

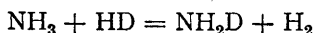
THE CATALYTIC INTERACTION OF AMMONIA WITH DEUTERIUM.

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In a previous communication ¹ an account was given of an exchange reaction between deuterium and ethylene. A number of similar reactions involving organic substances have since been investigated.² The subject matter of this paper deals with an exchange reaction between ammonia and deuterium which may be written



and which occurs at the surface of an iron catalyst.³ Apart from it being representative of a new group of exchange reactions it is of interest in connection with the catalytic synthesis of ammonia.

Experimental.

In previous experiments ⁴ it was found that even apparently outgassed material contains a certain amount of hydrogen absorbed in such a form as to become apparent by an exchange reaction when brought into contact with deuterium. A catalyst possessing a negligible amount of such occluded gas can be prepared by forming a metallic mirror by evaporation

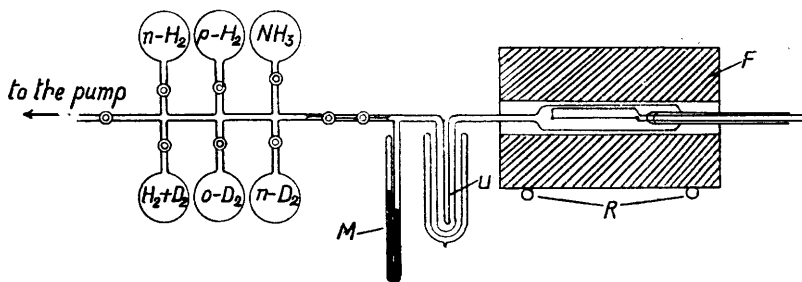


FIG. 1.

of an iron wire. Such mirrors when deposited at room temperature are readily prepared, reproducible in activity, reasonably active and stable.

The experimental arrangement is shown in Fig. 1. The reaction vessel (12 cms. long and 2 cms. in diameter) contained an axially mounted iron (electrolytic) wire 10 cms. long and 0.2 mm. in diameter arranged with leads in the usual way so as to permit of electric heating. The U-tube U

¹ A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.*, 1934, **146A**, 630.

² I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663, 1164.

³ Cf. also H. S. Taylor and J. C. Jungers, *J. Amer. Chem. Soc.*, 1935, **57**, 660.

⁴ A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1935, **31**, 821.

was cooled to -50°C . in order to keep tap grease and mercury from poisoning the catalyst. With these precautions the catalyst did not markedly decrease even after a week's use at 200°C .

Before deposition of the catalyst the reaction vessel was thoroughly outgassed in the furnace F at 350°C . (or using Pyrex vessels at 500°C .) the wire was being maintained at 900°C . The furnace was then removed by means of the rollers R and the wire heated to 1100°C – 1200°C . to evaporate the iron. This temperature was maintained (with continuous exhaustion) until a uniform mirror was formed. If the catalyst has once been poisoned (e.g., by admission of air to the reaction vessel) a new catalyst was prepared by evaporating fresh iron in the same vessel. The evaporation process could be repeated four or five times before the wire broke.

In order to obtain more information about the interaction of hydrogen and ammonia on this catalyst, the *ortho-para*-conversion and interaction of hydrogen and of deuterium and the decomposition of ammonia were investigated in addition to the exchange reaction between ammonia and deuterium.

To investigate the exchange reaction and the *ortho-para*-conversion, the micro-thermoconductivity method was employed, ammonia being frozen out in a trap cooled by liquid air.⁵ The decomposition of ammonia was determined by extracting samples of gas from the reaction vessel and measuring the pressure caused by this sample after freezing out the ammonia.

The following gases were used: ammonia (purified by fractional distillation *in vacuo*), deuterium (80 to 100 per cent. D), ortho-deuterium⁶ (100 per cent. D, prepared by adsorption on charcoal at 20°K . and subsequent evaporation), parahydrogen (prepared in a similar way) and a mixture of hydrogen and deuterium (containing only H_2 and D_2 molecules). All gases were free from oxygen, the hydrogens were initially purified by passage through palladium. The pressures of the gases admitted into the reaction vessel were measured by the manometer M (see Fig. 1).

The experiments to be described were carried out partly on the same catalyst, partly on different catalysts.

The Exchange Reaction between Ammonia and Deuterium.

Since in all experiments the rate of the exchange reaction was determined by measuring the decrease in the D-content of the deuterium originally added special care had to be taken to avoid the following sources of error. The D-content of the deuterium may decrease by an exchange reaction with hydrogen occluded or absorbed by the catalyst or formed by a catalytic decomposition of ammonia taking place on the surface of the catalyst. Separate experiments excluded the former possibility since—as has already been mentioned—no interchange could be observed with gases occluded by these catalysts. Thus there was only

TABLE I.

Temperature $^{\circ}\text{C}$.	Previous Treatment of the Catalyst.	Minutes.	Per Cent. D.
236	30 per cent. D	0	96
		5	96
		12	95
236	96 per cent. D	0	0
		6	1
		15	2

⁵ (a) A. Farkas, *Z. physik. Chem.*, 1933, **22B**, 344; (b) A. and L. Farkas, *Proc. Roy. Soc.*, 1934, **144A**, 467.

⁶ A. Farkas, L. Farkas and P. Harteck, *Proc. Roy. Soc.*, 1934, **144A**, 481
A. and L. Farkas, *ibid.*, 1935, **152A**, 124.

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a negligible decrease in the D-content of deuterium brought into contact with a catalyst previously exposed to hydrogen and practically no formation of deuterium after the catalyst has been in contact with deuterium (see Table I.).

By experiments on the rate of decomposition of ammonia it was found that in no case could the amount of uncondensable products formed account for more than a small fraction of the decrease in the D-content actually observed. On the same catalyst, for example, as referred to in Table II. at 233° C. and 15 mm. Hg of NH₃ the amount of uncondensable gas formed was 3 mm. in thirty minutes, *i.e.*, very little in comparison with the rate of the decrease in the D-content (see Table II).

TABLE II.

234° C., 16 mm. NH₃ + 15 mm. D₂

Minutes.	D-content in Per Cent.
0	96
9	34
15	23

Fig. 2 shows that the decrease in the D-content is actually due to an exchange. Curve *a* indicates the change in the D-content of 30 mm. deuterium when mixed with 26 mm. NH₃ at 233° C. After thirty minutes

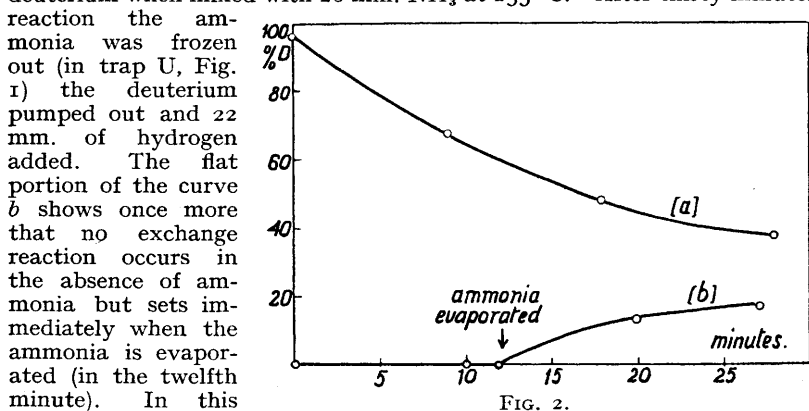


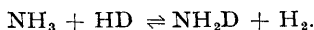
FIG. 2.

reaction the ammonia was frozen out (in trap U, Fig. 1) the deuterium pumped out and 22 mm. of hydrogen added. The flat portion of the curve *b* shows once more that no exchange reaction occurs in the absence of ammonia but sets immediately when the ammonia is evaporated (in the twelfth minute). In this case the D-content

of the hydrogen added naturally increases at the expense of the "heavy"

ammonia formed in the previous experiment.

The equilibrium constant of the reaction ⁷



$K = \frac{[\text{NH}_2\text{D}][\text{H}_2]}{[\text{NH}_3][\text{HD}]}$ could not be accurately determined by measuring the final D-content of a mixture of ammonia and deuterium for the following

TABLE III.

EQUAL PRESSURES OF D₂ (100 per cent. D) and NH₃.

Final D-content in Per Cent.	K.	$2K/3 = (\text{H/D})_h \cdot (\text{D/H})_a$.
40	1.5	1.0
35	2.1	1.5
30	3.0	2.0

reason. The value of the equilibrium constant obtained is very sensitive to the final D-content observed and an inaccuracy of a few per cent. in the determination of the final D-content may cause a considerable error in the determination of the

equilibrium constant (see Table III.).

⁷ A. Farkas, *J.C.S.* (in the press).

In the third column $(H/D)_h$ and $(H/D)_a$ represent the ratio of the H- and D-content in the hydrogen and ammonia respectively.⁷ The inaccuracy in the determination of the final D-content is due to the slight decomposition of ammonia (especially the formation of nitrogen). Another source of error is the strong adsorption of ammonia on the glass walls especially on those cooled to low temperatures (U tube), and thus the amount of ammonia taking part in the interchange is actually more than that calculated from the pressure readings. Both sources of error tend to produce a final D-content which is too low or an equilibrium constant which is too high. After allowing for this inaccuracy it was found that the equilibrium is definitely larger than the classical value of $3/2$ being at 220° - 230° C. about 2 to 3.* This provisional result which is in agreement with theoretical calculations requires confirmation by more accurate experiments.⁸

In order to exclude any uncertainty in the value of K the dependence of the rate of the exchange on pressure was investigated in mixtures with excess of ammonia in which the equilibrium D-content is very low.

The progress of the interchange at 200° - 210° C. at different deuterium pressures and constant ammonia pressures and at different ammonia pressure and constant deuterium pressures is shown in Figs. 3 and 4. It will be seen that whereas the relative rate of the interchange remains

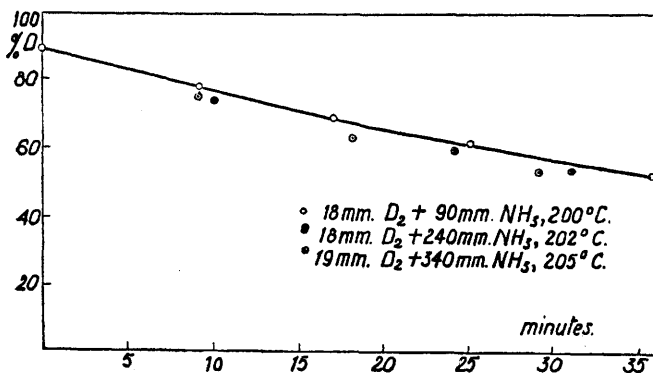


FIG. 3.

unaltered by changing the ammonia pressure, it decreases with increasing deuterium pressure.

In another series of runs the dependence of the rate of interchange was investigated at a varying total pressure but at approximately the same ratio $NH_3 : D_2$, see Table IV.

The measure for the relative rate of the exchange is the time (τ , in minutes) in which the original D-content has decreased by 25 per cent. and is given in column 5, whereas the measure for the absolute velocity being proportional to the deuterium pressure and $1/\tau$ is listed as P_{D_2}/τ in

* Such a value follows indirectly from exchange experiments between heavy water and ammonium salts. (Bonhoeffer and Brown, *Z. physik. Chem.*, 1933, 23B, 171, and A. Farkas, *Trans. Faraday Soc.*, in the press.)

⁸ Cf. also K. Wirtz, *Naturwiss.*, 1935, 23, 271.

TABLE IV.

Temperature °C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	P_{NH_3}/P_{D_2} .	25 Per Cent. Decrease in the D-content Reached in (τ).	P_{D_2}/τ .
203	17	64	3.8	11 mins.	1.55
201	39	119	3.0	17 "	2.29
203	54	246	4.5	22 "	2.45
208	82	326	4.0	29 "	2.83

column 6. Similar data for the experiments shown in Figs. 3 and 4 are given in Table V.

TABLE V.

Temperature °C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	25 Per Cent. Decrease Reached in (τ).	P_{D_2}/τ .
200	18	90	20 min.	0.90
202	18	245	19 "	0.95
205	19	340	17 "	1.11
214	13	236	17 "	0.76
210	29	228	23 "	1.26
212	51	243	31 "	1.64

From Tables IV. and V. we note that the absolute rate of the exchange reaction, *i.e.*, the number of atoms exchanged is practically independent of the ammonia pressure but increases approximately with the square root of the deuterium pressure.

The dependence of the rate of interchange on temperature is shown in

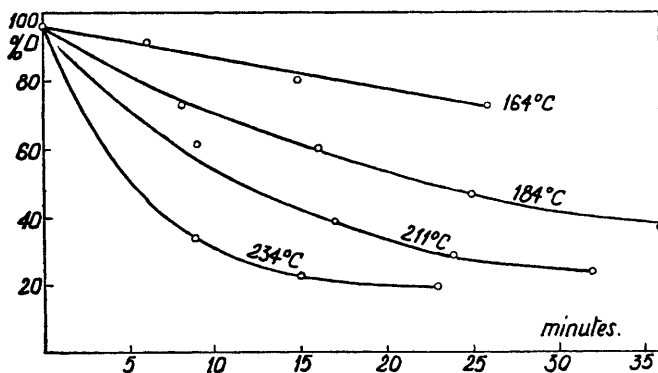


FIG. 5.

Fig. 5 for the temperature region 164°-234° C. and at 15-17 mm. of D_2 and NH_3 . (The curves for 211° and 234° refer to the catalyst in a slightly less active form.)

The apparent energy of activation (E)

was calculated from the dependence of the rate of exchange on temperature with the equation

$$\frac{d \log 1/\tau}{dT} = \frac{E}{RT^2}$$

τ denoting the time (in minutes) in which the original D-content has decreased by 25 per cent. (see Table VI.).

TABLE VI.

Temperature °C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	τ in Minutes.	Energy of Activation in Kg Cals.
170	15	15	20	14.4
196	15	15	8	
164	15	14	26	18.9
184	15	15	10	
201	14	16	5.5	
211	15	17	6.5	13.1
234	16	15	3.5	
			Mean	15.0

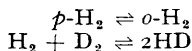
The *Ortho-para*-conversion.

In a series of previous publications⁹ it was shown that the catalytic *ortho-para*-hydrogen conversion on metals involves an atomic mechanism.

It was important to obtain some information about the catalytically active adsorption layer by this method since the "sorpative" capacity of this catalyst was hardly measurable. (There is no necessary connection between adsorptive capacity and catalytic activity. High adsorptive capacity is not always indicative of a high catalytic activity.)

On a fresh catalyst the *ortho-para*-hydrogen conversion occurred at room temperatures and a few mm. Hg pressure at a high velocity equilibrium being established within a few minutes. Under similar condition there was, however, no exchange reaction to be detected even after several hours.

Although it has already been shown that the reactions^{5b, 10}



proceed on a catalyst by the same mechanism namely by dissociation into atoms, it seemed desirable to show this including also the reaction $o\text{-D}_2 = p\text{-D}_2$ for the catalyst actually employed.

Fig. 6 shows the establishment of the equilibrium in these reactions at 10 mm. Hg pressure and 20° C. the logarithm of the "distance" from equilibrium (u), (taken as 10 at the beginning and 0 at the end), being plotted against the time. It will be noticed that though the individual reaction rates are different,

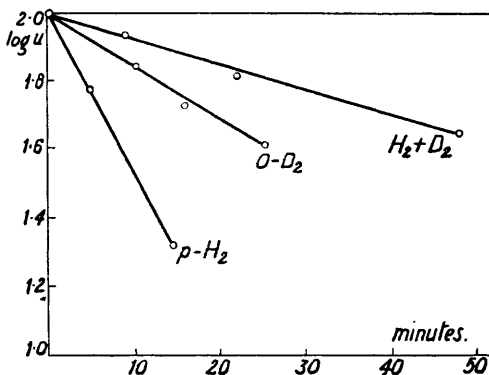


FIG. 6.

⁹ Bonhoeffer and Farkas, *Z. physik. Chem.*, 1931, **12B**, 231; A. Farkas, *ibid.*, 1931, **14B**, 371; Bonhoeffer, Farkas and Rummel, *ibid.*, 1933, **21B**, 225; Bonhoeffer and Farkas, *Trans. Faraday Soc.*, 1932, **28**, 242; A. Farkas, *Ortho-hydrogen, Parahydrogen and Heavy Hydrogen*, The Cambridge University Press, 1935.

¹⁰ E. Fajans, *Z. physik. Chem.*, 1935, **28B**, 239.

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the relative rates being 5 : 2 : 1 for *p*-H₂, *o*-D₂ and H₂ + D₂ respectively, these three reductions proceed with a very similar speed.

The temperature coefficient for these reactions are likewise very similar, indicating that in these processes practically the same energy of activation

TABLE VII.

Reaction.	Temperature °C.	Half-Life Time in Minutes.	Energy of Activation in Kg Cals.
<i>p</i> -H ₂ ⇌ <i>o</i> -H ₂ * at 18 mm. Hg.	85	8.5	8.1
	100	5	
	130	3	
	160	1.5	
<i>o</i> -D ₂ ⇌ <i>p</i> -D ₂ at 12 mm. Hg.	20	20	8.4
	40	8	
H ₂ + D ₂ ⇌ 2HD at 11 mm. Hg.	20	40	9.0
	40	15	

* Catalyst different.

is involved (see Table VII.). As expected slightly higher values are obtained for the reactions involving deuterium.

We note that this apparent energy of activation is considerably lower than that found for the exchange reaction between deuterium and ammonia. This

difference in the energies of activation is responsible for the fact that the conversion reaction takes place readily at temperatures which are 200° C. below those necessary for the exchange reaction.

It was found that the presence of ammonia inhibited the conversion of *para*-hydrogen, the inhibiting effect being dependent on the pressure of ammonia. Fig. 7 shows this effect at 82° and 122° C. and 15 mm. Hg of *para*-hydrogen, the velocity of the conversion in the absence of ammonia being taken as unity. The inhibiting effect at these temperatures is reversible *i.e.*, the original activity is restored as soon as the ammonia is removed.

In spite of this inhibition the conversion reaction is even in the presence of NH₃ much faster than the exchange as clearly shown by the following experiment.

In the thermo-conductivity cell employed for the analysis of hydrogen and deuterium mixtures hydrogen, normal deuterium and *ortho*-deuterium had the following "resistance" values (*i.e.*, the resistance of the wire in the thermo-conductivity cell when heated in the gas),

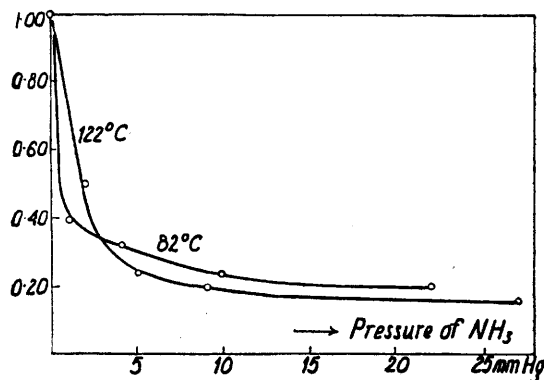


FIG. 7.

	Ω.	ΔΩ relative to <i>n</i> -D ₂
normal hydrogen (<i>n</i> -H ₂)	91.70 ohms.	- 12.19 ohms.
normal deuterium (<i>n</i> -D ₂)	103.91 "	0.00 "
<i>ortho</i> -deuterium (<i>o</i> -D ₂)	106.39 "	+ 2.48 "

Thus it was easy to show how much more quickly the conversion of *ortho*-deuterium proceeded than the interchange reaction in a mixture of $o\text{-D}_2 + \text{NH}_3$.

Fig. 8 shows the progress of these reactions in a mixture of 12 mm. $o\text{-D}_2 + 15$ mm. NH_3 over the temperature range 20° to 155°C ., the differences in the resistance values (relative to $n\text{-D}_2$, $\Delta\Omega$) being plotted as a function of time. At 155°C . there is slight exchange reaction to be observed proceeding a hundred times more slowly than the conversion; at 82°C ., however, there is practically no exchange reaction.

Whereas the inhibition of the *p*- H_2 conversion is reversible at 80°C . and upwards, at room temperatures the poisoning effect of ammonia persists even after removal of that gas. When ammonia is admitted to a fresh catalyst there is an immediate formation of some uncondensable

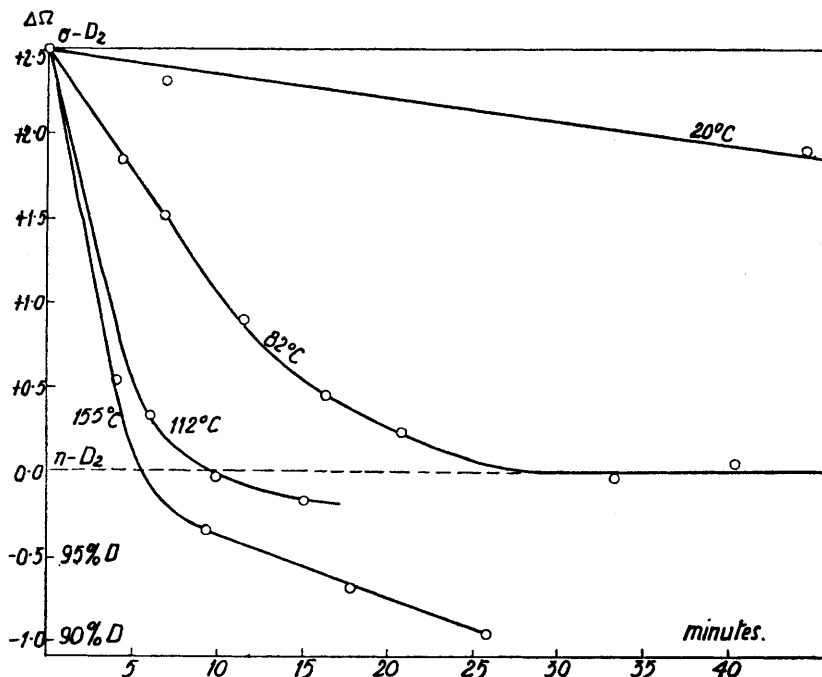


FIG. 8.

gas. Although it was not possible to analyse this gas owing to its small amount ($2 \cdot 10^{-4}$ c.cm. N.T.P.) it was shown that it was formed from the ammonia and not displaced by it from the catalyst in the following way. A newly formed catalyst was brought into contact with deuterium, its activity being measured by the catalytic conversion of $o\text{-D}_2$. The gas formed by admitting NH_3 was mixed with sufficient (100 per cent.) D_2 in order to obtain $4 \cdot 10^{-3}$ c.cm. (N.T.P.) of gas which was the minimum amount necessary for one measurement in the thermo-conductivity cell. The D-content of this sample was found to be 96 per cent. showing that the gas formed was not deuterium displaced by the ammonia from the catalyst. In the thermo-conductivity cell the resistance values for H_2 and N_2 are approximately equal and therefore it was not possible to decide whether the defect of 4 per cent. D was due to the presence of H_2 alone or to a mixture of $\text{H}_2 + \text{N}_2$. The poisoning effect is shown in Table VIII.

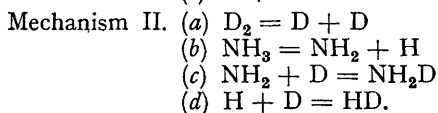
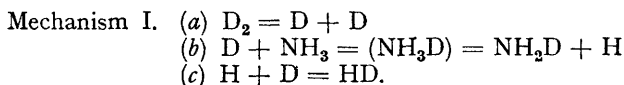
TABLE VIII.

Treatment.	Pressure in mm. Hg.	Half-Life of the Conversion in Minutes.
Fresh catalyst	0.06	2
3 mm. NH ₃ added and removed . . .	0.06	11
Fresh catalyst	2	3.5
NH ₃ added and removed	2	13
Pumped for 45 minutes	2	22
NH ₃ added and removed	2	24

Discussion.

We assume that this reaction is taking place between molecules adsorbed on the surface of the catalyst. As far as the ammonia is concerned this assumption is justified by the strong adsorption which causes the inhibiting effect of the *para-ortho*-conversion and the independence of the rate of the exchange reaction on the ammonia pressure. On the other hand from previous experiments ^{9,10} we know that the *ortho-para*-interconversion likewise takes place in the adsorption layer, and from the following it will be seen that there is a connection between the conversion and the exchange reactions.

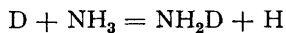
We can examine the following two reaction mechanisms ² making the further assumption that no transport processes between the gaseous phase and adsorption layer affect the actual reaction rate.



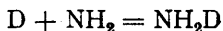
Mechanism I. is the heterogeneous analogue to the mechanism involved in the thermal interaction between NH₃ and D₂ occurring at 600° C. and upwards in the gaseous phase.⁷

In both mechanisms the activation of the deuterium is common. If the activation of the deuterium consists in dissociation (or at least in loosening the bond between the deuterium atoms) the *ortho-para*-conversion gives us a measure of this step since every dissociation and recombination process is necessarily connected with conversion. Actually it is found that the conversion reaction proceeds very much more quickly than the exchange reaction indicating clearly that II. (a) and (d) and I. (a) and (c) are not the rate determining steps. The dependence of the reaction rate on pressure suggests that neither is II. (b) rate determining since this reaction could not be accelerated by increasing D₂ pressure.

Thus we come to the conclusion that either the exchange reaction I. (b)



or the recombination reaction II. (c)



is the rate determining step depending whether mechanism I. or II. is valid. This is an interesting result since it shows that we have the same dependence of the rate of exchange on the pressure of NH_3 and D_2 (provided the ammonia is strongly adsorbed) whether ammonia is completely dissociated or not and that the kinetics of this reaction is compatible with both mechanisms.

Thus our problem reduces to enquiring how the ammonia is adsorbed.

Even at room temperatures a slight evolution of gas is observed when ammonia is brought into contact with a fresh iron surface. This cannot be due to a slow decomposition of ammonia into N_2 and H_2 since the formation of gas is only observed with a fresh catalyst and stops suddenly. It is more probably due to a reaction $\text{NH}_3 = \text{NH}_2 + \text{H}$ in which the radical NH_2 remains on the catalyst whereas the hydrogen is given up into the gas phase. This behaviour was actually observed by Frankenburger and Hodler,¹¹ who were able to show that on admitting ammonia to tungsten powder at 90° C. only hydrogen is evolved. It is also well known that at 500° C. nitride formation occurs which is not restricted to the surface of the iron but proceeds into the bulk phase. The formation of nitride and its reduction by hydrogen were demonstrated experimentally by Dünwald and Wagner.¹² Finally the experiments of Winter¹³ on the catalytic decomposition of ammonia on iron show definitely that the rate determining step is the decomposition of the nitride indicating that loosening of N—H bonds takes place before the nitride is decomposed.

The experimental evidence justifies the assumption that on the surface of the catalyst at 200° C. a large fraction of the ammonia is dissociated* and makes it probable that for the exchange reaction mechanism II. is responsible.

Thus we can form the following picture of the interaction of ammonia with deuterium (or hydrogen) on the catalyst.

In the absence of ammonia, hydrogen or deuterium are very easily dissociated on the catalyst as shown by the low activation energy for the conversion (8.9 kg. cal.). The conversion involves not only the dissociation process but also a migration of the hydrogen atoms since it is found that $\text{H}_2 + \text{D}_2 = 2\text{HD}$ reaction proceeds with a similar speed when compared with the conversion.†

If ammonia is added the greater part of the surface is covered cutting down the area accessible to hydrogen. At 20° C. a part of the ammonia covering the surface is decomposed into amide and hydrogen and the

¹¹ (a) Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, **28**, 229; (b) Frankenburger, *Z. Elektrochemie*, 1933, **39**, 45, 97, 269.

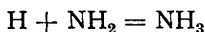
¹² Dünwald and Wagner, *Z. physik. Chem.*, 1934, **24B**, 53; Engelhardt and Wagner, *ibid.*, 1932, **18B**, 369.

¹³ Winter, *Z. physik. Chem.*, 1931, **13B**, 401.

* Whether the dissociation of ammonia proceeds according to $\text{NH}_3 \rightarrow \text{NH} + \text{H}_2$, $\text{NH}_2 \rightarrow \text{NH} + \text{H}$, $\text{NH} \rightarrow \text{N} + \text{H}$, and to what an extent these processes occur we cannot infer.

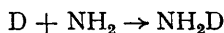
† It will be noticed, however, that the rate for the reaction $\text{H}_2 + \text{D}_2$ does not lie between that for the *ortho-para*-conversion of hydrogen and deuterium but is slower than either reactions. This effect (if not due to some impurity) might suggest that the migration involves a slightly larger energy of activation than the dissociation but in any case this difference is negligible being less than 1 k. cal.

hydrogen leaves the surface. The irreversibility of the inhibiting effect of ammonia is due either to a strong adsorption or to this surface amide formation, the hydrogen not being able to reduce the surface amide at these low temperatures. At higher temperatures (100° C.) the surface amide becomes reducible and the inhibition by ammonia becomes reversible. This reduction occurring according to



is the same reaction as the rate determining step in our mechanism II. of the exchange reaction. The actual exchange reaction however only becomes observable if the reduction proceeds with a very great speed as shown by the following example. Let us assume 1 cm.² of active surface in contact with 10²⁰ molecules of a mixture of D₂ and NH₃ (10²⁰ molecules are contained in 50 c.c. at 50 mm. Hg pressure). If the reduction of the 10¹⁵ molecules covering the surface of the catalyst takes place in one second the exchange reaction would require 10⁵ seconds. Thus the poisoning effect over this temperature range is due to the formation of the surface amide which also explains the fact why the *ortho-para*-conversion is not inhibited at higher pressures of ammonia. Through the dissociation process one part of the surface (namely that occupied originally by the third H-atom of the NH₃) remains always accessible to the hydrogen. A similar explanation might be advanced to explain the fact that no displacement of deuterium by ammonia is observed. (Cf. Tables IV. and V.)

Increasing the temperature (100° C. and upwards) the reduction of the amide occurs sufficiently rapidly and the exchange reaction appears. The activation energy for this exchange reaction is found to be 15 kg. cal. This is not the activation energy for the migration of hydrogen or deuterium which is much smaller namely 8 kg. cal.; it is more likely to be associated with the reaction



itself, whereas the back reaction, the dissociation, must have a smaller energy of activation not being the rate determining¹ step. It is therefore most probable that the greatest part of this energy of activation is due to the exothermicity of the reaction $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$.

The apparent energy of activation as calculated from the dependence of the reaction rate on temperature includes the heats of adsorption for the reactants. Owing to the strong adsorption of the ammonia we might assume that the adsorption layer is saturated with NH₃ over the whole temperature range and that therefore the heat of adsorption for NH₃ does not affect the true energy of activation. We do not know the exact heat of adsorption of D₂ but it will not be more than a few kg. cal. and therefore the true energy of activation will be somewhat larger than the apparent one. The concentration of deuterium will be rather low in the adsorption layer and this explains why the rate of exchange is approximately proportional to the square root of the deuterium pressure (Tables IV. and V.).

At still higher temperatures (over 300° C.) two new processes come into play, the decomposition of the surface nitride into molecular nitrogen and the migration of the nitride-N into catalyst the first reaction being responsible for the decomposition of ammonia, the second for the formation of iron nitride in bulk.

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Summary.

The exchange of hydrogen atoms between D_2 and NH_3 has been investigated on an iron catalyst at pressures of 30 to 400 mm. Hg and temperatures of 160° to 230° C.

The rate of the exchange reaction is independent of the ammonia pressure and increases with increasing D_2 pressure.

The apparent heat of activation is 15 kg cal.

The *ortho-para*-conversion of hydrogen and deuterium and the interaction $H_2 + D_2 = 2HD$ proceed much more quickly than the exchange reaction the activation for the conversion reactions being 8-9 kg cal. The *ortho-para*-conversion of hydrogen is inhibited by the presence of NH_3 .

It is suggested that the exchange reaction proceeds by the mechanism (all reactions occurring in the adsorption layer)

- (b) $NH_3 \rightarrow NH_2 + H$
- (a) $D_2 \rightarrow 2D$
- (d) $D + H \rightarrow 2HD$
- (c) $D + NH_2 \rightarrow NH_2D$

the step (c) being the slowest reaction and thus determining the rate. The reactions (a) and (d) are those involved in the conversion reactions. It is shown that this mechanism is in agreement with the experimental results.

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