

## The Theoretical Treatment of Chemical Reactions Produced by Ionization Processes Part I. The OrthoPara Hydrogen Conversion by AlphaParticles

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at  $13,700\text{ cm}^{-1}$ , which he has identified with the  $^3\Pi_1 \leftarrow ^1\Sigma^+$  transition. It would then accord with our interpretation of the bromine spectrum to assign the *B* (subsidiary) continuum of iodine to the  $^3\Pi_0+ \leftarrow ^1\Sigma^+$  transition, and the *A* (main) continuum to transitions from  $^1\Sigma^+$  to the predicted  $^1\Pi$  state. This assignment does not receive such good support from the Franck-Condon principle in the case of iodine as it does in the case of bromine. The Morse function predicts that the maximum of the  $^3\Pi_0+ \leftarrow ^1\Sigma^+$  transition of iodine should occur at  $19,000\text{ cm}^{-1}$ , which is between the experimental maxima of the *A* and *B* continua.

In the case of chlorine, the continuum with its maximum at  $30,000\text{ cm}^{-1}$  is generally ascribed to the  $^3\Pi_0+ \leftarrow ^1\Sigma^+$  transition; but Mulliken<sup>11</sup> has already pointed out that it might possibly be due to  $^1\Pi \leftarrow ^1\Sigma^+$ , since the  $U(r)$  curve for the upper state that was calculated quantum-mechanically by Gibson, Bayliss and Rice<sup>10</sup> lies somewhat above the Morse curve for  $^3\Pi_0+$ . If this is so, the continua that are associated with transitions to the  $^3\Pi_0+$  and  $^3\Pi_1$  states of chlorine are yet to be discovered, and it is interesting that the absorption curve of chlorine as measured by Halban and Siedentopf<sup>14</sup> has two humps or subsidiary max-

ima in the region of very low absorption coefficients on the long wave-length side of the maximum. This region of the chlorine continuum deserves further investigation.

This interpretation helps to remove two difficulties in the theory of the halogen spectra,<sup>13</sup> namely the apparently too great intensity of the "intersystem" transitions  $^3\Pi_0+ \leftarrow ^1\Sigma^+$ , and the apparent absence of  $^1\Pi \leftarrow ^1\Sigma^+$  transitions. The transitions have been estimated mainly from the intensities of the "*A*" continua, and if these are really due to the transition  $^1\Pi \leftarrow ^1\Sigma^+$ , transitions to the  $^3\Pi_0+$  states are less intense than had been thought. The confirmation of our interpretation will also have a consequence that may be of interest in the photochemistry of the halogens, for since the  $^1\Pi$  state dissociates into two atoms in their  $^2P_{1/2}$  state, the dissociation of halogen molecules by the absorption of light in the continuous region will produce mainly atoms in their ground state.

In conclusion, we would like to point out that the determination of the number of maxima in the  $\epsilon_1$  absorption curve by the method of temperature analysis affords a convenient method of deciding whether or not a given continuum is complex.

<sup>14</sup> H. v. Halban and K. Siedentopf, *Zeits. f. physik. Chemie* 103, 71 (1922).

## The Theoretical Treatment of Chemical Reactions Produced by Ionization Processes

### Part I. The Ortho-Para Hydrogen Conversion by Alpha-Particles

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The possible individual processes that may occur in a gaseous system under irradiation from alpha-particles have been examined from the theoretical standpoint. The ionization, clustering and the fate of the ions have been studied. The ortho-para hydrogen conversion under the influence of alpha-particles has been chosen as an example with which to illustrate the method of treatment. Recent experimental data by Capron have been analyzed to confirm his conclusion that atomic hydrogen is responsible for the large ratio of molecules converted to ions produced ( $M/N = (700\text{ to }1000)/1$ ). It is also shown

that clustering is unimportant in this case and that the paramagnetism of the ions is of negligible importance in producing the spin-isomerization. The role of mercury atoms in removing atomic hydrogen from the system is found to be negligible. Removal of atoms by three body collision of two atoms with molecular hydrogen is slow compared with removal at the walls of the reaction vessel. Analysis of this latter process shows excellent agreement with the experimental data on the conversion efficiency of the system.

IT is well known that alpha-particles in passing through various gaseous systems expend about one-half of their energy in ionization of the

molecules present and that therefore a corresponding amount of energy must be spent in excitation and dissociation of the molecules as

well as in producing translational energy. This experimental observation is in part confirmed by a theoretical calculation of Bethe<sup>1</sup> on the effect of alpha-particles on hydrogen atoms. His results indicate a 50 percent greater probability of excitation than for ionization. We might therefore expect in molecular systems a degree of reactivity due to excitation or dissociation independent of ionization, but there do not appear to be any experimental measurements to test this point. Such excitation of molecules may also arise during recombination of positive ions and electrons. In the absence of specific examination of effects due to such excitation,<sup>2</sup> we can only observe that the probability of reaction of such excited molecules should be the same as that of such species produced by photochemical excitation.

Into the details of the ionization processes under alpha-particle irradiation it is not necessary here to enter, since there is available a recent quantitative analysis of the whole ionization process as a function of sources of alpha-particles, their energy, range, ionization along a trajectory, secondary ionization and total ionization produced under given experimental conditions.<sup>3</sup> The positive ions formed in such processes by loss of a valence electron will have the valence properties of free radicals. As mass spectrographic evidence reveals, the primary positive ions which have lost a single electron are many times more numerous than any other and thus the discussion may, in general, be restricted to such processes. From mass spectrographic data also there are available, as appearance potentials, quantitative data on the energies required for the several ionization processes possible with a given molecule. Such data are readily available.<sup>4</sup>

The problem of the fate of the electron produced in the ionization process can be approached quite generally. Initially, the high speed of the electrons causes them to behave as ionizing agents, but ions so produced are included in the

total number of ion pairs ascribed to the action of a given alpha-particle. When the energies of the electrons have decreased to magnitudes of the order of dissociation energies of molecules in their path, electron attachment with accompanying dissociation to form an atom or radical and a negative ion from the original molecule sometimes occur. Studies of the formation of negative ions by electron attachment by Bradbury and others<sup>5</sup> are of especial use in this regard. At very low velocities, it emerges from such work that only molecules which possess what are virtually free valencies, i.e., orbital angular momenta or uncoupled spin, having the power of attachment of electrons. Diatomic molecules in  $^1\Sigma$  states and highly symmetrical polyatomic molecules show little or no electron affinity. The neutralization process whereby the electron disappears is discussed subsequently; consideration will also be given to the negative ion as a clustering center.

With respect to the positive ion fragment from the ionization process there are several possibilities. The ion may react with another molecule to form a new type of ion. It may also interact with such a molecule to exchange electrons in the collision process. This event needs especial examination in the case of spin-isomerization to be considered. The ion may act as a clustering centre for one or more neutral molecules attached to the ion by virtue of their polarization in the ion field. Finally, the neutralization process of the ion with one or other of the negatively charged species present together with the chemical consequences of such neutralization forms the concluding event in the processes immediately following ionization. These several alternatives will now be examined specifically in the one-component system which the ortho-para hydrogen mixture forms. This represents an especially favorable starting point since much is now known from the theoretical and practical standpoint concerning the ions and molecules involved.<sup>6</sup>

<sup>1</sup> Mott and Massey, *Theory of Atomic Collisions* (Oxford Press, 1933) pp. 185, 224; Bethe, *Ann. der Physik* **5**, 325 (1930); Blackett, *Proc. Roy. Soc. A* **135**, 132 (1932).

<sup>2</sup> The possibility of such effects was first emphasized by Wourzel, *J. de Phys. et le Rad.* **6**, 77 (1920).

<sup>3</sup> W. Mund, *L'Action Chimique des Rayons Alpha* (Hermann et Cie., Paris, 1935).

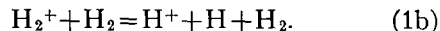
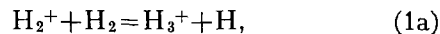
<sup>4</sup> H. D. Smyth, *Rev. Mod. Phys.* **3**, 347 (1931); H. Sponer, *Molekelspektren*, Vols. I and II (Julius Springer, 1935 and 1936).

<sup>5</sup> N. E. Bradbury, *Phys. Rev.* **44**, 883 (1933); *J. Chem. Phys.* **2**, 827, 840 (1934); N. E. Bradbury and H. E. Tatel, *J. Chem. Phys.* **2**, 835 (1934); F. Block and N. E. Bradbury, *Phys. Rev.* **48**, 689 (1935); L. B. Loeb, *Phys. Rev.* **48**, 684 (1935).

<sup>6</sup> Condon and Smyth, *Proc. Nat. Acad.* **14**, 871 (1928). E. Condon, *Phys. Rev.* **35**, 658 (1930). H. D. Smyth, *Proc. Roy. Soc. A* **102**, 283 (1922); *Phys. Rev.* **4**, 452 (1925); *Rev. Mod. Phys.* **3**, 347 (1931). W. Bleakney, *Phys. Rev.* **35**, 1180 (1930); **40**, 496 (1932). Brasefield, *Phys. Rev.* **31**,

## THE IONIZATION PROCESS

The products of ionization of hydrogen by alpha-particles have never been made the object of particular study. All that is definitely known is the number of ion pairs produced per alpha-particle and from this it is calculated that each ion consumes 33.0 electron-volts or about 100 percent more than the amount, 15.37 volts, necessary to produce the molecule ion,  $H_2^+$ . The products of ionization by electrons of controlled speeds have been very thoroughly investigated, with the aid of mass spectrographic methods.<sup>7</sup> From this it is known that up to speeds of 500 ev more than 90 percent of the primary products are the molecule ion,  $H_2^+$ , which first appears at 15.37 volts. At about 18 volts,  $H^+$ , appears weakly, while fast  $H^+$  ions are produced at 26 and again at 30 volts. These also are weak compared with  $H_2^+$ . At 15.9 volts, especially at high pressures, there is a plentiful production of  $H_3^+$  ions as a secondary effect, while, if the ion has some kinetic energy, the ion  $H^+$  also appears in quantity at high pressures. Such products may be attributed to secondary collisions described by the equations



The latter reaction requires an activation energy of at least 2.639 ev. With electron speeds from 11.5 to 15 volts there is definite evidence of atomic dissociation presumably by excitation of the molecule to the  $^3\Sigma$  state which subsequently dissociates into two H atoms. This effect is described by Smyth as "fairly strong."

It is evident that, at the relatively high pressures obtaining in alpha-particle work, all such ionization processes may occur along the track of the particle. Since, in such case, it is the singly-charged ions which predominate, we reason by analogy that the preponderant ion primarily produced by the alpha-particle is  $H_2^+$  and that this may represent upwards of 90 percent of the total primary ionization. The excess energy consumed but not in ionization may in large part have gone into the production of  $^3\Sigma$  molecules which immediately dissociate. Each pair of atoms thus formed would account for 12 volts.<sup>8</sup> On this basis one might expect approximately equal amounts of  $(2H)$  and  $H_2^+$  from the excitation and ionization processes respectively. The possible secondary processes will now be examined.

52 (1928). Hogness and Lunn, Proc. Nat. Acad. **10**, 398 (1924); Phys. Rev. **26**, 44 (1925). W. Lozier, Phys. Rev. **36**, 1417 (1930); **44**, 575 (1933). Dorsch and Kallmann, Zeits. f. Physik **53**, 80 (1929). Hughes and Skellett, Phys. Rev. **30**, 11 (1927). Dempster, Phil. Mag. **31**, 438 (1916); **3**, 115 (1927).

<sup>7</sup> Smyth, reference 4: Bleakney, Phys. Rev. **35**, 1180 (1930).

<sup>8</sup> Coolidge, James and Present, J. Chem. Phys. **4**, 187 (1936); W. Finkelnberg and W. Weizel, Zeits. f. Physik **68**, 577 (1931); N. D. Smith, Phys. Rev. **49**, 345 (1936).

THE FORMATION OF  $H_3^+$  BY SECONDARY COLLISION

The separation,  $d$ , between the centers of gravity of  $H_2$  and of  $H_2^+$  at the activated state is so large, because of the nature of their interaction energy, that each of the molecules may be assumed to rotate as freely as they do when they are far apart.

It is known that the interaction of a hydrogen atom with a hydrogen molecule requires about 7 kcal. of activation energy.<sup>9</sup> The activation energy of  $H_2 + H_2^+$  is probably small compared to this value since, at large distances, the molecule is attracted by ion-polarization forces to the ion and this attraction may persist to small distances. If it does so, an apparent activation will still arise from the rotational energy of the system as a whole. For a system rotating with a quantized angular momentum,  $j\hbar/2\pi$  the energy is increased, by the centrifugal forces, to an amount  $E_{\text{rot}} = j(j+1)\hbar^2/8\pi^2 m_H d^2$ .<sup>10</sup> Since the ion polarization energy is  $E_{\text{pol}} = -\alpha e^2/2d^4$ , these two potentials superposed give an activation energy and an activated state for every value of  $j$  different from  $j=0$ . The quantity  $\alpha$  is the polarizability of the hydrogen molecule. Following Eyring,<sup>11</sup> we obtain

<sup>9</sup> A. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930); Geib and Harteck, *ibid.*, Bodenstein Festband, 849 (1931).

<sup>10</sup> In this paper  $m$  with an appropriate subscript indicates the mass of the atom or molecule in grams, while  $M$  is the mass in atomic weight units.

<sup>11</sup> Eyring, J. Chem. Phys. **3**, 107 (1935); Eyring, Gershinowitz and Sun, J. Phys. Chem. **3**, 786 (1935).

for the rate of reaction

$$k = \frac{\kappa(2\pi m_{\text{H}_4} kT)^{\frac{1}{2}} h^{-3} [1 + \sum_{J=1}^{\infty} (2J+1) \exp - (E_{\text{rot}}^* - E_{\text{pol}}^*)(kT)^{-1}] kT h^{-1}}{(2\pi m_{\text{H}_2} kT)^{\frac{1}{2}} h^{-3} (2\pi m_{\text{H}_2^+} kT)^{\frac{1}{2}} h^{-3}}.$$

In this expression, the rotational and vibration partition functions for  $\text{H}_2$  and  $\text{H}_2^+$  have already been cancelled in the numerator and denominator. The starred energy symbols refer to the respective energies at the activated state, for which state the expression,  $j(j+1)h^2/8\pi^2 m_{\text{H}} d^2 - \alpha e^2/2d^4$ , has a maximum value. Hence, the distance,  $d^*$ , has the value,

$$d^* = (j(j+1)h^2/8\pi^2 m_{\text{H}} \alpha e^2)^{-\frac{1}{2}}, \quad (5)$$

and at this distance the activation energy becomes

$$E_{\text{rot}}^* - E_{\text{pol}}^* = j^2(j+1)^2 h^4 / 128 \pi^4 m_{\text{H}}^2 \alpha e^2. \quad (6)$$

Setting  $a^2 = h^4 / 128 \pi^4 m_{\text{H}}^2 \alpha e^2 kT$  we can write the quantity  $A$  inside the square brackets in the velocity equation as

$$A = 1 + \sum_{j=1}^{\infty} (2j+1) \exp -j^2(j+1)^2 a^2. \quad (7a)$$

Since the numerical value of  $a^2$  is small,  $2.74 \times 10^{-3} T^{-1}$ , the summation,  $A$ , may be replaced by the integral

$$A = \int_0^{\infty} (2j+1) \exp -j^2(j+1)^2 a^2 dj = \int_0^{\infty} (1/a) \exp (-y^2) dy = \sqrt{\pi}/2a = (\pi^{\frac{1}{2}}/2)(2\alpha kT)^{\frac{1}{2}} 8\pi^2 m_{\text{H}} e h^{-2}. \quad (7b)$$

Hence, our expression for the velocity of reaction becomes:

$$k = \kappa \left( \frac{m_{\text{H}_4}}{m_{\text{H}_2} m_{\text{H}_2^+}} \right)^{\frac{1}{2}} \frac{kT}{h} \cdot \frac{h^3}{(2\pi kT)^{\frac{1}{2}}} \cdot \frac{2\pi^2 m_{\text{H}_2} e}{h^2} (2\pi kT)^{\frac{1}{2}}$$

or  $k = \kappa 2\pi m_{\text{H}}^{\frac{1}{2}} e \alpha^{\frac{1}{2}} = 2.069 \times 10^{-9} \kappa$  cc per molecule per sec. or  $1.25 \times 10^{15}$  cc per mole per sec. It is evident that the velocity of this reaction is very high even when the possible rotation of the system is taken into account.

#### THE FORMATION OF $\text{H}^+$ BY SECONDARY COLLISION

In this reaction the process must be expressed by the equation,  $\text{H}_2 + \text{H}_2^+ = \text{H}_2 + \text{H} + \text{H}^+$  which consumes 60.9 calories of energy.<sup>12</sup> It occurs therefore only on collisions between molecules and ions in which the relative kinetic energy of impact is in excess of 60.9 kcal. It must therefore be a process of small probability with ions produced by electrons with velocities close to the ionization potential. The mass spectrographic data agree with this conclusion since  $\text{H}^+$  is first produced in quantity at about 18 volts  $\pm 0.3$ ; the secondary production requires that the impact contribute the necessary kinetic energy. It is also known that  $\text{H}^+$  ion tends to disappear in presence of hydrogen molecules to produce  $\text{H}_3^+$  presumably by a three body collision involving  $\text{H}^+ + \text{H}_2$ . This fact therefore renders the case of the  $\text{H}^+$  ion less important also in alpha-particle systems and enhances the relative importance of  $\text{H}_3^+$  ion.

<sup>12</sup> O. Burrau, Det. Kgl. Danske Vid. Selskab 7, 1 (1927); E. A. Hylleraas, Zeits. f. Physik 71, 739 (1931); G. Jaffe, ibid. 87, 535 (1934).

## THE FORMATION OF CLUSTERS

The general problem of clustering around ionic species may be formulated in terms of the equilibrium  $A + B^+ \rightleftharpoons A \cdot B^+$ , for which we may write the equilibrium constant  $K$  in terms of the partition functions,  $F$ , for the several species as follows:

$$K = (F_{AB^+} / F_A \cdot F_{B^+}) \exp -E_0/kT. \quad (9)$$

If  $d$  represents the distance between ion  $B^+$  and clustering molecule  $A$ , then  $E_0 = -\alpha e^2/2d^4$ . The partition function for the cluster is

$$F_{AB^+} = F_{\text{rot}_A} F_{\text{vib}_A} F_{\text{rot}_B} F_{\text{vib}_B} \frac{8\pi^2 I_{A \cdot B^+} kT}{h^2} \left( 2 \sinh \frac{h\nu_{A \cdot B^+}}{2kT} \right)^{-1} \frac{(2\pi m_{A \cdot B^+} kT)^{\frac{3}{2}}}{h^3}.$$

Here,  $I_{A \cdot B^+} = d^2(m_A m_B)/(m_A + m_B)$ . From this we deduce that

$$\begin{aligned} K &= \left( \frac{M_A + M_B}{M_A M_B} \right)^{\frac{3}{2}} d^2 \frac{(h^2 N / 2\pi kT)^{\frac{3}{2}} (8\pi^2 kT / Nh^2) \cdot 10^{16}}{2 \sinh h\nu_{A \cdot B^+} / 2kT} \exp \alpha e^2 / 2d^4 \\ &= 6.302 \times 10^{-24} \left( \frac{M_A + M_B}{M_A M_B} \right)^{\frac{3}{2}} \frac{d^2 \exp 277a/d^4}{\sinh h\nu_{A \cdot B^+} / 2kT} \text{ molecules per cc.} \end{aligned} \quad (10)$$

In this expression,  $a = (\alpha + \mu^2/3kT) \times 10^{-24} \text{ cm}^3$  where  $\alpha$  = the polarizability of the molecule  $A$  and  $\mu$  = the electric moment of molecule  $A$ . In the corresponding expression for  $K$  in moles per cc the numerical coefficient is 3.822.

For the frequency  $\nu_{A \cdot B^+}$  we assume a value  $100 \text{ cm}^{-1}$  or a value for  $h\nu_{A \cdot B^+} = 0.284 \text{ kcal}$ . The value of  $\sinh h\nu_{A \cdot B^+} / 2kT$  becomes for  $T = 300^\circ$ ,  $\sinh 0.238 = 0.240253$ . Including this in the numerical coefficient we obtain

$$K = 15.908 \left( \frac{M_A + M_B}{M_A M_B} \right)^{\frac{3}{2}} d^2 \exp 277a/d^4 \text{ moles per cc.} \quad (11)$$

The molecular concentration  $[A]$  when the partial pressure,  $P_A$ , of the species is expressed in atmospheres, for a temperature of  $300^\circ \text{ Abs.}$ , is  $[A] = 4.0600 \times 10^{-5} P_A$ . We can therefore express the ratio of concentrations of clustered ions to free ions quite generally by the expression

$$\frac{[A \cdot B^+]}{[B^+]} = 6.46 \times 10^{-4} \left( \frac{M_A + M_B}{M_A M_B} \right)^{\frac{3}{2}} d^2 P_A \exp 277a/d^4, \quad (12)$$

the distance  $d$  being expressed in A units, the polarizability  $a$  in  $10^{-24} \text{ cm}^3$ . Applying this equation to several types of clusters possible in the  $\text{H}_2 - \text{H}_2^+ - \text{H}_3^+$  system we obtain the following data:

(i)  $\text{H}_2 + \text{H}_2^+$ :  $d = 2.8\text{A}$ ;  $a = 0.8$ ;  $P_A = 1 \text{ atm.}$ ;

$$[\text{H}_2 \cdot \text{H}_2^+] / [\text{H}_2^+] = 6.46 \times 10^{-4} \times (2.8)^2 \exp 3.605 = 0.186;$$

(ii)  $\text{H} + \text{H}_3^+$ :  $d = 2.8\text{A}$ ;  $a = 0.663$ ;  $P_A = 1 \text{ atm.}$ ;  $[\text{H} \cdot \text{H}_3^+] / [\text{H}_3^+] = 0.116$ ;

(iii)  $\text{H}_2 + \text{H}_3^+$ :  $d = 2.8\text{A}$ ;  $a = 0.8$ ;  $P_A = 1$ ;  $[\text{H}_2 \cdot \text{H}_3^+] / [\text{H}_3^+] = 0.173$ .

We see, therefore, that, in hydrogen, approximately one ion in 5 to 9 will be present associated with one molecule; the probability of two molecules being associated falls to values of the order of one in 25 to 81.

## THE FORMATION OF NEGATIVE IONS

It is known from the data of Hylleraas<sup>13</sup> that the electron affinity of hydrogen atom is 16.48 kcal., so that  $H^-$  ions will be formed by interaction of electron with atomic hydrogen in the presence of a third body to dissipate excess energy as kinetic energy.

The formation of  $H_2^-$  ions may be examined by the method already employed by Pauling<sup>14</sup> for the treatment of the interaction of  $He+He^+$  to form  $He_2^+$ . The only difference in the two problems is that for  $H_2^-$  the nuclear charges are unity while they are two for the  $He_2^+$  case. Using the 1s hydrogen-like eigenfunctions  $a_1 = (Z^3/\pi)^{1/2}e^{-Zra_1}$ ,  $b_1 = (Z^3/\pi)^{1/2}e^{-Zrb_1}$ , where  $Z$  is a screening constant and  $r_{a_1}$  and  $r_{b_1}$  are the distances of electron (1) from nuclei  $a$  and  $b$  respectively, the eigenfunction which corresponds to the lowest energy state is:

$$\Psi = \frac{1}{6^{1/2}} \begin{vmatrix} a_1\alpha_1 & b_1\beta_1 & b_1\alpha_1 \\ a_2\alpha_2 & b_2\beta_2 & b_2\alpha_2 \\ a_3\alpha_3 & b_3\beta_3 & b_3\alpha_3 \end{vmatrix} + \frac{1}{6^{1/2}} \begin{vmatrix} a_1\beta_1 & b_1\alpha_1 & a_1\alpha_1 \\ a_2\beta_2 & b_2\alpha_2 & a_2\alpha_2 \\ a_3\beta_3 & b_3\alpha_3 & a_3\alpha_3 \end{vmatrix}.$$

Here  $\alpha$  and  $\beta$  are spin functions of the electron corresponding to  $S_Z = +\frac{1}{2}(h/2\pi)$  and  $-\frac{1}{2}(h/2\pi)$  respectively. The corresponding energy of the system is found to be:

$$E = -\frac{e^2}{a_0} Z \left\{ -\frac{3}{2} + \frac{1}{R} + \frac{1}{N} [-(3+2I-I^2)G - (1-2I-3I^2)J + L(aa, aa) + 2(1-I)L(aa, ab) + (2+I)L(aa, bb) - (1+3I)L(ab, ab)] + \frac{1}{2} \frac{(Z-1)}{N} [3+I+I^2+3I^3+2(1-2I-3I^2)J] \right\},$$

where  $N = (1+I-I^2-I^3)$  and the integrals

$$I = \exp -\rho \left( \frac{\rho^2}{3} + \rho + 1 \right) = \frac{1}{\pi} \int \exp -(\rho_a + \rho_b) d\tau, \quad G = \frac{1}{\pi} \int \rho_b^{-1} \exp -2\rho_a d\tau, \\ J = \frac{1}{\pi} \int \rho_a^{-1} \exp -(\rho_a + \rho_b) d\tau, \quad L(aa, bb) = \pi^{-2} \int \int \rho_{12}^{-1} \exp -2(\rho_a + \rho_b) d\tau_1 d\tau_2, \text{ etc.}$$

In these integrals, the screening constant  $Z$  times the separation,  $R$ , between the points  $a$  and  $b$  is  $\rho = ZR$  and  $\rho_{12} = Zr_{12}$ , where  $r_{12}$  is the distance between electrons 1 and 2. These integrals have been treated in the literature.<sup>15</sup> For a particular value of the internuclear separation,  $R_{a_0}$ , the screening constant  $Z$  is varied so as to make  $E$  a minimum. We obtain a minimum energy for  $R_{a_0} = 1.8A$ . Here  $E = 2E_H + 16.5$  kcal., i.e., an electron is repelled from  $H_2$  even at the most favorable internuclear separation. However, a better calculation would lead to an electron repulsion for  $H^-$  of 16.48 kcal. instead of the 37.36 kcal. of electron separation

which our calculation leads to. We assume, as did Pauling in the  $He_2^+$  case, that this type of calculation is in error by the same amount for all nuclear configurations. With this assumption, Pauling obtained excellent agreement with the experimental values for  $He_2^+$ . For this reason, we subtract  $(16.48+37.36)$  kcal. from all of our calculated energies. We now obtain a minimum energy of  $-37.4$  kcal. at  $R_{a_0} = 1.8A$ . This energy of  $H_2^-$  is plotted in Fig. 1. It is seen that there actually exist stable states for  $H_2^-$ . The zero point energy is about one kcal. However, from Fig. 1, it is evident that if an electron collides with  $H_2$  in accord with the Franck-Condon principle, it must possess an energy of around the energy of dissociation of  $H_2$  before it can form  $H_2^-$ . But this  $H_2^-$  possesses more vibra-

<sup>13</sup> Hylleraas, Zeits. f. Physik **65**, 209 (1930).

<sup>14</sup> Pauling, J. Chem. Phys. **1**, 56 (1933).

<sup>15</sup> Hirschfelder, Eyring and Rosen, J. Chem. Phys. **4**, 121 (1936).

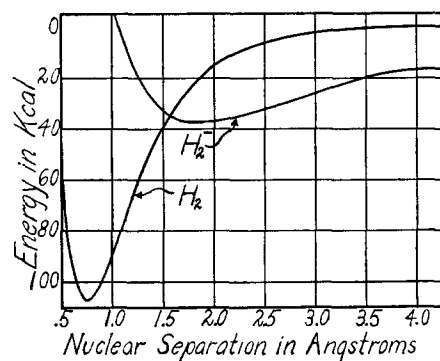


FIG. 1. Potential energy curves of  $H_2$  and  $H_2^-$ .

tional energy than is required to dissociate into  $H+H^-$  and therefore  $H_2^-$  could not be formed in this manner. If an H atom collides with  $H^-$ , it has more than enough energy to reach that part of the potential curve in which  $H_2+\epsilon$  is more stable than  $H_2^-$ . We, therefore, conclude that, (1)  $H^-$  can be formed by a three body collision between H,  $\epsilon$ , and another atom or molecule, without any activation energy.  $H^-$  may also be formed by a collision of an electron with  $H_2$  with an activation energy of about 4 to 6 ev (2)  $H_2^-$  stable states exist but they cannot be reached by electron collision with  $H_2$ . They might be formed by unusually favorable three body collisions between H,  $H^-$ , and a third atom or molecule. The probability for this ion to be formed is so low that it is not surprising that it has never been experimentally observed.

#### THE NEUTRALIZATION PROCESS

The process  $A^++B^-\rightarrow A+B$  has been observed experimentally and calculated theoretically<sup>16</sup> to have a specific reaction rate constant, expressed in cc per molecule per second, of  $\alpha \approx 10^{-6}$ , if the gas is air. For most other gases experiments give values of about this same magnitude. It is not ordinarily very specific since most gases contain sufficient impurity to combine to form the negative ions. However, in the case of unusually pure argon values as low as  $\alpha = 10^{-10}$  have been observed by Kenty.<sup>17</sup>

<sup>16</sup> E. B. Loeb and L. C. Marshall, J. Frank. Inst. **208**, 372 (1929); Thirkill, Proc. Roy. Soc. **A88**, 477 (1913); Harper, Cambridge Phil. Soc. Proc. **28**, 219 (1932); Eriksen, Phil. Mag. **18**, 328 (1909).

<sup>17</sup> Kenty, Phys. Rev. **32**, 624 (1928).

A value of  $\alpha$  as low as  $10^{-10}$  probably indicates that neutralization involves a third body in addition to the electron and positive ion while a value of  $10^{-6}$  would then indicate that no third body is necessary, the neutralization involving only a negative and positive ion.

The process of free electron capture necessarily involves three bodies, i.e., two molecules and an electron unless the resultant molecule dissociates. The third body is required to carry away enough energy to stabilize the electron-positive ion complex. If an electron is attached to a molecule to form a negative ion it may leak to a positive ion upon their near approach without having sufficient energy to escape subsequently into empty space. A stabilization collision in this case is unnecessary so that the process appears bimolecular. At atmospheric pressures such a mechanism is favored over a trimolecular one. If the molecule cannot form a negative ion then it can only stabilize the system, positive ion plus electron, if it is within a kinetic theory diameter of the positive ion when the latter is struck by the electron. Such three body collisions are much less frequent than the above type of bimolecular collision at atmospheric pressure. This would account for the slow rate in pure argon. That the third body must be in the neighborhood of the positive ion rather than the electron unless there are inelastic collisions can be seen as follows. As a consequence of the law of conservation of energy and momentum, an electron can only lose the fraction of its energy  $4m_e/m_{atom}$  in an elastic collision with an atom or molecule. To permit electron capture in this way the energy transferred must be of the order of  $kT$ . But since, in the neutralization process, the kinetic energy of the electron cannot be more than a small fraction of the ionization potential at points accessible to a third body any direct transfer of energy from the electron to the third body is negligible. This same argument applied to conservation of angular momentum excludes the possibility of the electron transferring energy to the rotational states of the molecules. The excitation of higher vibrational or electronic states of the neutral molecule is improbable but not excluded.

The electron-positive ion system is, of course, a very excited state of the molecule which is



being formed. This excited state may dissociate, or give the energy to other molecules. Radiation processes are of low probability compared to collision processes for taking up the excess energy and so can be ignored.

#### RECOMBINATION OF $H_3^+$ + ELECTRON

When  $H_3^+$  is neutralized, the resulting  $H_3$  surely dissociates since it is unstable. Initially, the  $H_3^+$  is in a singlet state. When the electron is coupled to the spin of the molecule, the total spin of the system must correspond to a doublet. Whatever electronic orbitals are involved one state, (1), of the doublet, i.e., energetically the lowest, corresponds to a binding between two of the three nuclei and this state dissociates to give  $H_2 + H$ . The other state, (2), of the doublet corresponds to a repulsion between all three atoms and hence a dissociation into three H atoms. The expression for the energy in which the spin has been properly considered and the approximations consist in neglecting certain orthogonality and multiple exchange terms are:<sup>18</sup>

$$E_1 = A + B + C - \left( \frac{1}{2}((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2) \right)^{\frac{1}{2}}, \quad (13a)$$

$$E_2 = A + B + C + \left( \frac{1}{2}((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2) \right)^{\frac{1}{2}}, \quad (13b)$$

and the occurrence of either is equally probable. The Greek letters correspond to the three single exchange bonds and Latin letters to the additive part, these states occur in pairs with equal probability of either occurrence, one yielding 3 hydrogen atoms, the other one atom and one molecule. Since the resulting molecule will be energy rich, it may dissociate on subsequent collision. The average yield from this neutralization process will therefore be more than two H atoms and less than 3 H atoms.

#### RECOMBINATION OF $H_2^+$ + ELECTRON

If the  $H_2^+$  reacts with  $H_2$  with the specific reaction rate of  $10^{15}$  cc per mole per sec. (as seems probable) the  $H_2^+$  has only a fleeting existence at atmospheric pressure of  $H_2$ . However, we may easily show what recombination processes take place between  $H_2^+$  and an electron.

$H_2^+$  is initially a doublet state. When the electron is coupled to the spin of the  $H_2^+$  the total system will be either a singlet or a triplet with relative probabilities of 1 and of 3, respectively. The singlet states of  $H_2$  are stable (excited or unexcited states) while the triplet states are all repulsive and correspond to the dissociation into two hydrogen atoms. The dissociation process is bimolecular while the capture to form the singlet state requires the presence of a third body and therefore does not occur as frequently. Often the singlet state will only result in excitation without the subsequent production of H atoms. The atom yield due to the triplet states will be  $\frac{3}{4} \times 2$  and that due to the singlet state will be somewhat less than  $\frac{1}{4} \times 2$ , the total being between 1.5 and 2.0 H atoms.

We do not consider the neutralization processes involving  $H_3^+ + H^-$  owing to the relatively low concentration of the latter species and since analysis shows that the atom yield cannot thereby be materially changed.

The general conclusion from the consideration of these neutralization processes is therefore that, the overwhelming majority of the neutralizations will involve  $H_3^+$  and produce 2 to 3 H atoms. Those processes involving  $H_2^+$  produce 2 H atoms as a maximum and in general yield between 1.5 and 2 H atoms per neutralization. Since in the formation of  $H_3^+$ , one H atom is already formed it is evident that the total net yield of atomic hydrogen will at least be from 3 to 4 H atoms per ion pair produced. Further, to the extent that the excitation processes occurring in the track of the alpha-particle may produce additional atomic hydrogen these minimum yields will be exceeded. Empirical evidence from our analysis of recent data by Lind and Livingston<sup>19</sup> on the alpha-particle reaction of hydrogen and bromine indicates that the *total* yield from ionization and excitation may reach 6 H atoms measured in terms of ion-pairs produced.

#### THE ORTHO-PARA CONVERSION

There remains for analysis the several effects of alpha particle, ions, ion-exchange and atomic hydrogen on the conversion of para to ortho

<sup>18</sup> London, *Probleme der Moderne Physik*, edited by Debye (Hirzel 1928) p. 104.

<sup>19</sup> Lind and Livingston, J. Am. Chem. Soc. **58**, 612 (1936). This work will be considered in detail in a later paper.

hydrogen at room temperatures as studied experimentally by Capron.<sup>20</sup>

### 1. Direct conversion by alpha particle

An alpha particle passes through the gaseous mixtures with velocities of the order of  $10^9$  cm per sec. Such a rapidly moving charged particle has associated with it a magnetic field as measured at the center of an  $H_2$  molecule of

$$H = -\frac{v}{c} \frac{2ea_s}{r^3(1-v^2/c^2)^{\frac{1}{2}}}.$$

Here  $r$  and  $a_s$  are the actual separation and the distance of closest approach of the alpha particle to the  $H_2$  molecule. The velocity of the alpha particle,  $v$ , is always small enough with respect to the velocity of light,  $c$ , that we may neglect the difference between  $(1-v^2/c^2)^{\frac{1}{2}}$  and unity. This field is identical with the field which Wigner<sup>21</sup> considered for the case of ortho-para conversion by paramagnetic molecules. Here we must let  $\mu_a = 2ea_s v/c$ , to use Wigner's terminology. Only the inhomogeneous part of the field is effective in producing spin-isomerism. This produces a coupling or uncoupling of the nuclear spins which is measured by the matrix components connecting the ortho with the para states. Realizing that the effect is very small, the eigenfunction for the molecule may be expanded in terms of the unperturbed rotational eigenfunctions and the coefficients evaluated by a standard perturbation method. The collision process is idealized in a manner suggested by the work of Kallmann and London,<sup>22</sup> i.e., the magnetic field is turned on with its greatest intensity for a length of time,  $t = a_s/3v$ . This method of Wigner gives a rough average of the effect and is better the shorter the time for the collision. Following Wigner we obtain for the probability of a transfer from the zero rotational level to the first

$$W = -\frac{4}{3} \frac{a_s^2 \mu_p^2 e^2}{(h/2\pi)^2 c^2 a_s^4} = \frac{2.66 \times 10^{-48}}{a_s^4}. \quad (15)$$

$W$  is only  $2.66 \times 10^{-16}$  if  $a_s = 1\text{\AA}$  and has decreased

to  $10^{-18}$  when  $a_s = 4\text{\AA}$ . We can calculate an upper limit for the number of molecules  $M$  which each alpha particle converts,

$$M_\alpha = R\rho \int_0^\infty W 2\pi r dr. \quad (16a)$$

Here  $R$  = range of the alpha particles,  $\rho$  = density of molecules in the gas. When  $r$  is less than some value,  $x$ , we assume that the molecules will certainly be converted and for  $r$  greater than  $x$  we use the value of  $W$  defined in the Eq. (15). Such an assumption leads to too large a value of  $M_\alpha$  regardless of what value of  $x$  is chosen. Therefore

$$M_\alpha < \rho R \int_0^x 2\pi r dr + R\rho(2\pi)2.66 \cdot 10^{-48} \int_x^\infty \frac{dr}{r^3}, \quad (16b)$$

$$M_\alpha < 2\pi R\rho(x^2/2 + 2.66 \times 10^{-48}/4x^4).$$

This expression is least when  $x = (2.66 \times 10^{-48})^{1/6}$ . Hence,

$$M_\alpha < 6.53 \times 10^{-16} R\rho. \quad (16c)$$

For atmospheric pressure, in  $H_2$  gas,  $R = 18.4$  cm ( $T = 15^\circ\text{C}$ ; radon) and  $\rho = 2.6 \times 10^{19}$  cm<sup>-3</sup>. Hence,  $M_\alpha < 3.1 \times 10^5$ . But the number of ion pairs formed by each  $\alpha$  particle,  $N$ , is

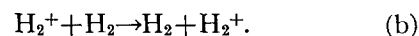
$$N = 2.2 \times 10^5;$$

$$\therefore M_\alpha/N = 1.5 \text{ as an upper limit.} \quad (17)$$

This is negligible in comparison with the experimentally observed value of  $M/N \approx 1000$ .

### 2. Ortho-para conversion by $H_2^+$ , $H_3^+$ and $H$

If  $H_2^+$  had a mean lifetime of a few collisions instead of the fleeting existence which we have already indicated in the preceding discussion, it might be supposed that, in collisions, an electron could be transferred from  $H_2$  molecules to  $H_2^+$  and this chain process would be efficient in converting para to ortho hydrogen.



Because the positive ion is of the same species as the molecule, this electron exchange is more efficient than electron exchanges between unlike ions and molecules. In the earlier experimental work on electron exchange it was thought that such a transfer would occur on a large fraction

<sup>20</sup> Capron, Ann. Soc. Sci. Bruxelles, **55**, 222 (1935).

<sup>21</sup> E. Wigner, Zeits. f. physik. Chemie **B23**, 28 (1933).

<sup>22</sup> H. Kallmann and F. London, Zeits. f. physik. Chemie **B2**, 207 (1929).

of the collisions. More recent work of Wolf<sup>23</sup> indicates that this exchange may require an activation energy of the order of the ionization potential of  $H_2$ . However, we shall prove that no spin isomerization takes place in  $H_2^+$  except during collisions or at the same time that electron jumps occur. The efficiency of the  $H_2^+$  for spin isomerization during collisions without electron transfer is similar in magnitude to that of other paramagnetic molecules.  $H_2^+$ , therefore, cannot contribute materially to the spin isomerization. The following is the proof that no spin isomerization occurs except during collision. The energy of coupling of the electron spin,  $S_e$ , with the nuclear spins,  $S_1$  and  $S_2$ , in  $H_2^+$  is:

$$Q = -\mu_p \mu_e \left[ \frac{S_e \cdot S_1}{r_1^3} + \frac{S_e \cdot S_2}{r_2^3} \right]. \quad (18)$$

Only the part of the energy which is antisymmetric with respect to the nuclei may contribute to the spin isomerization. The  $H_2^+$  (para) state is:

$$\Psi_{para} = \alpha_e(\alpha_1\beta_2 - \alpha_2\beta_1)\psi_e(x_e - x_1, x_e - x_2) \times \chi_0(x_1, x_2). \quad (19)$$

Here  $\alpha$  and  $\beta$  are the spin eigenfunctions of the electron  $e$ , and nuclei 1, and 2.  $\Psi_e(x_e - x_1, x_e - x_2)$  is the electronic eigenfunction of the molecule and  $\chi_0(x_1, x_2)$  is the nuclear eigenfunction.  $\Psi_e$ , as the notation indicates, is a function of the six components of the distance between the electron and the two nuclei, and  $\chi_0$  is a function of the nuclear coordinates only. The subscript on  $\chi$  indicates the rotational quantum number of the molecule as a whole. Operating on  $\Psi_{para}$  by the operator  $Q$ , we obtain:

$$Q\Psi_{para} = \left(\frac{h}{2\pi}\right)^2 \frac{1}{2} \mu_p \mu_e (r_1^{-3} - r_2^{-3}) \times [\Psi_{para} - \beta_e \alpha_1 \alpha_2 \psi_e \chi_0]. \quad (20)$$

As far as spin considerations go, the  $\beta_e \alpha_1 \alpha_2 \psi_e \chi_0$  will combine with the ortho  $H_2^+$  eigenfunction:  $\Psi_{ortho} = \beta_e \alpha_1 \alpha_2 \psi_e' \chi_1$ . The matrix element for this interaction is:

$$\Sigma \int \bar{\Psi}_{ortho} Q \Psi_{para} d\tau = \frac{1}{2} \mu_p \mu_e \int \chi_0 \bar{\chi}_1 d\tau_1 d\tau_2 \int \bar{\psi}_e' \times (r_1^{-3} - r_2^{-3}) \psi_e d\tau_e. \quad (21)$$

<sup>23</sup> Franz Wolf, *Zeits. f. Physik* **74**, 575 (1932); Ramsauer and Kollath, *Ann. der Physik*, **17**, 755 (1933).

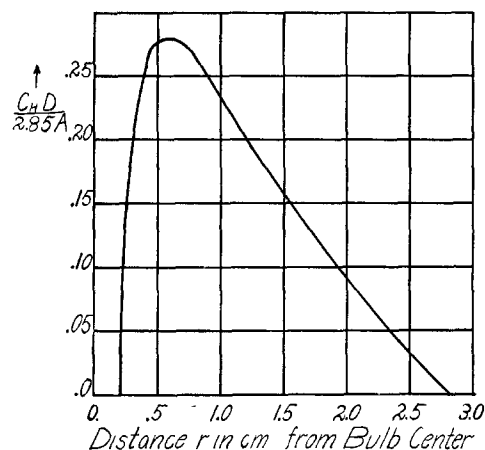


FIG. 2. Concentration of H atoms as a function of the distance from the center of the reaction vessel.

But if the electronic state  $\psi_e'$  is the same as that of  $\psi_e$ , i.e., there is no electron jump, then

$$\int \bar{\psi}_e' (r_1^{-3} - r_2^{-3}) \psi_e d\tau_e = 0 \quad (22)$$

since  $\psi_e$  is either symmetric or antisymmetric with respect to an interchange of nuclei. There are, therefore, no matrix components connecting ortho to para  $H_2^+$  except with electron jumps, and it follows that there cannot be any spin isomerization except during these electron jumps or during collisions with other molecules. The electron jumps require a considerable amount of activation energy and are, therefore, unimportant.

We next consider the probability of spin isomerization during collisions. Wigner's treatment of paramagnetic gases applies in this case without alteration. The exact position of the electron at the time of the collision is relatively unimportant as long as the electron does not spend a large portion of its time in the neighborhood of the nuclei. From the magnitude of the hyperfine structure separations in atoms, it is found that at the nucleus the magnetic field produced by the spin of an electron in a  $1s$  orbit, corresponds to the electron magnetic moment at a distance of one Bohr radius from the nucleus. We can, therefore, feel confident that the transfer of an electron during collision could not change the order of magnitude of the probability of spin isomerization. Using Wigner's formula, the

probability,  $W$ , of spin isomerization taking place during a single collision is

$$W = \frac{a_{H_2}^2 \mu_e^2 \mu_p^2}{3(h/2\pi)^2 10^{-48} a_s^6 v^2} = 1.840 \cdot 10^{-11} a_s^{-6}. \quad (23)$$

Here  $a_s$  is the distance of closest approach in Å. Since  $a_s$  is always greater than unity, it is evident that each  $H_2^+$  would have to have a preposterously long lifetime in order to affect the spin-isomerization. We find, therefore, that  $H_2^+$  can in no way contribute to  $M/N$  by direct conversion.

The probability that  $H_3^+$  will convert ortho into para hydrogen is completely negligible. Using the Wigner formula, we find that this conversion probability during a collision would be  $10^{-6}$  that of  $H_2^+$  since we must replace  $\mu_e$  by  $\mu_p$  for this case, and of course  $\mu_e/\mu_p \sim 1845$ .

The probability that H atoms will convert ortho into para hydrogen without exchange of atoms is, on each collision:  $W = 1.84 \times 10^{-11} a_s^{-6}$ . The collision diameter of  $H_2$  is 2.3 Å, and we may therefore take  $a_s = 2$  Å. Hence  $W = 3.0 \times 10^{-13}$ . We shall show that the mean lifetime of each H atom in the radiochemical experiment is less than one second and during this time it will suffer around  $10^{11}$  collisions. Therefore the probability that a H atom will convert an  $H_2$  molecule magnetically is less than three percent, and the  $M/N$  from this source is about one-tenth, i.e., completely negligible in comparison to the total  $M/N \sim 1000$ .

### 3. Ortho-para conversion by atomic hydrogen exchange

There remains for consideration only the influence of atomic hydrogen on the conversion process by the exchange reaction, and the data of the two previous sections indicate that this must be of major importance. The atomic hydrogen is produced in the ionization, excitation and neutralization processes already discussed. The net effect of the atomic species must depend on the relative rates of the exchange reaction,  $H + H_2(p) = H_2(o) + H$ , and the processes which remove atomic hydrogen from the system. Capron's data seemed to indicate that his reproducible results were obtained when the system contained the saturation concentration of mercury vapor. We, therefore, examined, by

statistical mechanics, the equilibrium in the system  $Hg + H = HgH$  and find that, at the low partial pressure of mercury vapor involved, the equilibrium is predominantly on the free atom side, so that, even though the *velocity* of interaction of Hg and H to form mercury hydride is competitive with the exchange process, no substantial diminution in H atom concentration can thereby be secured, since the molecule immediately dissociates again.

The intensity of alpha radiation falls off with the square of the distance from the source of radiation. To the approximation that the ionization is uniform over the alpha particle range between the source and outer wall, the H atoms formed in unit time per unit volume vary in the same manner. The concentration of atoms is depleted by diffusion of the atoms to the walls and also by three body recombinations with  $H_2$  as the third body. At the stationary state the following equation must be satisfied:

$$\frac{dC_H}{dt} = 0 = -D \left[ \frac{d^2 C_H}{dr^2} + \frac{2}{r} \frac{dC_H}{dr} \right] - k_1 C_{H_2} C_H^2 + \frac{aI}{4\pi(R_1 - R_2)r^2}. \quad (24)$$

Here,  $D$  is the diffusion coefficient of H in  $H_2$  gas.  $I$  is the total number of ion pairs produced per second in the reaction system and  $a$  is the total number of H atoms from all sources which are associated with the production of each ion pair.  $R_1$  is the radius of the reaction sphere and  $R_2$  that of the radon bulb. The rate constant,  $k_1$ , is the well-known constant for the three body recombination of H atoms on an  $H_2$  molecule. Actually, this process is negligible compared to the diffusion process as will presently be demonstrated. Assuming that  $k_1 C_{H_2} C_H^2$  can be neglected, the expression becomes

$$\frac{d^2 C_H}{dr^2} + \frac{2}{r} \frac{dC_H}{dr} + \frac{A}{r^2} = 0, \quad (25)$$

where  $A = aI/4\pi(R_1 - R_2)D$ . The solution may be written in the form

$$C_H = B - C/R - A \log R, \quad (26)$$

in which the constants  $B$  and  $C$  are determined in the following way. The concentration at the

wall may be taken as the number of H atoms reaching one square cm of the wall per second,  $D(dC_H/dr)$ , divided by the average velocity  $v$ , or  $(D/v) \cdot (dC_H/dr) = \lambda(dC_H/dr)$ . Here  $\lambda$  is the mean free path. Introducing this value into (26) for the concentration at the inner and outer wall, we obtain, after omitting negligibly small quantities:

$$C_H = \left[ -\frac{R_1 R_2}{R_1 - R_2} \left( \log \frac{R_1}{R_2} \right) \frac{1}{r} + \log R_1 + \frac{R_2}{R_1 - R_2} \log \frac{R_1}{R_2} - \log r \right] A$$

$$= \frac{aI}{4\pi D(R_1 - R_2)} \left[ -\frac{R_2}{R_1 - R_2} \left( \log \frac{R_1}{R_2} \right) \times \left( \frac{R_1}{r} - 1 \right) + \log \frac{R_1}{r} \right]. \quad (27)$$

From this equation we see that our assumption amounted to taking the concentrations as zero at the two boundaries. A plot of  $C_H$  against  $r$  is shown in Fig. 2. The factor  $D/2.85A$  occurs in the diagram since  $A$  varies with the individual

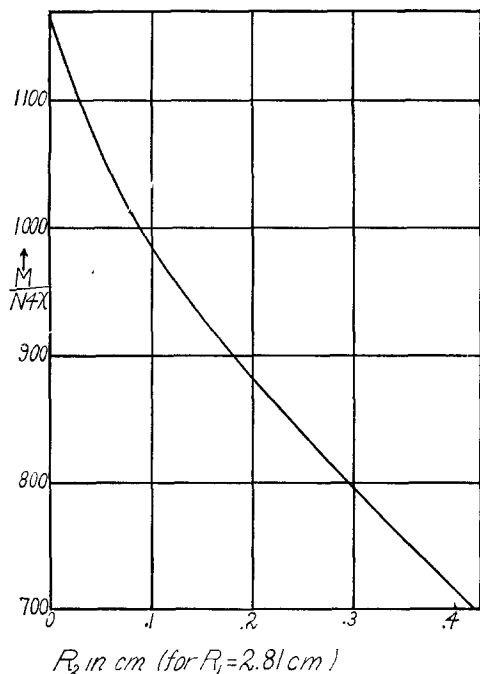


FIG. 3.  $M/N$  yield as a function of the radius of the reaction vessel. The ordinate should read  $M/NaX$ .

experiments and there is some uncertainty as to the best value of  $D$ .

Since the amount of ortho-para conversion per hydrogen atom is directly proportional to its mean life we require this latter quantity. It is evidently the number of hydrogen atoms in the vessel divided by the number formed by the alpha-particles,  $aI$ . The total number of hydrogen atoms  $H_T$  in the vessel is given by

$$H_T = 4\pi \int_{R_2}^{R_1} C_H r^2 dr$$

where  $C_H$  is the expression already obtained. Hence

$$H_T = \frac{aI}{D(R_1 - R_2)} \left[ \frac{1}{9} (R_1^3 - R_2^3) - \frac{1}{6} R_1 R_2 (R_1 + R_2) \log \frac{R_1}{R_2} \right] \quad (28)$$

and the mean life

$$\tau = H_T / aI. \quad (29)$$

Now, the rate of reaction  $H + H_2(p) = H_2(o) + H$  at room temperature is given by the expression: rate =  $(3/4) \times 8.5 \times 10^7 (C_H)(C_{H_2})$ , or  $2.59 \times 10^8 (C_H)$ , i.e., each H atom converts 2590 molecules per second with  $(C_{H_2}) = 1$  atm. From the values of  $\tau$  calculated from the above expression for various values of  $R_1$  and  $R_2$  we have constructed Figs. 3 and 4, in which  $M/N$  is set equal to  $2590\tau aX$ . The value of  $a$ , in accord with the conclusions of previous sections, is assigned the value  $\sim 6$ . The quantity  $X$  is the fraction of the total hydrogen present in the para form in excess of the equilibrium para concentration. Since Capron studied the conversion of 50 percent ortho: 50 percent para to the equilibrium mixture 75 percent ortho: 25 percent para, the value of  $X$  in his work was never in excess of  $\frac{1}{4}$ . Fig. 3 shows the variation in  $M/N$  as a function of the radius of the reaction vessel with the radius of the radon bulb constant at 0.2 cm. Fig. 4 shows  $M/N$  as a function of the radius of the radon bulb at a constant radius,  $R_1$ , of the quartz reaction vessel which we computed from Capron's reaction volume, 92 cc, to be 2.81 cm. It will be seen that the  $M/N$  yield calculated is exactly in the range

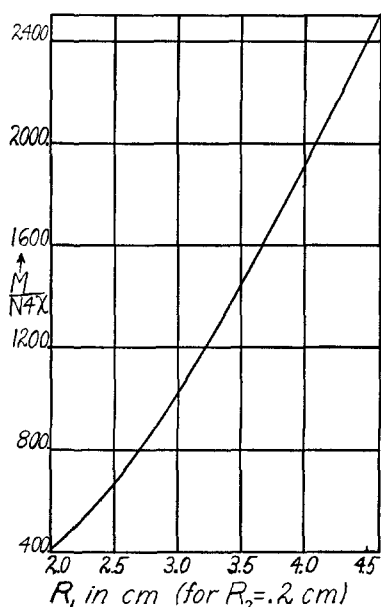


FIG. 4.  $M/N$  yield as a function of the radius of the capsule containing the radioactive material. The ordinate should read  $M/NaX$ .

of Capron's experimental observations when  $a=6$  and the concentration of parahydrogen is  $\sim 1/6$ . The values calculated depend obviously on the value assigned to  $D$ , the diffusion of H atoms in  $H_2$ ; we have used a value  $D=1.94$  cm/sec. which we derive from a value given by Smallwood<sup>24</sup> without reference to source. Alteration of this value will produce proportionate small variations in the value of  $M/N$ , as may be seen from equation (27) et seq.

For the homogeneous recombination of atomic hydrogen we use the expression,  $k_1 C_H^2 C_{H_2}$ , and, for the reaction constant  $k_1$ , use the value  $10^{16}$  cm<sup>6</sup> mol<sup>-2</sup> sec.<sup>-1</sup>.<sup>25</sup> This gives a velocity  $v=10^{16} \times (3.74 \times 10^{-13})^2 \times (2.46 \times 10^4)^{-1} = 5.69 \times 10^{-14}$  moles cc<sup>-1</sup> sec.<sup>-1</sup>. This represents a fraction

$$v/a(I/\text{volume}) = 5.69 \times 10^{-14}/6 \\ \times (2.75 \times 10^{-13}) = 0.034$$

of the atomic hydrogen which is produced, a negligible fraction as already assumed. In the preceding expression we have used six times the experimentally observed number of ion pairs as the total number of H atoms produced or disappearing per unit time. This alteration in the relative importance of wall and three body removal in the gas phase is caused by the low concentration of atomic hydrogen ( $\sim 10^{-13}$  mole cc<sup>-1</sup>). In the case investigated by Farkas and Sachsse<sup>26</sup> using excited mercury as the source of atomic hydrogen the gas phase reaction was alone important at pressures above 200 mm since the H atom concentration in their studies was  $\sim 10^{-10}$  mole cc<sup>-1</sup>.

The fact that the major removal of atomic hydrogen is at the vessel walls accounts for the observation of Capron that the  $M/N$  yield was dependent on the radon intensity and not on the square root of the intensity as would be required by the homogeneous recombination of atoms. The calculations of this section serve to show that the actual para hydrogen conversion is mainly governed by the dimensions of the radon bulb and the reaction vessel and the total pressure. Increase in the radon bulb size would increase the  $M/N$  yield. The calculations have been based on the assumption that the walls have a 100% percent efficiency of recombination. The observations of Capron would indicate that this is true when mercury is present but that in the absence of mercury, some reflection from the wall surface occurs with increased, though erratic, conversion.

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<sup>24</sup> Smallwood, J. Am. Chem. Soc. **56**, 1542 (1934). A quite recent value,  $D=1.80$  for this quantity has been obtained by Amdur, J. Chem. Phys. **4**, 339 (1936).

<sup>25</sup> Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 785 (1935).

<sup>26</sup> Farkas and Sachsse, Zeits. f. physik. Chemie **B27**, 111 (1934).