6. *The Thermal Interaction of Deuterium and Ammonia.*

By ADALBERT FARKAS.

A COMPARISON of the rates of certain reactions involving light and heavy hydrogen not only permits us to deduce conclusions with regard to the general theory of chemical change, but also affords a possibility of using heavy hydrogen as an indicator in elucidating the mechanism of complicated processes. We can also study a whole group of chemical reactions involving no other process than an exchange of hydrogen atoms, $H + XD \rightleftharpoons XH + D$.

Before the discovery of heavy hydrogen the thermal conversion of para- into orthohydrogen was the only example of this type of reaction: $H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$ (A. Farkas, *Z. Elektrochem.*, 1930, **36**, 782; *Z. physikal. Chem.*, 1930, *B*, **10**, 419), the exchange of hydrogen atoms, otherwise undetectable, being traceable by this process.

The homogeneous interaction between light and heavy hydrogen, involving the reactions $H + D_2 \rightleftharpoons HD + D$, $D + H_2 \rightleftharpoons HD + H$, was dealt with in a previous paper (A. and L. Farkas, *Proc. Roy. Soc.*, 1935, *A*, **152**, 124); and the present paper concerns the exchange reaction between deuterium and ammonia which takes place in the gas phase above 600°.

EXPERIMENTAL.

The experimental arrangement was practically the same as that already described (*idem, ibid.*).

A silica reaction vessel (vol. 68 c.c.) was heated in an electric furnace, the temperature of which was measured by a platinum–platinum-rhodium thermocouple. The ammonia and deuterium were mixed in the reaction vessel by admitting a certain pressure of each gas; then from time to time small samples of gas (0·003 c.c. at *N.T.P.*) were abstracted from the vessel by means of a capillary lock, and their deuterium contents analysed by the micro-thermoconductivity method (A. Farkas, *Z. physikal. Chem.*, 1933, *B*, **22**, 344; A. and L. Farkas, *Proc. Roy. Soc.*, 1934, *A*, **144**, 467) after the ammonia had been frozen out.

To detect any possible catalysis by the walls of the reaction vessel, the rate of the parahydrogen reconversion was measured and found to be the same (within the limits of experimental error) as that reported previously. Furthermore, the behaviour of heavy hydrogen and ammonia separately in the reaction vessel was investigated. With the former, scarcely any change was found in the deuterium content during 1 or 2 hours at the temperature at which the exchange experiments with ammonia were done, showing that an exchange reaction with hydrogen adsorbed or absorbed on the walls was negligible. With ammonia alone in the reaction vessel, its decomposition was investigated by measuring the amount of the uncondensable gas formed: at all temperatures the velocity of decomposition was negligible when compared with the exchange reaction, and therefore the amount of hydrogen and nitrogen formed did not affect the accuracy of the analysis of the deuterium content; *e.g.*, at 794° and 59 mm., the amount of ammonia decomposed in 36 minutes was only 5%, forming about 5 mm. of uncondensable gas, whereas the half-life period of the exchange reaction was found to be a few minutes at the same temperature (cf. p. 28).

In the first experiments the equilibrium between light and heavy hydrogen and light and heavy ammonia was determined. The complete equilibrium between the seven molecular species H_2, HD, D_2, NH_3, NH_2D, NHD_2, and ND_3 is given by the equations

$$H_2 + D_2 \rightleftharpoons 2HD \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$2NHD_2 \rightleftharpoons NH_2D + ND_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$2NH_2D \rightleftharpoons NHD_2 + NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$NH_3 + HD \rightleftharpoons NH_2D + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Assuming classical distribution of the H and D atoms in the equilibria (1), (2), and (3), such that

$$K_1 = [HD]^2/[H_2][D_2] = 4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$K_2 = [NHD_2]^2/[NH_2D][ND_3] = 3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$K_3 = [NH_2D]^2/[NHD_2][NH_3] = 3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

then the equilibrium constant

$$K_4 = [NH_2D][H_2]/[NH_3][HD] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which defines the equilibrium for low deuterium concentrations is identical with the expression

$$K_4 = 3[H/D]_h[D/H]_a/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $[H/D]_h$ and $[H/D]_a$ denote the ratio of the hydrogen to the deuterium content for hydrogen and ammonia respectively.

This type of isotopic equilibrium was first treated by Urey and Rittenberg (*J. Chem. Physics*, 1933, **1**, 137), and it was shown that, owing to the different zero-point energies, masses, moments of inertia, etc., of the isotopic molecules involved, the equilibrium constant would in general differ from unity, corresponding to equipartition, a value which is, however, reached at higher temperatures. For instance, the equilibrium constant of the reaction $HD + H_2O \rightleftharpoons HDO + H_2$, *viz.*, $K = [HDO][H_2]/[H_2O][HD]$, which is 2·9 at 20°, falls to 1·2 at 450° (L. and A. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071).

FIG. 1.

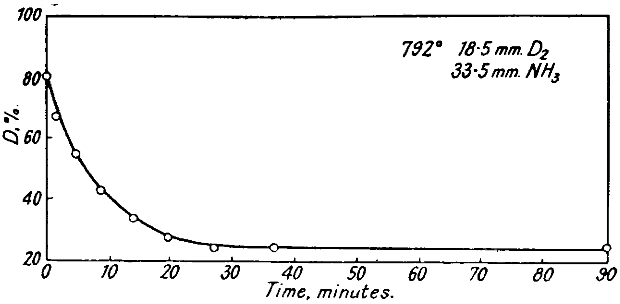


Fig. 1 shows the attainment of the equilibrium at 792° between 18·5 mm. D_2 (80%) and 33·5 mm. NH_3. In Table I the measurements are summarised, the equilibrium deuterium content of the ammonia, D_a, being calculated according to

$$D_a = (D_0 - D_h)2P_{D_2}/3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the significance of D_0 and D_h being clear from the table headings.

TABLE I.

Temp.	NH_3 press., mm. (P_{NH_3}).	D_2 press., mm. (P_{D_2}).	Original % D (D_0).	D, %, at equilibrium. In hydrogen (D_h).	In ammonia (D_a).	$[H/D]_h[D/H]_a$.
808°	49	59	80	35	36	1·04
820	38	57	80	37	43	1·28
750	66	66	80	32	32	1·00
710	55	56	80	34	37	1·14
792	33·5	18·5	80	24	21	0·84
788	26	26	88	34	36	1·09
						Mean 1·05

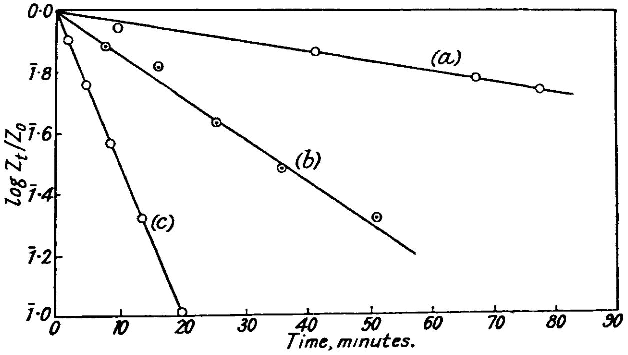
In these experiments the equilibrium is practically reached when the deuterium contents of the hydrogen and ammonia have become equal, *i.e.*, when $D_h = D_a$ or $[H/D]_h[D/H]_a = 1$ (or perhaps slightly higher).

In evaluating the following experiments, the value was assumed to be 1·00, *i.e.*, equilibrium was regarded as established when

$$P_{D_2}D_0 = (P_{D_2} + 1{\cdot}5\,P_{NH_3})D_h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The progress of the exchange reaction with time can be represented by $Z_t = Z_0e^{-k^*t}$, where $Z_t = D_t - D_h$ and $Z_0 = D_0 - D_h$ denote the excess concentrations of deuterium relative to equilibrium at times t and 0 respectively, and k^* is a constant depending on pressure and temperature. Fig. 2 shows that this relation is obeyed with some accuracy, the graphs of log Z_t/Z_0 against time being linear. From these lines, the half-life τ of the exchange reactions was determined, *i.e.*, the time required for Z_t to become halved; τ is related to k^* by the depression $\tau = (\log_e 2)/k^*$, and it is used to characterise subsequent reaction rates.

FIG. 2.



(*a*) 681°, 22 mm. D_2 + 72 mm. NH_3.
(*b*) 730°, 16 mm. D_2 + 54 mm. NH_3.
(*c*) 792°, 18·5 mm. D_2 + 33·5 mm. NH_3.

The dependence of the velocity on the pressures of ammonia and deuterium was investigated at 680—790°, with the following results :

Variation of deuterium pressure.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.
680°	10	207	45
680	21	191	38
681	22	185	48
680	40	207	47
682	65	208	45
727	16	114	15
727	17	95	18
727	31	106	19
725	40	86	20
722	107	105	15
790	4	22	6·2
788	26	26	6·2

Variation of ammonia pressure.

Temp.	p_D .	p_{NH_3}.	τ, mins.
681°	22	72	86
679	19	137	58
681	22	185	48
681	22	191	38
680	21	373	33
730	16	20	48
730	15	54	22
727	20	76	17
727	17	95	18
730	16	114	15
725	14	177	12
726	17	200	11
794	10	17	8
792	18·5	33·5	6

Alteration of the deuterium pressure over a range of 10—100 mm. did not appreciably affect τ, but increase of ammonia pressure decreased it.

From the dependence of reaction rate on temperature (see below), the apparent energy of activation (A) was calculated to be 62 kg.-cals. by means of the formula $1/\tau = \text{const.} \times e^{A/RT} \times 1/\sqrt{T}$, where the factor $1/\sqrt{T}$ is due to the fact that the concentration of the reactants is proportional to $1/T$ at constant pressure and that the number of collisions is proportional to $\sqrt{T}$.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.
681°	22	72	86
727	20	76	17
792	19	72	3

In Table II the rates of the exchange reactions between D_2 and NH_3 and between D_2 and H_2 are compared, the times of half change for the latter reaction (col. 5) being calculated on the basis of Farkas and Farkas's data (*loc. cit.*). In the temperature range 900—1000° Abs., the former reaction proceeds 30—40 times more slowly (col. 6) than the latter at the same temperature and pressure (col. 7; see p. 33).

TABLE II.

Temp.	p_{D_2}.	p_{NH_3}.	τ, mins.	τ, mins., for $H_2 + D_2$ reaction.	Ratio.	k_I/k_{II}.
788°	26	26	6·2	0·21	30	29
722	107	105	15	0·58	26	25
722	20	20	50	1·45	37	36
720	51	55	31	1	31	30
681	22	22	210	5·2	40	39

DISCUSSION.

There are four possible mechanisms for the interchange between ammonia and deuterium :

$$\text{I.}\ \left\{\begin{array}{ll} NH_3 & = NH_2 + H \\ D_2 & = D + D \\ NH_2 + D & = NH_2D \\ H + D & = HD \end{array}\right. \qquad \text{III.}\ \left\{\begin{array}{ll} D_2 & = D + D \\ D + NH_3 + M & = NH_3D + M \\ NH_3D + M & = NH_2D + H + M \end{array}\right.$$

$$\text{II.}\ NH_3 + D_2 = NHD_2 + H_2 \qquad \text{IV.}\ \left\{\begin{array}{ll} D_2 & = D+D \\ NH_3 + D & = NH_2D + H \\ H + D_2 & = HD + D \end{array}\right.$$

The dissociation mechanism according to (I) cannot contribute very much to the exchange reaction for the following reason (cf. A. and L. Farkas, *Proc. Roy. Soc., loc. cit.*). The maximum speed of this mechanism is given by the number of collisions between D atoms and NH_2 radicals, which is several orders of magnitude smaller than the number of exchange processes actually observed, even if we make the very improbable assumption that the dissociation constant for ammonia is 20 times larger than that for deuterium.

In the molecular exchange mechanism (II), τ should be proportional to the reciprocal of the ammonia pressure, whereas the variation found is much less.

Mechanism (III) is suggested by L. Farkas and Harteck's investigation (*Z. physikal. Chem.*, 1934, *B*, **25**, 257) on the stationary hydrogen-atom concentration in the photodecomposition of ammonia, in which they found evidence for a kinetic equilibrium $H + NH_3 \rightleftharpoons NH_4$. It is obvious that such a mechanism would lead to an exchange according to $D + NH_3 \rightleftharpoons NH_3D \rightleftharpoons NH_2D + H$, provided the fourth hydrogen atom is bound similarly to the other three. Further, they assume that association of $H + NH_3$ occurred at every ternary collision and required no activation energy.

Since it is now found that the apparent energy of activation is definitely larger than the energy necessary for the production of an atom by molecular dissociation, and the dependence of the reaction rate on pressure is much less than one would expect for a reaction involving ternary collisions, it may be concluded that the formation and dissociation of the ammonium radical does not lead necessarily to an exchange of atoms. A possible explanation for this behaviour is that the fourth hydrogen atom is bound with much less energy (according to Farkas and Harteck, 10 kg.-cals.) than the other three, and in the dissociation act the bond with this fourth atom is broken (Taylor and Jungers, *J. Chem. Physics*, 1934, **2**, 452).

On the basis of previous experiments on the relatively high reactivity of free hydrogen atoms, it was expected that the mechanism (IV), involving the attack of a deuterium atom on an ammonia molecule, would be the most probable one, and actually this mechanism accounts satisfactorily, as will be seen, for the kinetics of the exchange reaction between ammonia and deuterium if one assumes that in this mechanism the rate-determining step is the reaction $D + NH_3 \rightleftharpoons NH_2D + H$, which proceeds about 30—40 times more slowly than the step $H + D_2 \rightleftharpoons HD + D$.

In order to deduce the kinetic equation of this exchange reaction, we must investigate the dissociation equilibria $NH_3 = NH_2 + H$ and $D_2 = D + D$, and then calculate the stationary hydrogen- and deuterium-atom concentrations which are established by the exchange reactions $D + NH_3 = NH_2D + H$, $H + D_2 = HD + D$, etc.

The dissociation equilibrium of D_2 is known and is given by the expression

$$\log K_{D_2} = \log \frac{P_D{}^2}{P_{D_2}} = -\frac{Q_0}{4{\cdot}57T} + \frac{3}{2}\log \mathrm{T} + \frac{1}{4{\cdot}57}\int \frac{T}{T^2}\int C'_{D_2}\,dT + 2i_D - i_{D_2} \quad (12)$$

(Q_0 = energy of dissociation at absolute zero, C' = vibrational specific heat, i = chemical constant).

For the dissociation of NH_3 into NH_2 and H a similar expression is valid :

$$\log K_{NH_3} = \log \frac{P_H \, . \, P_{NH_2}}{P_{NH_3}} = -\frac{Q_0}{4{\cdot}57T} + \frac{5}{2}\log T + \frac{1}{4{\cdot}57}\int \frac{dT}{T^2}\int C'_{NH_3} dT$$

$$-\frac{1}{4{\cdot}57}\int \frac{dT}{T^2}\int C'_{NH_2}\,dT + i_H + i_{NH_2} - i_{NH_3} \quad . \quad . \quad (13)$$

but we have far less information for this equilibrium than for the preceding one.

The term $\frac{5}{2}\log T$ is introduced in (13) instead of $\frac{3}{2}\log T$ since the molar heats of the polyatomic molecules NH_3 and NH_2 are :

$$C_{p,\,NH_3} = \tfrac{8}{2}R + C'_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14a)$$

and

$$C_{p,\,NH_2} = \tfrac{8}{2}R + C'_{NH_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14b)$$

where the vibrational specific heats C'_{NH_3} and C'_{NH_2} are given by

$$C' = \sum_i \phi\left(\frac{h\nu_i c}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

ϕ denoting Einstein's function, h Planck's constant, k Boltzmann's constant, c the velocity of light, and ν_i the vibrational frequencies of the molecule (in cm.$^{-1}$). For NH_3, the following frequencies have been used : 3336, 3300 (double), 1630 (double), and 950 cm.$^{-1}$; and for NH_2, in the absence of better values, those of the similarly shaped H_2O, *viz.*, 3895, 3803, and 1635 cm.$^{-1}$.

The chemical constants have the following values :

$$i_H = -\,1{\cdot}28 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

$$i_{NH_2} - i_{NH_3} = \tfrac{3}{2}\log \frac{M_{NH_2}}{M_{NH_3}} + \log \frac{\bar{I}_{NH_2}}{\bar{I}_{NH_3}} + \log \frac{g_{NH_2}}{g_{NH_3}} \cdot \frac{s_{NH_3}}{s_{NH_2}} \quad . \quad . \quad (16b)$$

M denoting the mass, $\bar{I}$ the average moment of inertia ($\bar{I} = \sqrt{I_A I_B I_C}$), g the multiplicity, and s the symmetry number (3 for NH_3 ; 2 for NH_2).

The three moments of inertia for NH_3 are $I_A = I_B = 2{\cdot}8 \times 10^{-40}$ and $I_C = 4{\cdot}4 \times 10^{-40}$ g.-cm.^{2}. For NH_2 we obtain $I_A = 2{\cdot}7 \times 10^{-40}$, $I_B = 3{\cdot}0 \times 10^{-40}$, and $I_C = 0{\cdot}9 \times 10^{-40}$ g.-cm.^{2}, if we take the N–H and H–H distances and the angle between the two N–H bonds the same as in NH_3 (N–H = 1·02 ; H–H = 1·64 Å.).*

Assuming the ground state of NH_3 to be a singlet ($g_{NH_3} = 1$) and that of NH_2 a doublet ($g_{NH_2} = 2$), we obtain $i_H + i_{NH_2} - i_{NH_3} = 1{\cdot}1$.

The double integrals have the value of − 0·18 at the neighbourhood of $T = 1000°$ Abs., and we obtain for this temperature range

$$K_{NH_3} = -\frac{Q_0}{4{\cdot}57T} + \tfrac{5}{2}\log T - 1{\cdot}28 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Q_0 is not known accurately. An upper limit is given as 120 kg.-cals., since at a wavelength corresponding to this energy the spectrum of ammonia shows predissociation to $NH_3 = NH_2 + H$ (Bonhoeffer and Farkas, *Z. physikal. Chem.*, 1927, **139**, 337).

The average binding energy of the NH bond in ammonia is about 83 kg.-cals., but this does not necessarily imply that in the separation of the first hydrogen atom the same amount of energy is spent. It is more likely that the dissociation energy of this atom is

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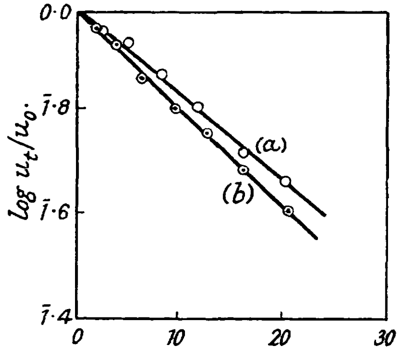
* The author has to thank Dr. Sutherland for the data concerning the NH_3 molecule.

much larger, for in water the dissociation energy for $H_2O = HO + H$ is 117 and that for $OH = O + H$ is 102 kg.-cals. (Bonhoeffer and Reichardt, *ibid.*, 1928, **139**, 75). Bonhoeffer and Harteck (" Grundlagen der Photochemie," Steinkopf, Dresden und Leipzig, 1933, p. 81) take the dissociation energy as 117 kg.-cals., which was deduced from the infrared spectrum of ammonia by Ellis (*Physical Rev.*, 1929, **33**, 27). With this value we obtain at 1000° Abs., $\log K_{NH_2} = -25{\cdot}6 + 7{\cdot}5 - 1{\cdot}3 = -19{\cdot}4$, or $K_{NH_2} = 4 \times 10^{-20}$, whereas the dissociation constant for D_2 is $K_{D_2} = 3{\cdot}7 \times 10^{-18}$ (Johnston and Long, *J. Chem. Physics*, 1934, **2**, 389).

Naturally, the value for K_{NH_2} so obtained is very uncertain, owing mainly to the uncertainty in the value of Q_0; *e.g.*, if we assume $Q_0 = 108$ kg.-cals., we obtain the same dissociation constant for ammonia as for deuterium.

Attempts to obtain some information about the dissociation of ammonia experimentally were made as follows. The thermal reconversion of para-hydrogen is caused by the reaction $H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H$, and the reaction rate is governed by the hydrogen-atom concentration (A. Farkas, *Z. physikal. Chem.*, 1930, *B*, **10**, 419). If ammonia is dissociated, its presence should increase the reaction velocity in proportion to the additional atoms produced by its dissociation. It was found that the rate of reconversion of 16 mm. of p-hydrogen was only increased 1·15-fold when 251 mm. of ammonia were added (see Fig. 3, in which u denotes the excess concentration of $p\text{-}H_2$ relative to equilibrium). From this experiment, we can conclude that on addition of ammonia the hydrogen-atom concentration is scarcely altered, and we are justified in assuming that it is governed by the dissociation of hydrogen, whereas the dissociation of ammonia is negligible.

FIG. 3.



(*a*) *Without* NH_3 *addition.*
(*b*) *With* NH_3 *addition.*

We can now estimate the stationary H- and D-atom concentrations established in a mixture of deuterium and ammonia if the exchange reactions (18) and (19) occur.

$$H + D_2 \overset{k_1}{\underset{k_2}{\rightleftharpoons}} HD + D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$D + NH_3 \overset{k_5}{\underset{k_6}{\rightleftharpoons}} NH_2D + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Naturally, as soon as some HD and NH_2D are formed, the reactions

$$H + HD \overset{k_3}{\underset{k_4}{\rightleftharpoons}} H_2 + D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$D + NH_2D \overset{k_7}{\underset{k_8}{\rightleftharpoons}} NHD_2 + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

followed by

$$D + NHD_2 \overset{k_9}{\underset{k_{10}}{\rightleftharpoons}} ND_3 + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

come into play. For the sake of simplicity, we will assume that there are only two forward and two backward reactions :

$$H + (\text{heavy hydrogen}) \rightleftharpoons D + (\text{light hydrogen}) \quad . \quad . \quad . \quad . \quad (23)$$

$$D + (\text{light ammonia}) \rightleftharpoons H + (\text{heavy ammonia}) \quad . \quad . \quad . \quad . \quad (24)$$

where the names " light " and " heavy " designate the mixture of the corresponding compounds. If we assign to forward and reverse reactions the same velocity constants, we have

$$k_{I} = k_1 = k_4 = 2k_3 = 2k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and

$$k_{II} = k_5 = k_{10} = \tfrac{3}{2}k_7 = \tfrac{3}{2}k_8 = 3k_9 + 3k_6{}^{*} \quad . \quad . \quad . \quad . \quad (26)$$

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* These two sets of velocity constants lead to the establishment of the equilibria (1), (2), (3), and (4).

Although from previous experiments we know that for the reactions (18) and (20) this is not exactly true, k_1/k_4 being $= 0{\cdot}48$, yet this simplification does not involve a great error in the calculation of the velocity constants, since that for the reactions (18) and (20) will turn out to be 30 times larger than that for the reactions (19), (21), and (22), and therefore the difference between the individual constants in one reaction might be neglected.

We will assume that at the beginning of the reaction a stationary H- and D-atom concentration is established which is invariant during the course of the reaction. Since the rate of the exchange reaction is much larger than the rate of dissociation and recombination of atoms, we might neglect the contribution of the last two processes to the alteration of the H- and D-atom concentration. The stationary concentration is reached if the production and consumption of H and D atoms by exchange is equal. If at the beginning of the reaction we start with 100% D_2 and pure NH_3 (pressures P_{D_2} and P_{NH_3}), then if the deuterium content of the hydrogen has decreased to u%, that of the ammonia has become $x = (1 - u)2P_{D_2}/3P_{NH_3}$. The numbers of hydrogen atoms produced and disappearing are given by (27) and (28) respectively :

$$[D]\{k_2[HD] + k_4[H_2] + k_5[NH_3] + k_7[NH_2D] + k_9[NHD_2]\} \quad . \quad . \quad (27)$$

$$[H]\{k_1[D_2] + k_3[HD] + k_6[NH_2D] + k_8[NHD_2] + k_{10}[ND_3]\} \quad . \quad . \quad (28)$$

For the stationary state these two expressions are equal.

If we introduce the simplification relating to the individual velocity constants, (25) and (26), and remember that as a consequence of (5)—(8)

$$[H_2] = (1 - u)^2P_{D_2} \quad . \quad . \quad . \quad (29a)$$

$$[HD] = 2(1 - u)P_{D_2} \quad . \quad . \quad . \quad (29b)$$

$$[D_2] = u^2P_{D_2} \quad . \quad . \quad . \quad . \quad . \quad (29c)$$

$$[NH_3] = (1 - x)^3P_{NH_3} \quad . \quad . \quad . \quad . \quad (30a)$$

$$[NH_2D] = 3(1 - x)^2xP_{NH_3} \quad . \quad . \quad (30b)$$

$$[NHD_2] = 3(1 - x)x^2P_{NH_3} \quad . \quad . \quad (30c)$$

$$[ND_2] = x^3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad (30d)$$

and

$$x = (1 - u)2 \,.\, P_{D_2}/3P_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

we obtain, by equating (27) and (28), for the ratio $f = [H]/[D]$:

$$f = \frac{[H]}{[D]} = \frac{k_{\text{I}}P_{D_2} \,.\, (1 - u) + k_{\text{II}}P_{NH_3}(1 - x)}{k_{\text{I}}P_{D_2}u + k_{\text{II}}P_{NH_3}x} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

or, introducing (31),

$$f = \frac{[H]}{[D]} = \frac{P_{D_2}(k_{\text{I}} - \frac{2}{3}k_{\text{II}})(1 - u) + k_{\text{II}}P_{NH_3}}{P_{D_2}(k_{\text{I}} - \frac{2}{3}k_{\text{II}})u + \frac{2}{3}k_{\text{II}}P_{D_2}} \quad . \quad . \quad . \quad . \quad . \quad (32a)$$

This ratio will define [H] and [D] during the reaction if we know either [H] or [D] or [H] + [D].

At the beginning of the reaction we have practically only deuterium atoms, their concentration being

$$[D]_0 = \sqrt{K_{D_2}P_{D_2}} \,\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

By the exchange reactions (23) and (24), hydrogen atoms are formed at the expense of these deuterium atoms. Since both types of atom disappear by forming H_2, D_2, and HD molecules

$$[D]_0 = [H] + [D] \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

if we assume that the recombination constants for H_2 and D_2 are equal and that for HD is twice as large.* The formulæ (32), (33), and (34) define [H] and [D] during the reaction.

Experimentally, the change in the deuterium content of the hydrogen (u) is measured, and this is governed by the equation

$$- du/dt = k_{\text{I}}\{[H]u - [D](1 - u)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

or, with $[H]/[D] = f$, as given by the equation (32a),

$$-\frac{du}{dt} = k_{\text{I}}[D]\left\{\frac{(k_{\text{II}}P_{NH_3} + \frac{2}{3}k_{\text{II}}P_{D_2})u - \frac{2}{3}k_{\text{II}}P_{D_2}}{P_{D_2}(k_{\text{I}} - \frac{2}{3}k_{\text{II}})u + \frac{2}{3}k_{\text{II}}P_{D_2}}\right\} \quad . \quad . \quad . \quad . \quad (36)$$

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* This is not exactly true, and involves the same simplification as formula (25).

If we introduce, instead of u, the excess concentration relative to equilibrium [cf. (11)]

$$Z = u - P_{D_2}/(\tfrac{3}{2}P_{NH_3} + P_{D_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (37)$$

we obtain

$$-\frac{dZ}{dt} = \frac{k_I k_{II}[D](\tfrac{3}{2}P_{NH_3} + P_{D_2})Z}{\tfrac{3}{2}P_{D_2}[(k_I - \tfrac{2}{3}k_{II})u + \tfrac{3}{2}k_{II}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (38)$$

or if we express [D] in terms of K_{D_2} and P_{D_2} according to equations (32), (33), and (34)

$$-\frac{dZ}{dt} = \frac{k_{II}(P_{NH_3} + \tfrac{2}{3}P_{D_2})\sqrt{K_{D_2}P_{D_2}}Z}{P_{D_2} + P_{NH_3}k_{II}/k_I} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (39)$$

This formula interprets the experimental data obtained for the reaction velocity (cf. $Z_t = Z_0e^{-k^*t}$, p. 27) since

$$k^* = \frac{k_{II}(P_{NH_3} + \tfrac{2}{3}P_{D_2})\sqrt{P_{D_2}K_{D_2}}}{P_{D_2} + P_{NH_3}k_{II}/k_I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (39a)$$

In order to find the values for k_I and k_{II}, it is the best to compare the velocity of the exchange reactions with that of the reaction $H_2 + D_2$ (cf. Table II), the rate of which is given by

$$dm/dt = 2k_1k_4\sqrt{K_{H_2}P_{H_2} + K_{D_2}P_{D_2}}m/(k_1 + k_4) \quad . \quad . \quad . \qquad (40)$$

with $m = [HD]_\infty - [HD]$.
If we put $k_I = k_1 = k_4$, we have

$$dm/dt = k_I \times 1{\cdot}65\sqrt{K_{D_2}P_{D_2}}m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (41)$$

since $P_{H_2} = P_{D_2}$ and $K_{D_2}/K_{H_2} = 1{\cdot}74$ at 1000° Abs.
If we put $P_{D_2} = P_{NH_3}$ in equation (39), we obtain

$$-dZ/dt = 1{\cdot}67Zk_Ik_{II}\sqrt{K_{D_2}P_{D_2}}/(k_I + k_{II}) \quad . \quad . \quad . \quad . \quad . \qquad (42)$$

The relative rate of the reactions between H_2 and D_2 and between NH_3 and D_2 is given by $(k_I + k_{II})/k_{II}$, which is 30—40 according to col. 6 of Table II. From these values, we find for the ratio k_I/k_{II} the figures listed in col. 7 of Table II. According to these figures it seems that the ratio k_I/k_{II} increases with decreasing temperature. Such a behaviour is to be anticipated if the slowness of the reaction $D_2 + NH_3$ compared with the reaction $H_2 + D_2$ is due to a higher energy of activation.

We can compare the dependence of the reaction velocity on the ammonia and the deuterium pressure, as found experimentally (see p. 28) and as given by formula (39), in the following way. From the measurements of the interaction between H_2 and D_2, we find $k_I\sqrt{K_{D_2}} = 0{\cdot}070$ at 1000° Abs. and 0·0168 at 953° Abs. (pressure in mm. Hg; time in minutes). With the values $k_I/k_{II} = 35$ and 40, we obtain $k_{II}\sqrt{K_{D_2}} = 0{\cdot}00200$ and 0·00042 at these two temperatures respectively. Using these values, we can calculate k^* according to formula (39a) and compare the calculated figures with those obtained from the experimental half-life times (τ) according to $k^* = (\log_e 2)/\tau$. The calculated and observed values of k^* are listed in Table III. Evidently, the dependence of the reaction rate on both the ammonia and the deuterium pressure is represented fairly well by formula (39) in the pressure range investigated, and the agreement between theory and experiment is therefore satisfactory.

The next question to decide is why reaction (19) is so much slower than (18). The kinetic cross-sections of ammonia and hydrogen (or deuterium) are very nearly equal. The collision frequency between two particles with masses m_1 and m_2, being proportional to $\sqrt{(m_1 + m_2)/m_1m_2}$, will differ in these two reactions by the factor $\sqrt{[(2 + 17)/2 \times 17][4 \times 1/(4 + 1)]} = 0{\cdot}67$. If we allow for this difference in the collision frequencies, we still find that reaction (19) proceeds about 25 times more slowly than reaction (18). This lower reactivity can be due either to a lower steric factor or to a higher activation energy. The activation energy for the reaction $D + NH_2$ can be estimated in

TABLE III.

Temperature 953° Abs.

p_{D_2}.	p_{NH_3}.	k^* (obs.).	k^* (calc.).	p_{D_2}.	p_{NH_3}.	k^* (obs.).	k^* (calc.).
22	72	0·0080	0·0072	10	207	0·0153	0·0186
19	137	0·0119	0·0123	21	191	0·0182	0·0153
22	185	0·0144	0·0147	22	185	0·0144	0·0148
22	191	0·0181	0·0151	40	207	0·0147	0·0136
21	378	0·0209	0·0258	65	208	0·0154	0·0121
			Temperature 1000° Abs.				
16	20	0·0144	0·0148	16	114	0·0460	0·0515
15	54	0·0313	0·0302	17	95	0·0383	0·0442
20	76	0·0406	0·0360	31	106	0·0363	0·0377
17	95	0·0384	0·0445	40	86	0·0345	0·0336
16	114	0·0460	0·0515	107	105	0·0460	0·0329
14	177	0·0575	0·0730				
17	200	0·0638	0·0766				

two different ways : (i) from the apparent heat of activation calculated from the dependence of the reaction rate on temperatures; (ii) from the relative rate of the reactions (19) and (18). The apparent heat of activation is 62 kg.-cals., and contains also half of the dissociation energy of D_2 (52 kg.-cals.) which is used up in the formation of the D atoms. By subtracting this figure, we obtain 10 kg.-cals. as the energy of activation of the reaction (19). This value is definitely higher than the average activation energy of the reactions (18) and $D + H_2 = HD + H$, which is about 6 kg.-cals.

From the relative rate of 25, we can estimate the additional heat of activation if we assume that the steric factors for (19) and (18) are equal. From the formula $\log_e 25 = \Delta A/RT$, we find the additional energy of activation (ΔA) at 1000° Abs. to be 6·5 kg.-cals., giving 12·5 kg.-cals. as the total energy of activation for the reaction (19).

The discrepancy between the energy of activation as calculated from the dependence of the reaction velocity on temperature and from the relative rate disappears if we assume that the steric factor for the interchange between D and NH_3 is only 1/4 of that of the reaction $H_2 + D_2$, which is about 0·07 (Farkas and Farkas, *loc. cit.*).

One might be inclined to regard this smaller steric factor as due to the fact that in the pyramidal ammonia molecule the area of attack for the deuterium atom is restricted to the position of the nitrogen atom, whereas any approach of the deuterium to the hydrogen atoms cannot lead to an exchange reaction. On the other hand, in the deuterium molecule both atoms are equally reactive. Such a connexion is, however, purely qualitative, since it was shown by Wigner (*Z. physikal. Chem.*, 1932, *B*, **19**, 203) that in the interaction of hydrogen atoms and molecules only those atoms are exchanged which are coming from a certain direction (determined by a relatively small spatial angle relative to the molecular axis), and we do not know the magnitude of this angle determining the favourable directions for the interchange $D + NH_3$.

A definite evaluation of the energy of activation and steric factor involved in reaction (19) could be carried out by using a wider temperature range. Geib and Steacie (*ibid.*, 1935, *B*, **29**, 215) investigated this interaction at room temperatures, the deuterium atoms being produced in a discharge tube; they found that at 100° the velocity is only 6 times slower than the exchange reaction between hydrogen atoms and molecules investigated by Geib and Harteck (*ibid.*, Bodensteinband, 1931, p. 849) with the same technique. These results cannot be reconciled with those of the present investigation carried out at high temperatures, since even an additional activation energy of only 3 kg.-cals. should make the reaction $D + NH_3$ go 60 times more slowly at 100° than the reaction $H + H_2$.

To obtain some more information about the exchange reaction (19) at low temperatures, the mercury-sensitised photo-reaction was investigated, in which the hydrogen (or deuterium) atoms are formed by impact with excited mercury atoms. Preliminary experiments[*] have given the following results (room temperature; pressure 50—100 mm.) : (1) The relative rates of the mercury-sensitised ortho-para conversion for H_2 and D_2 are in the ratio

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[*] For details, see a forthcoming paper in collaboration with Melville.

ca. 1·4 : 1; this result is in agreement with the experiments of A. and L. Farkas on the thermal conversion of ortho-deuterium, and shows that the activation energy for the reaction $D + D_2 = D_2 + D$ is practically the same as that for $H + H_2 = H_2 + H$. (2) The rate of the para-hydrogen conversion remains unaltered if ammonia is added or if the short-wave range of the mercury light is cut out by an acetic acid filter. (3) In the unfiltered mercury light, an exchange reaction is observed between NH_3 and D_2 proceeding about 5 times more slowly than the conversion of para-hydrogen. (4) This exchange reaction is practically completely stopped if the short-wave range of the mercury radiation is cut out.

The last two results are in agreement with earlier experiments carried out by Taylor and Jungers (*loc. cit.*), according to which the exchange reaction can be accounted for by a decomposition of ammonia in the short-wave light and by a subsequent regeneration of the ammonia molecule from NH_2 and D. Comparison of the relative rates of the para-hydrogen conversion and of the exchange reaction reveals that the collision efficiency of reaction (19) is at least 100 times smaller at room temperature than the collision efficiency of the reaction $H + H_2 = H_2 + H$. Such a relative collision efficiency is compatible with the results of the present investigation, but is in marked disagreement with those of Geib and Steacie. Whether, and to what extent, the relatively high collision efficiency found by these authors is due to processes other than the interaction of $D + NH_3$ in the gas phase, requires further investigation.

Finally, it is recorded that, including some preliminary experiments with methane and water at 1000° Abs., the following relative rates were found for the given exchange reactions :

$$\begin{array}{ccccccc} D_2 + H_2 & : & D_2 + CH_4 & : & D_2 + NH_3 & : & D_2 + H_2O \\ 100 & : & 20 & : & 3 & : & 1 \end{array}$$

This series does not agree with the experiments of Geib and Steacie by the atomic hydrogen technique at and above room temperature, since these authors find that the exchange reaction with methane is the slowest. No explanation can yet be given for this discrepancy, but the possibility of wall reactions cannot be ignored.

SUMMARY.

The kinetics of the exchange reaction between ammonia and deuterium have been investigated in the gas phase at 680—780° and at pressures of 10—400 mm. of mercury.

The progress of the reaction, the dependence of its rate on the partial pressures and on temperature, and its absolute rate can be satisfactorily explained by assuming that the rate-determining step $D + NH_3 = NH_2D + H$ occurs 30—40 times more slowly than the reaction $H + D_2 = HD + D$.

The atoms responsible for the exchange reaction are formed by the thermal dissociation of deuterium, that of ammonia ($NH_3 = NH_2 + H$) being negligible. The lower reactivity of deuterium atoms with ammonia than of hydrogen with deuterium is due to the fact that the energy of activation for the former reaction is 11 ± 1 kg.-cals., and may be partly due to a lower steric factor. This result is in agreement with some preliminary experiments on the mercury-sensitised photochemical exchange reaction between D and NH_3.

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