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# THE DECOMPOSITION OF AMMONIA BY IRON CATALYST.

## (Preliminary Report)

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The kinetics of the decomposition of ammonia is one of the interesting problems from the standpoint of catalysis, and it has been studied by many investigators. Most of the studies have been made by the 'flow method', using tungsten, copper, molybden, osmium, or platinum[1] as a catalyst, but few done by using a powder of iron.[2]

Under Prof. S. Horiba's guidance, by the static method the author tried to investigate the decomposition of ammonia, $2NH_3 \rightleftarrows N_2 + 3H_2$, in the presence of reduced iron used as a catalyst from the view-point of reaction velocity, measuring the change of pressure by means of a spring manometer.

## Experimental

### Materials.

Ammonia: Ammonia of Claude process was liquified with a mixture of alcohol and dry ice, dehydrated with metallic sodium, passed through KOH, fractionally distilled three times and then stored in a vessel.

Iron catalyst: Ferric nitrate of Kahlbaum was denitrated at 400°C. and the $Fe_2O_3$ thus obtained was reduced with hydrogen at 440°C. and used.

Nitrogen: Commercial nitrogen (from a bomb) collected from liquid air was purified as follows. Commercial nitrogen, from which the oxygen present was removed with pyrogallol, was dehydrated with sulphuric acid. Then by passing it through a heated copper mesh, NO was removed.

Hydrogen used for reduction: The hyrogen used was obtained by passing commercial electrolysed hydrogen over heated platinum asbestos and phosphorus pentoxide to remove the oxygen and the water present.

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[1] Dixon, *J. Am. Chem. Soc.*, **53**, 1763 (1931). Arnold and Burk, *J. Am. Chem. Soc.* **54**, 23 (1932). Kunsman, *Phil. Mag.* **10**, 1015 (1930). Chrisman, *Acta Physicochim. U. R. S. S.* **4**, 893 (1936). Hodler, *Trans. Farad. Soc.*, **31**, 229 (1932). Hailes, *Trans. Farad. Soc.*, **27**, 601 (1931). Wagner, *Z. Phys. Chem.* (B), **18**, 369 (1932). Burk, *J. Am. Chem. Soc.*, **56**, 1273 (1934).

[2] Elöd and Banholzer, *Z. Elektrochem.*, **32**, 555 (1926). Kunsman, *J. Am. Chem. Soc.* **50**, 2100 (1928); **51**, 688 (1929). Rubanik, *Acta Physicochim. U. R. S. S.* **3**, 945 (1935). Kobosev, *Acta Physicochim. U. R. S. S.* **4**, 829 (1936). Roiter, Gauchmann and Leperson, *Acta Physicochim.* **4**, 145 (1936).

### Apparatus.

The apparatus used is shown in Fig. 1. The reaction vessel (A) is heated by means of an electric furnace. The reaction vessel and the spring manometer B are made of Pyrex glass. The trap C in front of the reaction vessel is continuously cooled with a mixture of alcohol and dry ice not to let mercury flow into the vessel. To lessen the dead space capillary tubes are used outside the stopcocks A and B.

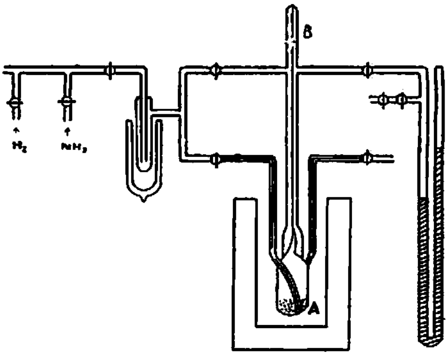

Fig. 1.

### Method of Measurement.

4.6183 g. of $Fe_2O_3$, being put in the reaction vessel as the catalyst, was reduced with hydrogen at 440°C. Then at the same temperature hydrogen was evacuated to $10^{-4}$ mm. by means of a pump, and then the trap (a Dewar vessel) in front of the reaction vessel was exchanged for another one, whose temperature was −40°C. Two minutes later, a given amount of ammonia was introduced and then the stopcocks a and b were quickly closed. This moment was taken as the zero time and the pressure read by means of the manometer as the initial pressure. As the decomposition proceeded, an increase in pressure caused the pointer of the manometer to incline to one side, and from the adjustment of this needle by introducing the air through the stopcock d the pressure in the vessel was indirectly measured.

## Experimental Results

1) Decrease in activity by continuous use: It is a well-known fact that the activity of a catalyst is decreased by its continuous use and in fact this phenomenon was observed in the present experiment as shown in Fig. 2. For example, evacuation was made for 18 hours at 440°C. after Expt. 29, and then Expt. 30 was carried out. Similarly, Expt. 31 was carried out after 20 hours' evacuation. It is seen from these two experiments that activity gradually falls.

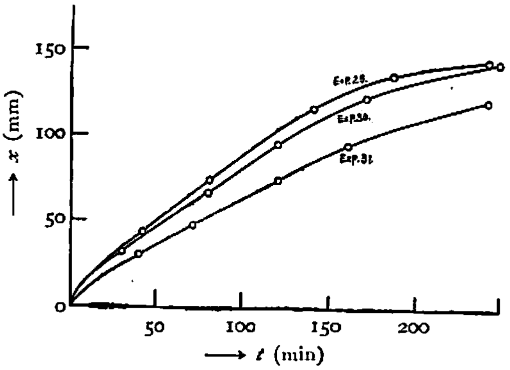

Fig. 2. Decrease in the activity by continuous experiments.
Expt. 29 $P_0=248.3$ mm. 390°C.
Expt. 30 $P_0=253.4$ mm. 390°C.
Expt. 31 $P_0=252.2$ mm. 390°C.

2) Recovery of activity by hydrogen reduction: A decrease in the activity of a catalyst by its continuous use may be ascribed to the fact that the decomposition product of ammonia exerts a retarding action by adsorbing

on the active centres too strongly to be desorbed even by long evacuation with a pump. If the decomposition product were $N_2$ or $H_2$, it would be desorbed merely by evacuation. Therefore, it is supposed that something different from $N_2$ or $H_2$, such as $Fe_xN$, is formed on the surface. Then, passing hydrogen over the catalyst at 440°C. for 24 hours after evacuation, it is found that the activity is recovered and that the curves of the same initial pressure are quite in good agreement. It is inferred that $Fe_xN$ being changed into $NH_3$ by passing $H_2$ over it the activity is recovered.

3) One of the typical examples is shown in Fig. 3 and Table I (Expt. 27). The curve, as a whole, consists of three parts—a curvature at the first stage, a straight line at the second, and again a curvature at the third.

The velocity constant of the first order reaction is expressed by

$$K_m = \frac{1}{t} \ln \frac{a}{a-x},$$

where $a$ is the initial number of mols and $a-x$ is the number of mols at a time $t$. In the present experiment $a$ represents the initial

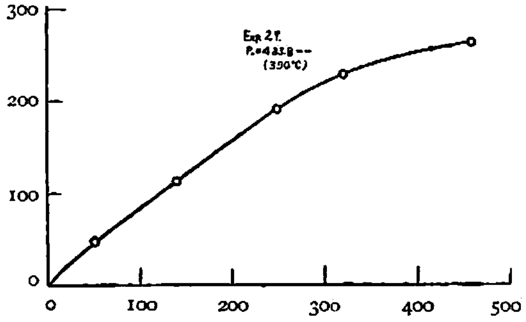

Fig. 3. One of the typical examples.

Table I.

Expt. 27 (390°C). With a catalyst reduced for 30 hrs at 440°C. $P_0$ 433.8 mm.

| $t$ (min) | $p'$ (mm) | $x$ (mm) | $K_m'$ | $v$ | $K$ |
|---|---|---|---|---|---|
| 0 | 433.8 | | | | 0.0001414 |
| 4.2 | 443.9 | 10.1 | 0.002436 | 2.404 | 1404 |
| 10 | 451.3 | 17.5 | 1788 | 1.750 | 1402 |
| 18 | 459.1 | 25.3 | 1450 | 1.405 | 1392 |
| 23 | 462.4 | 28.6 | 1287 | 1.243 | 1392 |
| 30 | 467.6 | 33.8 | 1174 | 1.126 | 1409 |
| 40.2 | 476.0 | 42.2 | 1106 | 1.049 | 1406 |
| 50 | 481.8 | 48.0 | 1019 | 0.960 | 0.0001403 |
| 100 | 516.1 | 82.3 | 914 | 0.823 | |
| 152 | 556.1 | 122.3 | 946 | 0.804 | |
| 206 | 597.6 | 163.8 | 9996 | 0.795 | |
| 253.5 | 628.5 | 194.7 | 1025 | 0.767 | |
| 300 | 651.5 | 217.7 | 1009 | 0.726 | |
| 360 | 676.3 | 242.5 | 988 | 0.674 | |
| 400 | 686.3 | 252.5 | 947 | 0.631 | |
| 460 | 695.0 | 261.2 | 870 | 0.568 | |

pressure and $x$ the increase in pressure. Turning $K_m$ to the common logarithm for convenience and representing it by $K_m'$, we have

$$K_m = 2.303\ K_m'.$$

As to Expt. 27, in the curve showing the relation between $K_m'$ (variable) corresponding to the velocity constant of the first order reaction and $v = x/t$, the retarded form first appears, and next the zero-order form and again what is like the retarded form as shown in Fig. 4.

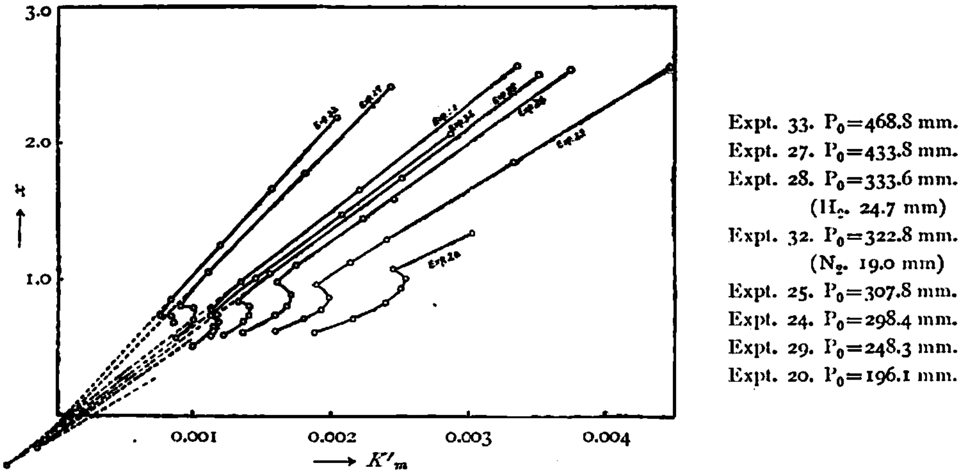

Fig. 4.

4) Other examples: Under various initial pressures, the similar curves appear. Expts. 23, 24, 25, 27, 29, and 33 were all carried out at 390°C. being reduced for 24 hours at 440°C. The results obtained show that the higher the

Table II.

Expt. 29 (390°C). With a catalyst reduced for 19 hrs. at 440°C. $P_0$ 248.3 mm.

| $t$ (min) | $p'$ (mm) | $x$ (mm) | $K_m'$ | $v$ |
|---|---|---|---|---|
| 0 | 248.3 | 0 | | |
| 3 | 255.9 | 7.6 | 0.004500 | 2.533 |
| 7 | 261.3 | 13.0 | 3337 | 1.857 |
| 15 | 270.0 | 21.7 | 2648 | 1.447 |
| 20 | 274.4 | 26.1 | 2412 | 1.305 |
| 30 | 282.4 | 34.1 | 2139 | 1.137 |
| 42 | 291.9 | 43.6 | 1996 | 1.038 |
| 50 | 298.2 | 49.9 | 1949 | 0.998 |
| 99.7 | 337.7 | 89.4 | 1944 | 0.896 |
| 155 | 373.7 | 125.4 | 1971 | 0.809 |
| 200 | 387.9 | 139.6 | 1794 | 0.698 |
| 240 | 393.5 | 145.2 | 1591 | 0.605 |

initial pressure is the sharper the inclination becomes and that if the initial linear parts of those curves are extrapolated, they converge. But the higher the initial pressure is, the closer the point where the line intersects the $v$-axis without converging on the $v$-axis comes to the $K_m'$ axis,[3] and the more clearly the zero-order form is observed.

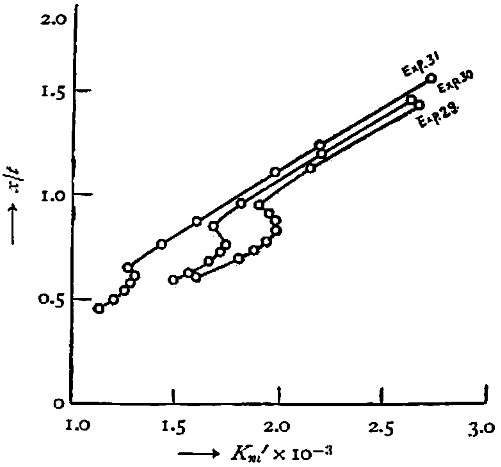

Fig. 5.

Change of the $K_m'$- $x/t$ curve by continuous experiments
Expt. 29. $P_0=248.3$ mm.
Reduced for 19 hrs. Expt. 390°C.
Expt. 30. $P_0=253.4$ mm.
Not reduced Expt. temp. 390°C.
Expt. 31. $P_0=252.2$ mm.
Not reduced Expt. temp. 390°C.

In a series of experiments carried out without any reduction, the curve tends to take such a type as shown in Fig, 5 (Expts. 29, 30 and 31).

5) When the temperature of decomposition is raised (Reduction temperature, 440°C.): The temperature of decomposition being raised to 410°C., 420°C., or 430°C., the reaction velocity was measured. The results obtained indicate that though the reaction velocity becomes larger with the rise of temperature, the type of the $K_m'$-$v$ curve is the same as before.

6) Measurement of the adsorption of hydrogen: the adsorption of hydrogen was measured and it was found that the

Table III.

Expt. 30 (390°C). $P_0$ 253.4 mm. With a catalyst evacuated for 18 hrs. at 440°C. without reduction.

| $t$ (min) | $p'$ (mm) | $x$ (mm) | $K_m'$ | $v$ |
|---|---|---|---|---|
| 0 | 253.4 | 0 | — | — |
| 5 | 265.3 | 11.9 | 0.004108 | 2.380 |
| 14 | 273.9 | 20.5 | 2617 | 1.464 |
| 22.5 | 280.5 | 27.1 | 2183 | 1.204 |
| 30.0 | 286.3 | 32.9 | 2013 | 1.097 |
| 42.0 | 294.0 | 40.6 | 1805 | 0.967 |
| 50 | 299.0 | 45.6 | 1723 | 0.912 |
| 100 | 337.1 | 83.7 | 1741 | 0.837 |
| 150 | 367.4 | 114.0 | 1730 | 0.760 |
| 247 | 397.8 | 144.4 | 1483 | 0.584 |

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[3] As to the discussion of this point, see the work of Dr. M. Kubokawa (This journal 11, 94 (1937)).

Table IV.

Expt. 31 (390°C). $P_0$ 252.2 mm. With a catalyst evacuated for 20 hrs. at 440°C. without reduction.

| $t$ (min) | $p'$ (mm) | $x$ (mm) | $K_m'$ | $v$ |
|---|---|---|---|---|
| 0 | 252.2 | 0 | — | — |
| 3.2 | 257.2 | 5.0 | 0.002719 | 1.562 |
| 7 | 260.9 | 8.7 | 2179 | 1.243 |
| 12.5 | 266.1 | 13.9 | 1970 | 1.112 |
| 20 | 270.1 | 17.9 | 1599 | 0.895 |
| 26 | 275.1 | 22.9 | 1590 | 0.881 |
| 32 | 278.8 | 26.6 | 1512 | 0.831 |
| 40 | 283.2 | 31.0 | 1424 | 0.775 |
| 52 | 289.0 | 36.8 | 1317 | 0.708 |
| 101 | 318.0 | 65.8 | 1300 | 0.651 |
| 150 | 343.3 | 91.1 | 1298 | 0.607 |
| 203 | 363.4 | 111.2 | 1244 | 0.548 |
| 280 | 382.0 | 129.8 | 1121 | 0.463 |

adsorbed amount was, though roughly, so small as to be neglected, i.e. 3.26 mm. in 42 minutes at 390°C. and under the initial pressure of 100.5 mm.

7) The case when hydrogen was introduced beforehand (Expt. 28 ; Fig. 4): One hour after the introduction of 24.7 mm. of hydrogen, ammonia being introduced, measurement was made. The type of the $K_m$-$v$ curve obtained is much the same.

Table V.

Expt. 28 (390°C). With a catalyst evacuated for 23 hrs. at 440°C without reduction. 333.6 mm. of $NH_3$ was admitted after the catalyst was left to stand 24.7 mm. hydrogen.

| $t$ (min) | $p'$ (mm) | $x$ (mm) | $K_m'$ | $v$ |
|---|---|---|---|---|
| 0 | 333.6 | — | — | — |
| 4 | 343.8 | 10.2 | 0.003372 | 2.550 |
| 10 | 350.2 | 16.6 | 2217 | 1.660 |
| 15 | 354.7 | 21.1 | 1892 | 1.406 |
| 23 | 360.6 | 27.0 | 1593 | 1.173 |
| 32 | 366.3 | 32.7 | 1400 | 1.022 |
| 40 | 372.5 | 38.9 | 1346 | 0.973 |
| 50 | 379.3 | 45.7 | 1280 | 0.914 |
| 100 | 410.3 | 76.7 | 1135 | 0.767 |
| 160 | 450.7 | 117.1 | 1174 | 0.732 |
| 210 | 476.4 | 142.8 | 1155 | 0.680 |
| 252 | 495.0 | 161.4 | 1140 | 0.640 |
| 310 | 514.8 | 181.2 | 1097 | 0.585 |
| 390 | 529.9 | 196.3 | 988 | 0.503 |

8) The case when nitrogen was introduced beforehand (Expt. 32; Fig. 4): One hour after the introduction of 19 mm. of nitrogen, ammonia, whose initial pressure was 322.8 mm., being introduced, measurement was made. The type of the curve is the same as before.

When hydrogen and nitrogen were introduced, the extrapolation of the first linear parts did not converge to one point, having some inclination different from the ordinary case.

9) The case when ammonia was introduced in the presence of the decomposition product of ammonia (Table 19, Expts. 39, 40 and 43; Figs. 11 and 12.): Expt. 39 is the case when, 253.6 mm. of ammonia being introduced in presence of 142 mm. of the decomposition product formed in Expt. 38, measurement was carried out at 410°C.

Expt. 40 is the case when, 253.6 mm. of ammonia being introduced in the presence of 200.6 mm. of the decomposition product formed in Expt. 42 being left to stand for 24 hours and then 97.1 mm. of ammonia introduced at 410°C., measurement was carried out at 410°C.

In all these cases, the initial linear part corresponding to the retarded form does not appear (Table 21).

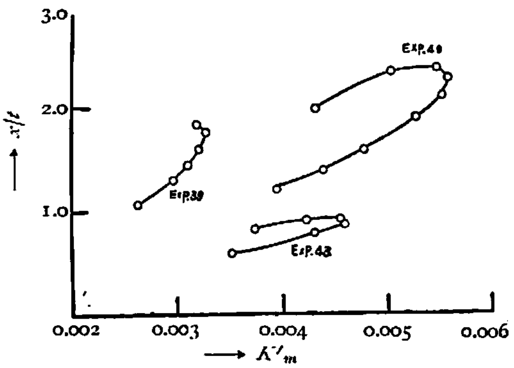

Fig. 6.

The case when the decomposition product of $NH_3$ was left to stand. 201.9 mm of the endproduct left to stand for 24 hrs.

Expt. 29, Expt. 38, end Product 142.3 mm $NH_3$ 253.6 mm at 410°C, Expt. 40. exp. 39, end Product 200.6 mm $NH_3$ $P_0$ 203.2 mm at 420°C, Expt. 43 Expt. 43, end Product 201.9 mm was left to stand for 24 hrs. $NH_3$ $P_0$ 97.1 mm at 410°C.

## Considerations of the Experimental Results

As the reaction in question proceeds stepwise in the following order—a reaction of retarded form and that of the zero order, the theory established by Prof. S. Horiba and Dr. T. Ri in their study of the decomposition of carbon monoxide can be applied in the present case (See p. 125).

As to the reaction of retarded form, it may be supposed that hydrogen and nitrogen, the decomposition products of ammonia, make retarding action by adsorbing on the active centres of the surface, of the catalyst. If so, when hydrogen or nitrogen is saturated beforehand, the initial linear part of the $K_m'$-$v$ curve is not to appear. In Expts. 28, 32, and 41, however, the part is clearly observed and so this supposition is not justified. If hydrogen and oxygen newly formed on the surface of the catalyst are considered to be atomic and active, it is another question. In Expts. 39, 40, and 43 carried out with the remaining decomposition products of ammonia the part in question does not appear and this may be ascribed to the fact that the reaction occurs halfway because the most highly active part has been covered.

As to the curve analogous to that of retarded form which appears after the reaction of the zero order, the question whether its appearance is ascribed either to the opposite reaction or to the reactivation of the poisoned active centres remains to be solved by further research.

## Summary

1) The decomposition velocity of ammonia in the presence of reduced iron has been measured at 390°—430°C.

2) Seeing from the $K_m'$-$v$ curve, the reaction in question is very complex and seems to proceed in the following order—a reaction of retarded form at the initial stage, that of the zero order and again that of retarded form.

3) It is supposed that the retarding action at the initial stage is caused by the fact that $Fe_xN$ which has been formed on the surface of the catalyst covers the highly active centres.

In closing, the anthor wishes to express his sincere thanks to Prof. S. Horiba for his kind guidance throughout this investigation.

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