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Kinetics of Ammonia Synthesis on Promoted Iron Catalysts

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As a result of the researshes of a number of investigators in the field of ammonia synthesis on iron catalysts, the mechanism of this process may, in the main, be considered elucidated. The majority of these authors are of the opinion that the rate-determining step of the overall reaction is the process of the binding of nitrogen by iron in the form of a surface nitride (Frankenburger[1]) or, employing the terminology of the adsorption theory of catalysis, the process of the activated adsorption of nitrogen (Taylor[2], Emmet and Brunauer[3]). The further stages of the process — the formation of a surface imide and its transformation into ammonia (directly or by way of the amide stage) — take their course considerably faster. In accordance with this conception it is assumed that the rate of decomposition of ammonia on iron is determined by the rate of desorption of nitrogen.

In many cases the slow processes of the sorption of gases by metals in the activated form may be connected with diffusion phenomena. It is, therefore, necessary to prove that the rate of the slow sorption of nitrogen by iron is actually the rate of the adsorption process and not, *e. g.*, that of diffusion along the grain boundaries on the inner surface. Emmet and Brunauer[3] found that the rate of sorption of nitrogen and the rate of the synthesis are of the same order of magnitude under identical conditions. The

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[1] Frankenburger, Z. Elektrochem., **39**, 45, 97, 269 (1933).

[2] Taylor, J. Am. Chem. Soc., **53**, 578 (1931).

[3] Emmet and Brunauer, J. Am. Chem. Soc., **56**, 35 (1934).

rate of sorption of nitrogen, however, is approximately 10^6 times smaller than that calculated according to the formula $Me^{-A_a/RT}$, where M is the number of impacts of the molecules on the surface, and A_a is the activation energy of adsorption.

At a first glance this result would seem to contradict the assumption that the slow process is the process of activated adsorption, but Temkin[4], by means of the transition state method, showed that the rate of activated adsorption should not be equal to $Me^{-A_a/RT}$. If we express the rate as $\alpha Me^{-A_a/RT}$, then for the case of the adsorption of a diatomic molecule, the theory gives the following equation for α:

$$\alpha = \frac{gLh^4}{16\pi^3 e^2 (kT_M)^2 Im},$$

where L is the number of elementary spaces per square centimeter of surface, I — the moment of inertia of the molecule, m — the mass of the molecule, T_M — the average temperature, g — the number of adsorption centers adjacent to the given one, and the remaining quantities have their usual meaning. Substituting

$$L = 10^{15}, \quad I = 1.38 \times 10^{-39}, \quad T_M = 450 + 273 = 723, \text{ etc.,}$$

we get $\alpha = 2 \times 10^{-5}$, *i. e.*, the theoretically anticipated rate of activated adsorption is of about the same order of magnitude as the rate of sorption of nitrogen which is observed experimentally. If we take into account the approximate character of the estimated magnitude of the surface, the non-uniformity of the surface, etc., this agreement may be considered satisfactory.

Kinetics of decomposition

The kinetics of the reverse process is the starting point for our treatment of the synthesis kinetics, since the process of decomposition can be studied in a pure form, while the process of synthesis is always accompanied by a reverse process as a result of the fact that the equilibrium under ordinary conditions is shifted to the side of dissociation of ammonia.

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[4] Temkin, J. Phys. Chem. (Russ.), **11**, 169 (1938).

The numerous investigations of the decomposition of ammonia on iron in the absence of hydrogen have no direct relation to the kinetics of the ammonia synthesis, since the interaction of ammonia and iron leads to the formation of the iron nitride phase, and thus the conditions of the process are quite different from the conditions of the synthesis. If excess hydrogen is present in the gas phase, the formation of a nitride is excluded. And it was under just such conditions that Winter[5] studied this process. He found that the rate of decomposition of ammonia on iron (studied by a flow method at temperatures from 500 to 700° C in the presence of excess hydrogen) may be expressed as follows:

$$-\frac{dP_{NH_3}}{dt}=k'\frac{P_{NH_3}^{0.9}}{P_{H_2}^{1.5}},$$

where t is the time of contact with the catalyst, and P_{NH_3} and P_{H_2} are the partial pressures of NH_3 and H_2, respectively. This equation differs but slightly from the following one:

$$-\frac{dP_{NH_3}}{dt}=k_2\frac{P_{NH_3}}{P_{H_2}^{1.5}}. \qquad (1)$$

To explain equation (1), Winter assumes that the stages of the decomposition process which leads to the formation of nitrogen adsorbed in an atomic state (N_{ads}) are so fast that in the course of the reaction the following equilibrium sets in:

$$NH_{3\,(gas)} \rightleftarrows N_{(ads)} + 1.5H_{2\,(gas)}. \qquad (a)$$

The conditions for this equilibrium may be obtained by combining the equilibria:

$$NH_{3\,(gas)} \rightleftarrows N_{(gas)} + 1.5H_{2\,(gas)} \qquad (b)$$

and

$$N_{(gas)} \rightleftarrows N_{(ads)}. \qquad (c)$$

This does not mean that process (a) is actually realized by way of processes (b) and (c). The partial pressure P_N of atomic nitrogen in the gas phase (N_{gas}) is a purely auxiliary quantity as the pressure of hydrogen in the quinhydrone electrode, the concentration of undissociated molecules in the derivation of the solubility product rule, and the like.

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[5] Winter, Z. physik. Chem., **13**, 401 (1931).

For equilibrium (b) we have:

$$\frac{P_{H_2}^{1.5} P_N}{P_{NH_3}} = K. \tag{2}$$

If we assume that adsorption takes place in the region of low degrees of covering and, consequently, obeys Henry's law, equilibrium (c) obeys the following equation:

$$\theta_N = aP_N, \tag{3}$$

where θ_N is the fraction of the surface covered with nitrogen, and a is the adsorption coefficient. Combining equations (2) and (3) we get:

$$\theta_N = aK \frac{P_{NH_3}}{P_{H_2}^{1.5}}. \tag{4}$$

Further, Winter assumes that the nitrogen is liberated according to an unimolecular law which corresponds to the scheme:

$$N_{(ads)} \rightarrow N_{(gas)},$$

and

$$2N_{(gas)} \rightarrow N_{2\,(gas)}.$$

According to such an assumption the rate of the process should be proportional to θ_N, and we arrive at equation (1).

An examination of the energy of activation of the process, however, reveals that Winter's interpretation cannot be accepted in its entirety. Indeed, let us denote the heat of process (a) by q, the heat of adsorption of atomic nitrogen, by q_N, and the activation energy of the desorption of nitrogen in the form of atoms, by E. It is evident that the rate of the reaction should be proportional to $e^{-E/RT}\theta_N$, and since the coefficient a is proportional to $e^{q_N/RT}$, and K in equation (2) is proportional to $e^{-q/RT}$, it follows from equation (4) that the rate of the reaction is proportional to

$$e^{-\frac{E-q_N+q}{RT}} \cdot \frac{P_{NH_3}}{P_{H_2}^{1.5}},$$

i. e., the apparent activation energy A is determined by the following equation:

$$A = E - q_N + q.$$

It is easy to see that

$$q = Q + \frac{1}{2} D_{N_2},$$

where Q is the heat of the reaction $0.5\,N_2 + 1.5\,H_2 = NH_3$ and D_{N_2} is the heat of dissociation of nitrogen into atoms. It can also be readily seen that $E \geqslant q_N$.

Consequently, Winter's assumptions lead to the conclusion that

$$A \geqslant Q + \frac{1}{2} D_{N_2},$$

and if we introduce the numerical values, 13,000 cals. (at 500° C) and 168,000 cals. for Q and D_{N_2}, respectively, we get

$$A \geqslant 97{,}000 \text{ cals.},$$

while Winter's experiments led to the quantity $A = 51{,}000$ cals. The difference of 46,000 cals., evidently, cannot be attributed to experimental error.

The above calculation is upheld by the consideration that the desorption of nitrogen in the atomic state is extremely improbable, since it requires the expenditure of a large quantity of energy. According to the current view, nitrogen is desorbed from the surface in the form of molecules, and the energy gained when the atoms unite to form molecules partially compensates the energy spent in severing the bonds of atomic nitrogen with iron, so that the energy of activation is less than the energy of bond rupture.

In accordance with the foregoing, the rate of the dissociation process is determined by the stage $2N_{(ads)} \rightarrow N_{2\,(gas)}$ and, consequently, within the frame of the concepts adopted by Winter, should be proportional to θ_N^2, *i. e.*, to the probability of finding two nitrogen atoms adsorbed on adjacent elementary spaces of the surface. But then, in accordance with equation (4), the rate of the dissociation process should be proportional to $\frac{P_{NH_3}^2}{P_{H_2}^3}$ which is in contradiction with the experimental data as expressed by equation (1).

We are convinced that the simple Langmuir conceptions of the adsorption kinetics do not make it possible to interpret Winter's results. At present it is becoming clear that these conceptions, which are based on the assumption of a uniform surface and neglect the forces of interaction between the adsorbed molecules, do not reflect the experimental data on adsorption equilibrium and the kinetics of adsorption on catalysts. The true relations may be very closely approximated by the following system of equations.

(a) Adsorption equilibrium:

$$\theta = \frac{1}{f} \ln a_0 p, \tag{5}$$

where θ is the degree of covering of the surface; p — the equilibrium pressure; and f and a_0 are constants.

(b) Rate of adsorption:

$$v = k_a P e^{-g\theta}, \tag{6}$$

where P is the gas pressure, and k_a and g are constants.

(c) Rate of desorption:

$$w = k_d e^{h\theta}, \tag{7}$$

where k_d and h are constants.

Equation (5) was obtained by Frumkin and Šlygin[6] for the hydrogen adsorption equilibrium on platinum black by means of electrochemical measurements (the method of polarization curves). Zeldowitsch[7] and Roginsky[8] found equation (6). Roginsky[8] pointed out the wide applicability of this equation. Equation (7) was obtained by Langmuir[9] in his study of the rate of evaporation of caesium and thorium from tungsten.

These equations are closely connected. All of them conform with the fact that, owing to the non-uniformity of the surface

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[6] Frumkin and Šlygin, Acta Physicochimica URSS, 3, 791 (1935).

[7] Zeldowitsch, Acta Physicochimica URSS, 1, 449 (1934).

[8] Roginsky, "Adsorption and Catalysis", in the Symposium "Problems of Kinetics and Catalysis", III, ONTI, Leningrad, 1937.

[9] Langmuir, J. Am. Chem. Soc., 54, 2798 (1932); J. Phys. Chem. (Russ.), 6, 161 (1935); Acta Physicochimica URSS, 1, 371 (1934).

or the action of considerable repulsive forces between the adsorbed molecules, the heat of adsorption decreases and the heat of activation of adsorption increases as the surface becomes covered. If we choose the assumption of non-uniformity of the surface, we find that equation (5) corresponds to a linear dependence of q on the number of adsorption centers possessing a heat of adsorption greater that the quantity q. It describes the region of average degrees of covering, when the weakest adsorbing centers are practically free of gas, and the strongest adsorbing centers are practically completely occupied. Here the heat of adsorption (differential) turns out to be a linear function of the degree of covering of the surface. If we further assume, in accordance with Polanyi's[10] conceptions, that the change in the energy of activation while passing from one adsorption center to another should amount to a certain fraction α of the change in the heat of adsorption similarly to the known relations in acid-base catalysis, hydrogen overvoltage, etc., then the activation energy of adsorption should also depend linearly upon the degree of covering of the surface. This dependence, in conjuction with the linear dependence of the heat of adsorption, leads to equations (6) and (7). The result does not depend on whether adsorption takes place in the form of atoms or molecules.

These conclusions will be examined in greater detail in a separate paper by Temkin.

The quantities f, g and h are connected by the following relations:

$$\frac{g}{f}=\alpha, \tag{8}$$

$$\frac{h}{f}=\beta \tag{9}$$

and

$$\alpha+\beta=1, \tag{10}$$

where α has the same meaning as above and β is the corresponding quantity in the relation between the activation energy of desorption and the heat of adsorption.

Roginsky[8] has shown that the kinetics of the adsorption of nitrogen on an iron catalyst, which were measured by Emmet

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[10] M. G. Evans and Polanyi, Trans. Farad. Soc., 32, 1333 (1936).

and Brunauer, are accurately described by equation (6). Owing to the close connection that exists between equations (5), (6) and (7), one must assume that the equilibrium should be described by equation (5), while the kinetics of desorption, by equation (7). Indeed, the experimental data of Emmet and Brunauer for the adsorption equilibrium conform to equation (5). These authors also found that the magnitude of the adsorption from pure nitrogen and from an equilibrium mixture of hydrogen, nitrogen and ammonia is exactly the same (at 450° C and pressures up to 50 atm.). Hence it follows that, for all practical purposes, only nitrogen is adsorbed from the mixture at the synthesis temperature.

Let us assume, with Winter, that the amount of nitrogen on the surface is determined by the equilibrium with hydrogen and ammonia in the gas phase. Then the nitrogen pressure which would correspond to equilibrium $(P_{N_2})_{\text{equil}}$ is given by the equation:

$$(P_{N_2})_{\text{equil}} = K' \frac{P^2_{NH_3}}{P^3_{H_2}}. \tag{11}$$

This quantity determines the degree of covering of the surface in accordance with equation (5):

$$\theta = \frac{1}{f} \ln a_0 K' \frac{P^2_{NH_3}}{P^3_{H_2}}. \tag{12}$$

Substituting this quantity for θ in equation (7) we get:

$$w = k_d e^{\frac{h}{f} \ln a_0 K' \frac{P^2_{NH_3}}{P^3_{H_2}}} \tag{13}$$

or

$$w = k_2 \left(\frac{P^2_{NH_3}}{P^3_{H_2}} \right)^{\beta}. \tag{14}$$

In order to make this equation identical with Winter's equation (1) we must assume that $\alpha = \beta = 1/2$. Such a value for α is quite usual (Volmer's overvoltage theory).

Schwab and Schmidt[11] found that the kinetics of the dissociation of ammonia on platinum are expressed by the equation:

$$-\frac{dP_{NH_3}}{dt} = k \frac{P^{1.4}_{NH_3}}{P^{2.3}_{H_2}},$$

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[11] Schwab and Schmidt, Z. physik. Chem., 3, 337 (1929).

which is almost the same as

$$-\frac{dP_{NH_3}}{dt}=k\left(\frac{P^2_{NH_3}}{P^3_{H_2}}\right)^{0.73}.$$

Thus **Schwab's** result may be explained if we assume that $\beta=0.73$.

We shall now show that our interpretation, in contrast to **Winter's**, leads to the correct value of the apparent activation energy. According to equation (13), for $\frac{h}{f}=1/2$, we have

$$w=k_d(a_0K')^{1/2}\frac{P_{NH_3}}{P^{1.5}_{H_2}}.$$

It will be readily seen that $(K')^{1/2}$ is proportional to $e^{-Q/RT}$, where Q is the heat of the process $0.5N_2+1.5H_2=NH_3$; that k_d is proportional to $e^{-A_d^0/RT}$, where A_d^0 is the activation energy of desorption at $\theta=0$ and $A_d^0=A_a^0+q^0$ (A_a^0 and q^0 are the activation energy of adsorption and the heat of adsorption, respectively, at $\theta=0$), and that a_0 is proportional to $e^{-q^0/RT}$. Thus the apparent activation energy is determined by the equation

$$-A=-(A_a^0+q^0)+0.5q^0-Q,$$

or

$$A=A_a^0+0.5q^0+Q.$$

Since $\frac{h}{f}=1/2$, the change of q with θ is twice as large as that of A_a. Furthermore, they have opposite signs: q decreases with θ, while A_a increases. Therefore, the expression for A will still hold if we introduce quantities that correspond to any value of θ, or average quantities, instead of A_a^0 and q^0. Consequently we may write: $A=A_a+0.5q+Q$, where A_a and q stand for average values.

If we make use of **Emmet** and **Brunauer's** data:

$$q=35{,}000,\quad A_a=16{,}000$$

and also of the value $Q=13{,}000$, we get $A=46{,}500$. This value, which differs markedly from that arrived at by employing **Winter's** conceptions ($A \geqslant 97{,}000$), is in satisfactory agreement with the experimental value $A = 51{,}000$ given above, as well as with that which ensues from our experiments: $A = 40{,}000$ (see below).

Synthesis kinetics

We can now obtain an equation for the rate of the synthesis by introducing the degree of covering of the surface, determined by equation (12), into the expression for the rate of adsorption, *i. e.*, into equation (6). We get:

$$v = k_a P_{N_2} e^{-\frac{g}{f} \ln a_0 K' \frac{P^2_{NH_3}}{P^3_{H_2}}} \tag{15}$$

or

$$v = k_1 P_{N_2} \left(\frac{P^3_{H_2}}{P^2_{NH_3}} \right)^{\alpha}. \tag{16}$$

As has been shown above, it follows from Winter's data that, for iron, $\alpha = 1/2$. Consequently, we arrive at the following equation:

$$v = k_1 \frac{P_{N_2} P^{1.5}_{H_2}}{P_{NH_3}}. \tag{17}$$

The retarding action of ammonia on the rate of the synthesis was already stated by Benton[12] from an analysis of the experimental data of Larson and Tour[13]. He explained it as resulting from the strong adsorption of ammonia on the surface of the catalyst. From our point of view the reason for the retardation of the reaction by ammonia is entirely different, namely, an increase in the ammonia concentration increases the amount of nitrogen on the surface as a result of equilibrium (a):

$$NH_{3\,(gas)} \rightleftarrows N_{(ads)} + 1.5H_{2\,(gas)}. \tag{a}$$

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[12] Benton, Ind. Eng. Chem., 19, 494 (1927).

[13] Larson and Tour, Chem. Met. Eng., 26, 647 (1922).

Ammonia as such is not adsorbed on the surface in noticeable amounts.

At a first glance the conception that ammonia is markedly adsorbed on iron catalysts appears to be upheld by the experiments of Ussatschew, Tarakanowa and Komarow[14] who observed a transitory increase in the ammonia concentration in the gas phase after the introduction of catalytic poisons. This effect was interpreted as being the result of the forcing off of adsorbed ammonia from the surface by the catalytic poison.

However, the effect observed by Ussatschew and his co-workers may be equally well explained from the point of view of the conception which has been developed above. The adsorption of a foreign substance (a poison) on the surface, which has a known amount of nitrogen adsorbed on it, should cause an increase in the equilibrium pressure of nitrogen for the given amount of nitrogen on the surface according to the known relations for the adsorption of mixtures. Thus, the equilibrium (a) should be shifted: nitrogen should disappear from the surface and appear in the gas phase in the form of ammonia. In other words, of the two rapid processes

$$NH_{3\,(gas)} \rightarrow N_{(ads)} + 1.5H_{2\,(gas)} \tag{a'}$$

and

$$N_{(ads)} + 1.5H_{2\,(gas)} \rightarrow NH_{3\,(gas)}, \tag{a''}$$

process (a′) slows down or ceases altogether owing to the covering up of the surface with the poison, while process (a″) proceeds as rapidly as formerly and leads to an increase in the concentration of ammonia in the gas phase at the expense of nitrogen which has been on the surface previously. This interpretation of Ussatschew's effect was proposed by Temkin in 1936 during the discussion which followed a report delivered by Kagan and Morozov who quoted the results obtained by Ussatschew and Benton to prove the strong adsorption of ammonia on ammonia catalysts. It was completely corroborated by the experiments of Morozov which were carried out in Kagan's laboratory taking

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[14] Ussatschew, Tarakanowa and Komarow. Z. Elektrochem., 40, 647 (1934).

into account the suggestions advanced at this discussion[15]. It was found that, if a nitrogen-hydrogen mixture is passed over the catalyst for a certain period of time and then pure nitrogen is substituted for it, the introduction of a poison (oxygen) as an addition to the nitrogen does not lead to the evolution of ammonia. However, as soon as hydrogen is introduced into the gaseous mixture, the appearance of ammonia in the gaseous phase is noticed immediately. These experiments prove beyond all doubt that the appearance of ammonia in the gaseous phase during the Ussatschew effect comes about as the result of a process of hydrogenation of the adsorbed nitrogen.

Let us now return to equation (17). Under ordinary conditions we do not observe the process of the synthesis so far removed from equilibrium that the reverse process may be neglected. Consequently, the observed overall rate of the synthesis is the difference between the rates of the forward and the reverse processes and should be expressed by the following equation:

$$\frac{dP_{NH_3}}{dt} = k_1 \frac{P_{N_2} P_{H_2}^{1.5}}{P_{NH_3}} - k_2 \frac{P_{NH_3}}{P_{H_2}^{1.5}} \tag{18}$$

which includes both the synthesis and the dissociation kinetics (under conditions which exclude the formation of an iron nitride phase).

At equilibrium $\frac{dP_{NH_3}}{dt} = 0$ and, consequently,

$$\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{k_1}{k_2}. \tag{19}$$

Upon introducing the usual equilibrium constant with the aid of the equation

$$\frac{P_{NH_3}}{P_{N_2}^{0.5} P_{H_2}^{1.5}} = K_p \tag{20}$$

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[15] Morozov and Kagan, Acta Physicochimica URSS, 8, 549 (1938).

we find that

$$\frac{k_1}{k_2} = K_p^2 \text{ [16]}. \tag{21}$$

Let us rewrite equation (18) in the following manner. As before, let us denote by $(P_{NH_3})_{equil}$ that partial pressure of nitrogen which would be in equilibrium with nitrogen and hydrogen at the partial pressures P_{N_2} and P_{H_2}, respectively. Then

$$(P_{NH_3})^2_{equil} = \frac{k_1}{k_2} P_{N_2} P^3_{H_2} \tag{22}$$

and equation (18) gives:

$$\frac{d \dfrac{P_{NH_3}}{(P_{NH_3})_{equil}}}{dt} = \frac{k_2}{P^{1.5}_{H_2}} \left[\frac{(P_{NH_3})_{equil}}{P_{NH_3}} - \frac{P_{NH_3}}{(P_{NH_3})_{equil}} \right]. \tag{23}$$

As a characteristic of the action of ammonia catalysts the efficiency is usually employed, *i. e.*, the ratio of the ammonia yield to the yield which corresponds to the attainment of equilibrium at the given temperature and total pressure. This quantity, which we shall denote by x, is not exactly equal to the ratio $\frac{P_{NH_3}}{(P_{NH_3})_{equil}}$, since $(P_{NH_3})_{equil}$ is determined by the values of P_{N_2} and P_{H_2} which correspond to the given degree of conversion and differ from those which correspond to equilibrium. However, if P_{NH_3} is only a small fraction of the total pressure, for simplicity in the calculations we may neglect the changes in P_{N_2} and P_{H_2} during the reaction, *i. e.*, put $\frac{P_{NH_3}}{(P_{NH_3})_{equil}} = x$ and consider the factor before the brackets

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[16] It might seem that equation (17) may be obtained from equation (1) and the equilibrium equation. However, this is not the case. Various equations for the rate of the synthesis may be written which, together with equation (1), give the equilibrium equation. For the derivation, it is essential to have a conception of the mechanism which leads to equation (1). Thus, for example, Winter's treatment of the mechanism leads to the rate equation of the synthesis $v = k_1 P^{0.5}_{N_2}$, which is also in accord with the requirements of thermodynamics.

on the right-hand side of equation (23) as a constant; integration of the equation

$$\frac{dx}{dt}=\frac{k_2}{P_{H_2}^{1.5}}\left(\frac{1}{x}-x\right) \tag{24}$$

gives

$$-\frac{1}{2}\frac{P_{H_2}^{1.5}}{t}\ln(1-x^2)=k_2. \tag{25}$$

From the time of contact t we may pass to the "space velocity" V which is defined as the ratio of the volume of the gas (reduced to standard conditions) which has passed through the catalyst during one hour to the volume of the catalyst. In the approximation under consideration we may disregard the change in the volume during the reaction. The time of contact is connected with the space velocity by the equation:

$$t=\frac{\varphi 273P}{TV}, \tag{26}$$

where φ denotes the free volume per unit volume of the catalyst (according to Rideal and Taylor φ is approximately 1/3). Furthermore, for mixtures of equivalent composition usually employed in synthesis,

$$P_{H_2}=0.75P. \tag{27}$$

Equations (25), (26), and (27) give:

$$k=-\frac{1}{2}P^{0.5}V\ln(1-x^2), \tag{28}$$

where

$$k=\frac{273\varphi k_2}{0.75^{1.5}T}. \tag{29}$$

The constant k in equation (28) should depend upon the temperature only.

For mixtures which are not equivalent in composition, we introduce the quantity γ which characterizes the deviation of the composition from the equivalent one:

$$\gamma=\frac{P_{H_2}}{0.75P}. \tag{30}$$

For this case we obtain:

$$k = -\frac{1}{2}\gamma^{1.5} p^{0.5} V \ln(1 - x^2). \tag{31}$$

Equations (28) and (31) are applicable to the synthesis at atmospheric pressure, since the assumptions which have been made during their derivation are fulfilled here.

It was the object of the experimental part of the present investigation to verify equations (28) and (31) experimentally.

Experimental

The kinetics of the ammonia synthesis were studied at atmospheric pressure making use of a flow method. A commercial iron catalyst, promoted with aluminium and potassium oxides, served as the catalyst. Electrolytic hydrogen and ordinary tank nitrogen were mixed in any desired proportions in a gas meter (volume 30 liters) over water. The gas meter was so designed (in the manner of a Mariot flask) that a constant pressure within it was ensured regardless of the amount of gaseous mixture removed.

The velocity of the gas was calculated from the duration of the experiment and the amount of gas that was passed. The speed of the gas flow was regulated by means of a rheometer. The gaseous mixture was dried by passing it through sulphuric acid and solid potassium hydroxide. It was then passed through a tube filled with nickel catalyst which was heated to 350°, where it was freed from oxygen. After this it was again dried with sulphuric acid and solid potassium hydroxide from which it was passed into the reaction tube. The apparatus was made entirely of glass and did not contain any rubber connections. The copper reaction tube was connected by means of a ground joint which was sealed with picein. The temperature required by the experiment was attained by immersing the reaction tube into an electrically heated bath containing a molten mixture of potassium and sodium nitrates which was continually stirred. The bath temperature was measured with a mercury thermometer and a copper-constantan thermocouple. The temperature fluctuations did not exceed one degree. The ammonia yield was determined by absorbing it in a standart acid solution with subsequent titration of the excess acid.

The catalyst was reduced in a current of hydrogen until a phosphorus pentoxide tube attached to the exit ceased to gain in weight. This also indicated tnat the gas was completely free of oxygen and water vapor. The reduction was carried out at a temperature of about 450° and lasted about 50 hours.

After reduction was completed an experiment began. These were carried out with a constant gas composition and at a constant space velocity at a temperature of 400° C until constant yields were attained. It was found that the catalyst reduced with hydrogen at first shows a gradual increase in yield during its treatment with the nitrogen-hydrogen mixture, after which the yield becomes constant under the given conditions.

In each experiment at least 10 liters of the gaseous mixture were passed through the catalyst under the conditions of the experiment before passing a measured amount of the mixture (usually 6 liters) through the absorbing solution for analysis. Each experiment was repeated.

Experimental results

Examination of equation (18) shows at once that the maximum rate of the reaction corresponds to a gas composition that differs from the equivalent one. At the initial stage of the process, when the ammonia content is considerably less than the equilibrium value, and the reverse reaction of dissociation may be disregarded, the maximum rate is determined by the maximum of the product $P_{N_2} P_{H_2}^{1.5}$ or, denoting the nitrogen content of the mixture by u, by the maximum of the expression $u(1-u)^{1.5}$. By the ordinary method of differential calculus we find that the maximum lies at $u=0.4$. Consequently, the maximum rate at the initial stage of the process corresponds to the composition $\frac{P_{H_2}}{P_{N_2}}=1.5$ and not to the equivalent composition $\frac{P_{H_2}}{P_{N_2}}=3$. One is easily convinced, however, that the difference in the yield is very small — namely, it comprises only 6% of the yield value.

As the yield approaches the equilibrium yield, the optimum composition approaches the composition $\frac{P_{H_2}}{P_{N_2}}=3$, since it is known that the equilibrium yield attains a maximum at the equivalent composition.

A slight increase in the yield, attained upon enriching the mixture with nitrogen, has already been noted by **Kozlov** and **Ivanov**.

The first series of experiments were set up to test this conclusion. The experiments were carried out at a temperature of 400° C and space velocity in the neighbourhood of 30,000 for different compositions of the nitrogen-hydrogen mixture.

Under these conditions the yields did not exceed 0.1%, *i. e.*, they were small in comparison with the equilibrium yield which amounted to 0.457% at 400° C and atmospheric pressure for an equivalent mixture. Table 1 gives the results of these experiments. Each value of the yield in the table is an average of the results of two individual experiments, with the exception of the value for $\frac{P_{H_2}}{P_{N_2}} = 1.5$ which is an average of the results of four individual experiments.

Table 1

The dependence of the yield upon the composition of the mixture at 400 °C and a space velocity of 30,000*

$\frac{P_{H_2}}{P_{N_2}}$	NH_3 yield in volume %
0.5	0.073
1.0	0.094
1.5	0.099
3.1	0.092
6.1	0.082
8.5	0.069

* In the experimental values of the yields a slight correction is introduced for deviations of the velocities from 30,000.

As can be seen from Table 1, experiment confirms the conclusion which has been drawn above. We did not employ the data of this series of experiments, however, in calculating the rate constants because the yields are somewhat lower than those in the experiments of the second series; this difference in the yields probably indicates a partial poisoning of the catalyst.

The results of the second series of experiments are given in Table 2. All the yield values are averages of the results of two individual experiments. The values of k given in the Table were calculated by equations (28) and (31).

Table 2

The dependence of the ammonia yield upon the space velocity, the temperature and the composition of the mixture

Temperature	Space velocity v	$\frac{p_{H_2}}{p_{N_2}}$	NH_3 yield in %	Efficiency x	Rate constant k
400	13,450	2.93	0.155	0.373	1.0×10^3
400	20,550	3.0	0.133	0.320	1.10×10^3
400	29.550	3.0	0.107	0.258	1.01×10^3
400	29,700	1.48	0.111	0.294	0.96×10^3
400	30,600	6.0	0.0925	0.259	1.21×10^3
450	29,800	3.0	0.134	0.629	7.73×10^3
450	20,000	3.0	0.157	0.738	7.84×10^3
450	9,100	3.0	0.199	0.934	(9.30×10^3)

The value of k at 450° C and $v = 9,100$ is enclosed in brackets because here the yield is so close to the equilibrium value that calculation of the constant becomes very inaccurate.

The values of the rate constants for different volume speeds and mixture compositions, which are given in the Table, show satisfactory constancy.

If we take into consideration only experiments with equivalent mixtures and discard the value of k enclosed in brackets, we obtain the following average values for k:

$$\text{at } 400^\circ \text{C} \qquad k = 1.04 \times 10^3,$$

and

$$\text{at } 450^\circ \text{C} \qquad k = 7.78 \times 10^3.$$

Making use of these quantities it is possible to calculate the apparent activation energy of the process. The Arrhenius equation is applicable to the dissociation rate constant k_2. If we take into consideration equation (29), we find that k should depend upon the temperature in the following manner:

$$k = \frac{B}{T} e^{-A/RT}, \tag{32}$$

where B is a constant.

Eliminating B, we obtain the equation

$$A = 4.57 \frac{T_1 T_2}{T_1 - T_2} \lg_{10} \frac{k_1 T_1}{k_2 T_2},$$

which, upon substituting the values given above for k, gives

$$A = 40{,}000 \text{ cals.}$$

The quantity A, though it is calculated from the rate of the synthesis, is the apparent activation energy of the dissociation, since it characterizes the temperature dependence of the quantity k_2.

Chrisman's experiments[17] on the dissociation of ammonia on a catalyst of the same type as ours (iron promoted with aluminium and potassium oxides) gave a value of 39,700 cals. for the activation energy of the dissociation, which is in complete agreement with our results. As has already been pointed out above, **Winter** obtained a somewhat higher value, 51,000 cals., for an unpromoted iron catalyst.

In order to find the apparent activation energy of the synthesis, *i. e.*, the quantity characterizing the change in the constant k_1 with the temperature, it is necessary to subtract $2Q = 26{,}000$ cals. from A, as can be easily seen from equation (21). The apparent activation energy of the synthesis is consequently equal to 14,000 cals.

The ammonia synthesis at pressures greater than atmospheric

The approximate integration of equation (18), which has been employed above, is not applicable at pressures greater than atmospheric.

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[17] **Chrisman**, Acta Physicochimica URSS, **4**, 899 (1936).

Let us carry out the integration of equation (18), without introducing any simplifying assumptions, for a process proceeding at constant pressure. We shall restrict ourselves here to the case of an equivalent mixture $\left(\frac{P_{H_2}}{P_{N_2}}=3\right)$. Let us denote the mole fraction of ammonia in the mixture by z,

$$z=\frac{P_{NH_3}}{P}, \qquad (33)$$

where P is the total pressure. Then

$$\left.\begin{aligned} P_{H_2}&=\frac{3}{4}P(1-z), \\ P_{N_2}&=\frac{1}{4}P(1-z), \\ P_{NH_3}&=Pz \end{aligned}\right\} \qquad (34)$$

and equation (18) gives:

$$\frac{dz}{dt}=k_1\frac{1}{4}\left(\frac{3}{4}\right)^{1.5}P^{0.5}\frac{(1-z)^{2.5}}{z}-k_2\left(\frac{3}{4}\right)^{-1.5}P^{-1.5}\frac{z}{(1-z)^{1.5}}$$

or

$$\frac{dz}{dt}=k_2\left(\frac{3}{4}\right)^{-1.5}P^{-1.5}\left[\frac{k_1}{k_2}\frac{1}{4}\left(\frac{3}{4}\right)^{3}P^{2}\frac{(1-z)^{2.5}}{z}-\frac{z}{(1-z)^{1.5}}\right]. \qquad (35)$$

The equilibrium yield z_{equil} under the given conditions, according to equations (20) and (34), is determined by the equation:

$$\frac{z_{\text{equil}}}{(1-z_{\text{equil}})^2}=L, \qquad (36)$$

where

$$L=\left(\frac{1}{4}\right)^{0.5}\left(\frac{3}{4}\right)^{1.5}PK_P \qquad (37)$$

or (see equation 21)

$$L=\left(\frac{1}{4}\right)^{0.5}\left(\frac{3}{4}\right)^{1.5}P\left(\frac{k_1}{k_2}\right)^{0.5}.$$

Thus, instead of equation (35), we obtain:

$$\frac{dz}{dt}=k_2\left(\frac{3}{4}\right)^{-1.5}P^{-1.5}\left[L^2\frac{(1-z)^{2.5}}{z}-\frac{z}{(1-z)^{1.5}}\right]. \qquad (38)$$

As the independent variable let us introduce, instead of the time of contact with the catalyst, t, the space velocity V, the definition of which has been given above. If the process took place without a change in volume, the relation between these quantities would be given by equation (26). In our case the reaction proceeds with a decrease in volume. We shall determine the space velocity according to the initial volume of the nitrogen-hydrogen mixture (the volume speed at the entry). It is easy to see that, if the initial volume of the nitrogen-hydrogen mixture was equal to U_0, and the volume occupied by the mixture at the same pressure after an amount of ammonia characterized by the mole fraction z had formed in the mixture was equal to U_z, we should have

$$\frac{U_z}{U_0}=\frac{1}{1+z}. \tag{39}$$

Let a volume U_0 of the gaseous mixture enter the catalyst over the period of one hour, and let a volume U_z, with an ammonia content equal to z, leave it. Let the volume of the catalyst be equal to W. Then the space velocity at the entry is determined by the equation:

$$V_0=\frac{U_0}{W}. \tag{40}$$

Let us increase the volume of the catalyst by an infinitely small amount dW. Then the time of contact increases by

$$dt=\frac{\varphi 273 P}{T}\frac{dW}{U_z}, \tag{41}$$

as can be seen from equation (26).

From equations (41) and (39) we obtain:

$$dt=\frac{\varphi 273 P}{T}\frac{dW}{U_0}(1+z), \tag{42}$$

and since, according to equation (40),

$$\frac{dW}{U_0}=d\left(\frac{1}{V_0}\right), \tag{43}$$

we have

$$dt=\frac{\varphi 273 P}{T}(1+z)\,d\left(\frac{1}{V_0}\right). \tag{44}$$

Substituting this expression for dt in equation (38), we obtain:

$$\frac{dz}{d\left(\frac{1}{V_0}\right)}=\frac{\varphi 273 P}{T}(1+z)\,k_2\left(\frac{3}{4}\right)^{-1.5}P^{-1.5}\left[L^2\frac{(1-z)^{2.5}}{z}-\frac{z}{(1-z)^{1.5}}\right], \quad (45)$$

or, introducing the constant k with the aid of equation (29),

$$\frac{dz}{d\left(\frac{1}{V_0}\right)}=kP^{-0.5}(1+z)\left[L^2\frac{(1-z)^{2.5}}{z}-\frac{z}{(1-z)^{1.5}}\right]. \quad (46)$$

Integration of equation (46) gives:

$$k=P^{0.5}\,V_0\int\limits_0^z\frac{dz}{(1+z)\left[L^2\frac{(1-z)^{2.5}}{z}-\frac{z}{(1-z)^{1.5}}\right]}$$

or

$$k=P^{0.5}\,V_0\int\limits_0^z\frac{z(1-z)^{1.5}\,dz}{(1+z)\left[L^2(1-z)^4-z^2\right]}. \quad (47)$$

If the experimental yield values are expressed as a function of space velocity at the exit, V_z, then in order to calculate k we can make use of the relation

$$V_0=V_z(1+z) \quad (48)$$

which follows from equation (39).

An exact analytical calculation of the integral in equation (47)

$$I(z)=\int\limits_0^z\frac{z(1-z)^{1.5}\,dz}{(1+z)\left[L^2(1-z)^4-z^2\right]} \quad (49)$$

is very cumbersome, and it is simpler to make use of methods of numerical integration, for example, of **Simpson**'s formula. If z is not too large, so that terms of the order of z^2 may be discarded in comparison with unity, while terms of the order of z are retained, an approximate integration may be carried out easily.

We may write:

$$I(z)\approx\int\limits_0^z\frac{z(1-2.5z)\,dz}{L^2(1-2z)^2-z^2}=\int\limits_0^z\frac{z(1-2.5z)\,dz}{[L(1-2z)+z]\,[L(1-2z)-z]}.$$

Integration by the usual method gives:

$$I(z)=\frac{1}{1-4L^2}\left\{2.5z+\frac{L+\frac{1}{L}+2.5}{2\left(2-\frac{1}{L}\right)}\ln\left[1-\left(2-\frac{1}{L}\right)z\right]-\right.$$
$$\left.-\frac{L+\frac{1}{L}-2.5}{2\left(2+\frac{1}{L}\right)}\ln\left[1-\left(2+\frac{1}{L}\right)z\right]\right\}. \qquad (50)$$

In order to test the equation of the synthesis kinetics at pressures greater than atmospheric, we made use of Larson and Taur's[13] data which were obtained with an iron catalyst promoted with aluminium and potassium oxides.

In Table 3 there are given the data of these authors for the temperature 420° C, and the rate constants which were calculated according to these data.

In this Table there are also given the values of the equilibrium yields (corresponding to $V_z=0$) calculated according to the data of Larson and Dodge[18]. These values were employed to calculate the quantity L. The constants were calculated by the equation:

$$k=P^{0.5}V_z(1+z)I(z), \qquad (51)$$

where $I(z)$ is determined by equation (50).

As can be seen from the Table, the equation expresses the data very well. In Table 4 equilibrium yield data of the same authors, as well as rate constants calculated according to the above equation for the temperature 450° C, are given. The values of z constituting more than 90% of the equilibrium yield were not used in the calculation of the rate constants, since they give unreliable results: a slight error in the value of z gives a marked change in k. Thus, at $P=31.6$ atm. and $V_z=5{,}000$, Larson and Taur found the values 0.0585 and 0.0600 for z. The first quantity gives $k=2.9\times10^4$, while the second, $k=3.9\times10^4$. Thus, a change in the yield of 2.6% changes the constant by 35%.

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[18] Larson and Dodge, J. Am. Chem. Soc., **45**, 2918 (1923).

Table 3

The synthesis of NH_3 at 420°C according to the data of **Larson** and **Taur**

Pressure P (in atm.)	Space velocity at the exit V_0	Volume percent of NH_3 100 y	Rate constant k
10	0	2.98	—
10	5,000	2.65	1.1×10^4
10	10,000	2.19	1.1×10^4
10	20,000	1.71	1.1×10^4
10	40.000	1.35	1.1×10^4
31.6	0	8.48	—
31.6	5,000	6.65	1.0×10^4
31.6	10,000	5.46	1.1×10^4
31.6	20.000	4.24	1.2×10^4
31.6	40,000	2.88*	1.0×10^4

* This value was calculated according to the efficiency value quoted by **Larson** and **Taur**, since the value of the percentage of ammonia given in their table is an evident misprint.

From Table 4 it is seen that, while the constants for 10 and 31.6 atm. agree with one another satisfactorily, the data for 100 atm. lead to lower values of the constant. It is necessary to take into account, however, that the experiments at 100 atm. were carried out in a different apparatus from the one in which the experiments at 10 and 31.6 atm. were carried out, and the difference in the conditions of reduction of the catalyst might have led to the difference in the activity.

In general it may be concluded that the experimental data of **Larson** and **Taur** agree satisfactorily with equation (18).

At the pressures which are employed in industry — 300 atm. and higher — it is necessary to take into account the deviation in the behaviour of the gases from the ideal gas laws. Therefore, the

Table 4

The synthesis of NH_3 at 450° according to the data of Larson and Taur

Pressure P (in atm.)	Space velocity at the exit V_s	Volume percent of NH_3 $100\,x$	Rate constant k
1	0	0.209	—
1	5,000	0.220	—
10	0	2.11	—
10	5,000	2.10	—
10	10,000	1.95	—
10	20,000	1.71	3.2×10^4
10	40,000	1.50	4.1×10^4
31.6	0	6.13	—
31.6	5,000	5.85	—
		(6.00)	—
31.6	10,000	5.41	3.5×10^4
31.6	20,000	4.66	4.0×10^4
31.6	40,000	3.71	4.1×10^4
100	0	16.43	—
100	5,000	14.10	1.9×10^4
100	10,000	11.60	1.9×10^4
100	20,000	9.50	2.3×10^4
100	40,000	7.00	2.3×10^7

equations derived above cannot be applied without additional complications. In equations (18) the partial pressures should be replaced by fugacities; furthermore the constants k_1 and k_2 should depend upon the pressure at large pressures.

The relation becomes quite simplified, however, if it is limited to an examination of small degrees of conversion. Here the composition of the mixture changes but slightly, so that the activity coefficients of the gases may be considered as constants. If the yield of ammonia is small in comparison with the equilibrium value, the reverse reaction may be disregarded. Thus equation (17) is applicable at large pressures also in the case of small degrees of conversion; k_1 however, will depend upon the pressure. Since the degree of conversion is small, P_{N_2} and P_{H_2} may be considered as constants. Then it follows from equation (17) that $P^2_{NH_3}$ should be proportional to t, and, consequently, the products $P^2_{NH_3}V$ or z^2V should be constant.

In Table 5 there are given data obtained by Kamzolkin, Jarlykov and Krasilshchikov in the Nitrogen Scientific-Research Institute for a Kazale type catalyst. From the Table it is seen that the product z^2V is actually approximately constant.

The constancy of the product z^2V shows that the rate of the synthesis is inversely proportional to the partial pressure of ammonia — a fact which has already been noticed by Benton.

Table 5

Synthesis of ammonia on Kazale catalyst at 400° and 800 atm.

Space velocity V	% NH_3 in the gas $100\,z$	z^2V
15,000	4.6	32
32,100	3.3	35
45,000	2.4	26
60,000	2.1	26

The optimum conditions of the synthesis process

Equation (18) may be used to find the optimum conditions for carrying out the process of the ammonia synthesis. It stands to reason that the values of the rate constants will differ for different catalyst samples; however, a number of corollaries of equation (18) do not depend upon the numerical value of the constants, but only upon the form of the equation.

Let us examine the question of the optimum temperature of the process. Fauser pointed out that, during the synthesis of ammonia, a temperature that decreases regularly throughout the catalytic mass is the most advantageous one.

Indeed, it is easy to see that while the ammonia content in the gaseous mixture is still small, a high temperature ensures the largest reaction rate. With an increase in the ammonia content in the gas phase, the approach to equilibrium limits the possibility of the further course of the process, and a lower temperature is the more advantageous. Fauser carried out a calculation of the optimum temperature curve making use of a cumbersome empirical equation for the reaction rate. Equation (18) permits this problem to be solved in a simple and graphical manner. Let us find a temperature at which the process proceeds with a maximum rate, as a function of the ammonia content.

Since

$$k_1 = b_1 e^{-A'/RT} \quad \text{and} \quad k_2 = b_2 e^{-A/RT}, \tag{52}$$

where A' is the apparent activation energy of the synthesis, we find that

$$\frac{d}{dT}\left(\frac{dP_{NH_3}}{dt}\right) = \left(k_1 \frac{P_{N_2} P_{H_2}^{1.5}}{P_{NH_3}} A' - k_2 \frac{P_{NH_3}}{P_{H_2}^{1.5}} A\right) \frac{1}{RT^2}.$$

The condition for the maximum

$$\frac{d}{dT}\left(\frac{dP_{NH_3}}{dt}\right) = 0$$

gives

$$\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{k_1 A'}{k_2 A}$$

(second solution: $T = \infty$ corresponds to the maximum rate of dissociation), or, in accordance with equation (21),

$$\frac{P_{NH_3}}{P_{N_2}^{0.5} P_{H_2}^{1.5}} \sqrt{\frac{A}{A'}} = K_P. \tag{53}$$

Thus, for a mixture with given partial pressures of NH_3, N_2 and H_2 the maximum rate will be attained at the temperature at which the equilibrium constant is equal to

$$\frac{p_{NH_3}}{p_{N_2}^{0.5}\, p_{H_2}^{1.5}} \sqrt{\frac{A}{A'}}.$$

If the ammonia content is small, this result may be expressed in a still simpler form, namely, it may be said that, if the process is carried out at an optimum temperature, the quantity

$$p_{NH_3} \sqrt{\frac{A}{A'}}$$

is an equilibrium yield corresponding to the given temperature. The ratio of the ammonia content to the equilibrium value, *i. e.*, the value of the efficiency, is consequently equal to $\sqrt{\frac{A'}{A}}$. Thus the process should be carried out not at a constant temperature, but at a constant efficiency.

Employing the values $A = 40{,}000$ cals. and $A' = 14{,}000$ cals., which were calculated above, we find that

$$\sqrt{\frac{A'}{A}} = 0.59.$$

Let us note that these conclusions do not depend upon the proportion of nitrogen and hydrogen in the initial mixture. The question of the optimum composition has been considered above.

It is expedient to limit ourselves to these brief considerations, taking into account that equation (18) cannot be strictly applied to the synthesis at large pressures, since it does not take into account the deviation of real gases from the simple gas laws.

Summary

During the synthesis of ammonia on iron, the stage determining the rate of the overall process is the process of the activated adsorption of nitrogen on the surface free of adsorbed nitrogen. The amount of nitrogen on the surface is determined by the equilibrium with hydrogen and ammonia in the gas phase, since the hydrogenation of the adsorbed nitrogen into ammonia proceedes rapidly.

The rate of dissociation of ammonia is determined by the rate of desorption of nitrogen. The equation obtained by Winter for the rate of dissociation of ammonia (1) cannot be explained on the basis of simple Langmuir conceptions, *i. e.*, assuming that the surface is uniform and the forces of interaction between adsorbed molecules may be neglected.

For a non-uniform surface, or in the presence of repulsive forces between adsorbed molecules in the region of average degrees of covering of the surface, equations must be employed for the adsorption equilibrium and the rates of adsorption and desorption, which differ from the usual Langmuir equations, — namely, equations (5) to (10). Winter's equation may be derived with the aid of these equations. Furthermore, in contrast to Winter's original treatment of this equation, the proposed derivation gives a theoretical value of the activation energy which is in good agreement with the experimental value.

The same equations give an equation for the rate of the synthesis (16). Furthermore, it follows from Winter's results that $\alpha = 0.5$.

The considerations developed give a new interpretation of the inhibiting action of ammonia during the synthesis, and also of the effect discovered by Ussatschew.

The rate of the synthesis, taking into consideration the reverse process is expressed by equation (18).

This equation is upheld by the experimental data of the authors, as well as by the data of Larson and Taur. The apparent activation energy of the synthesis process is equal to $\sim 14{,}000$ cals., and that of the dissociation process, to $\sim 40{,}000$ cals.

Analysis of equation (18) makes it possible to draw some conclusions regarding the optimum conditions for carrying out the process (the optimum temperature conditions, optimum composition of the gaseous mixture)[19].

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[19] This paper was presented at the conference of young research workers of the Karpov Institute of Physical Chemistry in May 1938 (see "Uspekhi Khimii" Russ., 7, 1092, 1938).