[COMMUNICATION FROM THE RARE AND PRECIOUS METALS EXPERIMENT STATION OF THE DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, IN COÖPERATION WITH THE MACKAY SCHOOL OF MINES, UNIVERSITY OF NEVADA]

# CHEMICAL ACTION PRODUCED BY RADON[1]
# III. THE DETERMINATION BY A CHEMICAL METHOD OF THE MEAN EFFECTIVE PATH OF ALPHA PARTICLES IN SMALL SPHERES[2]

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

RECEIVED JULY 27, 1923

1. In studying the relation between ionization and chemical reaction in gases containing radon, the ionization cannot be measured, but must be calculated from the quantity of radon and the mean path of the $\alpha$ particles in the gas being acted upon.[3] The desirability of an exact knowledge of the mean path of the $\alpha$ particles is therefore apparent. The problem is simplified by using *spherical* reaction vessels. The mean path of all $\alpha$ particles projected (by radon) from all points within the sphere in all directions in straight lines until they strike the wall is $0.75 \times r$ (where $r$ is the radius of a sphere). The mean path from all points on the inner surface (RaA and C) in all directions until the wall is again reached is $0.5 \times r$. But doubt exists as to the actual proportions of RaA and RaC that are on the wall when emitting $\alpha$ particles, which evidently would affect the length of path of the $\alpha$ particles emitted and hence the quantity of ionization. It appears impossible to settle this point with existing data on the rate of diffusion of active deposit; and while the direct determination can be made for RaC by means of its $\gamma$ radiation, it is not possible for RaA. Saturation current methods of determining the ionization are also not applicable since the imposition of an electrical field would influence the deposition of active deposit.

The following indirect chemical method therefore appears to have promise, since it had already been shown by one of us[3] that the rate of chemical combination of hydrogen and oxygen under the influence of radon mixed with them in spheres of different sizes is directly proportional to the radius of the sphere, and hence to the mean linear path of the $\alpha$ particles.

The proposed method based on the mean path principle is, in brief, to make a series of manometric measurements of the velocity of combination of electrolytic hydrogen and oxygen in the same sphere under two different

[1] The term *radon* is adopted for radium emanation, according to the recommendation of the International Committee on Chemical Elements. THIS JOURNAL, **45**, 868 (1923).

[2] Published with the permission of the Director of the Bureau of Mines.

[3] Lind (a) THIS JOURNAL, **41**, 547 (1919); (b) American Chemical Society Monograph No. 2, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., N. Y., **1921**, p. 105.

conditions: (A) with the radon confined at the center of the reaction vessel in a minute $\alpha$-ray bulb, which may be regarded provisionally as a point source of $\alpha$ radiation in all directions; (B) with the radon mixed in the reaction sphere with the hydrogen and oxygen. The sphere must, of course, be small enough for the $\alpha$ particles of shortest range to pass entirely across it in the given gases at the highest pressure employed.

In simplest terms, the velocity of chemical reaction in B will be proportional to the effective mean path of the $\alpha$ particles in the sphere, which is sought; while the velocity in A will be proportional to a path which must be the radius $r$ itself. Therefore, the ratio $\frac{\text{chem. velocity (B)}}{\text{chem. velocity (A)}}$ represents a fraction of the radius which is the mean path sought in B. A number of corrections are to be applied which are considered later.

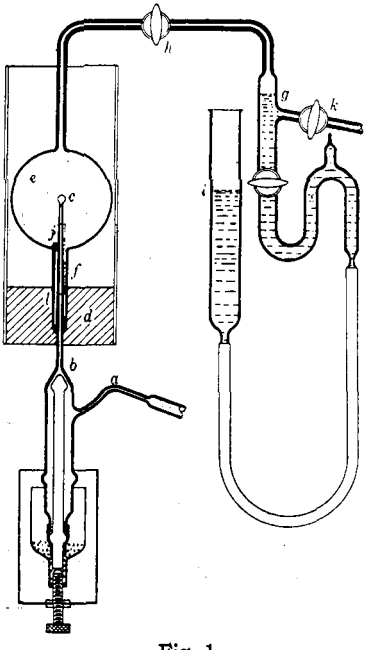


Fig. 1

**2. The Experimental Method.**—The apparatus used for Method A is shown in Figs. 1 and 2. Radon was collected from a solution containing 220 mg. of radium element as 50% radium barium chloride, $Ra(Ba)Cl_2$, dissolved in 5% hydrochloric acid. The method used to obtain radon purer than is needed for therapeutic purposes has been previously described.[4] The radon and residual gases must, after purification, occupy a volume not exceeding 1 to 2 cu. mm. at a pressure of 1 to 2 atmospheres. The electrolytic mixture of hydrogen and oxygen (dry) is first introduced through the stopcocks *k* and *h* to give the desired pressure in *e*. The purified radon is then passed from the purification train (not shown) through the capillary tube *a* past a ground glass valve *b*. Finally *b* is closed so as to confine the radon in front of the mercury just at the neck of the $\alpha$-ray bulb *c*.[5] The ground glass valve *b* is adopted from Taylor,[6]

[4] (a) Lind, *Am. Chem. J.*, **47**, 406 (1912); (b) *Sitzb. Wien Akad.*, **120**, IIa, 1714, (1911).

[5] To minimize the danger of puncturing *c* (Fig. 2) by sparking through, as a result of the accumulation of unipolar charge, a very fine platinum wire (*l*) was sealed through the capillary wall between *d* and *f* making contact with the mercury in the capillary and continuing at the other end well up into *e*. A blank test showed that this small quantity of platinum does not catalyze measurably the combination of hydrogen and oxygen.

[6] Taylor, THIS JOURNAL, **37**, 30 (1915).

but without his silica rod temperature compensator. By making the bore of the capillary between $b$ and $c$ and hence the volume of mercury very small, it was found that temperature compensation could be dispensed with over a range of 10°, which was two or three times the actual maximum fluctuation.

Owing to the difficulty of blowing an $\alpha$-ray bulb on a very short capillary, it was found necessary to make the glass in-seal $d$ at a greater distance from $c$ than could be allowed for the radius of the reaction sphere $e$. Consequently a dead arm (for radiation but open to hydrogen and oxygen) occurs in the annular space along $f$. Attempts to fill in $f$ with inert material failed; mercury has the disadvantage of contributing vapor to $e$ so that a deposit of oxide formed on $c$, owing to the oxidizing conditions in the intense ionization region around it, resulting in a prohibitive increase of stopping power of $c$ for $\alpha$ rays. Attempts to fill in $f$ with fused salt also failed, because the salt (eutectic mixture of lead chloride and silver chloride) upon solidifying broke the thin capillary. The dead arm had, therefore, to be filled with the electrolytic gas, which introduces a correction that will be treated subsequently.

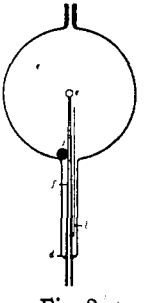

Fig. 2

In the reaction sphere $e$ small areas of a mixture of potassium and sodium oxides were fused flat upon the wall in two or three places for desiccation. The manometric measurements of the course of the reaction were made by reading at $g$, separated from $e$ by a 0.5mm. capillary 10 cm. long and by a stopcock $h$ to prevent diffusion of mercury vapor into $e$.[7] Except at the time of readings the mercury level is raised into the capillary. The mercury levels at $g$ and in the leveling bulb at $i$ were read with a cathetometer without detaching from the apparatus so as to avoid disturbing the mercury setting at $c$ which is very delicate.

The procedure B is identical with A just described except that in B the radon is allowed to mix with the hydrogen + oxygen in $e$ by breaking $c$. This is accomplished (after Procedure A has been followed for 2 or 3 days so as to obtain a good set of velocity constants) by lifting the "magnetic capsule" $j$ with an electro-magnet and allowing it to fall against $c$ which is readily crushed owing to its extreme thinness (about 0.0025 mm.). This "magnetic capsule" is merely a soft iron pin (3 mm. long and 2 mm. in diameter) enclosed in a glass shell of total volume 0.2 cc. In method B the dead arm $f$ is then filled with mercury (from the manometer) exactly up to the shoulder, thus making the reaction vessel $e$ a perfect sphere.

The general procedure just described not only furnishes a convenient method of continuing B from A with the same radon and the same elec-

[7] Use of a liquid-air trap to stop mercury vapor during the short reading intervals when $h$ is open was found unnecessary.

trolytic gas, but also possesses the great advantage of making the comparison of the two velocities independent of any $\gamma$-ray measurement of the quantity of radon (which is the same in both cases, taking into account, of course, the decay factor).[8]

The pumps used for evacuation were a mercury vapor diffusion pump of Pyrex glass backed up by a Gaede rotary oil pump. A vacuum of $10^{-5}$ mm. (neglecting mercury vapor) was attained in the system before the purification and introduction of radon was begun.

The manometric measurements were never begun until radon had been in place for 4 hours to insure equilibrium with and definite position of RaA and RaC. The initial pressure $P_0$, and $E_0$ the initial quantity of radon refer, of course, to the same zero time $t_0$.

**3. Experimental Results and Calculations.**—For the sake of confirmation, two independent experiments were made using reaction spheres of different diameters and $\alpha$-ray bulbs of slightly different dimensions. In Table I the dimensions of both are given. The factors primarily controlling the velocity are the quantity of radon present, the pressure of the reacting gases, and the dimensions of the reaction vessels. The other

TABLE I

DIMENSIONS OF REACTION SPHERES AND OF $\alpha$-RAY BULBS FOR EXPTS. 1 AND 2

| | Reaction sphere | | | $\alpha$-Ray bulb[9] | | | |
|---|---|---|---|---|---|---|---|
| | | | | Diameter of | | | |
| | Diameter Cm. | Volume Cc. | Vol. of dead arm Cc. | bulb Cm. | neck Cm. | tip Cm. | Wall thickness Cm. |
| Expt. 1..... | 3.563 | 23.69 | 1.16 | 0.159 | 0.063 | 0.042 | 0.00025 |
| Expt. 2..... | 4.259 | 40.46 | 1.07 | .145 | .047 | .046 | .00025 |

[8] $\gamma$-Ray measurements of the radon were made in order to give an absolute value to the velocity constants reported, but they are not regarded as very accurate because in passing radon over the ground-glass valve *b* some of it invariably was trapped by the rough surfaces. This rendered heavy screening of *b* necessary during the subsequent $\gamma$-ray measurement, thus introducing uncertainties not arising in the ordinary $\gamma$-ray measurement of Rn.

[9] The measurements of the bulb, neck and tip were made by means of a calibrated micrometer eye-piece (1 div. = 0.00234 cm.); those of the wall thickness by viewing the edge of the broken wall (1 div. = 0.000124 cm.). A preliminary measurement of the wall thickness to determine before use, the suitability of each bulb, was made radiometrically by means of a zinc sulfide screen after introducing radon.[10] The value obtained for wall thickness by the radiometric method was about twice as great as that by the microscopic method. The discrepancy is probably ascribable to the failure of the screen to render $\alpha$-rays visible at the extreme ends of their paths. Although the discrepancy involved in the two methods of measurement is but 1 to 6 mms. of the total path in air, the employment of a difference method magnifies the error to one of 2-fold. Hence, for accurate purposes the microscopic method is preferable. It has the disadvantage that it can only be applied after destruction of the bulb, so that the radiometric method will still be essential for preliminary examination in selecting suitable bulbs. The factor for converting glass into air equivalent, used later in the corrections, is 1 cm. air at 20° and 760 mm. = 0.0056 mm. of glass.

[10] Ref. 4a, p. 397. Ref. 3b, p. 76.

dimensions given in Table I are of secondary importance in later calculating the various corrections involved.

In Table II will be found the experimental results in detail for Expt. 1, and immediately following them a summary of results from Expt. 2, obtained in the same way. The calculations of the velocity constants from the observed changes of pressure involve only the two equations previously given.[11]

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

and

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{\log \frac{P_1}{P_2}}{E_0 (e^{-\lambda t_1} - e^{-\lambda t_2})} \qquad (2)$$

Equation 1 is the form for calculation from the initial pressure $P_0$ to any pressure $P_t$ through the entire interval of time. Equation 2 is the form for the usual "point to point" method of calculation to show absence of trend in the constant. $\frac{k\mu}{\lambda}$ and $\left(\frac{k\mu}{\lambda}\right)'$ may be regarded, for present purposes, merely as velocity constants, without regard to the significance of the separate symbols.

TABLE II

COMPARISON OF VELOCITIES FOR $2H_2 + O_2 = (2H_2O)$ UNDER THE INFLUENCE OF RADON

Experiment 1

Vol., 23.69 cc. Diam., 3.563 cm. $E_0$ for A, 0.1101 curie; for B, 0.0733 curie

A. In $\alpha$-ray bulb at center of reaction sphere

| Time | | | Velocity constant | |
|---|---|---|---|---|
| Days | Hrs. | $P(2H_2 + O_2)$ Mm. Hg | $\frac{k\mu}{\lambda}$ | $\left(\frac{k\mu}{\lambda}\right)'$ |
| 0 | 0 | 540.3 | .. | .. |
| 0 | 6.00 | 515.9 | 9.50 | 9.50 |
| 0 | 15.00 | 483.9 | 9.41 | 9.35 |
| 1 | 11.00 | 424.6 | 9.47 | 9.52 |
| 1 | 23.75 | 394.8 | 9.47 | 9.45 |
| | | | | Av. 9.46 |

B. After breaking $\alpha$-ray bulb and allowing radon to mix with $H_2$ and $O_2$

| | | | | |
|---|---|---|---|---|
| 0 | 0 | 404.8 | .. | .. |
| 0 | 7.92 | 394.0 | 6.43 | 6.43 |
| 1 | 6.00 | 367.4 | 6.57 | 6.62 |
| 2 | 6.50 | 343.8 | 6.64 | 6.75 |
| 2 | 18.00 | 334.5 | 6.66 | 6.81 |
| | | | | Av. 6.65 |

For Expt. 2, carried out in the same way between pressure limits of hydrogen plus oxygen (A) 579.7 to 458.1 mm. in 2 days and 0.5 hour, and (B) 453.5 to 358.4 mm. in 7 days and 11.5 hours, the velocity consts. obtained

[11] Ref. 3a, pp. 536, 543. Ref. 3b, pp. 96, 108.

were: A, $\frac{k\mu}{\lambda} = 7.05$; $\left(\frac{k\mu}{\lambda}\right)' = 7.05$, with $E_1 = 0.1094$ curie. B, $\frac{k\mu}{\lambda} = 4.64$; $\left(\frac{k\mu}{\lambda}\right)' = 4.63$, with $E_0 = 0.0690$ curie.

**4. Discussion of Results.**—This is the first instance in which the manometric course of a gas reaction produced by radon in an $\alpha$-ray bulb has been determined. While the manipulation involved is far more difficult than that for mixtures (Method B), it is nevertheless essential to use $\alpha$-ray bulbs in some cases. It is, therefore, gratifying to know that with suitable manipulation they can be used as a source of $\alpha$ radiation which obeys satisfactorily the theoretical previsions.

A direct comparison of the two velocities, Methods A and B for Expts. 1 and 2, as just reported, shows that radon is more effective when radiating from the center than in the mixture in the proportions: $\frac{9.46}{6.65} = 1.42$ and $\frac{7.05}{4.63} = 1.52$, which are direct experimental efficiency factors. According to the statements of Section 1, their reciprocals, 0.704 and 0.657, would represent values[12] for the fraction $f$ of the radius being sought, if the average path equal $f \times r$. Evidently the values cannot be accepted without a number of corrections, which largely remove their disagreement.

In order to avoid complication, a full treatment of all the corrections involved in both methods (A) and (B) is presented in a separate paper.[13] It suffices here to enumerate them. The corrections which apply to the $\alpha$-ray bulb are (1) for tip and neck, (2) correction to zero diameter, (3) for wall thickness and oblique passage of $\alpha$ particles through it. Those applying to the reaction sphere are (4) dead arm for Method A, (5) average intensity of ionization as dependent on the pressure of the reacting gases, (6) recoil atom effect (absent in Method A). By applying these corrections, as shown in detail in the subsequent paper, a final value for that fraction of the radius which is equivalent to the mean path is obtained. That from Expt. 1 is $0.615\ r$ and from Expt. 2 is $0.609\ r$, which values, within the limits of error may be regarded as identical, $(0.61 \pm 0.01)\ r$. This value has been corrected to the following conditions of ionization: sphere of 2 cm. diameter containing air at 320 mm. and 0°. Theoretically, the value $0.61\ r$ holds accurately only for these conditions, and the drift or

[12] Similar results were obtained in two single experiments by Scheuer [*Compt. rend.*, **159**, 423 (1914)] but were not of such a character that they could be used to obtain an accurate value of $f$. Scheuer stated the differences in velocity in terms of $M/N$ values. This is, of course, an error, arising from his employment of the Duane and Laborde formula for calculating ionization in both cases which is not at all permissible for the $\alpha$-ray bulb. Evidently, it is the length of path and the resultant ionization which is increased by use of the $\alpha$-ray bulb; the $M/N$ ratios remain constant.

[13] Bardwell and Doerner, THIS JOURNAL, **45**, 2593 (1923).

diffusion of active deposit to the wall should depend on the length of path times the density of the gas traversed. That one is not dealing with normal diffusion is evident from the results of Debierne.[14] So far as these and previous experimental results show, the proportion of active deposit on the wall is constant through quite a range of pressures and diameters. For example, if drift or diffusion has a determining influence, one would expect in Expt. 2 (when both the diameter and pressure were larger than in Expt. 1) to obtain a larger value of $f$, yet one slightly smaller was obtained. As far as is known at present the fraction of active deposit on the walls may be maintained practically constant by some other influence than diffusion. We assume, therefore, that the mean linear path traversed by $\alpha$ particles in the sphere is constant over a fairly wide range of pressure. The ionization itself, however, will change with pressure along a given path according to the Geiger ionization curve. We give in Table III, therefore, some interpolated values of average intensity of ionization. These data may be used for any other gas or mixture of gases by reducing to the basis of air by means of the specific ionization.

TABLE III[a]

AVERAGE INTENSITY OF IONIZATION FOR RADON MIXED WITH AIR IN A BULB OF 2 CM. DIAMETER AT 0°

| | | | | | |
|---|---|---|---|---|---|
| Pressure in mm. of Hg..... | 100 | 300 | 500 | 700 | 900 |
| Ion pairs $\times 10^4$ per cm..... | 2.51 | 2.55 | 2.58 | 2.60 | 2.62 |

[a] The number of ions per centimeter of path is based on the value $2.37 \times 10^5$ for the total path in air for Radium C. H. Fonovits-Smereker has recently reported [Sitzb. Akad. Wiss. Wien. $II_a$, 131, 355–63 (1923)] a value $2.20 \times 10^5$. The values in Table 3 may be converted by multiplying by the factor 2.20/2.37, if desired.

It remains to discuss the probability of the result obtained. By referring to Table IV, it will be seen that the value 0.61 $r$ lies well within

TABLE IV

| Assumed proportions on the wall of Radon % | RaA % | RaC % | Resulting av. path of $\alpha$ particles in sphere $r\times$ | Conclusion |
|---|---|---|---|---|
| 0 | 0 | 0 | 0.750 | Maximum possible |
| 0 | 0 | 100 | .667 | Possible |
| 0 | 100 | 100 | .583 | Minimum possible |
| 100 | 100 | 100 | ( .500) | Impossible |
| 0 | 84.0 | 84.0 | .61 | Found |
| 0 | 77.2 | 90.8 | .61 | Found |
| Assuming chemical reaction proportional to linear path (not to ionization) of $\alpha$ particles. | | | ( .53) | Impossible |

the theoretical limits (0.58 to 0.75 $r$), which is a further independent confirmation of the average-path theory of $\alpha$-ray chemical action. An in-

[14] Debierne, "*Le Radium*," **6**, 97 (1909).

terpretation of the result is possible from the standpoint of distribution. For 90.8% RaC[15] on the wall at the time of $\alpha$-ray emission, the value 0.61 $r$ will be satisfied by 77.2% of RaA on the wall. This distribution is intermediate between that to be expected if deposition were controlled solely by the rate of reaching the wall (taking into account the decay rates of RaA, and RaC through RaB) and that previously assumed by Lind[3] of 100% deposition of both RaA and RaC. The value 0.61 $r$ will be used in all future calculations for gas mixtures in small spheres, unless otherwise stated, and will later be used for correcting some previous calculations.

The last line of Table IV will not be clearly understood without reference to the following paper but, in brief, means that a full consideration of the complete or partial suppression of $\alpha$ particles owing to their oblique passage at different angles through the wall of the $\alpha$-ray bulb, with regard merely to their subsequent *linear* paths through the gas phase and without reference to ionization at all, leads to a value 0.53 $r$ for the average linear path in mixtures, which is less than 0.58 $r$, the lowest theoretically possible. Hence, the mere *linear relations* without resort to *ionization*, are incapable of explaining the quantity of chemical combination observed. This is further evidence in support of the ionic-chemical hypothesis.

It is a pleasure to acknowledge the valuable assistance of Professor J. C. Jones of the University of Nevada in making the microscopic measurements of the wall thickness of the $\alpha$-ray bulbs.

## Summary

1. By means of a chemical comparison method consisting of the measurement of the velocities of combination of electrolytic hydrogen and oxygen under the influence of radon in equilibrium with RaC, (A) when confined in an $\alpha$-ray bulb at the center of the reaction sphere, (B) when mixed with the gases, it was found that the mean effective path of the $\alpha$ particle (in mixtures) is 0.61 $\pm$ 0.01 $\times$ the radius.

2. The direct micrometer measurement of the walls of $\alpha$-ray bulbs showed them to be about half as thick as indicated by the zinc sulfide screen radiometric method.

RENO, NEVADA

[15] Ref. 3a. Ref. 3b, p. 205.