111. Experimental Determination of Overall and One-direction Rate of Ammonia Synthesis Reaction.

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The overall rate r in the neighbourhood of equilibrium of the ammonia synthesis reaction,

was observed in conjunction with the relevant one-direction rate $\vec{r}_e$ or the number of acts per unit time of the atom group on the left of the above chemical equation transferred at equilibrium to the state of the right, with the purpose of finding the stoichiometric number¹⁾²⁾ of the rate-determining step of the reaction, which will be the subject of the subsequent paper^{3)*)}.

The r may be expressed in terms of the ammonia partial pressure x as that,

$$r = \frac{dx}{dt} \quad (2)$$

where t is time, or alternatively perhaps, it vanishing at equilibrium when $x = x_e$, in the form,

$$r = r_1(x_e - x) \quad (3)$$

where r_1 is a constant in the neighbourhood of equilibrium as verified theoretically in the latter paper³⁾.

We have from (2) and (3) by integration, that,

$$\log(x_e - x) = -r_1 t + \text{const.}, \text{ for } x < x_e, \quad (4.s)$$

$$\text{or} \quad \log(x - x_e) = -r_1 t + \text{const.}, \text{ for } x > x_e, \quad (4.d)$$

i.e. for the synthesis or the decomposition respectively. The r_1 was determined experimentally according to the latter relation by following x with t .

The $\vec{r}_e$ was observed having recourse to ammonia of shifted N^{15} according to the relation,

$$-x_e \frac{dz}{dt} = \vec{r}_e (z - z_\infty) \quad (5)$$

where z or z_∞ is the atomic fraction of N^{15} in ammonia or in nitrogen respectively, the left-hand side giving the rate of the

1) Horiuti: J. Res. Inst. Catalysis, Hokkaido, **1**, 8 (1948).

2) Horiuti and Ikusima: Proc. Imp. Acad., **15**, 39 (1939).

3) Enomoto and Horiuti: Proc. Japan Acad., **28**, 499 (1952).

*) Detailed account of the experiment including that of the stoichiometric number will be given in a paper submitted to the Journal of the Research Institute for Catalysis, Hokkaido University.

partial pressure decrease of heavy ammonia N^{15}H_3 and $\vec{r}_e$ correspondingly the fictitious rate of increase of the ammonia partial pressure which would be exhibited, if ammonia were evolved at the given experimental condition at that one-direction rate.

Taking z_∞ in (5) practically constant at the natural abundance during the progress of the latter N^{15} exchange reaction, on account of our experimental condition that normal nitrogen is present in huge excess over ammonia, we have, by integration that,

$$\vec{r}_e = \frac{x_e}{t} \log \frac{z_0 - z_\infty}{z - z_\infty} \quad (6)$$

Our series of experiments consisting of r_1 -determination according to (4) both from the synthetic and the decomposition sides, and of the isotopic observation of $\vec{r}_e$ according to (6) was carried out by keeping 1:3 nitrogen-hydrogen mixture, admixed with ammonia or not, statically over the catalyst as well as by circulating the former over the latter.

In the static series 28 gm doubly promoted commercial catalyst provided by the Tokio Industrial Experimental Station was reduced *in situ* in a reaction vessel of *ca.* 6 litre capacity at 480°C in 300 mmHg hydrogen atmosphere, daily replacing the gas for 6 months until the water condensation in a liquid air cooled trap at the withdrawal of the gas through the latter after one day's reduction became imperceptible.

The reduction as well as reaction (1), as observed in the course of the above reduction procedure, was found appreciably retarded by the presence of a minute amount of water formed.

The reaction vessel was now evacuated, 1420 cc NTP 1:3 nitrogen-hydrogen mixture then admitted, the synthesis now started at 450°C and 400 mmHg total pressure was followed by sampling occasionally the gas mixture (*ca.* 1% of the total) each at recorded time and by analysing it for x prevailing in the reaction vessel, colorimetrically by means of Nessler reagent.

After x was thus followed along with the synthesis up to the neighbourhood of equilibrium, a proper portion of ammonia was added to the resultant gas mixture to raise x above x_e and the decomposition now started was similarly followed towards equilibrium.

The result is shown in Fig. 1 (a) by circlets for synthesis and by double circlets for decomposition, the relevant linearity of $\log(x_e - x)$ or $\log(x - x_e)$ with time t required by (4) in Fig. 1 (b), and x_e and r_1 thereby determined by the method of least square in Table I.

The reaction vessel was again evacuated, 1:3 mixture admitted and after a certain amount of ammonia, as determined by the above described method of analysis, was formed, a proper portion of

Fig. 1 (a and b). Variation of ammonia partial pressure x with time t . Static series; 450°C, 400 mm Hg total pressure.

8.55% shifted ammonia admitted just to make up the resultant partial pressure at x_e , as found by the foregoing experiment, in a homogeneous mixture of the same total pressure (400 mmHg) as before. The z_3 was 4.77%, the admitted shifted ammonia being diluted by the normal one present beforehand.

This procedure of admission in the presence of normal ammonia was preferred, the further formation during the latter, as learned from the foregoing observation, being slow enough for the resulting uncontrollable dilution being negligible but not otherwise.

After a recorded time the whole content was extracted, ammonia in it being fixed in the form of ammonium sulfate for analysing it for the isotopic content by means of the mass spectrometer. The analysis has been kindly conducted by Dr. A. Sugimoto of the Scientific Research Institute, Tokio. This procedure was repeated 5 times for each isotopic analysis which required 6 mgm nitrogen content of the sample.

The reaction vessel was evacuated once more again, the former observation of x along with synthesis was repeated exactly at the same condition and with the same catalyst, the result being shown by dots in Fig. 1 (a) and 1 (b) which assured satisfactorily the reproducibility of the catalyst's activity.

In the circulation series 23 gm doubly promoted commercial catalyst provided by the Toa Synthesis Company Ltd. was reduced in a reaction vessel of 30 cc capacity at 520°C in a flow of dry hydrogen of 400 mmHg at 1 litre NTP/min rate for 120 hours, water vapor formed being steadily condensed out by liquid air.

The reduction was found initially 30 times quicker than in the static series as measured by the decrease of hydrogen pressure but so slow later as indetectable by the water condensation in the liquid air cooled trap for the last 5 hours' period.

The x was followed in this series both from the synthetic and the decomposition sides just as in the static series circulating 2600 cc

Table I
 x_e and r_1 values

Quantity	Series Reaction	Tem- perature	Static	Circulation		
			450°C	430°C	445°C	400°C
x_e mmHg	Synthesis		0.388±0.013	0.46±0.02	0.40±0.01	0.74±0.01
	Decomp.		0.388±0.015	0.44±0.02	0.40±0.02	0.70±0.02
$r_1 \times 10^2$ *) hr ⁻¹	Synthesis		0.55±0.06	132±12	162±30	36±6
	Decomp.		0.55±0.04	132±12	204±30	42±6

NTP gas mixture at 50 cc NTP/min rate and 404 mmHg total pressure but at three different temperatures i. e. 400°C, 430°C and 445°C of the reaction vessel. The r_1 and x_e were determined from the result similarly as in the static series as given, together with those of the latter series in Table I.

It is deduced from the result that $\log r_1$ runs linearly with $1/T$, the appropriate "activation energy" i.e. $RT^2 \frac{d \log r_1}{dT}$ amounting to 33 Kcal.

The isotopic determination of $\vec{r}_e$ was conducted at 404 mmHg total pressure and 430°C similarly as in the static series except that 8.55% shifted ammonia was added to the 2600 cc NTP 1:3 mixture in the absence of normal one, the circulation device here being

Table II
 z and $\vec{r}_e$ values
 $z_\infty = 0.38\%$

Series	t hr.	z_0 %	z %	$\vec{r}_e \times 10^3$ *) mmHg hr ⁻¹
Static 450°C 400 mmHg	84	4.77	3.00	2.38 ± 0.08
	120	"	2.40	2.50 ± 0.08
	84	"	3.11	2.21 ± 0.04
	84	"	3.34	1.83 ± 0.04
Circulation 430°C 404 mmHg	0.87	8.55	2.52	702 ± 60

available for mixing the components homogeneously before contact with the catalyst. The $\vec{r}_e$ deduced from the observation of z according to (6) taking z_∞ at the natural abundance i.e. at 0.38% is shown in Table II side by side with that of the static series.

The overall as well as the one-direction rate is remarkably smaller in the static than in the circulation series as shown in Table I and II. This might be inferred, besides alternatively from the possible inherent difference of the catalyst due to that of the source, from above observed facts i.e. that (i) the water vapor retards both the reduction and reaction (1) and that (ii) the initial rate of the reduction is *ca.* 30 times as large in the circulation series as in the

*) The absolute value may be obtained by multiplying the given value by the ratio of the total quantity of gas present to the total pressure i.e. by 1420 cc NTP/400 mmHg or 2600 cc NTP/404 mmHg respectively in the case of the static and the circulation series.

static one, assuming that the curves of the reduction rate against time in both the cases, running monotonously down as qualitatively observed, may be reduced congruent with each other, by multiplying the abscissa of the latter by $1/30$ according to (ii). One day's period of reduction for the detection in the latter series extends now to $24/30=0.8$ hour on the reduced scale, which is much smaller than 5 hours' one for that in the former. Admitting that the quantity of water just to escape the detection is approximately the same in both the cases, the rate of the water formation at the detection must have been greater in the latter to cover the shorter reduced time interval.

It follows now that the reduction was much more incomplete in the latter series and hence reaction (1) must have been more seriously retarded according to (i) or r_1 and $\vec{r}_e$ there diminished as actually observed.

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