STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP OF AMMONIA SYNTHESIS ON IRON CATALYSTS

Comment on the papers of J. HORIUTI and N. TAKEZAWA and T. KODERA and N. TAKEZAWA

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Some time ago there appeared in this periodical two publications[1)2)] containing criticism of the report of an investigation entitled "Stoichiometric Number and Reaction Mechanism of the Ammonia Synthesis"[3)], which we published in 1959. In the present publication we shall deal with the main points of this criticism.

The determination of the stoichiometric number of the rate-determining step of the ammonia synthesis was made in two ways:

a. First series of measurements:

Near the equilibrium of the ammonia synthesis we measured simultaneously, and on one and the same portion of catalyst, the rates of the ammonia synthesis and of the exchange reaction

$$N^{15}H_3 + N_2^{28} \rightleftarrows N^{14}H_3 + N_2^{29} \qquad (I)$$

b. Second series of measurements:

Near the equilibrium of the ammonia synthesis we measured, simultaneously on two series-arranged catalyst beds and in one and the same gas stream, both the rate of the ammonia synthesis and the rates of the exchange between N_2^{30} and N_2^{28} (exchange reaction II) and the exchange between N_2^{30} and NH_3. The rates of the ammonia synthesis and the exchange between N_2^{30} and NH_3 were measured on the first catalyst bed, the rate of the exchange between N_2^{30} and N_2^{28} on the second.

All these reaction rates can be characterized under the given conditions by first-order reaction rate constants. The accuracy of the determination of these constants is largely determined by the location of the equilibrium. This applies in particular to the constants for the ammonia synthesis.

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The criticism referred to above is directed to two points in particular:

1. The accuracy of the determination of the reaction rate constant of the ammonia synthesis reaction in conjunction with the determination of the location of the equilibrium.
   In the criticism it is said that this determination is not accurate enough to justify the conclusion that the stoichiometric number of the rate-determining step of the ammonia synthesis is unity[1].
2. The assumption that at the end of the second catalyst bed the equilibrium
   $$N_2^{30} + NH_3 \rightleftarrows N_2^{29} + N^{15}H_3$$
   has been reached.
   Calculation on the basis of the small differences which exist at this point as compared with the state of equilibrium, leads the critics to another stoichiometric number, which is greater than unity[1)2)].

I. The Accuracy of the Determination of the Reaction Rate Constant of the Ammonia Synthesis

In the first series of our experiments the equilibrium concentration of the ammonia was determined by carrying out tests at an extremely low space velocity (*ca.* 1000 h^{-1}), at the same temperature and pressure as used in the velocity measurements; in the second series of experiments the ammonia concentration at equilibrium was equalized to the concentration at the end of the second catalyst bed.

HORIUTI *et al.* and KODERA *et al.* contend that under the experimental conditions used by us the equilibrium is not actually reached, which results in too high values of k_{synth} and hence in too low values of the stoichiometric number. According to these authors, the accuracy in the determination of the ammonia concentration at equilibrium required for a sufficiently accurate determination of the stoichiometric number is 0.1%. However, to reach this conclusion they started from the supposition that the temperatures mentioned in the heads of the published tables are the exact temperatures prevailing throughout each run, whereas in reality they are only approximate values. Further, this demand regarding the accuracy of determination was derived from an experiment which gave a k_{synth} value that was not used by us (see Table 1 in our publication[3]), owing to the close approximation to the equilibrium in this experiment.

In Table 1 we now give the temperatures and pressures measured in each experiment, the ammonia concentration determined experimentally, and the concentration that can be calculated from the temperature and pressure measured if equilibrium is assumed.

TABLE 1. Stoichiometric Numbers Calculated from Equilibrium Values of Ammonia Synthesis Reaction

(compare Tables 1 and 2 of publication[3]; data in parenthesis have not been used for calculation of k_{synth})

	Temp. (°C)	Pressure (atm.)	NH_3 content at equilibrium vol. −%		Stoichiometric numbers			
					γN_2–N_2	γN_2–NH_3	γN_2–N_2	γN_2–NH_3
			Experimental*)	Calculated from exp. temp. and pressures**)	as in our publication		on the basis of calculated equilibrium values	
Series 1: Catalyst I:						***)		***)
	429.0	7.5⁰	2.16	2.16				
	428.5	7.5⁰	2.18	2.18				
	430.0	7.5⁰	2.15	2.14		1.05		0.99
	(428.0	7.4⁵	2.18	2.18)		1.07		
	426.0	7.5⁸	2.27	2.27				
	Catalyst II:							
	(427.0	7.5⁰	2.21⁵	2.21⁵)		0.93		0.93
	425.0	7.4³	2.26	2.26		0.87		0.87
	(423.0	7.5³	2.34	2.34)		0.88		0.88
	425.0	7.4⁸	2.27	2.27				
Series 2: in the head of this table the temperature was erroneously stated to be 425°C (instead of 429°C).								
Run					***)	***)	****)	****)
1.1	428.5	7.5⁸	2.17⁷	2.20				
1.2	429.5	7.5⁸	2.19⁴	2.18	1.02	0.91	0.98	0.88
1.3	429.0	7.5⁸	2.21²	2.19	0.99	1.30	0.93	1.23
1.4	429.0	7.5⁸	2.19²	2.19	0.92	0.94	0.92	0.94
1.5	429.0	7.5⁸	2.17⁸	2.19				
2.1	428.5	7.4⁴	2.12⁰	2.16				
2.2	429.0	7.4⁴	2.11⁴	2.15	0.99	1.02	1.13	1.16
2.3	429.0	7.4⁴	2.11⁹	2.15	0.97	0.93	1.10	1.05
2.4	429.0	7.4⁴	2.12⁰	2.15	1.18	1.15	1.31	1.28

*) Identical with the ammonia content of the gas flowing at low space velocity through the reactor in series 1; identical with $NH_{3\,outlet}$ in series 2.

**) Use was made of HABER's-formula[4]:

$$\log K_p = \frac{2098.2}{T} - 2.509 \log T - 1.006.10^{-4}T + 1.859.10^{-7}T^2 + 2.10.$$

***) Use was made of the mean values of k_{synth} found in the runs on the respective catalysts.

****) The values of k_{synth} found in the respective runs were used in the calculation.

This table shows that the measured concentrations are, indeed, in good agreement with the calculated equilibrium values, as is stated in our publication This is to be expected in view of the temperature constancy (our publication mentioned a constancy of within 1°; actually the variations during a run never exceeded 0.3°C) and the very low heat production on the catalyst bed*).

Calculation of the stoichiometric number by the use of the calculated values of the equilibrium of the ammonia synthesis reaction produces values that are practically identical with those calculated on the basis of experimental ammonia concentrations (see Table 1).

That the equilibrium of the ammonia synthesis reaction must have been reached in the places referred to above also appears from the calculation of the degree of conversion by means of the space velocity applied and of the experimental velocity constant: the value found is over 0.999.

Another proof of the correctness of the temperature and pressure measurements is in the fact that the determination of the degree of conversion at

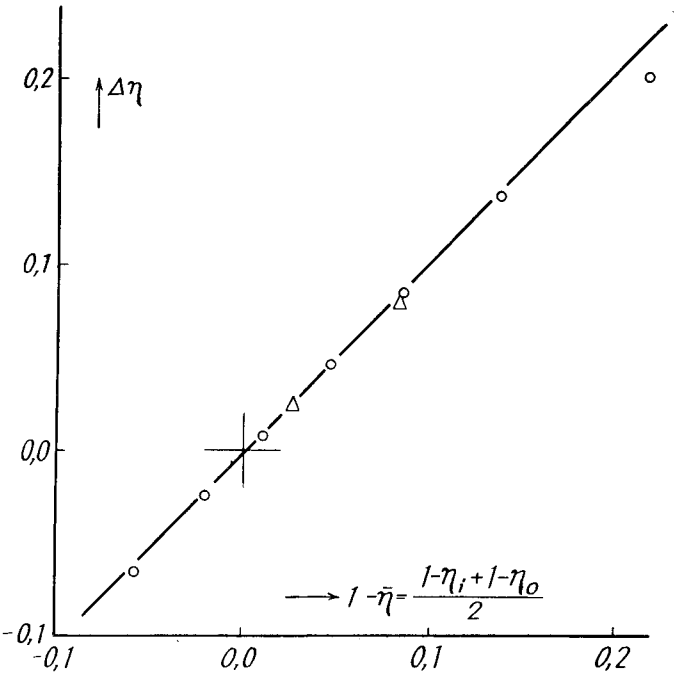

Fig. 1. Conversions in the ammonia synthesis reaction near to the equilibrium.

*) Calculations of the rise in temperature owing to reaction heat in the catalyst bed as compared with the temperature in the fluidized bed produces values of ΔT smaller than 0.02 °C.

constant space velocity as a function of the mean distance to the calculated equilibrium leads to a figure the straight line in which passes through the origin (see Fig. 1).

The correctness of the equilibrium values used is also demonstrated in the fact that the calculated rate constants do not depend on the distance to the equilibrium (Table 1 in our publication[3]). This would certainly have been the case if in the calculation a wrong equilibrium value had been used.

II. The Accuracy of the Measurements Relating to the Reaction

$$N_2^{30} + NH_3 \rightleftarrows N_2^{29} + N^{15}H_3$$

HORIUTI *et al.*[1] and KODERA *et al.*[2] contend that in the second series of experiments the N^{15} equilibrium in the N_2–NH_3 exchange was not reached at the end of the second catalyst bed.

The N^{15} contents of the ammonia experimentally found at the end of the second catalyst bed are given in Table 2.

TABLE 2. N^{15} content of ammonia at the end of the second catalyst bed as compared with the equilibrium condition (being assumed to be the mean of the overall contents of N^{15} at "inlet", "middle" and "outlet" of the reactor)

Run :	1.2	1.3	1.4	2.2	2.3	2.4
N^{15} in NH_3-outlet :	101.9%	98.8%	101.8%	93.9%	92.7%	94.5%

The spread in the results of the first run is slight, though naturally greater*) than the reproducibility of the mass spectrometric determination, which was 0.01%; it is of the same order as the spread in the measurements of N_2^{30} and N_2^{29} at "inlet" and "middle" (which, as is known, must be equal). This was about 1.1% on an average. It must therefore be concluded that in run 1 the isotope equilibrium is actually reached.

The deviation in the results of run 2 is, admittedly, larger than had been expected. However, we can by no means see proof in this of the equilibrium not having been established, but conclude that the accuracy of our measurement of the isotope concentration in these experiments was not so great as in run 1. That a measuring error is the cause of this deviation is proved by the fact that the experimental value of $k^{30}_{N_2+NH_3}$ and the space velocity applied lead to

*) For instance, entrance of air owing to leakage during the decomposition of NH_3 on platinum reduces the N^{15} content.

a degree of conversion on the second catalyst bed which is greater than 0.99.

Table 3 gives the results of the calculation of the stoichiometric number made with the aid of values of $k^{30}_{N_2+NH_3}$ derived from measurements on the first catalyst bed, (a) on the assumption that the concentration of N^{15} in the ammonia at the outlet of the second catalyst bed is equal to the equilibrium value, (b) on the basis of an equilibrium value of N^{15} in the ammonia calculated from the mean of the overall contents of N^{15} in the three gas samples taken along the gas stream: "inlet", "middle" and "outlet". From this table it is seen that the lower accuracy of the N^{15} measurements found in runs 2.2, 2.3 and 2.4 does not affect the value of the stoichiometric number.

TABLE 3. Stoichiometric Numbers Calculated from Equilibrium Values of the Exchange Reaction: $N_2^{30}+NH_3 \leftrightarrows N_2^{29}+N^{15}H_3$

Run	Values of $\frac{N^{15}}{N^{15}+N^{14}} \cdot 100$ at equilibrium		Stoichiometric number	
	(a) experimental: N^{15} in $NH_{3\,outlet}$	(b) calculated as the mean of the overall values in "inlet", "middle" and "outlet"	based on (a) as in publication [3]	based on (b)
1.2	1.095	1.075	0.91	0.94
1.3	1.041	1.054	1.30	1.27
1.4	1.069	1.050	0.94	0.97
2.2	1.100	1.172	1.02	0.90
2.3	1.086	1.172	0.93	0.80
2.4	1.110	1.175	1.15	1.02

In their publications HORIUTI *et al.*[1] and KODERA *et al.*[2] arrive at a stoichiometric number greater than untiy by means of a deliberate choice of data in Table 2 (viz. from the runs 1.3, 2.2, 2.3, 2.4, in which the experimental spread leads to a lower value of the N^{15} concentration in the ammonia). From the arguments mentioned above, it is quite clear that this procedure is not allowed. The occurrence of some figures higher than 100% (which "thermodynamic absurdity" is noted by HORIUTI *et al.*) proves that we have indeed to do with an experimental spread. As shown in Table 3 this spread no way affects the conclusion that the stoichiometric number of the rate determining step of the ammonia synthesis reaction is unity.

The said authors also take exception to our experiments because of the alleged small reproducibility of the catalytic activity.

The fact that the k_{synth} value is a function of the temperature of the pre-reactor has already been accounted for in our original publication[3], (p. 322). Owing to the extreme sensitivity of the catalyst to impurities, the use of a very

ideal purification (*e.g.* with a pyrophoric iron catalyst as getter) will cause the reaction rate to be strongly accelerated. With extremely pure synthesis gas the formation of ammonia proves noticeable even at room temperature[5].

It should be remarked in addition that in our method—contrary to what is the case in others—the determination of the stoichiometric number is not influenced by the presence of poisons, if any, because k_{synth} and $k_{exchange}$ are determined in the same gas stream. The same applies to the determination of the ratio between the activities of the first and second catalyst beds.

Conclusions

1. In opposition to the calculations by the critics it is demonstrated that the measurement of the ammonia synthesis equilibrium fits in very well with what can be expected from experimental conditions and the location of the equilibrium. The values of the stoichiometric number of the rate-determining step that can be calculated from these data are always equal to unity (see Table 1).
2. The accuracy of the N^{15} measurements is sufficient to justify the conclusion that the equilibrium of exchange reaction I has been established at the end of the second catalyst bed. The experimental error in this determination does not affect the conclusion that the said stoichiometric number is unity (see table 3).
3. It is pointed out that the experimental method used by us is adapted to the extreme sensitivity to traces of poison exhibited by the catalytic ammonia synthesis.

References

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