[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE POISONING ACTION OF WATER VAPOR AT HIGH PRESSURE ON IRON SYNTHETIC AMMONIA CATALYSTS

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Introduction

The mechanism of the poisoning action of water vapor and of oxygen on pure and promoted iron catalysts was first studied by Almquist and Black.[1] They found that during the passage of mixtures of 3:1 hydrogen–nitrogen gas containing 0.016% or more water vapor over iron synthetic ammonia catalysts at 444°, appreciable amounts of oxygen were retained by the catalysts. Concurrently with the addition of this oxygen, the activity of the catalyst toward the synthesis of ammonia at one atmosphere pressure decreased. According to an extrapolation from the data of Eastman and Evans,[2] ordinary massive iron is not oxidized at this temperature by a water vapor–hydrogen mixture containing less than about 16% of water vapor. Accordingly, Almquist[3] concluded that oxygen taken up by the catalyst was in the form of a "surface oxide" resulting from the interaction of water vapor and the active surface iron atoms of high degree of unsaturation. By assuming that this oxide phase was the same as ordinary Fe_3O_4, he calculated that the difference in free energy between crystalline iron and the more active surface iron atoms is of the order of 12,000 calories per gram atom of iron. By making the further assumptions that the active atoms taking part in the surface oxide formation are also responsible for most of the ammonia synthesis, and that the combination of active iron atoms and oxygen atoms occurs in the ratio of one to one, he calculated that in the pure iron catalyst approximately one atom out of every two thousand is active toward ammonia synthesis, whereas in the iron catalysts promoted with aluminum one atom out of every two hundred is active.

The investigations described in this paper were undertaken for the purpose of extending the experiments of Almquist and Black to higher pressures. It is well known that the activity of a synthetic ammonia catalyst at high pressures cannot be predicted from its activity at one atmosphere, since the variation of the efficiency of a catalyst with pressure is different for each individual catalyst. As Almquist and Black pointed out, catalyst 921, an iron catalyst promoted with aluminum, is slightly more active at atmospheric pressure than catalyst 922, an iron catalyst promoted with both Al_2O_3 and K_2O, whereas at 100 atmospheres' pressure

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[1] Almquist and Black, THIS JOURNAL, **48**, 2814 (1926).

[2] Eastman and Evans, *ibid.*, **46**, 896 (1924).

[3] Almquist, *ibid.*, **48**, 2820 (1926).

catalyst 922 is 50% more active than catalyst 921. Furthermore, it was observed in the previous poisoning work that the higher the activity of a catalyst at one atmosphere pressure on pure 3:1 gas, the greater the amount of surface oxide it is capable of picking up. Accordingly, it seemed that a comparison of the activities of several synthetic ammonia catalysts with the amounts of oxide formed in the presence of small percentages of water vapor in the hydrogen–nitrogen mixture at pressures up to 100 atmospheres would probably give some clue to the cause of the pressure coefficients in synthetic ammonia catalysts and would at the same time furnish additional information concerning the mechanism of the poisoning of iron catalysts by water vapor.

Apparatus

The apparatus used in the present experiments was designed to permit the passage, at a definite rate, of a known mixture of hydrogen, nitrogen, and water vapor over an activated synthetic ammonia catalyst at pressures between 1 and 100 atmospheres, and to obtain a complete analysis of the gases leaving the catalyst bomb. The difference between the water content of the influent and effluent gases has been considered to be a measure of the amount of water vapor reacting with the catalyst to form oxide.

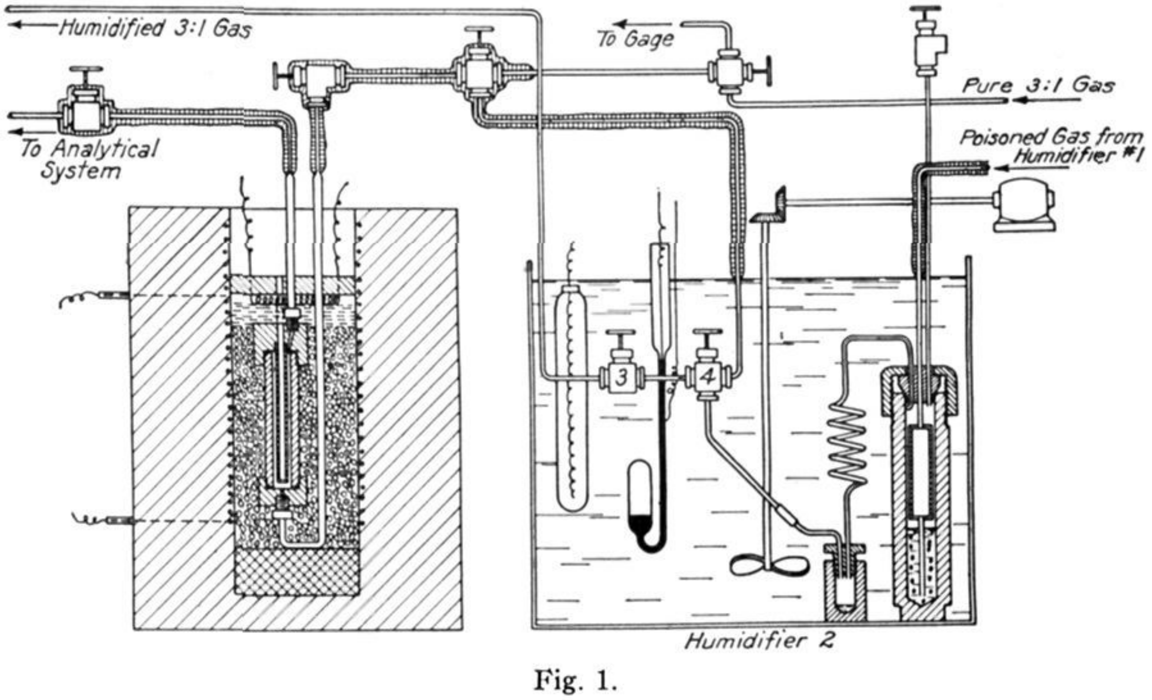

Fig. 1.

The high pressure supply of 3:1 hydrogen–nitrogen gas was the same as that described in a number of publications from this Laboratory.[4] It was obtained by burning electrolytic hydrogen in a limited supply of air and compressing the resulting 3:1 gas mixture to 2500 or 3000 lb. By means of an automatic pressure regulator[5] working in conjunction with an especially constructed pressure gage, any pressure between 30 and 100 atmospheres could be automatically maintained in the reaction bomb. The compressed gas mixture was freed of oxygen and carbon monoxide by passage over hot cop-

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[4] Larson and Dodge, THIS JOURNAL, **45,** 2918 (1923).

[5] Larson and Karrer, *J. Ind. Eng. Chem.*, **14,** 1012 (1922).

per and hot nickel, respectively. It was then passed through an ice-bath for condensing most of the water, and finally dried by passage through a series of five bombs, the first two filled with soda lime, the next with anhydrous aluminum oxide gel and the last two with pieces of fused potassium hydroxide. The resulting gas contained only a few thousandths of a per cent. of water vapor and was checked for purity during the runs by passage over a pilot catalyst maintained at 444° by a bath of boiling sulfur.

From the purifiers, the 3:1 gas mixture passed into the apparatus shown in Fig. 1. By appropriate adjustment of valves, the pure dry gas could be sent either directly into the reaction bomb or through a trap into humidifier No. 1 (not shown in diagram), then into humidifier No. 2 and finally into the reaction bomb. The first of the two humidifiers was maintained at a temperature approximately 5° above that of the final humidifier. Temperature was maintained accurately in the latter to ±0.1°. Calibration runs indicated that complete humidification was obtained without attendant mist or spray formation.

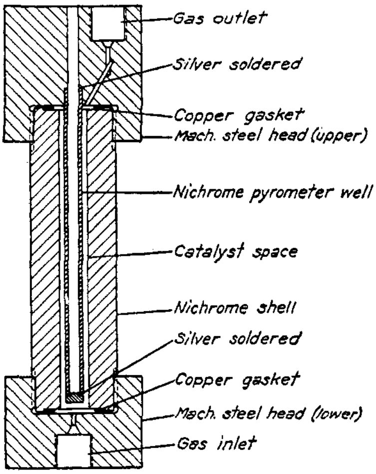

Fig. 2.

The reaction bomb containing the catalyst is shown in Fig. 2. It was made of nichrome steel and was so designed as to permit the placing of the 16-mesh catalyst particles in a thin layer around a thermocouple well extending the full length of the bomb. Uniform external heating was obtained by packing the bomb with mossy copper into an electric furnace as shown in Fig. 1. The furnace contained an alundum core wound with nichrome wire and packed with a thick layer of "85% Magnesia" into an outer iron jacket. An auxiliary heater on the top of the furnace permitted the temperature gradient along the length of the furnace to be kept down to 3°. The temperature of the bomb was measured by an alumel–chromel thermocouple in conjunction with a Leeds and Northrup type K potentiometer and was maintained by hand regulation of the furnace to ±3° during a particular run. All other temperatures were read by thermometers checked against calibrated Bureau of Standards thermometers.

Procedure

At the beginning of a series of runs the catalyst bomb containing approximately 5.3 cc. of the desired catalyst was packed into the electric furnace and connected as shown in Fig. 1. The catalyst was reduced with a 3:1 hydrogen–nitrogen mixture at one atmosphere pressure for a number of hours at temperatures below 450°. It was finally brought to a steady reactive state toward ammonia synthesis at 100 atmospheres' pressure.

In each run, at a given time, t_0, poisoned gas from the humidifiers was substituted for the stream of pure gas that had been passing through the reaction bomb at the desired temperature and pressure. At the same time, a stream of the high pressure humidified gas was reduced to one atmosphere by valve 3, and passed through a weighed phosphorus pentoxide tube into a wet gas meter. This blank run was used as a check on the water vapor content of the poisoned gas. The passage of poisoned gas through the catalyst bomb was continued until analysis of the exit gas showed a constant percentage of ammonia. Both the blank and poisoning runs were then terminated simultaneously. The rate of gas passage was regulated to 5000 space velocity. The total volume of gas passing the reaction bomb was measured by a carefully calibrated and frequently checked wet gas meter. The exit gas from the bomb passed first through an apparatus for quantitatively determining the water vapor, then through a series of boric acid solutions for absorbing all of the ammonia and finally into a wet gas meter. At frequent intervals during each run the following data were recorded: the temperature of the water in each of the gas meters, the barometric pressure, the temperature of the final humidifier, the readings of the gas meters and the concentration of ammonia in the exit gas. The method adopted in the present experiment for analyzing a stream of gas for water vapor in the presence of large concentrations of ammonia seems of sufficient general interest to merit a rather detailed description.

Method for the Determination of Small Concentrations of Water Vapor in a Gas Containing Large Percentages of NH_3.—Ammonia reacts with most of the usual chemical drying agents including phosphorus pentoxide, dehydrite and calcium chloride. Consequently none of these substances is suitable as a drying material for determining small quantities of water vapor in a gas containing large and variable amounts of ammonia. As pointed out by Almquist and Black,[1] fused potassium hydroxide will take up water vapor without absorbing ammonia. However, for the present experiments the quantities of water vapor were so small that it was found impracticable to prepare tubes of fused potassium hydroxide that would quantitatively absorb all of the water vapor during the hour run and would, at the same time, permit the free passage of the desired flow of approximately 420 cc. of gas per minute. Consequently, U-tubes filled with 20-mesh fused and crushed potassium hydroxide particles were used only for removing the water from the few samples of gas analyzed for ammonia during each run. The main portion of the exit gases was analyzed for water vapor by the apparatus shown in Fig. 3.

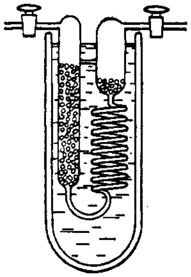

Fig. 3.

A U-tube filled with glass beads was immersed in an alcohol–carbon dioxide bath at −78°. In each run the first of the gas passing through the tube contained sufficient ammonia to permit the condensation of a considerable amount of liquid ammonia in the bottom of the bead tube. The water vapor of the gas passing into the U-tube was found to be completely absorbed by the liquid ammonia. At the end of each run, the liquid ammonia remaining in the U-tube was removed by flushing with a few liters of pure dry 3:1 hydrogen–nitrogen gas. The tube was permitted to come to room temperature, wiped carefully with alcohol and weighed. The slight excess gas pressure in the tube was then released, care being taken not to blow any liquid particles of water out of the tube. After being reweighed, the bead tube was flushed free of all adsorbed and dissolved ammonia. This latter was collected in distilled water and titrated against 0.01 N sulfuric acid, using sodium alizarin sulfonate as indicator. From these data, the total weight of water passing the catalyst could readily be obtained. Blank runs in which as much as 500 mg. of moisture was passed into the tube showed quantitative absorption of the water vapor.

Experimental Results

Data were obtained on fresh samples of three catalysts designated in the present work as 922, 921 and 918 and identical with the similarly numbered catalysts used by Almquist and Black. All of the catalysts consisted essentially of metallic iron. Catalyst 921 contained 1.31% Al_2O_3; catalyst 922 was promoted with 1.05% Al_2O_3 and 0.25% K_2O; catalyst 918 was a sample of pure iron containing no promoter. All were obtained by reducing with 3:1 hydrogen–nitrogen gas Fe_3O_4 prepared by a fusion method already described.[6] Their activities as ammonia catalysts under various temperature and pressure conditions have been described by Almquist and Crittenden.[7]

The manner in which the percentage of ammonia formed by a catalyst varies with time during a poisoning experiment is illustrated in Fig. 4. The curves are of the same general type as those shown by Almquist and Black for one atmosphere poisoning. A definite and constant activity toward the catalytic synthesis of ammonia is reached within a few minutes after the change from pure to poisoned gas. The constancy of this level was checked in several experiments by running on poisoned gas for as long as two hours without obtaining any indication of a further decrease in the activity of the catalyst. The activity of a promoted catalyst returns practically to its original value within less than an hour after changing from poisoned to pure gas. However, a definite decrease in the activity of the promoted catalysts on repeated poisoning and reduction could be detected. Thus in the course of twelve poisoning runs of approximately one hour duration each and the reduction of the oxide formed, the doubly promoted catalyst 922 gradually decreased from an activity corresponding to 12.5% ammonia produced at 100 atm., 450° and 5000 space velocity to one corresponding to 9.96% ammonia produced under similar conditions. The singly promoted catalyst 921 also became less active though not so rapidly as catalyst 922; during eighteen poisoning runs it decreased

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[6] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[7] Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

from a conversion of 8.88% ammonia to one of 7.56% ammonia. The catalytic activity on poisoned gas also decreased. In the above-mentioned runs on catalyst 922 in the presence of 0.32% water vapor, the percentage of ammonia in the exit gas dropped from the value 2.3 to 1.34, whereas that produced by catalyst 921 decreased from 2.92 to 2.27% ammonia. This decrease in activity with long exposure to poisoned gas is probably a manifestation of the same property by virtue of which a doubly promoted catalyst is found to be much less active if reduced at 100 atmospheres' pressure than if reduced at one atmosphere, the high partial pressure of water vapor present during reduction acting effectively the same as a long-continued poisoning run.

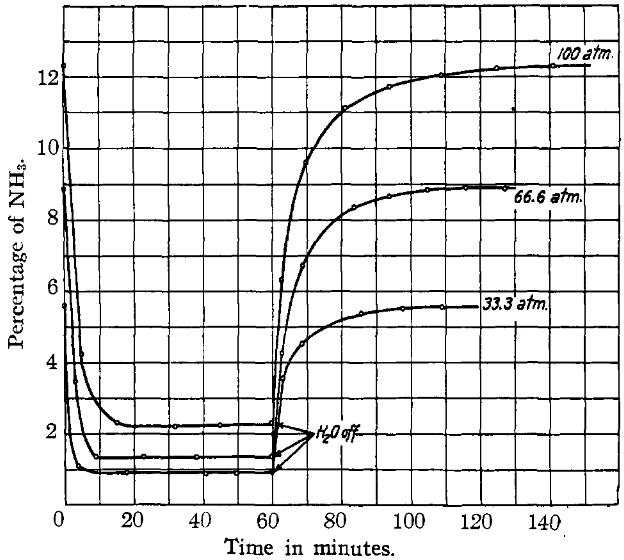

Fig. 4.—Effect of 0.32% water vapor on the activity of catalyst 922 at various pressures.

In Fig. 5 are shown curves based upon measurements made at 33, 66 and 100 atmospheres, representing the change of efficiency with pressure for catalysts 921 and 922, both when operating on pure and on poisoned gas. It is evident that the presence of 0.32% water vapor caused the doubly promoted catalyst 922 to decrease by not only a larger percentage of its activity than did the singly promoted catalyst 921, but to an actually lower level than catalyst 921. However, since the slope of the pressure efficiency curve for catalyst 922 is based upon an average of several successive runs during which the catalytic activity changed materially, no significance can be attached to the apparent similarity between the slopes of the pressure efficiency curves on poisoned gas runs of catalysts 921 and 922.

Unfortunately, the activity of the pure iron catalyst 918 decreased very rapidly. It was possible to make only two 100-atmosphere poisoning runs on a given charge of the catalyst and even in these the catalyst was effecting only a 1% conversion to ammonia at 100 atmospheres, 450° and 5000 space velocity.

The results of the poisoning experiments are summarized in Table I. Here are shown the average amounts of oxide formed on the 5 cc. of catalyst used under the different experimental conditions encountered. The average of several blank runs is also shown. During these latter runs the procedure of the regular poisoning experiments was followed, though no catalyst was placed in the reaction bomb. All blank values were within the range −0.6 mg. and +0.4 mg. There are also shown a few runs at temperatures other than 450°.

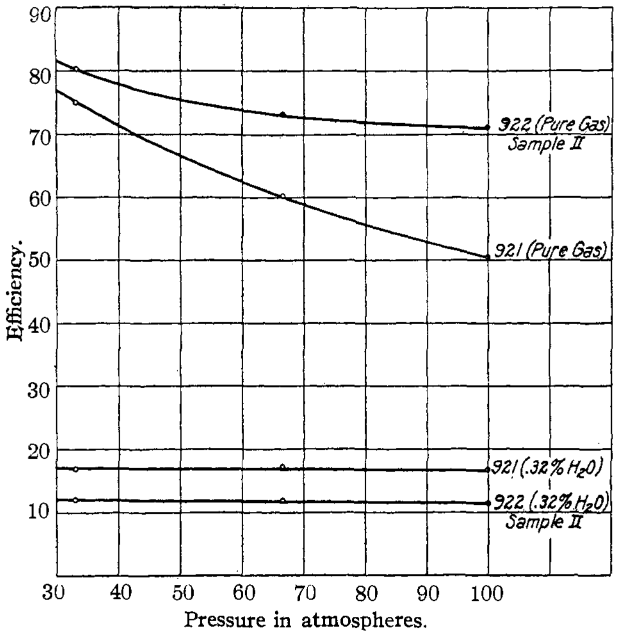

Fig. 5.—Variation with pressure of the efficiency of singly and doubly promoted iron catalysts on pure and poisoned 3:1 gas.

It is estimated that each individual reading might involve an error as large as ±3 mg. The values obtained as an average of several readings are, however, more reliable. The maximum deviation from the mean in the four blank runs was 0.6 mg.; in the two runs on catalyst 918 it was 0.8 mg.

The results recorded in Table I seem to warrant the following conclusions.

1. The amount of oxygen picked up by a particular catalyst at 450° is approximately proportional to the $\sqrt{P_{H_2O}}/\sqrt{P_{H_2}}$ throughout the range of P_{H_2O} and P_{H_2} values used in the present experiments.

2. At high pressure promoted synthetic ammonia catalysts take up much more oxygen than do pure iron catalysts. It will be noted that the experimental errors were too large to permit a decision as to whether the singly or doubly promoted catalyst picked up the more oxygen.

3. The temperature coefficient of the surface oxide formation is small. Only two runs were made at 400 and one at 500°. The sign of the temperature coefficient is accordingly uncertain.

4. The oxygen content of the catalyst is present as oxide and not as "adsorbed" water molecules, since the number of the latter would doubtless be a function of the absolute P_{H_2O} and not of $\sqrt{P_{H_2O}/P_{H_2}}$.

TABLE I

SURFACE OXIDE RETAINED BY VARIOUS CATALYSTS

5000 Space Velocity

						Ratio of total Fe atoms to active Fe atoms	
Catalyst	Temp., °C.	H_2O in 3:1 gas, %	Press., (atm. abs.)	No. of expts. averaged	Mg. of H_2O retained by catalyst as oxide	Present expts., 1–100 atm.	1 atmosphere, Almquist and Black
918	450	0.34	100.0	2	0.3	11,000	1680
921	450	.08	100.0	1	4.1	810	404
	450	.33	100.0	8	11.3	294	218
	450	.48	100.0	1	13.1	253	183
	450	.33	66.6	2	10.1	328	218
	450	.32	33.3	2	7.5	443	218
	400	.33	100.0	2	7.3	455	...
	470	.33	100.0	1	8.0	415	...
	500	.33	100.0	1	10.4	319	...
922	450	.08	100.0	1	5.0	636	441
Sample I	450	.33	100.0	6	12.3	259	253
	450	.32	66.6	3	11.9	267	253
	450	.32	33.3	2	10.1	315	253
922	450	.08	100.0	1	5.3	590	441
Sample II	450	.33	100.0	4(1)[a]	10.6(8.0)[a]	295(391)[a]	253
	450	.48	100.0	1	13.7	228	...
	450	1.23	33.3	1	21.9	143	...
	450	0.33	1.0	2(3)[a]	7.0(8.2)[a]	447(381)[a]	253
Blank runs	450	.32	100.0	4	−0.2	...	...

[a] In a number of runs the oxide retained by the catalyst was also determined by reduction. The quantity of oxide so determined is given in parentheses.

Discussion

The oxide formed on the promoted iron catalysts in the present experiments is believed to be due predominantly to the production of a surface oxide only and not to the formation of solid solutions of oxygen or iron oxide in iron. The evidence in favor of this conclusion is two-fold. In the first place, the rate of formation and of removal of a large part of the oxide in the poisoning experiments is very rapid. Experiments showed, in fact, that most of the oxide was formed during the first seven or eight minutes after the initial contact of the poison with the catalyst and removed in a similar period after the replacing of the poisoned gas by pure gas. No oxide was formed during that period in which the exit ammonia value had attained the constant low value. This is certainly not characteristic of the manner in which water would distribute itself throughout the mass of catalyst as a uniform solution of oxygen or iron oxide in iron. In the second place, the amount of oxide is some ten-fold greater in the case of the promoted catalysts than in the case of pure iron catalysts, in spite of the fact that the rate of reduction and hence presumably also of oxidation of the pure iron at 450° is several fold greater than that of promoted iron. Were the oxide present in the form of solid solution, it would seem logical to expect the pure iron sample to reach saturation more rapidly than the promoted iron samples, and to retain an equal amount of oxygen.

It is interesting to note that the 0.1% surface oxide formed on doubly promoted catalysts in the present experiments at 450° with 0.32% water vapor is about the same as reported recently by Krings and Kempkens[8] to be formed at 700° by the exposure of pure iron samples to a mixture of steam and hydrogen containing approximately 30% water vapor, a percentage slightly smaller than is necessary to form the stable ferrous oxide. In view of the fact that the ten-fold greater $\sqrt{P_{H_2O}}$ in their experiments as compared to ours would tend to compensate for their using pure iron at 700° in contrast to promoted iron at 450°, it seems very probable that the 0.1% oxygen content reported by them to be the maximum amount of oxide formed on the iron samples without converting them partially to the ferrous oxide phase is a surface oxide.

In Table I are compared the ratios of total iron atoms to iron atoms picking up oxygen atoms under the various conditions of pressure and water vapor concentration used in the present experiments. It is here assumed that no more than one oxygen atom is picked up by a single iron atom. The ratios similarly calculated from the work of Almquist and Black for one atmosphere poisoning experiments are shown in the same table. Considering the difficulties involved in the oxide determination in the high pressure experiments, the agreement is satisfactory.

Almquist and Black conclude that the percentage of ammonia obtained in their experiments is inversely proportional to the oxide content of the catalyst. Furthermore, they point out that the oxide content of a particular catalyst varies approximately as the square root of the partial pressure of water vapor to which it is exposed. If these statements are true, it follows that at any given temperature and pressure the product of

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[8] Krings and Kempkens, *Z. anorg. allgem. Chem.*, **183**, 225 (1929).

the percentage of ammonia and either the oxide content of the catalyst or the square root of the partial pressure of water vapor must be a constant. In Table II such products have been calculated both for the poisoning results of Almquist and Black and for our own high pressure results.

TABLE II

VARIATION OF CATALYTIC ACTIVITY WITH WATER CONCENTRATION

Catalyst	Pressure, atm.	P_{H_2O}, atm.	Mg. of H_2O retained as oxide = X	% NH_3	$K = (\sqrt{(P_{H_2O})}) \times (\% NH_3)$	$K' = (X) \times (\% NH_3)$
921	1	0.0004	4.8	0.205	0.00410	0.98
	1	.0008	6.6	.170	.00481	1.12
	1	.0016	9.4	.120	.00480	1.13
	1	.0032	12.2	.093	.00526	1.13
	1	.0048	14.5	.075	.00519	1.11
	100	.08	4.1	4.40	1.24	18.1
	100	.33	11.3	2.45	1.41	27.7
	100	.48	13.1	2.16	1.50	28.3
922	1	.0008	6.1	0.110	0.00311	0.67
	1	.0032	10.7	0.060	.00339	0.64
Sample I	100	.08	5.0	2.10	.60	10.5
922	100	.33	12.3	1.10	.63	13.5
Sample II	100	.08	5.3	2.30	.65	12.2
922	100	.33	10.6	1.34	.77	14.2
	100	.48	13.7	0.97	.67	13.3

Since deviations from constant values do not exceed the experimental errors, the results may be significant. It does not seem desirable to attempt to construct an *ad hoc* explanation to account for this peculiar relationship, for no reliable kinetic data have yet been obtained to account for the rate of synthesis of ammonia either at high or low pressures. It may be of interest to point out, however, that if the rate of ammonia formation is assumed proportional to some function of the hydrogen and nitrogen pressure, and inversely proportional both to the partial pressures of ammonia and partial pressures of water vapor as expressed by the equation

$$\frac{dP_{NH_3}}{dt} = \frac{kf_1(P_{N_2})\,f_2(P_{H_2})}{P_{NH_3}\,P_{H_2O}} \tag{1}$$

then on integration, assuming the partial pressures of nitrogen and hydrogen constant during the short time of contact, one obtains the relationship $P_{NH_3} = k'\sqrt{t}/\sqrt{H_2O}$, in agreement with the results shown in Table II. Equation 1 is also in accord with the known inhibiting action of ammonia on the rate of synthesis.[9] It is intended, of course, to apply over only a limited range of partial pressures of water vapor. Such an equation is consistent with the assumption that the surface atoms responsible for most of the ammonia synthesis are covered a large fraction of the time by either ammonia (or its resulting nitride) or water (or its resulting oxide).

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

The time during which such points would be free to participate in the synthesis of ammonia would then be inversely proportional both to the ammonia and water vapor partial pressures as expressed in the above equation. The known increase in oxide content of the surface with the partial pressure of water vapor would on this basis have to be accounted for by assuming that most of the oxide formed by the catalyst in the presence of high percentages of water vapor is located on other than those atoms active toward ammonia synthesis.

The excess free energy attributed by Almquist to the active surface atoms may be an important factor in the mechanism of ammonia synthesis. Frankenburger[10] has calculated that an excess free energy of 12,000 calories or more per gram atom of active iron would permit the formation of Fe_2N on the active iron atoms on the catalyst surface by a pressure of three or four atmospheres of nitrogen at 377°, assuming the dissociation pressure of Fe_2N to iron and nitrogen to be 50,000 atmospheres. It should be pointed out that the calculation of Frankenburger yields the above result only if one assumes one active iron atom for each nitrogen molecule reacting, as for example would be the case in the reaction

$$Fe_{(active)} + 3Fe + N_2 = 2Fe_2N$$

We have made similar calculations for the formation of surface Fe_4N at 444° using the recently determined[11] value for the dissociation pressure of Fe_4N into nitrogen and Fe of 5000 atmospheres. They show that to form surface Fe_4N according to the equation

$$Fe_{(active)} + 7Fe + N_2 = 2Fe_4N$$

pressures of 100 atmospheres of N_2 would be necessary when the active iron atoms concerned are those requiring 0.32% water vapor in 3:1 hydrogen–nitrogen gas to produce surface FeO. These results are consistent with the hypothesis advanced above that most of the oxide formed on the catalyst in the presence of high percentages of water vapor is located on other than those atoms active toward ammonia synthesis.

The reduction by hydrogen of surface Fe_2N formed by the reaction of nitrogen and surface iron atoms possessing sufficiently high excess free energies was advanced by Frankenburger as a possible mechanism of the catalytic synthesis of ammonia. This type of mechanism still seems very probable. However, in view of the results of the recent study[11] of the dissociation pressures of various iron nitrides, it is much more likely that the intermediate nitride is Fe_4N than Fe_2N.

Summary

The poisoning of synthetic ammonia catalysts by water vapor has been studied at 450° at pressures as high as 100 atmospheres and at various

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[10] Frankenburger, Ullmann, "Enzyklopädie der Technischen Chemie," Berlin, 1928, Vol. I, p. 393; also *Z. Elektrochem.*, **34**, 632 (1928).

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

partial pressures of water vapor between 0.08% and 0.64%. The amount of oxygen retained by the catalyst is proportional to $\sqrt{P_{H_2O}/P_{H_2}}$. Very active catalysts are capable of retaining more oxygen than less active catalysts. The poisoning of both doubly and singly promoted catalysts by water vapor is almost entirely reversible, though a slight permanent injury to the catalyst results. A probable mechanism of ammonia synthesis consists in the reduction by hydrogen of surface Fe_4N formed by the reaction of nitrogen molecules with surface iron atoms having average free energies sufficiently in excess of those of normal iron atoms.

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ACETAMIDE AND FORMAMIDE AS SOLVENTS FOR THE ELECTRODEPOSITION OF METALS

BY L. F. YNTEMA AND L. F. AUDRIETH

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The possible application of formamide and acetamide as suitable media for the electrodeposition of metals from solutions of their salts has been suggested by various investigators,[1] but has thus far been given only little attention. That such a suggestion is based upon excellent theoretical considerations becomes evident from a survey of the physical and chemical properties of both of these substances. That such an investigation is highly desirable becomes increasingly apparent from the stress which has recently been laid upon solvent chemistry and solvents, in particular, non-aqueous ones.

Their differentiation on the basis of their acidity and basicity, as developed by Conant and Hall,[2] has thus far been limited to a consideration of liquid ammonia, water, alcohol and glacial acetic acid. Ammonia is regarded as the most basic of these in view of its great tendency to unite with the hydrogen ion or proton to form the ammonated hydrogen ion, the ammonium ion. Consequently, ammonium salts[3] and acid amides[4] act as acids in liquid ammonia. Glacial acetic acid, because of its tendency to part with the proton more readily, is considered the most acidic of the four above-mentioned solvents. This characteristic of acetic acid accounts for two of its most unexpected properties. Certain acids, such as perchloric acid, have been found to be "stronger" in acetic acid solution than in a less acidic solvent, such as water. On the other hand, compounds such as acetamide, which are usually considered as neutral substances re-

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[1] Walden, *Z. physik. Chem.*, **46**, 103 (1903); **54**, 129 (1905); **55**, 683 (1906).

[2] Conant and Hall, THIS JOURNAL, **49**, 3047, 3062 (1927).

[3] Franklin, *ibid.*, **27**, 820 (1905); Browne and Houlehan, *ibid.*, **33**, 1742 (1911).

[4] Franklin and co-workers, *J. Phys. Chem.*, **24**, 81 (1920); THIS JOURNAL, **44**, 486 (1922); **47**, 1485 (1925).