

# CATALYSIS MECHANISM AND KINETIC EQUATION OF AMMONIA SYNTHESIS ON DOUBLY-PROMOTED IRON CATALYSTS

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## ABSTRACT

On the basis of the theoretical analysis (including the EHMO approximation calculation and the derivations of differential rates) of many known experimental facts, the modes of activation of  $N_2$  and  $H_2$  and the mechanism of  $^{28}N_2$ - $^{30}N_2$  isotopic exchange have been put forward, together with the proposal of the kinetic mechanism of two rate controlling steps of ammonia synthesis on doubly-promoted iron catalysts, i.e. to form adsorbed molecular  $N_2^{\delta}$  and to form  $NH_x$  ( $x = 0, 1, 2$ ) from reaction of  $N_2^{\delta}$  with  $2H^{\delta}$ . The relative concentrations between  $N_2^{\delta}$  and  $NH_x$  vary with catalyst composition and reaction conditions (pressure, temperature, gas composition). From the proposed molecular catalysis mechanism, a kinetic equation of ammonia synthesis on doubly-promoted iron catalyst can be derived. This equation, except the hydrogen adsorption constant term, is in agreement in mathematical form with the extended kinetic equation given by Temkin in 1963<sup>[1]</sup>, but there are significant differences in kinetic mechanism and in the physical meaning of certain microscopic parameters. This equation has already been used in plantoperation designs in China.

## INTRODUCTION

The catalysis mechanism and kinetic equation of ammonia synthesis is a very important fundamental theoretical research with a history of about 70 years, which is also of significance in industrial production. At the suggestion of Prof. Ozaki, Chairman of the 7th International Congress of Catalysis, a post-congress symposium on nitrogen fixation was held recently in Tokyo<sup>[2]</sup>. At this symposium, attention was focused on whether the activation of  $N_2$  passes through the molecular adsorption type and whether hydrogen participates in the process of dissociation of  $N_2$  on industrial catalyst. The concepts of the present author were dealt with briefly in the contributed paper of the 7th International Congress of Catalysis<sup>[2a]</sup>, but neither detailed discussion of the mechanism combined with the experimental results especially with the new data offered at this symposium, nor the derivation of kinetic equation from the proposed microview molecular mechanism have appeared<sup>[3b]</sup>, which will be discussed in detail in this paper.

### I. CATALYSIS MECHANISM OF AMMONIA SYNTHESIS AND THE RATE CONTROLLING STEPS

We believe that the catalysis mechanism of ammonia synthesis on doubly-promot-

ed iron catalyst probably runs like the following.

(1) *The association coordination adsorption of N<sub>2</sub>*

Dinitrogen is inclinedly adsorbed by the adsorption center (111) plane of  $\alpha\text{-Fe}^{[3a,3b]}$ . Both the nitrogen atoms carry negative charges but there are more negative charges on the exo-N of adsorbed N<sub>2</sub>. The results of EHMO calculation show that the overlap population (o.p.) between N<sup>o</sup> and N<sup>r</sup> decreases originally from 1.8 to 0.89.

(2) *The induced activation chemisorption of H<sub>2</sub><sup>[3a,3b]</sup>*

The adsorption type of pure H<sub>2</sub> on iron is Fe—H<sup>-δ</sup> (o.p. ≈ 0.6), which is of strong chemisorption. However, when N<sub>2</sub> and H<sub>2</sub> are adsorbed on the same metal, H<sub>2</sub> might be activated by weak chemisorption with induced polarization to form H<sub>2</sub><sup>+δ</sup> or 2H<sup>+δ</sup> in the vicinity of the exo-N<sup>-δ</sup> of the inclinedly adsorbed N<sub>2</sub><sup>-δ</sup> (o.p. of Fe—H<sup>+δ</sup> ≈ 0.2). If a negative charge oxide ion or AlO<sub>2</sub><sup>-</sup> ion of the K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub> promoter is also near by, the induced polarization to form H<sup>+δ</sup> is expected to be greatly increased<sup>1)</sup>. The forming of Fe—H<sup>+δ</sup> is fast and this reaction soon comes to an equilibrium state.

(3) *The reaction between adsorbed N<sub>2</sub><sup>-δ</sup> and adsorbed 2 H<sup>+δ</sup> (or H<sub>2</sub><sup>+δ</sup>)*

The formation of H<sup>+δ</sup> induced by N<sub>2</sub><sup>-δ</sup> will further weaken the bond order of adsorbed N—N (the o.p. of N—N decreases to 0.62 from original value 0.89), and thus the reaction between N<sub>2</sub><sup>-δ</sup> and 2H<sup>+δ</sup> may automatically break the bond of N—N to form (N) and (NH<sub>2</sub>)<sup>o</sup> or (NH) and (NH)<sup>o</sup>. The symbols ( ) and ( )<sup>o</sup> represent A set cluster (1,2,3,4) and B set cluster (1,3,5,8) of the active center respectively<sup>[3a]</sup>.

(4) *Fast hydrogenation of NH<sub>x</sub> (x = 0, 1, 2) to form NH<sub>3</sub>*

The steps (1) and (3) mentioned above are the rate-controlling steps. This assumption agrees with the observed stoichiometric number,  $n=1^{[4]}$ .

## II. THEORETICAL ANALYSIS OF EXPERIMENTAL DATA AND

### DISCUSSION OF KINETIC MECHANISM

The existence of adsorbed N<sub>2</sub> on Fe catalysts without K<sub>2</sub>O promoter has been proved in many experiments. For example, N<sub>2</sub> can be detected by displacement of chemisorbed dinitrogen <sup>30</sup>N<sub>2</sub> with gas phase dinitrogen <sup>28</sup>N<sub>2</sub> even at 380°C<sup>[5]</sup>; N<sub>2</sub><sup>+</sup> can be checked in FIM<sup>[6]</sup>; the N<sub>2</sub>H<sub>x</sub> exists in IR<sup>[7]</sup>. The thermal desorption rate of adsorbed nitrogen at room temperature shows that the principal adsorption type is N<sub>2</sub><sup>[2d]</sup>.

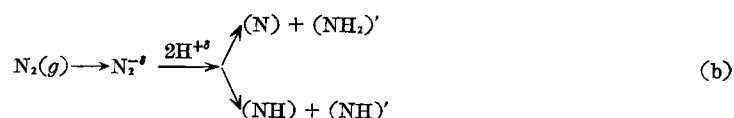
However, there is no direct experimental evidence of molecular adsorbed N<sub>2</sub> on the iron catalysts containing promoter K<sub>2</sub>O at high temperature. Even if a trace amount of adsorbed N<sub>2</sub> can be detected, the problem whether it is the active adsorption state in this catalysis reaction, i.e., whether it passes through N<sub>2</sub> state in the process of the dissociation of dinitrogen, is open to discussion.

Recently, Ertl pointed out<sup>[2c]</sup> that the dissociation of N<sub>2</sub> on iron single crystal consists of two steps.

1) Huang Kaihui, "The Active Adsorption Type of Hydrogen of Ammonia Synthesis on Iron Catalysts", paper presented at the Scientific Symposium of Xiamen University, 1979, (to be published).



The sticking coefficient of the first step is about of the order  $10^{-2}$  while the overall effective sticking coefficient for atomic nitrogen from dinitrogen molecule (gas) is of the order  $10^{-7}$ . This means that the rate of dissociation of adsorbed  $\text{N}_2$  is much lower than that of molecular adsorption of gas  $\text{N}_2$ . We have noticed the fact that the rate of ammonia synthesis on pure iron catalyst is almost the same as that of molecular adsorption of  $\text{N}_2(\text{g})$  on the same catalyst<sup>[41]</sup>, i.e. the rate of ammonia synthesis is higher than that of  $\text{N}_2$  auto-dissociation which obviously is not the principal path of ammonia synthesis reaction. Moreover, the rate of adsorption of  $\text{N}_2$  may increase in the presence of dihydrogen<sup>[43]</sup>. So we consider that, owing to the coexistence of  $\text{H}_2$  and  $\text{N}_2$ , the dissociation of  $\text{N}_2$  has another parallel step (b) with a rate which is much higher than that of step (a)<sup>[3a,2e]</sup>:



The experiments made by Boudart et al.<sup>[2b]</sup> and Topsøe, Dumesic et al.<sup>[9]</sup> show that on Fe/MgO catalyst with particle size of iron ranging from 0.7 to 30 nm, the ammonia synthesis turnover frequencies and the adsorption amount of  $\text{N}_2$  are higher on the larger particles than on the smaller ones. But the adsorption of hydrogen is different. Especially in the case of 1.5 nm small particle, hydrogen adsorption increases greatly with the increase of temperature, while the amount of adsorbed nitrogen and activity of ammonia synthesis are small and will depress slightly with decreasing temperature (in Fig. 4B, Ref. [9]). If we assume that the principal type of adsorbed hydrogen is  $\text{H}^{-\delta}$ , when  $\text{N}_2^{\delta}$  is deficient, this result can be easily understood. By pulse gas chromatography<sup>[10]</sup>, the retention volumes of hydrogen in nitrogen above 400°K are considerably greater than those in argon. This also illustrates the presence of induced chemisorption between hydrogen ( $\text{H}_2^+$  or  $2\text{H}^{+\delta}$ ) and  $\text{N}_2^{\delta}$ .

Recently, Toyoshima pointed out<sup>[2d]</sup> that when the nitrogen equilibrium reaction was performed at the temperature ranging from 350—450°C with the coexistence of  $\text{N}_2$  and  $\text{H}_2$ , the exchange reaction rate between  $^{28}\text{N}_2$ — $^{30}\text{N}_2$  is expressed as:

$$\begin{aligned} r_e &\propto \exp(-33.0/RT) P_{\text{N}_2}^{0.5} \quad (\text{for Fe-K}_2\text{O-Al}_2\text{O}_3), \\ r_e &\propto \exp(-36.0/RT) P_{\text{N}_2}^{0.5} P_{\text{H}_2}^{0.25} \quad (\text{for Fe-Al}_2\text{O}_3). \end{aligned}$$

This can be used to explain the presence of molecular adsorbed  $\text{N}_2$  and the promotive effect of  $\text{H}^{+\delta}$  on the dissociation of  $\text{N}_2$ .

If we assume that the mechanism of isotopic exchange consists of the following steps: (i) the molecular adsorption of  $^{30}\text{N}_2$  (gas) or  $^{28}\text{N}_2$  (gas); (ii) the dissociation of  $^{30}\text{N}_2$ ,  $^{28}\text{N}_2$  into  $^{15}\text{N}$  and  $^{14}\text{N}$  respectively; (iii) the surface migration of  $^{15}\text{N}$  and  $^{14}\text{N}$  to a neighboring adsorption site; (iv)  $^{15}\text{N} + ^{14}\text{N} \rightleftharpoons ^{15}\text{N}-^{14}\text{N}$ ; (v) the desorption of  $^{29}\text{N}_2$ . The relation between its exchange rate and  $P_{\text{N}_2}$  must be  $r_e \propto P_{\text{N}_2}$ , no matter which is the rate-controlling step; this is in contradiction with the result of the experiment described above.

Thus, we may assume that a new mechanism of isotopic exchange between  $^{28}\text{N}_2$ — $^{30}\text{N}_2$



were obtained under equilibrium condition with respect to ammonia synthesis or decomposition. It is reasonable to assume that if the step of hydrogenation of N is in equilibrium, the equilibrium constant is  $K_2$ . The ratio of forward and reverse rate constants of hydrogenation of  $N_2$  is  $K_1$ . Thus we obtain

$$K_1 = \frac{\theta_{NH}^2}{P_{N_2} K_{H_2} P_{H_2}}, \quad (1)$$

$$K_2 = \frac{\theta_N^2 K_{H_2} P_{H_2}}{\theta_{NH}^2}. \quad (2)$$

(For  $K_{H_2} P_{H_2} \ll 1$ , see section IV). Solving (1) and (2), we obtain

$$\theta_N = K_1^{1/2} K_2^{1/2} P_{N_2}^{1/2}. \quad (3)$$

Assuming that the migration of  $^{15}N$  is the rate controlling step, then

$$r_e \propto \theta_N \propto P_{N_2}^{1/2}. \quad (4)$$

This result shows that the exchange rate bears no relation with  $P_{H_2}$  although the hydrogen participates in the dissociation of  $N_2$ .

And on pure iron catalysts, the rate of hydrogenation of  $N_2^{-\delta}$  must be taken into account. The exchange rate is dependent of  $H_2$  ( $r_e \propto P_{N_2}^{1/2} P_{H_2}^{-0.25}$ ,  $P_{H_2} < 1$ ), which means that the presence of small amount of  $H_2$  would promote the hydrogenation dissociation of  $N_2$ , increase both the concentration  $\theta_N$  and the exchange rate. But if the larger amount of  $H_2$  is present, it would increase the NH by hydrogenation of N, thus decreasing the exchange rate.

On iron catalysts with promoter  $K_2O$ , the presence of  $H_2$  may greatly increase the overall exchange rate<sup>[11]</sup>, forming larger amount of  $NH_x$  than iron catalysts without  $K_2O$ . The promotive effect may be manifold, namely, (i) it can lower the work-function of  $\alpha$ -Fe and thus enhance the activation degree of  $N_2$ . The result of EHMO calculation shows that the VSIE of Fe depresses while the activation of  $N_2$  increases, resulting in more negative charges on  $N'$ ,  $N''$  and lower N—N bond order; (ii) according to the dipole reaction, dipole-dipole reaction, the dipole of  $K^+AlO_2^-$ ,  $K^+FeO_2^-$  may contribute to the formation of  $N_2^{-\delta} \cdots H^{+\delta}-Fe$ ; (iii) it may increase the surface concentration of  $NH_x$ , N. The stabilization energy of dipole-dipole reaction has been estimated in our unpublished work<sup>1)</sup>.

The thermal desorption rates after adsorbing nitrogen at room temperature suggest the presence of molecular nitrogen and atomic nitrogen on Fe— $Al_2O_3$  and Fe— $Al_2O_3$ — $K_2O$  catalyst respectively<sup>[2a]</sup>. However, in terms of this rate-expressing only, we can not exclude the presence of a small amount of molecular nitrogen on Fe— $Al_2O_3$ — $K_2O$  catalyst. The experiment is made in a static equilibrium condition in which  $N_2$  automatically dissociates into N in a quite long time and it differs from the flowing kinetic condition of ammonia synthesis. At low or atmosphere pressure, the principal adsorption types of nitrogen may be  $NH_x$  on doubly iron catalyst. The adsorption degree and workfunction of iron increase with the increase of pressure, and thus the rate of dissociation of  $N_2$  depresses when the relative content of  $N_2$  vs  $NH_x$  may increase.

1) It is the same as the footnote on p. 801.

The presence of  $\text{NH}_x$  at low pressure or atmosphere pressure had been detected by XPS<sup>[12,13]</sup>, but the detection of the kinetic adsorption type of  $\text{N}_2$  depends on further development of kinetic spectra technique.

There are some other important facts which can be used to explain the dissociation of  $\text{N}_2$  by the hydrogenation of  $\text{N}_2$  rather than by automatic decomposition of  $\text{N}_2$  (gas). For example, (i) the inverse hydrogen isotopic effect of ammonia synthesis on iron catalysts<sup>[14]</sup> was early explained with the assumption of main adsorbed species  $\text{NH}$ . The  $\text{D}_2$  enhances the forming of  $\text{ND}$  in thermodynamic stability constant, thus the rate of ammonia synthesis is greater in  $\text{D}_2$  than in  $\text{H}_2$ . But the assumption of the main adsorbed species  $\text{NH}$  is in contradiction with the data obtained by XPS<sup>[12]</sup>. According to the mechanism of ammonia synthesis proposed in this paper, we can well explain this inverse isotopic effect<sup>1)</sup>; (ii) from the data of Dumesic, Boudart et al.<sup>[15]</sup>, the initial activity of ammonia synthesis on  $\text{Fe-MgO}$  catalyst activated by pure  $\text{N}_2$  is lower than that on the same catalyst activated by coexistence of  $\text{N}_2$  and  $\text{H}_2$ , which may be contributed to the fact that the rate of hydrogenation of  $\text{N}$  is lower than that of  $\text{NH}_x$ . So the microscopic path of ammonia synthesis is likely to pass through the hydrogenation of  $\text{N}_2$  to  $\text{NH}_x$ ; (iii) we agree with Ozaki<sup>[2a]</sup> who said the fact that the rate of hydrogenation of adsorbed  $\text{N}_2$  formed at low temperature on doubly-promoter catalyst is higher than that of hydrogenation  $\text{N}$  formed at high temperature on the same catalyst, would show the former adsorption type ( $\text{N}_2$ ), which may be the real intermediate in the ammonia synthesis.

### III. DERIVATION OF KINETIC EQUATION

The kinetic equation put forward by Temkin-Pyzhev in 1939 is a significant achievement in the research of reaction kinetics and mechanism of ammonia synthesis, and it has been widely applied to industrial ammonia plant designs, but its mechanism can not explain the inverse isotopic hydrogen effect of this reaction, if without the assumption of the main adsorbed species. Temkin himself also discovered that the equation could not describe the macroscopic kinetics at low pressure. In 1963, he proposed a new extended kinetic equation<sup>[1]</sup>. However, the postulation transition state ( $\text{N}_2\text{H}_2$ ), ( $\text{N}_2\text{H}_4$ ) have not been proved by any experimental facts on doubly-promoted catalysts. His postulation that  $\text{H}_2$  reacts directly with adsorbed nitrogen without prior activation seems to be questionable because of the large dissociation energy of  $\text{H}_2$  (103 Kcal/mole). Moreover this would, we estimate<sup>1)</sup>, predict a normal kinetic isotopic hydrogen effect, which is in contradiction with experimental facts.

The purpose of this work is to derive a kinetic equation of ammonia synthesis on doubly-promoted iron catalysts, which can describe the macroscopic kinetics both at middle and low pressure, the microscopic molecular mechanism of which can reasonably be accepted.

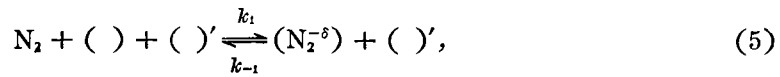
According to the above-mentioned mechanism, we can write out the differential

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1) Huang Kaihui, "The Calculation Hydrogen Isotopic Effect of Ammonia Synthesis on Iron Catalysis by Absolute Theory", paper presented at the Scientific Symposium of Xiamen University, 1979 (to be published).

equation of the rate of various elementary steps as follows,

(1) *The adsorption of N<sub>2</sub>*



where ( ) and ( )' represent A set and B set of active centers respectively.

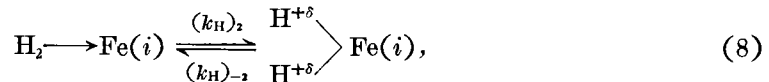
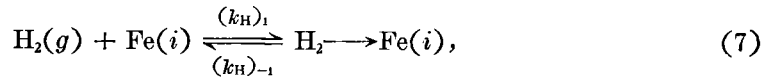
The difference between the rate of adsorption and that of desorption is

$$R = k_1 P_{\text{N}_2} [( )] [( )'] - k_{-1} [(\text{N}_2)] [( )'] \quad (6)$$

or

$$R = k_1 P_{\text{N}_2} \theta_A \theta_B - k_{-1} \theta_{\text{N}_2} \theta_B. \quad (6a)$$

(2) *The activation adsorption of dihydrogen*



where Fe(*i*) is the iron atom neighboring the exo-N'' of adsorbed N<sub>2</sub><sup>-δ</sup>.

When the adsorption of H<sub>2</sub> reaches to a equilibrium state, we obtain

$$(k_{\text{H}})_1 P_{\text{H}_2} (1 - \theta_{\text{H}_2} - \theta_{\text{H}}^2) = (k_{\text{H}})_{-1} \theta_{\text{H}_2}, \quad (9)$$

$$(k_{\text{H}})_2 \theta_{\text{H}_2} = (k_{\text{H}})_{-2} \theta_{\text{H}}^2. \quad (10)$$

Solving (9) and (10),

$$\theta_{\text{H}} = \left[ \frac{K'_{\text{H}_2} K''_{\text{H}_2} P_{\text{H}_2}}{1 + K'_{\text{H}_2} P_{\text{H}_2} + K''_{\text{H}_2} K'_{\text{H}_2} P_{\text{H}_2}} \right]^{\frac{1}{2}}, \quad (11)$$

where

$$K'_{\text{H}_2} = \frac{(k_{\text{H}})_1}{(k_{\text{H}})_{-1}}, \quad K''_{\text{H}_2} = \frac{(k_{\text{H}})_2}{(k_{\text{H}})_{-2}}. \quad (12)$$

At the step of adsorption of molecular H<sub>2</sub> (Eq. 7.) the entropy depresses with the degree of adsorption ( $\Delta S < 0$ ), and the adsorption heat of this process is low ( $\Delta < 0$ ).

From

$$\Delta Z^0 = \Delta H^0 - T \Delta S^0 = -RT \ln K'_{\text{H}_2},$$

we obtain

$$K'_{\text{H}_2} P_{\text{H}_2} \ll 1. \quad (13)$$

At the step of dissociation of adsorbed H<sub>2</sub> (Eq. 8), the degree of vibration increases after the dissociation of H<sub>2</sub>, i.e.  $\Delta S > 0$ ; but the dissociation energy of H<sub>2</sub> is great (103 Kcal/mole), and the bond formed by Fe—H<sup>+δ</sup> is a weak chemisorption (o.p. of Fe—H<sup>+δ</sup>: 0.2 compared with o.p. of Fe—H<sup>+δ</sup>: 0.6). So  $\Delta H > 0$ . From above, we can obtain

$$K''_{\text{H}_2} P_{\text{H}_2} \ll 1. \quad (14)$$

Substitute (13), (14) in (11),

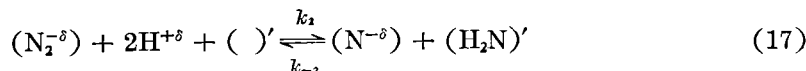
then

$$\theta_H = (K'_H K''_H P_{H_2})^{\frac{1}{2}} = K_{H_2}^{1/2} P_{H_2}^{1/2}, \quad (15)$$

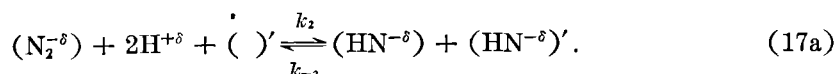
where

$$K_{H_2} = K'_H K''_H = \frac{(k_H)_1}{(k_H)_{-1}} \cdot \frac{(k_H)_2}{(k_H)_{-2}}. \quad (16)$$

(3) *The reaction between adsorbed  $N_2^{-\delta}$  and  $H^{+\delta}$*



or



The difference between the positive and the inversed directions can be expressed as

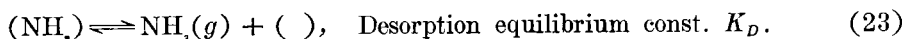
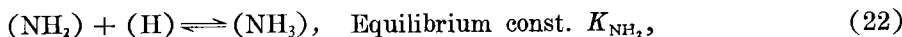
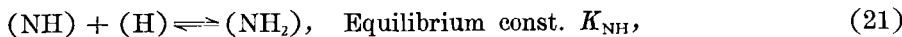
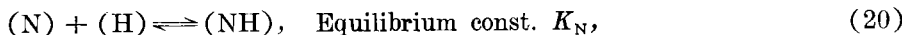
$$R = k_2(\theta_{N_2})\theta_H^2\theta_B - k_{-2}\theta_N\theta'_{NH_2} \quad (18)$$

or

$$R = k_2(\theta_{N_2})\theta_H^2\theta_B - k_{-2}\theta_{NH}\theta'_{NH} \quad (19)$$

(4) *Fast equilibrium of the hydrogenation of  $NH_x$  ( $x = 0, 1, 2$ ).*

The hydrogenation on A set of the active center.



From (20) to (23), we obtain,

$$\theta_N = \frac{P_{NH_3}\theta_A}{K_{NH_3}\theta_H^3}, \quad (24)$$

$$\theta_{NH} = \frac{K_N P_{NH_3}\theta_A}{K_{NH_3}\theta_H^2}, \quad (25)$$

$$\theta_{NH_2} = \frac{K_N K_{NH_2} P_{NH_3}\theta_A}{K_{NH_3}\theta_H}, \quad (26)$$

$$\theta_{NH_3} = \frac{K_N K_{NH} K_{NH_2} P_{NH_3}\theta_A}{K_{NH_3}} = \frac{P_{NH_3}\theta_A}{K_D}, \quad (27)$$

$$K_{NH_3} = K_N K_{NH} K_{NH_2} K_D. \quad (28)$$

Adding hydrogenation of  $(NH_x)$  on to the B set of active center, by similar derivation, we obtain  $K'_N, K'_{NH}, K'_{NH_2}, K'_D, \theta'_N, \theta'_{NH}, \theta'_{NH_2}, \theta'_{NH_3}, K'_{NH_3}$ , equivalent to (20a) to (28a) respectively.

(5) *Derivation of overall kinetic equation*

We assume that the rate controlling slow steps are the adsorption of  $N_2$  and the



reaction between  $N_2^{-\delta}$  and  $H^{+\delta}$ .

When the reaction reaches to a stationary state,

then 
$$\frac{d[N_2^{-\delta}]}{dt} = 0.$$

From (6a), (18) or (19), we obtain,

$$k_1 P_{N_2} (1 - \theta_{N_2}) \theta_B + k_{-2} \theta_N \theta'_{NH_2} = k_{-1} \theta_{N_2} \theta_B + k_2 \theta_{N_2} \theta_H^2 \theta_B \quad (29)$$

or

$$k_1 P_{N_2} (1 - \theta_{N_2}) \theta_B + k_{-2} \theta_{NH} \theta'_{NH} = k_{-1} \theta_{N_2} \theta_B + k_2 \theta_{N_2} \theta_H^2 \theta_B. \quad (29a)$$

Substituting  $\theta_N$  (24),  $\theta'_{NH_2}$  (26a) into (29), when (29) is simplified and solved, we obtain,

$$\frac{1 - \theta_{N_2}}{\theta_{N_2}} = \frac{k_{-1} + k_2 \theta_H^2}{k_1 P_{N_2} + k_{-2} \frac{P_{NH_3}^2}{K_{NH_3} K'_{NH_2} K'_D \theta_H^4}} = u. \quad (30)$$

Substituting  $\theta_{NH}$  (25),  $\theta'_{NH}$  (25a) into (29a), we obtain,

$$\frac{1 - \theta_{N_2}}{\theta_{N_2}} = \frac{k_{-1} + k_2 \theta_H^2}{k_1 P_{N_2} + k_2 \frac{P_{NH_3}^2}{K_{NH_3} K_{NH_2} K_D K'_{NH} K'_{NH_2} K'_D \theta_H^4}} = u'. \quad (30a)$$

Let

$$K = K_{NH_3} K'_{NH_2} K'_D, \quad (31)$$

$$K' = K_{NH} K_{NH_2} K_D K'_{NH} K'_{NH_2} K'_D. \quad (32)$$

Substituting  $K$ ,  $K'$  into (30), (30a), we obtain the same form of  $\frac{1 - \theta_{N_2}}{\theta_{N_2}}$ , rearranging further, we obtain,

$$\theta_{N_2} = \frac{k_1 P_{N_2} + k_{-1} \frac{P_{NH_3}^2}{K \theta_H^4}}{k_1 P_{N_2} + k_{-1} + k_2 \theta_H^2 + k_{-2} \frac{P_{NH_3}^2}{K \theta_H^4}}, \quad (33)$$

$$1 - \theta_{N_2} = \frac{k_{-1} + k_2 \theta_H^2}{k_1 P_{N_2} + k_{-1} + k_2 \theta_H^2 + k_{-2} \frac{P_{NH_3}^2}{K \theta_H^4}}. \quad (34)$$

When the reaction is in stationary state, the overall reaction rate may be described as the rate difference between positive and inverse of any elementary steps, as shown in (6a). Substituting (33), (34) and (15) into (6a), we obtain,

$$R = \frac{k_1 k_2 K_{H_2} P_{N_2} P_{H_2} - k_{-1} k_{-2} \frac{P_{NH_3}^2}{K K_{H_2}^2 P_{H_2}^2}}{k_1 P_{N_2} + k_{-2} \frac{P_{NH_3}^2}{K K_{H_2}^2 P_{H_2}^2} + k_{-1} + k_2 K_{H_2} P_{H_2}}. \quad (35)$$

The parameters of  $k_1$ ,  $k_2$ ,  $k_{-1}$ ,  $k_{-2}$  vary with adsorption coverage degree ( $s$ ). This is an important electronic effect that cannot be omitted.

In accordance with the treatment of the heterogeneous surface proposed by

Temkin<sup>[1]</sup>, the rate constants vary with coverage ( $s$ ) as follows:

$$\begin{aligned} k_1 &= k_1^0 e^{-\alpha f s}, & k_{-1} &= k_{-1}^0 e^{\beta f s}, \\ k_2 &= k_2^0 e^{\beta' f s}, & k_{-2} &= k_{-2}^0 e^{-\alpha' f s}, \end{aligned} \quad (36)$$

where  $f$  is the coefficient connected with adsorption heat of  $N_2$  which varies linearly with coverage ( $s$ ). For example, the adsorption heat of  $N_2$  is,  $Q_{N_2} = Q_{N_2}^0 - fRTs$ , where  $\alpha$  or  $\beta$  is the coefficient connected with adsorption activation energy or desorption activation energy both of which vary linearly with coverage ( $s$ ) respectively, such as:  $E_{N_2(A)} = E_{N_2(A)}^0 + \alpha fRTs$ , where  $E_{N_2(A)}$  is adsorption activation energy.  $E_{N_2(D)} = E_{N_2(D)}^0 - \beta fRTs$ , where  $E_{N_2(D)}$  is desorption activation energy.

From the definition of adsorption heat of  $N_2$  ( $Q_{N_2}$ ), we obtain

$$Q_{N_2} = E_{N_2(D)} - E_{N_2(A)}.$$

Hence

$$\alpha + \beta = 1.$$

These activation energies varying linearly with coverage can be explained from microscopic viewpoints, i.e. the workfunction of iron increases with adsorption coverage of  $N_2$ . So further adsorption of  $N_2$  must possess greater energy for electron of metal anti-back to  $\pi^*$  orbitals of  $N_2$ . The process of desorption is the reversal course. On the other hand, the forming of  $H^{+\delta}$  and the process of the reaction between  $N_2^{-\delta}$  and  $H^{+\delta}$ , may be effective by increasing the workfunction. So the activation energies of  $k_2$  depress with the coverage ( $s$ ), e.g.,

$$k_2 = k_2^0 e^{\beta' f s}.$$

Hence, the inversal process is,

$$k_{-2}^0 = k_{-2}^0 e^{-\alpha' f s} \quad \text{and} \quad \alpha' + \beta' = 1.$$

Because all the reaction steps are on the same surface, it is reasonable to assume that  $\alpha \cong \alpha'$ ,  $\beta \cong \beta'$ . From the treatment of experimental data by the sequential procedure to be described in the next paragraph, we can obtain  $\alpha = 0.495$ . It means that all the rate controlling steps must be taken in the powerful catalysts and the catalyst must possess the dual character of electron donor and electron acceptor simultaneously i.e.,

$$\alpha = \beta \cong 0.5.$$

Substituting (36) into (30), we can obtain,

$$ds = \frac{1}{f} \frac{du}{u}. \quad (37)$$

Substituting (36) into (35), and integrating from  $s = 0$  to  $s = 1$ , then changing variable  $s$  to  $u$  on the basis of (37), we found that the integral range is from  $u=0$  to  $u = \infty$ , where  $u = 0$  is equivalent to  $s = 0$  or  $\theta_{N_2} = 1$  (see (30)), i.e. the most active adsorption sites will be all covered, where  $u = \infty$  is equivalent to  $s = 1$  or  $\theta_{N_2} = 0$  (see (30)), i.e. the least active centers will all be vacant. The surface is probably an induced heterogeneous surface model rather than a heterogeneous adsorption sites model. Applying the mathematical method for integration similar to the method proposed by Temkin, we obtain,

$$R = \frac{1}{f} \frac{\pi}{\sin \alpha \pi} \times \frac{(k_1^0 P_{N_2})^{1-\alpha} (k_{-1}^0)^\alpha \left(1 - \frac{k_{-1}^0 k_{-2}^0}{k_1^0 k_2^0} \frac{P_{NH_3}^2}{KK_{H_2}^3 P_{N_2} P_{H_2}^3}\right)}{\left(\frac{k_{-1}^0}{k_2^0 K_{H_2} P_{H_2}} + \frac{k_{-1}^0 k_{-2}^0}{k_1^0 k_2^0} \frac{P_{NH_3}^2}{KK_{H_2}^3 P_{N_2} P_{H_2}^3}\right)^\alpha \left(\frac{k_{-1}^0}{k_2^0 K_{H_2} P_{H_2}} + 1\right)^{1-\alpha}}. \quad (38)$$

The constant terms of this equation can be simplified as follows: We assume the elementary step of adsorption of  $N_2$  reaches equilibrium,

then

$$\frac{k_1}{k_{-1}} = \left(\frac{\theta_{N_2}}{P_{N_2} \theta_A}\right)_{eq}, \quad (39)$$

where  $(P_{N_2})_{eq}$  is the equilibrium partial pressure of  $N_2$  which differs from pressure of  $N_2$  under reaction condition. Other terms have the same definition as below. Assuming the elementary step of the hydrogenation of  $N_2^{\delta}$  reaches equilibrium, we obtain,

$$\left(\frac{k_2}{k_{-2}}\right) = \left(\frac{\theta_N \theta'_{NH_2}}{\theta_{N_2} \theta_H^2 \theta_B}\right)_{eq}. \quad (40)$$

Substituting (36) into solved (39), (40), we obtain

$$\frac{k_1 k_2}{k_{-1} k_{-2}} = \frac{k_1^0 k_2^0}{k_{-1}^0 k_{-2}^0} = \left[\frac{\theta_N \theta_{NH_2}^2}{P_{N_2} \theta_H^2 \theta_A \theta_B}\right]_{eq}. \quad (41)$$

Substituting (24), (26a), (15), (31) into (41), we obtain

$$\frac{k_{-1}^0 k_{-2}^0}{k_1^0 k_2^0} \frac{1}{KK_{H_2}^3} = \frac{1}{K_{NH_3}^0}, \quad (42)$$

where

$$K_{NH_3}^0 = (P_{NH_3}^2 / P_{N_2} P_{H_2}^3)_{eq} / K_{NH_3}.$$

Similarly

$$\frac{k_{-1}^0}{k_1^0} \frac{k_{-2}^0}{k_2^0} \frac{1}{K' K_{H_2}^3} = \frac{1}{K_{NH_3}^0}, \quad (43)$$

where  $K'$  can be seen from (32). Since (42) and (43) have the same form, the macroscopic kinetic can not distinguish the mechanisms from (N),  $(NH_2)'$  or  $(NH)'$ ,  $(NH)'$ . Substituting (42) into (36), we obtain

$$R = \frac{1}{f} \frac{\pi}{\sin \alpha \pi} \times \frac{(k_1^0 P_{N_2})^{1-\alpha} (k_{-1}^0)^\alpha \left(1 - \frac{P_{NH_3}^2}{K_{NH_3}^0 P_{N_2} P_{H_2}^3}\right)}{\left(\frac{k_{-1}^0}{k_2^0 K_{H_2} P_{H_2}} + \frac{1}{K_{NH_3}^0} \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}\right)^\alpha \left(\frac{k_{-1}^0}{k_2^0 K_{H_2} P_{H_2}} + 1\right)^{1-\alpha}}. \quad (44)$$

Eq. (44) is the kinetic equation of ammonia synthesis on doubly-promoted catalysts. This equation has the same mathematical form as Temkin extended equation (1963)<sup>(11)</sup> except the hydrogen adsorption constant term. But obviously there are important differences between Temkin's extended equation (1963) and ours in both the kinetic mechanism and the physical meaning of some kinetic parameters. By using sequential procedure, we have found that the kinetic parameter calculated in (44) is more reasonable than that calculated by Temkin's extended equation (1963)<sup>(1)</sup>. More-

1) It is the same as the footnote on p. 805.

over, Eq. (44) can be used to explain the inverse isotopic hydrogen effect whereas the Temkin extended equation predicts a normal isotopic hydrogen effect which is in contradiction with experimental data.

#### IV. DETECTION OF KINETIC EQUATION

The first draft of the derivation of (44) from the microscopic viewpoint of molecular catalysis, was completed in 1977. This derivation has aroused interest in the practical aspect of this equation among some chemical engineers<sup>1)</sup>. By using an industrial iron catalyst (A110) made in China, Liu Deming et al.<sup>[16]</sup> have obtained 24 sets of experimental kinetic data for ammonia synthesis reaction under  $70 \leq P$  (atm)  $\leq 300$ ,  $320^\circ \leq t^\circ\text{C} \leq 500^\circ$ ,  $100 \leq V$  (NTP/HR)  $\leq 320$ . Treatment of these data by means of sequential procedure shows that compared with four other well-known kinetic equations (namely, that given by Cappelli et al., Temkin et al. (1939), Buzzi Fararis et al., and Nielsen et al.), it not only has a maximum post probability (see Fig. 2), but also enables production rate data to be described faithfully by applying a lot of this residual difference  $y_i - y_i$  versus  $y_i$  (values predicted from Eq. (40)).

Eq. (44) has already been in use for plant operation designs in NCC Research Institute at present, and has the following strong points: The imitation degree between the calculation and industrial data is excellent in many respects, such as the output of ammonia, the temperature distribution activity distribution of catalyst bed, etc. On the other hand, if we use old Temkin-Pyzhev equation, the correction coefficient of activity of ammonia synthesis with the length of catalyst bed would appear with abnormal distribution.

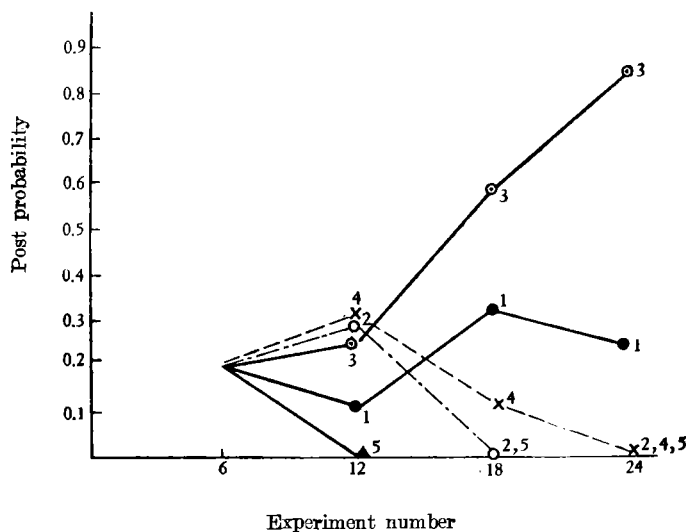


Fig. 2. Comparison of five kinetic equations by sequential procedure.  
 1. Cappilli model, 2. Temkin model, 3. Eq. (44) of this paper or Temkin extended equation, 4. Buzzi Ferraris model, 5. Nielsen model.

1) In early 1978, first draft of this article was preprinted by NCC Research Institute of Technology.

Since the kinetic parameters of (44) have more definite physical meaning, by using sequential procedure and calculating parameters with the help of electronic computer, Eq. (44) may be of some service in the selection of new type of catalysts, in the study of the influence of impurities on reaction parameters, as well as in automatic process control.

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