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ON THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA.

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I. Introduction.

The photolysis of ammonia by ultraviolet rays is one of the photochemical reactions earliest studied by many investigators.1)~19),20) Since Warburg measured the quantum yield of the reaction in 1911, a number of studies on this line have been done from various standpoints. Accordingly, the behavior of the reaction in the photolysis has been made fairly clear and yet its mechanism is uncertain.

The present author intended to elucidate (i) the heterogeneity of the reaction (wall-effect), (ii) the effect of pressure, and (iii) the relation between these two, making experiments by the two methods: thermal analysis of the Budde-effect and ammonia-condensing method.

Until now the Budde-effect (photo-expansion)21)~26) has meant thermal expansion caused by recombination heat of the free atoms generated by the photoche-

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mical dissociation of halogen, and the very effect has been studied only about halogen. The present author, extending the meaning, signifies by it "thermal expansion in a photochemical reaction involving no chain reaction". The occurrence of such thermal expansion as this at the moment of exposure in all photochemical reactions will be properly expected, but experimental difficulty due to smallness of the expansion has so far confined the measurement only to halogen. A compound other than halogen, therefore, was first studied in the present research.

II. Experimental.

A) Materials.

Ammonia used was prepared by purifying synthetic ammonia supplied in a bomb. Ammonia which was preliminarily dried with soda lime and potassium hydroxide was collected in a trap cooled with dry-ice. After repeated vacuum distillations with liquid oxygen it was condensed on metallic sodium, dried for long hours, solidified in another trap, and evaporated after residual non-condensable gas was completely removed.

Nitrogen: Sodium azide was first dried by evacuation at 250°C., and then decomposed above 280°C.

B) Apparatus.

Light source: A hydrogen discharge tube of 3 kw. was first used, but its light intensity was insufficient for the measurement of the Budde-effect, and in the present experiment zinc spark was used. The electrodes were discs of zinc with V-shaped edges 5 mm. thick and 8 cm. in diameter. The distance between the two electrodes was 1.6 mm.; the primary current of the transformer was 13.0 amp., being kept constant throughout the experiment. The time of illumination was within 20 sec. at one run, and during the time light intensity could be kept constant by adjusting the resistance of the primary circuit. Every time illumination was made, the electrodes were little by little rotated so that a fresh part might be supplied.

Manometer: The manometer was much the same with what was first used by Dr. W. Jono in his study of explosion reaction,27) and is called electric capacity differential manometer, to which the change in capacity due to the displacement by pressure change of a mica membrane used as one of the poles of the condenser was applied. The construction of the condenser is shown in Fig. 1. The condenser consists of the two parts, A and B, made of brass 5 cm. in diamerer. On K, the upper part of A, a mica membrane G 0.1 mm. thick, whose surface has been Pt-sputtered, is stretched and

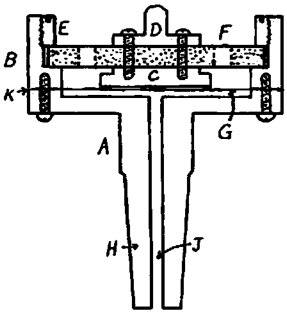

Fig. 1.

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27) W. Jōno, *Rev. Phys, Chem. Japan* (Japanese edition), 9, 1 (1935).

fixed with Apiezon wax W and pressed with a ring B. C, a brass plate, is one of the poles and F a glass plate. This condenser is put in a glass vessel A as shown in Fig. 3. The both poles of the condenser are connected with the electric circuit at the position of C in Fig. 2. In Fig. 2, A, B and D are accumulators of large capacity; V is a vacuum tube 201 A; L_1 and L_2 are coils 12 cm. in diameter; R_1 is a 100 ohm fixed resistance; R_2 and R_3 are 100 ohm variable resistances. The galvanometer[28] used is of short period and high sensibility: period, 0.22 sec. and current sensibility, 3×10^{-8} amp. The change of capacity of the condenser, C, is turned to that of the plate current by V, and by means of the galvanometer G the change is recorded on sheets of bromide paper or observed on scale. This manometer was used in sensibility of $10^{-3}\sim10^{-4}$ mmHg. All the accumulators kept electric current flowing for long hours before use.

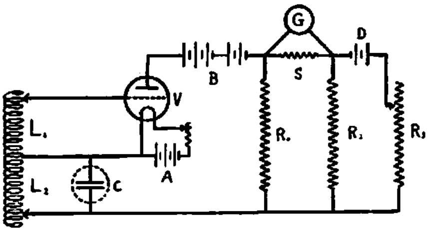

Fig. 2.

Reaction vessels: The two vessels used are cylindrical tubes of soft glass, each bottom of which has a window of plane quartz plate, and they are 5.4 cm. and 3.5 cm. in diameter, 7.1 cm. and 8.0 cm. in length, and 167 cc. and 85 cc. in volume respectively (reaction vessel No. 1 and 2).

C) Experimental methods.

1) The Budde-effect and the cooling constant. Thermal analysis of the Budde-effect.

In Fig. 3, closing the stopcock *c*, *e*, and *f*, and opening *a*, *b*, *d*, and *g*, the parts A and R were completely evacuated by means of a mercury pump. Then closing *g* and opening *e*, ammonia of a given pressure was introduced into them and *d* closed. For a while after the introduction of ammonia, when *a* was closed, the pressure of A rapidly decreased and it indicated that ammonia was being adsorbed on the metal in A. Therefore it was left alone for several hours until it was saturated and equilibrium was established, and then the measurement was made. Next, closing *a* and illuminating for a few seconds, light was shut off. The pressure change during the time was photographed and the time

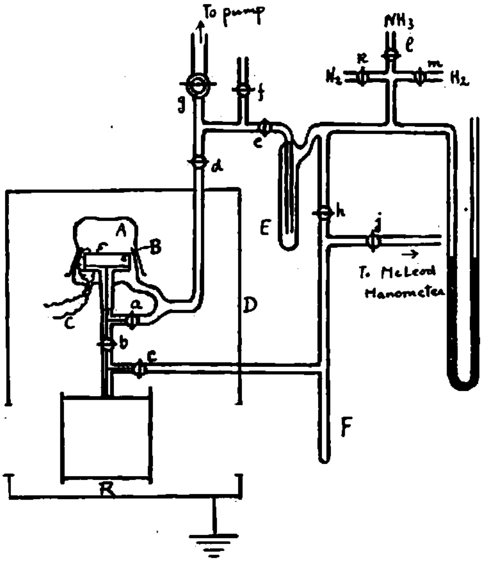

Fig. 3.

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[28] The galvanometer has been planned and made by Dr. K. Sassa, in the Geophysical Laboratory of the Kyoto Imperial University.

mark made by means of a tuning-fork (frequency : 26.2). The time-pressure curve obtained at the moment of exposure has a general form as shown in Fig. 4, ΔP_t is the pressure increase caused by the reaction heat and ΔP_d that by the increase in the number of molecules due to decomposition. In the case of long exposure after the temperature of the reacting gas had reached a stationary state, the increase in pressure was caused only by that in the number of molecules, and the time-pressure curve obtained was linear as shown in Fig. 5.

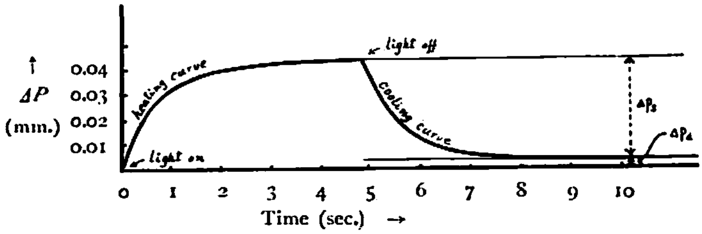

Fig. 4. Time-pressure curve at the moment of light on and off.

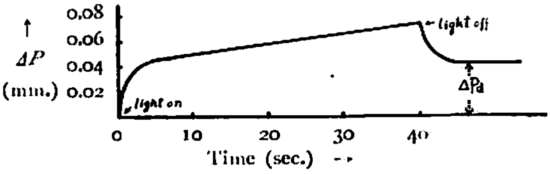

Fig. 5. Time-pressure curve in long exposure.

From the cooling curve in Fig. 4 after the shutting off of light, the cooling constant k is obtained according to the following equation,

$$k = \frac{2.303}{t} \log \frac{\Delta P_t}{\Delta P} \qquad (1)$$

ΔP in this equation is, of course, equivalent to the $\Delta P - \Delta P_d$ in Fig. 4. The cooling constants determined at various pressures for reaction vessel No. 1 and 2 are shown in Fig. 6.

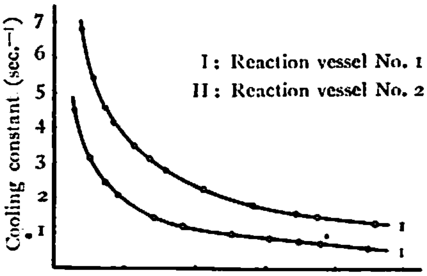

Fig. 6. Cooling constants at various ammonia pressures.

Thermal analysis of the Budde-effect.

Let us consider the heat amount to be concerned with the following reaction,

$$NH_3 + h\nu \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2.$$

It has been admitted that when ammonia absorbs ultraviolet rays (2200—1900Å) it dissociates by predissociation into NH_2 and atomic hydrogen and also that the quantum yield of the decomposition is in average 0.25. Therefore this reaction can be expressed by

i) $NH_3 \rightarrow NH_2 + H$

ii) $NH_2 + H$ — (through certain processes) $\rightarrow NH_3$

and iii) $NH_2 + H$ — („) $\rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$.

In the process (i), 133 kcal. per mol is absorbed and in (ii) the same quantity is evolved. It is well known that the process, (i)→(iii), is endothermic by 11 kcal. and it follows that the ammonia which decomposes into N_2 and H_2 makes an exothermic reaction evolving 122 kcal. The amount of heat evolved in the whole reaction is as follows:

$$Q = 133 \times 0.75 + 122 \times 0.25 = 130 \text{ kcal.}$$

Accordingly, so far as the quantum yield is not so much different from 0.25, this value of Q can be regarded as the reaction heat.

It is considered that the reaction heat dissipates in the following two ways: the case when the heat dissipates on the walls owing to the conduction and convection after being evolved in the gaseous phase and the case when it is evolved on the walls from the beginning. In the former case, of course, the reacting gas is heated, while in the latter the heat does not contribute to the heating of the reacting gas because of large difference between the heat capacity of the reacting gas and that of the wall. Consequently, when the above-mentioned Q is taken to be the heat of reaction, the reaction velocity $\frac{dx}{dt}$[29] in photo-stationary state to be obtained from the following equation by the method of the thermal analysis of reaction velocity[30] will be the reaction velocity in the homogeneous gaseous phase:

$$K\frac{dx}{dt} = k(\Delta P_s) \tag{2}$$

where $$K = \frac{nRQ}{s\sigma V^2} \tag{3}$$

and n, s and σ are the number of moles, the specific weight and the specific heat of the reacting gas respectively, V the volume of the reaction vessel and R the gas constant. Substituting in this equation the numerical values the homogeneous reaction velocity is obtained from the following expression:

$$\frac{dx}{dt} = 1.43 \times 10^{-7} \cdot k(\Delta P_s) \text{ mol} \cdot \text{sec}^{-1} \text{ (for the reaction vessel No. 1)} \tag{4}$$

$$\frac{dx}{dt} = 0.724 \times 10^{-7} \cdot k(\Delta P_s) \text{ mol} \cdot \text{sec}^{-1} \text{ (for the reaction vessel No. 2)} \tag{5}$$

Thus, the "homogeneous reaction velocity" expressed by $\frac{dx}{dt}$ means the velocity of the *whole* reaction involving (i), (ii) and (iii) in the *gaseous* phase, while the "decomposition velocity" measured by the under-mentioned methods — (2) and (3) — will be expressed by $\frac{dx_d}{dt}$ as the velocity of actual decomposition into N_2 and H_2 through reactions (i) and (iii).

(2) Measurement of the decomposition velocity by the ammonia-condensing method.

In Fig. 3, closing b and opening e and h, ammonia of a given pressure was introduced in the reaction vessel. Closing h, F was cooled with liquid oxygen to solidify ammonia and was evacuated completely through g, opening b and j. When the residual pressure read by

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29) For the photolysis of ammonia is a reaction of zero order and the decomposition velocity and the homogeneous reaction velocity are constant with time, it is not always necessary to write them in differential form as here.

30) S. Horiba. *Rev. Phys. Chem. Japan*, 11, 439 (1937).
Eq. (2) is a special case $\left(\frac{d(\Delta P)}{dt} = 0\right)$ of the general form $K\frac{dx}{dt} = k(\Delta P) + \frac{d(\Delta P)}{dt}$ in the method of the thermal analysis.

means of a McLeod manometer became below 3×10^{-5}mm., evacuation was stopped, and after it was confirmed that the pressure of non-condensable gas did not change, closing j and evaporating ammonia. After such a precaution illumination was done for a given time. After shutting off light, ammonia was again solidified and the pressure of non-condensable gas was read. Calculating the difference between the pressures before and after the illumination ($P_f - P_i$) and assuming that the gas was a mixture such as $H_2 : N_2 = 3 : 1$, the decomposition velocity of ammonia, $\frac{dx_d}{dt}$, was determined.

3) Measurement of the decomposition velocity by the pressure increase caused by the increase in the number of molecules.

In the case of pure ammonia, the decomposition velocity can be accurately determined by the above-mentioned ammonia-condensing method. But when the reacting gas is a mixture of ammonia and nitrogen the method is not applicable. In this case, the pressure increase ΔP_d caused by illumination for a given time was measured directly by means of an electric capacity differential manometer.

III. Experimental Results.

A) The influence of the pressure of ammonia on the homogeneous reaction velocity.

The expansion ΔP_d under various pressures of ammonia was measured by the above-mentioned method (II, C, 1). The light intensity was kept the same under each pressure and the amount of light absorbed also constant above 50 mm. of ammonia.

1) The case when the larger reaction vessel was used.

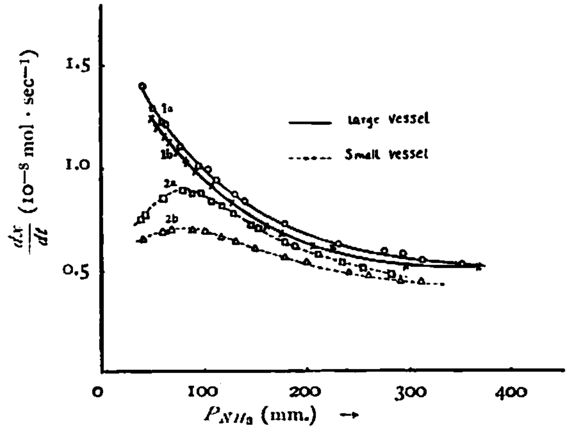

Fig. 7. Homogeneous reaction velocity.

Curve 1a. Large reaction vessel and small illuminated area.
Curve 1b. Large reaction vessel and large illuminated area.
Curve 2a. Small reaction vessel and small illuminated area.
Curve 2b. Small reaction vessel and large illuminated area.

Using reaction vessel No. 1 (D = 5.4 cm.), the effect produced by variation in the illuminated area was examined.

a) When a small portion in the centre was illuminated.

The illuminated area was 2 cm. in diameter in the front (or F.D. = 2 cm.) and 1 cm. at the back (or B.D. = 1 cm.) and the side wall effect was made as little as possible. The experimental results obtained are given in Table 1 and Fig. 7 (Curve 1a).

Table I.

I	II	III	VI	V	VI
Exp. No.	P_{NH_3} (mm.)	ΔP_s (mm.)	k (sec.$^{-1}$)	$k(\Delta P_s)$ (10^{-2}mm. sec.$^{-1}$)	$\frac{dx}{dt}$ (10^{-8}mol. sec^{-1}.)
1	51.4	0.028	3.25	9.10	1.30
2	61.0	0.0305	2.82	8.60	1.23
3	77.0	0.0332	2.37	7.86	1.12
4	94.4	0.0347	2.05	7.12	1.02
5	105.5	0.0363	1.90	6.90	0.99
6	114.0	0.0371	1.78	6.60	0.94
7	128.3	0.0380	1.63	6.20	0.89
8	143.0	0.0388	1.50	5.82	0.83
9	186.0	0.0408	1.20	4.90	0.70
10	234.0	0.0429	1.05	4.50	0.64
11	265.8	0.0450	0.96	4.32	0.62
12	289.0	0.0462	0.90	4.16	0.60
13	312.2	0.0470	0.85	3.97	0.57
14	349.1	0.0467	0.77	3.62	0.52
15	60.0	0.0304	2.86	8.70	1.24
16	48.8	0.0272	3.36	9.14	1.31
17	40.3	0.0248	3.95	9.80	1.40
18	32.0	0.0214	4.84	10.35	1.48

b) When the illuminated area was made larger.

The illuminated area was F.D. = 3 cm. and B.D. = 1.5 cm. The results obtained are given in Table II and Fig. 7 (Curve 1b). As seen from the curve, the homogeneous reaction velocity slightly falls over the whole range of pressure, but even at low pressures no marked change is noticed.

Table II.

I	II	III	IV	V	VI
Exp. No.	P_{NH_3} (mm.)	ΔP_s (mm.)	k (sec.$^{-1}$)	$k(\Delta P_s)$ (10^{-2}mm. sec.$^{-1}$)	$\frac{dx}{dt}$ (10^{-8}mol. sec.$^{-1}$)
1	48.8	0.0262	3.36	8.8	1.26
2	53.4	0.0272	3.15	8.6	1.23
3	86.0	0.0336	2.18	7.3	1.05
4	67.0	0.0306	2.61	8.0	1.14
5	75.5	0.0318	2.40	7.6	1.09
6	85.6	0.0325	2.24	7.28	1.04
7	92.7	0.0339	2.07	7.02	1.00
8	63.3	0.0298	2.75	8.2	1.17
9	84.0	0.0330	2.22	7.3	1.04
10	111.1	0.0355	1.95	6.46	0.93
11	134.4	0.0376	1.58	5.94	0.85
12	165.0	0.0386	1.32	5.10	0.73
13	182.3	0.0390	1.22	4.76	0.68
14	206.0	0.0410	1.13	4.63	0.66
15	229.0	0.0428	1.06	4.50	0.64
16	260.0	0.0445	0.98	4.36	0.62
17	298.6	0.0490	0.88	4.30	0.62
18	356.5	0.0542	0.76	4.12	0.59

2) The case when the small reaction vessel was used.

The results obtained by using reaction vessel No. 2 (D = 3.5 cm.) show that the homogeneous reaction velocity falls at pressures lower than about 100 mm. and also that the side-wall effect clearly begins appearing.

a) When the illuminated area was small.

The illuminated area was F.D. = 2.6 cm. and B.D. = 1.6 cm. The results obtained are given in Table III and Fig. 7 (Curve 2a).

Table III.

I	II	III	IV	V	VI
Exp. No.	P_{NH_3} (mm.)	ΔP_s (mm.)	k (sec.$^{-1}$)	$k(\Delta P_s)$ (10^{-2}mm. sec.$^{-1}$)	$\frac{dx}{dt}$ (10^{-8}mol. sec^{-1}.)
1	39.0	0.0163	6.6	10.8	0.78
2	43.0	0.0177	6.24	11.0	0.80
3	60.2	0.0236	5.14	12.1	0.88
4	78.0	0.0290	4.38	12.7	0.92
5	86.7	0.0305	4.07	12.4	0.90
6	97.8	0.0330	3.77	12.4	0.90
7	107.6	0.0342	3.57	12.2	0.88
8	117.7	0.0356	3.35	11.9	0.86
9	129.4	0.0365	3.15	11.5	0.83
10	145.0	0.0365	2.92	10.7	0.77
11	150.9	0.0367	2.85	10.5	0.76
12	180.5	0.0370	2.50	9.3	0.67
13	191.0	0.0367	2.41	8.9	0.64
14	217.0	0.0393	2.21	8.7	0.63
15	236.7	0.0397	2.06	8.2	0.59
16	254.0	0.0393	1.97	7.8	0.56
17	282.8	0.0378	1.85	7.0	0.51

b) When the illuminated area was large.

The illuminated area was F.D. = 3 cm. and B.D. = 2.6 cm The results obtained are given in Table IV and Fig. 7 (Curve 2b). The light intensity was a little different from that in the case of (a), and so the corrected values are given in the seventh column.

Table IV.

I	II	III	IV	V	VI	VII
Exp. No.	P_{NH_3} (mm.)	ΔP_s (mm.)	k (sec.$^{-1}$)	$k(\Delta P_s)$ (10^{-2}mm. sec.$^{-1}$)	$\frac{dx}{dt}$ (10^{-8}mol. sec.$^{-1}$)	$\frac{dx}{dt}$ correc. (10^{-8}mol. sec.$^{-1}$)
1	42.0	0.0163	6.32	10.3	0.745	0.674
2	56.0	0.0200	5.37	10.8	0.78	0.705
3	66.0	0.0227	4.84	11.0	0.795	0.72
4	91.7	0.0280	3.94	11.0	0.795	0.72
5	102.6	0.0301	3.65	11.0	0.795	0.72
6	116.2	0.0308	3.38	10.4	0.75	0.68
7	132.3	0.0316	3.11	9.8	0.71	0.643

8	145.7	0.0322	2.91	9.4	0.68	0.615
9	180.0	0.0342	2.52	8.6	0.625	0.565
10	200.9	0.0356	2.33	8.3	0.60	0.543
11	215.5	0.0358	2.21	7.9	0.58	0.525
12	236.4	0.0371	2.08	7.7	0.56	0.506
13	262.0	0.0384	1.94	7.45	0.54	0.488
14	288.5	0.0390	1.83	7.14	0.517	0.468
15	312.0	0.0400	1.73	6.92	0.50	0.453
16	336.4	0.0412	1.65	6.80	0.493	0.446

From the comparison between Curves 2a and 2b in Fig. 7, it is seen that the homogeneous reaction velocity is, as a whole, considerably small in Curve 2b and that the difference between those two curves becomes larger below 200 mm.

B) The influence of the pressure of ammonia on the decomposition velocity.

The decomposition velocity was examined under various conditions as the function of pressure by the method already mentioned (II, C, 2). Above 50 mm. pressure of ammonia, the amount of light absorbed is constant, so that the decomposition velocity is to be the relative equantum yield.

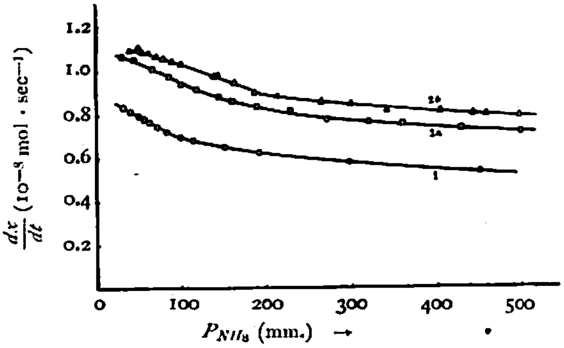

Fig. 8. The change of the decomposition velocity (the relative quantum yield) with ammonia pressure.

Curve 1. Large reaction vessel and small illuminated area.
Curve 2a. Small reaction vessel and small illuminated area.
Curve 2b. Small reaction vessel and large illuminated area.

1) The case when the larger reaction vessel was used.

The experimental conditions were quite the same as in (A, 1, a), i.e., reaction vessel No. 1 being used and the illuminated area being F. D. = 2 cm. and B. D. = 1 cm.

As shown in Table V and Fig. 8, as the pressure of ammonia is decreased from such high pressures as about 700 mm., the decomposition velocity increases slowly and almost linearly, but rapidly from about 80 mm. At pressures higher than 100 mm. this result agreed quite well with that of Wiig, but at lower pressures the result obtained was quite the reverse. Therefore, experiments were carefully repeated, but the fall of the quantum yield at low pressures was never observed and, on the contrary, increase in velocity was ascertained with sufficient reproducibility.

Table V.

The influence of the pressure of ammonia on the relative quantum yield. Total volume 600 cc. Time of illumination 20 sec. P_f-P_i, the pressure of non-condensable gas produced, is given in the third column, the value of this pressure converted into the pressure of ammonia decomposed per sec. in the fourth, and the decomposition velocity in the fifth.

I	II	III	IV	V
Exp. No.	P_{NH_3} (mm.)	P_f-P_i (10^{-3}mm.)	$\frac{d(\Delta P_d)}{dt}$ (10^{-4}mm. sec.$^{-1}$)	$\frac{dx_d}{dt}$ (10^{-8}mol. sec.$^{-1}$)
1	28.6	9.75	2.44	0.86
2	38.5	9.38	2.34	0.825
3	48,3	9.05	2.26	0.80
4	56.9	8.90	2.22	0.785
5	64.5	8.63	2.16	0.763
6	72.5	8.27	2.07	0.73
7	85.3	8.15	2.04	0.72
8	99.4	7.92	1.98	0.70
9	112.6	7.75	1.94	0.685
10	148.0	7.50	1.88	0.664
11	24.5	9.85	2.46	0.87
12	40.3	9.40	2.35	0.83
13	73.0	8.55	2.14	0.756
14	117.0	7.80	1.90	0.67
15	193.0	7.10	1.77	0.625
16	295.5	6.42	1.60	0.565
17	448.1	5.75	1.44	0.51
18	711.0	4.02	1.01	0.356

2) The case when the small reaction vessel was used. Using the reaction vessel No. 2, similar experiments were carried out.

a) When the illuminated area was small.

The experimental conditions were the same as those in (A, 2, a).

The results obtained are given in Table VI and Fig. 8 (Curve 2a).

Table VI. Total volume 518cc. Time of illumination 20 sec.

I	II	III	IV	V
Exp. No.	P_{NH_3} (mm.)	P_f-P_i (10^{-3}mm.)	$\frac{d(\Delta P_d)}{dt}$ (10^{-4}mm. sec.$^{-1}$)	$\frac{dx_d}{dt}$ (10^{-8}mol. sec.$^{-1}$)
1	30.0	14.4	3.60	1.09
2	43.0	14.2	3.55	1.08
3	62.9	13.5	3.36	1.02
4	84.2	12.9	3.23	0.98
5	97.8	12.3	3.08	0.93
6	113.8	12.1	3.03	0.92
7	137.0	11.9	2.98	0.90
8	156.5	11.4	2.85	0.86
9	188.6	11.2	2.80	0.85
10	225.4	10.9	2.73	0.83
11	265.4	10.1	2.53	0.77
12	317.6	9.9	2.48	0.75
13	364.2	9.7	2.43	0.74
14	430.0	9.4	2.35	0.71
15	500.0	9.0	2.25	0.68
16	558.8	8.7	2.18	0.66

b) When the illuminated area was large.

The experimental conditions were the same as those in (A, 2, b). Ths results obtained are given in Table VII and Fig. 8 (Curve 2b).

Table VII.

Total volume 518 cc. Time of illumination 20 sec.

I	II	III	IV	V	VI
Exp. No.	P_{NH_3} (mm.)	P_f-P_i (10^{-3}mm.)	$\frac{d(\Delta P_d)}{dt}$ (10^{-4}mm. sec.$^{-1}$)	$\frac{dx_d}{dt}$ (10^{-8}mol. sec.$^{-1}$)	$\frac{dx_d}{dt}$ correc. (10^{-8}mol. sec.$^{-1}$)
1	32.7	16.1	4.03	1.22	1.10
2	45.6	16.5	4.13	1.25	1.13
3	50.4	16.1	4.03	1.22	1.10
4	62.4	16.0	4.00	1.21	1.10
5	72.2	15.6	3.90	1.18	1.07
6	78.0	15.4	3.85	1.17	1.06
7	90.8	15.3	3.83	1.16	1.05
8	101.6	15.0	3.75	1.14	1.03
9	137.2	14.1	3.53	1.07	0.97
10	214.2	12.8	3.20	1.97	0.88
11	362.8	12.6	3.15	0.95	0.86
12	139.1	14.3	3.58	1.08	0.98
13	159.5	13.7	3.43	1.04	0.94
14	185.2	13.1	3.28	0.99	0.90
15	222.3	12.5	3.13	0.95	0.86
16	296.0	12.4	3.10	0.94	0.85
17	344.0	11.8	2.95	0.89	0.81
18	403.0	12.0	3.00	0.91	0.82
19	446.5	11.7	2.93	0.89	0.81
20	495.5	11.5	2.88	0.87	0.79

C) The effect of adding nitrogen.

All the results described above were obtained with pure ammonia. In connection with this, to see how the homogeneneity or heterogeneneity of the reaction varies in case of adding nitrogen to ammonia of a given pressure is an interesting matter in the interpretation of the experimental results obtained with pure ammonia.

Using reaction vessel No. 2 and under much the same conditions as (A, 2, a) and (B, 2, a), a series of experiments were carried out concerning the homogeneous reaction velocity and the decomposition velocity in case of adding nitrogen successively to ammonia of 50.1 mm. The experimental results will be described below.

1) The effect of adding nitrogen on the homogeneous reaction velocity.

As in the case with pure ammonia; the photo-expansion $\varDelta P_s$ and the cooling constant k under various pressures were first determined and the homogeneous reaction velocity was calculated by the method of thermal analysis. In the case of a gas mixture the value of K in equation (5), however, varies according as the ratio of mixing. In the present case, therefore, $\frac{S_{NH_3}\sigma_{NH_3}P_{NH_3}+S_{N_2}\sigma_{N_2}P_{N_2}}{P_{NH_3}+P_{N_2}}$ was used in place of $s\sigma$ in equation (5). (Consequently, the value of K for each mixture is different and $\frac{dx}{dt}$ is not proportional to the product $k(\varDelta P_s)$.)

The results obtained are given in Table VIII and Fig. 9. It is seen that as the mixed amount of nitrogen is increased, so is the homogeneity of the reaction.

Table VIII.

I	II	III	IV	V	VI
Exp. No.	Total pressure (mm.)	$\varDelta P_s$ (mm.)	k (sec.$^{-1}$)	$k(\varDelta P_s)$ (10^{-1}mm. sec.$^{-1}$)	$\frac{dx}{dt}$ (10^{-8}mol. sec.$^{-1}$)
1	50.1	0.0193	7.02	1.36	0.99
2	90.0	0.0330	4.98	1.64	1.05
3	148.0	0.0523	3.60	1.88	1.12
4	192.3	0.0685	2.98	2.04	1.18
5	244.0	0.087	2.40	2.09	1.19
6	286.5	0.105	2.10	2.20	1.24
7	341.3	0.129	1.78	2.30	1.28
8	384.3	0.143	1.60	2.29	1.27

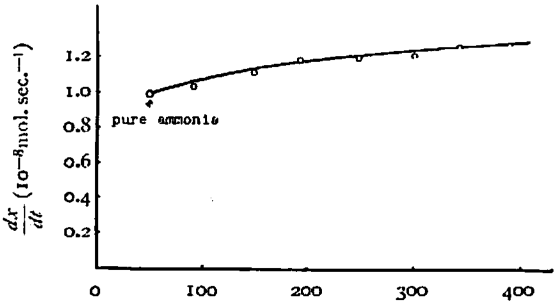

Fig. 9. The influence of adding nitrogen on the homogeneous reaction velocity.

2) The effect of adding nitrogen on the decomposition velocity.

The change of the decomposition velocity caused by adding nitrogen was examined by the method (II, C, 3). The results are given in Table IX and Fig. 10.

Table IX.

Volume 85cc. Time of illumination 20 sec.

I	II	III	IV	V
Exp. No.	Total pressure (mm.)	ΔP_d (10^{-3}mm.)	$\frac{d(\Delta P_d)}{dt}$ (10^{-3}mm. sec.$^{-1}$)	$\frac{dx_d}{dt}$ (10^{-9}mol. sec.$^{-1}$)
1	50.1	38.0	1.90	0.95
2	70.0	37.6	1.88	0.94
3	77.5	38.2	1.92	0.96
4	90.0	38.3	1.92	0.96
5	95.4	36.2	1.81	0.91
6	122.7	38.4	1.92	0.96
7	148.4	40.0	2.00	1.00
8	151.6	37.6	1.88	0.94
9	192.5	39.6	1.98	0.99
10	224.7	40.6	2.03	1.02
11	244.0	38.6	1.93	0.97
12	245.5	40.2	2.01	1.01
13	284.8	40.4	2.02	1.01
14	285.9	40.6	2.03	1.02
15	316.0	41.0	2.05	1.03
16	340.0	40.2	2.01	1.01
17	342.5	41.4	2.07	1.04
18	387.0	40.2	2.01	1.01

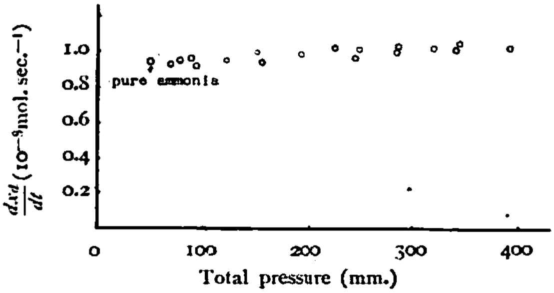

Fig. 10. The influence of adding nitrogen on the decomposition velocity.

From these results it is concluded that, though the addition of nitrogen increases the homogeneity of the reaction, it only slightly affects the quantum yield. That the quantum yield was independent of added nitrogen, as maintained by Warburg, was here confirmed. No investigation has been carried out on an ammonia-nitrogen mixture since done by Warburg.

IV. Discussion.

1) Summary of the experimental results.

i) The homogeneity of the reaction which is expressed by "the homogeneous reaction velocity $\frac{dx}{dt}$" in Fig. 7, decreased in the case of the smaller vessel or the large illuminated area. The decrease in the homogeneity, of course, indicates the increase in the wall effect.

ii) The quantum yield was larger in the case of the smaller vessel or the large illuminated area (Fig. 8).

iii) The quantum yield in any case increased slowly with decreasing pressure of ammonia at relatively high pressures. This increase became somewhat rapid below a certain pressure which shifted to a higher pressure with an increasing wall effect. (Fig. 8)

iv) The addition of nitrogen did not decrease the quantum yield (Fig. 10), while it increased the homogeneity of the reaction (Fig. 9).

2) Discussion of the experimental results.

a) As already mentioned, the photochemical decomposition of ammonia has been studied by many investigators from various points of view. Before we discuss the present results, we wish to state briefly some of the recent researches performed under similar conditions and purposes.

Wiig measured the quantum yields at various pressures using two reaction vessels 2.5 cm. and 4 cm. in diameter and he found that in both cases the value reached the maximum (0.3 for the former vessel and 0.28 for the latter) in the pressure range 80–100 mm., falling rapidly at the lower pressure side and slowly at the higher pressure side, and that the quantum yield was smaller in the large vessel in the whole range of pressure. And he assumed that the whole reaction did not take place in the gaseous phase at low pressures and proposed a series of reactions as follows :[31]

$$NH_3 + h\nu \rightarrow NH_2 + H \qquad (1)$$

$$H + H + M \rightarrow H_2 + M \text{ (or at wall)} \qquad (2)$$

$$NH_2 + H + M \rightarrow NH_3 + M \text{ (or at wall)} \qquad (3)$$

$$NH_2 + NH_2 \rightarrow N_2H_4 \qquad (4)$$

$$NH_2 + NH_2 \rightarrow N_2 + 2H_2 \qquad (5)$$

$$N_2H_4 + H \rightarrow NH_3 + NH_2 \qquad (6)$$

According to him, the fall of the quantum yield at higher pressures is ascribed

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[31] In fact, Wiig adopted a triple collision mechanism instead of binary collision in process (4).

to the predominance of the homogeneous regeneration of ammonia ((3), (4) and (6)) over the recombination process (2) on the wall; while the fall below 100 mm. is due to the occurence of the regeneration of ammonia on the wall.

From this consideration Wiig predicted that the addition of an inert gas to ammonia at a pressure of about 100 mm. should result in a decreased quantum yield and that, likewise, the addition of a foreign gas to ammonia at pressures of 10∼40 mm. so as to make the total pressure about 100 mm. should give an increased quantum yield. And he said that these effects would account for Warburg's constant yield of 0.23 at total pressures of 800∼900 mm. of ammonia, nitrogen and hydrogen.

b) But Wiig's result that the quantum yield falls below 100 mm. is doubtful from the under-mentioned experiments made by Welge and Beckmann, and also it seems to conflict with the result obtained by Wiig himself and the present author that the quantum yield decreases in the case of a large vessel.

Welge and Beckmann[4)32)] have recently found that as the amount of decomposition of ammonia becomes less than 10^{-3} mm. the composition of non-condensable gas (H_2, 75%; N_2, 25%) approaches 100% H_2. In the experiments made by Wiig, the amount of decomposition was sometimes small ($<10^{-3}$ mm.) at low pressures, and regarding it as a mixture of $H_2:N_2=3:1$, the quantum yield was calculated to be 0.1∼0.2. From the above consideration, therefore, it is inferred that the true value may be several times larger.

In the present experiments, on the other hand, a relatively large amount of products ($>10^{-3}$ mm.) was treated with, and so the ratio of H_2 to N_2 could be regarded as 3:1 throughout the experiments. Accordingly, the present experimental result obtained at low pressures—somewhat rapid increase in the quantum yield with decreasing pressures—will be quite reliable. This fact also coincides well with the fact that the quantum yield falls when the reaction vessel larger in diameter is used or when the illuminated area is small, because in these three cases it is supposed that the wall effect will increase. From this consideration the following conclusion is drawn:

The "side" wall effect acts to make the quantum yield larger.
It will be seen later why the wall effect is confined to the side wall.

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32) They concluded from this fact and others that the reaction is almost heterogeneous (processes (2) and (3)), hydrazine produced being strongly adsorbed on the wall, and also that as the reaction proceeds the regeneration of ammonia and production of nitrogen takes place by some reactions between N_2H_4 and H.

c) In order to make the above conclusion more valid, it is necessary to confirm that the wall effect, in fact, is increased by decreasing pressure, by increasing the diameter of reaction vessel and by increasing the illuminated area. In the latter two cases this was experimentally confirmed directly from the decrease in the homogeneous reaction velocity. (Summary of the experimental results, (i)). In the first case it will be seen as follows.

In Fig. 7, as the pressure is decreased the differences between the homogeneity in the smaller and larger vessels and that between the cases of smaller and larger illuminated areas in the smaller vessel become more remarkable. Let us compare this decrease in the homogeneous reactions with the increase in the decomposition velocity (relative quantum yield).

In Fig. 8, the point where sudden rise of the curve is observed lies at 80～100 mm. in the case of the larger reaction vessel (Curve 1), while in the case of the smaller vessel it lies at about 150 mm. in a small illuminated area (Curve 2a) and at 200 mm. in a large one (Curve 2b), and thus it gradually shifts to higher pressures. And it seems that at those (low) pressures the wall reaction suddenly increases.

From these considerations it is inferred that the decrease in pressure at low ammonia pressures, as well as the enlargement of the reaction vessel in diameter and the illuminated area, causes the wall effect and the quantum yield to increase.

d) On the inhomogeneity of the light absorption.—As to the homogeneous reaction velocity, it remarkably falls with increasing pressure (Fig. 7). This is because of the facts that ammonia strongly absorbs light under these conditions and the absorption becomes inhomogeneous along the direction of light with increasing pressure. The light absorption of ammonia at various pressures as a function of the thickness of absorbing layer in the case of zinc spark is graphically shown in Fig. 11.[10] Thus, as the pressure of ammonia increases, light is absorbed in greater and greater degree near the front wall and so the reaction on the front wall becomes predominant.

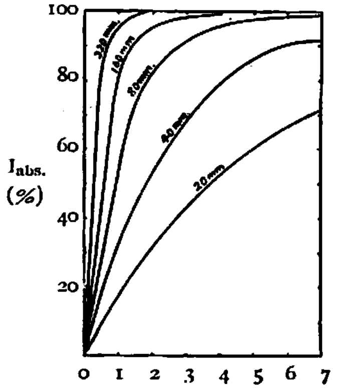

Fig. 11.

$I_{abs.}=I_0(1-e^{-[NH_3]as})$
$a=157\,cm^{-1}$. Litre. mol^{-1}.

In this case an increase in the quantum yield should be analogically expected from the case of the side wall. Contrary to this expectation, however, the quantum yield falls in fact with increasing pressure. It is difficult to make a simple interpretation of this fact, but it seems probable that it is caused by some other factor due to the inhomogeneity of the light absorption than the simple front wall effect or by the difference of property between the dark surface and the surface exposed to light.

As there are such undesirable factor, the discussion on the wall effect in the other section has been confined only to the " side " wall.

e) Wiig's prediction relating to the effect of added inert gas was completely disproved by the present experimental results obtained by studying the effect of added nitrogen which could be regarded as an inert gas. As seen from Fig. 10, in the range of total pressure of 50~100 mm. the quantum yield was almost constant instead of any increase ; and above 100 mm. it increased, though slightly, instead of decreasing. Thus Wiig's theory must be dismissed.

Though the fact that the quantum yield was increased by the addition of nitrogen in spite of increased homogeneity seems apparently contradictory to the above conclusion that the wall effect acts to make the quantum yield larger, this discrepancy should be ascribed to different efficiency of an ammonia molecule and a nitrogen molecule as a third body in the recombination processes, NH_2+H+M and $H+H+M$. This point will be discussed in the following section.

f) In summarizing the above considerations, the author adopts the same processes (1)~(6) as those proposed by Wiig although from the different experimental grounds. In the process (4), the third body, *M*, has hitherto been taken into consideration, but the author considers it unnecessary.[33] And also he assumes that the processes (2) and (3) proceed in a triple collision and on the wall, while the processes (4), (5) and (6) are independent of the wall effect. Then the effect of wall on the quantum yield was determined by the extent to which either of the two processes (2) and (3) would be promoted more highly by the wall.

Now, if the ratio of efficiencies of an ammonia molecule and a nitrogen molecule as a third body in the process (3) to those in the process (2) is expressed by $\left(\frac{NH_2+H}{H+H}\right)_{NH_3}$ and $\left(\frac{NH_2+H}{H+H}\right)_{N_2}$ respectively, and the ratio corresponding to the wall by $\left(\frac{NH_2+H}{H+H}\right)_{Wall}$, then assuming

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[33] e.g., Kimball, *J. Chem. Phys.*, 5, 310 (1937).

$$\overset{\text{I}}{\left(\frac{NH_2+H}{H+H}\right)_{NH_3}} > \overset{\text{II}}{\left(\frac{NH_2+H}{H+H}\right)_{\text{Wall}}} \doteqdot \overset{\text{III}}{\left(\frac{NH_2+H}{H+H}\right)_{H_2}},$$

almost the whole experimental results can be accounted for as will be described below. It may be easily considered that an ammonia molecule is a third body so good in the recombination process (3) as to be able to make I>II.

The following four facts caused by increased wall effect—i) the relatively rapid increase in the quantum yield at low pressures with decreasing pressure, (ii) the fact that the quantum yield in the smaller vessel was larger than in the larger one, (iii) the fact that the increase in the illuminated area caused the quantum yield to increase, and (iv) the fact that, when the diameter of the reaction vessel or the illuminated area was enlarged, the pressure below which somewhat rapid increase in the quantum yield with decreasing pressure began to appear, shifted to the higher pressure side—can be accounted for by assuming that the role of the ratio I decreased and that of II increased.

On the other hand, the fact that by addition of nitrogen the quantum yield was not appreciably affected can be accounted for by the assumption that the ratio of III is approximately the same as that of II.

In spite of the qualitativeness of the above discussion, the author believes that the heterogeneous character of the reaction is, at least, to some extent made clear in this study.

V. Summary.

1) The Budde-effect has been measured under various conditions and the homogeneity of the reaction determined by the method of the thermal analysis of this effect. The reaction has been found to be remarkably heterogeneous, that is, to be a wall reaction.

2) The relative quantum yield under various conditions have been measured and it has been confirmed that the quantum yield increases instead of decreasing even below a pressure of 100 mm.

3) It has been concluded that the side-wall effect makes the quantum yield larger.

4) The effect of the addition of nitrogen has been studied and a slight increase in the quantum yield found.

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