Reaction Rates in the Synthesis of Ammonia. I. Dependence upon Reaction Pressure and Hydrogen-Nitrogen Ratio

By Hiroshi UCHIDA and Michio KURAISHI

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Introduction

Many workers[1-6] have measured the rate of the reaction of ammonia synthesis. P. H. Emmett[3] and R. M. Adams[5] measured the ammonia concentration in exit gases over a wide range of space velocities, pressures, and temperatures using mixtures of different ratios of hydrogen to nitrogen of 3, 1, and 1/3. However, they confined the measurements to one kind of catalyst. H. Kobayashi[4] recently made extensive measurements with four kinds of catalysts under varying conditions of pressure, flow rate, and temperature, but used only a mixture of the ratio of 3 throughout the experiments. As for the ammonia concentration relating to hydrogen-nitrogen ratio, A. Nielsen[6] carried out the measurements with a triply promoted catalyst, but only at a pressure of 330 atm., at a space velocity of 15×10^3 and a temperature of 450°C.

No one, so far as we are aware, has ever published results sufficient to estimate the rate of the ammonia synthesis varying the ratio of hydrogen to nitrogen as well as the kind of catalyst. The authors have conducted the measurements with both of a singly and a triply promoted catalyst over an extended range of these conditions.

Our results have been to test the practical utility of the rate equations proposed by M. I. Temkin[2] and by M. Shindo[7], each based on different concepts as to the rate determining step. We have also attempted to modify the Temkin's equation to represent the experimental results more adequately, though not completely.

Experimental

A mixture of hydrogen and nitrogen was obtained in ratio of 3 by introducing ammonia gas over an ammonia catalyst at 500°C and in order to obtain the mixtures of different composition either hydrogen or nitrogen was added from a cylinder. After having been compressed, the mixtures were purified by passing over palladium-asbestos at 200°C followed by cooling and subsequent drying through solid caustic potash. Fig. 1 is a diagram of the reactor. The catalyst chamber is made of copper tube, 27 mm. in outer dia. and 15 mm. in inner dia., inserted with an iron thermo-couple of 7 mm. in dia. The gas feed was directed downward on an electric heating nichrome coil wound on the copper tube, then upwards first into the preheating zone where copper granules of 2 mm. dia. were packed and finally through the catalyst bed.

Measurements of the rate of the ammonia synthesis were carried out with both a singly and a triply promoted catalyst, i.e. Fe_3O_4 containing 5% Al_2O_3 (Cat. No. 1) and 4% Al_2O_3, 1% CaO, 1% K_2O (Cat. No. 2). The catalysts were prepared according to a procedure previously reported by G. Shima and one of the authors.[8] The latter catalyst is in current industrial use in this country. The catalysts were screened to obtain par-

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[1] A. T. Larson and R. S. Tour, *Chem. Met. Eng.*, 26, 683 (1922).

[2] M. I. Temkin and V. Pyzhev, *Acta Physicochim.*, (U.S.S.R.) 12, 327 (1940).

[3] P. H. Emmett and J. T. Kummer, *Ind. Eng. Chem.*, 35, 677 (1943).

[4] H. Kobayashi and H. Kubota, *Bull. Faculty Eng.* Hokkaido Univ., 5, 118 (1951).

[5] R. M. Adams and E. W. Comings, *Chem. Eng. Progr.*, 49, 359 (1953).

[6] A. Nielsen, "Advances in Catalysis and Related Subjects," Academic Press Inc., 5, 1 (1953).

[7] M. Shindo, *Bull. Faculty Eng., Hokkaido Univ.*, 3, 136 (1949), *Mem. Muroran Univ. Eng.*, 1, 75 (1950).

[8] G. Shima and H. Uchida, *Rept. Chem. Ind. Res. Inst.*, Tokyo, 45, 369 (1950).

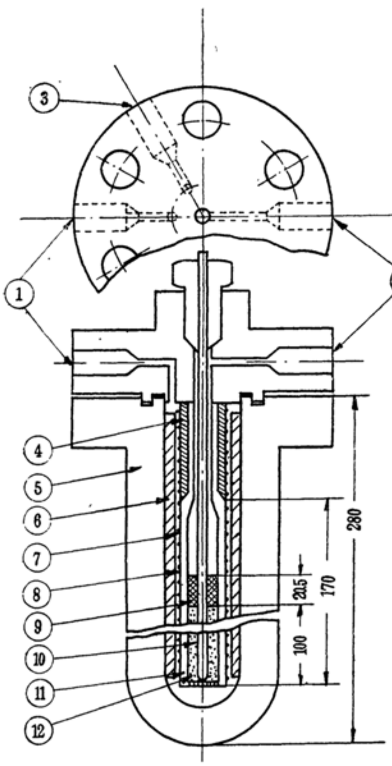

Fig. 1. Reactor.

1. Gas inlet
2. Gas outlet
3. Furnace lead
4. Asbestos
5. Steel shell, $100\phi/50\phi$
6. Silica tube
7. Nichrome heater
8. Mica
9. Catalyst
10. Preheating zone
11. Catalyst chamber, $27\phi/15\phi$
12. Thermocouple well $7\phi/5\phi$

ticles which passed a 1.5 mm. mesh sieve, but were retained on the 1 mm. mesh. About 3 cc. of these specimens, weighing 7.25 g., was placed in the catalyst chamber just to fill 20.5 mm. at the height of the catalyst bed.

The catalysts were reduced in a current of the gas mixture of the ratio of 3 under 50–100 kg./cm^2 at space velocities of $3\sim5\times10^4$ and the reduction was continued until no more increase of ammonia concentration at 425°C under 100 kg./cm^2 was observed after further six hours reduction.

Temperature was measured both at the higher place near the inlet of the catalyst bed and at the lower place near the outlet. During the synthesis, the temperature difference through the catalyst bed remained usually less than 1°C, however it was not successful in retaining a difference less than 7°C, when the reaction temperature was higher than 500°C and the space velocity higher than 10^5. The gaseous products were reduced to an atmospheric pressure and their volumes were measured after ammonia was absorbed in sulfuric acid which was determined as usual.

The measurements were made with both of the two catalysts at 6 to 7 different temperatures from 350°C to 525°C and at space velocities from 5×10^3 to 5×10^5 hr^{-1}., (1) using a mixture whose ratio of hydrogen to nitrogen was 3, under the pressure of 50, 100 and 150 kg./cm^2, and (2) using other mixtures of the ratio of 7, 5, 2, 1 and 1/3 under a constant pressure of 100 kg./cm^2.

Results

Some of the experimental results* are shown in Figs. 2–9 presenting the ammonia concentration or the conversion efficiency as functions of the space velocity, the reaction pressure, and the initial gas composition.

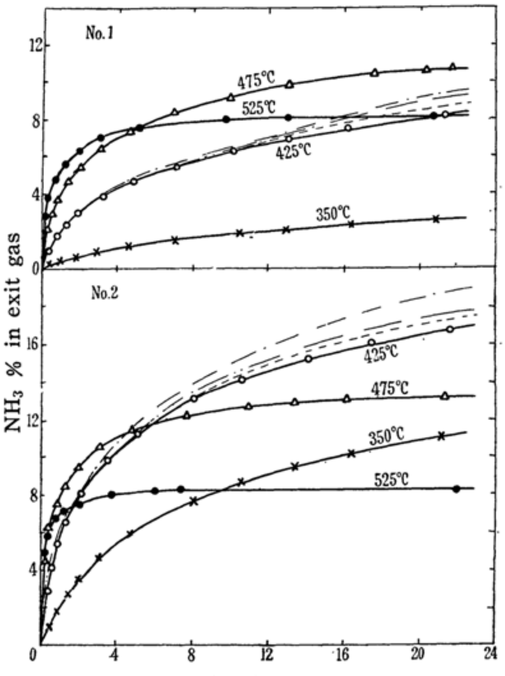

Fig. 2. Relation between reciprocal space velocity and ammonia %.
—○— Experimentally determined
- - - - - Estimated from Eq. (5)
— - — - Estimated from Temkin's Eq.
— — — — Estimated from Shindo's Eq.

When the results concern the use of a mixture of a constant ratio of hydrogen-nitrogen ratio of 3, the ammonia concentration increases, as is well known, with the increasing pressures, but differently according to the kind of catalyst.[1,4,9] A greater increase of conversion percentage and a smaller decrease of efficiency with the increasing pressure are observed with Cat. No. 2 than with Cat. No. 1 (Fig. 3). To the extent that the space velocity is sufficiently high and at the same time the temperature low, the ammonia

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9) H. Uchida and K. Ogawa, *Rept. Chem. Ind. Res. Inst.*, Tokyo, **46**, 114 (1951).

* A paper providing the results described in full will be published in *Rept. Chem. Ind. Inst.* Tokyo.

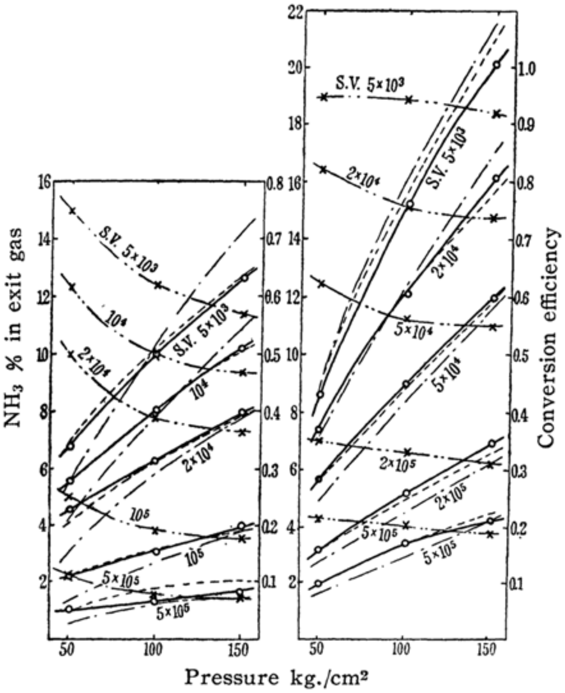


Fig. 3. Effect of pressure on ammonia % and conversion efficiency with catalyst No. 1 and No. 2. $N_2/H_2=1/3$, 450°C; left, No. 1, right, No. 2.

—○— %NH_3 determined experimentally
----- %NH_3 estimated from Eq. (5)
—·—·— %NH_3 estimated from Temkin's Eg.
—··—··— Conversion efficiency

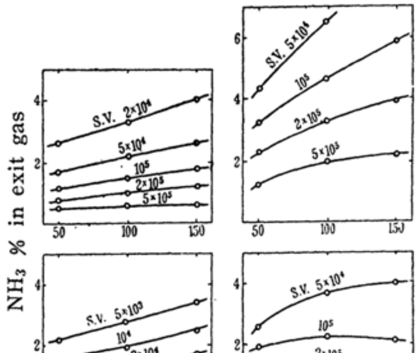


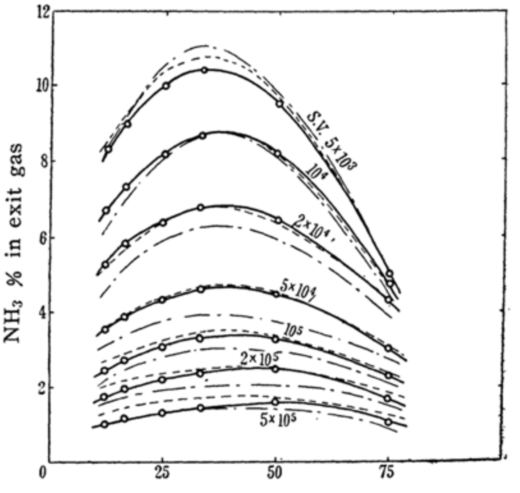
Fig. 4. Effect of pressure on ammonia % at low temperature and high space velocity. $N_2/H_2=1/3$.
above, left; No. 1, 400°C. above, right; No. 2, 400°C. below, left; No. 1, 350°C. below, right; No. 2, 350°C.

concentration remains, however, almost constant, irrespective of the different pressure. Ranges of the space velocity and the temperature in which this constancy holds are different between the two catalysts.**

A. Nielsen has shown an evidence of a maximum of the ammonia concentration together with a minimum of the conversion efficiency with respect to the initial nitrogen percentage, at limited pressure, space velocity, and temperature. In a wider range of space velocity and temperature, as shown in Figs. 5-8, the ammonia concentration and the conversion efficiency are expressed as functions of the initial nitrogen percentage at a pressure of 100 kg./cm² with each of the two catalysts. The maximum ammonia percentage tends to shift with increasing space velocities towards higher nitrogen percentages from 25%, in the neighbourhood of which the maximum is observed at high temperature and low space velocities, say, at the conditions closely approaching equilibrium. The maximum also tends to shift alike with lower temperatures, even at low space velocities.

** The space velocity below which the concentration begins to increase with the pressure is 5×10⁵ at 400°C, 1×10⁵ at 350°C with Cat. No. 1, while 2×10⁵ at 350°C with Cat. No. 2.

(Fig. 5a)



(Fig. 5b)

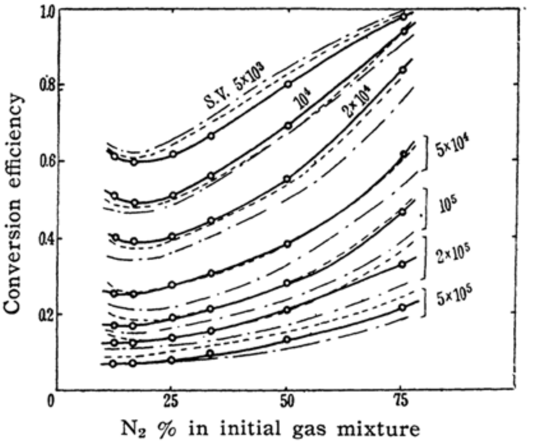
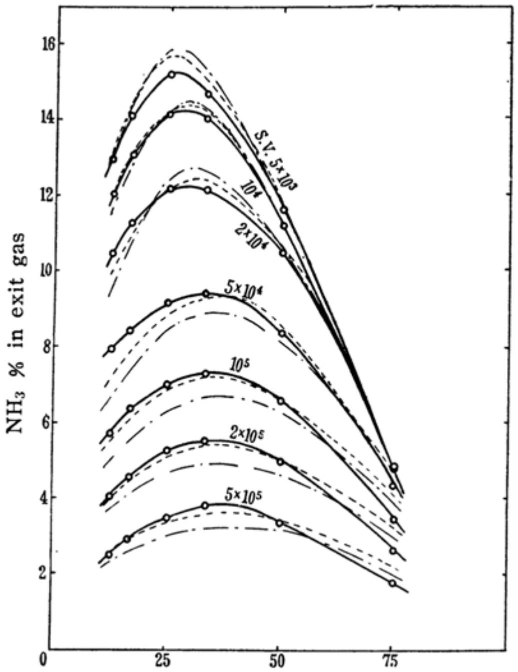


Fig. 5. Dependence of ammonia % and conversion efficiency upon initial gas composition, 100 kg./cm², 450°C, Catalyst No. 1.
—○— Experimentally determined
----- Estimated from Eq. (5)
—·—·— Estimated from Temkin's Eq.

(Fig. 6a)



(Fig. 6b)

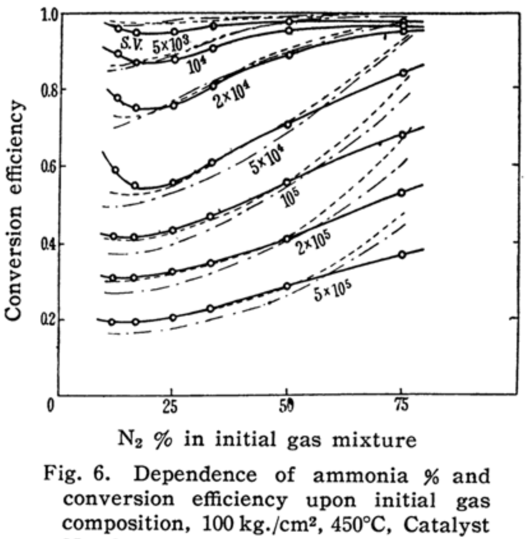


Fig. 6. Dependence of ammonia % and conversion efficiency upon initial gas composition, 100 kg./cm², 450°C, Catalyst No. 2.
—○— Experimentally determined.
----- Estimated from Eq. (5).
—·—·— Estimated from Temkin's Eq.

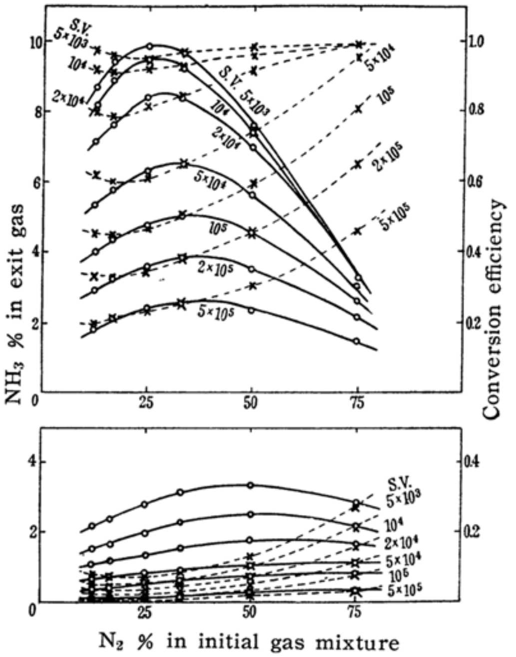


Fig. 7. Depenence of ammonia % and conversion efficiency upon initial gas composition, 100 kg./cm², catalyst No. 1. above, 500°C. below, 350°C.
—○— NH_3 %.
--×-- Conversion efficiency,

The shifting is observed to be more rapid with Cat. No. 1.* At a low temperature and at a high space velocity such as 350°C and 5×10^5, it shifts further through 75% with Cat. No. 1 and 54% with Cat. No. 2. At lower space velocities, the minimum of the conversion efficiency appears at 20–25% nitrogen percentage independent of the temperature. With increasing space velocity, it tends to shift towards a lower nitrogen percentage, and more rapidly at a higher temperature. When a comparison is made between the two catalysts at a constant temperature, the minimum lies at a lower percentage of nitrogen with Cat. No. 2.

S. L. Kiperman[10] pointed out that the ammonia concentration z was in the relation of a straight line with space velocity at a normal pressure, when space velocity is very high. As shown in Figs. 2 and 9, this relation is found also valid at the high pressure in the range of extremely small values of 1/S.V. According to the present observations,

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* The maximum is obtained at 25—26% nitrogen percentage at 500°C, 5×10^3 S.V. with both of the catalysts, and shifts to 48% with Cat. No. 1 and 33% with Cat. No. 2 at 350°C, 5×10^5 S.V., to 40% and 32% at 500°C, 5×10^5 S.V., respectively.

[10] S. L. Kiperman and V. S. Granovskaya, *Chem. Abstr.*, **45**, 9346 (1952), **47**, 6749 (1953).

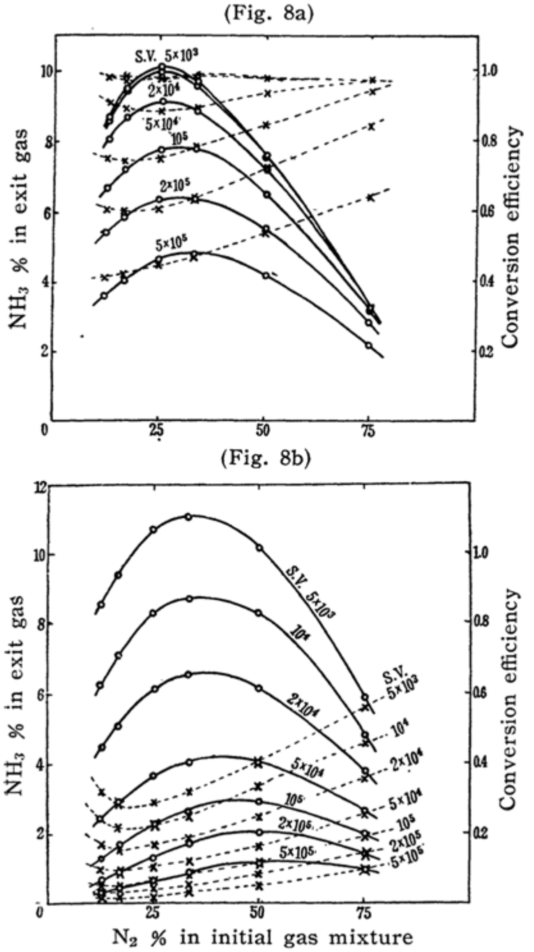

Fig. 8. Dependence of ammonia % and conversion efficiency upon initial gas composition, 100 kg./cm², catalyst No. 2. above, 500°C. below, 350°C.
—○— NH_3 %.
--×-- Conversion efficiency.

it extends towards lower space velocities with lower temperatures, with increasing pressure, and with higher hydrogen percentage. The results may be expressed in terms of the conversion efficiency as follows: the lower the efficiency becomes, the wider is the range at which the linear relation holds.

The proportionality factor between z and 1/S.V. increases with the increasing nitrogen pressure in the mixtures of different hydrogen-nitrogen ratios at a constant total pressure, though it remains constant independent of the different total pressure when a mixture of the ratio of 3 is used.

Discussion

A number of the rate equations for the ammonia synthesis have been proposed.[2,3,4,7,10,11)

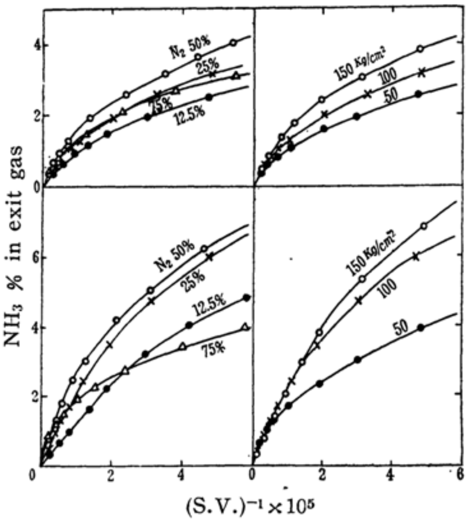

Fig. 9. Relation between ammonia % and reciprocal space velocity at earlier stage of the reaction.
above left, No. 1, 100 kg./cm², 400°C;
above right, No. 1, $N_2/H_2=1/3$, 400°C
below left, No. 2, 100 kg./cm² 350°C;
below right, No. 2, $N_2/H_2=1/3$, 350°C

Among them, the equations by P. H. Emmett,[3) H. de Bruijn,[11) and S. L. Kiperman[10) were in accordance with M. I. Temkin's[2) on the basic assumption that the adsorption rate of nitrogen determines the rate of the synthesis. Likewise H. Kobayashi's[4) agrees with M. Shindo's[7) on assuming the rate of formation of ammonia from NH or NH_2 on the catalyst surface as the rate determining step. The equations by M. I. Temkin and by M. Shindo are here taken as the representatives and their conformity with the experimental results will be checked.

For a flow reactor at a constant temperature and pressure, the reaction rate is in general given by Equation (1)

$$U=dN/A\cdot dl. \tag{1}$$

On rearranging

$$U=dz/273\cdot R\cdot c_m(1+z)^2 d(1/S_0), \tag{2}$$

where U is reaction rate, moles NH_3/hr. m³ catalyst, N is flow rate of ammonia, moles NH_3/hr, A is cross sectional area of catalyst bed, m², l is bed length, m, z is mole fraction of ammonia, R is gas constant, c_m is mean compressibility factor of gas mixture at N. T. P., and S_0 is space velocity based on influent gas, 1/hr.

According to M. I. Temkin and M. Shindo, the rate of the ammonia synthesis is given in terms of activity by Eqs. (3) and (4) respectively.

$$U=k_1\frac{a_{N_2}\cdot a_{H_2}^{3/2}}{a_{NH_3}}-k_2\frac{a_{NH_3}}{a_{H_2}^{3/2}}, \tag{3}$$

[11) H. de Bruijn, *Disc. Faraday Soc.*, 8, 69 (1950).

$$U=k_1\frac{a_{N_2}{}^{1/2}\cdot a_{H_2}{}^{3/2}}{a_{NH_3}}-k_2, \qquad (4)$$

where k_1 and k_2 are respective rate constants for a forward and a reverse reaction, and a_i, activity of the i th component. Combining (2) with (3) or (4), rate constant k_T* from Eq. (3) and k_S from Eq. (4) are expressed respectively by:

$$k_T=\left(\frac{\nu_{H_2}{}^{3/2}}{c_m\cdot\nu_{NH_3}}\right)\frac{P^{1/2}\cdot S_0}{2^{3/2}\cdot 273\cdot R}\int_0^z\frac{z[2-z-2\alpha(1+z)]^{3/2}\cdot dz}{(1+z)^2\left\{\left(\frac{K_P\cdot P}{4}\right)^2[2\alpha(1+z)-z][2-z-2\alpha(1+z)]^3-z^2\right\}}$$

$$k_S=\left(\frac{\nu_{NH_3}}{c_m\cdot\nu_{N_2}{}^{1/2}\cdot\nu_{H_2}{}^{3/2}}\right)\frac{S_0}{273\cdot R}\int_0^z\frac{K_P\cdot z\cdot dz}{(1+z)^2\left\{\left(\frac{K_P\cdot P}{4}\right)[2\alpha(1+z)-z]^{1/2}[2-z-2\alpha(1+z)]^{3/2}-z\right\}}$$

where P, total pressure in atm., K_P, equilibrium constant, ν_i, fugacity coefficient of the ith component, α, mole fraction of nitrogen in the initial gas. Using either of the equations, k_T and k_S are evaluated by means of numerical integration. The obtained values of k_T's and k_S's are not always equal over the measured range of space velocity. For the sake of convenient comparison of the calculated value with the experimental, one value of k is chosen among many values so that z evaluated in use of the k may best approximate to the experimental data over the measured range of space velocity. The values of z thus obtained from Temkin's are illustrated in Fig. 2 together with those from Shindo's, in a dotted and dashed, and a double dotted and dashed line respectively, at 100 kg./cm², 425°C. Temkin's equation gives a good approximation at low z to the experimental data while Shindo's equation rather a better one at higher z.

The pressure being varied, the rate of the forward reaction is proportional to 1.5 power of the total pressure by Temkin's while it is proportional to one power by Shindo's. In this respect, the former equation agrees better with Cat. No. 2, while the latter agrees better with Cat. No. 1.

With respect to Temkin's equation, S. Kodama[12] has come to the conclusion that the nitrogen percentage at which a maximum ammonia concentration is obtained shifts towards the higher percentage with increasing space velocity; from the value of 25% (where S.V.=0) asymptotically to a critical value of 40%. Shindo's equation leads us, however, to the conclusion that the nitrogen percentage remains always at 25% independent of the value of space velocity. The experimental data are in agreement with what was expected from Temkin's equation, the percentage shifting towards the higher with increasing space velocity, but are not exactly so because of the further shifting through the critical value of 40%.

Taking into account the varying dependence of the conversion upon the pressure with respect to the kind of catalyst, the authors propose a modification on Temkin's equation as follows:

$$U=k\frac{1}{(1+k_{NH_3}\cdot a_{NH_3})^{1/2}}\left[\frac{a_{N_2}\cdot a_{H_2}{}^{3/2}}{a_{NH_3}}-\frac{a_{NH_3}}{K^2\cdot a_{H_2}{}^{3/2}}\right], \qquad (5)$$

where k_{NH_3} is a constant characteristic of the catalyst in use.* The modification suggests different degrees of covering of ammonia, depending on the kind of catalyst. It is derived from M. Shindo's fundamental concept on resistivity caused by covering of ammonia on the catalyst surface as well as H. Kobayashi's by which a characteristic degree of the covering dependent on the kind of the catalysts is assumed. Shindo's equation has been improved by H. Kobayashi by means of the above concept and has attained to a better agreement with the latter's experiments with respect to change of pressure.

The values of z or conversion efficiency calculated in the use of Equation (5) are shown in Figs. 2, 3, 5, and 6, being compared with the experimental as well as the calculated by Equations (3) and (4) respectively. In Fig. 2, the deviation from the experimental data (full line) becomes less on Equation (5) (dashed line) than in the case of both Equation (3) (dotted and dashed line) and Equation (4) (double dotted and dashed line), though it remains yet in the region of extremely low as well as extremely high space velocity. With respect to z dependent upon the pressure, the values evaluated by Equation (5) agree well with the observed on both catalysts, except for those observed at higher space velocities

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* M. I. Temkin (*Chem. Abstr.*, 45, 3699 (1951)) improved recently his equation to make it more applicable on varying pressures by introducing another factor. The correction has a less important effect as compared with that due to fugacity.

[12] S. Kodama and K. Fukui et al., *J. Chem. Soc., Japan* (*Ind. Sect.*) 54, 157 (1951).

* The values of k_{NH_3} were calculated by means of trial and error to agree most to the observed data at different temperatures and found to be 0.76 and 0.11 with Cat. No. 1 and No. 2 respectively.

and at the same time at lower temperatures, at which z remains constant independent of the pressure. As for the representation of z as a function of the hydrogen-nitrogen ratios of the gas mixtures, Equation (5) is no more satisfactory than Equation (3). It deviates somewhat from the experimental data with Cat. No. 2, though it approximates closer to those with Cat. No.1 (Figs. 5 and 6).

Temkin's equation together with Equation (5) is thus often in disagreement with the experimental results, pronouncedly at higher space velosities. From the basic concept of M. I. Temkin, S. L. Kiperman proposed the following equation:

$$U=k'\cdot a_{N_2}-k''\frac{a_{NH_3}^{2}}{a_{H_2}^{3}} \tag{6}$$

and interpreted his experimental results at a normal pressure in an earlier stage of the reaction i.e. at low z situated far from the equilibrium.

Combining Equations (2) and (6), it can be readily shown that z should be nearly proportional to 1/S.V.,[*] and the proportionality factor between them should also be proportional to the nitrogen pressure. This prediction is confirmed as shown in Fig. 9 left (at a space velocity of 5×10^5) as well as Fig. 7 below (at space velocities higher than 1×10^5), in both of which the mixtures of varying hydrogen-nitrogen ratio are used at a constant pressure. However, the fact that the factor remains constant irrespective of the varying total pressures when a mixture of the constant ratio is used, seems unable to be interpreted in any way.

Equation (6) calls for the shift of the nitrogen percentage, at which the maximum z is obtained, towards the higher percentages through the critical value of 40% nitrogen at extremely high space velocities, i.e. at low values of z.

Summary

This series of experiments presents the well known fact about the different concentration increases as well as the different decreases of the conversion efficiency with the increasing pressure depending upon the kinds of catalysts in greater detail. At extremely high space velocities, the ammonia concentration remains constant independent of the change of the total pressure when the mixture of a constant gas ratio (H_2 : N_2=3 : 1) is used; however, it increases with increasing nitrogen pressure when the mixtures of different initial compositions are used at a constant pressure.

As predicted by Temkin's equation, the nitrogen percentage or hydrogen percentage, at which a maximum ammonia concentration or a minimum conversion efficiency is observed, shifts towards the higher percentage with the increasing space velocity; however, the nitrogen percentage corresponding to the maximum shifts further through the critical value predicted by Temkin. The shifting is more or less rapid depending on the kind of catalyst. To the extent that the space velocity is very high and the total pressure remains constant the equation by S. L. Kiperman can represent the shifting in a better agreement together with the observed proportionality between the ammonia concentration and the reciprocal space velocity.

The rate equations of M. I. Temkin and M. Shindo, which are based on different concepts, have been compared with the present results, and neither M. I. Temkin's nor M. Shindo's (unimproved) is in satisfactory agreement with the results. An equation based on the concept by M. I. Temkin and provided with another factor characteristic of the kind of catalyst has been proposed. The equation is in better agreement with the experimental results concerning the ammonia concentration expressed as functions of the space velocity and the pressure. The maximum of the ammonia concentration or the minimum of the conversion efficiency related to the ratio of hydrogen to nitrogen is represented in a somewhat better agreement with the singly promoted catalyst, while yet unsatisfactorily with the triply promoted.

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Research Institute, Tokyo

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[*] A. Nielsen has found that $z^2\times$(S.V) approaches a limiting value when S.V. is increased higher than 1×10^5, as a consequence of Temkin's equation. According to our observations, $z\times$(S.V.), instead of $z^2\times$(S.V.), approaches that value.