# A "New" General Mechanism of Ammonia Synthesis and Decomposition on Transition Metals

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The heterogeneous catalytic synthesis (and decomposition) of ammonia is among the most important reactions in science and technology. As a reaction it has played, and continues to play, a key role in the development of a large number of thermodynamic and kinetic principles stemming from both its intrinsic and its industrial importance. Every time new methods, tools, or concepts have appeared in the field of heterogeneous catalysis, they have been applied to this system. Examples of these are the concepts of gas equilibrium,[1] activated adsorption,[2] structure sensitivity,[3] stoichiometric number,[4] nonuniform surfaces,[5] the measurement of surface area,[6] surface composition and distributions,[7] and the usage of isotopic[8] and spectroscopic techniques.[9] In particular, in recent years various surface science techniques have been applied successfully to this reaction system over well-defined surfaces, and in this way the effect of promoters, for instance, has been elucidated.[10] These various topics are covered in a number of reviews.[11] This account will deal with another important chapter in the history of this well-studied reaction: the kinetics and mechanism of the reaction elucidated by means of the dynamic approach which was initiated by the author over 20 years ago.[12]

In the case of the decomposition of ammonia on a tungsten surface, the rate is expressed by the equation[13]

$$-d(NH_3)/dt = k(NH_3)/(1 + b(NH_3))$$

where $k$ and $b$ are constants and $(NH_3)$ is the concentration of ammonia. In chemical engineering this equation is usually interpreted with the Haugen–Watson theory, in enzyme kinetics with the Michaelis–Menten theory, and in physical chemistry, with the Langmuir–Hinshelwood theory. In all of these cases it is assumed that the reactant is being chemisorbed by the catalyst and that the reaction rate is proportional to the amount of reactant adsorbed on the catalyst. However, although the kinetic equation may be interpreted by these mechanisms, it has been experimentally demonstrated by the following dynamic treatment that they are actually not valid.

In most studies of heterogeneous catalysis the catalyst itself has been considered to exist in a black box, and only the entrance and exit of the black box have been examined. On the basis of indirect information obtained from the kinetic behavior outside the black box, the mechanism of a reaction that takes place in the black box may be discussed from conjectures. Since catalysis is a dynamic process, its mechanism is better elucidated by a dynamic approach, examining what is actually happening on the working catalyst surfaces.[12]

The author studied the mechanism of the catalytic decomposition of germane, $(GeH_4)$ on germanium, $GeH_4 \rightarrow Ge + 2H_2$, some years ago.[14] By direct adsorption measurements it was shown that the number of hydrogen atoms adsorbed on the working germanium surface is equal to that of germanium surface atoms. The rate of hydrogen desorption is the rate-determining step since the chemical potential of the chemisorbed hydrogen on the working germanium catalyst is much higher than that of ambient hydrogen gas. Although much attention has been focused on this catalytic reaction in recent years in connection with the chemical vapor deposition technique, our earlier work was the first example where direct adsorption measurements were carried out during the course of the reaction to identify the amounts and structures of the adsorbed species and to compare the reactivity of each to the overall reaction rate. This dynamic approach has been successfully applied to various catalytic reactions since

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then to elucidate their mechanisms.[15]

## Mechanism of Ammonia Decomposition on Tungsten

In the case of the decomposition of ammonia on tungsten it is found that the following equations for the reaction rate give reasonable representations of the experimental data. In both cases $r$, the rate of reaction, is a function only of $P_{NH_3}$, the partial pressure of ammonia.[13]

$$r = k'P_{NH_3}^m \qquad (1)$$

or

$$r = kP_{NH_3}/(1 + KP_{NH_3}) \qquad (2)$$

where $k$, $k'$, $K$, and $m$ ($0 \leq m \leq 1$) are constants. Kinetic expressions such as (1) and (2) have been observed in the decomposition of ammonia on tungsten, on molybdenum,[13] and even on iron and platinum at higher temperatures.[16] It was also observed by Egawa et al.[17] that rate equation (1) or (2) was observed over the terrace sites of ruthenium (1, 1, 10), whereas the rate equation of the Temkin–Pyzhev mechanism, as will be discussed later in eq 8, exhibited over its step sites under similar reaction conditions. These various cases suggest that rate equations (1) and (2), which are independent of hydrogen pressure, are general expressions for ammonia decomposition.

The dynamic approach can be illustrated with the case of ammonia decomposition on tungsten. When ammonia is introduced onto a clean tungsten surface, hydrogen is evolved and chemisorption of nitrogen takes place. The mechanism of the reaction was elucidated by measuring the rate of the overall reaction as well as the concentration of chemisorbed species and the pressures of the ambient gases during the course of reaction.[13] The decomposition of ambient ammonia gas to form chemisorbed nitrogen and hydrogen gas is rapid at first and subsequently slows down as more nitrogen is chemisorbed. On the other hand, nitrogen desorption is slow at the beginning and then becomes more rapid, finally reaching its steady state. During such a process no appreciable hydrogen is chemisorbed (in any form) above 973 K.

The results may be recalculated to estimate the rate ($r_a$) of nitrogen uptake from ammonia onto the surface and that ($r_d$) of nitrogen desorption from the surface to form nitrogen gas, both rates being expressed by the number of nitrogen atoms per second per surface tungsten atom, as shown in Figure 1. If the number of surface tungsten atoms is denoted as $n_W$, and those of ammonia, nitrogen gas molecules, and adsorbed nitrogen atoms as $n_{NH_3}$, $n_{N_2}$, $n_{N(a)}$, respectively, then

$$-(1/n_W)(dn_{NH_3}/dt) = (1/n_W)(dn_{N(a)}/dt) + (2/n_W)(dn_{N_2}/dt) = r_a + r_d \qquad (3)$$

The parameters $r_a$ and $r_d$ are plotted against nitrogen coverage in Figure 1 under the reaction conditions at 1073 K. The rate of supply of chemisorbed nitrogen from ammonia is proportional to the ammonia pressure, and it decreases as the nitrogen coverage increases whereas the rate of nitrogen desorption increases. The rate of nitrogen desorption is approximated by the Langmuir[18] equation

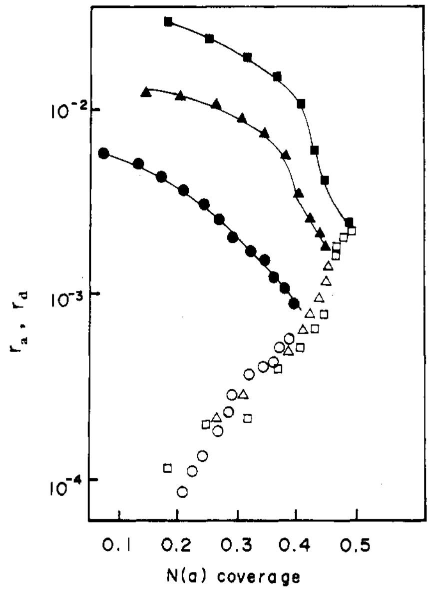

**Figure 1.** Rates of nitrogen chemisorption ($r_a$) from ammonia and nitrogen desorption ($r_d$) plotted against nitrogen coverage on tungsten. $T$ = 1073 K; $P_{NH_3}$: (●,○) $1.7 \times 10^{-6}$, (▲,△) $5.1 \times 10^{-6}$, (■,□) $9.8 \times 10^{-6}$ Pa. Open points refer to adsorption experiments and closed points refer to desorption experiments.

$$r_d = k_d \exp(h\theta_N) \qquad (4)$$

where $k$ and $h$ are constants and $\theta_N$ is the coverage of nitrogen. This rate is only dependent upon the nitrogen coverage and temperature, and not upon the ammonia pressure. The steady state is the point where the two curves of $r_a$ and $r_d$ intersect, and the rate of the overall reaction observed agrees well with this point.[17]

The rate of the overall decomposition reaction is first order with respect to ammonia at lower ammonia pressure and approaches zero order at higher ammonia pressures. The rate is always zero order in hydrogen pressure, which is quite different from the Tempkin–Pyzhev mechanism as will be discussed later.

When the adsorption isotherm of nitrogen on tungsten is studied, it is readily concluded that the nitrogen chemisorbed during the course of reaction is markedly more than that in adsorption equilibrium with ambient nitrogen gas. There is a chemical potential drop between the ambient nitrogen gas and chemisorbed nitrogen. The fact that hydrogen does not affect the rate of nitrogen desorption, its chemisorbed amount, or the overall reaction rate throughout the wide range of coverage and reaction conditions strongly suggests that no equilibrium among ambient ammonia ($NH_3$(g)), hydrogen ($H_2$(g)), and chemisorbed nitrogen (N(a)) is realized.

The rate ($r_a^A$) that nitrogen is chemisorbed from ammonia is approximately expressed by the equation

$$r_a^A = k_a^A P_{NH_3} \exp(-g'\theta_N) \qquad (5)$$

and the rate ($r_a^A$) of its desorption, by eq 4. Therefore the amount of nitrogen chemisorbed or its coverage in

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[15] E.g.: Tamaru, K. *Dynamic Heterogeneous Catralysis*; Academic: New York, 1978. Tamaru, K., et al. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2913; **1982**, *78*, 845, 1473; *Surf. Sci.* **1983**, *130*, 29; **1985**, *145*, 1; **1985**, *155*, 153; *J. Catal.* **1985**, *94*, 353.

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[17] Egawa, C.; Nishida, T.; Naito, S.; Tamaru, K. *J. Chem. Soc., Faraday Trans. 1* **1982**, *80*, 1595.

[18] Langmuir, I. *J. Am. Chem. Soc.* **1932**, *54*, 2798; *Acta Physicochim. USSR* **1934**, *1*, 371.

the steady state of the reaction ($\theta_N^{ss}$) is determined by equating eq 4 and 5 to yield

$$\theta_N^{ss} = \frac{1}{h + g'} \ln \left( \frac{k_a^A}{k_a^N} P_{NH_3} \right) \quad (6)$$

Thus $\theta_N^{ss}$ is independent of hydrogen pressure. Consequently, the rate of the overall reaction ($V$) under the condition of a steady state is obtained as follows:

$$V = r_d^N = k_d^N \exp(h\theta_N^{ss}) = k_d^N(KP_{NH_3})^{m'} = k_d^N KP_{NH_3}/(1 + KP_{NH_3}) \quad (7)$$

where $m'$ is equal to $h/(h + g')$, and $K$ is equal to $k_a^A/k_d^N$. Equation 7 is exactly what has been observed kinetically over a tungsten surface.[13]

In this manner it was demonstrated that, although the kinetic expression of ammonia decomposition over tungsten obeys the Langmuir–Hinshelwood mechanism, it is not to be interpreted by the mechanism, but by the dynamic balance mechanism between the supply and desorption of chemisorbed nitrogen.

## Ammonia Decomposition on Different Transition Metals

The decomposition of ammonia on iron and also on many transition metals is generally treated as consisting of two kinetically significant steps, chemisorption of nitrogen from ammonia with simultaneous splitting of hydrogen and desorption of the chemisorbed nitrogen thus supplied. The kinetic expression for ammonia decomposition on transition metals, in many cases, is given by the following empirical equation:

$$r = k(P_{NH_3}^2/P_{H_2}^3)^\alpha \quad (8)$$

where $P_{H_2}$ is the pressure of hydrogen, and $k$ and $\alpha$ are constants. This kinetic expression is very interesting in the sense that the rate of forward reaction is strongly retarded by hydrogen, which is one of the reaction products. According to the Temkin–Pyzhev mechanism,[19] eq 8 may be obtained by assuming that nitrogen desorption is the only rate-determining step and that a quasi-equilibrium between gaseous ammonia, chemisorbed nitrogen, and gaseous hydrogen exists in the steady state of the reaction:

$$NH_3(g) \rightleftarrows N(a) + {}^3/_2H_2(g) \quad (9)$$

Furthermore, eq 8 assumes that the rate of nitrogen chemisorption ($r_a$) obeys the Zeldovich–Roginsky[20] equation as given by empirical eq 10, whereas that of desorption by the Langmuir equation given by eq 4:

$$r_a = k_a^N P_{N_2} \exp(-g\theta_N) \quad (10)$$

where $k_a^N$ and $g$ are constants (although their values are actually influenced by the presence of hydrogen[21]). Consequently, the following nitrogen adsorption equilibrium may be obtained by equating the two rate equations (10) and (4):

$$\theta_N = \frac{1}{h + g} \ln \left( \frac{k_a^N}{k_d^N} P_{N_2} \right) \quad (11)$$

Equations 4, 10, and 11 may be obtained by assuming that the heat and the activation energy of adsorption vary linearly with coverage over a moderate range of $\theta_N$. Therefore, the partial pressure of nitrogen, which determines the nitrogen coverage in the steady state of the reaction, is not the nitrogen pressure in the ambient gas, but it is the "virtual pressure" of nitrogen ($P_{N_2}{}^*$). This virtual pressure is that pressure of nitrogen which would be in equilibrium with the pressures of ammonia and hydrogen observed in the ambient gas:

$$P_{NH_3}^2/(P_{N_2}{}^*P_{H_2}^3) = K_A \quad (12)$$

where $K_A$ is the equilibrium constant of the reaction $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$.

The rate of the overall reaction, consequently, is determined by eq 4, 11, and 12 as follows:

$$V = r_d^N = k_d^N \exp(h\theta_N^{ss}) = k(P_{NH_3}^2/P_{H_2}^3)^\alpha \quad (13)$$

where $\alpha$ is equal to $h/(g + h)$ and $k$ is equal to $k_d[k_a^N/(k_d^N K_A)]^\alpha$. This mechanism, proposed by Temkin and Pyzhev,[19] has been supported by various experimental observations, as is explained in various review articles.[11]

## A Parameter Indicating Which Mechanism Is Operative

In the Temkin–Pyzhev mechanism the decomposition rate expression contains a dependence on the hydrogen pressure, showing a marked retardation by hydrogen, whereas in the case of the decomposition on tungsten, the rate expression is independent of hydrogen pressure, being only dependent on ammonia pressure. In the case of platinum and iron the decomposition at higher temperatures and lower hydrogen pressures proceeds via the tungsten-type mechanism, whereas at lower temperatures and higher hydrogen pressures the decomposition proceeds via the Temkin–Pyzhev mechanism.[16] Over the ruthenium (1,1,10) surface, the former mechanism is operative on its terrace sites, whereas the latter mechanism is operative on the step sites under similar reaction conditions.[17]

It should be noted here that the apparent activation energy of the overall decomposition reaction is generally high at lower reaction temperatures and low at higher temperatures. Also the effect of hydrogen pressure on the overall rate of the reaction becomes smaller at higher temperatures. These observations suggest a change in the reaction mechanism.[22]

Under these circumstances many questions arise: Why are there two classes of behavior, one represented by (1) or (2) and the other by (8)? Under what conditions are these two different rate equations manifested? What determines the transition between the two mechanisms? Why do the terrace and step sites behave differently kinetically?

For the decomposition of ammonia, the rate ($r_a^A$) of nitrogen chemisorption from ammonia under steady state should balance its rate of consumption. The latter is composed of two contributions: the rate ($r_d^N$) of desorption of chemisorbed nitrogen to form nitrogen molecules, and the rate ($r_d^A$) of hydrogenation of chemisorbed nitrogen to re-form ammonia. The supply of chemisorbed nitrogen from gaseous nitrogen molecules is normally negligible during the decomposition reaction; that is

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(19) Temkin, M.; Pyzhev, V. *Acta Physicochim. USSR* **1940**, *12*, 327.

(20) Zeldovich, Ya. *Acta Physicochim. USSR* **1934**, *1*, 449. Roginsky, S. Z. "Adsorption and Catalysis" *Symp. Prob. Kinet. Catal. III*, Leningrad, 1937.

(21) Tamaru, K. *Actes Cong. Int. Catal., 2nd*, **1960**, **1961**, 325.

(22) Kunsmann, C. M. *J. Am. Chem. Soc.* **1929**, *51*, 688.

$$2r_a^A = 2f_d^A + r_d^N \qquad (14)$$

The coefficient 2 is added to $r_a^A$ and $r_d^A$ in eq 14 because the net disappearance and formation of two ammonia molecules result in the formation and disappearance of one diatomic nitrogen molecule, respectively.

If the nitrogen chemisorbed from ammonia mostly goes back to ammonia before it desorbs to form nitrogen molecules, then $2r_d^A$ is much larger than $r_d^N$. Consequently, the ratio $r_a^A/r_d^A$ approaches unity, which results in a quasi-equilibrium which is represented by eq 9. The free energy drop ($-\Delta G$) or the driving force of the step, which is determined by the ratio of the forward and backward reaction rates[23,24]

$$-\Delta G = RT \ln (r_a^A/r_d^A) \qquad (15)$$

becomes nearly zero as expected in eq 9. This is indeed the case in the Temkin–Pyzhev mechanism.

On the other hand, if $2r_d^A$ is much smaller than $r_d^N$, most of the nitrogen that is supplied from ammonia will go to dinitrogen molecules to be desorbed before it is hydrogenated back to ammonia. This is the case in the tungsten-type mechanism, and there is an appreciable chemical potential drop in the step involving supply of chemisorbed nitrogen from ammonia, $NH_3(g) \rightarrow N(a) + {}^3/_2H_2(g)$. The rate of the overall reaction is expressed by eq 7, and the quasi-equilibrium among chemisorbed nitrogen, ambient ammonia, and hydrogen is no longer realized.

From this discussion, it is clear that the ratio, $r_d^N/2r_d^A$, which is expressed as $\gamma$, is a parameter that determines which of the two mechanisms is operative. If $\gamma \gg 1$, then the tungsten-type mechanism corresponding to rate equation 7 should be operative, whereas if $\gamma \ll 1$, then the Temkin–Pyzhev mechanism should be observed. This criterion certainly applies to ammonia decomposition and its synthesis.

## Unification of the Two Mechanisms: The Transition Condition

The rate ($r_d^A$) of hydrogenation of chemisorbed nitrogen on various metals to form ammonia has not been widely studied in a quantitative manner. In the case of a standard ammonia synthesis catalyst the author studied the rate expression as a function of the partial pressure of hydrogen and nitrogen coverage and obtained the following expression:

$$r_d^A = k_d^A P_{H_2} \exp(h'\theta_N) \qquad (16)$$

where $h'$ is a constant.[25]

He also obtained the rate ($r_d^N$) of nitrogen desorption in the form of eq 4, and the values of the constants $h$ and $h'$ in eq 4 and 16, respectively, were approximately the same. Therefore, the following equation may be obtained:

$$\gamma = k_d^N/(k_d^A P_{H_2}) \qquad (17)$$

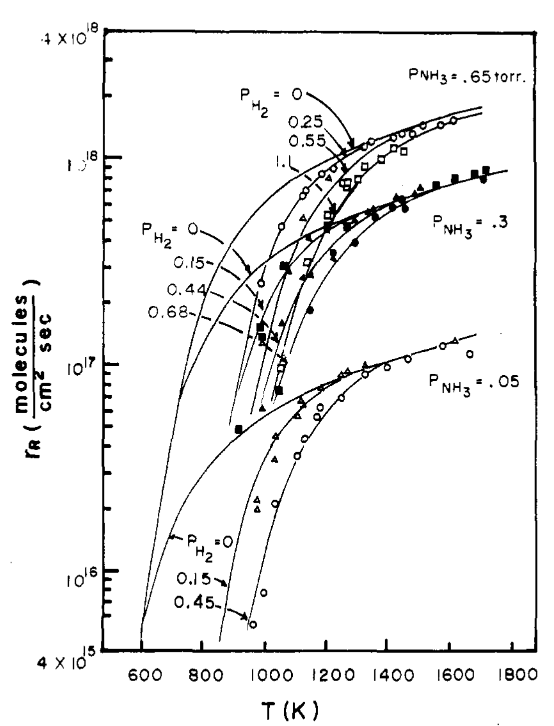

**Figure 2.** Plot of rate of ammonia decomposition versus $T$ in $NH_3$–$H_2$ mixtures for three pressures of $NH_3$ with variable $H_2$ pressures as indicated. Solid curves are those calculated from an expression of the form of eq 19.

In the case of a palladium foil, Obuchi et al.[26] also studied the rate of hydrogenation of the chemisorbed nitrogen that was supplied by the NO–$H_2$ reaction and suggested the following kinetic expression:

$$r_d^A = k_d^A P_{H_2} \theta_N \qquad (18)$$

The rate ($r_d^N$) of nitrogen desorption is proportional to the nitrogen coverage on iron and palladium, rather than to its square.[27] Consequently, we may take $\gamma$ as equal to eq 17 for this case also. The activation energy for nitrogen desorption is normally considerably higher than that for the hydrogenation of chemisorbed nitrogen, as will be shown later. Consequently, the value of $\gamma$ will become larger at higher temperatures and lower hydrogen pressures, whereas it will become smaller at lower temperatures and higher hydrogen pressures, and will be independent of ammonia pressure.

From this, we may derive several important conclusions: (1) The Temkin–Pyzhev mechanism will occur at lower temperatures and higher hydrogen pressures. (2) The tungsten-type mechanism would prevail at higher temperatures and lower hydrogen pressures. (3) The transition temperature between the two mechanisms at constants pressure is independent of ammonia pressure.

Such conclusions are beautifully demonstrated to be true in the case of ammonia decomposition on platinum as is given in Figure 2 and eq 19, both of which are the results of elaborate work by Loeffler and Schmidt.[16]

$$r = 9.87 \times 10^{18} e^{-4300/RT} P_{NH_3} / [1 + 4.35 \times 10^{-5} e^{16700/RT} P_{NH_3} + 9.85 \times 10^{-6} e^{27700/RT} P_{H_2}{}^{3/2} (+1.25 \times 10^{-3} e^{12600/RT} P_{N_2})] \qquad (19)$$

where the unit of pressure is Torr and the units of rate ($r$) are ammonia molecules cm$^{-2}$ s$^{-1}$.

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(23) Tamaru, K. *Dynamic Heterogeneous Catalysis*; Academic: New York, 1978; p 13.

(24) Boudart, M.; Djega-Mariadassou, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University Press: Princeton, NJ, 1984; p 80.

(25) Tamaru, K. *Proc. 3rd Int. Cong. Catal., Amsterdam 1964* **1965**, p 664.

(26) Obuchi, A.; Naito, S.; Onishi, T.; Tamaru, K. *Surf. Sci.* **1982**, *122*, 235.

(27) Ertl, G.; Huber, M. *J. Catal.* **1980**, *61*, 537.

At lower temperatures and higher hydrogen pressures, as is shown in the figure, the rate of reaction becomes clearly hydrogen pressure dependent, demonstrating a marked retardation by hydrogen, as is given by the Temkin–Pyzhev mechanism (eq 8). At higher temperatures, on the other hand, the rate of reaction becomes independent of hydrogen pressure, being only dependent upon ammonia pressure, as is the case in the tungsten-type mechanism. The transition temperature ($T_{tr}$) between the two mechanisms becomes higher by increasing the pressure of hydrogen and is indeed independent of ammonia pressure as is shown in the figure. These were all predicted by the "new" unified mechanism of the reaction.

There is considerable evidence for a shift in reaction mechanism that is affected by temperature and hydrogen pressure. In the case of an iron catalyst Loeffler and Schmidt obtained only tungsten-type rate expression between 600 and 1250 K at low hydrogen pressures.[16] This rate expression was independent of hydrogen pressure. However, it is generally accepted that the decomposition of ammonia on iron catalysts obeys the Temkin–Pyzhev kinetics at low temperatures and high hydrogen pressures. Kunsmann studied the thermal decomposition of ammonia on an iron catalyst many years ago and observed that "the effect of hydrogen varies with the temperature of the catalyst, being small at high temperatures (the activation energy is 84 kJ/mol), but large at low temperatures (activation energy is 210 kJ/mol)".[22] Actually, Takezawa and Toyoshima reported for an ammonia synthesis catalyst a kinetic expression[28]

$$V = k(P_{NH_3}/P_{H_2}^{0.5})^{0.75} \qquad (20)$$

at 752 K. This is considerably less hydrogen pressure dependent than the rate expression of the Temkin–Pyzhev mechanism, which they obtained at lower temperature (693 K):

$$V = k(P_{NH_3}/P_{H_2}^{1.5})^{0.4} \qquad (21)$$

In the case of ammonia decomposition over vanadium nitride McGill and Sebba reported that, although the kinetics of the reaction obey the Temkin–Pyzhev mechanism at $P_{H_2} = 93$ kPa and $P_{H_2} = 27$ kPa, at lower pressures of hydrogen the partial pressure of hydrogen has little effect on the rate of reaction.[29]

The effect of hydrogen pressure on the rate of decomposition and the change in the activation energy of the overall decomposition reaction with temperature both support the behavior predicted by the general mechanism presented here. Consequently, rate equation (19) describes a shift between the Temkin–Pyzhev and the tungsten-type mechanisms. It does not describe a Langmuir–Hinshelwood mechanism as originally proposed.[16]

In recent years much experimentation in ammonia synthesis and decomposition has been carried out on well-defined crystal planes of single-crystal metal surfaces in ultrahigh-vacuum vessels. The surface area of the catalyst is small in those cases, and the reaction is generally carried out at comparatively higher temperatures under lower pressures of reactants, including hydrogen. Therefore, under such reaction conditions the tungsten-type mechanism will be more probable.

Weinberg and co-workers recently studied the decomposition of ammonia on platinum and discussed the mechanism of the reaction.[30] They carried out steady-state treatments of the elementary steps involved in the reaction, taking the experimental data available on each of the steps into consideration. The steady-state mass balance equation for the reactants and the products was solved by employing an iterative scheme. They also studied the $NH_3 + D_2$ exchange reaction over the catalyst and demonstrated a much higher rate of exchange than nitrogen production from ammonia at lower temperatures, whereas a much slower rate of exchange at higher temperatures. These results are consistent with the proposed shift between the two mechanisms, because the hydrogen exchange reaction should be much faster than nitrogen desorption in the Temkin–Pyzhev mechanism, whereas it should be much slower in the tungsten-type mechanism. Thus, in the latter case, as soon as ammonia is dissociatively adsorbed on tungsten, it goes on to desorb as nitrogen without going back to ammonia.

Weinberg et al. also studied the decomposition on the platinum (110)-(1×2) surface. The reaction probability on this surface is greater than that on the polycrystalline surface, but the kinetics are qualitatively similar. It was observed on the surface that the predominant surface species during ammonia decomposition are nitrogen adatoms. The surface is saturated with nitrogen adatoms below 400 K, but its coverage decreases at higher temperatures, becoming less than 0.1 above 600 K.

## Transition Temperature of the Two Mechanisms

The transition temperature of the two mechanisms may be determined by taking $\gamma = 1$. If we take the equations as follows

$$k_d^N = k_{d0}^N \exp(-E_d^N/RT) \qquad (22)$$

$$k_d^A = k_{d0}^A \exp(-E_d^A/RT) \qquad (23)$$

the transition temperature ($T_{tr}$) is given by the following equation:

$$T_{tr} = \frac{E_d^N - E_d^A}{R \ln [k_{d0}^N/(k_{d0}^A P_{H_2})]} \qquad (24)$$

In the case of a platinum surface $E_d^N - E_d^A$ may be estimated to be 27 700 cal/mol, as will be given later, from the values of $E_d^N$ and $E_a^N$, using the equation

$$E_d^A = E_a^A - 0.5(Q_A - Q_{ads}^N) \qquad (25)$$

where $Q_A$ and $Q_{ads}^N$ are the heat of reaction for 2 mol of ammonia synthesis (ca. 24 000 cal/mol) and that of nitrogen adsorption. According to the results of Loeffler and Schmidt, $T_{tr}$ is 1160 K at the hydrogen pressure of 0.45 Torr, which gives $k_{d0}^N/k_{d0}^A = 0.98 \times 10^5$.

Thus $T_{tr}$ may be calculated under various pressures of hydrogen. For example, at $P_{H_2} = 0.15$ Torr, $T_{tr}$ becomes 1107 K, which looks reasonable in Figure 2. If we employ the stoichiometric mixture of one atmospheric pressure ($P_{H_2} = 570$ Torr), $T_{tr}$ becomes 1555 K,

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(28) Takezawa, N.; Toyoshima, I. *J. Phys. Chem.* **1966**, *70*, 594.

(29) McGill, W. J.; Sebba, F. *J. Catal.* **1963**, *2*, 104.

(30) Tsai, W.; Vajo, J. J.; Weinberg, W. H. *J. Phys. Chem.* **1985**, *89*, 3243. Vajo, J. J.; Tsai, W.; Weinberg, W. H. *Ibid.* **1985**, *89*, 3243; private communication.

which is too high for the tungsten mechanism to be the case under normal conditions.

In the case of an iron surface, Loeffler and Schmidt observed only the tungsten-type mechanism for the ammonia decomposition between 600 and 1250 K and ammonia pressure between 0.05 and 1 Torr, and they gave the following rate equation

$$r = \frac{k_R K P_{NH_3}}{1 + K P_{NH_3})} \qquad (26)$$

where $k_R$ (molecules cm$^{-2}$ s$^{-1}$) = $1.57 \times 10^{28}$ exp($-$49600/$RT$) and $K$ (Torr$^{-1}$) = $6.7 \times 10^{-9}$ exp(39600/$RT$). In a manner similar to the treatments carried out for platinum, it is easily concluded that $k_R$ corresponds to $k_d^N$ and that $K$ corresponds to $k_a^A/k_d^N$, which gives $k_d^N$ and $k_a^A$ as follows:

$$k_d^N = 1.57 \times 10^{28} \exp(-49600/RT) \qquad (27)$$

$$k_a^A = 1.05 \times 10^{20} \exp(-10000/RT) \qquad (28)$$

The activation energy for nitrogen desorption from an iron surface is, accordingly, estimated to be almost 50 kcal/mol, which is reasonable from the literature.[11]

The activation energy for the hydrogenation of chemisorbed nitrogen ($E_d^A$) on iron may be estimated by eq 25. Thus $E$ becomes 23 000 cal/mol, which gives $E_d^N - E_d^A = 26600$ cal/mol. Therefore, the numerator of eq 24, $E_d^N - K_d^A$, is approximately the same for platinum and iron. As to the denominator of eq 24, the $k_{d0}^N$ for platinum is $2.23 \times 10^{23}$, whereas that for iron is $1.57 \times 10^{28}$, which is much larger than the former. The value of $k_{d0}^A$ for iron is not known, but since the hydrogenation of chemisorbed nitrogen proceeds even at 433 K on the platinum, the $k_{d0}^A$ for platinum seems to be not much smaller than that for iron. Under these circumstances, it is reasonably concluded that the $T_{tr}$ for iron would be considerably lower than that for platinum. The kinetics of ammonia decomposition on iron, given by Loeffler and Schmidt, indeed demonstrate that $T_{tr}$ for iron is lower than 600 K under the reaction conditions employed, which is definitely much lower than that for platinum.

The results reported by Takezawa and Toyoshima strongly suggest that $T_{tr}$ for the triply promoted ammonia synthesis catalyst is below 775 K under mild conditions. It is to be noted here that the author first proposed a similar shift of reaction mechanisms over the synthesis iron catalyst under mild conditions in 1964.[25] He measured the values of $k_d^N$ as well as $k_d^A$ over the ammonia synthesis catalyst and discussed the shift of the reaction mechanisms. In this sense, quotation marks have been added to the word "new".

At lower temperatures some nitrogen or partially hydrogenated nitrogen may be covering the catalyst surface in the steady state of the reaction. The activation energy for nitrogen desorption and the heat of adsorption of nitrogen will be considerably less, which would make $T_{tr}$ lower.

In the case of the ammonia decomposition on a stepped surface of ruthenium (1,1,10), it was concluded that the reaction proceeds via the Temkin–Pyzhev mechanism on the step sites, whereas it proceeds via the tungsten-type mechanism on the terrace sites. The values of $k_d^N$ and $k_d^A$ in eq 17 are not known for both the step and terrace sites. It is only known that nitrogen desorption and also the N–H dissociation take place more readily at the step sites than on the terrace sites. Since the experimental results suggest that the $T_{tr}$ is lower on the terrace sites than on the step sites, the ratio $k_d^N/k_d^A$ should be larger for the terrace sites than for the step sites.

## Behavior of Nitrogen on a Platinum Surface

According to Loeffler and Schmidt, the rate of ammonia decomposition on a platinum wire may be expressed by eq 19. The fourth term in the denominator is negligibly small in most cases, and at lower temperatures the third term in the denominator becomes predominant, which results in the Temkin–Pyzhev rate expression:

$$r = 1.00 \times 10^{24} e^{-32000/RT} P_{NH_3}/P_{H_2}^{1.5} \qquad (29)$$

At higher temperatures, however, the first two terms in the denominator become predominant to give the tungsten-type mechanism, or eq 7:

$$r = \frac{9.87 \times 10^{18} e^{-4300/RT} P_{NH_3}}{1 + 4.35 \times 10^{-5} e^{16700/RT} P_{NH_3}} \qquad (30)$$

In the tungsten-type mechanism the rate of reaction is given by eq 7:

$$r = \frac{k_d^N K P_{NH_3}}{1 + K P_{NH_3}} = k_d^N[(k_a^A/k_d^N)P_{NH_3}]^\alpha \qquad (31)$$

where $K$ corresponds to the ratio $k_a^A/k_d^N$. We may thus obtain the values of $k_d^N$ as well as $k_a^A$ from the empirically obtained parameters in eq 29:

$$k_d^N = 2.23 \times 10^{23} \exp(-21000/RT) \qquad (32)$$

$$k_a^A = 9.87 \times 10^{18} \exp(-4300/RT) \qquad (33)$$

Thus the activation energy for nitrogen desorption on platinum at the reaction temperatures may be estimated to be 88 kJ/mol.

In the case of Temkin–Pyzhev mechanism on platinum catalyst, the rate of the reaction is expressed by eq 13, 19, and 29:

$$r = k_d^N \left[ \frac{k_a^N}{k_d^N} \frac{P_{NH_3}^2}{P_{H_2}^3 K_A} \right]^\alpha = 1.00 \times 10^{24} \exp(-32000/RT) P_{NH_3}/P_{H_2}^{1.5} \qquad (34)$$

Consequently, $\alpha = 0.5$, and the equilibrium constant of nitrogen adsorption, $k_a^N/k_d^N$, becomes 19.4 exp($-$22000/$RT$)$K_A$. The heat of the reaction in $K_A$ (or $Q_A$) at high reaction temperatures is estimated to be 110 kJ/mol from the value at 298 K and the heat capacities of nitrogen, hydrogen, and ammonia. Thus the heat of adsorption of molecular nitrogen on platinum at the reaction temperatures may be calculated to be 18 kJ/mol from $k_a^N/k_d^N$ (or $Q_A$ − 22000 cal/mol) and the activation energy for adsorption, 70 kJ/mol. In this manner the kinetic behavior of ammonia decomposition and the "new" mechanism may be used to estimate the heat as well as the activation energy for the nitrogen adsorption on platinum. These quantities are not easily determined experimentally from adsorption experiments, as molecular nitrogen is not found to chemisorb on platinum. According to the calculations, the reason for this is seemingly the high activation energy for adsorption and the low heat of adsorption. Weinberg and co-workers also estimated the activation energy for adsorption of molecular nitrogen to be 67 kJ/mol at $\theta_N = 0$ and the heat of its adsorption as 25 kJ/mol at their reaction temperatures.[30] They also estimated the activation energy for desorption of nitrogen from the platinum (110)-(1×2) surface as 108–117 kJ/mol, which is independent of nitrogen coverage.

## Conclusion

The rate of catalytic decomposition of ammonia is often markedly retarded by hydrogen, as given by eq 8. Under these conditions the reaction is successfully explained by the well-known Temkin–Pyzhev mechanism, which assumes that the desorption rate of chemisorbed nitrogen is rate determining.

The kinetic equation of the reaction on tungsten, on the other hand, is expressed by eq 1 and may well be independently explained by the Langmuir–Hinshelwood mechanism, which assumes that the rate is proportional to the amount of ammonia molecules adsorbed on the catalyst surface. However, examination of the behavior of nitrogen chemisorbed directly under the reaction conditions reveals that the mechanism of the reaction is not accurately described by the Langmuir–Hinshelwood mechanism, but rather by a dynamic balance between the supply and desorption of chemisorbed nitrogen.

It has now been demonstrated for the first time that the two mechanisms are the limiting cases of a "new" general mechanism. If the chemisorbed nitrogen that is supplied from ammonia is readily hydrogenated to re-form ammonia before it is desorbed to form nitrogen molecules, then the quasi-equilibrium of eq 9 is realized in the steady state of the reaction. In this case the reaction proceeds via the Tempkin–Pyzhev mechanism and shows a marked retardation by hydrogen. On the other hand, if the chemisorbed nitrogen is mostly desorbed before it is hydrogenated, then the tungsten-type behavior should be observed, for which there is no retardation by hydrogen. Accordingly, the kinetics of ammonia decomposition on metals is determined by whichever of the two rates, hydrogenation and desorption of chemisorbed nitrogen, would be faster. If the former is much faster than the latter (which is the case, in general, at lower temperatures and higher hydrogen pressures), then the Temkin–Pyzhev mechanism occurs, whereas if the latter is much faster than the former (which is the case, in general, at higher temperatures and lower hydrogen pressures) the tungsten-type behavior is observed. In such a manner, ammonia decomposition on metals generally proceeds between the two limiting cases. The activation energy for adsorption and the heat of adsorption of nitrogen on platinum can be estimated on the basis of the general mechanism.

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# *Additions and Corrections*

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**Josef Michl* and Erik W. Thulstrup**: Ultraviolet and Infrared Linear Dichroism: Polarized Light as a Probe of Molecular and Electronic Structure.

On p 198, the twist angle in 4,4′-dibromobiphenyl derived from IR dichroic measurements is incorrectly stated to be 30–40°. The correct value is 60–85°.