Heat Transfer and Kinetics in a Catalyst Bed of Rectangular Cross Section:

Air Oxidation of Nitric Oxide with Silica Gel

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The results of an investigation of heat transfer and reaction kinetics in a fixed-bed catalytic reactor of slab geometry are described. The particular reaction studied is the air oxidation of nitric oxide with silica gel. Conversions and catalyst-bed temperatures were observed in the experimental, nonisothermal slab reactor, but only a sample of these data are reported and analyzed here.

A mathematical analysis of the processes occurring in a slab reactor has been developed which leads to a design method for such reactors that permits prediction of catalyst-bed temperatures and conversions from a knowledge of specific reaction rates and the physical properties of the system. The design method involves a step-by-step procedure but requires a small number of steps. To evaluate the accuracy of the design method and to illustrate its use, the specific reaction-rate data together with published thermal-conductivity data have been used with the method to predict the results of a run on the experimental nonisothermal reactor. Good agreement between calculated and observed temperatures and conversions was obtained.

Specific reaction rates, derived from integral conversions in an experimental, isothermal reactor, are reported.

The studies of heat transfer in catalytic converters made in recent years have advanced remarkably our knowledge of this important problem in chemical engineering design. For the most part these studies have been confined to cylindrical beds, but there are certain advantages to converters of other shapes; for example, a slab bed (one of rectangular cross section with heat transfer through two opposite sides) may be enlarged greatly in an area without increasing the distance through which heat must flow, and also the mathematical analysis is somewhat simpler than for cylindrical converters. The purpose of this work was, therefore, the study of heat transfer and kinetics in a catalyst bed of rectangular cross section. The particular reaction, the air oxidation of nitric oxide with silica gel, was selected because the analysis was relatively easy and because a wide variation in reaction rates throughout the converter was anticipated. The second reason constitutes a severe test of theory and experiment.

Since conditions for the slab bed required operating in a range of temperature at which isothermal-rate data for this catalytic reaction were not available, and since the catalyst could not be assumed to be identical to that of previous investigations, it was necessary to measure such rates as well.

RANGE OF VARIABLES

For the runs in the slab bed the following were studied:

Entering gas temperatures: 81° to 136°C.
Air flow rates: 0.029 to 0.125 g. moles air/(sq. cm.)(min.)
Mole fraction nitric oxide in feed: 0.022 to 0.152

The temperature of the coolant for removal of the heat of reaction was close to that of the entering gas. The extent of conversion of nitric oxide was 42 to 82%.

The catalyst used was refrigeration-grade silica gel, 14 to 20 mesh, with a density of 0.680 g./cc.

APPARATUS, ANALYSES, AND PROCEDURE

Reactor System

Nitric oxide was generated continuously by the reaction of sodium nitrite with sulfuric acid, and air was supplied by a compressor. The reactant streams were separately purified by passage through silica gel and measured with calibrated orifice meters before being mixed in a tee upstream of the reactor. The air stream was also separately preheated approximately to the reactor coolant temperature in an electrically heated section of pipe. The flow rate of each stream was controlled with a globe valve.

Suitable thermocouples and manometers were provided so that temperatures and pressures were known at the orifices and at the entrance to the reactor. The controlled flow rates determined the composition of the gases entering the converter; no independent analyses for nitric oxide were made.

Reactor

The reactor (Figure 1) was constructed of two standard 8-in. aluminum structural channels with their plane surfaces opposed, spaced by two stainless steel bars. The web thickness of the channels was only 0.51 cm. to promote heat transfer through the walls. The stainless steel bars were 5.1 cm. in vertical dimension to minimize heat flow in this direction. Asbestos gaskets coated with gasket cement were placed between the channels and the bars, and the assembly was bolted together tightly. The resulting rectangular cross section for the catalyst was 2.26 cm. wide and 10.2 cm. high. The length was 91.5 cm., with the catalyst occupying the space between 17.6 and 74.0 cm. from the entrance. The spaces before and after the catalyst were empty. Since the position of the assembly was horizontal, the catalyst was held in place by screens. Total catalyst weight was 885 g.

Thermocouples were provided through-

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out the bed to permit measurement of lateral temperature gradients at several longitudinal positions. The measurement should lie between the gas and solids temperatures, but the difference between these cannot be great under the conditions used here (later shown to be less than 1°C.). The couples were introduced through stainless steel, high-pressure tubing soldered into ¼-in. holes drilled in the top bar. Small stuffing boxes at the tops of these tubes prevented leakage of the gas where the wires entered. The couples were located in the bed with special supports to assure that movement was practically impossible and that the lead wires lay in straight, vertical (isothermal) paths.

Thermocouples were carefully located at the center of the catalyst and 0.40 and 0.80 cm. out from the center in a lateral direction. The lateral gradient thus measured was observed with such thermocouples at axial positions 3.1, 18.1, 31.8, and 48.3 cm. along the catalyst for the first forty runs. Subsequent runs all were the same except that the 18.1 position became 18.8 cm.

The whole reactor was mounted in a steel shell which contained the coolant. Water, a calcium chloride brine boiling at about 119°C., and another boiling at about 132°C. were used as coolants. The coolants were boiled slowly in the reactor shell by heat from the reactor and from two immersion heaters controlled with variable autotransformers.

The catalyst was charged to the reactor with care to insure accurate thermocouple positioning and to eliminate the possibility of subsequent catalyst-bed shrinkage.

Analyses

Continuous analysis of the reactor effluent for nitrogen dioxide was accomplished photometrically, advantage being taken of the ability of the compound to absorb blue light. Calibration of the photometer was accomplished by passing known mixtures of nitrogen dioxide and air through the apparatus, the calibrations taking the form of plots of nitrogen-dioxide concentration vs. instrument reading. Allowance for nitrogen tetroxide, present in equilibrium with nitrogen dioxide in appreciable quantity at room temperature, was made by calculation based on published equilibrium constants (5) and the fact that nitrogen tetroxide is transparent to blue light. A standardizing procedure was employed to eliminate drift.

Procedure

The catalyst was activated by passing a slow stream of dry air through the bed for 2 hr. while the catalyst temperature was maintained at 130°C. The effluent air was cooled in a glass tube immersed in a salt-ice bath, and no condensation was observed after this 2-hr period.

Prior to each day's runs fresh silica gel was charged to the reactant purifiers, the system was checked for gas leakage, reactant supply circuits were carefully purged, and the coolant was brought to the desired temperature. Air and nitric oxide flows were then begun and adjusted to the desired rates. When steady state behavior was obtained, the following readings were made:

1. Photometer: gas inlet and outlet temperatures, pressure, instrument settings and reading.
2. Voltages of the twelve thermocouples in the catalyst.
3. Temperature of the gas stream immediately ahead of the bed.
4. Pressure in the precatalyst mixing space. In the case of those runs with boiling-water coolant this measurement was made with a separate set of runs without other observations.
5. Air flow rate.
6. Nitric oxide flow rate.
7. Ambient temperature and coolant temperature.

A detailed description of the apparatus and procedure is given by Jaffer (7).

TABLE 1. REPRESENTATIVE DATA, RUN C-3

Gas inlet temperature	100°C.
Coolant temperature	100°C.
W_A	2.76 g. moles/min.
W_{NO}	0.383 g. moles/min.
y°_{NO}	0.1215
n°_{NO}	0.00418 moles nitric oxide/unit mass feed
X_1	0.00040 moles nitric-oxide conversion/unit mass feed
X_2	0.00242 moles nitric-oxide conversion/unit mass feed
X_3	0.00254 moles nitric-oxide conversion/unit mass feed
X_3/n°_{NO}	0.61
Pressure (before catalyst)	1.311 atm.
Pressure (after catalyst)	1.029 atm.

Bed temperatures, °C.

	$x = 0$	$x = 0.40$ cm.	$x = 0.80$ cm.
$y = 3.1$ cm.	122	122	117
$y = 18.1$ cm.	141	137	121
$y = 31.8$ cm.	139	135	122
$y = 48.3$ cm.	130	127	116

SLAB-BED DATA

Eighty-six runs were made in the slab-bed reactor under the conditions described earlier. The temperature of the coolant except in a few cases was close to that of the entering gas.

The data of a representative run are given in Table 1. All data are reported in detail by Jaffer (7).

The homogeneous reaction before and after the catalyst was minor but could not be neglected. It is thus important to observe in Table 1 and elsewhere that the following designations were made:

X_1: conversion at bed entrance, basically a measured quantity differing from zero by a small amount

X_2: conversion at bed exit, a value calculated from X_3 and differing from it by a small amount

X_3: conversion measured at photometer.

The details of these small corrections are given in the appendix.

The reproducibility of these data was established in two ways: simple repetition of six runs and repetition after disassembly, catalyst removal and replacement, and changes in thermocouple vertical position and support construction detail for three runs. In all nine cases all temperatures were within 2°C. of the original (most were identical), and conversion was within 1% of the original. There is thus no evidence of loss of catalyst activity or movement of thermocouples in the bed.

The fact that measured catalyst bed temperatures were reproducible despite appreciable changes in vertical positioning of several thermocouples indicates that relatively little heat was transferred through the stainless steel bars; that is, slab behavior was closely approached. Similarly, no changes resulted from substantial modifications to thermocouple-support design, indicating that these supports did not affect temperature measurements.

INTERPRETATION OF DATA

For these data the concern is primarily with solving the differential equation describing the problem and with using with this solution suitable parameters for the heat transfer and heat generation quantities which appear therein. It should be noted that all mass transfer aspects of this problem have been neglected. The geometry is shown in Figure 2.

The heat balance on a differential catalyst volume may be written

$$K_f \frac{\partial^2 T_g}{\partial x^2} - G c_p \frac{\partial T_g}{\partial y} + C_1 T_s + C_o = 0 \qquad (1)$$

In this equation one assumes negligible axial heat conduction; negligible solids heats conductivity*; no lateral concentration gradients; conduction

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* Singer and Wilhelm (9) have shown that, in heat exchangers at least, solid-to-solid conduction is important only for highly conductive particles.

through the fluid all in one plane, that is no correction for the corner; and heat generation function linear in the solids temperature, that is $C_o + C_1T_s$. The heat balance on the solid phase may be written as a simple algebraic equation when the solids conductivity is neglected:

$$C_1T_s + C_o + h_v\,(T_g - T_s) = 0 \quad (2)$$

This may be solved immediately to yield

$$T_s = \frac{C_o + h_vT_g}{h_v - C_1} \quad (3)$$

The boundary conditions are

$$T_g(x{=}w,0) = 0 \quad (4)$$

$$\frac{\partial T_g}{\partial x}\,(0,y) = 0 \quad (5)$$

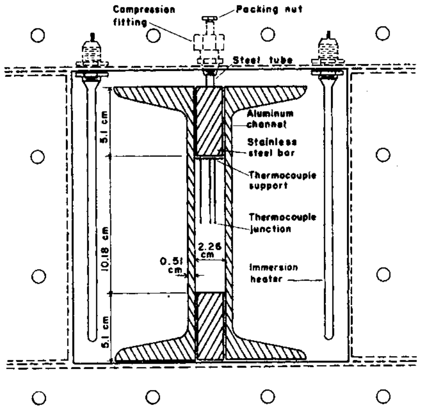

Fig. 1. End view of slab bed converter.

$$T_g(x{=}w,y) = T_w \quad (6)$$

The solution of this equation with the further assumption of constant properties is obtained by the Laplace transform and is

$$T_g = \frac{T_w + \frac{c}{b}}{\cos w\sqrt{b}}\cos x\sqrt{b} - \frac{c}{b} + \sum_{n=0}^{\infty} \frac{2(-1)^n}{\left(n+\frac{1}{2}\right)\pi}\left(\frac{T_w\alpha^2 + c}{b-\alpha^2}\right)\cos\alpha x \left(\exp\frac{b-\alpha^2}{a}y\right) \quad (7)$$

in which

$$\alpha = (n + 1/2)\,\frac{\pi}{w},\ a = \frac{G\,c_p}{K_f},$$

$$b = \frac{C_1h_v}{K_f(h_v - C_1)},\ c = \frac{C_oh_v}{K_f(h_v - C_1)}$$

There is no doubt that the use of this equation and others like it for catalyst beds of other shape, such as that used by Singer and Wilhelm (9), is most severely impaired by the assumption that the heat-generation function is linear in the solid temperature. This assumption is almost never a good one for extensive conversions, and it is particularly bad for the reaction here considered. In most exothermic reactions the effects of conversion and of temperature counter each other to a certain extent, at least, and so an approximation to a linear dependence on temperature may be had. In this reaction both high temperature and conversion decelerate the reaction, and the approximation to linearity is not good.

This difficulty can be overcome by limiting the application of Equation (7) to axial segments of the bed, each one of which is short enough to give a reasonably good approximation to the linearity sought. In practice, as judged by the treatment of these runs, the number of segments required is not large. Three or four should suffice in most cases. However, of course, the first boundary condition [Equation (4)] must be replaced for segments other than the first by an approximation as follows:

$$T_g(x{<}w,0) = \beta\cos\frac{\pi x}{2w} + \gamma\cos\frac{3\pi x}{2w} \quad (8)$$

in which β and γ are constants determined to fit the gradient of T_g at the end of the previous segment, which is found with Equation (7). This is a purely empirical correction, of course, and any convenient values of x (such as those to give easy reading of the cosines) are recommended. It should be noted that a discontinuity in T_g at the wall is permitted in the first set of boundary conditions. This discontinuity can give some difficulty if the value of T_w is large with this new boundary condition because it would distort the gradient. It is thus recommended that T_w be small, and in the cases applied T_w was 0.

This adds two terms to the previous equation, and so this final equation expressing the behavior of a slab bed is

$$T_g = \frac{T_w + \frac{c}{b}}{\cos w\sqrt{b}}\cos x\sqrt{b} - \frac{c}{b} + \sum_{n=0}^{\infty} \frac{2(-1)^n}{\left(n+\frac{1}{2}\right)\pi}\left(\frac{T_w\alpha^2 + c}{b-\alpha^2}\right)\cos\alpha x \left(\exp\frac{b-\alpha^2}{a}y\right) + \beta\cos\frac{\pi x}{2w}\exp\frac{b-\frac{\pi^2}{4w^2}}{a}y + \gamma\cos\frac{3\pi x}{2w}\exp\frac{b-\frac{9\pi^2}{4w^2}}{a}y \quad (9)$$

in which α, a, b, and c have the same meanings as before. This equation applies to all segments, even the first, if β and γ are taken to be zero for this one.

The results of the application of this equation to run C-3, the data for which are given in Table 2, will be described. Since the modified Reynolds number for this run is 31, the results of Singer and Wilhelm (9) and of Argo and Smith (*1*) lead to an estimate of K_f = 0.0223 cal./(min.)(cm.)(°C.) for the particle size and flow conditions involved. The heat transfer studies of Baumeister and Bennett (3) lead to an estimate for h_v of 9.85 cal./(min.)(cc.)(°C.), which is consistent with the mass transfer studies of Wilke and Hougen (*12*). The value of ΔH for this reaction is −13,562 cal./g. mole nitric oxide according to Giauque and Kemp (5). This figure, reversed in sign for the heat-generation function, was taken as constant over the temperature range involved. The heat of reaction per mole must be multiplied by the appropriate rate of reaction (read from one of figures in the appendix) to yield the heat-generation function. This was re-evaluated for each segment, and the segments used corresponded to those used in the experimental measurements. The details of the calculation method are best considered as a method of design and will be thus described in a subsequent section. The columns in Table 2 headed $T_{g,\text{avg}}$ have bearing on the design method only, since no such measurements were made.

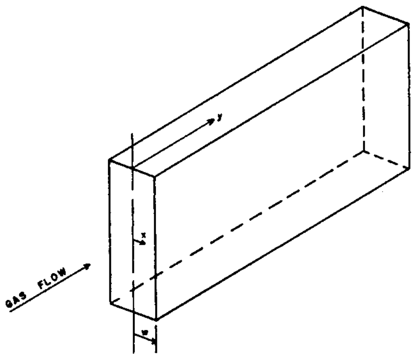

Fig. 2. Geometry of slab bed converter.

When one considers the complexity of the system involved, the results ap-

TABLE 2. CALCULATED BEHAVIOR OF RUN C-3 AND COMPARISON WITH MEASURED FIGURES GIVEN IN PARENTHESES*

Segment	Length from entry, cm.	Assumed $T_{g_{Avg}}$	Calc. $T_{g_{Avg}}$	Conv. %	$T_g(x=0)$	$T_g(x=0.40)$	$T_g(x=0.80)$
1	3.1	113	112.7	16	115.3 (122)	115.1 (122)	112.5 (117)
2	18.1	132	130	36	142 (141)	138 (137)	125 (121)
3	31.8	132	129	47	141 (139)	137 (135)	123 (122)
4	48.3	123	124	55	138 (130)	135 (127)	124 (116)
End	56.4	123	126	59 (61)			

* It should be remembered that measured temperatures should lie between T_g and T_s and thus would be expected to be a little higher than the calculated values of T_g. However the difference between T_g and T_s cannot be large under the conditions here considered. A simple consideration of Equation (3) with the parameters for the conditions here met indicates that T_s and T_g are about 1°C. apart at most.

pear to be good. The conversion result is particularly so, although this is not so severe a test as it might first be considered, since the reaction is very slow at high conversion.

DESIGN METHOD

Equations (7) and (9) may be used as the basis of a design method for a slab reactor in the following sequence. (The description is based on an exothermic reaction.) The rate data for this particular case are described in the appendix.

1. With the specification of all entrance conditions, calculate from suitable data the reaction rate at the entrance.
2. Considering only the first axial segment, assume (a) an average T_g, (b) a maximum T_g, and (c) the extent of conversion for the end of this segment.
3. Calculate rate of reaction, defined by assumed average T_g and conversion at end of segment. Using average rate (entrance and end), calculate the conversion. Repeat 3 and 2(c) until a check is obtained.
4. Calculate the heat-generation function at entrance and lowest temperature and at the exit and highest temperature.
5. Evaluate C_o and C_1 for the segment. Note that this involves T_s, which can be solved with Equation (3) from the values of T_g.
6. Assuming knowledge of the parameters K_f, h_v, G, and c_p, evaluate a, b, and c.
7. Calculate the integral average value of T_g from the appropriate operation on Equation (7). Repeat steps 2(a), 2(c), 3, 4, 5, and 6 until a check with the assumed values is found.
8. Calculate T_g at $x = o$ using Equation (7). This should also check, but an exact agreement is not essential. A serious disagreement will require a repeated trial to this point.
9. Calculate T_g at one intermediate value of x and use this and T_g at $x = o$ to evaluate β and γ of Equation (8).
10. Proceed to the next axial segment and use Equation (9) instead of Equation (7).

It should be noted that conversion calculations are based on a mean rate in which the rates at entrance average temperature and exit average temperature are considered. The heat-generation function, however, is evaluated with rates at the entrance conversion and entrance wall temperature and the exit conversion and maximum temperature. This was done in an attempt to get the extremes of the rates, since the rate is fastest (with this reaction) at the lowest temperature and lowest conversion and slowest at the highest temperature and highest conversion. This is a refinement which may not be necessary; it is probably satisfactory to use average temperatures throughout, which would simplify the design method. Despite the necessity of assuming three items, the calculation is fairly fast after some practice.

The calculated figures in Table 2 were computed with this method.

CONCLUSIONS

The apparatus and procedure described proved to be effective in permitting the observations of temperature distributions and conversions for the catalytic oxidation of nitric oxide in a slab bed. Eighty-six runs were made, although only one is described in detail here.

A mathematical analysis led to equations describing the distribution of temperatures throughout the catalyst bed as functions of fundamental properties, flow conditions, and the rate of heat generation. These equations may be adapted to the formulation of a design method with which the temperature distributions and conversions may be predicted. This method requires the consideration of axial segments of the bed, but the number of such segments is small and thus the method is a relatively fast one.

The design method was used in conjunction with isothermal rate data given in the appendix to predict with good accuracy the results observed, although those of only one run are described.

ACKNOWLEDGMENT

J. H. Jaffer, Jr., gratefully acknowledges the financial assistance of E. I. du Pont de Nemours and of the Research Corporation.

NOTATION

a = $G\,c_p/K_f$, constants in Equations (7) and (9), cm.$^{-1}$
b = $C_1h_v/K_f(h_v-C_1)$, constant in Equations (7) and (9), cm.$^{-2}$
C_o = constant in catalyst-bed heat-generation function, cal./(min.)(cc.)
C_1 = constant in catalyst-bed heat-generation function, cal./(min.)(cc.)(°C.)
c = $C_oh_v/K_f(h_v-C_1)$, constant in Equations (7) and (9), °C./sq. cm.
c_p = heat capacity of gas phase at constant pressure, cal./(g.)(°C.)
F = reactor feed rate, g./min.
G = superficial mass velocity of gas in catalyst bed, g./(min.)(sq. cm.)
h_v = volume-based coefficient of heat transfer between solid particles and gas in catalyst bed, cal./(min.)(cc.)(°C.)
K_f = effective thermal conductivity of gas phase in catalyst bed, cal./(min.)(cm.)(°C.)
k_h = reaction-rate constant for uncatalyzed oxidation of nitric oxide g. moles nitric oxide converted/(min.)(cc.)(atm.^{3})
n^o = total moles of reactor feed per unit mass of feed, dimensionless
n^o_{NO} = moles of nitric oxide in reactor feed per unit mass of feed, dimensionless
$n^o_{O_2}$ = moles of oxygen in reactor feed per unit mass of feed, dimensionless
p = absolute pressure, atm.
R = specific rate of oxidation of nitric oxide over silica gel, g.-moles nitric oxide converted/(min.)(atm.^{2})(cc.)
r = rate of oxidation of nitric oxide over silica gel, g. moles nitric oxide converted/(min.)(cc.)
T_g = temperature of gas phase in catalyst bed, °C. above reactor wall temperature at inlet end
$T_{g_{avg}}$ = average temperature of gas phase (averaged in the lateral direction). °C. above reactor wall temperature at inlet end
T_s = temperature of solid phase in

catalyst bed, °C. above reactor wall temperature at inlet end
T_w = gas temperature at reactor wall, °C. above reactor wall temperature at inlet end
V = volume, cc.
V_B = total catalyst-bed volume, cc.
W_A = air flow rate, g. moles/min.
W_{NO} = nitric oxide flow rate, g. moles/min.
w = half width of slab catalyst bed, cm.
X = extent of conversion, moles nitric acid converted per unit mass of reactor feed, dimensionless
X_1 = value of X at catalyst-bed entrance
X_2 = value of X at catalyst-bed exit
X_3 = value of X at point of analysis
x = lateral distance from central plane of slab-shaped bed, cm.
y = axial distance through catalyst bed, cm.
y°_{NO} = mole fraction nitric acid in reactor feed, dimensionless
α = $(n + 1/2)\ \pi/w \quad n = 0, 1, 2,$ cm.$^{-1}$
β = constant in Equation (8), °C.
γ = constant in Equation (8), °C.

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Manuscript received July 7, 1958; revision received February 17, 1960; paper accepted February 18, 1960.

APPENDIX

A-I. Observations on the Homogeneous Reaction

The homogeneous oxidation of nitric oxide which occurs in the empty space before the catalyst and between the catalyst and the photometer is not negligible and must be taken into account in interpreting both the slab-reactor data and the isothermal-bed data discussed below. The rate equation for the third-order homogeneous reaction in a flow system is

$$\frac{dV}{F} = \frac{(n^{\circ} - \frac{1}{2}X)^3}{p^3 k_h\,(n^{\circ}_{NO} - X)^2\,(n^{\circ}_{O_2} - \frac{1}{2}X)}\,dX \tag{A-1}$$

The rate constants as listed by Glasstone, Laidler, and Eyring (*6*) and the U.S. Bureau of Standards (*11*) were used in calculations based on this equation.

The photometer was located downstream of the catalyst bed, of course, and its measured value is the reported X_3 of the tables. The conversion at the exit of the catalyst bed, X_2, was obtained by successive application of Equation (A-1) in integrated form over portions of the volume between the catalyst-bed exit and the photometer. This procedure was employed to allow for the fact that the gas left the catalyst bed at temperatures as high as 172°C., although the photometer was close to room temperature. The temperature in the photometer chamber was, of course, known. Since the precise pattern of temperature change between the converter and photometer was not known and had to be estimated, there are errors in this procedure. However the over-all contributions of such errors are small because the differences between X_2 and X_3 are small; it is a correction to a correction.

With regard to precatalyst conversion in the slab reactor, it was recognized that large errors could result from direct application of Equation (A-1) because of incomplete mixing of the reactants early in the unpacked volume upstream of the catalyst. Consequently a number of runs were made in which the gas mixture immediately upstream of the catalyst bed was bypassed around the catalyst and sent directly through the photometer. The conversions read at the photometer were then adjusted to those at the catalyst-bed entrance by means of the integrated form of (A-1). Details are given by Jaffer (*7*). Some error was undoubtedly involved in the use of these data; however, again, it is only a correction to a correction.

The geometry of the reactor system used to obtain isothermal rate data was such that virtually perfect mixing in the precatalyst unpacked volume could be safely assumed. Hence precatalyst conversion was computed directly with the integrated form of Equation (A-1).

A-II. Determination of Isothermal Rates

Isothermal rate data for the oxidation of nitric oxide over silica gel have been reported (*2, 4, 8, 10*) for different temperatures than used here and with silica gel preparations which may well be different. Hence isothermal rate measurements were undertaken with the present catalyst and in the higher temperature region of interest here.

The range of variables for the isothermal conversion data were

Temperature	96° to 172°C.
Air flow rates	0.029 to 0.17 $\frac{\text{g. moles}}{\text{(min.) (sq.cm.)}}$
Mole fractions, nitric oxide	0.0177 to 0.146
Conversions	9 to 89%

Isothermal Reactor System. This system was similar to the slab-reactor system except for the following: air was supplied from a compressed air tank rather than a compressor, reactant stream flow rates were controlled with needle valves and measured with rotameters, and both air and nitric oxide streams were separately preheated.

Isothermal Reactor. (Figure A-1) The catalyst was contained in four parallel copper tubes, each 3/16 in. O.D., 0.314 cm. I.D., and about 61 cm. long. The packed length of each tube was 58.4 cm., resulting in a total catalyst volume of 18.0 cc., including voids, and a catalyst weight of 12.0 g. Such small tubes were used to ensure relatively fast heat transfer, and the parallel arrangement was used to give total flow rates which could be measured accurately. Loss of catalyst was prevented by tightly rolled cylinders of wire mesh inserted into fittings which connected the above tubes to a manifold. The catalyst density was 0.655 g./cc.

Thermocouples were placed along the length of these tubes, the couple junctions being located as near as possible to the

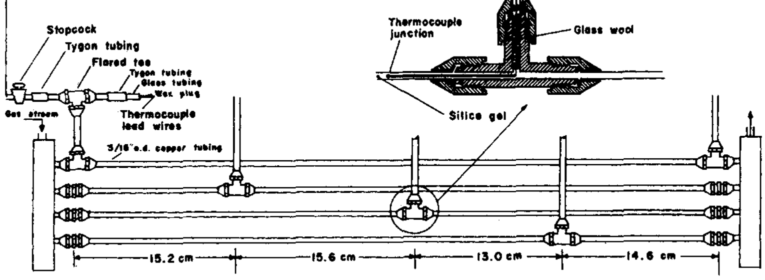

Fig. A1. Isothermal reactor.

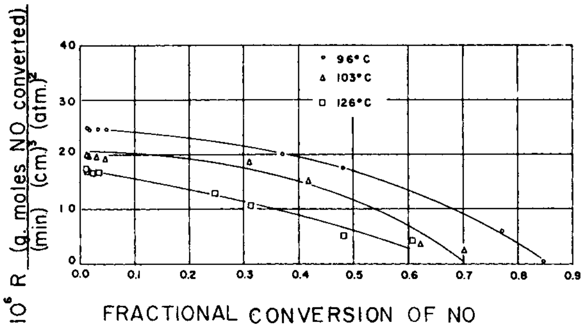

Fig. A2. Specific rate of oxidation of nitric oxide over silica gel $n^\circ_{NO} = 0.001$.

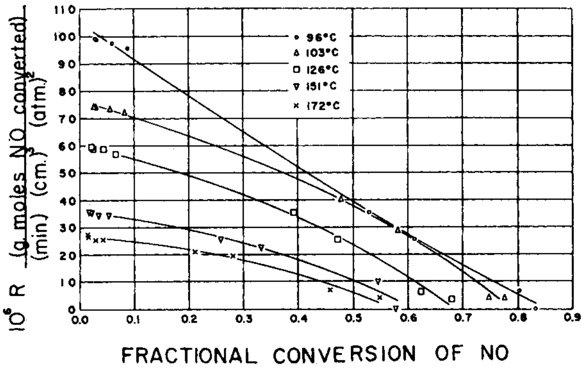

Fig. A3. Specific rate of oxidation of nitric oxide over silica gel $n^\circ_{NO} = 0.002$.

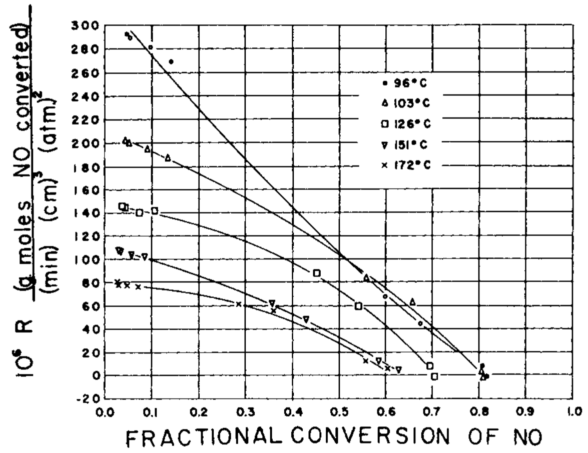

Fig. A5. Specific rate of oxidation of nitric oxide over silica gel $n^\circ_{NO} = 0.004$.

axes of the tubes. (See Figure A-1.) The lead wires were removed through legs of tees inserted in the tubes, care being exercised to avoid leakage of gas and to bring the leads out through an isothermal zone. These tees also led to a manometer for pressure measurement. The whole assembly was immersed in an agitated oil bath which was heated by an immersion heater.

Isothermal Runs. The catalyst was activated in the same manner as in the nonisothermal runs, and operation of the unit was essentially the same. The following data were recorded:

1. Photometer, same as for slab converter.
2. Air flow rate.
3. Nitric oxide flow rate.
4. Ambient temperature.
5. Pressures at four positions along the reactor (one connection proved sluggish).
6. Temperatures at five points along the catalyst bed.
7. Temperature of the cooling bath.

More details of the apparatus and procedure are given by Jaffer (7); however, the analytical procedure was basically the same as described before.

Isothermal Data. Eighty-five isothermal runs were made at the conditions described earlier.

The data of a representative run are given in Table A-1. All the data are given in reference (7).

For all practical purposes isothermal conditions were, indeed, maintained. In some cases the temperature of one station differed from the others or from the bath by 1°C., in four cases by 2°C., and in one case by 3°C.

A pair of runs at essentially identical conditions but at quite different times were made for each of the five temperatures. The worst disagreement in any of these was 57.5 vs. 58.1% conversion; the others were in considerably better agreement. It is thus clear that there is no evidence of loss of catalyst activity.

Interpretation of the Isothermal Data. The basic relationship by which specific reaction rates were obtained from the isothermal data is

$$X_2 - X_1 = \int_0^{V_R/F} r\, d(V/F) \qquad \text{(A-2)}$$

The fact that the feed rate, rather than catalyst volume, was varied experimentally introduced a complication. Both X_1 and X_2 varied with feed rate: X_1 because of varying residence time available for homogeneous reaction in the precatalyst volume and X_2 because of changes in X_1 and varying residence time in the catalyst bed. A mathematical analysis (7) was developed to take these factors into account.

Since total pressure varied over the length of the isothermal bed as well as from run to run, and since the effect of

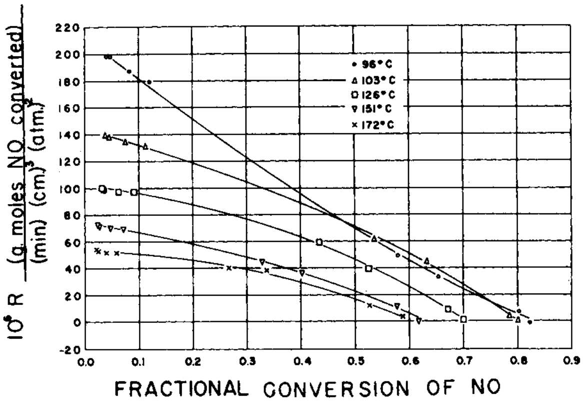

Fig. A4. Specific rate of oxidation of nitric oxide over silica gel $n^\circ_{NO} = 0.003$.

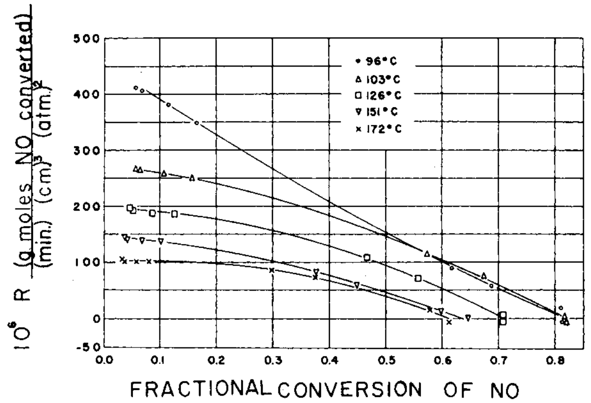

Fig. A6. Specific rate of oxidation of nitric oxide over silica gel $n^\circ_{NO} = 0.005$.

TABLE A-1. REPRESENTATIVE DATA OF ISOTHERMAL RUNS, RUN I—14

Coolant temperature	96° to 97°C.
W_A	0.00887 g. moles/min.
W_{NO}	0.00152 g. moles/min.
y°_{NO}	0.146
n°_{NO}	0.00500 moles nitric-oxide converted/unit mass feed
X_1*	0.000807 moles nitric-oxide converted/unit mass feed
X_2*	0.00401 moles nitric-oxide converted/unit mass feed
X_3*	0.00421 moles nitric-oxide converted/unit mass feed
X_3/n°_{NO}	0.843

Station through bed	1	2	3	4	5
Pressure, atm. abs.	1.029	—	1.020	1.013	1.007
Temperature, °C.	96	96	96	96	96

* X_3 is a measured quantity; X_2 is calculated from it as a correction for the homogeneous reaction. X_1 is calculated for the homogeneous reaction.

pressure was not specifically studied in this investigation, it was necessary to assume a pressure dependence on the basis of available data. Although there is little agreement in the literature in this regard, proportionality of the rate to the square of absolute pressure represents a reasonable compromise between reported correlations (*2, 4, 8, 10*). This relationship was assumed in deriving the reaction rates reported here.

Rates of Isothermal Reaction. The calculated rates of isothermal reaction are plotted in Figures A-2, 3, 4, 5, and 6. The ordinate is R, for use in the equation

$$X_2 - X_1 = \frac{1}{F}\int_0^{V_R} R\, p^2\, dV \qquad \text{(A-3)}$$

The abscissas are fractional conversions and the parameter temperature. A separate curve is given for each value of n°_{NO}.

Tabulated values are given by Jaffer (*7*). No empirical or semitheoretical equation has been found to correlate these rates, although there is evidence for strong adsorption of nitrogen dioxide in the practically zero rates at high conversions. Negative rates shown in some curves and in the tables at very high conversions reflect slight errors, of course. Such rates are, for all practical purposes, zero. The absence of a significant effect of gas-phase diffusion on this catalytic reaction has been reported by Baker *et al.* (*2*); accordingly any effect of velocity of flow has been neglected in interpreting these rate data.

Comparison of these results with those of others is difficult because conditions were not at all comparable. While the temperature range is considerably different from that used by Baker, Wong, and Hougen (*2*), their results and these seem to be consistent. For $n^{\circ}_{NO} = 0.003$, a conversion of 0.578, and a temperature of 60°C., the equation given by Baker, Wong, and Hougen predicts a rate of 0.000065 g. moles nitric oxide converted/(min.) (cc.) at 1 atm. An extrapolation of the present results to 60°C. yields a rate of 0.000075. The temperature dependence of this reaction is the same in direction as that observed by all previous workers. The decrease of the temperature dependence at higher temperatures conforms to the observations of Kurin and Blokh (*8*) and the theoretical treatment of Glasstone, Laidler, and Eyring (*6*).

It will be noted that for high initial nitric oxide concentrations and high conversion of nitric oxide, reaction rates at 103°C. are shown to be higher than those at 96°C. Such a reversal of the effect of temperature on the reaction has not been reported previously. No successful attempt has been made in the present investigation to explain this phenomenon; the effect is not large and occurs only at high conversion of nitric oxide.

A good verification of the method and of the accuracy of these rate data is that they can be used to reproduce by calculation the integral conversion data observed with excellent agreement. In run I-14 the measured value of X_2 was 0.00401; when one integrates Equation (A-3) with these rate data, the calculated value is 0.00412. The absolute magnitude of the rate in this calculation varied thirty-fold from entrance to exit of bed.

Multicomponent Diffusion Problems

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Analysis of four three-component diffusion problems by means of the Stefan-Maxwell equations is presented. In three of these problems heterogeneous chemical reactions are occurring at a catalytic surface. Characteristic curves are presented for the better understanding of the analytical solutions. The results of one of the exact solutions are compared with those by the effective diffusion-coefficient approach.

The equations describing the diffusion in a ν-component mixture of gases are the Stefan-Maxwell equations (*1*):

$$\nabla x_i = \sum_{j=1}^{\nu} (c\,\mathcal{D}_{ij})^{-1}(x_i\vec{N}_j - x_j\vec{N}_i)$$
$$i = 1, 2, ---, \nu \qquad (1)$$

The derivation of Equation (1) from the kinetic theory of gases has been given by Curtiss and Hirschfelder (*3*). Only $\nu - 1$ of these equations are independent because $\Sigma x_i = 1$.