[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Role of Ions in the Radiation Induced Exchange of Hydrogen and Deuterium[1]

BY SYDNEY O. THOMPSON AND OLIVER A. SCHAEFFER

RECEIVED JULY 26, 1957

The α-particle induced reaction expressed by the over-all equation $H_2 + D_2 \rightarrow HD$ has been investigated. It is found that the reaction has a large yield, 18,000 molecules are formed for each ion pair at 100 mm. pressure of hydrogen. The reaction is extremely sensitive to trace impurities so that the yield for pure hydrogen is probably higher. The addition of trace amounts of xenon or krypton markedly inhibits the reaction, while moderate amounts of added argon, neon or helium have little effect on the reaction. In addition, it is found that none of the rare gases influence the thermal or photochemical induced exchange. The reaction is interpreted as due to an ion chain mechanism involving H_3^+ as the chain propagator.

Introduction

For some time in the discussion of the chemical effects of ionizing radiation it has been popular to describe most if not all of the chemical changes as due to reactions of the free radicals formed by the radiation. There has been little concern of the nature of the role of ions in such systems. The ions are often dismissed as of only transitory existence and hence of no consequence. The experimental facts available at present are for the most part well described by such an hypothesis; however, there is little in the experimental facts of radiation chemistry which clearly defines the role of either ions or radicals.

One must go back to the work of Lind[2] to find serious mention of the role of ions. Lind interpreted the chemical changes as due to the reactions of ions with neutral molecules through the intermediary of clusters. In this way he interpreted the chemical yield per ion pair for a large number of reactions. Lind's approach suffered from the difficulty of often requiring large clusters as intermediates, when it could be shown on theoretical grounds that the formation of such clusters is very unlikely. Because of this, ion molecule reactions did not receive further serious consideration. The concept of atoms and radicals as intermediates became a more acceptable way of interpreting the chemical effects.

The radicals could be formed either directly by excitation or in the process of ionization and subsequent neutralization. Essex[3] and co-workers conducted a number of researches to understand the part played by the ions in forming the radicals and in this way initiating the chemical reactions. Recent studies of elementary ion reactions[4] in a mass spectrometer ion source show that ion–molecule reactions have an extremely high probability of occurrence; the cross section is several times as large as the usual gas kinetic cross section with reaction at every collision. These studies indicate clearly that at low pressures ions react directly with molecules to produce chemical changes. In addition, Meisels, Hamill and Williams[5] find that the radiolysis of methane can be more clearly understood if the results are interpreted as due to the reactions of ions and molecules.

The present experiments were undertaken to determine the part ions play at moderate pressures in a relatively simple system. The reaction chosen was that of the isotopic exchange between hydrogen and deuterium gas. Previous investigators have studied the exchange initiated thermally,[6] photochemically[7] and by ionizing radiation.[8] The thermal and photochemical reactions are well known to be atom chains, and the radiation induced reaction has been interpreted[9a] as being due to atom chains also.[9b] According to this interpretation, six atom chains are initiated for each ion pair produced; two from electronic excitation, one from the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$, and three from the neutralization of H_3^+. The reaction was thought to be initiated by ionization and carried out by atom chains.

The plan of the present experiments was to initiate exchange in an equimolar mixture of H_2 and D_2 with ionizing radiation, controlling the ions present by the admixture of rare gases. As will be shown, rare gases do not affect the atom reaction but a rare gas will charge-exchange with ions in the system, lowering the concentration of ions with higher ionization potentials and increasing the concentrations of ions with lower ionization potentials than the rare gas used. In this way one can vary the concentration of the different ionic species and determine the extent that ions play in the chemical exchange. The present work shows that ion chains rather than atom chains are the major factor in the radiation induced exchange of pure H_2 and D_2.

Experimental

The exchange was induced by the α-particles from polonium-210. All the gases irradiated were of the highest purity commercially available. The rare gases were used without further purification, while the hydrogen and deuterium were purified by passing through a palladium thimble heated to 700°. The deuterium was 99.5% isotopically pure. The mixtures of the gases were made manometrically to an accuracy of about one per cent.

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., Inc., New York, N. Y., 1928.

[3] H. Essex, *J. Phys. Chem.*, **58**, 42 (1954).

[4] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

[5] G. G. Meisels, W. H. Hamill and R. R. Williams, *ibid.*, **25**, 790 (1956).

[6] See *e.g.*, A. Farkas, "Light and Heavy Hydrogen," Cambridge University Press, Cambridge, England, 1935.

[7] L. Farkas and H. Sachsse, *Z. physik. Chem.* **B27-28**, 111 (1934-1935).

[8] See *e.g.*, P. C. Capron, *Soc. Sci. Bruxelles, Ann.*, **55**, 222 (1935), and for a recent investigation L. M. Dorfman and F. J. Shipko, *J. Phys. Chem.*, **59**, 1110 (1955).

[9] (a) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936); (b) the work of Capron and Eyring, *et al.*, was for the o-p hydrogen conversion which should follow the same mechanism as the isotopic exchange as Eyring, *et al.*, show that the possible magnetic interactions are too small to be significant.

The irradiation cell (Fig. 1) was a Pyrex right cylinder, 3.2 cm. high by 4.3 cm. in diameter with a volume of 46.5 cc. The end of the cylinder in front of the α source was closed by a 2.8 mg./cm.^{2} mica window, sealed on with a plastic thermal setting cement. The radiation source[10] used was a disc whose central area, 2.5 cm. in diameter, had polonium-210 deposited on it. The source was rigidly attached to the cell with a clamp. The air gap between the polonium deposit and the mica window was 3 mm. The construction permitted one to estimate the energy of the α-particle entering the gas and consequently the primary ion pair production from the loss in energy of the α-particle due to absorption by the gas. The pressure of hydrogen in the cell was maintained at about 100 mm. The rare gases were usually added in minor amounts. Under these conditions the energy absorbed by the hydrogen was not changed by the addition.

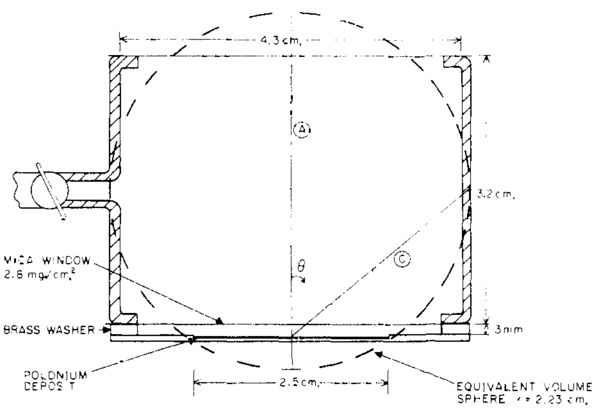

Fig. 1.—Schematic diagram of irradiation cell.

The polonium α-source strength was 25.9 millicuries for the first experiments and ~2 millicuries for the last; all the data were corrected for the decrease in activity so as to be comparable to the initial source strength. The polonium-210 half-life of 138.4 days was used for this correction.

The exchange reaction is quite sensitive to the presence of trace amounts of impurity. It was necessary to pump out the cell for about three hours with a vacuum of 5×10^{-7} mm. of Hg to obtain reproducible results. After the pump-out, the gas mixture was added to the cell, irradiated for a given period, and then the mixture was analyzed with a mass spectrometer.

The mass spectrometer was used exclusively as a comparator; all samples were measured in relation to known standards. As the spectrometer itself equilibrated the samples slightly, the irradiated samples were compared to the original unirradiated mixture. The HD formed by the irradiation was obtained by difference. This procedure gave a precision of ±0.2% when the HD content of the sample was approximately 10%.

The analysis for the isotopic molecules of hydrogen was modified when foreign gases were present. For admixtures of helium, neon, argon, krypton and nitrogen a series of calibration curves were made for different percentages of foreign gas in the mixtures. In the case of helium, calibration curves for H_2 + He, D_2 + He, H_2 + D_2 + He and H_2 + D_2 + HD + He were made. When xenon was present in amounts less than one per cent., the sample was calibrated directly against an unirradiated sample with the same xenon content. For larger amounts of xenon, the xenon was removed by condensing in a liquid nitrogen trap.

Radiation Exchange.—The yield of HD from the equimolar mixture of H_2 and D_2 was studied as a function of intensity of the α-source. In Table I it is seen that the yield is essentially independent of the intensity of the source and only dependent on the total number of α-particles passing through the cell. The production of HD in Table I and subsequently throughout this paper is expressed as mole per cent. HD. By this is meant the per cent. of the irradiated mixture that is HD or equivalently the per cent. of the originally equimolar mixture of H_2 and D_2 that has exchanged. It is now relatively easy to compare the results of experiments with different source strengths.

TABLE I

EFFECT OF YIELD WITH IONIZING STRENGTH

Radiation source strength, mc.	Time of irradiation, min.	Mole % HD total yield	Mole % HD per mc.-hr.
14.7	30	9.7	1.32
7.4	60	10.2	1.38
7.4	60	9.7	1.31
18.2	30	13.9	1.52
9.1	60	13.3	1.46

The reproducibility of the irradiation technique is shown in Table II to be the same as the reproducibility of the analysis. To monitor the system continually and to check for possible impurity contamination of the irradiation cell, a control H_2–D_2 mixture with no added rare gas was irradiated and analyzed after every two or three irradiations. A number of the results listed in Table II are such control experiments. It can also be seen from Table II that in the range 100 to 280 mm. the mole per cent. HD formed has little pressure dependence.

TABLE II

REPRODUCIBILITY OF IRRADIATION OF H_2–D_2 MIXTURES WITH POLONIUM-210 AT ROOM TEMPERATURE FOR 30 MIN.

Hydrogen pressure (mm.)	Source strength (mc.)	Mole % HD formed	Mole % HD formed (cor. to 25.9 mc.[a])
103	25.8	19.1	19.1
103	15.9	12.0	19.6
106	25.9	19.4	19.4
106	24.3	18.2	19.5
106	25.4	18.7	19.1
107	25.0	18.4	19.1
155	19.7	15.1	19.8
240	22.4	16.5	19.2
280	23.5	17.0	18.9

[a] A polonium-210 half-life of 138.4 d. was used to make this correction.

The kinetics can be expressed by the equation

$$\ln [(HD_e - HD_t)/HD_e] = kt \qquad (1)$$

where

HD_e is the concn. of HD at thermodynamic equilibrium
HD_t is the concn. of HD at a time, t
t is the irradiation time
k is the constant which expresses the over-all kinetics of the reaction

That the reaction follows this kinetic relation has been observed previously by other investigations.[8,11] The amount of HD formed is directly proportional to the radiation dose up to a conversion of 15% of the mixture of H_2 and D_2 to HD.

The effect of rare gases on the exchange reaction induced by α-particles is seen in Figs. 2 and 3. The rare gases with ionization potentials higher than hydrogen, namely, helium, neon and argon,

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[10] The source was supplied by Mound Laboratory, Miamisburg, Ohio, operated by Monsanto Chemical Co.

[11] L. M. Dorfman and H. C. Mattraw, *J. Phys. Chem.*, **57**, 723 (1953).

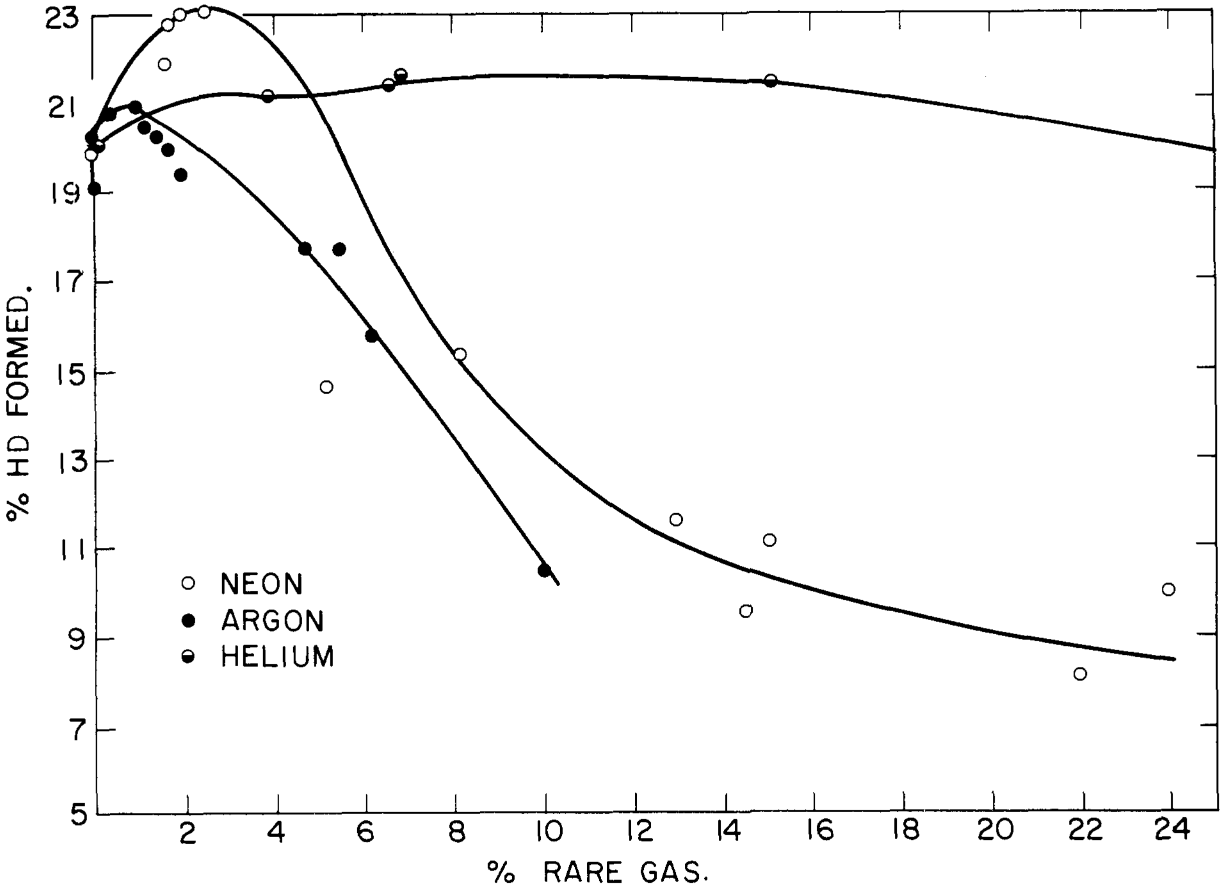

Fig. 2.—Influences of added helium, neon and argon on the amount of HD found by α-irradiation.

do not appreciably affect the rate of the exchange when present in concentrations below 2%. At high concentrations these gases markedly decrease the rate of the exchange reaction. In the case of helium more than 20% had to be added to show any measurable change in the exchange rate. Neon was the only added gas which showed a measurable increase in the rate of exchange. Neon showed the maximum effect at 3% concentration where the exchange rate was 10% above the exchange rate for pure hydrogen.

The addition of krypton or xenon, which have ionization potentials below that of hydrogen, causes a marked decrease in the rate of exchange. For 2% added krypton the rate of the exchange is reduced to one tenth of its value for the pure hydrogen, while with the same amount of added xenon no measurable HD was found during a half-hour radiation.

In order to investigate the effect of xenon more carefully experiments were performed with long irradiation times. The results of these irradiations are in Fig. 4. The addition of one part per million by volume of Xe reduces the exchange to about one half its value for pure hydrogen. For this reason the experiments were performed in the order of increasing xenon content.

Thermal and Photochemical Exchange.—As seen from the previous experiments the addition of

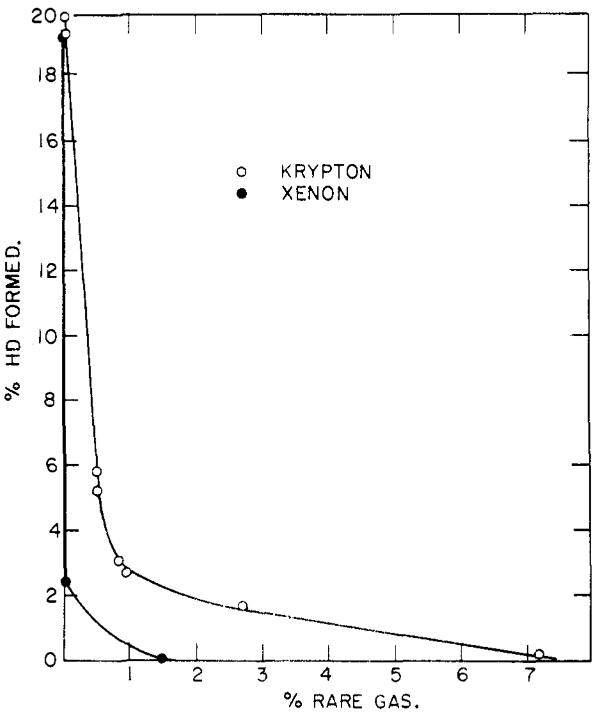

Fig. 3.—Influence of added krypton and xenon on the amount of HD formed by α-irradiation.

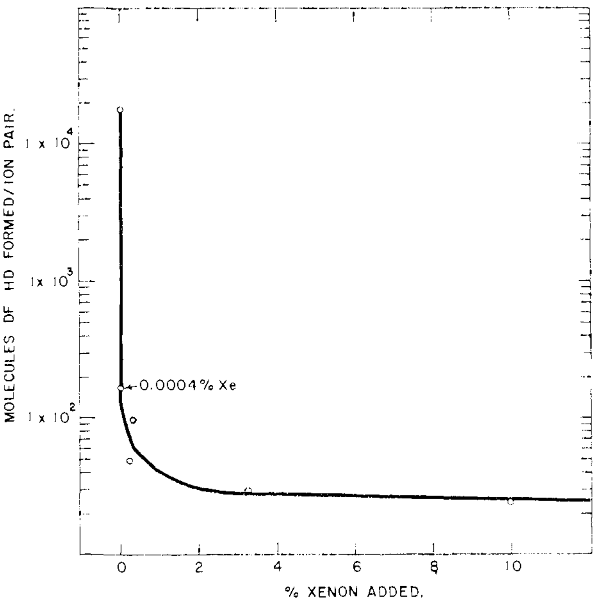

Fig. 4.—Ion yield of the H_2, D_2 exchange with added xenon.

the rare gases shows marked effects on the radiation induced exchange rate. If the exchange is due principally to ions, the effects can be interpreted on the basis of reactions between the added rare gas and the different ionic species. On the other hand, the rare gases may influence the atom chain reaction as a third body in atom recombination. For this reason, the thermal and mercury photosensitized exchange reactions which are known to take place by way of atom chains were studied in the presence of rare gases.

The exchange experiments initiated thermally were carried out in a quartz vessel at 460°. Mixtures of H_2, D_2 and rare gas were prepared in the same manner as for the irradiation experiments. Samples were removed periodically and analyzed with a mass spectrometer. The results are presented in Fig. 5. It is seen that 10% or 48% neon or 10% krypton have no effect on the rate of the exchange.

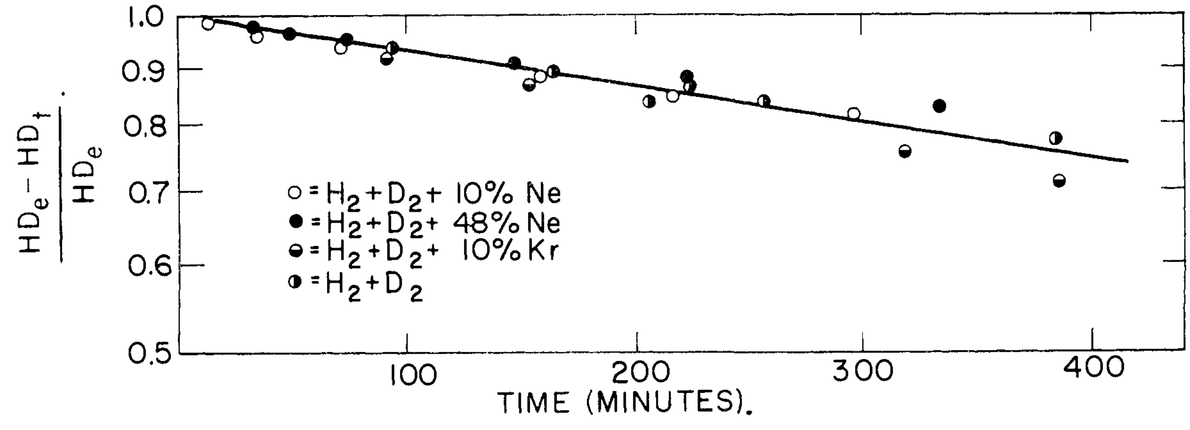

Fig. 5.—Log plot of fraction of HD formed with time, for the thermal reaction in quartz at 460°.

A low pressure mercury arc lamp which operated at about 30° was used for the photochemical study. The results of this study with about 10% added helium, argon, krypton and xenon showed that the addition of rare gases does not alter the rate of the photochemical induced exchange.

The thermal and photochemical induced exchange experiments clearly show that rare gases do not affect the atom chain exchange reaction between hydrogen and deuterium.

Discussion

Mechanism of the Reaction.—From the result that added rare gases have no appreciable effect on well-known atom chain reactions, the mercury photosensitized reaction at room temperature or the thermal reaction at elevated temperature, one would expect the rare gases to have little if any effect on a radiation induced reaction if the reaction proceeded by way of an atom chain. Yet the results of these experiments show that even trace amounts of xenon have a large inhibiting effect on the radiation induced reaction. One must, for this reason, abandon the atom chain mechanism as being responsible for any major portion of the reaction we observe. It is also clear from the large yields of product HD that the reaction is a chain reaction of such a sort that xenon and krypton can serve to break the chain while argon, neon and helium are ineffective at moderate concentrations. These facts suggest strongly an ion chain mechanism. The added gases which inhibit the reaction, xenon and krypton, both have lower ionization potentials than any of the possible chain carriers, H^+, H_2^+ or H_3^+, and will be able to exchange charge with the chain carrier and stop the chain propagation. On the other hand, argon, neon and helium all have higher ionization potentials than the chain carriers and will not greatly affect the chain propagation. This is in agreement with the observed results for moderate additions of the rare gases.

The primary ionization in hydrogen gas will produce predominantly H_2^+ which will react almost immediately with the hydrogen to form H_3^+; hence, the most likely chain carrier is H_3^+.

A very plausible reaction mechanism is then

Initiation reaction	$H_2^+ + H_2 \longrightarrow H_3^+ + H$
Chain propagation	$H_3^+ + D_2 \longrightarrow H_2D^+ + HD$
Chain termination	$H_3^+ + (-) \longrightarrow H_2 + H$

where (−) is some negative carrier either an electron, a negative ion, or the wall of the reaction vessel.

Ion Yield.—With this reaction scheme in mind, it is of interest to estimate the chain length from the present experimental results. Because of the geometry, dictated more or less by the form of the polonium α-source, certain simplifying assumptions are necessary. The geometry is shown schematically in Fig. 1. It is clearly seen that the path length of the α particle in the gas varies a great deal with the angle with which it traverses the cell. At large angles, θ, the path becomes small. However, insofar as ion production is concerned, there is a compensating effect in that for large angles the α-particle loses more energy in the mica and so is more strongly ionizing in the gas. The actual number of ions formed per α-particle is more constant than would at first seem to be the case. In Fig. 6 are plotted the calculated ion yield per α-particle as a function of the angle of entering the cell.[12] The plot has a cut off at 57° caused by absorption in the mica.

The number of molecules exchanged per ion pair, M/N is given by

$$M/N = M/fI_t n \qquad (2)$$

where f is the fraction of the α's which traverse the cell, I_t is the total number of ion pairs formed per α-particle, n is the disintegration rate of the polonium α-source in α's per minute.

The value of f was estimated by assuming that all α's with angles, θ, of less than 57° would traverse the cell. The geometrical efficiency is given by $f = {}^1/_2(1 - \cos\theta)$. For $\theta = 570$, f is 0.22. The average number of ions formed was estimated to be 4500 ions per α particle from Fig. 6.

In this way the M/N values of Fig. 4 were calculated. It is difficult to compare the results of the present experiments with the earlier work, because of the different geometries and because of the very likely variation in purity of the gases used. Capron,[8] for example, found that in order to get reproducible results he had to have a saturation pressure of mercury vapor present. In so doing the mercury vapor is an impurity of constant and relatively high concentration so that small variations in other impurities are not important. Dorfman and Shipko[8] also found the exchange to be highly sensitive to impurities.

Calculation of Chain Length.—The impurities probably inhibit the exchange reaction by either forming negative ions and neutralizing the ion chain carriers or by directly exchanging charge with the ion chain carriers. In the absence of impurities the reaction will terminate on the walls of the reaction vessel. For pure hydrogen the ion yield or chain length will be given by the average number of exchange collisions an H_3^+ makes in diffusing to the wall. A comparison of a calculated chain length to our values of M/N will show to what extent the effect of impurities have been eliminated from our results. Also a similarly calculated chain length for the atom process will show that the atom process is much slower than the ion one.

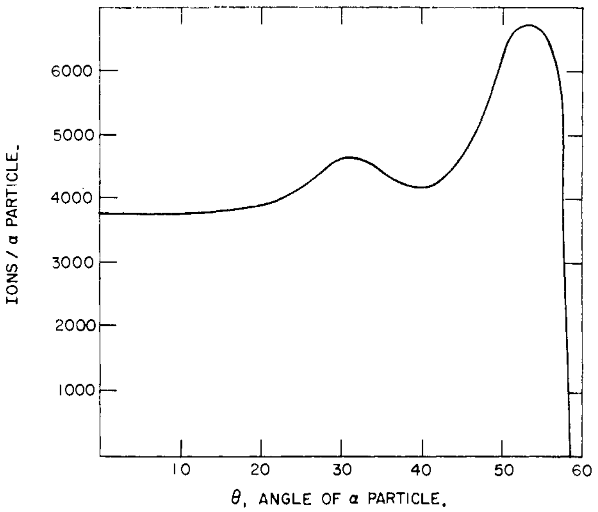

Fig. 6.—Plot of the number of ions produced in the cell as a function of the angle of entry of the α-particle.

To simplify the computation assume that the cell is a sphere with the same volume as the cell used, bathed uniformly in the α-particle radiation. This approximation should be acceptable as the cell is not too far from a sphere as seen in Fig. 1, where the dashed line represents the boundary of the equivalent volume sphere. The cell will not be uniformly bathed in radiation; however, the local radiation intensity will be strongly $1/r^2$ dependent, r being the distance from the α source. The $1/r^2$ dependence introduces an error in that more ions are formed nearer to the wall than assumed and hence the calculation based on uniform radiation is too high. It should, however, be within an order of magnitude of the correct result. The diffusion of the ions to the walls under these conditions is given by the well known relation for spherical diffusion

$$\left(\frac{\partial(H_3^+)}{\partial t}\right)_r = D\left(\frac{2}{r}\frac{d(H_3^+)}{dr} + \frac{d^2(H_3^+)}{dr^2}\right) \qquad (3)$$

At the steady state, this is just balanced by the rate of ion production, I, ions per cc. so that one obtains

$$I = D\left(\frac{2}{r}\frac{(dH_3^+)}{dr} + \frac{d^2(H_3^+)}{dr^2}\right) \qquad (4)$$

The integrated form of (4) is

$$(H_3^+) = \frac{I}{6D}(r^2 - R^2) + \frac{2IR^3}{3D}\left(\frac{1}{r} - \frac{1}{R}\right) \qquad (5)$$

where R is the radius of the vessel. In integrating the boundary conditions were used that the value of (H_3^+) at the wall was zero and that the total diffusion to the wall is equal to the total production of (H_3^+) in the vessel. Equation 5 gives the steady-state ion concentration as a function of the radius of the vessel. To obtain the number of collisions each ion makes in diffusing to the wall, one calculates an average life time and then multiplies by the collision frequency to obtain the desired result.

The average lifetime of an H_3^+ ion is the total number of H_3^+ ions in the vessel divided by the

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(12) The range-energy curves used are those given in E. Segre, "Experimental Nuclear Physics," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1953. The W value used was 36.3 volts per ion pair, W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **97**, 1668 (1955).

total H_3^+ production rate. The total number of H_3^+, $(H_3^+)_T$, ions is given by integrating (5)

$$(H_3^+) = \int_0^R (H_3^+)\, 4\pi r^2 dr \qquad (6)$$

Performing the integration, one obtains

$$(H_3^+)_T = \frac{16\pi}{45}\frac{IR^5}{D} \qquad (7)$$

The total production rate of H_3^+, P, is

$$P = \frac{4\pi}{3} R^3 I \qquad (8)$$

So, then, the average lifetime, τ, of an H_3^+ ion becomes

$$\tau = 4R^2/15D \qquad (9)$$

The collision frequency can be obtained from the kinetic expression

$$\frac{d(HD)}{dt} = k(H_3^+)(H_2)$$

To numerically evaluate the chain length, M/N, the following constants were used. The diffusion coefficient D was taken from work of Persson and Brown.[13] Their value of $D_a p$ = 700 cm.^{2} mm. Hg/sec. was used. The value of k for the kinetic expression was taken from Stevenson and Schissler[4] to be the same as for the similar reaction $H_2^+ + H_2 = H_3^+ + H$, $k = 1.4 \times 10^{-9}$ cm.^{3}/molecule-sec. Using these values, M/N is calculated to be $1.8_5 \times 10^7$ molecules of HD formed per H_3^+ ion.

Our value of 2×10^4 is still low from the calculated value of 2×10^7 by a factor of a thousand. It is interesting to note in this connection that Persson and Brown[13] could only obtain a diffusion controlled neutralization of charge in hydrogen with specially purified hydrogen. Consequently, it is to be expected that if one irradiated extremely pure hydrogen the M/N value would increase to the order of 10^7, for the pressure and vessel size used in our experiments.

For comparison the same computation can be made, assuming that the ions are only initiators of chains, the chain carriers being H atoms. This changes the value of k to 1.4×10^{-16} and D to 1.94.[9] Then assuming each ion initiates six chains[9] one calculates M/N to be 40. This latter value is very close to the value observed with added xenon (see Fig. 4).

Summary

The radiation induced exchange reaction of H_2 and D_2 previously has been interpreted as due solely to atom processes.[8,9,14] Nevertheless our results show that while Kr and Xe have no effect on H atom processes, they do lower the H_2, D_2 exchange reaction rate to an almost imperceptible level. A reasonable conclusion is that atom-induced reaction chain effects are insignificant compared with ion induced chains. The presence of adequate Xe or other added gas which can either exchange charge or form negative ions presumably reduces the exchange exclusively to an atom-induced process as may be inferred by the close agreement between chain length under such conditions and the estimated length of an atom chain.

UPTON, L. I., NEW YORK

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(13) K. B. Persson and S. C. Brown, *Phys. Rev.*, **100**, 729 (1955).

(14) W. Mund, P. Uyskens and R. Lories, *J. chim. phys.*, **48**, 202 (1951).