Catalytic Decomposition of Nitric Oxide

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Catalytic decomposition of nitric oxide at a concentration of 0.404 and 0.432% by volume in nitrogen was studied in a tubular flow reactor. The packing consisted of alumina pellets impregnated with 0.1% by weight of platinum oxide and 3.0% by weight of nickel oxide. Tests were conducted at pressures of 1 to 15 atm. and temperatures from 800° to 1,000°F. A rate equation correlating the data as a function of temperature, pressure, and compositions was developed. A reaction mechanism compatible with the rate equation is proposed.

Although the catalytic decomposition of nitric oxide is of both practical and theoretical interest, there is very little information on the subject in the literature. The bulk of the experimental studies on catalytic decomposition occurred during the period between 1923 and 1934. The efforts were directed mainly toward decomposition of pure nitric oxide at pressures of 1 atm. or less and at temperatures from 1,100° to 2,500°F. With the exception of Muller and co-workers (*11*) and Schwab and co-workers (*17*), who used a variety of metals and metal oxides for catalysts, the investigators mainly studied platinum catalysts.

In general (*8, 11, 17, 22, 23*) the data indicated that the reaction was first order with respect to nitric oxide and was retarded by adsorbed oxygen. The rate equation to describe such behavior could be written as follows:

$$r = -\frac{dp_{\mathrm{NO}}}{d\theta} = k\left(\frac{p_{\mathrm{NO}}}{p_{\mathrm{O_2}}}\right) \qquad (1)$$

Another form of the rate equation was presented as

$$r = -\frac{dp_{\mathrm{NO}}}{d\theta} = k\left(\frac{p_{\mathrm{NO}}}{1 + ap_{\mathrm{O_2}}}\right) \qquad (2)$$

Bachman (*2*) proposed from his studies however that in the temperature range of 1,900° to 2,500°F. the reaction was second order with respect to nitric oxide but was also retarded by oxygen to give a rate equation of the form

$$r = -\frac{dp_{\mathrm{NO}}}{d\theta} = k\left[\frac{(p_{\mathrm{NO}})^2}{p_{\mathrm{O_2}}}\right] \qquad (3)$$

In later work the Armour Research Foundation (*1*) screened a large number of catalysts to determine their effectiveness in decomposing nitric oxide which was present in nitrogen at a concentration of 0.2% by volume. Their tests were mainly qualitative and were conducted for the purpose of applying the results to the treatment of exhaust from automobile engines. Later Fraser and Daniels (*6*) in 1958 reported on the catalytic decomposition of diluted nitric oxide over metal oxides with low surface areas. In this work the temperature was varied from 1,300° to 1,900°F., and helium was used to dilute the nitric oxide to 10% by volume. A zero-order reaction rate was obtained, and this was attributed to the complete occupation of active sites because of the high concentration of nitric oxide.

Some work has also been done on the high-pressure decomposition (*3, 4, 5, 7, 16*) of pure nitric oxide. Studies were made at pressures up to 800 atm. and temperatures up to 575°F. Products of the decomposition were found to be nitrogen, oxygen, and various oxides of nitrogen. Mechanism and rate studies were not made, but it was ascertained qualitatively that the rate of decomposition increased with increases in temperature and pressure.

The purpose of the present work was to develop further knowledge about the kinetics and mechanism of the catalytic decomposition of nitric oxide, especially for the case of low concentrations of nitric oxide in nitrogen. Selection of the temperature range of 800° to 1,000°F. was made on the basis of possible application of the results to the dissociation of nitric oxide in the exhaust gases from internal combustion engines.

EQUIPMENT

Reactor

The reactor used in the flow studies of the decomposition of nitric oxide in nitrogen was constructed from type 304 stainless steel tubing. It had an outside diameter of ⅝ in., an inside diameter of 0.495 in., and a length of 46 in. Catalyst was supported in the central section of the reactor to a maximum depth of 15.5 in. A uniform temperature was maintained in the catalyst bed for all lengths up to the maximum by means of heaters mounted externally.

Reactor Accessories

Figure 1 shows a schematic diagram of the reactor system. In order to allow conditioning of the feed gas before entrance to the reactor a preheater section consisting of a 15 ft. length of ¼-in., stainless steel tubing coiled to a length of about 9 in. was mounted just upstream from the reactor. The outflow leg of the tube had a heater mounted on its external surface which allowed a variable energy input up to 700 w. A porcelain tube which had two 1,650-w. heaters mounted on its exterior was used as a shield over the outflow leg. The whole assembly of preheater and exit tube was located inside a cylindrical shield made from a porcelain tube closed at the top. The external portion of this porcelain outer shield was wrapped with a 2,200-w. heater, and finally the whole assembly was insulated with microquartz and Fiberglas and covered with aluminum foil.

Measurement of Pressure and Temperature

Pressures above 10 lb./sq. in. gauge were measured with a gauge which had a maximum reading of 400 lb./sq. in. and was located at the exit of the reactor. For pressures below 10 lb./sq. in. gauge a differential pressure gauge was used and was connected by a manifold system to six pressure taps equally spaced along the length of the reactor. When used only for measurement of the exit pressure rather than pressure differences along the reactor, the gauge was connected between the reactor exit and the manifold vent. Both gauges were stipulated by the manufacturer to be accurate to within 0.5% of the full scale reading, and this accuracy was confirmed by checks with a pressure balance and a mercury manometer.

Temperatures in the preheater, the line connecting the preheater to the reactor, and the reactor were measured with ten chromel-alumel thermocouples. They were checked over the range of 700° to 1,100°F. against a standard platinum-platinum-10%-rhodium thermocouple which had been calibrated by the National Bureau of Standards.

Feed and Product Analysis

Analysis of the feed and discharge gases was accomplished by means of a gas

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chromatograph. A procedure using a column packed with dry silica gel was developed (*15*), and a known sample of nitric oxide in nitrogen was used each day to obtain a calibration factor. The analysis of the standard sample was checked by a chemical method in accordance with American Society for Testing Materials specification No. D1608-58-T.

Measurement of Gas Flow

Rotameters for measuring the flow of product gas from the reactor and carrier gas from the chromatograph had been calibrated for air. Corrections for nitrogen and helium were made according to the manufacturer's recommendations.

Catalyst Data

Qualitative experiments were conducted to select a catalyst for use in the study of the decomposition of nitric oxide. A nickel-platinum catalyst was among the most effective tested and gave the most reproducible results. Descriptions of these preliminary experiments are available (*13*), and properties of the catalyst are tabulated in Table 1.

Before tests were conducted with a new charge of catalyst it was dried and activated in place at 1,050° to 1,110°F. in the presence of a low flow of high-purity, dry nitrogen at atmospheric pressure. Drying time usually extended over a period of two or three days.

Table 1. Properties of the Girdler G-43 Catalyst

Data obtained from the catalyst manufacturer*

Surface area	188.4 sq. m./g.
Pore volume associated with a maximum pore diam. of 800 A	0.27 cc./g.
Packed specific weight	68 ± 4 lb./cu. ft.
Composition:	
Active agents as oxides	
Pt	0.1%
Ni	3.0
Carrier	
Fe_2O_3	0.07
Na_2O	0.02
SiO_2	0.10
SO_3	3.50
MgO	0.20
CaO	0.35
Al_2O_3	95.76

Measurements of pellets:

Length	0.138 ± 0.004 in.
Diameter	0.1225 ± 0.0005 in.

Surface area measurement by Union Oil Company

167 sq. m./g.	2 runs
172 sq. m./g.	

* Chemical Products Division of the Chemetron Corporation.

EXPERIMENTAL PROCEDURE

Prior to a run each Variac associated with the reactor heaters and preheater was set at a voltage which gave approximately the desired temperature of operation. The thermocouple in the preheater, the one in the connecting line to the reactor, and the four central thermocouples in the reactor were connected to a recording potentiometer. By observation of the continuous record of the thermocouple emf's the approach to the final operating temperature was conveniently regulated. Meanwhile the feed stream was adjusted to the desired operating pressure. Two or three hours were generally required for the system to reach steady state.

About 1 hr. before the first sample was taken from the discharge stream the flow of the product stream was adjusted to a predetermined setting on the rotameter without changing the pressure. As discussed this was accomplished by means of a regulator valve on the cylinder of the reactant gas and a back-pressure valve on the reactor exit. A product sample was obtained by opening the sampling port and allowing the gas to flow through the sampling cell and subsequently through a nitric-oxide scrubber before expulsion to the atmosphere. During this period the temperature and pressure in the reactor and the flow rate of the product stream were measured and recorded. If all the variables were steady, the filled sample cell was removed and attached to the entrance section of the chromatograph column. A second sampler was then placed on the sample port of the reactor. When the base line of the chromatograph recorder had become steady, the contents of the first sampler were analyzed, and at the appearance of the final elution peak the second sampler was taken from the reactor. In this manner three samples were taken under steady operating conditions from the reactor. The time interval between samples was 20 to 35 min. and was governed by both the analysis time and the steadiness of the operating conditions. If the three samples were found to agree satisfactorily by inspection of the elution peaks, the feed rate was adjusted to a new value, but the temperature and pressure were held constant. After a change in feed rate about 1½ hr. were required for reestablishment of steady state. When a series of runs had been completed, the reactor was put in stand-by condition by adjusting the temperature to approximately 800°F. The pressure of the reactor was reduced to atmospheric, and calibration samples were withdrawn from the feed-stream sampling port. Finally the exit valves on the reactor were closed, and the entire system was pressurized to about 50 lb./sq.in. gauge with nitrogen.

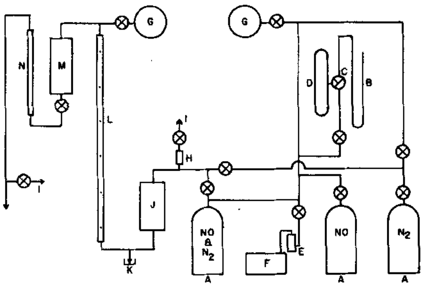

Fig. 1. Flow diagram of reactor assembly: A = compressed gas, B = manometer, C = stopcock, D = McLeod gauge, E = trap, F = vacuum pump, G = Bourdon gauge, H = check valve, I = sample port, J = preheater, K = safety disk, L = reactor, M = cooler, and N = rotameter.

After a series of experiments had been completed on a particular bed of catalyst, the reactor was allowed to cool. The top was opened, and after the depth of the void space above the catalyst was measured, the catalyst was emptied into a vial and weighed.

Reactor Operation

The work reported here is based upon a reactor operated as an integral unit at constant pressure and temperature and at steady state. Longitudinal mixing by diffusion and radial gradients of concentration and velocity were neglected. It was observed experimentally that no fouling of the catalyst occurred, in which case the design equation becomes simply

$$F dx = r dw \qquad (4)$$

The integral form of Equation (4) is

$$\frac{w}{F} = \int_0^x \frac{dx}{r} \qquad (5)$$

Values of x vs. w/F were obtained experimentally and plotted on Cartesian coordinates. It was assumed that the changes in feed rate for a given weight of catalyst did not affect the basic mechanism of the reaction, namely that diffusion was not a rate-controlling factor, so that the curves were graphically differentiated to obtain the rate in accord with the expression

$$r = \frac{dx}{d\left(\frac{w}{F}\right)} \qquad (6)$$

This is the same as the differentiation of Equation (5) with the assumption that the use of F as the independent variable rather than w has no effect in the treatment. The rate obtained by use of the relation in Equation (6) was for the surface reaction and was only slightly affected by resistance to internal diffusion in the pores. Analy-

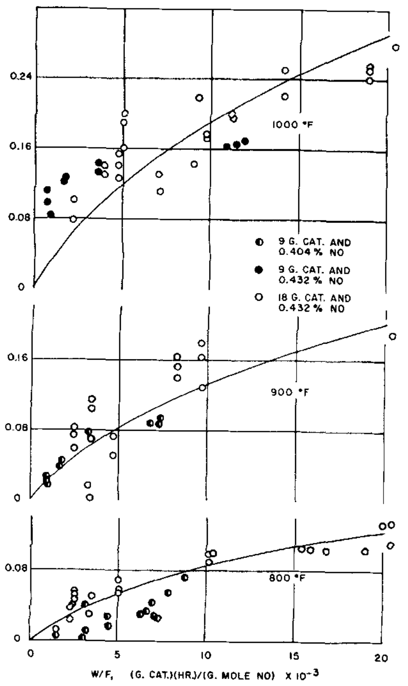

Fig. 2. Conversion of nitric oxide xs. w/F at 1 atm.

sis by use of the Wheeler model (*20*) based upon Thiele's work (*19*) showed that for fractional conversions greater than 0.04 the fraction of surface available was always greater than 0.93.

Values of r obtained as a function of x were used to test a series of postulated rate equations. The final test of a selected rate equation was to compare the results of the integration of Equation (5) with experimental data.

Temperature Control

The main source of difficulty in conducting the experiments was the control of temperature. Control was manual and subject to fluctuations in line voltage which were not eliminated until the last part of the experimental program. When the reactor was operated in the temperature range of 800° to 1,000°F. a difference in setting of approximately 5 v. was required to change the temperature by 100°F. Once the operating temperature was obtained for a given pressure, it was controllable to ± 2°F. at a point when no fluctuation in line voltage occurred.

There were times when temperature changes during intervals between samples were as great as 10°F. When those variations were observed, samples were not taken until the operating temperature was steady for at least 10 min. within the limits of ± 2°F.

In accordance with thermocouple readings the temperature difference over the length of the catalyst bed did not exceed 3°F. The temperature profile was assumed to be linear between thermocouples, and an arithmetic average of the point measurements was used to obtain the temperature of the catalyst bed. That temperature in turn was considered to be the same as that at the center of the catalyst. A computation showed that the maximum temperature difference between the main gas stream and the center of a pellet was less than 1°F. The temperature gradient was small because of the very low rates of reaction for the low concentrations of nitric oxide.

Pressure Control

When the total pressure in the reactor was above 1 atm., it was measured with a gauge and controlled to within ± 0.1 atm. For the studies at atmospheric pressure the differential manometer was used. At this pressure the pressure drop was less than 0.007 atm. for the maximum flow rate. Since the absolute pressure of the surroundings varied from 0.968 to 0.974 atm., the average pressure for the atmospheric runs was taken as 0.975 ± 0.01 atm. but reported as 1 atm.

For all other conditions of temperature, pressure, and flow rate the maximum pressure drop through the reactor was less than 0.01 atm., and this change was neglected.

Feed Rate

The maximum errors in the measurements of feed rate varied from ± 3% at the lower rates to ± 1% at the higher rates. These were largely due to uncertainties in reading the rotameter scale.

Feed and Product Composition

The composition of the feed gas was either 0.404 or 0.432% nitric oxide in nitrogen to within ± 1%. Analyses of the mixtures by gas chromatography showed the absence of water and other impurities which could be separated from nitrogen or nitric oxide. Impurities which were not separable from nitrogen or nitric oxide were negligible.

The fractional conversion of nitric oxide in the reactor was obtained from the following relation between chromatogram areas:

$$x = \frac{\text{area \% NO in feed stream} - \text{area \% NO in product stream}}{\text{area \% NO in feed stream}} \qquad (7)$$

Equation (7) states implicitly that the calibration factor to convert the area per cent to volume per cent is the same for both the feed and product streams. Knowledge of the fractional conversion of the nitric oxide allowed computation of the per cent of oxygen in the product stream. The amount of oxygen present was not in excess of 0.2%. Therefore its contribution to the nitrogen peak was negligible.

Assuming that the gases behaved as mixtures of perfect gases and that only nitrogen and oxygen were the decomposition products of nitric oxide, one can use the following equations to relate conversions and partial pressures:

$$p_{NO_0} = (\text{\% NO in feed by chromatographic analysis}) \left(\frac{\pi}{100}\right) \qquad (8)$$

$$x = \frac{p_{NO_0} - p_{NO}}{p_{NO_0}} \qquad (9)$$

$$p_{O_2} = \frac{(p_{NO_0})(x)}{2} \qquad (10)$$

$$p_{N_2} = p_{N_{2_0}} + \frac{(p_{NO_0})(x)}{2} = \pi - (p_{NO_0})\left(1 - \frac{x}{2}\right) \qquad (11)$$

$$\pi = p_{NO} + p_{O_2} + p_{N_2} \qquad (12)$$

Weight of Catalyst

The catalyst pellets were weighed and counted before and after use, and these data are listed in Table 2. The ratio of the weight of catalyst charged to the reactor to that after use was reproducible to within ± 6%, and the weight after use was used to calculate the w/F ratio noted in Equation (5). Loss in weight was because of loss of moisture and fines in the activation of the catalyst.

EXPERIMENTAL RESULTS

Data Correlation

Values of x were plotted as functions of w/F for parameters of constant temperature and pressure. Figures 2, 3, and 4 are plots of data from studies with 9 or 18 g. of catalyst in the reactor. The solid curves in each figure are plots of a generalized equation which is to be discussed. Tabular summaries of all the data collected are available (*14*).

TABLE 2. DATA ON PACKING OF G-43 CATALYST BEDS IN THE REACTOR

Packing no.	No. of pellets	Bed height*, (in.)	Weights,† Input (g.)	Output
1	250	4.0	10.14	8.99
2**	500	8.0	20.05	17.97
3	500	7.6	20.05	18.00

* After activation and use.

† Weight difference between input and output due to removal of moisture and dust in activation of catalyst.

** This catalyst charge was used in studies at 1 and 8 atm. and the other 18-g. charge at 15 atm.

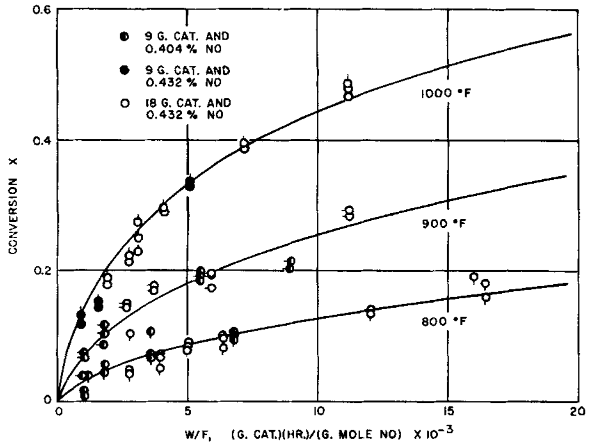

Fig. 3. Conversion of nitric oxide vs. *w/F* at 8 atm.

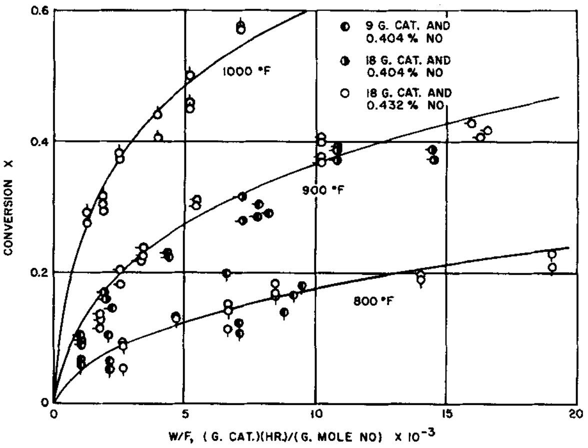

Fig. 4. Conversion of nitric oxide vs. *w/F* at 15 atm.

In the correlation of the data for x as a function of w/F it was assumed that:

1. Side reactions and the reverse reaction in the equation $2NO \rightleftarrows N_2 + O_2$ were negligible.
2. The gas system was a mixture of perfect gases.
3. The adsorption and reaction constants were functions only of temperature.
4. Diffusion steps were always rapid and at equilibrium.
5. Only one of the possible chemical steps was rate controlling, while all the others were at equilibrium. In the derivations adsorption was considered as a chemical step.
6. The law of mass action applied to all reactions including those involving active sites on the catalyst.

In consideration of the above assumptions various models of the possible controlling reaction were considered. The rate equations based on these models were examined by means of a least squares method (*10*) on a Burroughs 220 digital computer. Since the integrated equations for w/F as a function of x contained transcendental terms which were complex and difficult to linearize, the general least-squares method was inapplicable. To circumvent this problem the least-squares method was applied directly to the rate equations, which could easily be linearized. Rate and conversion data for the analyses were obtained from curves of x vs. w/F that had been smoothed by eye.

The calculations were made initially with individual curves as well as combinations of curves from the data at 1,000°F. The constants obtained were substituted into the integrated equations for the particular models, and the resulting curves were compared with experimental data points. Equations which obviously did not give fits to the experimental data were eliminated from further consideration. Continuation of this procedure showed that the only rate equation to fit all of the curves individually was of the form

$$r = \frac{A(p_{NO})^2}{(1 + B\sqrt{p_{O_2}})^2} \qquad (13)$$

The coefficients A and B obtained from the computer in fitting individual curves as well as all the curves were varied and scattered. It was then necessary to use trial-and-error calculations to correlate the coefficients of Equation (13) as orderly functions of temperature and pressure.

Evaluation of Constants in Equation (13)

Equation (13) was substituted into Equation (5) and the latter integrated:

$$\frac{w}{F} = \frac{1}{A}(p_{NO_0})^2\left[\frac{x}{1-x} + B\sqrt{2(p_{NO_0})}\left(\frac{\sqrt{x}}{1-x} - \frac{1}{2}\ln\frac{1+\sqrt{x}}{1-\sqrt{x}}\right) + \frac{B^2(p_{NO_0})}{2}\left(\ln|1-x| + \frac{x}{1-x}\right)\right] \qquad (14)$$

The nature of the constants A and B in Equations (13) and (14) has been noted (*9*). The quantity A is composed of several factors and is described by

$$A = kS\,K_{NO}^2\,L \qquad (15)$$

in which for these investigations L is a function of the total pressure of nitrogen. The quantity B is the square root of the adsorption equilibrium constant for oxygen on the catalyst and is described by

$$B = \sqrt{\left(\frac{C_O^2}{C_s^2\,p_{O_2}}\right)_{equil}} \qquad (16)$$

Because of the large concentration of nitrogen relative to nitric oxide and oxygen and the experimental observation that nitrogen was adsorbed on the catalyst, it was necessary to modify Equation (13) to account for the competitive adsorptivity of the nitrogen. This effect was incorporated in the constant A; thus A was taken to be a function of temperature and pressure, while B was considered to be a function only of temperature.

A correlation of A as a function of temperature and pressure gave an equation of the form

$$A = 39.7\,e^{\frac{-3,080}{T}} - 17.3\left(e^{\frac{-2,740}{T}}\right)(p_{N_2})^{1/2} + 3.18\left(e^{\frac{-3,010}{T}}\right)(p_{N_2}) \qquad (17)$$

The units of A are (g. moles NO)/(g. catalyst) (hr.) (atm.)^2 with T expressed in °R. and pressures in atmospheres. For B the temperature dependence was found to be given by the relation

$$B = 0.0135\,e^{\frac{11,100}{T}} \qquad (18)$$

The units of B are atm.$^{-1/2}$, and T is temperature in °R.

Values of A and B are given in Table 3 and were used in Equation (14) to obtain curves of w/F as a function of x. These curves are plotted in Figures 2, 3, and 4 and give a clear picture of their correlation with experimental points. Data beyond a value of 20,000 for w/F are not included because of the increasing effect of diffusion in the main gas stream.

DISCUSSION OF RESULTS

Assumptions

Several factors, such as catalyst fouling, diffusion, and the reverse reaction, were neglected in the derivation of the rate equations presented. Experimental data indicated that catalyst fouling did not occur for periods up to 48 days at least. Relative to diffusion, rough estimates following the methods discussed by Smith (*18*) showed that the effect of diffusion on the partial pressure of oxygen was less than 1% for w/F less than 20,000. Experimental data for x as a function of w/F also showed that the effects of diffusion in the main gas stream were negligible for values of w/F less than 20,000 because for a given w/F approximately the same value for x was obtained for different values of w. With respect to the reverse reaction, available data (*21*) show that relative to the forward reaction it is essentially negligible in the temperature range of 800° to 1,000°F.

Accuracy of Data

One of the major sources of error in the rate studies was introduced by fluctuations in line voltage which affected temperature control. It is believed that in some instances temperature fluctuations in the reactor were as high as ± 10°F. over a 10-min. period.

Another source of error was in the sampling of the reaction products. Although reactor samples were usually analyzed within 15 min., it was occasionally necessary to store the samples in a glass sampler for 20 min. This was sufficient time for oxygen, which was a product of the decomposition reaction, to react partially with the remaining nitric oxide to form nitrogen dioxide. Calculations showed that up to 5% of the nitric oxide could be oxidized in a period of 30 min. at room temperature. Therefore the samples were analyzed as rapidly as possible to minimize that source of error. Not only was the homogeneous reaction a possible source of difficulty, but a heterogeneous reaction in the presence of the silica gel in the chromatographic column could have occurred. The heterogeneous reaction was minimized however by the nature of the chromatographic analysis. First the sample was introduced (*15*) by way of a glass cell having a volume of about 3 cc. The resultant chromatograms suggested complete mixing (*12*) of the contents of the cell and the helium carrier gas which was flowing at the rate of 40 to 50 cc./min. That mixing then provided significant dilution of the already dilute reactants. Retention time for the nitrogen-oxygen system was about 90 sec. and about 170 sec. for the nitric oxide, which suggests a rapid separation of the oxygen from the entering nitric oxide. An estimate of the presence of nitrogen dioxide was obtained directly in the chromatographic analysis. In the column that was used the nitrogen dioxide peak would have appeared after that of nitric oxide, and no area greater than 2% of the nitric oxide area was observed with the particular chromatographic techniques. Within the errors of the experimental work then the combined effect of the homogeneous and heterogeneous reactions between nitric oxide and oxygen was not considered significant.

TABLE 3. VALUES OF A AND B IN THE EQUATION $r = \dfrac{A(p_{NO})^2}{(1 + B\sqrt{p_{O_2}})^2}$

Temperature, (°F)	B	A 1 atm.	A 8 atm.	A 15 atm.
800	94	1.8	0.21	0.19
900	50	2.15	0.34	0.36
1,000	28	2.6	0.55	0.62

In general the over-all error in chromatographic analysis was magnified in terms of conversion of nitric oxide and could have been excessively high at lower conversions as may be seen from Equation (7). For example with an error of ± 5% in the product analysis an uncertainty of ± 45% would result for a 10% conversion of nitric oxide and an uncertainty of ± 20% for a 20% conversion. The scatter of the data, especially for the pressure of 1 atm., was partly attributable to these uncertainties at low conversion. Because of the large quantity of data however the errors at low conversion should have been significantly reduced by the smoothing and correlating processes.

CONCLUSION

The rate of the heterogeneous decomposition of nitric oxide over a platinum-nickel catalyst supported on activated alumina was found to be second order with respect to nitric oxide, retarded by atomic oxygen, and further retarded by the excess nitrogen in the system.

The rate equation

$$r = \frac{A(p_{NO})^2}{(1 + B\sqrt{p_{O_2}})^2} \qquad (13)$$

is applicable for the decomposition of nitric oxide present in nitrogen at concentrations of less than 0.5% within the temperature range of 800° to 1,000°F. and a pressure range of 1 to 15 atm. Retardation by the atomic oxygen is expressed in terms of an adsorption term $B\sqrt{p_{O_2}}$ in the denominator of the rate expression, whereas the retardation by the nitrogen is included in a factor A in the numerator and is considered to cause a decrease in the number of available active sites per unit weight of catalyst.

A bimolecular surface reaction between two adsorbed nitric oxide molecules is suggested by the rate equation, but the sequential steps in the reaction have not been uniquely defined. One series of reaction steps compatible with Equation (13) is given as follows:

$$NO + s \rightarrow NOs \qquad (19)$$

$$2NOs \rightarrow N_2 + 2Os \qquad (20)$$

$$2Os \rightarrow O_2 + 2s \qquad (21)$$

In this series of equations s is an empty active site on the surface of the catalyst, and NOs and Os are adsorbed NO and O, respectively. Equation (20) represents the rate-controlling step. The actual rate equation for this step could be presented as

$$r = \frac{kS\,K_{NO}{}^2\,L\,(p_{NO})^2}{(1 + K_{NO}p_{NO} + \sqrt{K_{O_2}p_{O_2}})^2} \qquad (22)$$

If the term representing the adsorbed nitric oxide is small compared with other terms in the denominator, Equation (22) then reduces to the form of Equation (13).

ACKNOWLEDGMENT

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NOTATION

a = constant in rate equation
A = constant in rate equation, (g. moles NO)/(g. catalyst) (hr.) (atm.)^2
B = constant in rate equation, atm.$^{-1/2}$
c = constant
C = concentration of empty or occupied sites, as designated, g. moles/g. catalyst
F = feed rate to reactor, g. moles NO/hr.
k = specific reaction rate constant in consistent units
K = adsorption equilibrium constant
L = concentration of active sites, g. moles/g. catalyst
p = partial pressure, atm.
r = rate of conversion in consistent units
s = designation of an empty active site
S = number of adsorption sites equidistant from a given site
T = absolute temperature, °R.
x = fractional conversion of NO
w = weight of catalyst, g.

θ = time, hr.
π = total pressure, atm.

Subscripts

o = initial conditions
s = designation of an empty active site

LITERATURE CITED

1. Armour Research Foundation, Report No. 8, *ARF Project No. C711* (February, 1957).
2. Bachman, P. W., and G. B. Taylor, *J. Phys. Chem.*, **33**, 447 (1929).
3. Briner, E., and N. Bouboff, *Compt. Rend.*, **156**, 228 (1913).
4. ————, *J. Chim. Phys.*, **11**, 597 (1914).
5. Briner, E., and A. Wroczynski, *Compt. Rend.*, **149**, 1372 (1910).
6. Fraser, J. M., and F. Daniels, *J. Phys. Chem.*, **62**, 215 (1958).
7. Granier-Mayence, J., J. Robin, and S. Robin, *Compt. Rend.*, **236**, 1011 (1953).
8. Green, T. E., and C. N. Hinshelwood, *J. Chem. Soc.*, **129**, 1709 (1926).
9. Hougen, O. A., and K. M. Watson, "Chemical Process Principles, Part Three. Kinetics and Catalysis," p. 923, Wiley, New York (1947).
10. *Ibid.*, p. 938.
11. Muller E., and H. Barck, *Z. Anorg. Allgem. Chem.*, **129**, 309 (1923).
12. Porter, P. E., C. H. Deal, and F. H. Stross, *J. Am. Chem. Soc.*, **78**, 2999 (1956).
13. Sakaida, R. R., Ph.D. thesis, Calif. Inst. Technol., Pasadena, California (1960).
14. Sakaida, R. R., Y. I. Wang, R. G. Rinker, and W. H. Corcoran, Am. Doc. Inst., Washington 25, D. C., Document 6891 (1961). A copy of this document may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress, Washington 25, D. C.
15. Sakaida, R. R., R. G. Rinker, R. F. Cuffel, and W. H. Corcoran, *Anal. Chem.*, **33**, 32 (1961).
16. Scheuer, O., *Wien. Ber.* (11a), **123**, 931 (1914).
17. Schwab, G., R. Staeger, and H. H. Baumbach, *Z. Physik. Chem.*, **B21**, 65 (1933).
18. Smith, J. M., "Chemical Engineering Kinetics," p. 234, McGraw-Hill, New York (1956).
19. Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).
20. Wheeler, A., "Catalysis," Vol. 2, P. H. Emmett, ed., p. 138, Reinhold, New York (1955).
21. Yost, D. M., and H. Russell, Jr., "Systematic Inorganic Chemistry," p. 25, Prentice-Hall, New York (1946).
22. Zawadski, J., and T. Badzynski, *Roczniki Chem.*, **11**, 158 (1931).
23. Zawadski, J., and G. Perlinsky, *Compt. Rend.*, **198**, 260 (1934).

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Interfacial Area in Liquid-Liquid Mixing

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In predicting interfacial area in liquid-liquid systems there are several published reports which give different results. Differences in methods of measurement of interfacial area and impeller design and location account for some of these discrepancies.

For one pair of liquids, 40 parts by volume of ethylhexanol and 60 parts water, it was found that over wide ranges of impeller size to tank size ratio (0.27 to 0.67) that equal power per unit volume gave equal interfacial area per unit volume.

A familiar rule-of-thumb for scaling up a mixing operation is to hold constant the energy input per unit volume. When mixing involves the creation and maintenance of interfacial area between two immiscible liquids, the rule has been supplanted by dimensionless correlations of interfacial area, impeller diameter, and Weber number (*2*, *3*, *5*, *6*). In the model system reported here energy input per unit volume appears to be a more valid criterion than the dimensionless grouping. Specifically it has been found that the average interfacial area per unit volume is proportional to the 0.4 power of energy input per unit volume for a number of geometric variations.

EXPERIMENTAL

The system used for the correlation of interfacial area with power input consisted of 40 parts by volume of 2-ethylhexanol and 60 parts of water. The alcohol was commercial grade (interfacial tension, 13.9 dynes/cm.; density 0.834 g./cc.; refractive index, 1.431 at 20°C.).

As in previous studies (*1* to *5*, *7*, *8*) light transmission was used as a measure of particle size. The apparatus is patterned after that of Trice and Rodger (*7*). Essentially a beam of light is led through a glass probe into the suspension. Another probe transfers light transmitted by the suspension to a photocell (Figure 1). The signal from the photocell is amplified, compared with the initial beam, and recorded.

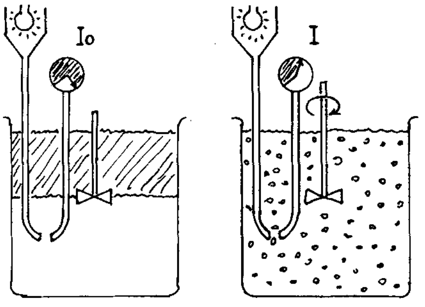

Fig. 1. The light beam transmitted by the glass probe is interrupted by a 0.9 cm long path through the continuous phase (I_o) or by the agitated suspension (I).

For measurement of power input a Chemineer ELB kit was used. The basic kit (*9*) consists of a ball-bearing mounted motor and variable speed reducer, various impellers and baffles, an 8- and a 16-gal. tank. The maximum of three baffles, symmetrically located, was used in the above tanks and also in a 1-gal. tank. The dynamometer is simply a two-pan balance, one pan of which is connected by a wire to an arm from the speed reducer mounting.

LIGHT TRANSMISSION AS A MEASURE OF INTERFACIAL AREA

Three groups of workers have reported the measurement of interfacial area of liquid-liquid dispersions (*1*, *4*,

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