(\frac{k\mu}{\lambda}\right)''_{\text{found}}$
		Expt. I			
200	114.6	314.6	1.57	128	125
150	112.3	262.3	1.75	143	138
140	111.6	251.6	1.80	147	142
130	110.9	240.9	1.85	151	148
120	110.0	230.0	1.92	157	157
110	109.2	219.1	1.99	163	163
100	108.0	208.0	2.08	170	175
90	106.6	196.6	2.18	178	193
		Expt. II			
80	119	199.0	2.49	197	199
70	119	189.0	2.70	214	219
60	119	179.0	2.98	236	237
50	119	169.0	3.38	268	259
40	119	159.0	3.98	316	283

and 2, applying a 3% correction for lower intensity of ionization in such a small bulb at low pressures, this reduces to 81.7 and 79.1, respectively. In Experiment I at a pressure of 109 mm., the total velocity constant is double this value. Thus recoil atoms are producing as much combination of electrolytic gas as are α-particles. But the recoil atom is wasting energy upon the water vapor and foreign gas (introduced with radon) in proportion to their pressures and stopping powers relative to the electrolytic gas. There are present 4 mm. of water vapor and 2.5 mm. of foreign gas (as-

sumed to be carbon dioxide), equivalent therefore to 13 mm. of electrolytic mixture. Thus, in pure electrolytic mixture, the recoil-atom effect equals the α-ray effect at 122mm. pressure, a value comparable with, and in fair agreement with 118 mm. previously found.[2] In a bulb exactly 1 cm. in diameter, the two effects are equal at 117mm. pressure.

The second, third, fourth and fifth columns of Table IV, Expt. I, are calculated as follows: taking the recoil-atom effect equal to the α-ray effect and equal to 122 at 122mm. pressure the recoil-atom effect (R) for other pressures may be calculated from the expression: $R = 122 \times \frac{P}{P + 13}$. The corresponding α-ray effect is equal to the pressure (P). Values of $\left(\frac{k\mu}{\lambda}\right)''$ calcd. may then be calculated as: $\left(\frac{k\mu}{\lambda}\right)''$ calcd. $= 81.7 \times \frac{\alpha + R}{\alpha}$.

In Expt. II the recoil-atom effect is treated as constant = 119, since there is no water vapor present and the residual pressure of foreign gas is less than a millimeter.

The new results are in agreement with the theory proposed in Part II, from high pressures down to about 50 mm. Below this pressure the experimentally found velocity constants continue to rise but are not concordant among the several experiments attempted. In all cases the finally observed pressure exceeded 1.50 mm.[12] Various corrections for foreign gas, water vapor and possible back reaction are unsatisfactory, hence comparison between theoretical and experimental values is not made for pressures below 40 mm. where those corrections become unduly large.

Summary

1. The velocity constants for the combination of electrolytic gas in a 1cm. bulb show no abnormal increase at low pressures when the radon is confined at the center of the sphere in an α-ray bulb which completely stops the recoil atoms. Thus the earlier view is directly supported that it is recoil atoms which produce the excess reaction observed when radon is mixed with the gases under conditions otherwise the same.

2. Revision of the data for the combination of electrolytic gas in bulbs of various sizes has eliminated an apparent discrepancy between the recoil-atom effect and the law of the inverse square of the diameter. Expressing the diameter in centimeters and the initial radon in curies, the mathematical relation for α-ray effect is: $\left(\frac{k\mu}{\lambda}\right)'' \times D^2 \div \frac{\alpha + R}{\alpha} = 78.4$.

3. A further study was made of the recoil-atom effect in small spheres at very low pressures. The experimental results confirm those previously

[12] Lack of equivalence of $2H_2 + O_2$ if real, must have arisen from some radiation effect, as the same mixture had been carefully tested by sparking in place and found to be correct within 1 part per 1000.

reported down to pressures where the observed velocity of reaction is three times the normal velocity. For electrolytic mixture of hydrogen and oxygen the α-ray effect equals the recoil-atom effect at 117mm. pressure, in a bulb 1 cm. in diameter. The departures from the calculated values at very low pressures remain to be explained.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PHARMACEUTICAL LABORATORY OF THE UNIVERSITY OF UTRECHT]

THE VOLUMETRIC ANALYSIS OF HYDRAZINE BY THE IODINE, BROMATE, IODATE AND PERMANGANATE METHODS

BY I. M. KOLTHOFF

RECEIVED JUNE 9, 1924 PUBLISHED SEPTEMBER 5, 1924

Recently W. C. Bray and E. I. Cuy[1] published the results of their investigation on the quantitative titration of hydrazine. As the author also made in the past few years an investigation about the accuracy of a number of rapid oxidimetric methods for the determination of hydrazine, he thinks it a useful supplement of the communication of Bray and Cuy to describe his results.

All the substances used were purified before the stock solutions were prepared. Commercial hydrazine sulfate was recrystallized twice from water and then dried at 140°. In accordance with results of acidimetric titrations, it proved to be pure. It may be remarked here, that hydrazine sulfate is a very suitable substance to serve as a standard in acidimetric titrations. As the second dissociation constant of hydrazine is very small,[2] its salts are strongly hydrolyzed in aqueous solutions and can be accurately titrated to the basic salts with the use of methyl red as indicator: $2N_2H_4.H_2SO_4 + 2NaOH \longrightarrow (N_2H_5)_2SO_4 + Na_2SO_4 + 2H_2O$.

So with pure hydrazine sulfate one can easily determine the titer of sodium hydroxide, sodium carbonate, etc.

The potassium bromate and iodate were purified by recrystallization from water and were dried at 140°. The products obtained proved to be pure.[3] The iodine was sublimed according to the usual methods and its 0.1 N solution in 0.2 N potassium iodide was standardized against pure arsenious oxide. The potassium permanganate was a high grade commercial sample and was not further purified.

[1] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

[2] From the results of Sommer and Weise [*Z. anorg. allgem. Chem.*, **94**, 51 (1916)] on the solubility of the hydrazine salts the approximate value for the second dissociation constant of hydrazine is calculated to be 2.8×10^{-13}.

[3] Compare Kolthoff, *Pharm. Weekbl.*, **56**, 644 (1919).