Note on the Effect of Alpha Particles on Paraffin. By WILLIAM T. RICHARDS, Ph.D. (Communicated by Prof. Sir E. RUTHERFORD.)

[*Received* 25 August, *read* 25 October 1926.]

Duane and Scheuer (*Le Radium*, **10**, 33, 1913) found, by measurements of the amount of gas mixture evolved by the action of alpha particles on water and ice, that the number of molecules acted upon divided by the number of ion pairs formed was 0·96 in the former case and only 0·05 in the latter. Since this seemingly anomalous result is the only satisfactory published comparison between the behaviour of solids and liquids under the action of alpha particles, a short research of the same type has been undertaken with a substance of somewhat different properties. Paraffin was chosen for this purpose because of the vigorous action to be expected (cf. Lind, *Science*, **40**, 304 (1924) footnote), because of its simple empirical formula, because a previous investigation of so complex a molecular structure had not been undertaken, and because it may be obtained liquid and solid at ordinary temperatures without important change in chemical composition.

Apparatus.

The apparatus consisted, in essence, of a reaction chamber connected by a short capillary tube to a standardized burette which, in turn, was connected to a gas pipette and eudiometer chain terminating in a Ramsay pipette. The eudiometer served also as a means of evacuation. Control measurements showed that quantities of gas of the order of 1 c.c. could be measured with an error of about 0·004 c.c. Since measurements were made over water to secure constant aqueous tension in the burette system, any water vapour evolved by the alpha particle action could not have been detected.

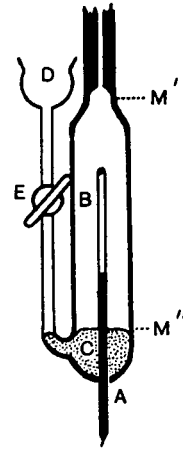

Fig. 1.

The reaction chamber is illustrated in Figure 1. It was made of glass, having a capacity between the limits M' and M'' of about 1·0 c.c. A represents an orifice which permitted the introduction of an alpha ray tube B, and was subsequently tightly sealed with hard wax. The wax was protected from the action of alpha rays by a layer of mercury C which was introduced through the funnel tube D. When liquid paraffin was used it was introduced through D to the level M', and the tap E closed.

https://doi.org/10.1017/S0305004100011658 Published online by Cambridge University Press

When solid paraffin was used it was melted on the inner wall of the reaction chamber in a uniform coating before the tube B was in place, and the side tube leading to D was then filled with mercury.

The liquid paraffin was obtained commercially as "refined medicinal paraffin." The solid was a good grade of hard paraffin wax with a melting point at about 50° C. The two are not, of course, chemically identical, but it is necessary only that they should both have the empirical formula C_mH_n, with m and n of comparable magnitude in each case, for the results to have significance. Impurities to the amount of 5 % would not have affected the results.

Experiments.

Solid Paraffin. 48·3 mg. of emanation were employed to cause the action, contained in an α-ray tube having a range of 4·5 cm. $\pm$ 0·5 cm. The colour of the substance changed, after long continued exposure to the radiation, from white to a brown tinged with violet.

Table I, in which θ represents time in hours and v volume in c.c. of gas evolved, shows the measurements obtained calculated (with appropriate temperature and aqueous tension corrections) for 760 mm. and 12·6° C.

TABLE I.

θ	v	$\frac{\Delta v}{\Delta \theta}$	$\log_{10}\frac{\Delta v}{\Delta \theta}$
0	0	—	—
19·5	0·58	0·0298	$\bar{2}$·474
91·3	2·04	·0203	$\bar{2}$·308
114·8	2·24	·0085	$\bar{3}$·930
140·5	2·42	·0070	$\bar{3}$·845
163·8	2·55	·0056	$\bar{3}$·747

These measurements are represented graphically in Figure 2. The second point has been omitted since it involves too long an interval of time to give a reliable average value.

A series of measurements was also made on the pressure change at constant volume due to emanation in a small evacuated tube lined with paraffin. This method has the advantages of eliminating the uncertainty of range of the α-ray tube, and of showing the additional effect due to the action of recoil atoms. Since, however, the results obtained show no tendency not revealed in Table I, and since corresponding measurements cannot be made with liquids, they will not be detailed. 0·35 c.c. of gas were evolved per mg. of emanation decayed over a period of 29 hours, the volume being given under standard conditions.

Liquid Paraffin. 22·0 mg. of emanation were employed in an α-ray tube having a range of 4·5 ± 0·5 cm. (unfortunately not the same tube as that used in the solid determination). Fifteen minutes after the introduction of the tube small bubbles, which had formed on its surface, began to rise slowly through the liquid. A microscopic examination of the surface of the tube failed to show the action of single alpha particles. After two weeks a black shell, resembling carbon in appearance and properties, collected on a small part of the tube surface. Table II shows the measurements obtained, v being expressed at 12·6° C. and 760 mm. as before.

TABLE II.

θ	v	$\frac{\Delta v}{\Delta \theta}$	$\log_{10} \frac{\Delta v}{\Delta \theta}$
0	0	—	—
1·42	0·033	0·024	$\bar{2}$·380
5·33	·080	·012	$\bar{2}$·079
23·17	·139	·0033	$\bar{3}$·519
26·67	·151	·0033	$\bar{3}$·519
48·00	·188	·0018	$\bar{3}$·255
100·00	·225	·0007	$\bar{4}$·851
144·50	·249	·0006	$\bar{4}$·740

These measurements also are represented graphically in Figure 2.

Errors. That the deviation from linearity of the rate of evolution of the gas in liquid paraffin is not due to systematic error in the apparatus is apparent by a careful consideration of the method of procedure, and is confirmed by the much greater regularity in the solid, where the method was identical. That it is not due to the solubility of hydrogen in paraffin is obvious, as this would influence the results in the opposite direction; the invalidity of this objection is confirmed by the immediate appearance of bubbles which rose very slowly, undiminished in size, to the surface of the liquid. The greatest error in the quantitative comparison of these results is the ranges of the two α-ray tubes which could be determined, as usual, within 10 °/₀ only. This does not, however, affect the rate of evolution of gas in each determination.

Analysis of the gas. Attempts to analyse the exceedingly limited quantity of gas obtained indicated that it was only hydrogen. A satisfactory analysis was not obtained, however, and the nature of the gas is of no importance for the main thesis of the work. It must be borne in mind here, as in other parts of this paper, that radium emanation can be obtained only in limited quantities, and that experiments with it cannot be repeated with the ease and precision possible in most chemical processes.

Comparison of Results.

The following results are the basis for comparison:

State	θ	$(mg)_0$	Δmg	v	$\frac{v}{\Delta mg}$
Solid	163·8	48·3	34·2	2·440	0·0713
Liquid	144·5	22·0	14·6	0·238	0·0163

Here θ represents the number of hours over which action was observed, $(mg)_0$ the number of mg. of radon at the commencement of action, Δmg the amount of radon decayed during action, and v the volume of gas generated expressed under standard conditions.

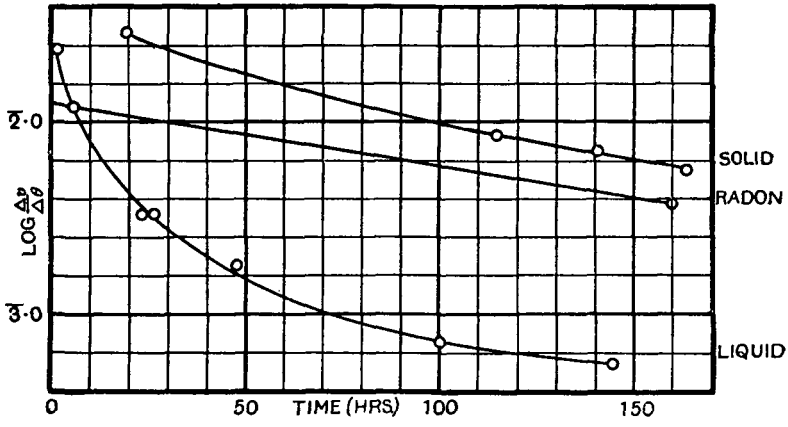

Fig. 2.

In the discussion below, the action due to β and γ rays is assumed to be negligible.

The values for $\frac{v}{\Delta mg}$ given above show, even as they stand, a striking difference from the results of Duane and Scheuer (*loc. cit.*) on ice and water. Whereas these investigators found only $\frac{1}{20}$ of the action in the solid state which they observed in the liquid, the variation here observed is by a factor of 4 in the opposite direction. A part of this latter divergence is clearly attributable to the mutual irregularity in time-action coefficient made clear by a comparison of the curves in Figure 2. This remains to be explained.

In order to treat this irregularity it is necessary to make only the almost axiomatic assumption that chemical action observed is proportional not only to the amount of emanation decayed (Ramsay's Law), but also to the amount of substance present if the latter be

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small. From this, and from the following measurements, may be calculated the relative numbers of molecules instantaneously accessible to α-rays in solid and liquid. The measurements are: inside diameter of the reaction chamber, 0·62 cm.; its length, 3 cm.; length of active portion of the α-ray tube, 1·5 cm.; its diameter 0·1 cm. Taking the range of the average alpha particle in paraffin, calculated from Bragg's Law, to be ·0024 cm., the ratio $\frac{0{\cdot}0141 \text{ c.c.}}{0{\cdot}0012 \text{ c.c.}}$ is obtained. Thus 12 times as many molecules of solid as of liquid paraffin are subjected to $\frac{34{\cdot}2}{14{\cdot}6}$ or 2·3 times as many mg. of emanation, and we should expect to find $\frac{12}{2{\cdot}3}$ or 5·1 as great a volume of gas generated from the solid as from the liquid under the conditions of the experiment. This number is in fair agreement with the $\frac{7{\cdot}13}{1{\cdot}63}$ or 4·4 ratio actually observed for the gas volume generated in the two cases. The calculated value is based on the further assumption that mixing is so incomplete as to be negligible in the liquid. This is partly justified by the concordance obtained; it is further substantiated by the high viscosity of the liquid, and by a consideration of the nature of its decomposition products.

Thus, with a liquid of high viscosity, there appears to be an accumulation of decomposition products in the volume of alpha particle action which acts as a partial screen without producing gas in doing so. If this is virtually unaffected by such weak mixing agencies as are available in the liquid, it must be more noticeable at the surface of the tube than at the outer circumference of the volume of action, and the ultimate black coating of a part of the tube is accounted for. A modification of the usual procedure for the decomposition of liquids for very viscous liquids is therefore seen to be necessary. The slight deviation from linearity of solid paraffin may be even more plausibly accounted for on the basis given above.

Corrections for this effect in the liquid may be made from data already at hand. An extrapolation along the line of emanation decay from the initial rate of gas evolution should give the rate of evolution at the discontinuation of the experiment if the supply of liquid paraffin had been unlimited. If the initial rate is taken as that observed between 1·42 and 5·33 hours, when lack of adjustment to temperature and aqueous tension changes has surely been overcome, the result fixes a minimum for the quantity of gas so evolved. Such an extrapolation, which is indicated in Figure 2, gives a value of 1·08 c.c. at 12·6° C. for 160 hours of action by 15·4 mg. of emanation, or 0·0674 c.c. per mg. emanation at 0° C.

On the other hand, a correction may be made on the basis of the number of molecules available to action, as calculated above, which gives $5{\cdot}1 \times 0{\cdot}0163$ or 0·0830 c.c. of gas per mg. emanation. Although the methods by which each of these corrected values has been obtained are open to question, their average result, 0·0702 c.c. per mg. emanation, agrees well with the 0·0712 c.c. which was found in the solid determination, and must be given more weight than the uncorrected value. Evidently, then, the state of aggregation does not play an important part in the chemical effect of alpha particles on some substances, and divergencies from this conclusion must be attributed to secondary action wherever possible. This carries with it the corollary that the ionization relations in solids and liquids are comparable, a result which has been demonstrated for gases and liquids by previous investigations of a similar character.

A quantitative reconciliation between these results and those of the previous investigators on water cannot here be attempted. The divergence may, however, be descriptively accounted for by a consideration of the chemical and mechanical aspects of the two reactions studied. The mobility in water is sufficiently great to effectively separate a large proportion of the decomposition products which, in ice, remain practically without change of position. Whether it be supposed that they combine according to the laws of probability and their space distribution after formation, or whether recombination into their respective molecules be considered from the point of view of the free energies of the reactions involved, or both, the reformation of water is clearly favoured over paraffin under approximately similar conditions. Hence, with the latter, the mobility of the medium is not important.

According to Geiger (*Proc. Roy. Soc.* **83** A, 565 (1910)), a diminution of the paths of the alpha particles from the decay of radon by 2·6 cm. of air should affect their combined energy by a factor of 0·6, whereas the experiments with solid paraffin at constant volume indicate that 0·2 of the destructive energy of radon is effective with an α-ray tube of 4·5 cm. range. This discrepancy must be laid to the fact that the common method of measuring range gives the maximum value only; that this does not correspond to the average range is demonstrated by the collection of black coating on only a small part of the tube surface after long action in liquid paraffin. This is an added argument against the quantitative measurement of chemical action by α-ray tubes; they may be made to give comparable values, but their absolute values are uncertain. It is interesting to note that the amount of gas, 0·35 c.c. per mg. emanation, obtained from solid paraffin without an α-ray tube, corresponds closely to the value 390 c.c. per curie found by Duane and Scheuer (*loc. cit.*) in the decomposition of water, since it seems

to indicate a general similarity in the ionic mechanism of the two processes.

Lecture Demonstration.

A small trough of two microscopic cover glasses enclosing, between suitable cemented metal supports, an α-ray tube containing 20 or more mg. of emanation, shows clearly on the screen rising bubbles due to the intense chemical action when filled with liquid paraffin and mounted in a projecting lantern focussed on the tube.

Summary.

1. It has been shown that the action of alpha particles on paraffin is independent of the state of aggregation of the substance.

2. Defects in the customary procedure for the decomposition of liquids and solids by the emanation tube method are discussed.

3. A lecture demonstration of the chemical effect of alpha particles is described.

It is a pleasure to express my thanks to Sir Ernest Rutherford for calling my attention to the violent action of alpha particles on paraffin, and to the International Education Board whose Fellowship made possible my short stay in the Cavendish Laboratory.