Effect of Water Vapor on the Catalytic Oxidation of Nitric Oxide

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Extension of the kinetics of the catalytic oxidation of nitric oxide on activated carbon and silica gel confirms the rate-controlling step postulated by previous workers. The effect of variables including water vapor on the reaction rate is expressed by an equation containing the constants *a*, *b*, *c*, and *w*, which have been evaluated for both catalysts at 30°, 45°, and 60°C. The effect of water vapor is to reduce the reaction by reversible adsorption on the active sites of the catalyst. The value of *w* is dependent on temperature but independent of water-vapor concentration up to a relative humidity of 20%. Above 20% the value of *w* for activated carbon increases greatly with relative humidity, in agreement with the effect of capillary adsorption at high water contents.

In the Wisconsin process for nitrogen fixation, ambient air is heated to about 2,500°K. in a reversing pebble-bed furnace (*4*). At this temperature nitrogen and oxygen combine to form nitric oxide. The heat of reaction and heat losses are supplied by the combustion of an admixed fuel gas, and the resultant gaseous product contains about 2% nitric oxide along with the combustion products, including water vapor.

The nitric oxide is further oxidized to nitrogen dioxide by passing the gases through a fixed bed of silica gel or activated carbon. Water vapor, however, retards the catalytic rate of this secondary oxidation and thus reduces the capacity of the reactor. A rate equation for the catalytic oxidation of nitric oxide in a flow system having been previously established (*1*, *7*) in terms of pressure, temperature, and gas composition by use of silica gel and activated-carbon catalysts in a fixed bed, the purpose of the present investigation was to determine quantitatively the effect of water vapor on the kinetics of this same catalyzed reaction in order to decide how much water vapor it is economical to remove before the gas passes into the secondary reactor.

PREVIOUS WORK

Previous work on the catalytic oxidation of nitric oxide was carried out by Baker, Wong, and Hougen (*1*) and Rao and Hougen (*7*), who found that the apparent rate-controlling chemical step in the catalytic oxidation was a surface reaction between molecular oxygen in the gas phase and an adsorbed complex of nitric oxide. The catalytic reaction was postulated to occur through the following sequence of steps:

1. equilibrium formation of a nitric oxide dimer in the gas phase

$$2NO \rightleftarrows (NO)_2$$

2. equilibrium activated adsorption of the nitric oxide dimer

$$(NO)_{2(gas)} + (\text{active site}) \rightleftarrows (NO)_{2(ads)}$$

3. surface reaction between the adsorbed dimer and oxygen in the gas phase (This is the rate-controlling step.)

$$(NO)_{2(ads)} + O_{2(gas)} \rightleftarrows NO_{2(ads)} + NO_{2(gas)}$$

4. equilibrium desorption of nitrogen dioxide

$$NO_{2(ads)} \rightleftarrows NO_{2(gas)} + (\text{active site})$$

According to this postulation, the rate equation is expressed as follows:

$$r = \frac{p_{NO}{}^2 p_{O_2}}{a + b p_{NO}{}^2 + c p_{NO_2}} \qquad (1)$$

The kinetics of the homogeneous reaction has been investigated by Bodenstein (*3*), Hasche and Patrick (*5*), Trautz (*8*), and Treacy and Daniels (*9*). The last investigators postulated that the rate-controlling step was the reaction $NO_3 + NO \rightleftarrows 2NO_2$, where NO_3 was an intermediate complex resulting from the equilibrium oxidation of nitric oxide. Trautz first proposed that $(NO)_2$ was the intermediate complex. Either postulation accounts for the negative temperature coefficient of the over-all homogeneous reaction velocity constant based on a third order reaction rate equation.

$$2NO_{(gas)} + O_{2(gas)} \rightleftarrows 2NO_{2(gas)} \qquad (2)$$

$$r_H = k_H p_{NO}{}^2 p_{O_2}$$

Since the rate of homogeneous reaction at all degrees of conversion is small relative to the reaction rate catalyzed by silica gel and negligible with activated carbon, the exact form of the homogeneous rate equation is not essential when it is used in correcting the total reaction rate to obtain the catalytic reaction rate; hence, the simple third-order equation was used for the homogeneous reaction. The constant k_H in the third-order equation (2) was determined by Hasche and Patrick (*5*) and by Rao (*7*).

	30°C.	45°C.	60°C.
(*5*)	3,733	3,420	3,140
(*7*)	4,413	4,068	3,408

In this study the values obtained by Rao were used, as they were obtained on the same experimental equipment as was used in this investigation.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The experimental equipment was adapted from that used by Rao in his study of the catalytic oxidation of nitric oxide under essentially dry conditions (*7*). The principal modifications were the addition of equipment for introducing, controlling, and measuring the amount of water vapor in the feed. A photograph of the equipment is shown in Figure 1 and a flow chart in Figure 2.

The experimental reactor was of the series-integral type. This type is particularly advantageous in kinetic studies where available methods of analysis are not sufficiently accurate to permit the use of a differential-type reactor, and it has the additional advantage of permitting several simultaneous analyses to be made at several points in the reactor under the same constant conditions of entering feed. Constants in the rate equation were thus obtained from an integrated equation rather than by graphical differentiation.

The reactor consisted of four sections of ¾-in. stainless steel pipe each 6 in. long. Valves permitted by-passing the gas stream from any section directly to the outlet manifold. Control of the reactor pressure was maintained by a needle valve on the outlet manifold. The reactor assembly was immersed in a controlled-temperature bath to maintain nearly isothermal reaction conditions. The inlet air was measured by a calibrated orifice meter and the nitric oxide feed by a calibrated Fischer-Porter Flowrator.

The content of water vapor in the feed was controlled by bubbling a portion of the feed air through a column of water. The air streams were then recombined and the dew point was determined by use of a continuously recording dew-point hygrometer. The hygrometer used in the present work was constructed by Bickling (*2*).

The photometric analyzer used for the analysis of gases containing nitrogen dioxide was similar to that used in many other studies. It consisted of a Pyrex tube

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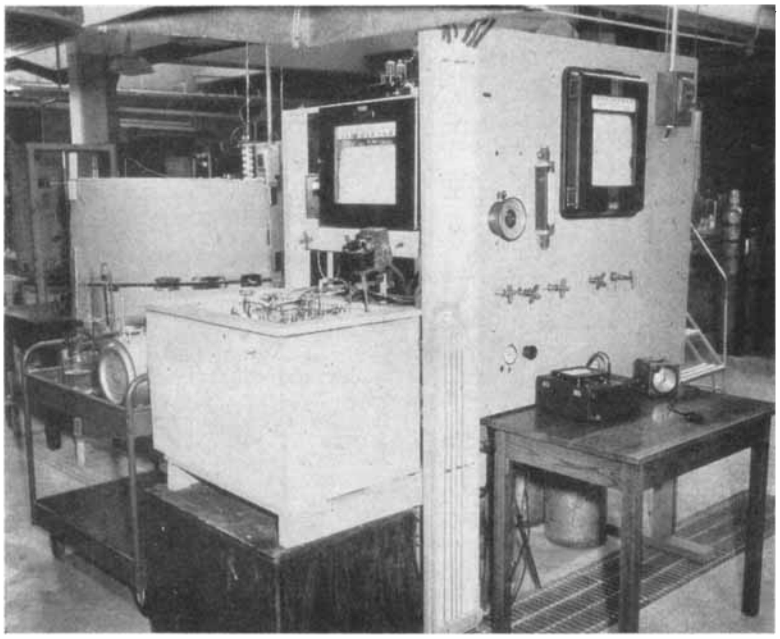

Fig. 1. Experimental equipment.

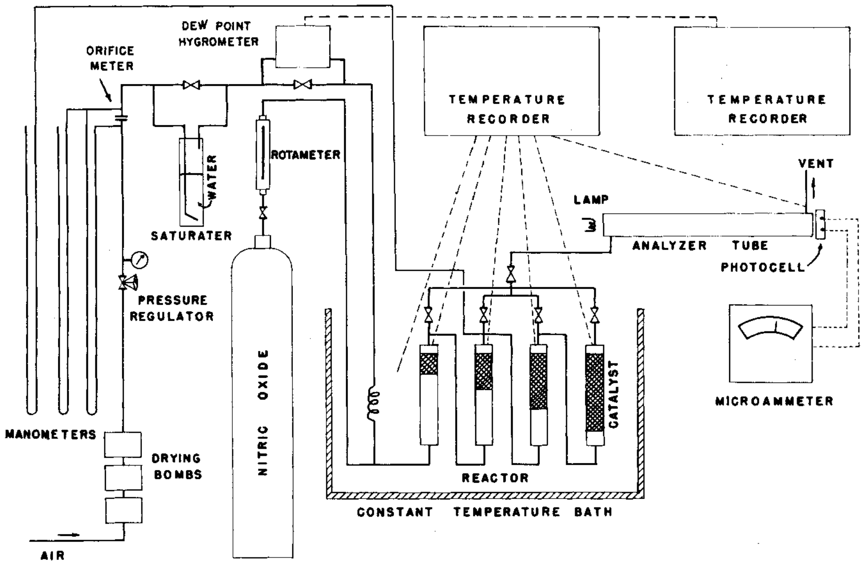

Fig. 2. Flow sheet, catalytic oxidation of nitric oxide.

1½ in. in diameter and 18 in. in length with flat ends. Outlets were located in the wall of the tube approximately ½ in. from each end.

The light source was an ordinary flashlight reflector powered by a 5-cell Edison battery. An ammeter and variable resistance in the lamp circuit permitted regulation of the light intensity. The light was filtered through a mixed solution of 2.5N calcium chloride and 0.4N copper chloride. This solution transmits light in the range of wave lengths from 460 to 600 mμ. Light of this frequency is absorbed by nitrogen dioxide but not by nitric oxide or nitrogen tetroxide. A barrier-layer type of photocell mounted opposite the light source permitted measurement of the intensity of the light passing through the tube.

The analyzer was calibrated by passing a carefully measured flow of air and nitric oxide over sufficient activated-carbon catalyst to give complete conversion (above 99%). From the established composition of the gas in the analyzer a series of points was obtained by varying the total pressure in the photometric cell. Several duplicate calibrations gave excellent agreement with points falling on the same line. During the experimental runs the entire flow from the reactor was passed continuously through the analyzer as a rapid, convenient, and continuous means of monitoring the product composition.

The nitric oxide used in these experiments was obtained from the Matheson Company in steel cylinders initially at 480 lb./sq. in. Compressed air was the source of oxygen.

The activated-carbon catalyst was Columbia activated carbon, grade CXA, obtained from the Carbide and Carbon Chemicals Company. The carbon was crushed and screened to 11 to 20 mesh before use and had a bulk density of 0.48 g./cc. The silica-gel catalyst, consisting of a 16- to 20-mesh granular gel with a bulk density of 0.69 g./cc., was obtained from the Davison Chemical Company. Both catalysts were dried for 1 hr. at 120°C. before being weighed and loaded into the reactor.

During the experimental work flow rates, pressure, temperature, and dew point of the feed were adjusted according to a predetermined experimental schedule and the system was allowed to reach steady state conditions before data were recorded.

Steady state conditions were assumed when no changes occurred in operating conditions and in fraction conversion after several hours of operation. Several identical pairs of runs preceded alternately by a run made at a higher partial pressure of water vapor and one at a lower partial pressure eliminated the uncertainty of nonequilibrium adsorption or of moving-band adsorption; furthermore the fact that there was no change in catalyst activity with either silica gel or activated carbon was established by periodically repeating a standard run. Flow rates of reactants, reaction temperature, reaction pressure, and dew point of the feed air were recorded. Analyses of the reacting gases were made at four points in the reactor by successively by-passing each section of the reactor, starting with the last section.

In the calculation of conversion it was necessary to take into account the equilibrium between nitrogen dioxide and nitrogen tetroxide and also to correct for the extent of the homogeneous reaction which occurred in the sampling lines and in the photometric analyzer cell. The extent of conversion in the free space of the reactor itself and in the prereactor space was found to be negligible. The homogeneous rate equation may be integrated to give the following equation if total moles and mole fraction of oxygen are assumed to be constant. This assumption is good for the low concentrations of nitric oxide used in this study. The complete data are presented in the thesis of Kircher (6).

$$F_t\, dy_{\mathrm{NO}} = -r_{\mathrm{H}}\, dV$$

$$\frac{V}{F_t} = \frac{1}{k_{\mathrm{H}}\pi^3 y_{\mathrm{O}_2(avg)}}\left[\frac{1}{y_{\mathrm{NO}}''} - \frac{1}{y_{\mathrm{NO}}'}\right] \quad (3)$$

REEVALUATION OF THE RATE CONTROLLING CHEMICAL STEP

The rate-controlling chemical step of the catalytic oxidation of nitric oxide has been reported by previous investigators as mentioned above. In order to confirm these decisions, a series of experiments was made with the dew point of the feed-gas stream below −25°C. Rates of reaction were determined by graphical differentiation of plots of conversion vs. catalyst-to-feed ratio.

As an academic exercise the rate-controlling chemical step was selected from sixty-seven postulated rate equations. A few of these equations were formally identical, and others could be eliminated by inspection of the experimental data. The remaining equations, of which there were thirty-three, were tested by a least squares fit of the data. In most cases this calculation produced one or more negative coefficients. Since negative constants are not permissible under the assumptions of the derivation, such a result was taken as an indication that the particular rate equation was not consistent with the data, and was hence eliminated from further consideration. Several equations involving only two constants, both of which were assigned positive values by the least squares calculation, gave poor fits to the data and were also eliminated. Equations postulating the adsorption of nitrogen tetroxide gave poorer agreement than those assuming adsorption of nitrogen dioxide and were likewise eliminated. Six equations remained, all of which were based on surface-reaction–controlling processes. The equation which best agreed with the experimental data was the one previously selected by Rao and by Baker and Wong. Two other equations, which were based on the assumption of NO—O_2 complex, were about equally satisfactory in the range of conditions studied.

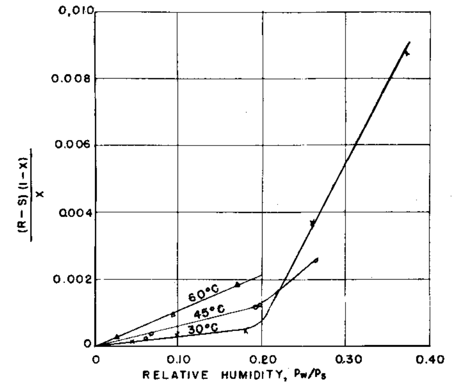

Fig. 3. Water-vapor adsorption term; catalyst, activated carbon; × 30°C., ○ 45°C., △ 60°C.

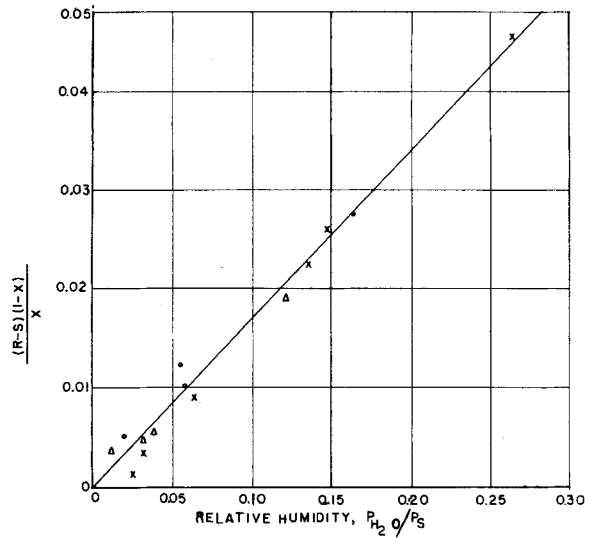

Fig. 4. Water-vapor adsorption term, effect of relative humidity; catalyst, silica gel; × 30°C., ○ 45°C., △ 60°C.

EFFECT OF WATER VAPOR

The effect of water vapor in reducing the rate of catalytic oxidation of nitric oxide may be accounted for in either of two ways: by assuming that the water vapor reduces the activity of the catalyst or that, by reversible adsorption, water molecules occupy active sites on the surface of the catalyst. The experimental data confirm the second theory. The effect of water vapor can be accounted for by the inclusion of the additional adsorption term wp_{H_2O} in the denominator of the rate equation.

$$r = \frac{p_{NO}^2 p_{O_2}}{a + bp_{NO}^2 + cp_{NO_2} + wp_{H_2O}} \quad (4)$$

In evaluating the effect of water vapor and determining the constant w, the use of direct experimental data relating conversion to catalyst-to-feed ratio was considered more reliable than obtaining rates by methods of graphical differentiation. This direct method involves integration of the rate equation.

$$Fdx = rdW$$

$$\frac{w}{F} = \int_0^x \frac{[a + bp_{NO}^2 + cp_{NO_2} + wp_{H_2O}]}{p_{NO}^2 p_{O_2}} dx \quad (5)$$

Partial pressures of the reactants may be expressed in terms of conversion x as follows:

$$p_{NO} = \frac{N_{NO}(1 - x)\pi}{(1 - 1/2xN_{NO})}$$

$$p_{O_2} = \frac{(N_{O_2} - 1/2xN_{NO})\pi}{(1 - 1/2xN_{NO})} \quad (6)$$

$$p_{NO_2} = \frac{xN_{NO}\pi}{(1 - 1/2xN_{NO})}$$

where N_{O_2}, N_{NO} = initial mole fraction of O_2 and NO in the feed. However, the integration of this equation can be greatly simplified for low concentrations of NO and high concentrations of O_2 by neglecting the small change in the total number of moles and assuming a constant average value for the mole fraction of oxygen. Under these assumptions, Equation (5) may be integrated to give

$$\frac{W}{F} = \frac{1}{m^2 n}\left\{(a + wp_{H_2O})\frac{x}{1 - x} + bm^2 x + cm\left[\frac{x}{1 - x} + \frac{\ln(1 - x)}{x}\right]\right\} \quad (7)$$

When the reaction takes place in the presence of water vapor, the partial pressure of water vapor remains constant and the integrated equation may be written

$$\left(\frac{W}{F}\right)_w = \left(\frac{W}{F}\right)_0 + \frac{1}{m^2 n}\left(\frac{x}{1 - x}\right)wp_{H_2O}$$

or

$$wp_{H_2O} = m^2 n\left[\left(\frac{W}{F}\right)_w - \left(\frac{W}{F}\right)_0\right]\frac{1 - x}{x}$$

$$= (R - S)\frac{1 - x}{x} \quad (8)$$

where

$(W/F)_w$ = experimental value in the presence of water vapor
$(W/F)_0$ = calculated value, absence of water vapor assumed

The values of $(R - S)[(1 - x)/x]$ for both catalysts are plotted in Figures 3 and 4 against relative humidity p_{H_2O}/p_s. If w is independent of partial pressure, straight lines should result for equitemperature conditions. For silica gel it will be observed (Figure 4) that a straight line results for conditions up to 25% relative humidity and that the results are independent of temperature. This is characteristic of the equilibrium-adsorption isotherm for water vapor on silica gel.

With activated carbon the isothermal lines are not coincident (Figure 3) and a sudden break occurs at a relative humidity of about 20%, an indication that below 20% relative humidity the *adsorption-equilibrium* constant is independent of partial pressure but that as the relative humidity increases above 20%, the value of w increases rapidly. This behavior is consistent with the capillary-adsorption curves characteristic of activated carbon. For clarity, the results on activated carbon below relative humidities of 20% have been replotted in Figure 5.

SUMMARY OF RATE-EQUATION CONSTANTS

Catalyst: Activated Carbon

Temperature, °C.	a	b	c	w
30	0.000283	0.521	0.00646	0.0812
45	0.000187	0.824	0.00658	0.0634
60	0.000181	0.942	0.01363	0.0544

Catalyst: Silica Gel

Temperature, °C.	a	b	c	w
30	0.00398	3.109	0.242	4.06
45	0.00876	3.435	0.174	1.80
60	0.01597	3.382	0.176	0.865

The same rate-controlling step was obtained for both silica gel and activated carbon by all three sets of investigators (*1, 6, 7*); however, in this investigation higher initial reaction rates were obtained with both silica gel and activated carbon than in previous studies (*1, 7*), with corresponding different numerical values for the constants a, b, and c. With any batch of catalyst, however, the activity remained constant during the period of investigation. For precision these numerical constants require evaluation for each specific catalyst. It should also be stated that greater precaution was taken in this last investigation in removing water from the gas stream and from the catalyst for tests made with dry gases.

For activated carbon, values of conversion calculated from these constants deviated by an average of ±1.9% from experimental values; for silica gel the average deviation was ±1.4%. The range of variation for calculated values was ±6% from experimental values.

The effect of water vapor on percentage conversion as a function of catalyst-to-feed ratio or reciprocal space velocity has been calculated and is shown in Figure 6 for activated carbon and in Figure 7 for silica gel at relative humidities up to 20%. The additional catalyst required to compensate for the presence of water vapor, plotted as function of dew point, is shown in Figure 8 for activated carbon and in Figure 9 for silica gel. The additional catalyst is expressed as a fraction of that required when no water vapor is present. These results are given for 95% conversion of nitric oxide with 3% nitric oxide in the entering feed, an isothermal reaction temperature of 30°C., and a reaction pressure of 1 atm. For example, at a dew point of −20°C. 17% more activated carbon is needed than for a dry gas; at a dew point of 0°C. 100% more catalyst is required. For silica gel, 30% more is required at a dew point of −20°C. than for the dry gas and 220% more at a dew point of 0°C. These figures apply to a reaction temperature of 30°C. It is evident that silica gel is much more sensitive to the partial pressure of water vapor than is activated carbon below a relative humidity of 20%.

SUMMARY

In these experiments on the catalytic oxidation of dilute nitric oxide, the apparent rate-controlling chemical step and the corresponding form of the rate equation as obtained by previous investigators has been confirmed. The quantitative effect of water vapor on the reaction rate has been established for both silica gel and activated carbon catalysts. In the presence of water vapor the reaction-rate equation is

$$r = \frac{p_{NO}^{2} p_{O_2}}{(a + b p_{NO}^{2} + c p_{NO_2} + w p_{H_2O})} \qquad (9)$$

The effect of water vapor is to reduce the reaction by reversible adsorption on the active sites of the catalyst. The value of w is dependent on temperature but independent of water-vapor concentra-

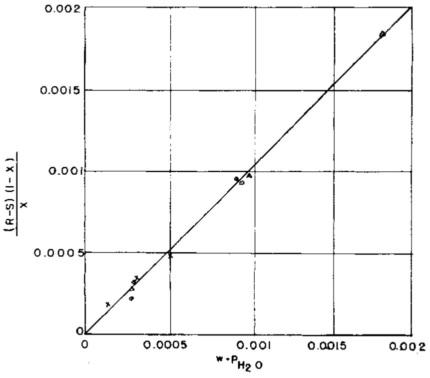

Fig. 5. Water-vapor of adsorption term at relative humidity below 20%; catalyst, activated carbon.

× 30°C., w = 0.0812
○ 45°C., w = 0.0634
△ 60°C., w = 0.0544

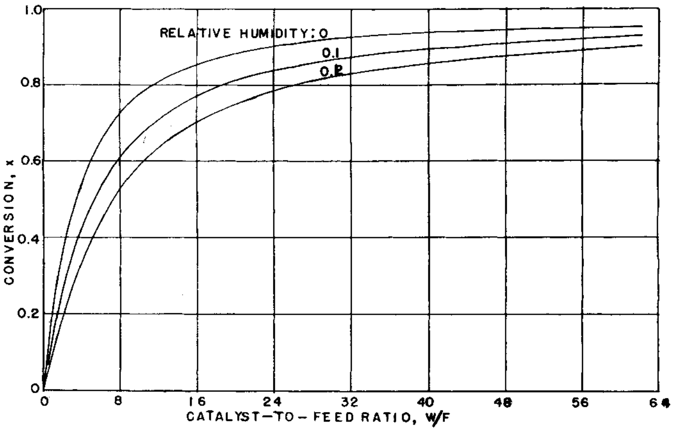

Fig. 6. Effect of water vapor on the conversion of nitric oxide.

Catalyst: activated carbon
Pressure: 1.0 atm.
Temperature: 30°C.
Feed: 3% nitric oxide in air

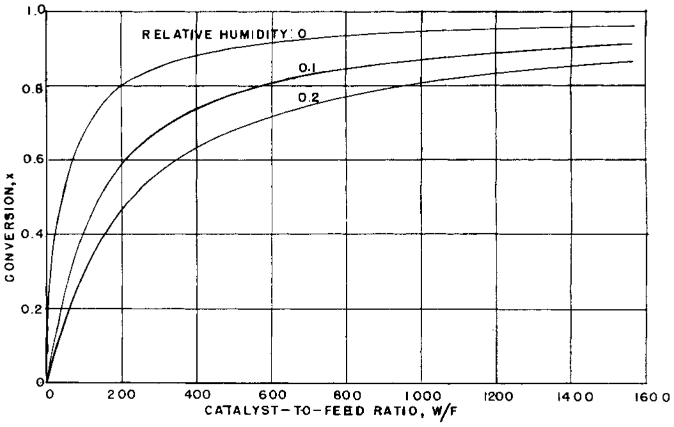

Fig. 7. Effect of water vapor on the conversion of nitric oxide.

Catalyst: Silica gel
Pressure: 1.0 atm.
Temperature: 30°C.
Feed: 3% nitric oxide in air

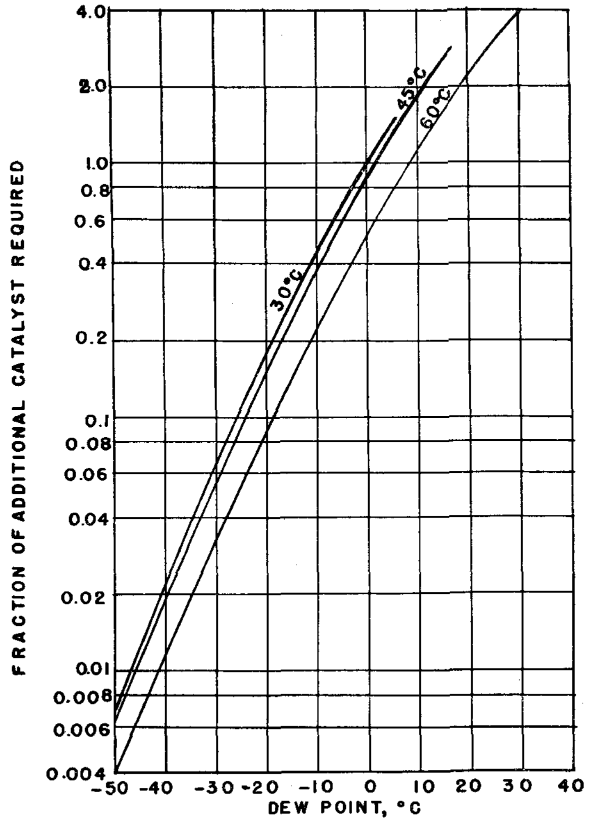

Fig. 8. Effect of dew point on the fraction of additional catalyst required.
Catalyst: activated carbon
Pressure: 1.0 atm.
Feed: 3% nitric oxide in air
Conversion: 95%

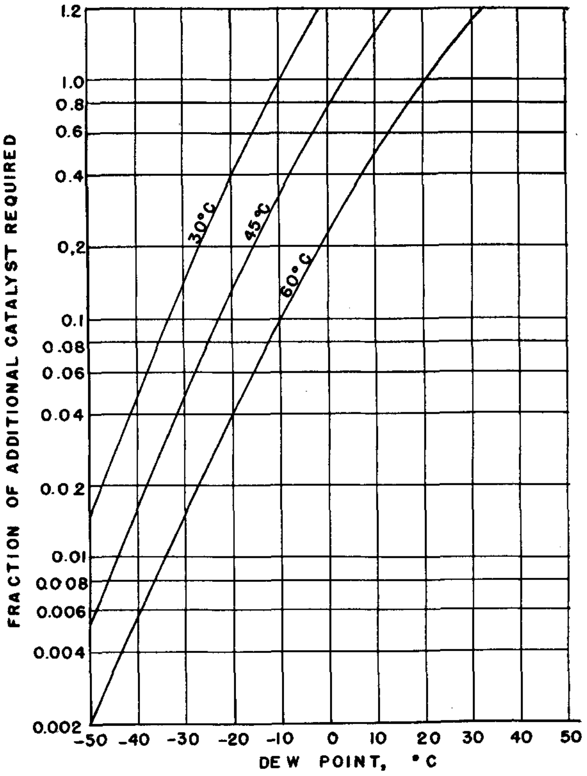

Fig. 9. Effect of dew point on the fraction of additional catalyst required.
Catalyst: silica gel
Pressure: 1.0 atm.
Feed: 3% nitric oxide in air
Conversion: 95%

tion up to a relative humidity of 20%. At relative humidities above 20% the value of w for activated carbon increases greatly with relative humidity, apparently corresponding to the effect of capillary adsorption.

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NOTATION

a = rate-equation constant
b = rate-equation constant
c = rate-equation constant
F = feed, g.-moles of nitric oxide/hr.
F_t = total feed, g.-moles/hr.
k_H = homogeneous reaction velocity constant
m = initial partial pressure of nitric oxide, atm. = $N_{NO}\pi$
n = average partial pressure of oxygen, atm. = $(N_{O_2} - \frac{1}{4}N_{NO})\pi$
N_A = initial mole fraction of subscript component
π = total pressure, atm.
p_A = partial pressure of subscript component, atm.
p_s = vapor pressure of water, atm.
R = $m^2n(W/F)_w$ (experimental value in the presence of water vapor)
r = catalytic rate of reaction, g.-moles of nitric oxide reacted/(g. of catalyst)(hr.)
S = $m^2n(W/F)_O$ (calculated value, absence of water vapor assumed)
V = volume of reactor, liters
W = mass of catalyst, g.
w = rate-equation constant
x = conversion, moles of nitric oxide reacted/mole of nitric oxide feed
y_A = mole fraction of subscript component

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