to be: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2}$, and for higher oxygen pressures: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}$. As in the case of the chlorine-sensitized oxidation of carbon monoxide, it has not yet been possible to develop a mechanism for the reaction capable of explaining the experimental rate law over the whole range. The two reactions have been compared and have been found to be very similar in several important respects. It has been concluded, therefore, that probably very similar mechanisms will be found to apply to both chlorine- and phosgene-sensitized oxidations.

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# The Reduction by Hydrogen and the Thermal Decomposition of Nitrides Made by the Reaction of Ammonia with Various Promoted and Unpromoted Iron Synthetic Ammonia Catalysts

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Phase rule investigations[1] have in the last few years shown that at least two nitrides of iron are formed by passing ammonia over iron in the temperature range 400 to 525°. At 450° and one atmosphere pressure, for example, an ammonia–hydrogen mixture containing between 30 and 70% ammonia will convert the iron into a body-centered cubic nitride whose composition is close to that of $Fe_4N$; ammonia percentages ranging from 70 to 100% will convert the $Fe_4N$ into an hexagonal nitride whose composition varies with the percentage of ammonia from one approximating $Fe_3N$ to one that closely corresponds to $Fe_2N$. As a part of a study being made of the mechanism by which iron catalysts are able to effect the synthesis of ammonia, the rates and nature of the decomposition and of the reduction by hydrogen of the various nitrides, prepared both from active and from inactive iron ammonia catalysts, have been determined.

## Experimental

The various nitrides were prepared by passing suitable ammonia–hydrogen mixtures at about 400° over finely divided iron synthetic ammonia catalysts obtained by the reduction in hydrogen of fused $Fe_3O_4$. Portions of each nitride preparation were analyzed by a modified Kjeldahl method; usually samples were also taken for x-ray photographs. Table I gives the composition of the samples and in some cases the nature of their x-ray pattern. Samples for both x-ray and chemical analysis were obtained in an oxygen-free nitrogen atmosphere.

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[1] Emmett, Hendricks and Brunauer, THIS JOURNAL, **52**, 1456 (1930); Lehrer, *Z. Elektrochem.*, **36**, 383 (1930); Eisenhut and Kaupp, *ibid.*, **36**, 392 (1930); Lehrer, *ibid.*, **36**, 460 (1930); Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, **53**, 1778 (1931).

TABLE I

COMPOSITION OF IRON NITRIDE SAMPLES

| Designation of nitride | Source of iron from which the nitride was made[a] | Nitrogen in sample, %[b] | X-Ray analysis |
|---|---|---|---|
| A-1 | Cat. 973 | 5.91 | Only $Fe_4N$ lines |
| A-2 | Cat. 973 | 11.00 | Only $Fe_3N$-$Fe_2N$ lines |
| B-1 | Cat. 984 | 6.04 | Only $Fe_4N$ lines |
| B-2 | B-1 | 10.81 | |
| B-3 | Cat. 984 | 7.53 | $Fe_3N$-$Fe_2N$ 50% $Fe_4N$ 50% |
| B-5 | Cat. 984* | 5.64 | |
| C-1 | Cat. 921 | 6.02 | Only $Fe_4N$ lines |
| C-2 | C-1[c] | | |
| D-1 | Cat. 920 | 6.01 | Only $Fe_4N$ lines |
| D-2 | Cat. 920* | 7.89 | |
| D-3 | D-2 | 6.02 | |
| E-1 | Iron oxalate[d] | | |

[a] The samples designated by * were 8–14 mesh; all others were ground to pass a 200-mesh screen. The catalysts were obtained by the reduction in hydrogen of variously promoted fused magnetites: 984 contains 2.92% $Al_2O_3$ and 1.05% $K_2O$; 921, 1.05% $Al_2O_3$; 920, 0.2% $K_2O$; 973, 0.15% $Al_2O_3$. [b] The formula $Fe_4N$ corresponds to 5.90% nitrogen; $Fe_2N$, to 11.14% nitrogen. [c] C-1 was flushed with $N_2$ at 100° for two hours. [d] This $Fe_4N$ sample was made by Mr. Brunauer and used by him in phase rule studies.

The decomposition experiments were carried out in an all-glass apparatus, the evolved nitrogen being measured in a gas buret at about atmospheric pressure. The furnace used was fitted with an aluminum block. When once adjusted the furnace could be kept at a given temperature by controlling it with hand rheostats, the variation being about 2° during a decomposition run. The experimental uncertainty in each determination of the amount of nitrogen evolved per five minutes per gram of iron was about 0.03 cc.

The reduction experiments were carried out by bringing the nitride samples to the desired temperature in a stream of nitrogen and then quickly replacing the nitrogen with pure hydrogen. The exit gas was analyzed continually for ammonia.

## Results on the Thermal Decomposition of the Nitrides of Iron

(a) **$Fe_4N$ Decomposition.**—The general nature of the decompositions of the various $Fe_4N$ samples can be judged from the types of curves shown in Fig. 1. The decompositions seem to be autocatalytic, the rates being low at first and increasing as a function of time. One peculiar exception to this rule was noted. The decomposition rate of the $Fe_4N$ made from a doubly promoted catalyst was in a certain temperature range practically independent of the nitrogen content of the sample. This is illustrated in a run on sample B-3, Fig. 1. The first portion of the curve represents the decomposition of a little $Fe_3N$ known to be present. The rate of nitrogen evolution after the sample had attained a composition corresponding to $Fe_4N$ was practically constant at 0.28 to 0.32 cc. of nitrogen per g. of Fe for about thirteen hours; when about 95% of the nitrogen had been evolved the rate decreased rapidly, dropping from 0.3 cc. to less than 0.01 cc. per five minutes per gram of Fe in about one and one-half hours. This zero order solid decomposition made possible the determination of the temperature coefficient of nitrogen evolution from $Fe_4N$.

Temperature coefficients were determined on four $Fe_4N$ samples, three of them being taken from nitride preparation B-1 and the fourth from an 8–14 mesh sample designated as B-5. The logarithms of the rates of decomposition in these temperature coefficient runs are shown plotted against $1/T$ in Fig. 2. Each point on these curves represents an hour's decomposition run at a given temperature; no change in rate was observed in any of these cases during the hour's run. It is evident however that the temperature coefficient calculated by going back from a higher to a lower temperature is considerably smaller than that obtained by going from a lower to a higher temperature. Thus in run 26 the slope of the line connecting points a, b and c corresponds to 69,000 calories and that connecting points d, e and f, 52,000 calories; however, one connecting points c and d indicates an energy of activation of only 42,000 calories. The real energy of activation of the decomposition is apparently between the two extreme values. From the combined results it is concluded that the energy of activation for the reaction $Fe_4N = 4Fe + 1/2N_2$ is about 50,000 calories.

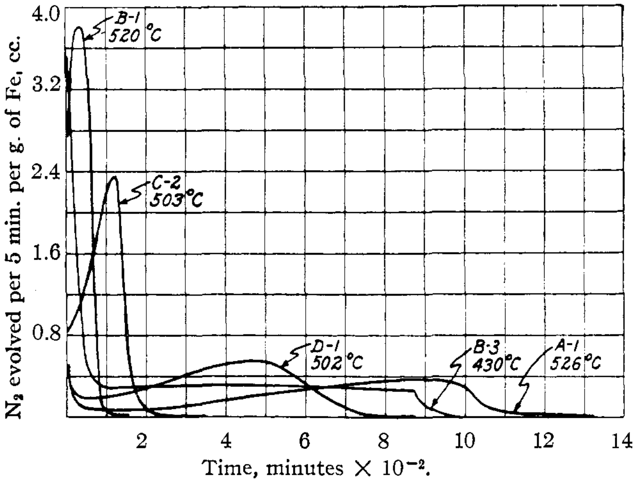

Fig. 1.—Rate of decomposition of $Fe_4N$ prepared from various iron synthetic ammonia catalysts.

In the course of the experiments on thermal decomposition it became evident that some unknown factor was causing the rate of decomposition of the $Fe_4N$ made from doubly promoted catalysts to vary from run to run. In particular, it became evident that the first run (always made within twenty-four hours after preparing the $Fe_4N$ sample) gave higher results than any of the succeeding runs. The cause of this decrease after the initial run was not satisfactorily ascertained. Increased precautions in excluding possible traces of water vapor and of oxygen from the sample during its storage after the first run seemed to decrease the effect; however, it was still very much in evidence in the last few experiments made. To illustrate the magnitude of the disturbing factor and at the same time show the relative approximate rates of decomposition of the various nitrides studied, the logarithms of the maximum rates observed are plotted against 1/*T* in Fig. 2. It must of course be borne in mind that only in the case of the zero order decompositions of the doubly promoted sample is such a method of comparing rates quantitative. Runs 36, 38 and 13 on sample B were all "first runs," as was also run 41 on sample D; a comparison of the rates in these four runs indicates that $Fe_4N$ prepared from an active synthetic ammonia catalyst, B, decomposes much more rapidly than that made from a comparatively inactive catalyst, D. Unfortunately the runs on the pure iron catalyst (2 and 4, Fig. 2) and on the catalyst promoted with $Al_2O_3$ (10 and 11, Fig. 2) are either "second" runs or made several days after the preparation of the samples. Hence rate comparisons involving these two last catalysts are not warranted. The decomposition of the $Fe_4N$ made from iron obtained by the reduction of ferric oxalate was by far the slowest of all nitride samples tried (Run 6).

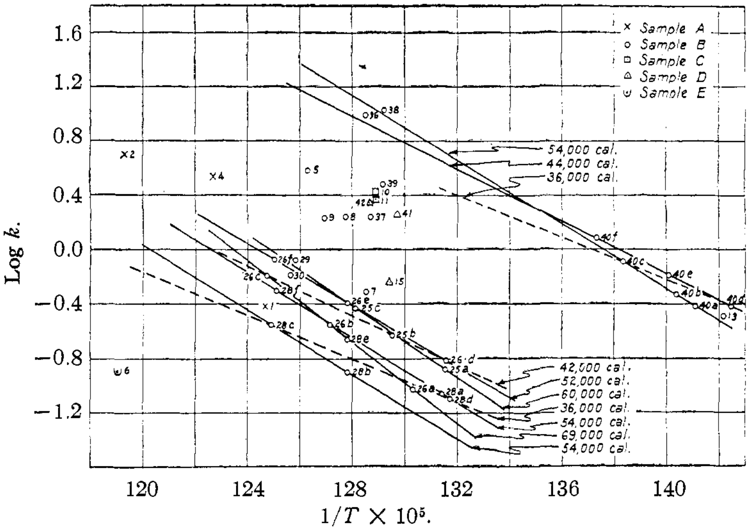

Fig. 2.—Variation of the rate of decomposition of $Fe_4N$ with the temperature and with the type of catalyst used as a source of iron. The temperature coefficient of $Fe_4N$ decomposition as determined by runs 25, 26, 28 and 40 is expressed in terms of the energy of activation, *E*, involved in the decomposition.

Since it appeared that traces of poison might affect the rate of decomposition of the nitrides quite appreciably, a few experiments were made in which poisons were deliberately added to the nitrides and the effect on the rate noticed. The addition of about 0.2 cc. of either hydrogen sulfide or oxygen to the doubly promoted $Fe_4N$ sample at the end of run 28 produced no appreciable change in rate; however, an additional 1.3 cc. of hydrogen sulfide caused the rate to drop immediately from 0.25 to 0.014 cc. per five-minute period.

(b) **$Fe_2N$ Decomposition.**—Typical decomposition curves for $Fe_2N$ samples are shown in Fig. 3. The decomposition is of a non-autocatalytic nature, decreasing rapidly with the evolution of nitrogen until a composition close to that of $Fe_3N$ is reached. The rate of decomposition of $Fe_3N$ into $Fe_4N$ is much slower than the initial $Fe_2N$ rate, is many times faster than the decomposition of $Fe_4N$, and at several temperatures is nearly independent of the fraction of the sample decomposed.

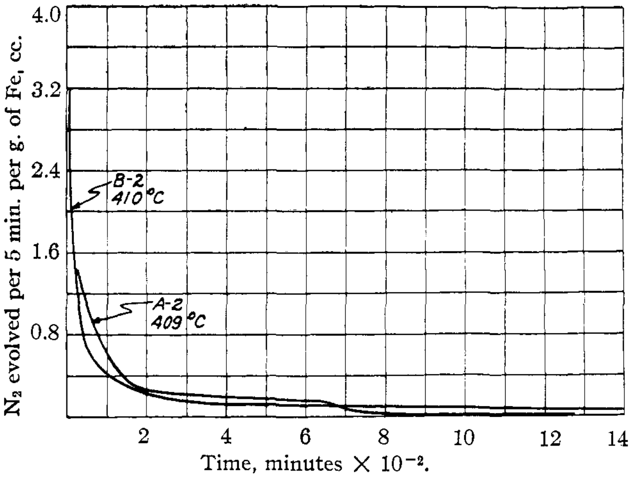

Fig. 3.—Rate of decomposition of $Fe_2N$ into $Fe_4N$.

## Reduction of the Iron Nitrides by Hydrogen

The $Fe_2N$ samples prepared from the various catalysts reduce much more rapidly in hydrogen at about 180° than do the $Fe_4N$ samples. Typical $Fe_4N$ reduction curves, as shown in Fig. 4, indicate that the reaction is slightly if at all autocatalytic. A distinct maximum in the curve was always obtained about ten or fifteen minutes after the beginning of a two-hour reduction run; this apparent maximum might, however, be due to the adsorption of ammonia by the samples, since these were initially carefully flushed with nitrogen to zero ammonia content at the temperature of the run. The agreement between successive reduction runs is illustrated by runs 33 and 34 at 245°.

Two reduction curves for $Fe_2N$ shown in Fig. 4 are characterized by unusually sharp maxima. x-Ray photographs of samples which during a similar run were removed before reaching the maximum reduction rate and at two successive points after reaching the maximum showed increasing amounts of Fe, decreasing amounts of $Fe_2N$ and $Fe_3N$, and no $Fe_4N$. The photographs were not sufficiently clear to permit differentiation between $Fe_2N$ and $Fe_3N$.

## Discussion

Mittasch, Kuss and Emert[2] have studied the rate of ammonia decomposition over $Fe_2N$ and compared it with the rate of nitrogen evolution from $Fe_2N$ *in vacuo*. In the course of their work they measured the rate of nitrogen evolution from a sample of promoted iron synthetic ammonia catalyst that had been converted into $Fe_2N$. The decomposition curves for 350 and 400° published in Fig. 8 of their article permit one to estimate approximately the rates of decomposition of the $Fe_4N$ portion of their nitrides at these two temperatures. The temperature coefficient calculated from the curves corresponds to about 45,000 calories energy of activation for the $Fe_4N$ decomposition, which agrees satisfactorily with the average value, 50,000 calories, found in the present work. They point out that the $Fe_2N$ decomposed at practically a constant rate until about one-half the nitrogen was evolved. Our own results showed similarly constant rates for $Fe_3N$ and $Fe_4N$ under favorable conditions but not for $Fe_2N$.

Winter[3] has recently studied the rate of ammonia decomposition over iron. In the course of his experiments he found that the energy of activation of the decomposition was about 50,000 calories per mole of ammonia. Furthermore, the kinetics he obtained indicated that the slow step in the reaction was the escape of nitrogen from the surface of the catalyst. It is interesting to note that the temperature coefficient of the decomposition of $Fe_4N$ in our own experiments corresponded to an energy of activation of about this same value.

On several different occasions attempts have been made to correlate the rate of surface reactions with the frequency, $f$, with which the energy of a surface atom or molecule has an opportunity to readjust itself. Thus, for example, Topley[4] pointed out that if it be assumed that the molecules of adsorbed ammonia on tungsten or platinum have a chance to readjust their energies $10^{12}$ times per second, then from the known areas of metal involved it can be shown that the observed rate can be accounted for by assuming that the fraction $e^{-E/RT}$ of these energy changes will result in the adsorbed ammonia molecules picking up the observed energy of activation $E$. The value $10^{12}$ is about the magnitude of the "restrahlen"

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(2) Mittasch, Kuss and Emert, *Z. Elektrochem.*, **34**, 829 (1928).

(3) Winter, *Z. physik. Chem.*, **B13**, 401 (1931).

(4) Topley, *Nature*, **128**, 115 (1931).

vibration frequencies for solids. In an analogous way it is interesting to show by calculation whether or not the observed rate of nitrogen evolution in the zero order decomposition of $Fe_4N$ made from a doubly promoted catalyst can be accounted for by similar postulates. If every nitrogen atom (or molecule) on the surface of the $Fe_4N$ sample gets a chance to change its energy content $f$ times per second, and if all atoms (or molecules) picking up the 50,000 calories per mole average energy of activation noted in the present work escape from the surface, then the rate $r$ of nitrogen evolution in cc./min./g. of iron will be given by the equation $nfe^{-E/RT}$ (60) $= r$, where $n$ is the number of cc. of nitrogen constituting a monomolecular surface layer on 1 g. of iron, $f$ is the atomic vibration frequency for Fe (about $10^{12}$ times per second), and $E$ is the energy of activation observed in the present experiments for the thermal decomposition of $Fe_4N$. An approximate value for $n$ obtainable from the poisoning experiments of Almquist and Black[5] and from some recent adsorption experiments of Emmett and Brunauer[6] is 1 cc. of nitrogen per gram of iron. Inserting 50,000 calories for $E$ and $10^{12}$ for $f$, the calculated value of $r$ is 0.17 cc. per minute per gram of iron at 430°. The experimental value is 0.06 cc. per gram. This agreement is of course much better than the accuracy with which the values of $E$ or of $n$ are known. It indicates however that the observed rate is of the right magnitude to be explained on such a basis.

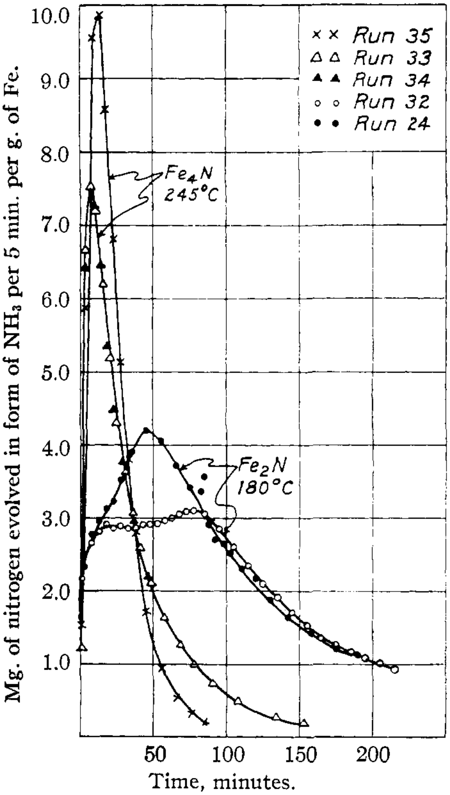

Fig. 4.—Rate of reduction of $Fe_4N$ and $Fe_2N$ by hydrogen.

Attention should be called to one other interesting experimental observation in connection with the thermal decomposition of $Fe_4N$ made from a doubly promoted catalyst. In a decomposition experiment on sample B-3 shown in Fig. 1 and in three other similar experiments on $Fe_4N$ samples from this same doubly promoted catalyst, an abrupt decrease in the rate

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(5) Almquist and Black, THIS JOURNAL, **48**, 2814 (1926).

(6) Emmett and Brunauer, *ibid.*, **55**, 1738 (1933).

of nitrogen evolution occurred at the end of the run. The volume of gas evolved after the beginning of this abrupt rate decrease was in all cases about that estimated to correspond to a monomolecular surface layer, being between 1 and 3 cc. of nitrogen per gram of iron. This is in accord with the hypothesis that the escape of nitrogen from the surface of the iron is the slowest step in the decomposition, the sudden break in the rate curve being naturally associated with the point at which all except the surface nitrogen has escaped. However, if the rate of diffusion of nitrogen through iron at 430° is sufficiently great, then the 1 to 3 cc. of nitrogen evolved after the break might include some of the dissolved nitrogen as well as nitrogen adsorbed on the surface of the iron.

The reduction curves for $Fe_2N$ shown in Fig. 4 can be explained as a summation of two non-autocatalytic reactions: $3/2H_2 + 3Fe_2N = 2Fe_3N + NH_3$ and $3/2H_2 + Fe_3N = 3Fe + NH_3$. The very sharp maxima in the $Fe_2N$ reduction curves seem more consistent with this interpretation than with the conclusion that the reduction of $Fe_2N$ proceeds to Fe in one step and is autocatalytic.

In one experiment on the reduction of $Fe_2N$ part of the experimental points were obtained by flushing out any adsorbed ammonia between each five-minute reduction period. These points and those obtained without such flushing lay equally well on the reduction curve, thus showing definitely that the adsorption of ammonia is not sufficiently large to account for the initially low ammonia values obtained at the start of each $Fe_2N$ reduction run..

## Summary

The rates of decomposition and of reduction by hydrogen of $Fe_4N$ and $Fe_2N$ made from active and from rather inactive iron synthetic ammonia catalysts have been determined. The decomposition of $Fe_4N$ entails an energy of activation of about 50,000 calories. $Fe_4N$ prepared from active catalysts decomposes more rapidly than that prepared from less active catalysts.

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