4. $Al_2(CH_3)_6$ and $Si_2(CH_3)_6$ have ethane-like structures. The silicon compound has the bond lengths and angles expected for a normal covalent structure. In the aluminum compound the C–Al–C bond angles are 115° or larger. The Al–Al bond is surprisingly short in comparison with the Si–Si bond length.

5. The structural question of what makes two $Al(CH_3)_3$ molecules join is still a question.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 4, 1941

[CONTRIBUTION OF THE FERTILIZER RESEARCH DIVISION, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

The Catalytic Decomposition of Ammonia over Iron Synthetic Ammonia Catalysts

BY KATHARINE S. LOVE AND P. H. EMMETT[1]

The catalytic decomposition of ammonia has been studied by many workers. In only a few instances, however, have such studies been concerned with the decomposition over iron synthetic ammonia catalysts. The present work had as its primary object the elucidation of the kinetics of ammonia decomposition over several of the many iron catalysts prepared and studied in the U. S. Department of Agriculture. The results obtained point toward a complexity of the ammonia synthesis and decomposition reactions over iron that heretofore has not been recognized. The present work is believed to represent progress in unravelling some of the many complex aspects of these reactions over iron but much additional painstaking work is needed for a complete understanding of ammonia catalysts.

Apparatus and Procedure

The apparatus and procedure were similar to those described by E. Winter.[1a] A flow system at approximately atmospheric pressure was employed. Mixtures of hydrogen, nitrogen and ammonia were led over the hot catalyst. In a few experiments helium was substituted for nitrogen. The undecomposed ammonia was absorbed in half normal sulfuric acid and the excess acid titrated with standard alkali. The rate of decomposition was estimated as the difference between the ammonia flow at the entrance and at the exit. Each entering gas was measured by a separate flowmeter. Through a multiple capillary arrangement each flowmeter could accurately cover the range 50 to 500 cc. of gas per minute. All of the capillaries were thermostated at 30°. By thus keeping the temperature constant and correcting for pressure changes, satisfactory precision could be obtained. The manometer measuring the flow of ammonia was made from tubing 12 mm. in diameter. It was long enough to allow a pressure difference of 100 cm. of nujol and was kept at constant temperature. Mercury was used in the auxiliary manometers for measuring the pressure at the exit of each flowmeter. Synthetic ammonia which had been selected for its purity was dried over fused potassium hydroxide. The hydrogen was electrolytic. The nitrogen was atmospheric (Linde) and was purified by passage first through one tube of hot copper and after mixing with the hydrogen stream through a second. The hydrogen–nitrogen mixtures were then passed through tubes containing soda lime, through a trap immersed in liquid air and finally through a phosphorus pentoxide tube. The copper had been reduced at 800° and then oxidized and reduced again at a lower temperature. The temperature of the catalyst was measured by a thermocouple placed in a glass well extending through the body of the catalyst.

Most of the results reported here are on the decomposition over three iron synthetic ammonia catalysts: Catalyst 931, doubly promoted with 1.3% Al_2O_3 and 1.59% K_2O; Catalyst 954 singly promoted with 10.2% Al_2O_3; and pure iron Catalyst 973, containing 0.15% Al_2O_3 as impurity. The decomposition was also measured over iron supported on Al_2O_3.

Experimental Results

Decomposition on Catalyst 931.—The initial period of reduction of each sample of 931 included about twenty-four hours at 400° and twenty-four to seventy hours at 430 to 450°. The space velocities during reduction were 15,000, 3600, 2400 and 1000 for samples A, B, C and D, respectively. Immediately before each run on this and other catalysts, the catalyst was reduced at the temperature of the run for at least one hour. Between runs the cold catalyst stood in hydrogen at a pressure 1.5 cm. of mercury higher than atmospheric. Unless stated otherwise, the data on the decomposition over all of the catalysts were obtained under conditions of temperature and gas composition which preclude formation of the iron nitrides.[2,3]

An apparent energy of activation of 43,800 ±

---

[1] Present address: Department of Chemical and Gas Engineering, The Johns Hopkins University, Baltimore, Maryland.

[1a] E. Winter, *Z. physik. Chem.*, **B13**, 401 (1931).

[2] Emmett, Hendricks and Brunauer, THIS JOURNAL, **52**, 1456 (1930).

[3] Brunauer, Jefferson, Emmett and Hendricks, *ibid.*, **53**, 1778 (1931).

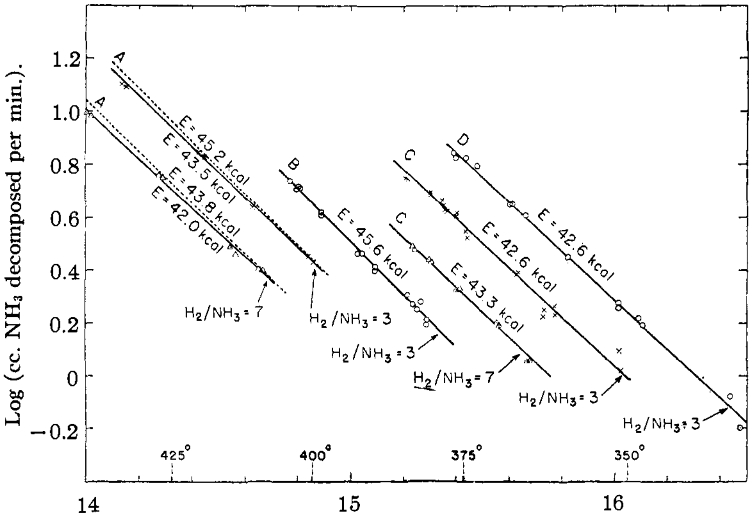

Fig. 1.—Temperature dependence of rate of ammonia decomposition over samples A (0.8 cc.), B (1.5 cc.), C (5.0 cc.) and D (12.5 cc.) of iron catalyst 931 ($Fe-K_2O-Al_2O_3$). Dotted curves have been corrected for the small change in composition of the gas in passing through the catalyst; total flow, 400 cc./min.; no nitrogen as diluent. Apparent energy of activation expressed in kilogram calories per mole of ammonia.

2000 cal. was obtained for the reaction on unsintered samples of 931 throughout the temperature range 335 to 430°. There appeared to be no trend in the value for the energy of activation with the temperature of the catalyst or with the composition of the gas used. Figure 1 shows a series of typical runs during which the entering gas mixture was held constant and the rate of decomposition observed at different temperatures. The rates shown are not corrected for the change in composition of the gas mixture occurring as it passes the catalyst. To show the magnitude of the error this lack of correction entails, curves giving the corrected rates for sample A are shown by the dotted lines in Fig. 1. The apparent energies of activation calculated from the slopes of the corrected curves are about 1800 cal. higher than those from the slopes of the uncorrected ones. The method of making the correction will be given later.

One run with a sample of catalyst that had been converted to Fe_4N, and with such a gas mixture and temperature that the Fe_4N was not reduced, gave an apparent energy of activation of 53,000 cal. A similar run over the Fe_3N-Fe_2N phase gave 42,000 cal. Sintering the catalyst at 550° raised the apparent energy of activation somewhat. Values of 47,400 and 50,000 cal. were obtained over a sintered catalyst.

In order to determine the dependence of the decomposition upon the partial pressure of ammonia in the gas mixture, experiments were conducted in which the temperature, the hydrogen flow and the total flow were held constant and the ammonia flow varied. Nitrogen was used as a diluent after it had been established that this would yield the same results as helium. In a like manner the dependence of the rate upon the partial pressure of hydrogen was obtained. These experiments covered the temperature range 347–430°.

In Fig. 2 the rate of reaction is shown as a function of the ammonia fraction in the entering gas. The solid lines are uncorrected, the dotted line is corrected for the change in composition of the gas passing the catalyst. The slope, *m*, of all the lines is 0.6 within our experimental

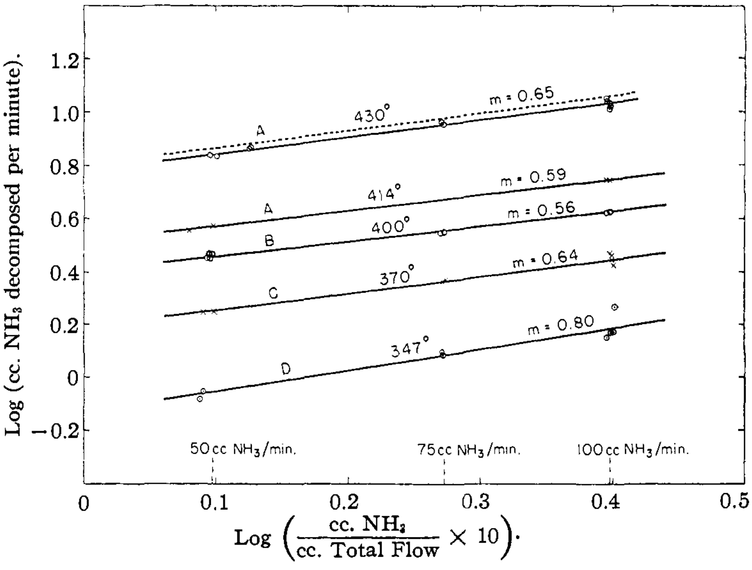

Fig. 2.—Rate of ammonia decomposition *vs.* its mole fraction over samples A (0.8 cc.), B (1.5 cc.), C (5.0 cc.) and D (12.5 cc.) of iron catalyst 931 ($Fe-K_2O-Al_2O_3$). Dotted curve has been corrected for the change in composition of the gas in passing through the catalyst; total flow, 400 cc./min.; hydrogen flow, 300 cc./min.; nitrogen as diluent.

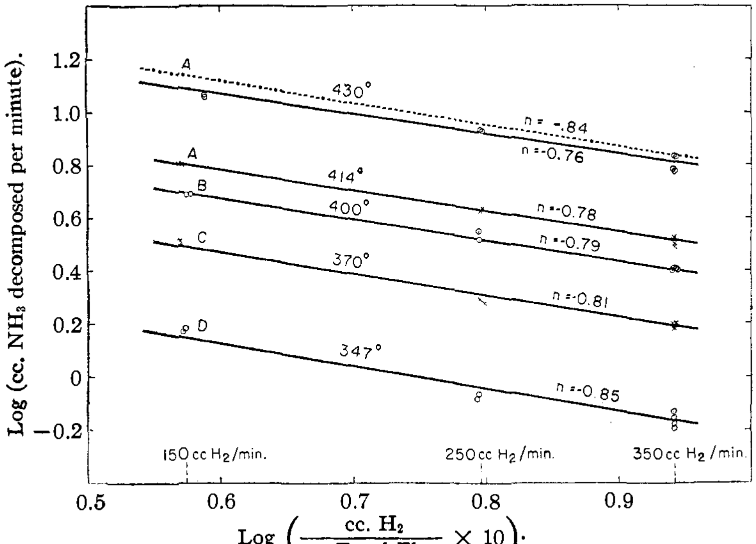

Fig. 3.—Rate of ammonia decomposition *vs.* the mole fraction of hydrogen over samples A (0.8 cc.), B (1.5 cc.), C (5.0 cc.), D (12.5 cc.) of iron catalyst 931 ($Fe-K_2O-Al_2O_3$); total flow, 400 cc./min.; ammonia flow, 50 cc./min.; nitrogen as diluent. Dotted curve has been corrected for the change in composition of the gas in passing through the catalyst.

error.[4] The rate of ammonia decomposition is, accordingly, directly proportional to $(P_{NH_3})^{0.6}$. Similarly from curves of Fig. 3[5] we find the rate inversely proportional to a power of the partial pressure of hydrogen between 0.8 and 0.9 (after the correction for change in gas composition on passing the catalyst has been made).

The rates of decomposition shown by the solid lines in Figs. 2 and 3 have been corrected for variations in temperature but not for the slight change in composition of the gas as it passes the catalyst. In order to get some idea as to the maximum error due to this change, the observed rates of reaction in a few runs of relatively large decomposition in Figs. 1, 2 and 3 were corrected in the following manner. The gas mixture that existed after one-half the observed decomposition had taken place was regarded as the mixture with which the observed rate was obtained. The observed rate for this average mixture was then corrected to the rate for the entering mixture on the assumption that the rate of decomposition is proportional to the *m*th power of (NH_3) and the *n*th power of (H_2), *m* and *n* being taken from the uncorrected curves in Figs. 2 and 3. The corrected rates are shown by the dotted curves.

In a series of experiments the composition of the entering gas, the total flow and the temperature were held constant while the change in rate with time was observed. Two interesting effects have been noted: (1) usually there was a sharp rise in rate at the beginning of the run. Run 1, Fig. 4, was an unexplained exception to this rule. A continuous nineteen hour reduction between runs 3 and 4 did not eliminate the effect. (2) In certain experiments after the reaction had continued three hours or longer, the ammonia was cut off and the catalyst reduced for eighteen minutes. The ammonia was then turned into the gas stream again, and, after six minutes had elapsed for equilibration, the exit gas sampled. After this short reduction, there was always ob-

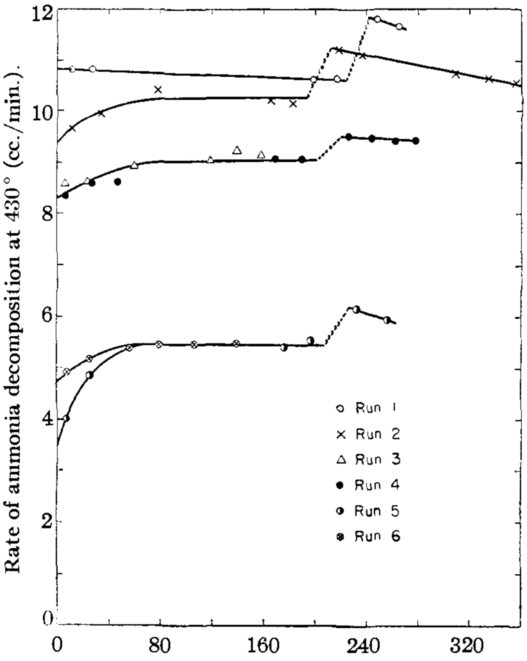

Fig. 4.—Rate of ammonia decomposition *vs.* time on sample A (0.8 cc.) of iron catalyst 931 ($Fe-K_2O-Al_2O_3$). Dotted lines indicate period of reduction by pure hydrogen; 300 cc. hydrogen and 100 cc. ammonia per minute, runs 1, 2, 3 and 4; 350 cc. hydrogen and 50 cc. ammonia per minute, runs 5 and 6.

---

[4] The 347° run can be given little weight because the rate of ammonia decomposition was quite small and one point on the curve seems to be considerably in error.

[5] The two points on the solid curve for 430° at log (H_2 fraction $\times 10^2$) = 0.589 were obtained with a gas mixture close to the equilibrium mixture required to form Fe_4N, a fact which may have influenced the spread of points at log (H_2 fraction $\times 10^2$) = 0.942. The two low points at 0.942 were obtained after the two at 0.589.

served first an increase in rate and then a slow decrease toward the rate existing prior to the short reduction.

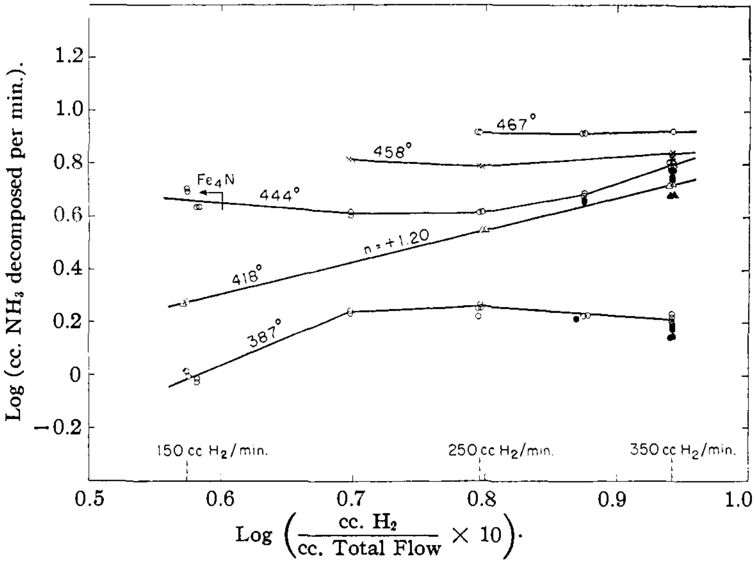

Fig. 5.—Rate of ammonia decomposition *vs.* mole fraction of hydrogen over a sample (1.55 cc.) of iron catalyst 954 (Fe–Al_2O_3): total flow, 400 cc./min.; ammonia flow, 50 cc./min.; nitrogen as diluent. Solid triangles and circles are for data taken by going from low to high hydrogen flows.

Within one minute after the ammonia was turned into the gas stream, a small though decided drop in temperature of the catalyst was observed, but within six minutes the temperature became fairly steady. It will be noted that in run 2 of Fig. 4 the rate was still high 144 minutes after the short reduction. The rates shown in Fig. 4 have been corrected for slight temperature variations. Other runs not shown in Fig. 4 indicate that a short reduction period after the reaction had continued only forty to fifty minutes had little effect upon the activity of the catalyst.

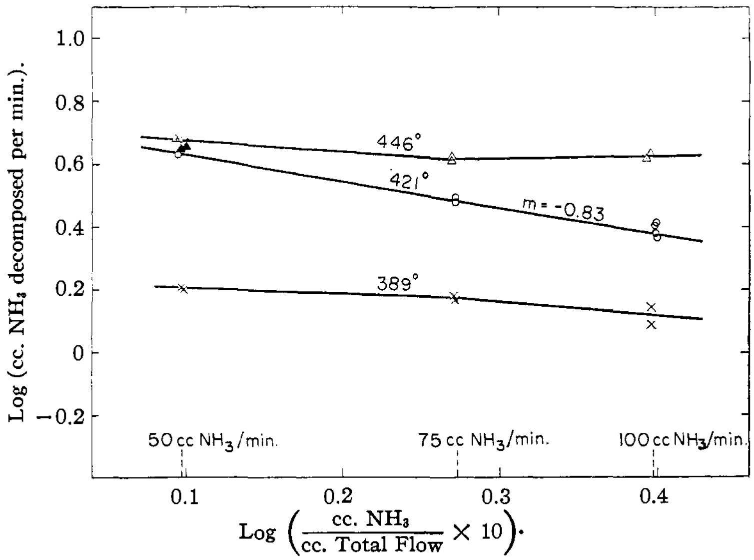

Fig. 6.—Rate of ammonia decomposition *vs.* its mole fraction over a sample (1.55 cc.) of iron catalyst 954 (Fe–Al_2O_3); total flow, 400 cc./min.; hydrogen flow, 300 cc./min.; nitrogen as diluent. Solid triangles are for data taken by going from high to low ammonia flows.

Decomposition on Catalyst 954.—In all decomposition runs on 954 shown in graphs of this report except those in Fig. 13, one 1.55 cc. sample of catalyst was used. The preliminary treatment consisted of nineteen hours reduction at 400°, twenty-seven hours at 450° and twenty hours at 485° at a space velocity of 8000. The rate of the reaction on this catalyst differs greatly from that on catalyst 931 in its dependence upon temperature, ammonia partial pressure and hydrogen partial pressure. Over a considerable range of temperature and gas composition the rate of ammonia decomposition increases with increasing partial pressure of hydrogen, and decreases with increasing ammonia partial pressure. For example, at about 420° throughout the range of gas compositions used, the rate is inversely proportional to $(NH_3)^{0.8}$ and directly proportional to $(H_2)^{1.2}$ (Figs. 6 and 5, respectively). The solid triangles and solid circles in these two figures represent rates observed on return to a higher H_2–NH_3 ratio from a lower one.

When experiments were conducted to observe the dependence of the rate upon temperature, low apparent energies of activation were obtained. Furthermore, when the rate was observed at a lower, then a higher, and finally the lower temperature, the rate on return to the lower temperature was decidedly smaller than the initial rate at this temperature. Figure 7 gives the experimental points of three such runs. The points of each run are numbered in chronological order. The figures above the solid lines give the

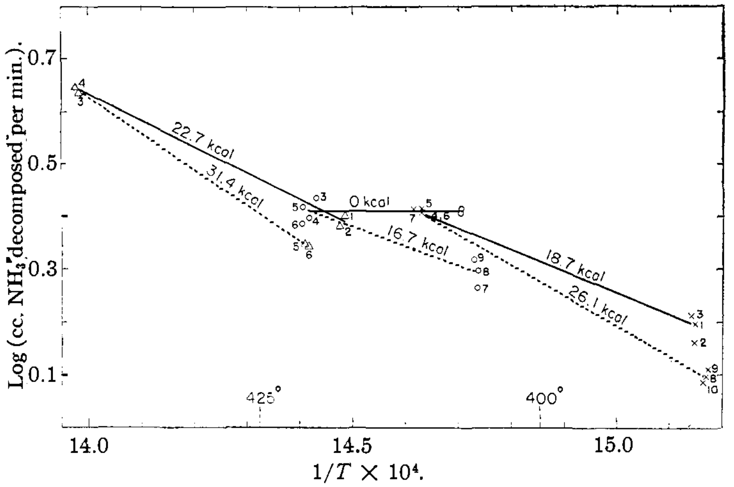

Fig. 7.—Temperature dependence of rate of ammonia decomposition over a sample (1.55 cc.) of iron catalyst 954 ($Fe-Al_2O_3$); hydrogen flow, 300 cc./min.; ammonia flow, 100 cc./min.; no nitrogen as diluent. Numbers indicate the chronological order of data for a given temperature dependence run. Dotted lines are for data taken by going from high to low temperatures.

apparent energies of activation in going from lower to higher temperatures; those over the dotted lines, the apparent energies of activation in going from higher to lower temperatures. With the gas mixture used in these experiments, 300 cc. of hydrogen and 100 cc. ammonia per minute, the apparent energy of activation seems to pass through a minimum between 400 and 425°. This is shown also in Fig. 8 which represents the same gas mixture. Here the experimental points designated by circles (the triangles will be discussed later) were selected from rate *vs.* temperature and rate *vs.* ammonia partial pressure runs by taking only those rates observed while going from lower to higher temperatures, or lower ammonia partial pressure to higher ammonia partial pressure.

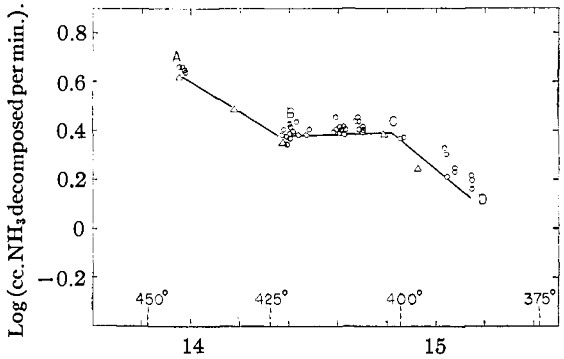

Fig. 8.—Temperature dependence of rate of ammonia decomposition over a sample (1.55 cc.) of iron catalyst 954 ($Fe-Al_2O_3$); circles, data taken from lower to higher temperatures or from lower to higher ammonia partial pressures; triangles, data from 180 minute point in time *vs.* activity runs; hydrogen flow, 300 cc./min.; ammonia flow, 100 cc./min.; no nitrogen as diluent.

Experiments in which the temperature, partial pressures of ammonia and hydrogen, and total flow were held constant and the rate of reaction was observed as a function of time gave some interesting results on catalyst 954. A number of such runs are shown in Fig. 9. In most of these the ammonia was turned off after three or more hours of running, the catalyst reduced for eighteen minutes, and the ammonia turned on again. With a flow of 350 cc. of hydrogen and 50 cc. ammonia per minute there is no decrease in rate with time nor any appreciable increase after the eighteen-minute reduction period in the temperature region 393–417°; but in the range 428–490° the rate decreases slightly at the beginning of the run and jumps to approximately the initial rate after the short reduction. The drop back to the rate reached just before the reduction is fairly rapid in most cases. In several runs the reduction time was varied from five to eighteen minutes. No great difference in rate increase was noted.

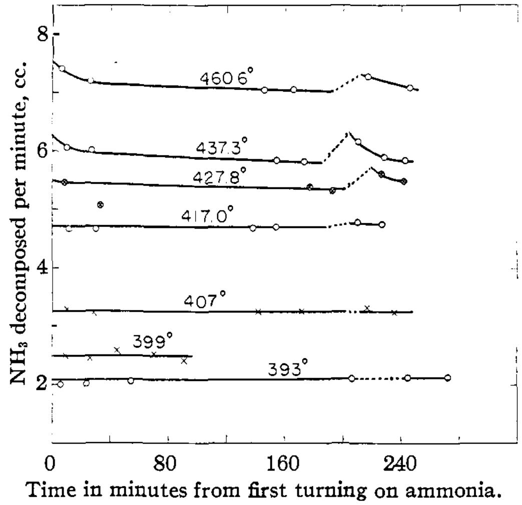

Fig. 9.—Activity *vs.* time runs on a sample (1.55 cc.) of catalyst 954 ($Fe-Al_2O_3$); hydrogen flow, 350 cc./min.; ammonia flow, 50 cc./min.; no nitrogen as diluent. Dotted lines indicate period of reduction by pure hydrogen.

Three rate–temperature curves are shown in

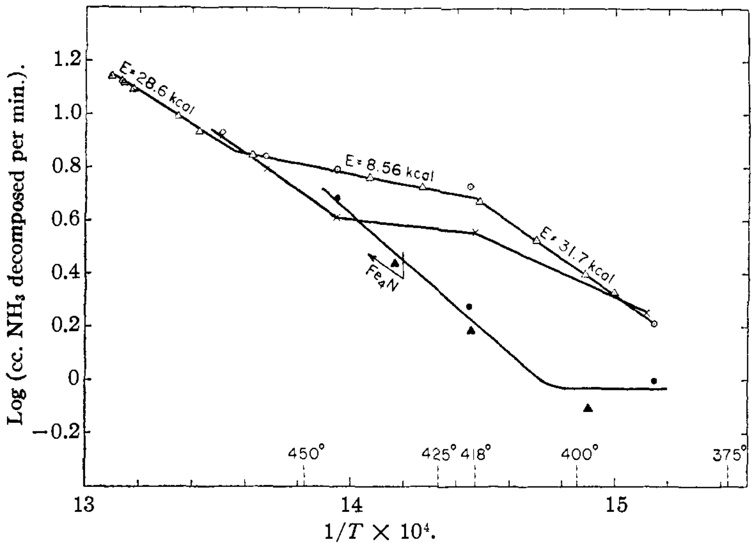

Fig. 10.—Temperature dependence of rate of ammonia decomposition over a sample (1.55 cc.) of catalyst 954 ($Fe-Al_2O_3$): △, from 180 minute point on time *vs.* activity runs; hydrogen flow 350 cc./min., ammonia flow 50 cc./min., no nitrogen; ▲, from 180 minute point on time *vs.* activity runs, hydrogen flow, 150 cc./min.; nitrogen flow, 200 cc./min., ammonia flow, 50 cc./min.; ○, × and ● from runs in Fig. 5 for hydrogen flows of 350, 250 and 150 cc. hydrogen/min., respectively.

Fig. 10. The rates indicated by open triangles were taken at the 180-minute point from runs of the gas composition and of the type shown in Fig. 9; those indicated by solid triangles were taken, likewise at the 180-minute point, from similar runs in which a flow of 150 cc. hydrogen, 50 cc. ammonia and 200 cc. nitrogen per minute was used. The open circles, crosses, and solid circles are the rates shown by the curves in Fig. 5 at the points at which the hydrogen flow was 350 cc., 250 cc., and 150 cc. per minute, respectively. Figure 10 shows that between 400 and 430° rates for a given partial pressure of ammonia are higher, the higher the partial pressure of hydrogen. Rates taken at the 180-minute point from time *vs.* activity curves are represented by triangles in Fig. 8 and are probably more accurate than those designated by circles because of the long time allowed for equilibration in case of the former. The apparent energy of activation for the reaction may, therefore, be negative between 403 and 423° when a flow of 300 cc. hydrogen and 100 cc. ammonia is used.

All curves shown for catalyst 954 are based on the gas mixtures entering the catalyst chamber. The rates are not corrected for slight fluctuations in composition of the gas mixture or in temperature because of the uncertainty in the kinetics and temperature coefficients over this catalyst. In every case, however, the fractional decomposition is so small and the temperature variations so slight that corrections would not alter the general shape of the curves.

Decomposition on Catalyst 973.—The two curves in Fig. 11 and two of the four in Fig. 12 represent the decomposition on a 5-cc. sample of catalyst 973 that had been initially reduced at a space velocity of 2400 for seventy-four hours at temperatures ranging from 389 to 402°. The temperature during reduction had been purposely kept low because the pure iron catalyst sinters readily. Two of the four curves shown in Fig. 12 represent runs with only 4.5 cc. of the catalyst after the reduction had been extended to 425–450° for six hours. The curves of Fig. 12 connect points obtained by averaging data from several runs.

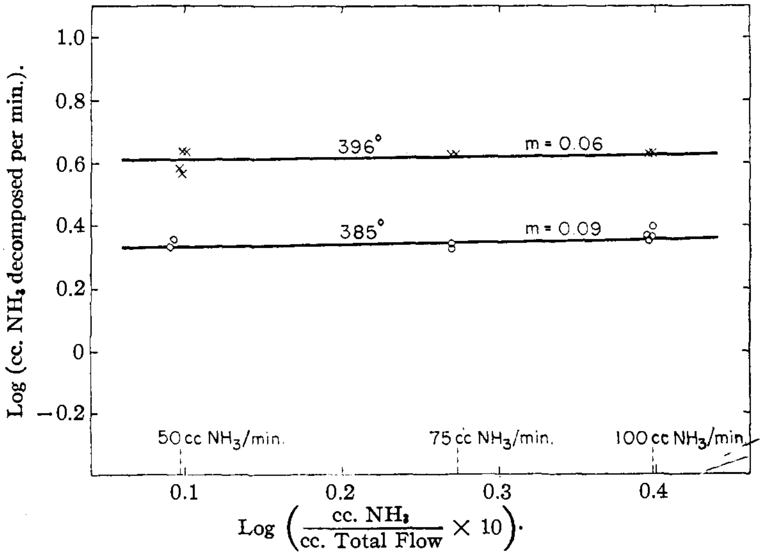

Fig. 11.—Rate of ammonia decomposition *vs.* its mole fraction over a sample (5 cc.) of catalyst 973: total flow, 400 cc./min.; hydrogen flow, 300 cc./min.; nitrogen as diluent.

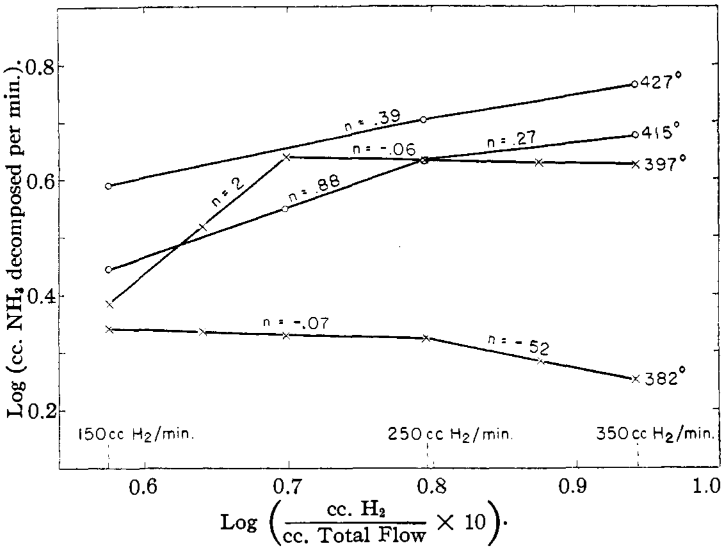

Fig. 12.—Rate of ammonia decomposition *vs.* mole fraction hydrogen over 5 cc. (×) and 4.5 cc. (O) samples of pure iron catalyst 973: total flow, 400 cc./min.; ammonia flow, 50 cc./min.; nitrogen as diluent. The points shown were obtained by averaging data from a number of runs.

The decomposition on catalyst 973 shows irregularities and trends similar to those shown by the decomposition on 954. A rate–time run at 418° with a flow of 300 cc. of hydrogen and 100 cc. of ammonia showed an initial decrease in rate, and a subsequent increase when ammonia was turned in again after a short reduction period. The rate at 427° increased with the partial pressure of hydrogen as for the decomposition on 954 at 418°. The curve representing the decomposition at 397° in Fig. 12 is very similar to the one in Fig. 5 representing the reaction on catalyst 954 at 387°. With a flow of 300 cc. of hydrogen and 100 cc. of ammonia per minute, in the temperature range 400–483°, a decrease in rate on return from higher to lower temperatures was observed. The apparent energy of activation varied from 26,000 to 42,000 cal. depending on the temperature range, and the order with respect to temperature of observing rates. On a sintered sample with a flow of 560 cc. of hydrogen and 100 cc. of ammonia per minute in the temperature range 473–523°, on the other hand, no decrease in rate on return to lower temperature was observed and the apparent energy of activation was 54,000 cal.

Decomposition on an Iron Catalyst Supported on Alumina.—To facilitate intercomparison of our results with those of Winter, a few experiments were conducted with a catalyst made by soaking alumina gel in ferric nitrate, igniting it and then reducing it in hydrogen at 500–550°.

The rate of decomposition of ammonia varied as $1/(P_{H_2})^{0.85}$ at 535° with a gas mixture in which the solid phase was iron, and as $1/(P_{H_2})^{1.1 \text{ to } 1.25}$ when the gas composition corresponded to that necessary for the conversion of the catalyst to Fe_4N. The apparent temperature coefficient was 50,600 cal., the rate with a flow of 350 cc. of hydrogen and 50 cc. of ammonia per minute being 1.1 cc. at 520°, 2.14 cc. at 530° and 3.02 cc. at 546°.

Rate of Decomposition *vs.* Mesh Size.—The development of a method for measuring the total (inner plus outer) surface[6] of a catalyst enabled us to make some interesting observations relative to the influence of the mesh size of synthetic ammonia catalysts on their activity toward ammonia decomposition. A 10–14 mesh and a 35–40 mesh sample of singly promoted catalyst 954 were reduced according to the usual fixed schedule up to 475°. These samples were shown by surface area measurements[7] to have approximately the same total surface, the surface of the 35–40 mesh sample being only 15% greater than that of the larger mesh sample. On the other hand, the geometric or outer surface area of the smaller mesh sample ought to have been three times as large as that of the 10–14 mesh sample. On each of these samples the decomposition of ammonia from a mixture containing 75% hydrogen and 25% ammonia was determined by the procedure used in the other reaction rate runs in the present work. The rate of decomposition on the 35–40 mesh sample was 0 to 10% less than on the 10–14 mesh, whereas if the rate had been proportional to the geometric surface area, it should have been about 300% greater for the finer mesh sample. It therefore appears that the entire inner surface, or some given fraction of it, is actually able to take part in the catalytic decomposition about as readily as the outer surface of the catalyst.[8] Similar observations on two other catalysts have been reported. Juliard[9] found that changing the

---

(6) Committee on Catalysis, National Research Council, 12th Report, Chapter V, John Wiley and Sons, New York, N. Y., 1939.

(7) Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(8) Emmett and Brunauer, *Trans. Am. Electrochem. Soc.*, **71**, 383 (1937).

(9) Juliard, *Bull. soc. chim. Belg.*, **46**, 549 (1937).

size of particles of cobalt catalysts fourteen-fold from 0.05 to 7.0 mm. had no effect on the rate of hydrocarbon synthesis; Cawley and King[10] found similarly no change in the activity of a molybdenum oxide catalyst for the hydrogenation of tar when the particle size was changed from $^1/_8$–$^1/_4$ to $^1/_{16}$–$^1/_8$ inch.

Addition of Alkali to a Reduced Fe–Al_2O_3 Catalyst.—One other application of the surface area measurement technique was made in the present work. When it became evident that the rate–temperature curves for the singly promoted catalyst 954 were so radically different from those of the doubly promoted 931 and that the surface of the former was much greater than that of the latter, the idea of trying to incorporate alkali on the surface of a reduced singly promoted catalyst suggested itself. To this end a series of experiments was carried out in which nitrogen adsorptions at −183°, carbon dioxide adsorptions at −78°, and the rate of ammonia decomposition at several temperatures were used in detecting the accumulation of alkali on the surface of the catalyst and its effect on the catalyst efficiency. The alkali was added to a reduced 1.5-cc. sample of catalyst 954 by allowing the catalyst to come in contact with first 1.5 cc. of 0.117 *N* solution of potassium hydroxide and then with 1.5 cc. of 0.33 *N* solution. The water was evaporated from the catalyst and the catalyst reduced in hydrogen at 450° after each addition.

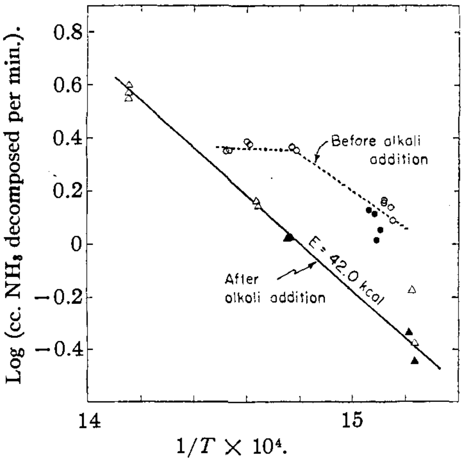

Fig. 13.—Effect of addition of K_2O to a reduced sample (1.6 cc.) of catalyst 954 (Fe–Al_2O_3) upon the temperature dependence of the rate of ammonia decomposition over the catalyst: hydrogen flow, 150 cc./min.; ammonia flow, 50 cc./min.; no nitrogen as diluent.

The effects of the two alkali additions on the activity of the catalyst are shown in Fig. 13. Clearly the alkali changed the rate–temperature curve from the type characteristic of Fe–Al_2O_3 catalysts to the type characteristic of the doubly promoted Fe–K_2O–Al_2O_3 catalysts. At low temperatures the activity seems to be less than before; at higher temperatures, greater. The temperature coefficient of the ammonia decomposition on the catalyst is much greater after the addition of alkali than before.

The adsorption of nitrogen at −183° and 200 mm. pressure before the addition of alkali was 7.4 cc. compared to 3.90 cc. after the addition. The total surface area, therefore, decreased by 50%. The carbon dioxide adsorption at −78° and 200 mm., judging from repeated carbon dioxide adsorption isotherms on other samples of 954, would also have been approximately 7.4 cc. before the additions of alkali. After the additions 3.87 cc. of carbon dioxide was physically adsorbed and 1.90 cc. was chemisorbed.[11] Thus the alkali promoter covered about one-half the total surface on the assumption that each surface alkali molecule is capable of holding one chemisorbed carbon dioxide molecule.

These preliminary results definitely point to the possibility of producing a doubly promoted catalyst by impregnating the reduced iron catalyst with alkali rather than adding the alkali to the unreduced fused iron oxide as in the usual procedure. The work is, however, insufficient to show whether or not the alkali addition can be carried out in such a manner as to retain both the large surface area of the singly promoted catalyst and the higher activity of a doubly promoted catalyst at both high and low temperatures.

Discussion

Many of the previous experiments on the kinetics of ammonia decomposition over iron have been made in static systems in which the initial gas was pure ammonia.[12,13] Although such systems may be very useful in the absence of complications due to nitride formation, they lead to very complex results with metal catalysts on which a series of nitrides may form. The recent work by Kiyama[14] clearly illustrates the complexity of

---

[10] Cawley and King, *Dept. Sci. Ind. Research* (*Brit.*), "Fuel Research," Tech. Paper **45** (1937).

[11] Emmett and Brunauer, THIS JOURNAL, **59**, 310 (1937).

[12] Kunsman, *Science*, **65**, 527 (1927); *ibid.*, **51**, 688 (1929).

[13] Kunsman, Lamar and Deming, *Phil. Mag.*, **10**, 1015 (1930).

[14] Ryo Kiyama, *Review of Phys. Chem. of Japan*, XIII, 125 (1939).

the factors causing pressure increases when pure ammonia is allowed to decompose over iron in a static system. In view of the fact that the initial reaction may be the reaction between iron and ammonia to form iron nitride, such reaction rate determinations in static systems are not suitable for obtaining the kinetics of ammonia decomposition.

Only the experiments by Winter[1a] using a flow system have been carried out in such a manner as to give kinetics for the decomposition of ammonia over iron. On an iron catalyst supported by aluminum oxide he found that the rate of decomposition of ammonia was proportional to $P_{NH_3}/(P_{H_2})^{3/2}$. His measurements were apparently made in a temperature range and with a gas composition corresponding to region A B, Fig. 8. In interpreting the mechanism by which the decomposition of ammonia might lead to a kinetic expression of this sort Winter suggested the following series of reactions:

$$NH_{3gas} = NH_{3ads.} \qquad (1)$$

$$H_{2gas} = 2H_{ads.} \qquad (2)$$

$$NH_{3ads.} = N_{ads.} + 3H_{ads.} \qquad (3)$$

$$N_{ads.} = N_{gas} \qquad (4)$$

$$2N_{gas} = N_{2gas} \qquad (5)$$

and pointed out that the equilibrium constant for reaction (3) may be written as

$$K_1 = \frac{(N_{ads.})(H_{ads.})^3}{(NH_{3ads.})}$$

and, consequently

$$(N_{ads.}) = K_2 \frac{(NH_{3gas})}{(H_2)^{1.5}}$$

If the slow step in the decomposition of ammonia is the process represented by equation (4), the rate of ammonia decomposition would be expected to be proportional to $NH_3/(H_2)^{1.5}$.

Temkin and Pyzhev[15] pointed out recently that the mechanism proposed by Winter to explain his kinetic results is impossible since it entails as a slow step the breaking of a Fe–N bond whose energy is of the order of 90,000 calories. Since the apparent energy of activation for ammonia decomposition obtained by Winter was 54,000 cal., it can be shown that the reaction represented by equation (4) cannot be a step in the actual decomposition of ammonia over iron.

To clarify this situation Temkin and Pyzhev have suggested that the rate of escape of nitrogen molecules from the surface of the catalyst depends very strongly on the fraction of the surface covered by adsorbed nitrogen. They propose the use of several equations for expressing the adsorption equilibrium between gaseous nitrogen and iron, and for representing the rate of adsorption and desorption of nitrogen. The equations[16] are as follows

$$\theta = \frac{1}{f} \ln a_0 p \qquad (6)$$

$$v = k_a P e^{-g\theta} \qquad (7)$$

$$w = k_d e^{h\theta} \qquad (8)$$

where θ is the fraction of surface covered; p, the equilibrium pressure of nitrogen; v, the rate of adsorption; P, the instantaneous nitrogen pressure; w, the rate of desorption; and f, a_0, k_a, g, k_d and h are constants.

Roginsky has pointed out that equation (7) is applicable to the data of Emmett and Brunauer[17] for the rate of adsorption of nitrogen, and Temkin and Pyzhev have stated that equation (6) conforms to the equilibrium data of Emmett and Brunauer. Using the three above equations Temkin and Pyzhev propose an explanation for the kinetics of ammonia decomposition that agrees with the results obtained by Winter, and at the same time gives an approximately correct value for the energy of activation. At equilibrium, according to equation (6), the fraction of the surface covered with an adsorbed gas is related exponentially to the partial pressure of the gas being adsorbed. For example, in the adsorption of nitrogen on iron the pressure represented by p in equation (6) would refer to the partial pressure of gaseous nitrogen in contact with iron.

In applying these equations to the kinetics of ammonia decomposition Temkin and Pyzhev make the assumption that the adsorption of nitrogen on iron in the presence of an ammonia–hydrogen mixture will be the same as it would be at equilibrium with the partial pressure of nitrogen equivalent to the existing partial pressure of ammonia and hydrogen in the gas mixture. Thus, since the equilibrium constant for ammonia synthesis is $K_3 = (NH_3)^2/(H_2)^3(N_2)$ the partial pressure of nitrogen can be represented as being equal to $(NH_3)^2/K_3(H_2)^3$. Accordingly, in equation

---

(15) Temkin and Pyzhev, *Acta Physicochim.*, *U. R. S. S.*, **12**, 327 (1940).

(16) Equation (6) is reported to have been obtained by Frumkin and Slygin [*Acta Physicochim.*, *U. R. S. S.*, **3**, 791 (1935)]; equation (7) by Zeldowitsch [*ibid.*, **1**, 449 (1934)]; and Roginsky ["Adsorption and Catalysis," in the Symposium "Problems of Kinetics and Catalysis," III, ONTI, Leningrad (1937)]; and equation (8) by Langmuir [THIS JOURNAL, **54**, 2798 (1932); *J. Phys. Chem.* (Russ), **6**, 161 (1935)].

(17) Emmett and Brunauer, THIS JOURNAL, **56**, 35 (1934).

(6) Temkin and Pyzhev replace the pressure p by the equivalent pressure of ammonia and hydrogen to yield

$$\theta = \frac{1}{f} \ln a_0 \frac{(NH_3)^2}{K_3(H_2)^3} \tag{9}$$

Temkin and Pyzhev assume that the slow step in the decomposition is the rate of escape of nitrogen molecules from the surface of the catalyst. The rate of ammonia decomposition is then expressed by equation (8) in which θ is replaced by the value from equation (9) to yield equations (10) and (11)

$$w = k_d e^{\frac{h}{f} \ln a_0 \frac{(NH_3)^2}{K_3(H_2)^3}} \tag{10}$$

$$w = k_1 \left(\frac{(NH_3)^2}{(H_2)^3}\right)^{\beta} \tag{11}$$

where β is equal to the ratio of the two constants h and f. This equation is identical with the one obtained by Winter for the rate of ammonia decomposition provided we assume that β is equal to one-half. The detailed analysis by Temkin and Pyzhev of the temperature dependence of the constants of equation (10) using the values of Emmett and Brunauer[17] for the heat of adsorption and energy of activation of adsorption of nitrogen on promoted iron catalysts, leads to a satisfactory value for the energy of activation for the decomposition of about 46,500 cal.

It is pertinent to inquire at this point how well the theory and postulates of Temkin and Pyzhev can be applied to the reaction rate measurements reported in this paper for the decomposition of ammonia over catalyst 931. From Figs. 2 and 3 it is evident that the rate of ammonia decomposition over this catalyst in the neighborhood of 400° is represented approximately by the equation:

$$\frac{-d(NH_3)}{dt} = k \frac{(NH_3)^{0.6}}{(H_2)^{0.9}} \tag{12}$$

This would be obtained by the theory advanced by Temkin and Pyzhev, if β in equation (11) is taken as three-tenths rather than one-half. Furthermore, by reasoning analogous to that used by them, it can be shown that the energy of activation for the decomposition of ammonia according to equation (12), would be about 48,000 cal. It seems, therefore, that their proposed theory would explain sufficiently well the kinetic expression that we have obtained for ammonia decomposition over iron catalyst 931.

It is interesting to note that equation (12) can be arrived at in another way. If we assume with Temkin and Pyzhev that the slow step in ammonia decomposition is the escape of the nitrogen molecules from the surface, we would expect the rate of ammonia decomposition to be proportional to (N)(N). In previous experiments it has been found by Emmett and Brunauer[17] that the amount of nitrogen adsorbed on the surface is proportional to one-sixth power of the partial pressure of the nitrogen in the gas phase. Now, assuming that the concentration of nitrogen atoms on the surface is determined by the partial pressure of nitrogen equivalent to that which would be in equilibrium with the ammonia–hydrogen mixture used, these equations follow

$$\begin{aligned} \frac{-d(NH_3)}{dt} &= k_2(N)(N) = k_3(N_2)^{1/6}(N_2)^{1/6} \\ &= k_3(N_2)^{1/3} = k_4 \frac{(NH_3)^{0.67}}{(H_2)^{1.00}} \end{aligned} \tag{13}$$

This equation is in agreement with the results indicated by the curves shown in Figs. 2 and 3.

Our results on catalyst 931 unlike those obtained by Winter over iron supported on alumina do not indicate an inhibitive effect of hydrogen greater than the inverse first power of the hydrogen partial pressure. Therefore one might be tempted to explain the kinetic results obtained in the decomposition over catalyst 931 in the usual way[18] by saying that the hydrogen is so strongly adsorbed as to make the rate of ammonia decomposition inversely proportional to the hydrogen partial pressure. This procedure meets with several difficulties. In the first place there is no indication that hydrogen is as strongly adsorbed as nitrogen in the temperature range in which ammonia decomposition over iron occurs. On the contrary, the experiments of Emmett and Brunauer[17] indicate that even at high pressures from equilibrium mixtures of nitrogen, hydrogen and ammonia the amount of nitrogen adsorbed is for a given partial pressure of nitrogen substantially the same as from pure nitrogen. This certainly does not indicate any strong preferential adsorption of hydrogen on iron in the temperature range in which the present experiments were carried out. Furthermore, it is very difficult to devise a mechanism for the decomposition which involves a dependence of the rate upon a power of the ammonia partial pressure between 0 and 1 if the slow step is assumed to be the rate of escape of nitrogen molecules and if the amount of adsorbed nitrogen is assumed proportional to the

---

[18] Hinshelwood, "Kinetics of Chemical Change," Clarendon Press, Oxford, 1940.

amount of adsorbed ammonia, the latter being expressed either by the Freundlich or the Langmuir adsorption equations. Accordingly, it seems that the fundamental assumptions of Temkin and Pyzhev relative to the kinetics of the catalytic decomposition of ammonia furnish a basis for understanding kinetic data for catalyst 931 that are otherwise difficult to interpret.

On turning to our experimental results on catalyst 954 we find a very surprising and unexpected behavior of the dependence of the rate of ammonia decomposition on the partial pressure of hydrogen, the partial pressure of ammonia and the temperature. The results do not seem explainable on the basis of any of the ideas suggested by Temkin and Pyzhev. Indeed, their complexity appears to defy accurate interpretation at the present time. Nevertheless, certain relationships and possible explanations can be pointed out even for the decomposition over 954.

Facts pertinent to the kinetics of the decomposition on catalyst 954 can be summarized with the help of Figs. 5, 6, 8, 9 and 10. A plot of log (rate of decomposition) against $1/T$ gives a curve having three distinct regions. In Fig. 8 these have been labelled as regions AB, BC and CD. From Fig. 10 it becomes evident that an increase in the ratio of ammonia to hydrogen causes the flat part of the curve, region BC, to shift to lower temperature. In the temperature region 400–420°, furthermore, the rate of ammonia decomposition follows kinetics that are almost the inverse of those usually obtained, the rate of 420° being proportional to $(H_2)^{1.2}/NH_3^{0.8}$.

Finally, as is evident from Fig. 9, a brief reduction period after the catalyst has reached a steady state results in a temporary but definite increase in activity only when the catalyst is operating above point C, Fig. 8.

It seems impossible to state with certainty the cause of the peculiar kinetics of ammonia decomposition over Fe–Al_2O_3 catalyst 954. The following is suggested as a possible picture. Catalyst 954, unlike catalyst 931, has been shown to be capable of holding —NH or possibly —NH_2 radicals on its surface at 100°.[19] This conclusion was inferred from the fact that chemisorbed nitrogen on catalyst 954 actually *increases* the hydrogen chemisorption instead of decreasing it volume for volume as it does on catalyst 931. This suggests that in the CD region (see Fig. 8) the surface may be covered with —NH or —NH_2 rather than —N, and that with such an adsorption some mechanism becomes possible that is faster than the one depending on $2(N)_{ads.} = N_{2gas}$ as the slow step. Possibly $2NH_{ads.} = N_{2gas} + H_{2gas}$, or $2NH_{2ads.} = N_2 + 2H_2$ may constitute the slow step in this low temperature region. The kinetics in region AB may conform to the hypothesis of Temkin and Pyzhev, region BC being merely a transition region between AB and CD.

The explanation here presented conforms to the reverse kinetics obtained at 420°—the rate being higher when the low ammonia–hydrogen ratio permits the $NH_{2ads.}$ (or $NH_{ads.}$) mechanism of region CD to operate. The data in Fig. 9 are consistent with the picture if one assumes that the equilibration of the surface with an ammonia–hydrogen mixture to form adsorbed NH_2 or NH radicals is faster than to form adsorbed nitrogen atoms. Finally to explain the postulated shift with increasing temperature from a surface covered with $NH_{2ads.}$ (or $NH_{ads.}$) to one covered with $N_{ads.}$ the series of steps represented by the following equation must be endothermic

$$NH_3 + Fe = \underset{\text{Surface}}{Fe\text{–}NH_2} + {}^1/_2H_2 = \underset{\text{Surface}}{Fe\text{–}NH} + H_2 = \underset{\text{Surface}}{Fe\text{–}N} + {}^3/_2H_2 \quad (14)$$

This is possible only if the heat of adsorption of nitrogen in equilibrium with the Fe–N surface is less than 26,000 cal. per mole. Thus

$$2Fe + 2NH_3 = \underset{\text{Surface}}{2Fe\text{–}N} + 3H_2 + x\text{ cal.} \quad (15)$$

$$N_2 + 3H_2 = 2NH_3 + 26{,}000\text{ cal.} \quad (16)$$

$$2Fe + N_2 = \underset{\text{Surface}}{2Fe\text{–}N} + y\text{ cal.} \quad (17)$$

x can be negative only if y is less than 26,000 cal. Actually on the singly promoted catalyst 921 (1.31% Al_2O_3), Emmett and Brunauer found that y was 35,000 cal. It is possible that on catalyst 954 (containing 10.2% Al_2O_3) y may be smaller than 35,000 calories. Furthermore, it is well known that the heat of adsorption of a gas on a solid frequently falls sharply with the fraction of the surface covered. It does not seem unreasonable that the heat of adsorption on that portion of the iron that is capable of yielding its nitrogen most rapidly may be less than 26,000 cal. If such be the case, then for a given ammonia–hydrogen mixture a shift to higher temperature will gradually result in the shift of the surface layer from $NH_{2ads.}$ (or $NH_{ads.}$) to $N_{ads.}$ by letting reaction (14) proceed from left to right.

---

(19) Brunauer and Emmett, THIS JOURNAL, 62, 1732 (1940).

The fact that the decomposition over 931 does not show a BC region but behaves as though it is in the AB region is consistent with the fact that 931 chemisorbs more nitrogen per unit iron surface at a given temperature and partial pressure of nitrogen than does 954 and with the inability of 931 to permit —NH or —NH_2 to be adsorbed on its surface.

Catalyst 973, as indicated in Figs. 11 and 12, appears to resemble catalyst 954 as far as the dependence of rate of ammonia decomposition on partial pressure of ammonia and hydrogen is concerned. The rate of decomposition on this pure iron catalyst at about 400° is practically independent of the partial pressure of ammonia and proportional to a power of H_2 varying between +2 and −0.6. The measurements made on this catalyst may be well summed up by saying that the kinetics in the range 380–430° appear in general to be characteristic of regions BC or CD. As regards possible formation of —NH or —NH_2 on its surface catalyst 973 is intermediate between catalyst 954 and catalyst 931.

Summary

Ammonia decomposition over three iron synthetic ammonia catalysts has been studied—catalyst 931 (1.3% Al_2O_3, 1.59% K_2O), catalyst 954 (10.2% Al_2O_3), catalyst 973 (0.15% Al_2O_3). The kinetics of the reaction over catalyst 931 were found to be very different from those of the reaction over catalysts 954 and 973.

Throughout the range of temperature and gas composition used the rate of the reaction over catalyst 931 is within experimental error proportional to $(P_{NH_3})^{0.6}/(P_{H_2})^{0.85}$. The apparent energy of activation is 45,600 ± 2000 cal.

Within a considerable range of temperature and gas composition the rate of the reaction over catalyst 954 is directly proportional to the partial pressure of hydrogen, indirectly proportional to the partial pressure of ammonia, and the apparent energy of activation is very small. At higher and lower temperatures the kinetics of the reaction more nearly approach those of the reaction over catalyst 931. The reaction kinetics over catalyst 973 are similar to those over catalyst 954.

Possible interpretations of the results are given.

BELTSVILLE, MARYLAND RECEIVED AUGUST 12, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Propionic Acid in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND THOMAS R. DEDELL[1]

The ionization constants of formic, acetic acids and water in dioxane–water mixtures have been determined from 0 to 50° by means of cells without liquid junction.[2] From the electromotive forces of the cells

$$H_2 \mid HP\ (m_1),\ NaP\ (m_2),\ NaCl\ (m_3),\ Dioxane\ (X),\ H_2O\ (Y) \mid AgCl\text{-}Ag$$

we have determined the ionization constant of propionic acid (HP) in these media over the same temperature range. From these results the free energy, heat content and entropy of ionization have been calculated.

In addition to these measurements of propionic acid solutions, we have summarized all our determinations of the ionization constants of formic, acetic acids and water in the dioxane–water mixtures by tabulating the constants of a suitable empirical equation. By means of equations derived from this one, all the thermodynamic functions which accompany the ionization processes may be computed.

Experimental Results

Three kilograms of Eastman Kodak Co. propionic acid was purified by fractional distillation in an all-glass column still. The final fraction of 400 g. distilled within 0.05°.

A solution of about four moles of the acid and a liter of water was prepared. The exact molality of this solution was determined by weight titration against standardized sodium hydroxide. The titrations checked to within 0.02%. The number of moles of propionic acid remaining in the solution was calculated and about half as many moles of standardized sodium hydroxide was added.

[1] This communication contains material from a dissertation presented by Thomas R. Dedell to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

[2] A complete bibliography is given in connection with Table III of this communication.