

STAT

Investigation of the Catalytic Oxidation of Amonia

by M. V. Polyakov, V. I. Urizko, and N. P. Galenko

Zhur Fiz Khim, Vol XXV, No 12, pp 1460-1468,  
Russian Mo per, 1951

STAT

Zhur. Fiz. Khim. Vol. XXV No. 12, 1951,  
 No. 1460-1468

STAT

INVESTIGATION OF CATALYTIC  
OXIDATION OF AMMONIA

M. V. Polyakov,  
 V. I. Urizko, and  
 N. P. Galenko

In a number of laboratory studies (1-3), in the catalytic oxidation of ammonia to nitrogen oxide, the existence of optimum temperatures and contact durations was established between the air-ammonia mixture and the catalyst -- a platinum screen.

At temperatures below the optimum and excessively large velocities of the gaseous stream, the yield of nitrogen oxide decreases because of passage of unreacted ammonia, while at temperatures above the optimum and excessively low velocities of the gaseous stream, a considerable part of the ammonia is converted not into nitrogen oxide but into nitrogen.

In several studies a linear correlation between temperature and contact duration was established which is optimum insofar as nitrogen oxide yield is concerned. Empirical formulas have been proposed to express this correlation (4,5).

In a number of investigations the anomalous effect of admixtures on the yield of nitrogen oxide was detected. For example, very small admixtures of hydrogen sulfide introduced under conditions other than optimum for nitrogen oxide production, increase the yield of the latter by 5 to 6 percent (6) and even by 20 to 30 percent (7). At the same time there is observed a shift of opti-

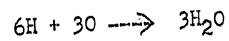
imum condition towards the lower temperatures (from 800 to 700 degrees Centigrade).

In several studies (8,9) intermediate products have been isolated, for example, imid, hydroxylamine, nitrous and nitric acid.

The thus derived natural laws and facts as well as their analogues have become the foundation of various hypotheses concerning the mechanism of catalytic oxidation of ammonia. Here we may mention only the concepts of a heterogeneous-homogeneous reaction mechanism, inasmuch as these concepts are most closely associated with the cited natural laws and facts.

According to one concept (10,11), there occurs on the surface of the catalyst a decomposition of ammonia to the imid and oxidation of the thus liberated hydrogen to water. Under conditions which are not optimum for the production of nitrogen oxide at excessively-high temperature levels and contact times, a heterogeneous conversion of imid into nitrogen takes place, and only the evaporation of imid at the proper time into the reaction space contributes (under optimum conditions) to its homogeneous conversion to hydroxylamine according to the equation  $\text{NH} + \text{H}_2\text{O} \longrightarrow \text{NH}_2\text{OH}$ , and thereafter through a number of intermediate stages into nitrogen oxide.

According to the concept of Markov (12), the atomic oxygen formed upon the surface of the catalyst yields with ammonia, under optimum conditions, first hydroxylamine and then nitrogen oxide and water:



Under conditions other than optimum, however, the hydroxylamine diffuses from the surface into space, where it causes the formation of atomic nitrogen. At excessively high temperature levels and contact durations this takes place in advance of the catalyst (diffusion of hydroxylamine against the gaseous stream), while at low values of these parameters, beyond the catalyst.

The concepts cited are based on experimental data on formation of hydroxylamine (13), which at low pressures is homogeneously converted beyond the catalyst not only into nitrogen and water, but also into nitrous and then nitric acid. This fact favors the first concept according to which there is heterogeneous formation of imid and not of hydroxylamine.

A wide-reaching substantiation as to the correctness of one or the other of these concepts resides in the fact that de-fixation of nitrogen under non-optimum conditions is not caused by decomposition of nitrogen oxide upon the catalyst surface; in our laboratory data obtained by other researchers were confirmed according to which this decomposition occurs approximately 200 times slower than the nitrogen de-fixation process.

The possibility of increasing nitrogen oxide yields under

non-optimum conditions by the use of poisons such as hydrogen sulfide also indicated the plausibility of a heterogeneous-homogeneous mechanism of ammonia oxidation. The poison affects the most active centers of the surface at which ammonia is decomposed to nitrogen, and thus contributes to the formation of imid, which is then homogeneously converted into nitrogen oxide. In connection with what has been stated hereinbefore, the question as to the actual optimum conditions has become of substantial importance, especially since this problem has been the subject of discussions over a period of many years.

Some investigators (14 -- 16) have contended that the optimum conditions observed are the results of other secondary causes and not of the decomposition of nitrogen oxide or of ammonia on the surface of the catalyst.

The main problem of the instant investigation was the determination of the real significance of optimum temperature and time of contact as reported in the literature in connection with oxidation of ammonia to nitrogen oxides.

#### Investigation Method

Figure 1 shows diagrammatically the unit which we have used for the study of catalytic oxidation of ammonia to nitrogen oxide with atmospheric oxygen, using platinum screens having a diameter of 0.8, 1.4, and 1.8 centimeters. The number of apertures for 1 square centimeter of the screen was 961. Concentration of ammonia in the ammonia-air mixture fluctuated within the limits of 8 and 8.5 percent.

The contact apparatus consisted of a quartz tube 21 centimeters long and 2 centimeters in diameter surrounded by a heating coil and heat insulating material. Within this tube was placed another tube 12.5 centimeters long held by means of a ground joint and having affixed at its end the platinum screen of a given diameter. The temperature within the contact apparatus was regulated by means of the electrical heating device and was measured by a platinum-platinum-rhodium thermocouple contained in a quartz casing and placed at a distance of 1 millimeter from the screen surface at its central part. Such a method of measuring the temperature of the reaction gases issuing through the screen eliminated to a considerable extent the complications which are usually unavoidably connected with the heating of the gases, not only by the externally-applied heat but also as a result of the strongly exothermic reaction.

→ Air

↓  
Excess NH<sub>3</sub>

Figure 1. Diagram of the unit for catalytic oxidation of ammonia.  
1, regulator; 2, canister with activated carbon; 3, buffer flask;  
4, bottle with sulfuric acid (oleum), trap, towers with NaOH and CaCl<sub>2</sub>; 5, rheometer; 6, mixer; 7, cylinder with liquid ammonia;  
8, buffer flask; 9, tower with NaOH; 10, rheometer; 11, mixer;  
12, contact apparatus

Determination of the ammonia and nitrogen oxide contents of the gaseous mixture was made gravimetrically by the evacuated flasks method of Gaillard. Methods of feed, purification, and formation of the ammonia-air mixture require no description; they are apparent from the drawing of Figure 1 showing the unit. It should be only mentioned that small amounts of admixed hydrogen sulfide and of other gases were fed into the contact apparatus through a special rheometer.

#### Results Obtained and Their Discussion

Yield of nitrogen oxide as a function of temperature and velocity of the gaseous stream was studied using platinum screens 0.8, 1.4, and 1.8 centimeters in diameter within the temperature range of 310 to 1040 degrees at space velocities 18 to 360 liters per hour.

To illustrate the correlations thus determined, Figure 2 shows a juxtaposition of a number of curves giving the relation of nitrogen oxide yields and temperature at space velocities of the gaseous stream, from 18 up to 360 liters per hour. Diameter of the screen was 1.4 centimeters. Analogous sets of curves were obtained with screens having a diameter of 0.8 and 1.8 centimeters.

% contact  
activation

Figure 2. Nitrogen oxide yield as a function of temperature and flow velocity of the ammonia-air mixture. Diameter of screen 1.4 centimeters. I. Flow velocity, 0.3 liters per minute. II. Flow velocity 0.5 liters per minute. III. Flow velocity 1.0 liters per minute. IV. Flow velocity 3.0 liters per minute. V. Flow velocity 6.0 liters per minute.

From Figure 2 it can be seen that: (1) with increasing temperature yield of nitrogen oxide increases at first, reaches an optimum at temperatures of the order of 750 to 850 degrees Centigrade, and decreases thereafter; (2) with increasing velocity of the gaseous stream the optimum shifts toward higher temperatures. The regular nature of this shift is apparent from Figure 3, in which the data of Figure 2 are plotted on coordinates  $lgz$  and  $T^{\circ}K$ , where  $z$  is duration of contact, while  $T$  is the absolute temperature. Values of  $z$  were calculated by means of four formulas proposed by V. I. Atroshchenko, G. K. Boreskov, Andrusov, and I. M. Libinson. The diameter of the screen is 1.4 centimeters.

Figure 3. Optimum duration of contact between reaction mixture and catalyst as a function of the temperature. Diameter of screen 1.4 centimeters. According to formula of: I, Atroshchenko; II, Boreskov; III, Andrusov; IV, Libinson

Figures 4 and 5 show two sets of straight lines obtained on using screens with a diameter of 1.8 and 0.8 centimeters. In these cases a linear correlation exists between  $lgz$  and  $T$ . The straight lines for  $z$ , calculated by means of the formula of I. M. Libinson, show inclination angles different from those of the straight lines obtained when  $z$  was calculated using the formulas of V. I. Atroshchenko, G. K. Boreskov, and Andrusov.



Figure 4. Optimum duration of contact between reaction mixture and catalyst as a function of the temperature. Diameter of screen 0.8 centimeters. According to formula of: I, Atroshchenko; II, Bereskov; III, Andrusov; IV, Libinson.

Figure 5. Optimum duration of contact between reaction mixture and catalyst as a function of temperature. Diameter of screen 1.8 centimeters. According to formula of: I, Atroshchenko; II, Bore-skov; III, Andrusov; IV, Libinson

Figure 6 shows a juxtaposition of straight lines obtained using the formula of V. I. Atroshchenko, in the case of screens of three different diameters -- 0.8, 1.4, and 1.8 centimeters. We see that inclination angle of the straight line corresponding to the screen 1.4 centimeters in diameter differs sharply from the almost identical angles of inclination of straight lines corresponding to screens having a diameter of 0.8 and 1.8 centimeters. This fact leads to the conclusion that the occurrence of optima depends not only on temperature and duration of contact but also on the walls of the quartz vessel, since screens having diameters of 0.8 and 1.8 centimeters were used in the same vessel, while screens having a diameter of 1.4 centimeters in a vessel having a larger surface area of the walls.

Figure 6. Comparison of curves I of figures 3, 4, and 5, calculated by means of the formula of Atroshchenko. Diameter of screens 1.4, 1.8, and 0.8 centimeters. Calculation of  $z$  according to formula of Atroshchenko: I, for screen  $d = 1.4$  centimeters; II, for screen  $d = 1.8$  centimeters; III, for screen  $d = 0.8$  centimeters.

In this connection, Figure 7 becomes of special importance. It shows the dependence of nitrogen oxide yield on linear velocity of the gaseous stream, at 650, 750, 850, and 950 degrees Centigrade in the case of screens 0.8 and 1.8 centimeters in diameter used in the same vessel. Solid line curves refer to the screen 0.8 centimeters in diameter while those in dotted lines to that having a diameter of 1.8 centimeters.

Diameters of screens 0.8 and 1.8 cm

% of contact  
activation

Velocity of gas flow l/min.  $\text{cm}^2$

Figure 7. Yield of nitrogen oxide as a function of linear flow velocity of reaction mixture at temperatures of 650, 750, 850, and 950 degrees Centigrade. Diameter of screens, 0.8 and 1.8 centimeters. 1, 650 degrees with 1.8 centimeter screen; 2, 650 degrees with 0.8 centimeter screen; 3, 750 degrees with 1.8 centimeter screen; 4, 750 degrees with 0.8 centimeter screen; 5, 850 degrees

(Figure 7, cont'd) with 1.8 centimeter screen; 6, 850 degrees with 0.8 centimeter screen; 7, 950 degrees with 1.8 centimeter screen; 8, 950 degrees with 0.8 centimeter screen.

We see that solid and dotted lines form continuous curves which are characteristic of the dependency of NO yield on contact duration; this dependence is clearly not affected by dimensions of the screen. Consequently the change in inclination of the straight line corresponding to the 1.4 centimeter screen (Figure 6) is also caused not by dimensions of the screen but by the surface size of/adjoining inner tube walls of the reaction vessel; these walls under certain conditions clearly participate in the reaction by contributing to the conversion of ammonia into nitrogen, and cause at high temperatures and low velocities of the gaseous stream (figures 2 and 7) the occurrence of optima.

A series of preliminary experiments was conducted with the purpose of determining the part played by nitrogen oxide decomposition in the de-fixation of nitrogen, which is observed under non-optimum conditions. A study was made of the correlation between the degree of nitrogen oxide decomposition and the temperature, at a velocity of the gaseous stream amounting to 11.7 liters per hour per square centimeter using a screen 1.8 centimeters in diameter; the mixture contained 8 percent nitrogen oxide, 92 percent air, and 8 percent nitrogen oxide, 92 percent nitrogen.

Experiments have shown that increase of temperature from 800 to 1100 degrees Centigrade results in a higher degree of nitro-

gen oxide decomposition which rises from 0.4 to 8 percent, and that consequently this decomposition cannot be the cause of nitro de-fixation under non-optimum conditions of catalytic oxidation of ammonia; the degree of this defixation within the indicated temperature interval reaches 70 to 90 percent.

Thus our experiments have confirmed the correctness of data obtained by other investigators (16), who had reached the conclusion that it is not possible to explain occurrence of optima by a decomposition of nitrogen oxide.

The validity of the explanation proposed in the present paper as being the actual cause has been verified in a large number of experiments devoted to the study of the decomposition of ammonia in tubes containing no catalyst and under conditions of poisoning of the tube walls by small amounts of admixed hydrogen sulfide utilized as the poison. We contemplated the discovery in this manner not only the cause of optima occurrence, but also to determine the mechanism of increase in nitrogen oxide yields, reaching 5 to 6 percent (6) and even 20 to 30 percent (7), and attained by the use of small admistures of a poison --- hydrogen sulfide. We assumed that this increase in the yield of nitrogen oxide is the result of a decreased de-fixation of ammonia on the walls of the quartz vessel due to the poisoning of these walls by the action of hydrogen sulfide.

However, before the experiments referred to were started, it was found that removal of the screen from the reaction vessel does not ensure complete removal of the platinum; the latter in

in the form of a dust covers a considerable portion of the walls, contributing thereby about 40 to 50 percent of the catalyst activity: the yield of nitrogen oxide decreases, following removal of the screen, from 91 to 95 percent to 40 to 50 percent.

This fact reveals the activation mechanism of a platinum catalyst over a period of many hours, which is attained by passing through the vessel the reaction mixture at temperatures of the order of 700 to 800 degrees Centigrade.

The mechanism of catalyst activation is clearly not limited to change of structure or surface area of the platinum screen. During the activation process a portion of the vessel walls becomes coated with platinum dust, which necessarily causes a considerable increase of catalyst surface and, what is not less important, a decrease of the wall surface taking part in defixation of ammonia and decreasing the yield of nitrogen oxide.

Curve II in Figure 8 illustrates what takes place on complete removal of the platinum by repeated treatment of the vessel with aqua regia and boiling distilled water. This curve shows decomposition of ammonia as a function of temperature in a vessel free of platinum (velocity of gaseous stream 1 liter per minute).

This decomposition (10 to 20 percent) is appreciable even at temperatures below 500 degrees Centigrade, and reaches almost 100 percent at temperatures of the order of 1000 degrees Centigrade.

Curve I of Figure 8 shows the dependence of nitrogen oxide yields on the temperature, under identical conditions and within

the same vessel, in catalytic oxidation of ammonia by means of a platinum screen. A comparison of the two curves leads to the conclusion that the right arm of curve I is the effect of de-fixation of ammonia down to nitrogen to which contributes the surface of quartz tube walls free from platinum dust. This platinum is precisely the cause of decrease in de-fixation by the vessel walls in comparison with what takes place under non-catalytic conditions of the process (curve II). Insofar as the left arm of curve I is concerned, it is connected primarily with the passage of unreacted ammonia which increases on decrease of the temperature. It must be assumed that even under optimum conditions we never have a hundred percent oxidation of ammonia to nitrogen oxide because a small portion of it is converted to nitrogen, in which process the walls of the vessel take part, while another portion passes through the screen without reacting.

% decomposition of  
ammonia

Figure 8. Comparison of curve showing yield of nitrogen oxide as a function of the temperature (I); with the curve showing degree of ammonia decomposition as a function of temperature (II). Space velocity of gaseous flow 1 liter per minute. Diameter of screen 1.4 centimeters. I, Oxidation of  $\text{NH}_3$ ; II, Decomposition of  $\text{NH}_3$ .

From figures 9 and 10 it can be seen that decomposition of ammonia in a vessel free of platinum follows a fully regular course. Figure 9 shows the dependence of ammonia decomposition, expressed in percent, on the temperature in the case of velocities of the air-ammonia mixture amounting to 0.5 liters per minute (curve I), 2 liters per minute (curve II), and 4 liters per minute (curve III), while Figure 10 shows the dependence of the percentage of ammonia decomposition on velocity of the air-ammonia stream at temperatures of 600 degrees Centigrade (curve I), 700 degrees Centigrade (curve II), and 800 degrees Centigrade (curve III).

% decomposition of  
ammonia

Figure 9. Degree of ammonia decomposition with participation of quartz vessel walls, as a function of temperature, at space velocity of gaseous stream of air-ammonia mixture amounting to 0.5 liters per minute (curve I), 2.0 liters per minute (curve II), and 4.0 liters per minute (curve III). Surface of walls 52 square centimeters. I, 0.5 liters per minute; II, 2.0 liters per minute; III, 4.0 liters per minute.

% decomposition of  
ammonia

Velocity of gas flow in l/min

Figure 10. Degree of ammonia decomposition with participation of quartz vessel walls as a function of space velocity of gaseous stream of air-ammonia mixture at a temperature of 600 degrees Centigrade (curve I), 700 degrees Centigrade (curve II), and 800 degrees Centigrade (curve III). Surface of walls 52 square centimeters. I, percent of  $\text{NH}_3$  decomposition at 600 degrees; II, percent of decomposition at 700 degrees; III, percent of  $\text{NH}_3$  decomposition at 800 degrees.

Satisfactory repetition of experiments on decomposition of ammonia is apparent from a comparison of curve II, Figure 8, and curve I, Figure 9. These curves were obtained at different times by different workers.

% decomposition of  
ammonia

Figure 11. Degree of ammonia decomposition with participation of quartz vessel walls as a function of temperature at space velocity of gaseous stream of nitrogen ammonia mixture amounting to 0.5 liters per minute (curve I), and 2 liters per minute (curve II).



(Figure 11 cont'd)

Surface of walls 52 square centimeters. I, 0.5 liters per minute; II, 2 liters per minute.

Figure 11 shows the percentage of ammonia decomposition as a function of the temperature for two velocities of the gaseous stream of nitrogen-ammonia mixture (8 percent of ammonia). Curve I relates to space velocity of 0.5 liters per minute while curve II relates to the velocity of 2 liters per minute.

Comparison of data shown in figures 11 and 9 leads to a conclusion concerning the participation of oxygen of the ammonia-air mixture in the exothermic oxidation of ammonia to nitrogen; it increases the rate of ammonia decomposition several times by comparison with that obtained on decomposition of ammonia in the presence of nitrogen.

% decomposition of  
ammonia

Figure 12. Degree of ammonia decomposition with participation of quartz vessel walls as a function of temperature without admixture of hydrogen sulfide (curve I), and with the air-ammonia mixture containing 0.1 percent hydrogen sulfide. Space velocity of gaseous stream 2 liters per minute. Surface of walls 52 square centimeters. I, without  $H_2S$ ; II, 0.1 percent  $H_2S$ .

Figure 12 shows a comparison of two curves which give the decomposition of ammonia as a function of temperature in a vessel free of platinum; curve I was obtained in the absence of hydrogen sulfide, while curve II was obtained in the presence of an admixture of this catalyst poison. Velocity of ammonia-air stream in both experiments was equal to 2 liters per minute. It can be seen from Figure 12 that a negligibly small admixture of hydrogen sulfide decreases decomposition of ammonia to less than one half. Hydrogen sulfide obviously poisons the surface of the quartz vessel walls which take part in this process. It is not difficult to visualize what must be the result of poisoning of vessel walls by hydrogen sulfide on catalytic oxidation of ammonia to nitrogen oxide. Under these conditions the hydrogen sulfide, by inhibiting decomposition of ammonia by the walls of the vessel, and thus contributing to its access to the catalyst surface, must increase the yield of nitrogen oxide.

Table I shows that this is actually the case. Results given in this table were obtained in two contact apparatuses connected in series with a total wall area equal to 176.5 square centimeters. The upper apparatus with an area of 59.3 square centimeters had been previously freed of the platinum screen and the platinum dust and served merely to increase the quartz surface preceding the catalyst. The lower apparatus contained platinum as usually used in performing experiments on catalytic oxidation of ammonia. Both apparatuses were heated by means of separate electrical coils. The air-ammonia mixture was fed into the upper apparatus, was heated to a definite temperature level, and reached

TABLE I

| Velocity of<br>gaseous stream<br>lit/min | Temperature of<br>upper apparatus<br>without catalyst<br>(degrees Centigrade) | Temperature of<br>lower apparatus<br>with platinum<br>screen. °C. | Percent of<br>hydrogen sulfide | Percent of oxidation<br>of ammonia to nitro-<br>gen oxide |
|--|---|---|--------------------------------|---|
|  | —   | 800   | —                              | 90.17   |
|  | 700   | 800   | —                              | 63.20   |
|  | 600   | 700   | —                              | 33.39   |
|  | 600   | 700   | 0.1                            | 49.07   |
| 0.5                                      | 600   | 700   | —                              | 27.76   |
|  | 600   | 700   | 0.1                            | 94.35   |
|  | 500   | 600   | —                              | 22.01   |
|  | 500   | 600   | 0.1                            | 79.77   |
|  | 800   | —   | —                              | 51.16   |

the catalyst in the lower apparatus. When an addition of hydrogen sulfide was used (0.1 percent) the entire mixture also first entered the upper apparatus and then the lower. Before a sample was taken for analysis the reaction mixture was passed through the apparatus for two to three hours.

It follows from Table I that increase of the area of quartz wall surface heated to 700 degrees Centigrade, and preceding the catalyst, results in a decrease of nitrogen oxide yield from 90.17 to 63.2 percent, while an addition of 0.1 percent of hydrogen sulfide increases the yield of nitrogen oxide from 27.76 to 94.35 percent, that is, by more than 60 percent.

It must be mentioned that in experiments conducted using the same two quartz apparatuses without a platinum screen, 51.46 percent nitrogen oxide was obtained, formed as a result of the presence of platinum dust deposited on the walls of the lower apparatus.

It is also of interest to note that an increase of hydrogen sulfide concentration up to 2 percent results in a pronounced drop of the nitrogen oxide yield. Under these conditions not only the walls of the vessel are poisoned but also the platinum catalyst, which leads to the appearance of ammonium nitrate and nitrite fumes, as this usually occurs when unreacted ammonia passes through the screen.

From Table I it follows that the main cause of nitrogen de-fixation and corresponding decrease of nitrogen oxide yields on catalytic oxidation of ammonia at excessively high tempera-

ture values and contact durations is the oxidation of ammonia to nitrogen, to which contribute the platinum free walls of the quartz vessel preceding the catalyst.

Thus, from all of the above-presented data it follows that occurrence of optima is connected not with the mechanism of the basic catalytic process but with a side reaction which is, however, difficult to eliminate completely. Thus in a number of investigations, external heating of the entire vessel walls or of only a portion thereof preceding the catalyst was omitted entirely, but optima and de-fixation associated therewith still were present. This is explained by the fact that strong heating of the catalyst (800 degrees Centigrade and higher) unavoidably results in heating of the walls preceding the catalyst to 400 -- 600 degrees Centigrade, that is, to a temperature at which considerable decomposition of ammonia takes place (see Figure 8), especially at excessively low velocities of the gaseous stream.

The most reliable means of counteracting the detrimental effect of the walls of the vessel preceding the catalyst would be, as follows from the present study, to cover completely all the heated portion of vessel walls with platinum or another material that is inert, or promotes not the decomposition but the oxidation of ammonia to nitrogen oxide. The foregoing relates to laboratory experiments. Insofar as manufacturing conditions are concerned, the problem requires additional study.

### Conclusions

1. The cause of the occurrence of optima in temperature and contact duration on catalytic oxidation of ammonia over platinum screens has been determined under laboratory conditions. The cause is the conversion of ammonia into nitrogen before it reaches the catalyst, the walls of reaction vessels participating in this conversion. The conversion occurs at an especially high rate at high temperatures and prolonged contact durations, which results in the occurrence of optima and a linear correlation between them under these conditions.

2. The cause of increased yields of nitrogen oxide on introduction of small admixtures of a poison-hydrogen sulfide, which increase the yield by 5 to 6 percent (6) and even by 20 to 30 percent (7), has been determined. Hydrogen sulfide poisons the walls of the reaction tube preceding the catalyst and thus decreases the percentage of ammonia decomposition and increases correspondingly the degree of its conversion into nitrogen oxide.

3. The cause of activation of the catalyst on passing over it the reaction mixture at conditions optimum for the production of nitrogen oxide, with respect to temperature (800 degrees Centigrade) and contact duration, has been determined. Under these conditions the catalyst surface is considerably increased due primarily to the coating of vessel walls with platinum dust, which concurrently results in a decrease of free surface area of the walls, and consequently a decrease of the percentage of ammonia decomposition prior to its contact with the

catalyst and a corresponding increase of nitrogen oxide yields.

4. From the fact that in the catalytic oxidation of ammonia to nitrogen oxide the optima and linear correlations between them are not characteristic of the basic reaction, it follows that it is necessary to re-examine and amend theories based upon these optima; it is also necessary to improve methods of laboratory and plant investigations, taking into account that at the walls of reaction apparatus an oxidation of ammonia to nitrogen and nitrogen oxide (pulverulent catalyst) occurs. A method has been proposed to eliminate this defect.

5. As a result of the oxygen taking part in de-fixation of nitrogen by the vessel walls free from platinum, there takes place (in advance of the catalyst) not a decomposition but an oxidation of ammonia to nitrogen if this is favored by temperature and contact duration under non-optimum conditions. This oxidative decomposition of ammonia has a heterogeneous-homogeneous mechanism (17); vessel walls merely initiate a homogeneous oxidation of ammonia to nitrogen in advance of the catalyst; an analogous process takes place also beyond the catalyst, as established by our investigations (11) and other researches (12). On the whole, the catalytic oxidation of ammonia constitutes a complex heterogeneous-homogeneous process. However, the place and mechanism of nitrogen oxide formation have remained undetermined by the outcome of the present study.

Academy of Sciences, Ukrainian SSR  
Institute of Physical Chemistry  
imeni L. V. Pisarzhevskiy, Kiev

Received for publication  
27 November 1950

## LITERATURE CITED

1. V. I. Malyarevskiy and N. Malyarevskaya-Kobachenka, Zhurnal Prikladnoy Khimii, 2, 7, 1928.
2. L. Andrussow, Z. Angew. Chem., 39, 321, 1926.
3. I. Ye. Adadurov and R. Ya. Vaynshtenker. Ukrainskiy Khimicheskii Zhurnal. 5, 1, 1930.
4. I. M. Libinson, Zhurnal Prikladnoy Khimii. 8, 342, 1931.
5. G. K. Boreskov, Zhurnal Prikladnoy Khimii. 5, 2, 1932.
7. M. V. Polyakov, F. M. Vaynshteyn and L. A. Kostyuchenko. Izvestiya IFKh Akademiya Nauk Ukrainskoy SSR, 14, 1947.
11. M. V. Polyakov and F. M. Vaynshteyn. Zhurnal Fizicheskoy Khimii, 15, 2, 1941.
12. V. I. Atroshchenko and S. I. Kargin. Tekhnologiya Azotnoy Kisloty (Technology of Nitric Acid), GOSKHEMIZDAT, 1949.
13. M. Bodenshteyn. Okisleniye Ammiaka (Symposium, Oxidation of Ammonia), ONTI, 1936, 119.
14. V. I. Atroshchenko, Zhurnal Prikladnoy Khimii. 8, 25, 1935.
15. V. I. Atroshchenko and Ye. G. Sedasheva. Zhurnal Prikladnoy Khimii, 14, 500, 1941.
17. M. V. Polyakov, Uspekhi Khimii, 3, 351, 1948.