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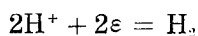
DETERMINATION OF STOICHIOMETRIC NUMBER OF AMMONIA SYNTHESIS REACTION

By

Saburo ENOMOTO and Juro HORIUTI

Introduction

One¹⁾ of the present authors has previously introduced the concept of the stoichiometric number relevant to the respective elementary reaction implied in an overall reaction or the number of times of the former to occur for every completion of the latter, deriving a general equation for that n of the rate-determining step in terms of observable quantities. IKUSIMA²⁾ in conjunction with him has determined, according to the equation, n of the hydrogen electrode process,



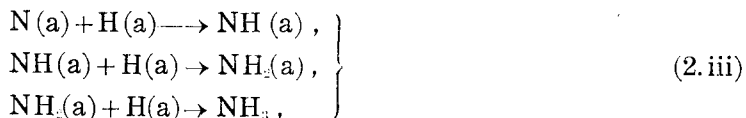
on platinum at 1, i.e. has shown that the rate-determining step, whatever it may be, should occur once for every over-all reaction specified by the latter chemical equation, where ε denotes electron.

A further account of the stoichiometric number might be given below with special reference to the ammonia synthesis reaction,



whose n is going to be determined.

Let us assume that the latter over-all reaction proceeds through the sequence of elementary reactions,



where (2.i) or (2.ii) is respectively the dissociative adsorption of nitrogen or hydrogen, to form adsorbed nitrogen atoms $\text{N}(\text{a})$'s or hydrogen atoms

1) HORIUTI, J. Res. Inst. Catalysis, Hokkaido University, **1**, 8 (1943).

2) HORIUTI and IKUSIMA, Proc. Imp. Acad. Tokyo, **15**, 39, (1939).

H(a)'s, and (2.iii) the successive combination of N(a) with H(a)'s to complete NH_3 . It follows that (2.i), (2.ii) and (2.iii) should occur respectively once, thrice, and twice for every over-all reaction (1) or for every act of transferring the atom group $\text{N}_2 + 3\text{H}_2$ into the state of 2NH_3 . This number of times, 1, 3 or 2 is called the stoichiometric number appropriate to the respective elementary reaction implied in the over-all reaction specified by (1).

The stoichiometric number n of the rate-determining step is now combined as mentioned above with the one-direction rate \bar{r} i.e. the number of acts per unit time of the atom group of the left hand side of the chemical equation transferred to the state of the right, the over-all rate r i.e. the excess of \bar{r} over its reversal and the free energy increase $\Delta\mu$ per mol of the over-all reaction by the equation,¹⁾²⁾

$$r = \bar{r} \left(1 - e^{\frac{\Delta\mu}{nRT}} \right) \quad (3)$$

where R is the gas constant and T the absolute temperature.

The r , \bar{r} , $\Delta\mu$ and n depend individually how the chemical equation of the over-all reaction is normalized, such as that both r and \bar{r} inversely proportional on one hand, $\Delta\mu$ and n proportional on the other hand respectively to the coefficient of any definite term in the chemical equation³⁾, thus leaving r/\bar{r} and $\Delta\mu/n$ as well as the relation between them stated by (3) invariant.

The purpose of the present work is to determine n of (1) in accordance with (3) in the presence of commercial synthesis catalyst at temperatures of their use but at several hundred mmHg total pressure.

We first develop below the fundamental equation (3) into an adequate form to the experimental determination of n and then describe the experiments arranged in accordance with the latter.

§ 1. Development of Fundamental Equation.

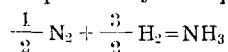
The $\Delta\mu$ in (3) may be specialized to (1) as that,

$$\Delta\mu = 2\mu^{\text{NH}_3} - (\mu^{\text{N}_2} + 3\mu^{\text{H}_2})$$

where μ^{NH_3} etc. are the chemical potentials of ammonia etc. respectively.

Expressing the latter in the form,

*) If the same over-all reaction is specified by the equation,



the stoichiometric number of (2.i), (2.ii) or (2.iii), is 1/2, 3/2 or 1 respectively.

$$\mu^{\text{NH}_3} = RT \log x + \text{const.}$$

etc. and remembering that $\Delta\mu=0$ at equilibrium, we have,

$$\Delta\mu = 2RT \log x/x_e - RT \log (P^{\text{N}_2}/P_e^{\text{N}_2}) (P^{\text{H}_2}/P_e^{\text{H}_2})^3 \quad (4)$$

where x , P^{N_2} and P^{H_2} are respectively the partial pressures of ammonia, nitrogen and hydrogen, suffix e denoting their particular values at equilibrium. P^{N_2} and P^{H_2} remaining sufficiently constant respectively at $P_e^{\text{N}_2}$ and $P_e^{\text{H}_2}$ in our present experimental condition,^{*)} the second term on the right of (4) may be neglected and hence (3) expressed in the form,

$$r = \bar{r} \left\{ 1 - \left(\frac{x}{x_e} \right)^{\frac{2}{n}} \right\}$$

Expanding the right of the above equation around the equilibrium point, where $r=0$, $\bar{r}=\bar{r}_e$ and $x=x_e$ with respect to the increments, $\bar{r}-\bar{r}_e$ and $x-x_e$, and neglecting terms of higher than the first order, we have that,

$$r = r_1 (x_e - x) \quad (5. a)$$

where,

$$r_1 = \frac{2\bar{r}_e}{nx_e} \quad (5. b)$$

is a constant.

We might express r practically by the actual increasing rate dx/dt of x with time t and \bar{r}_e , in consequence, according to (3), by the fictitious one supposed to be exhibited, if ammonia were evolved at that one-direction rate^{**)} . Eq. (5.a) gives now by integration that,

$$\log (x_e - x) = -r_1 t + \text{const.} \quad \text{for } x < x_e \quad (6. S)$$

or

$$\log (x - x_e) = -r_1 t + \text{const.} \quad \text{for } x > x_e \quad (6. D)$$

i. e. for the synthesis or the decomposition respectively.

The \bar{r}_e governs on the other hand the isotopic transfer or the ex-

*) The x being varied around x_e of several tenth mmHg magnitude, while the total pressure kept at *ca.* 400 mmHg in our present experiment, the relative variation of P^{N_2} and P^{H_2} or $RT \log (P^{\text{N}_2}/P_e^{\text{N}_2}) (P^{\text{H}_2}/P_e^{\text{H}_2})^3$ was safely negligible.

**) The rates r_1 and \bar{r}_e expressed in this manner are not specific to the capacity of the catalyst, but varies inversely proportionally to the total gas quantity present in contact with the latter, although their arbitrariness of this sort cancels each other with regard to the n -determination according to (5. b).

change reaction between ammonia and nitrogen at equilibrium as that,

$$-x_e \frac{dz}{dt_e} = \bar{r}_e (z - z_\infty) \quad (7)$$

where z is the atomic fraction of nitrogen isotope in ammonia, z_∞ that in nitrogen and t_e the time elapsed along with the progress of the exchange reaction at equilibrium of (1), provided that the latter proceeds through the sole agency of (1) and its reversal, but not concurrently through some other mechanism.

Eq. (6)^{***}), stating a law that $\log(x_e - x)$ or $\log(x - x_e)$ varies linearly with time in the neighbourhood of equilibrium, irrespective of the underlying mechanism, enables us experimentally to determine r_1 as well as x_e by following x with t , whereas (7) to find \bar{r}_e having recourse to N¹⁵ shifted ammonia at equilibrium of (1) with normal nitrogen and hydrogen.

Nitrogen isotope was preferred in this regard to that of hydrogen, because the exchange reaction between hydrogen and ammonia was immeasurably rapid at the present experimental condition, as extrapolated from the observation by one of present authors³⁾ at lower temperatures, indicating that the above necessary condition for the validity of (7) was not fulfilled.

Taking z_∞ constant at the natural abundance on account of the huge excess of nitrogen over ammonia (7) may be integrated as that,

$$\frac{\bar{r}_e}{x_e} = \frac{1}{t_e} \log \frac{z_0 - z_\infty}{z - z_\infty}$$

Substituting \bar{r}_e/x_e from the above expression into (5. b), we have,

$$n = \frac{2}{r_1 t_e} \log \frac{z_0 - z_\infty}{z - z_\infty} \quad (8)$$

which gives n in terms of observable quantities, r_1 and z at equilibrium of (1).

Our series of experiments consisting of r_1 -determination according to (6) both from synthetic and decomposition sides, and of z -determination was carried out by keeping 1:3 nitrogen-hydrogen mixture, admixed with ammonia or not, statically over the catalyst on one hand and by circulating the former over the latter on the other hand. Below will be described the details of the experiment and the result obtained.

***) (6) stands for (6. S) and (6. D) together. This manner of expression will be followed below throughout.

3) ENOMOTO, "Shokubai" ("The catalyst", printed in Japanese) 8, 47, (1952).

§ 2. Material.

Hydrogen was prepared by electrolysis of sodium hydroxide solution, passed over reduced nickel powder at 300°C for reducing contaminating oxygen to water, dried over calcium chloride and phosphorus pentoxide, filtered through the palladium thimble heated at 350°C and stored over platinum black for removing possibly existing catalytic poison.

Nitrogen was prepared by thermally decomposing purchased sodium azide, dried and stored similarly as hydrogen.

Ammonia from cylinder was dried over soda-lime, solid potassium hydroxide, condensed by liquid air, fractionated three times and then stored over platinum black.

Shifted ammonia was prepared by decomposing ammonium sulfate solution containing 8.55 atomic percent N^{15} offered by the Scientific Research Institute, Tokio, with alkali, purified and stored similarly as the normal one.

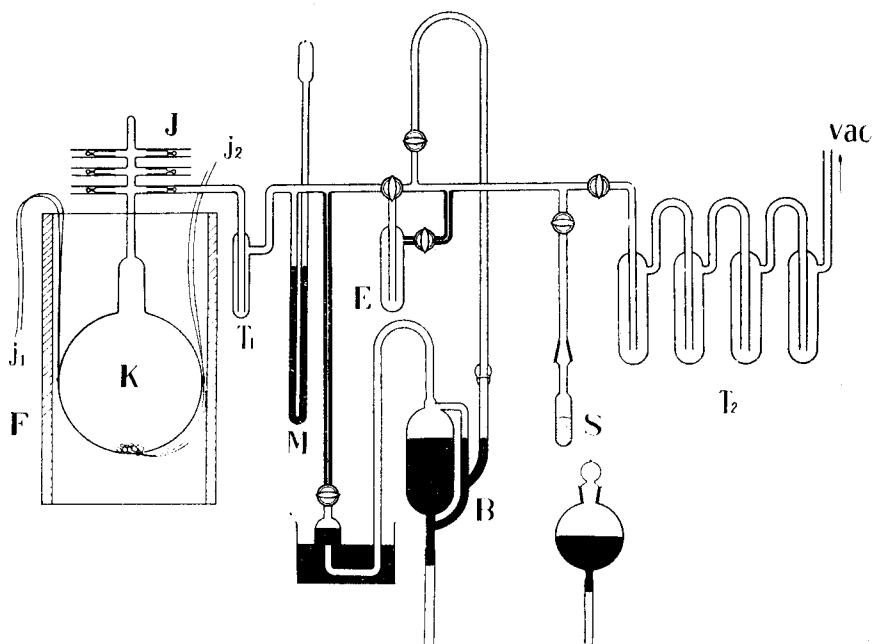


Fig. 1

Apparatus for static Series

K:—Reaction chamber. F:—Electric Furnace. E:—Sampling Bulb.
j₁, j₂:—Thermocouple. T₁, T₂:—Traps. M:—Manometer. B:—Taper Pump. J:—Breakable joints.

Doubly promoted ammonia synthesis catalyst provided by the Tokio Industrial Experimental Station (catalyst I) was used for static series and that from the Toa Synthesis Company (catalyst II) for the circulation one.

§ 3. Apparatus.

The apparatus for the static series is shown in Fig. 1. K is the reaction chamber of *ca.* 6 litres capacity containing 28 gm catalyst I, provided with several breakable joints J's and enclosed in the electric furnace F. The reaction chamber is attached with thermojunctions j's from outside, with the lower one at the catalyst inside the potentiometric temperature regulator being operated, to keep temperature automatically constant within several degree centigrade. T₁ is the trap, M the manometer, E the bulb of 36 cc capacity for sampling the gas in the course of the reaction, B the Töpler pump for returning the part of the sampled gas, noncondensable at liquid air temperature i.e. hydrogen-nitrogen mixture towards the reaction chamber and S a vessel containing 1 cc dilute sulfuric acid solution for fixing the ammonia sampled in E for analysis. T₂ is the train of traps for completely condensing out the total ammonia in the reaction chamber in the case of *z*-determination.

The apparatus for the circulation series is shown in Fig. 2. K is the reaction chamber of 30 cc capacity 2.2 cm wide, in which 23 gm catalyst II is placed in 3 cm layer between glass wool packings above and beneath, the above one being of 5 cm height. The reaction chamber was attached with thermojunctions j's from outside at the upper inlet and at the catalyst inside and enclosed in the electric furnace F, the temperature being controlled by hand, the period of reaction not very long in this case. T₁, T₂ and T₃ are traps, M is the manometer, E the sampling bulb of 52 cc capacity, and B the Töpler pump of the similar use as that of the static series. P is the all glass magnetic pump driven by water cooled coil D, V the valve rectifying the gas flow into the direction of arrows and C the flow meter. A is the train of bulbs of 4 litres total volume affording a sufficient capacity to the circuit. The apparatus is besides provided with the train of traps of the similar description as T₂ of the static series.

§ 4. Reduction of Catalyst.

Catalyst I was reduced at 480 °C in K in the static series admitting

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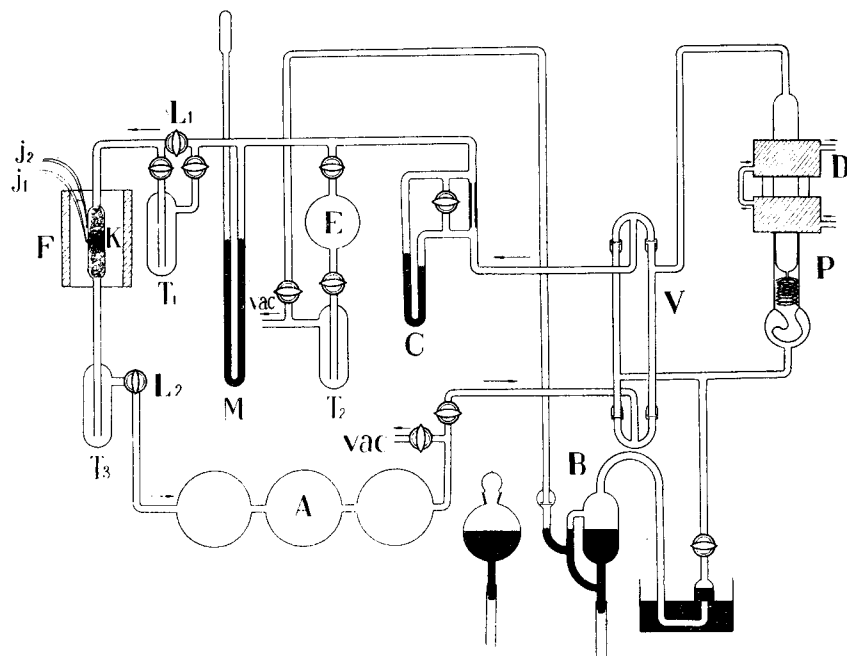


Fig. 2

Apparatus for Circulation Series

K:—Reaction chamber. F:—Electric Furnace. E:—Sampling Bulb.
 j_1, j_2 :—Thermocouples. T_1, T_2, T_3 :—Traps. M:—Manometer.
 B:—Töpler Pump. P:—Magnetic Pump. D:—Water Cooled Coils.
 V:—Rectifying Valve. C:—Flow Meter. A:—Train of Bulbs.

200–300 mmHg hydrogen and cooling T_1 with liquid air. The hydrogen was daily renewed for 6 months until the water condensation in T_1 at the withdrawal of the gas through the latter became imperceptible.

The above routine was occasionally interrupted and the rate of the reduction as well as of the synthesis was observed as follows: the reaction chamber was thoroughly evacuated, 300 mmHg hydrogen alone or 1 : 3 mixture of the same total pressure admitted and left at 450°C for several days leaving T_1 at room temperature, the content gas being sampled at intervals during the latter period into E, cooled by liquid air there, the noncondensable portion pumped out, the condensable one distilled into a vessel of 4 cc capacity provided with a manometer and then allowed to evaporate at 25°C for measuring the total pressure m_1 , less than the saturation pressure of water, and hence for determining the total quantity q of the portion according to the gas law.

In the case of 1 : 3 mixture admitted into the reaction chamber, the portion was further analysed for the ammonia content by cooling the vessel by 3/4 part of its total volume v at 0°C, leaving the remaining 1/4 part at 25°C and by reading the constant pressure m_2 finally attained after *ca.* 30 minutes. The ammonia fraction y and hence its quantity yq or that of water $(1-y)q$ were determined from the known fractions G and L of ammonia respectively

in coexistent vapor and liquid at equilibrium at the same temperature and pressure, attributing the decrease, $m_1 - (1/4 + 3/4 \times 298/273)m_2$ of the vapor quantity caused by the cooling, to the liquid formed, as that,

$$y = \left[\left(\frac{1}{4} + \frac{3}{4} \times \frac{298}{273} \right) m_2 G + \left\{ m_1 - \left(\frac{1}{4} + \frac{3}{4} \times \frac{298}{273} \right) m_2 \right\} L \right] / m_1$$

It was thus found that both the reduction and the synthesis were appreciably retarded as soon as the partial pressure of water vapor attained 0.15 mmHg but recovered reversibly on renewal of the content gas or on withdrawal of the water vapor present.

Catalyst II in K of Fig. 2 was reduced by circulating hydrogen over it at 1 litre per minute rate, 520°C and 300~400 mmHg total pressure for 120 hours, cooling T₁ by liquid air until the water condensation in T₃, when cooled for 5 hours, became similarly imperceptible^{*)}. It was found that the initial rate of reduction as measured by the total pressure decrease by means of manometer M was *ca.* 30 times as large as that of the static series similarly observed.

§ 5. ν_1 -Determination of the Static Series.

The reaction chamber K containing the catalyst I reduced as described in the forgoing section was evacuated to 10⁻⁴ mmHg and then 1420 cc NTP 1:3 mixture of nitrogen and hydrogen was admitted at 400 mmHg total pressure and 450°C^{**)} into the latter, the synthesis thus started being followed by sampling the gas mixture occasionally into E at recorded time after the admission and the quantity of each sample determined from the known capacity of E, reading manometer M. Ammonia in each sample was condensed in E by liquid air, the noncondensable part returned into K by Töpler pump B and the condensate distilled in vacuum into S containing the above mentioned absorbent to determine the quantity of the absorbed ammonia colorimetrically by means of Nessler reagent.

A control experiment has shown that the sampled gas was practically of the same composition with that inside K^{***)}. The reaction

^{*)} Actually T₃ was also cooled during the reduction procedure to prevent the possible intrusion of catalytic poison in the event of accidental stop of the circulation pump: the end point of the reduction was detected as described in the text by preliminarily transferring the condensate in T₃ into T₁ by distillation.

^{**)} The reading of the lower thermojunction attached at the catalyst [cf. §3]. The upper one was read somewhat higher than the latter was within 10°C.

^{***)} The known amount of ammonia (3.2 cc NTP) was admitted into E by distillation and then pumped by means of Töpler pump for 30 min into the tube communicated with K, the latter being preliminarily filled with 400 mmHg 1:3 mixture of nitrogen and hydrogen at room temperature. The gas was now sampled at the finish of the pumping into E just as in the case of ν_1 -observation and analysed. The partial pressure of ammonia 0.41 mmHg thus found was almost in coincidence with 0.40 mmHg calculated for the homogeneous mixture in 6500 cc joint total volume of K, T and tubings.

having thus been followed up to the neighbourhood of equilibrium, 1.2 cc NTP ammonia was added to the resultant gas mixture in K to raise its partial pressure up to *ca.* 0.7 mmHg, the decomposition now started being followed towards equilibrium similarly as above.

The gas in K was now pumped out, α -determination carried out as described in §7 with the same catalyst and then a fresh portion of 1:3 mixture admitted after thorough evacuation to follow the synthesis similarly again for keeping check with the activity of the catalyst.

The r_1 and x_e were determined first by fitting them by trial on the above x observation of the synthesis and the decomposition according to (6) i.e. on the linearity of $\log(x_e - x)$ or $\log(x - x_e)$ with t and then by determining the correction Δx_e and Δr_1 respectively to the trial values x'_e and r'_1 by the method of least square according to the relation,

$$\log(x'_e - x) + \frac{\Delta x_e}{x'_e - x} = -(r'_1 + \Delta r_1)t + \text{const.}$$

or

$$\log(x - x'_e) + \frac{\Delta x_e}{x'_e - x} = -(r'_1 + \Delta r_1)t + \text{const.}$$

derived from (6) by substituting x_e there by $x'_e + \Delta x_e$ and r_1 by $r'_1 + \Delta r_1$, and by expanding it with respect to Δx_e .

The effect of the sampling on the progress of the reaction was ignored, the loss of ammonia for each amounting only *ca.* 1% of the total quantity present in K at the moment.

§ 6. r_1 -Determination of Circulation Series.

The whole apparatus was evacuated to 10^{-1} mmHg, K being kept at required temperature of reaction, as read coincidently within a few degrees by means of thermojunctions described in §3, stopcocks L_1 and L_2 in Fig. 2 then closed to shut off K from the remaining part, 650 cc NTP nitrogen and 650×3 cc NTP hydrogen admitted into the latter and the magnet pump now operated to make up 1:3 homogeneous mixture, at a rate as would just cause the flow of 50 cc. NTP/min rate through the whole circuit inclusive of K.

After 30 minutes L_1 and L_2 were opened to start the reaction at 404 mmHg total pressure, the circulating gas being sampled from time to time by E each at recorded time. The procedures were besides just the same as that of the static series, except that ammonia was frozen out in the separate trap T_2 here, instead *in situ* in the sampler there.

The decomposition was now similarly followed by repeating the above procedure with the mixture of 650 cc NTP nitrogen and 650×3 cc NTP hydrogen, and 6 cc NTP ammonia, the latter being added to the former two components through Töpler pump B before the preliminary pump operation described above, which was then continued

for 30 minutes. The homogeneity thus attained was preliminary confirmed similarly as in the case of static series by sampling and analysing the gas mixture.

§ 7. *z*-Determination.

In the static series 0.74 cc NTP, 8.55% shifted ammonia was added to the 1:3 mixture at 400 mmHg pressure in K kept at 450°C containing 0.64 cc NTP ammonia at 0.180 mmHg partial pressure, just to set up the equilibrium of (1) at $0.180 \times (0.74 + 0.64) / 0.64 = 0.388$ mmHg or at z_0 according to the result of the foregoing experiment, the communicating breakable joint being then sealed off. The original shift diluted by the normal ammonia present beforehand down to $(0.74 \times 8.55 + 0.64 \times 0.385) / (0.74 + 0.64) = 4.77\%$ was taken z_0 in this case, where 0.385% was that of the natural abundance.

This procedure was preferred in this case to that of admitting shifted ammonia in the absence of normal one, because the rate in the presence was so small, as learned from the foregoing experiments that the incontrollable dilution by normal ammonia evolved further during the operation was negligible, whereas not otherwise.

After 3.5 or 5 days K was communicated again with the vacuum line by one of the breakable joints and the whole mixture inside pumped out through the train of traps cooled by liquid air. The ammonia condensed there was distilled over dilute sulfuric acid to fix it as ammonium sulfate. The above procedure was repeated five times exactly in the same manner, each with the same quantity of the new portion of the material, for securing ammonium sulfate sample containing total 6 mgr nitrogen, as required for each atomic shift determination by means of the mass-spectrometer.

In the circulation series 650 cc NTP nitrogen, 650×3 cc NTP hydrogen and 2.90 cc NTP, 8.55% shifted ammonia were preliminary mixed up by the pump operation described in the foregoing section, thus making up the homogeneous equilibrium mixture at 430°C and at 404 mmHg total pressure.

The mixture was now circulated over the catalyst at the latter condition for 52 minutes, and then completely withdrawn through the train of traps to condense out the ammonia present and to fix it as ammonium sulfate for *z*-determination; this procedure was repeated 3 times similarly as in the static series to make up the requisite amount of ammonia.

The isotopic analysis of the ammonium sulfate samples was kindly

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conducted by Dr. A. SUGIMOTO.

§ 8. Result.

The result of r_1 -observation of the static series at 450°C and 400 mmHg total pressure is shown in Table I and in Fig. 3, (a) by ○ of the synthesis, by ⊙ of the decomposition and by ● of the synthesis repeated for check as described in §5. The activity of the catalyst is satisfactorily reproducible as shown by the Figure. Fig. 3, (b) shows the linearity of (6) actually obeyed in the neighbourhood of equilibrium, appropriate r_1 and x_e values being given in Table III together with those of the circulation series.

TABLE I. Variation of Ammonia Partial Pressure
 x with Time t in Static Series.

Temperature :—450°C, Total Pressure :—400 mmHg.
Quantity of 1 : 3 Mixture Used :—1420 cc NTP.

Reaction	Synthesis		Decomposition	
Quantities	t (days)	x (mmHg)	t (days)	x (mmHg)
Observed Figures.	0.58	0.076	0	0.690
	0.79	0.090	0.17	0.664
	1.08	0.100	1.08	0.631
	2.12	0.150	2.17	0.609
	3.00	0.153	4.91	0.558
	3.96	0.173	5.00	0.557
	6.04	0.230	7.00	0.515
	7.06	0.243	9.00	0.480
	8.02	0.263	12.00	0.452
	10.81	0.298	13.09	0.450
	14.14	0.320	13.87	0.432
	15.10	0.344	19.08	0.420
	16.06	0.355	22.00	0.415
	17.00	0.365	27.00	0.400
	19.91	0.372	30.00	0.400
	21.91	0.375	33.00	0.398
	26.91	0.380		
	31.00	0.380		
Observed Figures of Check Experiment after α - Measurement (cf. §5)	4.87	0.191		
	5.87	0.220		
	7.87	0.271		
	10.87	0.297		
	12.87	0.318		
	16.87	0.378		

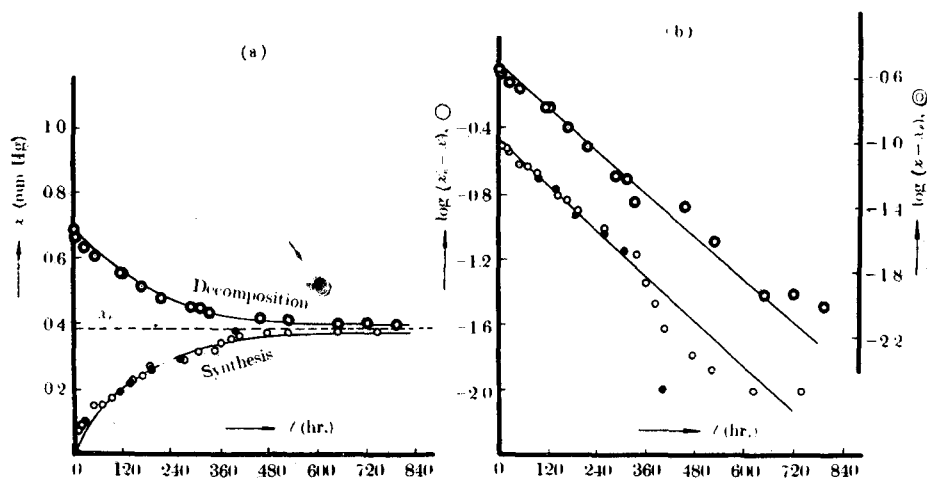


Fig. 3

r_1 and x_e Observation

Static Series: 450°C, 400 mmHg

○:—Synthesis, ⊙:—Decomposition, ●:—Synthesis for check

Dotted line in Fig. 3, (a) shows the coincident x_e values of the synthesis and of the decomposition.

Table II shows the result of similar observation of the circulation series at 400°C, 430°C and 445°C.

TABLE II. Variation of Ammonia Partial Pressure x with Time t of Circulation Series.

Total Pressure :—404 mmHg, Flow rate :—50 cc NTP/min.
Quantity of 1 : 3 Mixture Used :—2,600 cc NTP.

Temperature	400°C				430°C				445°C			
Reaction	Synthesis		Decomposition		Synthesis		Decomposition		Synthesis		Decomposition	
Quantities	t min	x mmHg	t min	x mmHg	t min	x mmHg	t min	x mmHg	t min	x mmHg	t min	x mmHg
Observed Figures.	0	0.440	0	1.598	15	0.065	0	1.100	0	0.093	0	0.933
	80	0.518	40	1.390	40	0.221	50	0.623	35	0.263	20	0.734
	100	0.547	75	1.251	60	0.271	70	0.597	60	0.367	50	0.463
	130	0.580	112	1.093	65	0.287	115	0.496	97	0.374	95	0.422
	145	0.595	150	0.962	95	0.341	190	0.464	120	0.380		
	185	0.609	195	0.900	125	0.420			150	0.390		
	265	0.654	230	0.868	200	0.443						
			265	0.826								

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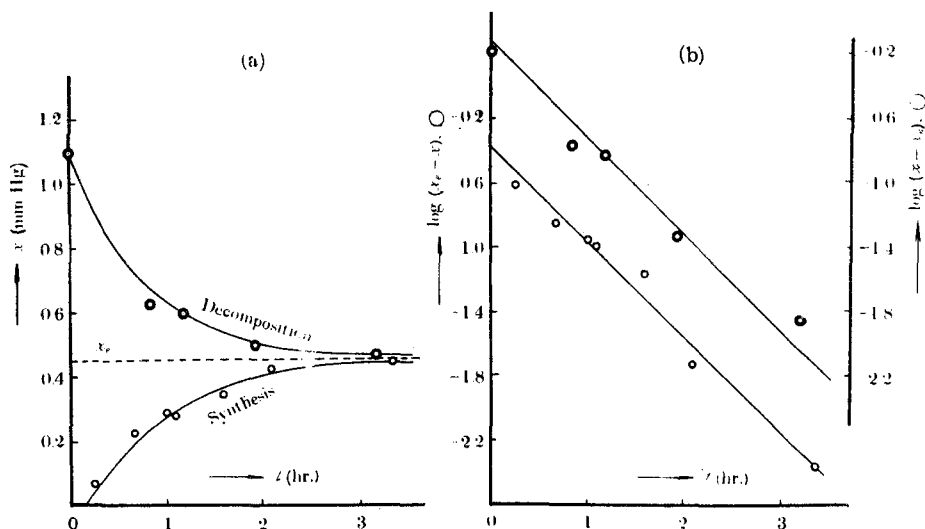


Fig. 4

r_1 and x_e Observation

Circulation Series: 430°C, 404 mmHg

○;—Synthesis, ⊙;—Decomposition

The result at 430°C only is shown in Fig. 4, (a) and 4, (b) similarly as that of the static series, those at two other temperatures being of the similar trend.

The x_e and r_1 values and their provable errors determined from above observations as described in §7 are summarized in Table III. Synthesis and decomposition values of x_e or r_1 coincide with each other almost within the probable error as shown in the Table.

It is found from r_1 -values of the circulation series that $\log r_1$ varies linearly with $1/T$, the appropriate "activation energy" $RT^2 \frac{d \log r_1}{dT}$ amounting to 33 Kcal.

TABLE III. x_e and r_1 Values.

Quantity	Re- action	Series Temp.	Static	Circulation			
			450°C	430°C	445°C	406°C	
x_e mmHg	Synthesis		0.388 ± 0.013	0.46 ± 0.02	0.40 ± 0.01	0.74 ± 0.01	
	Decompos.		0.388 ± 0.015	0.44 ± 0.02	0.40 ± 0.02	0.70 ± 0.02	
r_1 $\text{hr}^{-1} \times 10^2$	Synthesis		0.55 ± 0.06	132 ± 12	162 ± 30	36 ± 6	
	Decompos.		0.55 ± 0.04	132 ± 12	204 ± 30	42 ± 6	

The r_1 -values given in the Table are not specific to the catalyst, but particular to the total quantity of gas present as mentioned before*). Its absolute value i. e. the quantity of ammonia synthesized or decomposed per hr per 1 mmHg difference between x and x_e is obtained by multiplying the figures given in the Table by the ratio of the total gas quantity present in contact with the catalyst to the total pressure i. e. $1,420/400 = 3.55$ cc NTP mmHg⁻¹ or $2,600/404 = 6.43$ cc NTP mmHg⁻¹ for the respective series, as that,

$$r_1 = 0.0055^{**}) \times 3.55 = 0.019 \text{ cc NTP hr}^{-1} \text{ mmHg}^{-1} \quad (9. S)$$

for the static series at 450° and 400 mmHg total pressure and,

$$r_1 = 1.83^{**}) \times 6.43 = 12.0 \text{ cc NTP hr}^{-1} \text{ mmHg}^{-1} \quad (9. C)$$

for the circulation one at 445°C and 404 mmHg.

The weighted mean $x_e = 0.388 \pm 0.010$ mmHg at 450°C and 400 mmHg total pressure of the static series and that $x_e = 0.45 \pm 0.01$ mmHg at 430°C and 404 mmHg of the circulation one are compared respectively with 0.49 mmHg and 0.64 mmHg calculated at the respective conditions from the empirical formula of the equilibrium constant put forward by HABER⁴⁾ on the basis of experiments at the total pressure from 1 atm up,

$$\log K_P = 2098.2/T - 2.509 \log T - 1.006 \times 10^{-4}T + 1.859 \times 10^{-7}T^2 + 2.10$$

where $K_P = P_{e\text{NH}_3} / (P_{e\text{N}_2})^{1/2} (P_{e\text{H}_2})^{3/2}$ atm⁻¹ and $P_{e\text{NH}_3}$ etc. are partial pressures of ammonia etc. at equilibrium in atm***).

The observed z at equilibrium of (1) as well as n calculated according to (8), taking z_∞ at 0.385****) is shown in Table IV, the probable

TABLE IV. Observed Shift z and Stoichiometric Number n of Rate-Determining Step.

Series	r_1 *****) hr ⁻¹ × 10 ²	z_0 *****) %	z %	t_e hr	n
Static	0.55 ± 0.03	4.77 ± 0.14	3.00 ± 0.04	84	2.2 ± 0.2
450°C	"	"	2.40 ± 0.03	120	2.4 ± 0.2
400 mmHg	"	"	3.11 ± 0.003	84	2.1 ± 0.2
	"	"	3.34 ± 0.004	84	1.7 ± 0.2
Circulation 430°C, 404 mmHg	132 ± 8	8.55 ± 0.02	2.52 ± 0.003	0.87	2.3 ± 0.1

*) Cf. the foot-note on page 89.

**) Weighted mean of synthetic and decomposition values.

4) HABER, Z. Elek. chem. 20 (1914), 603.

***) It follows from the K_P expression in the text that,

$$K_P/760 = 16 x_e/3^3 (P_e - x_e)^2$$

where P_e is the total pressure at equilibrium in mmHg and further neglecting x_e^2 in the expansion of the above equation that, $x_e = P_e^2/(P_e + 16 \times 760/3^3 K_P)$

by which x_e values are calculated.

****) Natural abundance of nitrogen isotope N¹⁵.

*****) Weighted mean of the synthetic and decomposition values given in Table III.

*****) The probable error of the diluted shift was derived from that of the original one of ammonia ± 0.02 % as communicated by Dr. SUGIMOTO and the relative error ± 3% of the measurement of its quantity involved at dilution [cf. §7]

error of n there being derived from those of r_1 , z_0 and z neglecting that of t_c .

It is concluded from the result that $n=2$.

§ 9. Discussion.

The foregoing conclusion, $n=2$ would however be of any meaning with regard to the reaction mechanism only when (A) the observed synthesis, decomposition and N^{15} exchange are controlled by the genuine chemical reaction on the catalyst's surface and (B) Reaction (1) and its reversal are exclusively responsible for the exchange. We will discuss below the validity of these conditions with the present experiment, going back for the moment more reservedly to the standpoint of viewing (6) and (5.b) with $n=2$, the relations purely empirically established among observables, r_1 , x_e and \bar{r}_e .

If (A) were not fulfilled, the possible case would be that (a) the rate be controlled by the diffusion of the reactant of (1), or that (b) by that of the resultant or (c) the intermediary between any two of the above three extreme cases i.e. (A), (a) and (b). The case (a), which requires the diffusion of the resultant for being far rapider than that of the reactant, may however be safely excluded, inasmuch as the partial pressure and hence the diffusion rate of the reactant are overwhelmingly large, on the contrary to the requirement, compared with that of the resultant, admitted that diffusion constants of gaseous components are of much the same order of magnitude.

If now (b) were the case, the diffusion of the reactant as well as the surface reaction would be at equilibrium and hence the ammonia partial pressure at the surface equal to x_e . The steady rate of formation or consumption of ammonia would then be proportional to the difference between its partial pressure at the surface and that x in the bulk of gas, or to $x_e - x$ or $x - x_e$ respectively, leading formally to the same x versus t relation as (6.S) or (6.D), r_1 here being however proportional to the diffusion constant D . The inclination of $\log r_1$ against $1/RT$ should now be of the order of magnitude of RT or that of $\log D$ against $1/RT$, since the other factor of r_1 in this case may be taken independent of temperature. This case is now excluded since the inclination or the "activation energy" amounts to 33 Kcals as observed in §8.

If (c) were alternatively the case, of which that between (A) and (b) only remains now as possible one, $\log r_1$ would not vary linearly with $1/RT$ as actually observed, but run flat at higher temperatures

the inclination tending to that of $\log D$. We are hence led to the conclusion that the observed rates are controlled by the surface reaction at least in the circulation series.

With regard to the static series, r_1 of (9) reckoned per unit weight of the catalyst 0.019/28 at 450°C is *ca.* 800 times smaller than that 12/23 of the circulation series at 445°C. It is possible for the diffusion of being controlling in the static series, only when the effective depth of the diffusion layer adhering the catalyst's surface is altogether incredibly much more than 800 times as large here as that in the circulation series.

This is, besides, disproved by the fact mentioned in §4 that the reduction of the catalyst as well as Reaction (1) is appreciably retarded by a minute amount of water vapor, since the latter could hardly affect the diffusion constant or the rate.

The synthesis and the decomposition observed in both the static and circulation series must hence be governed by the surface reaction.

As to the exchange reaction simple consideration will show, similarly as in the case of the synthesis or the decomposition, that it should rather be controlled, if at all, by the diffusion of heavy ammonia molecules consisting of N^{15} than by that of heavy nitrogen.

The following argument shows further that the diffusion of ammonia is not controlling but atomic fraction z_s of N^5 in ammonia at the surface is even practically equal to that z in the bulk of gas i.e. that the exchange reaction is also practically controlled by the surface reaction.

Equating both the sides of (7) to the diffusion rate, $D'(z-z_s)$, we have,

$$-x_e \frac{dz}{dt} = \bar{r}_e (z - z_\infty) = D' x_e (z - z_s) \quad (10)$$

where $x_e(z-z_s)$ is the difference between the partial pressure of heavy ammonia $x_e z$ in the bulk of gas and that $x_e z_s$ at the catalyst's surface and D' a constant or the product of the diffusion constant and some factor depending on the geometry of the catalyst's surface.

The rate of the ammonia diffusion in the course of the synthetic reaction at the same catalyst may on the other hand be expressed by $D'(x_s - x)$, which gives, being equated to both the sides of (5.a) and r there expressed by dx/dt , that,

$$\frac{dx}{dt} = r_1 (x_s - x) = D' (r_s - x), \quad (11)$$

where x_s is the ammonia partial pressure at the surface.

The foregoing conclusion of the ammonia diffusion being practically at equilibrium requires now that $x_e - x \gg x_s - x$ or according to the above equation that,

$$r_1 \ll D'.$$

Substituting r_1 from (5.b) and putting $n=2$, we have that,

$$\bar{r}_e/x_e \ll D' \quad (12)$$

which, incorporated with (10) leads to the conclusion that $z - z_s$ is negligibly small compared with $z - z_\infty$ or to the above proposition.

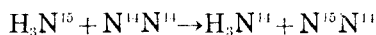
The conclusion, $n=2$ is now relevant to the surface reaction, giving a basic criterion to its mechanism.

We might inquire at this stage why the rate of reaction (1) is exceedingly small in the static series compared with that in the circulation one, besides attributing the situation to the possible difference of the catalyst due to the source, on the basis of the observed facts mentioned in §4 that (i) water vapor retards both the reduction and Reaction (1) reversibly and that (ii) the initial rate of reduction of the circulation series, is *ca.* 30 times as large as that of the static one, assuming that the curves of the reduction rate *versus* time, running monotonously down in both the cases as qualitatively observed, may be brought congruent with each other by multiplying the abscissa of the former by 1/30 according to (ii).

One day's period of the reduction for detection of the end point in the former case extends now to $24/30 = 0.8$ hour on the reduced scale, which is much smaller than the corresponding time interval 5 hours in the latter.

Admitting that the quantity of water just to escape the above detection is approximately the same in both the cases, the rate must be greater or the reduction poorer in the former case to cover the shorter reduced time interval. It follows that the amount of water formed during the r_1 -observation and hence the retardation of (1) according to (i) must have been then pronounced as observed.

The conclusion, $n=2$ would now confine the rate-determining step of Scheme (2) to (2.iii) in both the cases of the catalysts, provided that (B) were fulfilled. If not, but some elementary reaction, say, like that,



causes the exchange reaction side by side with (1), \bar{r}_e deduced from

z-observation according to (7) and hence n according to (5.b) would be too large including the contribution from the latter. It follows then that the true stoichiometric number appropriate to (1) must be equal to or less than 2, definitely invalidating (2.ii) of being rate-determining.

If we furthermore exclude such an elementary reaction curious enough concurrently sharing n by the comparable amount, even resulting invariably in the same integer 2 of it, irrespective of extent of the water vapor retardation or alternatively of the possible inherent difference of the catalysts, we are inevitably led to the conclusion that the rate-determining step, whatever it may be, must occur twice for every Reaction (1), which disproves (2.i) of being rate-determining as suggested to be by TEMKIN⁵⁾ and others.^{5),6)7)}

It is not however asserted that this should hold whole throughout the temperature and pressure range including that of the commercial plant, inasmuch as the prevailing rate-determining step to which a particular value of n is appropriate, may well switch from one over to the other elementary reaction along with the variation of condition.

The determination of n at higher total pressure is now in progress in this laboratory.

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The catalysts used were analysed after the completion of the experiments, the result being Al_2O_3 1.92%, K_2O 1.31%, SiO_2 1.58%, CaO 0.23%, MgO trace, ZrO_2 trace, for Catalyst I and, Al_2O_3 1.82%, K_2O 1.06%, SiO_2 0.41%, CaO 0.04%, MgO trace for Catalyst II.—*added at the proof.*

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