JOURNAL OF CATALYSIS 3, 68–79 (1964)

Rate Equation and Mechanism of Ammonia Synthesis at Industrial Conditions

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Received September 9, 1963

The ammonia synthesis reaction has been studied over a wide range of conditions, including conditions of vital importance for industrial use of the process. A reactor with a good approach to isothermal conditions has been used. A digital computer was used to analyze the results.

We find the Temkin-Pyzhev rate equation applicable in the range 370–495°C and 150–310 atm.

We realize that our kinetic data could hardly constitute a definite proof of a given reaction mechanism; however, they do confirm one mechanism out of a number of different ones. This mechanism has as its rate-determining step the chemisorption of nitrogen on a nonuniform surface on which is found as the main species chemisorbed nitrogen atoms. Somewhere between 370°C and 330°C there is a change in apparent energy of activation which may indicate a change in mechanism or surface coverage.

INTRODUCTION

The mechanism of ammonia synthesis on the surface of an iron catalyst is still subject to discussion. Emmett and Brunauer (*1, 2*) in measurements of adsorption and synthesis rate have shown that the chemisorption of nitrogen is sufficiently fast to be the first step of the synthesis reaction, and a rate equation for ammonia synthesis on promoted iron catalysts was formulated by Temkin and Pyzhev (*3*) on the assumption that the rate-determining step is the chemisorption of nitrogen on a nonuniform surface, presenting a linear distribution function of the surface sites with respect to heat of adsorption, activation energy of adsorption, and activation energy of desorption of nitrogen. Temkin and Pyzhev furthermore assumed that the main species on the surface are nitrogen atoms, the amount of which on the surface is determined by an equilibrium with hydrogen and ammonia in the gas phase.

The Temkin-Pyzhev rate equation, Eq.

$$r = k_1 P_{N_2} \left(\frac{P_{H_2}{}^3}{P_{NH_3}{}^2}\right)^\alpha - k_2 \left(\frac{P_{NH_3}{}^2}{P_{H_2}{}^3}\right)^\beta \quad (1)$$

(1) has been used to correlate a large amount of experimental data. Reference is given in this connection to a survey by Bokhoven *et al.* (*4*) and to a monograph by one of the authors (*5*). The Temkin-Pyzhev equation has been used with considerable success and some difficulties. One of the apparent difficulties of the Temkin-Pyzhev equation is that the rate constant turns out to depend on pressure. It should be kept in mind, however, that partial pressures, not fugacities, have normally been used so that deviations from ideal conditions are not taken into account. Temkin (*6*) has extended Eq. (1) to make it applicable for high pressures. When doing so he took into account the deviation from ideal gas conditions as well as the influence of pressure upon the rate constants for adsorption and desorption, arriving at the more general Eq. (2). Formally

$$r = \left[k_1{}^\circ a_{N_2} \left(\frac{a_{H_2}{}^3}{a_{NH_3}{}^2}\right)^\alpha - k_2{}^\circ \left(\frac{a_{NH_3}{}^2}{a_{H_2}{}^3}\right)^\beta\right] \exp\left[-(\bar{V}_a - \alpha \bar{V}_s)P/RT\right] \quad (2)$$

Eq. (2) is derived from Eq. (1) by replacing partial pressures by fugacities and further introducing the factor

$$\exp\,[-(\bar{V}_a - \alpha\bar{V}_s)P/RT]$$

in which $\bar{V}_s$ and $\bar{V}_a$ are the partial molar volumes of adsorbed nitrogen and of the transition state, and P is the total pressure. Livshits and Sidorov (*7*) have used this equation and found the corrected k° independent of pressure up to 400 atm.

Ozaki, Taylor, and Boudart (*8*) have proposed a new mechanism of ammonia synthesis. Their kinetic experiments include the pressure dependence and quite particularly the isotope effect on the synthesis rate. They concluded that the rate-determining step is nitrogen adsorption on a uniform or a nonuniform surface, the coverage of the surface consisting of adsorbed NH in equilibrium with hydrogen and ammonia in the gas. They expressed the opinion that the relative amount of adsorbed N and (NH) may well depend on the state of the surface such as the extent of removal of oxygen.

Enomoto and Horiuti (*9*) on the other hand have determined the stoichiometric number of the rate-determining step of ammonia synthesis to be two. This is incompatible with the chemisorption of nitrogen being rate-determining and requires one of the succeeding steps of the synthesis that occurs twice for every nitrogen molecule converted to be the slowest step. Rate equations on this basis have been developed by Shindo (*10*) and by Kobayashi and Kubota (*11*). Contrary to this, Bokhoven, Gorgels, and Mars (*12*) have found the stoichiometric number to be equal to unity. These authors determined the stoichiometric number by comparing the rate of synthesis reaction near equilibrium with the rate of exchange reactions, including also the exchange between N_2^{30} with N_2^{28}. While the experimental results by Bokhoven *et al.* are in disagreement with the results reported by Enomoto and Horiuti they are in agreement with other experimental evidence, as mentioned above. We particularly want to mention that Ozaki, Taylor, and Boudart point out that they find the observed rate constant to be identical for hydrogen and deuterium and that this is a strong argument against any assumption in which hydrogen is a reaction partner in the slow step of the synthesis.

Taking for granted that nitrogen chemisorption is the rate-determining step of the synthesis reaction, the aim of the present investigation was to find which one out of a number of proposed rate equations would give the best agreement with experimental measurements on ammonia synthesis at industrial conditions.

FORMULATION OF A RATE EQUATION

Boudart (*13*) and earlier, Ozaki *et al.*, discuss the various rate equations for ammonia synthesis as derived on the basis of different assumptions. In Fig. 1 we give as Eqs. (3) through (6) the rate equations from the article by Ozaki *et al.* (*8*), all of them derived on the assumption that the two-site chemisorption of nitrogen is rate-determining, but different with respect to the energy spectrum of the surface and the main species occupying the surface at synthesis conditions. As the derivations of these expressions is given by Ozaki *et al.* it is not repeated here. We shall only show how we combine the formulas into one, and formulate a rate expression on that basis.

	N	NH
UNIFORM SURFACE	$r = \dfrac{k' P_{N_2}}{\left[1 + K P_{NH_3}/P_{H_2}^{1.5}\right]^2} \quad (3)$	$r = \dfrac{k' P_{N_2}}{\left[1 + K' P_{NH_3}/P_{H_2}\right]^2} \quad (4)$
NON-UNIFORM SURFACE	$r = \dfrac{k_1 P_{N_2}}{\left[1 + K_0 P_{NH_3}/P_{H_2}^{1.5}\right]^{2\alpha}} \quad (5)$	$r = \dfrac{k_1 P_{N_2}}{\left[1 + K_0' P_{NH_3}/P_{H_2}\right]^{2\alpha}} \quad (6)$

FIG. 1. Equations (3)–(6).

By introducing the variable parameters

w and α we combine the four expressions (3) to (6) into Eq. (7). We now substitute

$$r = \frac{k_1 P_{N_2}}{[1 + K_3 P_{NH_3}/P_{H_2}^{w}]^{2\alpha}} \tag{7}$$

activities for partial pressures and introduce the equilibrium constant of the synthesis reaction through Eq. (8). The reciprocal reaction is introduced in Eq. (9) in which

$$K_a^2 = \frac{a^2_{NH_3,eq}}{a^3_{H_2,eq} a_{N_2,eq}} \tag{8}$$

$$r = \frac{k_1^\circ a_{N_2} - k_2^\circ a_{NH_3}^2/a_{H_2}^3}{NN} \tag{9}$$

for convenience the denominator has been substituted by NN. The denominator is given in Eq. (10). The equilibrium constant

$$NN = [1 + K_3 a_{NH_3}/a_{H_2}^{w}]^{2\alpha} \tag{10}$$

is introduced and k_1° is eliminated, giving us a reaction rate equation (11) in which r

$$r = \frac{k_2^\circ (a_{N_2} K_a^2 - a_{NH_3}^2/a_{H_2}^3)}{NN} \tag{11}$$

is the reaction rate expressed, for instance, as kg mole NH_3 produced per m^3 catalyst bed per hour.

We now introduce the fractional conversion f:

$$f = 2z/1 + z \tag{12}$$

in which z is the mole fraction of ammonia. Reference concerning Eq. (12) and also Eqs. (17) through (22) is given to pages 64–65 of Nielsen (*5*). We now have

$$r = \tfrac{1}{2} F_0 (df/dx) \tag{13}$$

in which F_0 is the feed rate in kg mole/m^2 hr. This gives

$$\frac{df}{dx} = \frac{2}{F_0} \frac{k_2^\circ (a_{N_2} K_a^2 - a_{NH_3}^2/a_{H_2}^3)}{NN} \tag{14}$$

After rearrangement of Eq. (14) and substitution of df with $(df/dz)\,dz$ equal to $2/(1 + z)^2\,dz$, integration is carried out between z_1 and z_2 on one side and 0 and L on the other, giving the equation

$$I = \int_{z_1}^{z_2} Y(z)dz = (2L/F_0)k_2^\circ \tag{15}$$

in which L is the length of the catalyst bed, and

$$Y(z) = \frac{2}{(1 + z)^2} \cdot \frac{NN}{a_{N_2} K_a^2 - a_{NH_3}^2/a_{H_2}^3} \tag{16}$$

The activities are introduced through Eqs. (17)–(19):

$$a_{NH_3} = P z \gamma_{NH_3} \tag{17}$$

$$a_{N_2} = P \gamma_{N_2} (a/3\gamma)(1 - b_2 z) \tag{18}$$

$$a_{H_2} = P \gamma_{H_2} a (1 - b_1 z) \tag{19}$$

in which

$$a = \frac{3\gamma}{3\gamma + 1}(1 - i_0) \tag{20}$$

$$b_1 = \frac{i_0 + 0.5 + (0.5/\gamma)}{1 - i_0} \tag{21}$$

$$b_2 = \frac{i_0 - 0.5 + 1.5\gamma}{1 - i_0} \tag{22}$$

with i_0 being the mole fraction of inerts (CH_4,A) and 3γ the ratio of hydrogen to nitrogen at conditions of complete dissociation of ammonia.

K_a is given by Eq. (23):

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \cdot 10^{-5} T + 1.848863 \cdot 10^{-7} \cdot T^2 + (2001.6/T) + 2.6899 \tag{23}$$

and the activity coefficients, γ_i, are calculated on the basis of Eq. (9) in the article by Gillespie and Beattie (*14*), from which the expression for K_a is also taken. We now have the elements to calculate the integral I given in Eq. (15) except for the parameters K_3, w, and α. The temperature dependence of k_2° and K_3 is introduced through Eqs. (24) and (25):

$$k_2^\circ = k_{20} \exp(-E_2/RT) \tag{24}$$

$$K_3 = K_{30} \exp(-E_3/RT) \tag{25}$$

We now have six unknown coefficients to determine from the experimental data. This was done by the digital computer GIER according to a procedure which will be described in a later section of this article. To summarize, the unknown coefficients are: k_{20}, E_2, K_{30}, E_3, w, and α.

EXPERIMENTAL PROCEDURES

A large amount of data on conversion efficiency obtained at different reaction conditions in this laboratory has previously been published by one of the authors (*5*). One of the reasons for carrying out a new set of experiments was the availability of more isothermal reactors equipped with controllers which keep temperature and pressure at a preset level and of the computer to analyze the results.

Reactants

Hydrogen and nitrogen of commercial grade from cylinders served as the raw synthesis gas components. Low pressure purification was accomplished by passing the individually metered combined stream of hydrogen and nitrogen over a reduced copper catalyst and a reduced nickel catalyst at 250°C and 8 atm gauge. The catalytic purifiers convert carbon monoxide and carbon dioxide into methane and water, and oxygen into water. The next purification step is a filter of activated carbon at room temperature and atmospheric pressure. The carbon bed removes traces of lubricants and other impurities of relatively high molecular weight such as trace amounts of chlorine compounds. Final purification was carried out after compression of the gas by passing the gas mixture over a composite bed of potassium hydroxide, a copper catalyst, silica gel, activated alumina, and activated carbon at room temperature and the synthesis pressure in question.

Catalyst

All of the experiments reported in this article were carried out on one sample of catalyst and frequent checks at standard conditions were inserted in the program to verify that no change in activity occurred.

Commercial type KM I R prereduced promoted iron catalyst was used for the experiment. This catalyst is essentially triply promoted based on the promoter set K_2O–CaO–Al_2O_3. The sample had been reduced in a commercial converter for manufacture of prereduced catalyst. Particle size of the catalyst at the time of its reduction was 3–6 mm. It should be mentioned in this connection that the intrinsic catalyst activity depends to a considerable extent on the particle size in which the catalyst is reduced. Reference is given in this connection to Nielsen (*5*). Upon termination of the experiment the surface area of the sample was determined by the BET method. We found a surface area equal to 8.57 m^2/g, which is in excellent agreement with the surface area to be expected for a catalyst of this type reduced in a particle size with an equivalent diameter of 4.6 mm. [See p. 84 of Nielsen, ref. (*5*)].

Prior to loading the catalyst in the converter the particle size was reduced to 0.3–0.7 mm. Catalyst volume was 2.5 cm^3.

The catalyst sample, already prereduced, was activated with synthesis gas while the pressure was kept at 150 atm until a temperature of 400°C was reached, after which the pressure was increased to 300 atm and the temperature to a maximum of 480°C. The temperature was then brought back to 450°C, still at a pressure of 300 atm, and after a few days at these conditions the activity was found to be constant.

Catalyst Bed

Figure 2 shows the dimensions of the catalyst bed. The dimensions and design of the converter have been chosen so as to obtain the highest possible degree of isothermicity and at the same time reasonably high gas velocities. The catalyst cross section area is only 0.2 cm^2, corresponding to a diameter of 0.5 cm. The catalyst is in direct contact with the heavy pressure shell of the converter, which has high thermal conductance. The heat transfer surface area per unit catalyst volume is as high as 8 cm^{-1}.

Three thermocouples of outer diameter 1 mm and with hot junctions 0.5, 4, and 10 cm above the catalyst support grid project through the bed. Temperatures are recorded on a potentiometric recorder. Temperature is controlled from a thermocouple placed on the outside of the pressure shell in close contact with the shell. Temperatures in the catalyst were adjusted to be almost uniform by changing the relative effects of 5 separate heating coils in the furnace surrounding the reactor. The highest temperature difference found in any of the experiments between any 2 of the 3 thermocouples was 18°C, but in more than half of the experiments this difference was below 5°C. A weighted mean

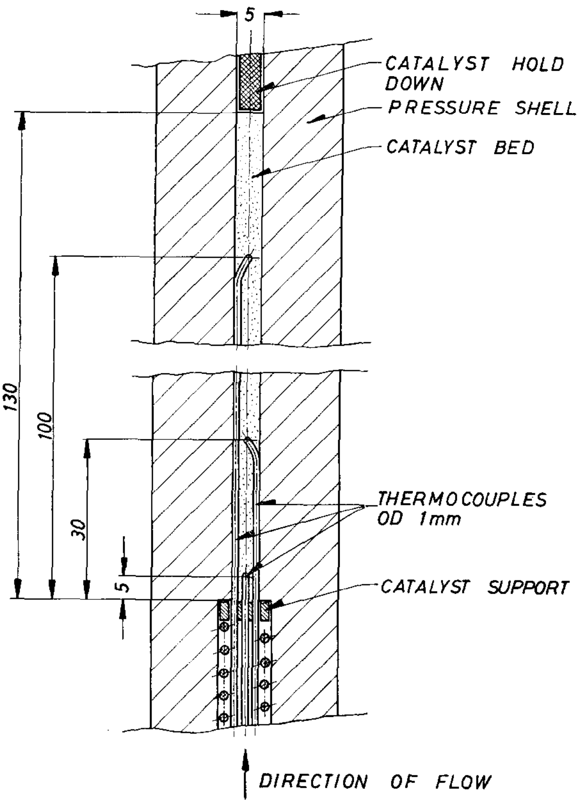

FIG. 2. Arrangement of catalyst bed in converter showing dimensions of bed and locations of thermocouples. All dimensions are in mm.

temperature was the one taken to represent the conditions. Constancy of temperatures to within 1°C was easily obtained.

Analytical Procedure

The ammonia in the gas leaving the reactor is determined by absorption in boric acid solution and titration with 0.1 *N* hydrochloric acid using bromophenol blue as indicator.

The H_2/N_2 ratio of the inlet gas was analyzed by a gas chromatograph. For the stoichiometric mixture the ratio of 3.0 has been used in the calculations in spite of the fact that there have been some smaller variations. The analysis deviating the most from the stoichiometric ratio and quoted as such showed 25.8% N_2.

Computer Evaluation of Results
AK-3 Program

A special program was made for the computer GIER for the analysis of the experimental data. The program performs an iterative adjustment of the six unknown rate constants: K_{30}, E_3, w, α, k_{20}, and E_2. Input to the program is a set of experimental data (10–30 runs) and a first guess on the values of the first four of the constants: K_{30}, E_3, w, and α.

Using these values, the program calculates k_2° for each run by a numerical integration of the rate expression using Simpson's formula. The calculated k_2° values are then expressed by Eq. (24).

The best values of k_{20} and E_2 are found by the method of least squares. The mean error is also calculated.

The program then starts improving the first values of the four constants above. This is made in a systematic way using the method of steepest descent in a search for the minimum in the mean error calculated above.

EXPERIMENTAL RESULTS

The following range of process conditions was covered by our experiments:

Pressure: 149–309 atm (abs.)
1 atm = 1.033 kg/cm^2 = 14.7 psi.

Temperature: 330–495°C.

Space velocity: 13,200–105,600 V/V/hr
at NTP and converter entrance.

Ratio H_2:N_2: 6.23–1.15.

No runs with inerts or ammonia at converter inlet were included in the present series.

The results of the 35 runs are given in Table 1. Omitted from Table 1 are some check runs at our standard conditions which were not used in the analysis to avoid giving unreasonable weight to measurements at one given condition.

TABLE 1
REACTOR OUTLET AMMONIA PERCENTAGE AS A FUNCTION OF PROCESS CONDITIONS
CATALYST VOLUME, 2.5 ML INLET NH_3, A, AND CH_4, 0.0%.

Run no.	Inlet gas flow (l/hr)	Temperature, weighted mean (°C)	Pressure (atm)	Inlet H_2:N_2 ratio	Space velocity (V/V/hr)	Outlet % NH_3
5	238.0	492	300	3.0	94,200	19.6
6	238.0	492	300	3.0	94,200	19.7
7	155.0	492	300	3.0	62,000	21.0
8	101.0	491	300	3.0	40,400	22.5
21	38.8	487	153	3.0	15,520	14.6
22	99.0	492	150	3.0	39,600	13.6
23	258.0	495	149	3.0	103,200	10.8
1	42.2	455	300	3.0	16,880	27.4
10	40.3	451	153	3.0	16,120	16.3
14	42.7	450	300	3.0	17,080	28.0
15	101.0	450	300	3.0	40,400	21.2
16	230.0	455	300	3.0	92,000	16.4
18	33.0	450	300	3.0	13,200	29.6
24	244.0	454	150	3.0	97,600	9.7
25	99.5	453	150	3.0	39,800	13.4
36	36.7	451	309	6.23	14,680	21.3
37	261.0	455	308	5.88	104,400	12.1
38	115.0	450	308	1.31	46,000	16.3
39	264.0	456	305	1.31	105,600	13.5
40	37.0	451	308	1.15	14,800	19.9
2	39.4	418	300	3.0	15,760	25.2
3	37.8	411	300	3.0	15,120	25.3
4	35.7	412	300	3.0	14,280	25.9
11	41.9	410	153	3.0	16,760	12.1
12	225.0	410	300	3.0	90,000	9.2
13	106.2	409	300	3.0	42,480	14.7
26	94.5	413	153	3.0	37,800	10.6
27	241.0	412	152	3.0	96,400	7.0
31	39.4	373	151	3.0	15,760	10.6
32	39.4	373	153	3.0	15,760	10.5
33	100.5	374	153	3.0	40,200	6.5
34	254.0	375	152	3.0	101,600	4.2
28	35.0	331	155	3.0	14,000	1.4
29	40.0	330	150	3.0	16,000	1.2
30	99.5	330	150	3.0	39,800	0.6

DISCUSSION OF CONVERSION MEASUREMENTS

There are several factors which influence the reliability of the experimental data reported in Table 1 and these will briefly be discussed below. A general reference in this connection is given to Nielsen (*5*), where a much more thorough discussion of factors influencing the reliability of laboratory measurements on the ammonia synthesis reaction is given.

Deviation from Isothermal Conditions

As mentioned above, in most of the experiments the temperature recorded from all 3 thermocouples located in the catalyst bed were within 5°C. Adding to this that we apply a weighted mean temperature in our analysis, such runs do not suffer in accuracy from deviation from isothermal conditions. In other runs, particularly those at high pressure and at the same time a high space velocity, the deviation was larger, and in a couple of cases as high as 17°C. To this it must be added that the temperature peak in the catalyst itself may be somewhat higher than in the thermocouple well, as analyzed in another case by Kjaer (*15*).

We have previously analyzed the difference between measured and calculated outlet ammonia percentages using the rate constants found in the experiment, and carrying out a stepwise calculation with the temperature variation taken into account, and this has shown a fairly small difference between measured and calculated outlet percentages. Reference is given to Nielsen (*5*).

Diffusion Restriction

In view of the fact that we have used catalyst particles in the size 0.3–0.7 mm we do not think diffusion restriction has effected measurements of the rate constants to any large extent. We do realize that in the runs at a high temperature and pressure in which production rate has been high, the catalyst in the inlet zone of the bed was not exploited to the full extent due to diffusion restriction. We may mention that by the use of another GIER program GEK-2 [Kjaer (*16*)] we have carried out a general kinetic converter integration with diffusion correction for an experimental run with particles of 0.75 mm equivalent diameter. The run in question was at 450°C, 317 atm, and a space velocity of 32,100 V/V/hr. On the basis of an average pore radius of 200 Å, a porosity of 0.5, and an assumed labyrinth factor of 0.3, we found the diffusion effectiveness factor 10% up the catalyst bed in the order of 0.5 and 20% up the catalyst bed in the order of 0.8; of course, for the main part of the bed the effectiveness factor was very close to 1.0. This program also calculates the temperature at the surface and center of the catalyst particles, and we found in the entrance part of the bed a few degrees over-temperature at the surface and very little difference between surface and center. For the main part of the bed the over-temperature was in the order of 1°C.

Filamentous Flow

The flow conditions existing in the laboratory reactor during the experiments were in the viscous region, or, for the higher space velocities, in the transition region between viscous flow and turbulent flow. Under such conditions complete mixing of the fluid between the particles cannot be taken for granted; however, bulk diffusion must have been important in evening out concentration gradients.

Wall Effect

Undoubtedly the gas has been flowing somewhat faster close to the reactor wall than for the average of the bed; however, we believe this effect is quite small as the catalyst particles have an irregular shape which seems to give a very excellent packing. The ratio of particle diameter to bed diameter, it would be recalled, is in the order of 0.1. It is admitted that the thermocouples do cause some irregularities in the packing and flow conditions.

Intrinsic Catalyst Activity Versus Catalyst Particle Size

As mentioned before, the intrinsic activity of an ammonia synthesis catalyst of a given type depends upon the particle size in which it is reduced. This is due to a self-poisoning by the water vapor diffusing out of the pore structure. While the catalyst particle size during the conversion experiments was 0.3–0.7 mm, this catalyst was reduced in size 3–6 mm, which should be kept in mind when transferring our data to industrial conditions.

TREATMENT OF EXPERIMENTAL DATA

The experimental data were analyzed with the GIER program AK-3 described above. One difficulty encountered was that the optimization depended only slightly upon the start value of K_{30} and the computer did not change K_{30} much within a reasonable computer time. The main reason for this is that, as it turned out, the second term in the bracket of the denominator NN is so much more important than the number 1 that the computer, so to say, lumps together k_{20} and K_{30}. The other reason is to be found in the fact that while K_{30} enters as a multiplier, w, α, and E_3 enter into exponents.

The facts that the number 1 in NN has very little importance and that w was found to be equal to 1.5 mean that at the process conditions at which our study was carried out, the more complicated formula we have used for all practical purposes becomes equivalent to the Temkin-Pyzhev rate equation, Eq. 2. In the Temkin-Pyzhev equation $k_2°$ and K_3 are combined. As pointed out by Brill and Tauster (*17*) the apparent energy of activation entering the Temkin-Pyzhev equation is not independent of α.

We counteracted the difficulty mentioned above by starting the computer with different entrance values of K_{30}, allowing GIER a certain maximum number of optimization cycles, generally 6, corresponding to 42 trials. We then plotted the mean error in ln (k_{20}) as a function of K_{30}. On the basis of such a plot we selected the entrance value of K_{30}.

The first analysis was made on 15 runs in the temperature range 330–418°C. After an approximate value of K_{30} had been selected, the computer was started on this basis and with a start value of $w = 1.50$ and $\alpha = 0.75$. After 6 cycles the mean error in ln (k_{20}) has been brought down from 0.7629 to 0.5860, and the optimum values of w and α were given as 1.44 and 0.75, respectively. Data for 20 runs in the temperature range 450–495° were then analyzed on the same basis, the computer being given a start value of $w = 1.5$ and of $\alpha = 0.75$. After 6 cycles the mean error in ln (k_{20}) had been brought down from 0.4189 to 0.3051, and w and α had been corrected to 1.49 and 0.75, respectively. While the agreement was considered rather satisfactory for the high-temperature range, this was not so for the low-temperature range. The low-temperature range data were analyzed by another GIER program AK-4 applying a polynomial making the activation energy a function of temperature. The mean error in ln (k_{20}) was as low as 0.1937, but in other respects the procedure was not quite satisfactory, w and α found by GIER for the optimum trial were 1.52 and 0.74, respectively.

A different approach was now made by plotting log $k_2°$ against $1/2.30 \cdot RT$ for the full temperature range. The $k_2°$ (experimental) values were those calculated by GIER on the basis of $K_{30} = 3.00 \times 10^{-6}$, $E_3 = -25\,000$ kcal/kg mole, $w = 1.50$, and $\alpha = 0.75$. The plot is shown in Fig. 3. Before making the plot the averages of log $k_2°$ and $1/2.30 \cdot RT$, respectively, were calculated for all groups of runs close to 330°C, 370°C,

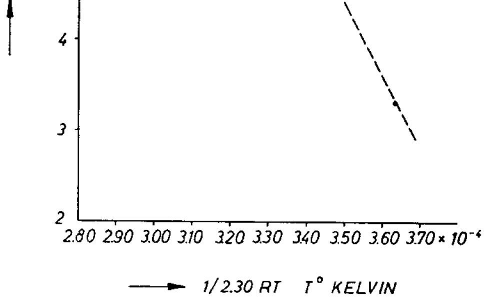

FIG. 3. Plot of $\log_{10} k_2°$ versus $1/2.30 \cdot RT$.

TABLE 2
ADJUSTED RATE CONSTANTS AND MEAN ERROR IN LN (k_{20}) FOR ENTRANCE VALUES OF K_{30} EQUAL TO 3×10^{-2}, 3×10^{-4}, AND 3×10^{-6}

K_{30}	E_3	w	α	k_{20}	E_2	$A = E_2 - 2\alpha E_3$	Mean error ln (k_{20})
3.07×10^{-2}	−19 361	1.564	0.640	2.12×10^{13}	17 249	42 300	0.2865
2.94×10^{-4}	−24 052	1.523	0.654	7.89×10^{10}	11 171	42 600	0.2880
2.96×10^{-6}	−29 241	1.454	0.661	4.60×10^{8}	4854	43 500	0.2940

410°C, 450°C, and 490°C. All of our runs are close to one of these temperatures.

It is apparent from Fig. 3 that the points corresponding to 370°C, 410°C, 450°C, and 490°C may quite well be approximated by a straight line, while the point representing the 330°C runs falls far below.

After that, all of the runs except the 3 runs at 330°C were analyzed by GIER program AK-3.

The entrance value of K_{30} of 3.0×10^{-6} had been determined mainly by an analysis of runs at 330°C, 370°C, and 410°C. As we found out that the points at 330°C should not be treated with the other data, this value may not be the best one. We therefore tried three final calculations with entrance values of K_{30} as follows: $K_{30} = 3.0 \times 10^{-2}$, $K_{30} = 3.0 \times 10^{-4}$, and $K_{30} = 3.0 \times 10^{-6}$. The lowest mean error in ln (k_{20}) in an analysis of all runs excepting the three at 330°C was 0.2865. The adjusted rate constants are given in Table 2.

In Table 3 we give $k_2°$, exp. and $k_2°$, calc. for the 32 runs corresponding to the best trial made by the computer. It will be noticed that there is no significant trend in the error in ln ($k_2°$), except with respect to temperature, which tends to indicate that the apparent energy of activation is not completely constant within the temperature range 370–490°C.

Before concluding the discussion of the derived rate data it should be mentioned that for the high-temperature range we also tried to start the computer off with the values $w = 1.00$ and $\alpha = 1.00$. After 6 cycles or 42 trials the computer had corrected w to 1.20 and α to 0.93. After an additional 6 cycles the computer had corrected w to 1.33, while α was still at 0.93. The mean error in ln (k_{20}), was however, 0.3240, considerably above the mean error in ln (k_{20}) found when starting the computer with 1.50 and 0.75 for w and α, respectively. This error, as mentioned above, was 0.3051.

TABLE 3
EXPERIMENTAL AND CALCULATED RATE CONSTANTS

Run no.	P (atm)	$k_2°$, exp. ($\times 10^{-8}$)	$k_2°$, calc. ($\times 10^{-8}$)	Error in ln ($k_2°$)
5	300	3.21	2.50	−0.25
6	300	3.27	2.50	−0.27
7	300	2.65	2.50	−0.06
8	300	2.22	2.46	0.10
21	153	1.27	2.32	0.60
22	150	2.77	2.50	−0.10
23	149	3.31	2.61	−0.24
1	300	1.44	1.40	−0.02
10	153	1.30	1.32	0.01
14	300	1.52	1.29	−0.16
15	300	1.46	1.29	−0.12
16	300	1.67	1.40	−0.17
18	300	1.47	1.29	−0.13
24	150	1.96	1.38	−0.35
25	150	1.88	1.36	−0.32
36	309	0.97	1.32	0.31
37	308	1.22	1.40	0.14
38	308	0.86	1.29	0.41
39	305	1.23	1.43	0.15
40	308	0.57	1.32	0.83
2	300	0.88	0.74	−0.17
3	300	0.84	0.65	−0.26
4	300	0.85	0.66	−0.25
11	153	0.53	0.64	0.19
12	300	0.39	0.64	0.50
13	300	0.57	0.63	0.10
26	153	0.86	0.68	−0.24
27	152	0.82	0.66	−0.22
31	151	0.37	0.31	−0.17
32	153	0.35	0.31	−0.13
33	153	0.29	0.32	0.10
34	152	0.27	0.32	0.19

Discussion

Rate Equation

It is apparent that the number 1 in NN is very small compared with the second term in the bracket. It seems that only when the content of ammonia is down in the order of 0.1%, does the second term take on a value of the same order of size as the number 1. For calculations on high-pressure ammonia synthesis one may therefore disregard the number 1 in NN. In our analysis, as reported above, we have found figures for w in the range 1.44–1.56. We take this to mean that our experiments are best correlated with $w = 1.50$. They certainly do not correlate as well if w is put equal to 1.00, which would be required if NH radicals were the main species on the surface.

Our equation thus reduces to the original Temkin-Pyzhev equation with a best value of α of about 0.75.

We wish to emphasize that we do not find any pressure dependence of our rate constant, which we ascribe to the fact that we use fugacities not partial pressures.

We find an apparent energy of activation of 42 300 kcal/kg mole for use in the Temkin-Pyzhev equation with $\alpha = 0.64$.

Mechanism

When discussing the mechanism of ammonia synthesis on an iron catalyst we want to take as our departure point the observation by Ozaki, Taylor, and Boudart (*8*) that the rate constant k as determined by them is identical for hydrogen and deuterium, which strongly points to a rate-determining step in which hydrogen is not a reaction partner. We further point to the fact that there is an abundance of kinetic data which appears well correlated by the Temkin-Pyzhev equation. Our data, which are referred to in detail above, are indeed in very good agreement with the Temkin-Pyzhev equation, and we wish to point out that they cover quite a large range of high-pressure operating conditions.

At the conditions of high-pressure synthesis within the range in which our experiments could be correlated the synthesis of ammonia from hydrogen and nitrogen is assumed to have as its rate-determining step the chemisorption of nitrogen molecules from the gas on a surface on which the main species are chemisorbed nitrogen atoms. It is apparent from Fig. 3 that the experimental results at 330°C do not fit into the same picture. Some difference in the mechanism apparently exists below a given temperature or transition region. Our data do not allow us to make any conclusions as to the mechanism of the synthesis below 370°C nor on a surface that is more poisoned by oxygen atoms than the one exposed by our catalyst. Our experiments are therefore in no way in disagreement with the results of Ozaki *et al.*, because their temperature range was 218–302°C and their experiments were carried out at atmospheric pressure and lower. Ozaki *et al.* point out the difference that may exist for synthesis on a very well reduced surface and on a moderately well reduced surface. While our experiments do not allow any conclusions as to the cause of the difference, synthesis experiments by Scholten, Konvalinka, and Zwietering (*18*) on a singly promoted catalyst point to the validity of the Temkin-Pyzhev equation in the temperature range 200–300°C and at atmospheric pressure. However, at temperatures below 200°C their data may indicate deviation from the Temkin theory.

We find an α value essentially below 1.0, and therefore our data show that the surface of our catalyst at the conditions of operation is not uniform. When keeping in mind the complexity of this surface, this is really not surprising. We picture this surface as a surface of iron crystals of a few hundred Å size extensively covered and intimately mixed with promoter compounds in their surface layers. The promoter compounds are also found in the interphases between the individual crystals, as otherwise these crystals would grow together at synthesis conditions. It is obvious to us that such a surface could hardly be uniform in a catalytic respect, one reason being that the electron work function must vary from one crystal to another due to the different amount of alkali promoters which may be assumed to be found on the different crystals and may be due to different crystal faces being exposed to the gas. Reference in this connection is given to Boudart (*19*), to Enikeev and Krylova (*20*), and to Gundry, Haber, and Tompkins (*21*).

As mentioned above and as shown by Fig. 3 the apparent energy of activation is probably not completely constant within the temperature range 370–490°C. There is no reason that it should really be. As pointed out by Taylor and Liang (*22*) and by Taylor (*23*), if the energy spectrum of surface sites active at one temperature is not the same as that active at another, the relative rates at such temperatures cannot be given a simple physical meaning.

The Temkin-Pyzhev equation assumes a nonuniform surface of the simplest type, namely one in which the heat of adsorption, q, of nitrogen, the activation energy of adsorption, E_a, and the activation energy of desorption, E_d, vary linearly with surface coverage. The value of α in this interpretation is equal to $\Delta E_a/\Delta q$. While this appears to be a good approximation there is no reason why it should represent an exact condition, and Scholten (*24*) has calculated α as a function of surface coverage for a given catalyst and found that it depends on nitrogen coverage and synthesis temperature. Particularly, α is supposed to vary from one type of catalyst to another, and this has also been found experimentally. Reference is given in this connection to an article by Frankenburg (*25*).

While we have concluded that the chemisorption of nitrogen is rate-determining in high-temperature ammonia synthesis we agree with the point made by Halsey (*26*) that the usual assumption that a particular step in a reaction is the rate-determining one is inapplicable or, as we should prefer, is far from granted. Only if one end of the energy spectrum on the surface represents the sites on which the reaction is mainly taking place, is the assumption of one rate-determining step justified. We think that that is the case in ammonia synthesis, and we think that this is also borne out by the very small amount of catalyst poisons needed to change the properties of the catalyst surface.

While we consider the catalyst surface to possess *a priori* heterogeneity we also think induced heterogeneity must play an important role. We picture the interphase between the catalyst and the fluid as being indeed a very busy place where not only molecules arrive and depart, but structural rebuilding is continuously going on. The establishment of strong covalent bonds must lead to renewed equilibrium positions of the surface atoms. In an article by Cook, Pack, and Oblad (*27*) the theory of structural adsorption is presented. Reference is also given to Schlier and Farnsworth (*28*), who, in examining a germanium surface of orientation (100) by low energy electron diffraction, found that an atomically clean surface gives, besides the pattern to be expected from a perfect surface, a pattern to which half order numbers had to be ascribed. Adsorption of oxygen removed this pattern. These observations were taken to mean that the unsaturated valences of the surface atoms of the atomically clean surface cause a displacement of the surface atoms so that adjacent rows are moved in opposite directions. This way a structure with double lattice distance is created.

In view of the complexity of the system we find it quite remarkable that a satisfactory rate equation covering a wide range of process conditions can be as simple as the Temkin-Pyzhev equation, with only three constants.

ACKNOWLEDGMENTS

We are grateful to Mr. Haldor Topsøe for permission to carry out this work and publish the results.

Operation of the high pressure unit was done by Mr. H. Bundgaard Nielsen, and we wish to thank him for careful and skilful experimental assistance.

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