ON THE VELOCITY OF THE THERMAL DECOMPOSITION OF AMMONIA ON A QUARTZ SURFACE

BY

J. A. CHRISTIANSEN AND EGGERT KNUTH

1. Introduction and Summary.

M. BODENSTEIN and F. KRANENDIECK[1] and later C. N. HINSHELWOOD and R. E. BURK[2] investigated the decomposition of ammonia in quartz-bulbs at about 800° C. The results of these two pairs of investigators do not agree in all respects but in one they agree completely: The reaction takes place exclusively or almost exclusively on the quartz-surface. B. and K. found, further, that the reaction is retarded by one of the products, but were unable to find any effect of added hydrogen or nitrogen. H. and B., on the other hand, succeeded in showing that added hydrogen had a retarding effect, and added nitrogen none at all. Finally B. and K. found proportionality between the initial velocity and the square root of the ammonia-pressure, while H. and B. found proportionality between the initial velocity and the first power of the ammonia-pressure.

The reason why the results differ is not quite clear. As, however, B. and K.'s quartz-bulb was much more permeable to hydrogen than that of H. and B. the difference may be traced to a difference between the surfaces.

We have repeated the experiments in so far as we have investigated the decomposition at pressures from 2 to 7 cm. and various temperatures without any addition of foreign gas. We made no direct experiments on the effect of in-

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[1] Nernst Festschrift, 1912, p. 99 and F. KRANENDIECK, Dissertation Hannover, 1912.

[2] Journal chem. Soc. (London) **127**, p. 1105 (1925).

creasing the quartz-surface, but still our experiments show that the reaction is at least to a large extent a wall reaction, as its velocity varies considerably with the preceding treatment of the bulb.

In a single run, however, the course seemed quite regular, and we succeeded in finding an expression for the degree of decomposition as a function of time, which conformed with the experiments up to about 95 % decomposition. From this expression we derived a reaction-mechanism, in which the radical NH played an essential part. Some preliminary experiments with the reaction products made the presence of this substance therein probable.

2. The Cinetic Experiments.

The construction of the apparatus appears from the following description. The electric furnace was a well insulated porcelain tube wound with nichrom-wire. To get a better temperature distribution the quartz-bulb which was provided with a thermometer-pocket was placed in a rather thick-walled iron tube inside the porcelain tube. The furnace was handregulated. Temperatures were measured by means of a platinum-platinumrhodium thermocouple. The heated volume of the bulb was 201 cm^3. the dead space including the free volume of the mercury manometer, about 14 cm^3. The heated surface of the bulb was about 200 cm^2. Pressures were measured by means of a rather short mercury manometer. It proved sufficiently accurate to measure only the uppermost of the two mercury surfaces in the manometer. The readings were made by means of a horizontal microscope (Leitz) with an ocular micrometer-scale, divided into 100 parts, each division corresponding to 0.05 mm. By suitable illumination we succeeded in getting the picture

of the mercury meniscus so sharp, that the readings were correct to 0.01 mm. and by tapping the manometer before each reading we avoided with about the same accuracy any lag in the movement of the mercury. The microscope could be moved up and down by means of rack and pinion, these movements being read with an accuracy of 0.05— 0.1 mm. The advantage of this arrangement was that the last 5 mm. of the total movement could be read with at least as great a relative accuracy as the first far greater movements.

The time was measured by means of a pocket chronograph, the button being pressed, and the meniscus read at the same time. The ammonia was taken from a container with the well known Diver's liquid, a solution of ammonium-nitrate in liquid ammonia. To prevent spray a suitable part of the connecting tubing between bulb and container was packed with cotton wool. An absorber containing conc. sulphuric acid served to protect the oil pump against ammonia.

By a suitable operation of the stopcocks the bulb could be pumped out and filled with ammonia to the desired pressure. The Diver's liquid was boiled out to remove traces of air. It may be mentioned in this connection that air (and oxygen) seemed to have an effect on the reaction. We tried to investigate this, but up till now the results have been very erratic. On account of the influence of the preceding treatment of the bulb on the velocity, well known from previous investigations, we decided to let the reaction-products from one experiment stay over night in the bulb, which remained heated. The next experiment was started by evacuating for about 10 minutes and refilling with ammonia.
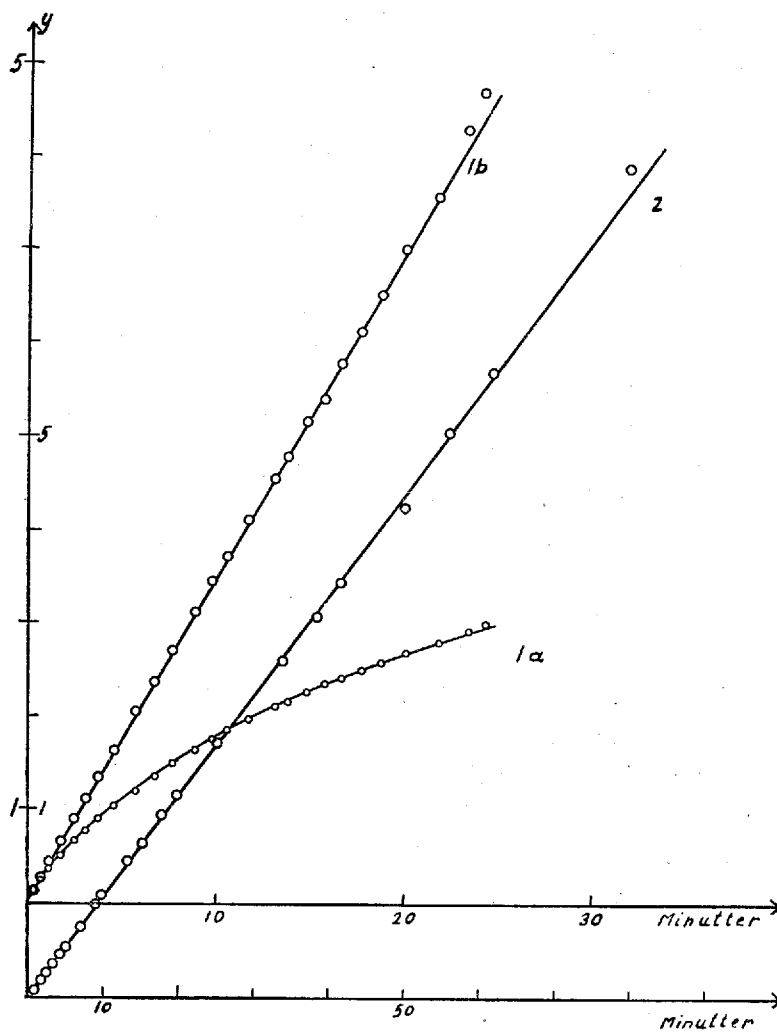
Fig. 1.

Curves 1 a and 1 b refer to experiment 124. The three last readings have not been plotted. Abscissæ: time in minutes, upper scale.

Ordinates 1 a: $\ln p_{NH_3}$, scale to the right.

Ordinates 1 b: k_1 times t calc., scale to the right.

Curve 2 refers to experiment 96. Abscissæ time in minutes, lower scale.

Ordinates: k_1 times t calc., scale to the left.

3. The Results of the Cinetic Measurements.

Our results are in accordance with H. and B.'s in so far as we also found that the initial velocity was proportional to the first power of the ammonia pressure. The general trend appears from fig. 1, curve 1 a where $\ln p_{NH_3}$ is plotted against time. The downward curvature is immediately explained by the retarding action of the hydrogen (H. and B.).

In the tables below are given the numerical results of some representative experiments. We selected such in which the temperature did not deviate more than 1° from the mean. As the temperature coefficient is rather low, this accuracy just suffices, although a better constancy would have been desirable. The pressures are corrected for variations in temperature only. On account of the rather large dead space this will make the absolute velocities low by about 7 $^0/_0$ but it will have no effect on the form of the curves. Other systematic errors might arise from the variation in total volume caused by the mercury-manometer and from lack of homogeneous distribution of the gases between the reaction vessel proper and the dead space. A rough estimate, however, showed these errors to be negligible.

Table 1.

Experiment 96.

Final pressure $P_\infty = 55.75$ mm. Hg; T° abs. $= 1062°$;
$k = 0.0535$; $f = 0.0050$; $g = 4.0$.

T° abs.	t exp. min. sec.	P_t mm. Hg	p_{NH_3} mm. Hg	t calc. min. sec.
1062	0 18	29.30	26.45	0 13
	0 52	29.90	25.85	0 38
	1 45	31.10	24.65	1 33
	2 28	32.10	23.65	2 20

T° abs.	t exp.	P_t	p_{NH_3}	t calc.
	min. sec.	mm. Hg	mm. Hg	min. sec.
	3 22	33.20	22.55	3 14
	4 17	34.30	21.45	4 12
	5 05	35.10	20.65	4 56
	7 06	37.20	18.55	7 03
	9 02	39.10	16.65	9 12
1062	9 52	39.80	15.95	10 06
	13 20	42.30	13.45	13 30
	15 14	43.50	12.25	15 18
	17 52	45.00	10.75	18 06
	19 53	46.00	9.75	20 11
	25 14	48.10	7.65	25 21
1061	34 00	50.50	5.25	33 35
	38 34	51.40	4.35	37 54
	41 46	52.00	3.75	41 24
	50 19	53.00	2.75	48 48
	56 15	53.70	2.05	56 15
1061	62 00	54,10	1.65	62 12
1061	80 27	54.90	0.85	82 16

Experiment 124.

Final pressure $P_\infty = 59.42$ mm. Hg; T° abs. $= 1157°$;

k = 0.347; f = 0.040; g = 5.5.

T° abs.	t exp.	P_t	p_{NH_3}	t calc.
	min. sec.	mm. Hg	mm. Hg	min. sec.
1157	0 23	35.00	24.42	0 25
	0 43	37.50	21.92	0 47
	1 10	40.00	19.42	1 16
	1 47	42.50	16.92	1 51
	2 32	45.00	14.42	2 37
	3 05	46.50	12.92	3 12
	3 47	48.00	11.42	3 53
	4 37	49.50	9.92	4 43
	5 45	51.00	8.42	5 54
1157	6 48	52.20	7.22	6 49
	7 47	53.10	6.32	7 45
	8 58	54.00	5.42	8 58
	9 51	54.60	4.82	9 54

T° abs.	t exp. min. sec.	P_t mm. Hg	p_{NH_3} mm. Hg	t calc. min. sec.
	10 40	55.00	4.42	10 41
1157	11 49	55.50	3.92	11 48
	13 10	56.00	3.42	13 11
	13 55	56.20	3.22	13 47
	14 55	56.50	2.92	14 49
	15 52	56.70	2.72	15 50
	16 45	56.90	2.52	16 37
	17 48	57.10	2.32	17 35
	18 59	57.30	2.12	18 47
	20 13	57.50	1.92	20 08
1157	22 00	57.70	1.72	21 48
	23 34	57.90	1.52	23 49
	24 25	58.00	1.42	25 00
	25 35	58.10	1.32	26 42
	26 48	58.20	1.22	27 48
	28 09	58.30	1.12	29 31

Experiment 131.

Final presssure $P_\infty = 36.50$ mm. Hg; T° abs. $= 1132°$;
k $= 0.133$; f $= 0.017$; g $= 4.0$.

T° abs.	t exp. min. sec.	P_t mm. Hg	p_{NH_3} mm. Hg	t calc. min. sec.
1132	0 11	19.00	17.50	0 10
	0 32	19.70	16.80	0 28
	1 06	21.00	15.50	1 06
	1 39	22.00	14.50	1 37
1132	2 13	23.00	13.50	2 12
	3 00	24.20	12.30	2 59
	3 33	25.00	11.50	3 34
1132	4 17	26.00	10.50	4 21
	5 09	27.00	9.50	5 15
1132	6 07	28.00	8.50	6 16
1132	9 39	30.50	6.00	9 36
	10 55	31.20	5.30	10 50
1132	11 29	31.50	5.00	11 27
	12 39	32.00	4.50	12 34
1132	13 58	32.50	4.00	13 53

T° abs.	t exp. min. sec.	P_t mm. Hg	p_{NH_3} mm. Hg	t calc. min. sec.
	15 26	33.00	3.50	15 23
	17 11	33.50	3.00	17 10
1132	18 27	33.80	2.70	18 30
1132	19 28	34.00	2.50	19 24
1132	21 09	34.30	2.20	21 00
1132	25 08	34.90	1.60	25 24
1132	32 16	35.50	1.00	33 12

Experiment 132.

Final pressure $P_\infty = 57.15$ mm. Hg; $T°$ abs. $= 1134°$;

$k = 0.135$; $f = 0.017$; $g = 4.0$.

T° abs.	t exp. min. sec.	P_t mm. Hg	p_{NH_3} mm. Hg	t calc. min. sec.
1134	0 25	31.00	26.15	0 25
	0 52	32.50	24.65	0 52
	1 22	34.00	23.15	1 23
	1 43	35.00	22.15	1 44
1134	2 30	37.00	20.15	2 32
	3 24	39.00	18.15	3 26
	4 47	41.50	15.65	4 48
	5 43	43.00	14.15	5 45
	6 37	44.25	12.90	6 39
1134	7 12	45.00	12.15	7 12
	8 33	46.50	10.65	8 34
1134	10 09	48.00	9.15	10 12
1134	11 24	49.00	8.15	11 29
1134	14 44	51.00	6.15	14 42
1134	18 34	52.60	4.55	18 25
1134	21 50	53.60	3.55	21 43
1134	25 03	54.30	2.85	25 00
1134	35 23	55.61	1.54	35 21
1134	50 06	56.40	0.75	52 24

The first column shows the absolute temperature, the second the time of reading, the third the pressure in mm. mercury. The fourth column shows the difference between

the final pressure and the pressure at time t, which is equal
to the ammonia pressure at that time.[1] The meaning of
the fifth will be explained later.

4. The Mechanism of the Reaction.

To determine the mechanism we applied the method
given by one of us.[2] The simplest way in which to account
for the retarding effect of hydrogen would be to assume
the following mechanism:

$$NH_3 \rightleftarrows NH + H_2 \ (\pm 1)$$
$$NH + NH_3 \rightarrow N_2 + 2H_2 \ (2).$$
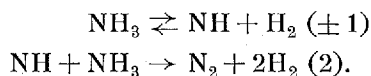
The corresponding expression for the reciprocal velocity $\frac{1}{v}$ is

$$\frac{1}{v} = \frac{1}{a_1 w_1} + \frac{1}{a_1 w_1} \cdot \frac{w_{-1}}{w_2}$$

where

$$a_1 = p_{NH_3}, \ w_1 = k_1, \ w_{-1} = k_{-1} \cdot p_{H_2}, \ w_2 = k_2 \cdot p_{NH_3}.$$

Taking a as the original pressure of ammonia and x as
the amount which has disappeared at time t we get a
differential equation between t and x which easily can be
integrated, giving t as a function of a, x and the two con-
stants k_1 and $\frac{k_{-1}}{k_2}$. Although the two constants could be
chosen so as to give good agreement with the experiments
over a large interval, it proved impossible to get agreement
over the complete range measured. It turned out, however,
that a slight modification of the expression, subtraction of

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[1] This is true even if the reaction $NH_3 \rightarrow NH + H_2$ has taken place
to any extent.

[2] J. A. CHRISTIANSEN, Z. physikal. Chem. **B 28** (1935) 303. See also
G.-M. SCHWAB, Z. physikal. Chem. **B 8** (1930) 141.

x times a third constant, gave practically complete agreement for the whole range, i. e. from 0 to about 95 % decomposition. This final expression can be written in the form

$$k_1 t = \left(1 + \frac{3}{2}\frac{k_{-1}}{k_2}a - \frac{3}{2}\frac{k_{-1}}{k_2}\frac{k_{-2}}{k_3}\right)\ln\frac{a}{a-x}$$

$$+ \frac{3}{2}\frac{k_{-1}}{k_2}\frac{k_{-2}}{k_3}\frac{x}{a-x} - \frac{3}{2}\frac{k_{-1}}{k_2}x.$$

After a suitable choice of the three constants

$$k_1, \quad \frac{3}{2}\frac{k_{-1}}{k_2} = f \quad \text{and} \quad \frac{k_{-2}}{k_3} = g$$

the values of t could be calculated from a and x. These are given in the tables as t calc. A glance at the tables and curves 1 b and 2 in fig. 1 shows the agreement obtained.

Differentiation of the above expression gives

$$k_1\frac{dt}{dx} = \frac{1}{a-x} + \frac{3}{2}\frac{k_{-1}}{k_2}\frac{x}{a-x} + \frac{3}{2}\frac{k_{-1}}{k_2}\frac{k_{-2}}{k_3}\frac{x}{(a-x)^2}$$

or

$$\frac{1}{v} = \frac{1}{k_1 p_{NH_3}} + \frac{1}{k_1 p_{NH_3}}\cdot\frac{k_{-1}p_{H_2}}{k_2} + \frac{1}{k_1 p_{NH_3}}\cdot\frac{k_{-1}p_{H_2}}{k_2}\cdot\frac{k_{-2}}{k_3 p_{NH_3}}.$$

Comparing with
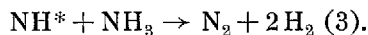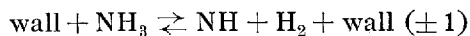
$$\frac{1}{v} = \frac{1}{a_1 w_1} + \frac{1}{a_1 w_1}\cdot\frac{w_{-1}}{w_2} + \frac{1}{a_1 w_1}\cdot\frac{w_{-1}}{w_2}\cdot\frac{w_{-2}}{w_3}$$

we get:

$$a_1 = p_{NH_3}; \; w_1 = k_1; \; w_{-1} = k_{-1}p_{H_2}; \; w_2 = k_2;$$
$$w_{-2} = k_{-2}; \; w_3 = k_3 p_{NH_3}.$$

This leads immediately[1] to the mechanism

[1] J. A. CHRISTIANSEN, Z. physical. chem. B 28 (1935) 303.

$$wall + NH_3 \rightleftarrows NH + H_2 + wall \; (\pm 1)$$

$$NH \rightleftarrows NH^* \; (\pm 2)$$

$$NH^* + NH_3 \rightarrow N_2 + 2H_2 \; (3).$$

To explain the results it is thus necessary to assume three steps instead of two. The essential point is the occurrence of the NH-radical which at once explains the strong retardation by hydrogen. It may be remarked here that the mechanism found is no chain mechanism in the ordinary sense of the word. With the nomenclature proposed by one of us[1], it should be called an open sequence of reactions, while a chain reaction would be called a closed sequence.

From our experiments and their mathematical treatment given above it can only be concluded that NH and NH* are two different forms of the radical. It might seem natural to assume that NH means an NH adsorbed on the quartz-surface and NH* the same radical in the vapour phase. A discussion of the temperature coefficients of the three constants in connection with our knowledge of the heat of formation of ammonia, however, does not support this view. Judging from the discussion it seems more probable, that both forms react in the adsorbed state. As, however, the determination of the temperature coefficients is not very accurate, and as for the present we consider the question of the two forms of the radical NH as being of secondary importance only, we refrain from entering more deeply into this matter, and restrict ourselves to giving the values of the constants at different temperatures in the section below.

[1] J. A. CHRISTIANSEN, Z. physical. chem. **B 28** (1935) 303.

5. The Dependency on Temperature of the Constants.

Table 2.

Exp.	$T°$ abs.	$t = 0$ p_{NH_3} mm. Hg	P_∞ mm. Hg	$\triangle$ mm. Hg.	k_1	f	g
96	1062	26.84	55.75	1.04	0.0535	0.0050	4.0
97	1065	28.65	59.85	1.28	0.0506	0.0051	2.7
104	1075	26.85	56.15	1.23	0.0720	0.0058	14.7
103	1077	26.70	55.50	1.05	0.0775	0.0065	14.7
98	1111	29.60	61.80	1.30	0.135	0.011	3.3
100	1113	28.30	58.80	1.10	0.125	0.011	3.3
99	1116	28.20	58.90	1.25	0.149	0.017	4.0
102	1117	28.10	59.10	1.45	0.171	0.014	3.6
101	1119	27.80	58.60	1.50	0.152	0.014	3.6
125	1129	27.20	56.60	1.10	0.172	0.017	4.0
126	1130	27.85	58.67	1.49	0.191	0.020	4.0
130	1129	17.64	36.20	0.46	0.133	0.017	4.0
129	1131	17.67	35.83	0.25	0.138	0.017	4.0
131	1132	17.92	36.50	0.33	0.133	0.017	4.0
132	1134	27.65	57.15	0.93	0.135	0.017	4.0
133	1135	27.47	57.40	1.23	0.137	0.014	4.0
124	1157	27.82	59.42	1.89	0.347	0.040	5.5

The first column gives the serial number of the experiment, the second the temperature. The third column gives the ammonia pressure (compare p. 11) extrapolated to time zero, and the fourth the final total pressure. The meaning of $\triangle$ in column 5 will be explained below. The columns 6, 7 and 8 give the three constants mentioned p. 12, k_1, f and g.

On account of the method of determination, the values of k_1 must be expected to be the most and the values of g the least accurate. Unfortunately time did not permit us to repeat experiments 103 and 104, the g-values of which differ so much from the rest, that we suspect them of being quite erroneous.

6. Experiments on the detection of NH.

Inspection of columns 3 and 4 in table 2 shows that the extrapolated initial ammonia pressure is a little less than half of the final pressure. The difference, $\triangle$, is given in column 5 in the table. On account of the difficulty in securing the initial pressure by extrapolation we will not lay too much strees upon this deviation, but it might mean that just after the start the dissociation $NH_3 = NH + H_2$ takes place to an extent which is not quite negligible. We therefore made some preliminary experiments to detect NH in the reaction-products.

The procedure adopted was the following:

Method a). Dry ammonia at a pressure of 5—10 mm. mercury was passed as fast as possible through a nearly white hot quartz-tube. Just behind the heated zone water vapor was admitted through a side-tube, the arrangement being that a constriction on the main tube to a large extent prevented back diffusion of the water vapour into the heated zone. The gas mixture was passed through a trap cooled with liquid air or carbon-dioxide + alcohol and the permanent gases pumped off with the oil-pump.

Method b). Dilute ammonia-water was evaporated and the vapours pumped through the quartz-tube at about 5—10 mm. and passed through the trap as before. The side-tube was closed.

Method c). This was method b) modified so as to admit a slow stream of air through the side tube.

We expected eventually formed NH to react with water, giving NH_2OH. Consequently the contents of the trap after each experiment were melted and the liquid tested

for hydroxylamine by the very sensitive method of J. Blom [1]. This method which consists in the oxidation of hydroxylamine into nitrous acid and detection of this by the Griess-reaction includes also a test for nitrous acid.

On cooling the trap with liquid air both method a) and b) gave weak but positive reactions for NH_2OH and stronger reactions for HNO_2. In one experiment with method a) we even got quite a distinct reaction for HNO_2 without any detectable trace of NH_2OH.

On cooling with carbon-dioxide the same two methods gave weaker reactions for HNO_2 and none at all for NH_2OH.

Of course we took every possible precaution to avoid the presence of air in the apparatus during the experiments, but naturally air had to be admitted after the melting and before the test.

We performed only one experiment according to c), in which we cooled by liquid air. This gave a very strong reaction for HNO_2 and none at all for NH_2OH.

There are several possibilities of explaining the formation of nitrous acid, but on account of lack of further experimental data we refrain from entering on a discussion of these. At any rate our experiments seem to us to indicate strongly the presence of NH in the products of thermal dissociation of NH_3. As mentioned above, there seems to be a distinct difference between the experiments with liquid-air cooling on one side and those with carbon-dioxide cooling on the other, in so far as the reaction for $NH_2OH + HNO_2$ is distinctly less in the latter case. This might indicate that NH is a gas whose "temperature of condensation" lies somewhere between -190 and $-80°C$.

[1] Ber. 1926 I, p. 121.

7. Other Investigations and Conclusive Remarks.

It appears from the above that, although our experimental results show a fairly complete agreement with those of H. and B., the hypotheses underlying the theoretical treatment are quite different. H. and B. assumed with Langmuir that the retardation by hydrogen is caused by a displacement on the quartz-surface of ammonia by the hydrogen, while we come to the conclusion that it is caused by a reversion of the first step in a sequence of reactions. We find it correct therefore to emphasize that, although we find our conclusion more natural than the assumption of H. and B. and also find rather strong support for our view in the numerical agreement between experiments and theory, we cannot on this basis assert that our view has been finally proved, since a more detailed treatment based on the views of H. and B. might perhaps lead to an alternative explanation of our results. If, however, the qualitative evidence for the intermediate formation of NH be confirmed by further experiments this would strongly support the correctness of our view.

In this connection it may be useful to mention the rather numerous investigations on the decomposition of ammonia on different surfaces which have appeared since the work of HINSKELWOOD and BURK, and whose underlying theoretical assumptions are analogous to those of these authors. It is true of course that the mechanisms on different surfaces may be quite different, but it is remarkable that the differences between the experimental results seem to be rather of a quantitative than of a qualitative nature. Espe-

cially the retardation by hydrogen is a common feature of nearly all the reactions.

Thus the later investigators[1][2][3] all agree upon the fact first found by H. and B. that hydrogen has a very strong retarding effect when the decomposition takes place on platinum.

On tungsten H. and B. found no retardation by hydrogen, while C. H. Kunsman[4] found some by hydrogen and almost none by nitrogen.

On molybdenum the same author[4] found distinct retardation by hydrogen and a small one by nitrogen, in direct opposition to R. E. Burk[5] who found just the reverse.

On copper E. Elöd and W. Banholzer[6] and J. K. Dixon[7] agree in finding a strong retardation by hydrogen and none by nitrogen.

On osmium E. A. Arnold and R. E. Burk[8] found a retardation by hydrogen and nitrogen. We must remark that we have not been able to follow the theoretical treatment of the experimental data in this paper in detail.

From an economic point of view the most important of the catalysts investigated is iron or rather iron mixed with iron nitrides[9]. The decomposition in this case has been investigated i. a. by E. Elöd and W. Banholzer[6] and

[1] G.-M. Schwab, Z. physik. Chem. 128 (1927) 161.

[2] G.-M. Schwab, Z. physik. Chem. B 3 (1929) 337.

[3] J. K. Dixon, Journ. am. chem. Soc. 53 (1931) 2071.

[4] Journ. am. chem. Soc. 50 (1928) 2100.

[5] Proc. national Acad. science, Wash. 13 (1927) 67.

[6] Z. Elektrochem. 32 (1926) 555.

[7] Journ. am. chem. Soc. 53 (1931) 1763.

[8] Journ. am. chem. Soc. 54 (1932) 23.

[9] G. Hägg, Nova acta regiae societatis scientiarum Upsaliensis (4) 7 (1929) 3. Further references see E. Winter l. c. p. 416.

by E. WINTER[1] who agree in finding a strong retardation by hydrogen.

It is thus seen that in nearly all cases a retardation by hydrogen has been noted, while only in one case (Os) a retardation by nitrogen has been found with any certainty. On account of this qualitive agreement between the behaviour of different catalysts it therefore seems to us to be of general interest to note that in one case (W) A. MITTASCH and W. FRANKENBURGER[2] report a direct proof of the formation of a surface-layer of NH on the catalyst, and we might take this as additional evidence in favour of our views concerning the mechanism of the reaction.

We would also call attention to the work of M. BODENSTEIN[3] on the oxidation of ammonia, as it seems that the reactions occurring may be explained by the primary formation of NH. This would lead us to expect a certain parallelism between the decomposition and the oxydation of ammonia on different catalysts, and from the paper by I. E. ADADUROW and T. I. SSOKOOLWA such a parallelism seems actually to have been found[4]. We must remark, however, that the original paper has not been accessible to us.

Finally we wish to offer a remark concerning the detection of the intermediate product NH. It is well known that intermediate products occurring in a sequence of reactions on account of their very short life in the reacting mixture are often very difficult to detect directly. That it seems to

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[1] Z. physikal. chem. **B 13** (1931) 401.

[2] Z. Elektrochem. **35** (1929) 927.

[3] Z. Elektrochem. **41** (1935) 466. Comp. the paper by M. BODENSTEIN on the same subject in the report of the 9 th Internat. Congress of pure and applied Chem. Madrid 1934.

[4] Chem. Zentralbl. 1932 I 341.

be easier in this case might be due to the circumstance that the N-atom is to a certain extent apt to be univalent, a property which from our knowledge of this atom may be expected. Thus the "even" radical NH might be expected to have a longer life than e. g. the "odd" radical NH_2, and thence be more easily detected.

<div align="right">

Chemical department A
Royal Technical College of Denmark.
Copenhagen, August 1935.

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