14p

NASA TECHNICAL NOTE

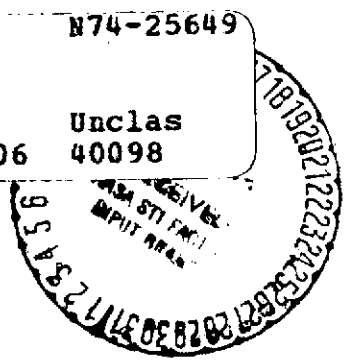
NASA TN D-7687

NASA TN D-7687

(NASA-TN-D-7687) CATALYTIC OXIDATION OF TRACE LEVELS OF METHANE IN OXYGEN IN A TUBULAR REACTOR (NASA) 21 p HC $3.00
CSCL 07C

N74-25649

Unclas
H1/06 40098



# CATALYTIC OXIDATION OF TRACE LEVELS OF METHANE IN OXYGEN IN A TUBULAR REACTOR

*by Marvin Warshay and Christopher L. Caenepeel*

*Lewis Research Center*
*Cleveland, Ohio 44135*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JUNE 1974

| 1. Report No. | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| NASA TN D-7687 | | |

| 4. Title and Subtitle | 5. Report Date |
|---|---|
| CATALYTIC OXIDATION OF TRACE LEVELS OF METHANE IN OXYGEN IN A TUBULAR REACTOR | JUNE 1974 |
| | 6. Performing Organization Code |

| 7. Author(s) | 8. Performing Organization Report No. |
|---|---|
| Marvin Warshay and Christopher L. Caenepeel | E-7595 |
| | 10. Work Unit No. 502-25 |

| 9. Performing Organization Name and Address | 11. Contract or Grant No. |
|---|---|
| Lewis Research Center<br>National Aeronautics and Space Administration<br>Cleveland, Ohio 44135 | |

| 12. Sponsoring Agency Name and Address | 13. Type of Report and Period Covered |
|---|---|
| National Aeronautics and Space Administration<br>Washington, D.C. 20546 | Technical Note |
| | 14. Sponsoring Agency Code |

15. Supplementary Notes

16. Abstract

An experimental investigation of catalytic oxidation of trace levels of methane in oxygen was conducted in a tubular reactor. Two noble metal solid catalysts were explored: a 1-percent platinum on gamma alumina and a 0.5-percent rhodium on gamma alumina. For each catalyst the activity was determined as a function of temperature, pressure, space velocity, and methane concentration. The rhodium catalyst was considerably more active than the platinum catalyst. For each catalyst mass transfer had a pronounced effect upon activity at low space velocity.

| 17. Key Words (Suggested by Author(s)) | 18. Distribution Statement |
|---|---|
| Chemical reactors<br>Oxidation<br>Reactor design<br>Reaction kinetics<br>Catalytic activity | Unclassified - unlimited<br>Category 06 |

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of Pages | 22. Price* |
|---|---|---|---|
| Unclassified | Unclassified | 21 | $3.00 |

* For sale by the National Technical Information Service, Springfield, Virginia 22151

# CATALYTIC OXIDATION OF TRACE LEVELS OF METHANE IN OXYGEN IN A TUBULAR REACTOR

by Marvin Warshay and Christopher L. Caenepeel*

Lewis Research Center

## SUMMARY

An experimental investigation of catalytic oxidation of trace levels of methane ($CH_4$) in oxygen ($O_2$) was conducted in a tubular reactor. Two noble metal solid catalysts were explored: a 1-percent platinum (Pt) on gamma alumina ($Al_2O_3$) and a 0.5-percent rhodium (Rh) on gamma alumina. For each catalyst, the activity was determined as a function of temperature, pressure (134 to 685 $kN/m^2$), space velocity $S_v$ (500 to 12 000 $hr^{-1}$), and $CH_4$ concentration (5 to 25 ppm). The temperature range investigated for each catalyst was different, being governed by the temperature range over which appreciable conversion occurred. The highest temperatures reached were 535 K with the Rh catalyst and 741 K with the Pt catalyst. At these temperatures approximately 90 percent methane conversion to carbon dioxide occurred in each case.

The following conclusions were reached: (1) The Rh catalyst is more active than the Pt catalyst. (2) The first-order reaction rate form correlates the data quite well over the temperature ranges investigated for each catalyst. (3) For each catalyst mass transfer had a pronounced effect on activity at low space velocities. The lowering of the space velocity caused the reaction rate constant to drop over two orders of magnitude.

---

*Assistant Professor of Chemical Engineering, California State Polytechnic College, Pomona, California; Summer Faculty Fellow at the Lewis Research Center in 1971 and 1972.

# INTRODUCTION

The hydrogen-oxygen alkaline fuel cell has been successfully employed for aerospace applications. For the Apollo program an intermediate temperature version of this type of fuel cell was used for on-board power. For current space applications, the hydrogen-oxygen alkaline fuel cell is undergoing intensive development. One of the chief goals is extended cell life. The NASA Space Shuttle Fuel Cell ultimately will be required to operate reliably for 10 000 hours.

One of the factors limiting alkaline fuel cell life has been its extreme sensitivity to reactant impurities. Thaller, Post, and Easter (ref. 1) reported rather serious effects on cell performance resulting from trace impurities, such as carbon dioxide, which lead to the formation of potassium carbonate and limit cell life. Recent experiments (unpublished experiments by M. Warshay) have shown that traces of methane ($CH_4$) contained in the oxygen ($O_2$) reactant are quite reactive at the cathode and thereby contribute to the alkaline cell decay problem resulting from carbonation of the electrolyte.

One means of solving this problem is to devise a method of removing the trace hydrocarbon impurities contained in the oxygen feed. Catalytic oxidation of the hydrocarbons followed by scrubbing out of the resulting carbon dioxide ($CO_2$) is a method under consideration. The need to obtain design data for the catalytic oxidizer led to the present experimental investigation.

Very little data have been published on the oxidation of trace levels of hydrocarbons in oxygen. Marshall (ref. 2) reported results of an investigation of catalytic oxidation of 1 percent $CH_4$ in $O_2$ conducted at low space velocities. His primary aim was to screen five oxidation catalysts in order to obtain conversion against temperature curves for each catalyst-flow rate combination. Although he did not specifically study the effect of mass transfer, he did note that higher space velocity increases the catalyst efficiency, which is directly related to the effect of mass transfer. His work suffered from rather large temperature gradients along the axis of his reactor. The temperature difference from the ends to the middle varied between 90 and 324 K.

The need to monitor trace hydrocarbons in air or in other atmospheres led to a number of investigations of the catalytic oxidation of major gaseous hydrocarbons. However, the details of many of these investigations have been kept proprietary by the catalyst manufacturers and/or by manufacturers of monitoring instruments. Two noteworthy studies that have been published are by Anderson, et. al. (ref. 3), and Rosenbaum, Adams, and King (ref. 4). In reference 3, which was primarily a rapid screening of methane oxidation catalysts, it was demonstrated that catalyst preparation affects catalytic activity (the rate constant). The effectiveness of supported catalysts of the same chemical composition varied widely with method of preparation and type of support. Reference 4 has some limited data on high-temperature catalytic oxidation of trace concentrations of methane in air. An important finding in this work was that no decrease in

catalytic activity was detected in 2 years of continuous operation using the Baker F catalyst.

In a research on catalytic oxidizers by Lesieur (unpublished NASA contractor report), four noble metal catalysts were tested using oxygen containing approximatly 55 ppm $CH_4$. The catalysts tested were 0.5 percent rhodium on alumina, 0.5 percent palladium on alumina, 0.5 percent platinum on alumina, and 10.0 percent platinum on alumina. The rhodium catalyst was the most active one. The other catalysts either had lower activity (lower rate constants) or decayed more rapidly. Although experiments were conducted over a broad range of space velocities, Lesieur made no systematic attempt to use space velocity variation to study the effect of mass transfer on activity. In sereral cases the effects were obscured because changes in temperature, pressure, and $S_v$ were made simultaneously. Lesieur concludes that the catalysts were independent of space velocity, a result with which we disagree. For what Lesieur interprets as decay appears to us to be, at least in part, a space velocity or mass transfer effect.

The type of catalyst, the catalyst bed size, reactant concentration, and the operating conditions are the variables that determine the chemical conversion and the capacity of the bed. Two noble metal solid catalysts were investigated: a 1 percent platinum on alumina and a 0.5 percent rhodium on alumina. For each catalyst the activity was determined as a function of temperature, pressure (134 to 685 $kN/m^2$), space velocity $S_v$ (500 to 12 000 $hr^{-1}$), and methane concentration (5 to 25 ppm). The highest temperatures investigated were 535 K with the rhodium catalyst and 741 K with the platinum catalyst. The aim of this investigation was to obtain relations among these variables which could be used to design a catalytic reactor. A secondary aim was to express these relations in terms of useful kinetic expressions such as rate constants. In this investigation, mass transfer was specifically explored to determine the extent of its effect upon rate.

## SYMBOLS

| | |
|---|---|
| $a$ | reaction order |
| $C_A$ | concentration of reactant A at any time, mole per unit volume |
| $C_{A_0}$ | concentration of reactant A initially or entering, mole per unit volume |
| $C_i$ | concentration of methane in oxygen, ppm |
| $F_{A_0}$ | initial feed of reactant A to reactor, mole per unit time |
| $k$ | rate constant for first-order reaction, $time^{-1}$ |
| $p$ | pressure |

| | |
|---|---|
| $r$ | statistical regression coefficient |
| $r_A$ | rate of reaction of reactant A |
| $S_v$ | space velocity |
| $T$ | absolute temperature |
| $V$ | volume of reactor occupied by reacting fluid |
| $v_0$ | initial volumetric feed rate, volume per unit time |
| $X_A$ | conversion, fraction of reactant A converted into product |
| $\epsilon$ | fractional change in volume as result of reaction |

## EXPERIMENTAL CONSIDERATIONS

The experiments were conducted in a multizone heated, fixed catalytic bed, tubular reactor (fig. 1). The stainless-steel walls of the reactor were 2.54-centimeter outside diameter and 0.165-centimeter thick. Coils of Nichrome heating wire were used to deliver heat to both the preheater portion of the tube and the catalytic bed portion. The Nichrome wire was encased in thin-walled stainless-steel tubing. To provide maximum contact these heating coils were tightly wound around the outside of the tube and then brazed. In addition to a preheater heating coil and a catalytic bed heating coil, a third coil was used to heat the portion of the tube past the bed in order to reduce end heat losses. To reduce radial heat losses, the reactor was wrapped with aluminum foil and then with asbestos insulation. Autotransformers were used to control the three heated sections of the tube.

To improve heat transfer to the gas, the preheater was packed with 0.476-centimeter perforated stainless-steel packing chips. Chromel/Alumel thermocouples were used to measure temperature at various locations in the tube. Temperatures were recorded on a multipoint potentiometer. Temperature variation axially was kept to only a few degrees Kelvin (at steady-state conditions). In addition, the multithermocouple probe located at the preheater exit indicated that there was no radial temperature gradient.

The 1 percent platinum on alumina particles (0.635 cm) used in this investigation were supplied by the Chemetron Corp. The 0.5 percent rhodium on alumina particles (0.3175 cm) were supplied by Engelhard industries. The porosities measured were 0.683 for the platinum catalyst and 0.632 for the rhodium catalyst.

Flow rates were measured with rotameters. Calibrated bourdon tube pressure gages indicated pressure.

The exit gases from the reactor were cooled and fed continuously into a nondispersive infrared analyzer. The analyzer was equipped to analyze for $CO_2$ and for total

hydrocarbon content of the gas down to 0.1 ppm by volume.

## DISCUSSION OF RESULTS

In this section the results are discussed in terms of temperature effects, space velocity and mass transfer effects, pressure and concentration effects, and kinetics. Following these subsections is a brief summary and a discussion of the significance of these results.

### Treatment of Data

A reasonable way to express or define catalyst activity is in terms of a kinetic rate constant. In general, the kinetic rate constant is a superior index of catalyst efficiency than is chemical conversion, which does not take into account the duration of exposure to the catalyst. As can be seen in equation (1), the rate constant k is valuable in relating flow rate $F_{A,0}$ reactor volume V, and conversion of reactant A (methane in our case) $X_A$.

In a plug flow reactor the steady-state material balance for a reaction component is made for a differential element of volume dV as follows (see ref. 5):

$$F_{A_0} dX_A = (-r_A)\, dV$$

Integrating results in

$$\frac{V}{F_{A_0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

For an irreversible reaction of order a

$$\frac{V}{F_{A_0}} = \int_0^{X_A} \frac{dX_A}{kC_A^a} \qquad (1)$$

where

$$C_A = C_{A_0} \frac{(1 - X_A)}{(1 + \epsilon_A X_A)}$$

in the general case, with $\epsilon_A$ representing the fractional change in volume as the result of reaction.

In our case, because the reacting medium is so dilute, $\epsilon_A$ is essentially zero. Also, because so many catalytic reactions are first order (a = 1), first-order rate constants were calculated for all the data. Substituting for $C_A$ in equation (1) and rearranging result in

$$\frac{C_{A_0} V}{F_{A_0}} = \frac{1}{k} \int_0^{X_A} \frac{dX_A}{1 - X_A}$$

Therefore,

$$k = S_V \ln \left( \frac{1}{1 - X_A} \right) \tag{2}$$

where

$$S_V = \frac{F_{A_o}}{C_{A_o} V} = \frac{v_o}{V}$$

For a catalytic reactor bed V equals the total volume occupied by the catalyst multiplied by the porosity of the catalyst. As is the customary practice, the data were plotted as log k against 1/T to obtain the classical Arrhenius temperature dependency of the rate constants. The correlation coefficient r calculated in the least-squares calculation provides a quantitative measure of correlation in each case. It should be stressed that while a correlation coefficient close to 1 represents good correlation, it does not

represent a proof of first-order behavior.

## Temperature

The high temperature increased the catalytic rate of oxidation of methane, a result that was expected. It is the classic response. All the data indicate this. More important than this is the clear superiority of the rhodium catalyst over the platinum catalyst over the entire range of temperatures investigated. This can be seen by comparing figures 2(a) and (b), which are Arrhenius plots of the data. At an $S_v$ of approximately 6000 reciprocal hours, a temperature of 512 K was required to attain 90 percent conversion with the rhodium catalyst while a temperature of 705 K was required with the platinum catalyst. The small difference in concentration under which these Pt and Rh experiments were conducted do not affect the conclusion. This will be made clear in a later section on concentration effects. Comparing any other results for the platinum and rhodium catalysts conducted at similar conditions yields the same conclusion. The rhodium catalyst is much more active than the platinum catalyst.

## Space Velocity Effects - The Role of Mass Transfer

In a heterogeneous system, since more than one phase is present, the movement of material from phase to phase must be considered in the overall rate equation. In general, the expression describing the overall rate must include mass-transfer terms in addition to the usual chemical kinetic terms of homogeneous reactions. As has already been pointed out in the introduction, the fact that mass transfer plays a role in catalytic reactions is often overlooked. For example, for gas phase reactions catalyzed by solid catalysts, reactants must first diffuse from the main body of the fluid to the exterior of the catalyst surface. In addition, with porous catalysts the reactants must diffuse into the interior of the pellet to reach the much larger surface area. Following the activated adsorption and the chemical reaction at the surface, the products must desorb, diffuse out of the pores, and then transfer into the main gas stream. Thus, in this idealized description of the rate process as a series of successive steps, either a slow mass transfer step, slow adsorption or desorption steps, or a slow chemical reaction step could dominate the overall reaction rate, that is, become the rate-controlling step. Furthermore, as conditions are changed another rate step may take over to become dominant. (Rather than speak in terms of the relative rates of the various steps it is quite common to refer to the relative resistances of the steps. This avoids confusion over whether you're referring to the overall rate or to the rate of an individual step. We shall adopt this convention in this discussion.)

For the present catalytic oxidation investigation no attempt has been made to develop a detailed overall rate expression. These expressions are usually complicated series-parallel relations involving the individual steps in the process. For design purposes we have chosen to adopt a simple first-order form and then investigate possible mass-transfer effects on the overall rate, expressing these effects in terms of changes in the rate constant.

The significant effects on rate illustrated in figures 3 to 5 are indications of the importance of mass transfer. For instance, in figure 3 the rate constants for the rhodium and platinum cases changed markedly with change in space velocity even during isothermal isobaric conditions. At constant temperature and pressure there would have been no change in the overall rate constant if the chemical reaction were rate controlling.

At low space velocities the rate constant is very much lower than at the higher space velocities where each curve appears to be approaching a constant value. The higher space velocities were achieved simply by increasing the gas velocity through the reactor for each catalyst bed. Mass-transfer coefficients increase with increase in velocity (ref. 6). Apparently a point was reached at the highest space velocities where the mass transfer coefficient ceased to be a controlling factor.

Figure 4 indicates that the mass-transfer effect is most significant at the highest temperatures where the difference between the rate constant of the low and high space velocity cases is greatest. This is understandable. At the lower temperatures the chemical reaction is a much larger resistance than at the higher temperatures. So is the mass-transfer resistance greater at lower temperatures. However, the temperature effect on the chemical reaction resistance is more pronounced than is the temperature effect upon the mass-transfer resistance. Consequently the chemical resistance becomes rate controlling at lower temperatures.

Figure 5 provides additional evidence of the influence of mass transfer on the overall rate. The oxidation rates were measured for two different lengths of platinum catalyst beds of the same diameter. At the same $S_v$ the longer bed would have a higher gas velocity and, consequently, a higher mass-transfer rate. The mass-transfer coefficient increases with velocity. Thus, if mass transfer is a controlling factor, the rate constant curve for the longer bed should be higher than that for the shorter bed, which is the case in figure 5.

## Concentration and Pressure

For a simple first-order homogeneous chemical reaction, the reaction rate constant is independent of both concentration and pressure. This is readily discerned from equation (2). The situation is not so straightforward when dealing with heterogeneous systems containing a solid catalyst. Here, the response to concentration and pressure of

the overall rate will be governed by the particular response to concentration and pressure of the rate-controlling step. For example, the adsorption step could be first order, the desorption step could be zero order, while the chemical reaction step could be yet some other order. As we have indicated earlier, there are many possible rate-controlling steps. Not only could their response to pressure and concentration be different, but an individual step's response to pressure or concentration could change as that variable is changed. Finally, to add to the complexity, as catalytic conditions are changed, one step can take over from another as the rate-controlling step. (See ref. 5 for further discussion.)

As previously mentioned, we have chosen to correlate our data with a first-order rate. According to active-site theory, at very low pressures with adsorption controlling, the overall reaction is essentially first order. The apparent independence of the rate constant with moderate change in reactant concentration indicates that with respect to concentration our choice of the first-order rate is consistent. The results for the rhodium platinum catalysts (fig. 6) indicated that the rate constants were essentially independent of concentration over the ranges investigated (6.8 to 21.8 ppm $CH_4$ in $O_2$ for the Rh catalyst and 5.8 to 19.9 ppm for the Pt catalyst).

On the other hand, the results indicate that for neither the platinum nor rhodium (fig. 7) catalysts is the rate constant independent of pressure. Furthermore, the particular responses of the two catalyst beds to pressure were different. For the platinum catalyst bed (fig. 7(a)) an increase in pressure increases the rate constant at low temperatures. For the rhodium catalyst bed (fig. 7(b)) the opposite effect prevails at the lower temperature: an increase in pressure decreases the rate constant. However, at higher temperatures the response of the rhodium catalyst bed to pressure appears to be reversing (if we accept the extrapolated lines in fig. 7(b)); an increase in pressure increases the rate constant.

The inverse response to pressure at low temperatures of the rhodium catalyst bed was somewhat unexpected especially in view of the platinum experiments, which had been conducted first. The low-temperature response of the rhodium catalyst to pressure is uncommon. However, a plausible explanation is that the phenomenon is due to surface reaction controlling combined with adsorption of interfering species at the active sites.

## Kinetics

From the results discussed in the previous sections for both the rhodium and platinum catalysts it is obvious that the first-order assumption correlates the data quite well. The lowest correlation coefficient calculated from 10 different sets of data was 0.9045.

However, the high degree of linearity of the Arrhenius plots should not be misin-

terpreted as proof of first-order behavior. It merely indicates that it is a reasonably good correlation of the rate constant with respect to $S_v$, temperature, and conversion. Other assumed reaction orders might have also correlated the data as well. The only real evidence of first-order behavior was the independence of the rate constant with respect to concentration.

One thing that the Arrhenius plot might indicate about order is that different reaction orders are governing over different temperature regions, that is, the mechanism is changing with changing temperature. In that case, the assumption of first-order behavior would result in a straight line over the temperature portion where the reaction was first order and some other sloped line or curve where another order prevailed. In addition, the simplicity of the first-order relation should not be misinterpreted. It does not mean that the physicochemical phenomena occurring in the catalyst beds are simple. For each catalyst a single first-order equation will not describe the oxidation of methane for all possible conditions. This has already been made evident by the investigations into mass transfer and pressure effects, both of which resulted in a series of curves. Prudent use of the simple first-order rate relations representing highly complex phenomena would call for avoidance of large extrapolations out of the regions investigated.

In general, therefore, the complete, detailed rate equation for solid-catalyzed fluid reactions accounts for many processes, some involving transport phenomena, others chemical reactions. To have determined the detailed rate equation would have required additional, very time consuming investigations delving into chemisorption, chemical mechanism, and diffusion in the bulk gases as well as in the pores. However, the design goals of the present investigation did not call for this type of detailed study. The simple kinetic expression containing a rate constant that lumps several physicochemical effects suffices as long as none of the major ones (e.g., the rate-controlling processes) are overlooked.

The decay of the catalytic bed activity must be empirically determined. For the rhodium bed the more active one, some investigation of decay was made. No degree of decay could be measured after 1 month of operation. This corresponded to approximately 200 hours of contact time. In other words, no decay rate could be established in so short a time interval. For so clean a gas as the propulsion grade oxygen used, it would not be surprising if the catalyst bed could last for quite a few years of operation. However, to establish the decay rate, a period much longer that 1 month would evidently be required.

## SUMMARY OF RESULTS

The most significant result is that the rhodium catalyst is much more active than the platinum catalyst for methane oxidation. The most unusual aspect of these results, however, is that as a consequence of mass transfer control of the reaction rate, increasing residence time may actually produce a decrease in conversion. In other words, under certain conditions passing the gas through the catalytic reactor more quickly will actually increase the conversion of methane to carbon dioxide. As had been discussed in the INTRODUCTION, the influence of mass transfer in heterogeneous catalysis is often ignored. Apparently the complexity of the heterogeneous systems involving many potentially important processes is not appreciated. The knowledge that a change in a variable will most definitely reduce the chemical reaction resistance does not necessarily insure an improvement in the overall process. As we have seen, although the lowering of the gas flow did decrease the chemical resistance, it simultaneously increased the mass-transfer resistance by causing the mass-transfer coefficient to decrease.

For design purposes this means that to reduce the mass-transfer resistance, it is best to operate at higher gas velocities out of the region where the rate is extremely sensitive to space velocity $S_v$. This is achieved by designing for high gas flow rates by keeping the diameter of the catalyst bed as small as is feasible. Other considerations, of course, also influence the diameter. For instance, for the 22.9-centimeter-long, 2.31-centimeter-diameter bed of rhodium, a fairly typical size, operation at an $S_v = 6000$ would eliminate mass transfer as a major part of the resistance. If conditions were then to call for higher conversion, a larger bed would be required. One could achieve this larger bed in two ways: by increasing the bed length or the bed diameter. In each case the residence time would be increased. Increasing the bed diameter would decrease the linear velocity, which could, in turn, decrease the mass-transfer rate. If the mass-transfer rate were decreased significantly, it could adversely affect the conversion. Therefore, all other considerations being equal, it is better to increase the bed length than its diameter.

## CONCLUSIONS

The following conclusions were reached:

1. The 0.5 percent rhodium on gamma alumina catalyst is much more active in the oxidation of trace levels of methane in oxygen than is the 1 percent platinum on gamma alumina catalyst.

2. The first-order reaction rate form correlates the data quite well over the temperature ranges investigated for each catalyst.

3. For each catalyst at low space velocities mass transfer had a pronounced effect activity. The lowering of the space velocity caused the reaction rate constant to drop over two orders of magnitude.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 6, 1974,
502-25.

## REFERENCES

1. Thaller, L. H.; Post, R. E.; and Easter, R. W.: Effects of Carbon Dioxide on Trapped Electrolyte Hydrogen-Oxygen, Alkaline Fuel Cells. NASA TM X-52812, 1970.

2. Marshall, Derry W.: Catalytic Oxidation of Methane at Low Space Velocities. AFFDL-TR-66-56, Air Force Systems Command, (AD-803267) June 1966.

3. Anderson, R. B.; Steen, K. C.; Feenan, J. J.; and Hofer, L. J. E.: Catalytic Oxidation of Methane. Ind. Eng. Chem. vol. 53, no. 10, Oct. 1961, pp. 809-812.

4. Rosenbaum, E. J.; Adams, R. W.; and King, H. H., Jr.: Monitoring Trace Hydrocarbons in Air by Catalytic Oxidation and Nondispersive Infrared Analysis. Anal. Chem., vol. 31, no. 6, June 1959, pp. 1006-1008.

5. Levenspiel, Octave: Chemical Reaction Engineering. John Wiley and Sons, Inc., 1962.

6. Frossling, Nils: The Evaporation of Falling Drops. (Uber die Verdungstun Fallender Tropfen). Beitrage zur Geophysik, vol. 52, 1938, pp. 170-216.

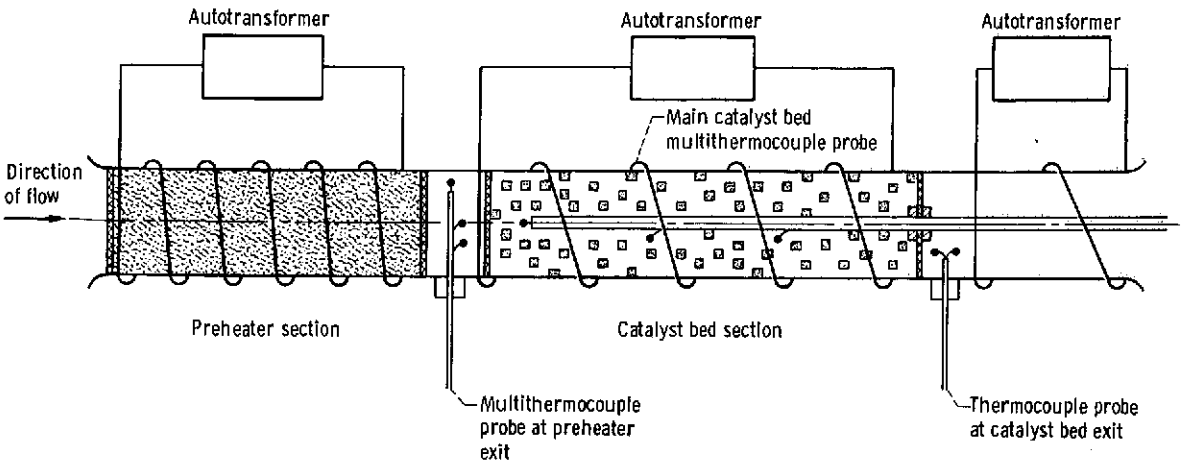
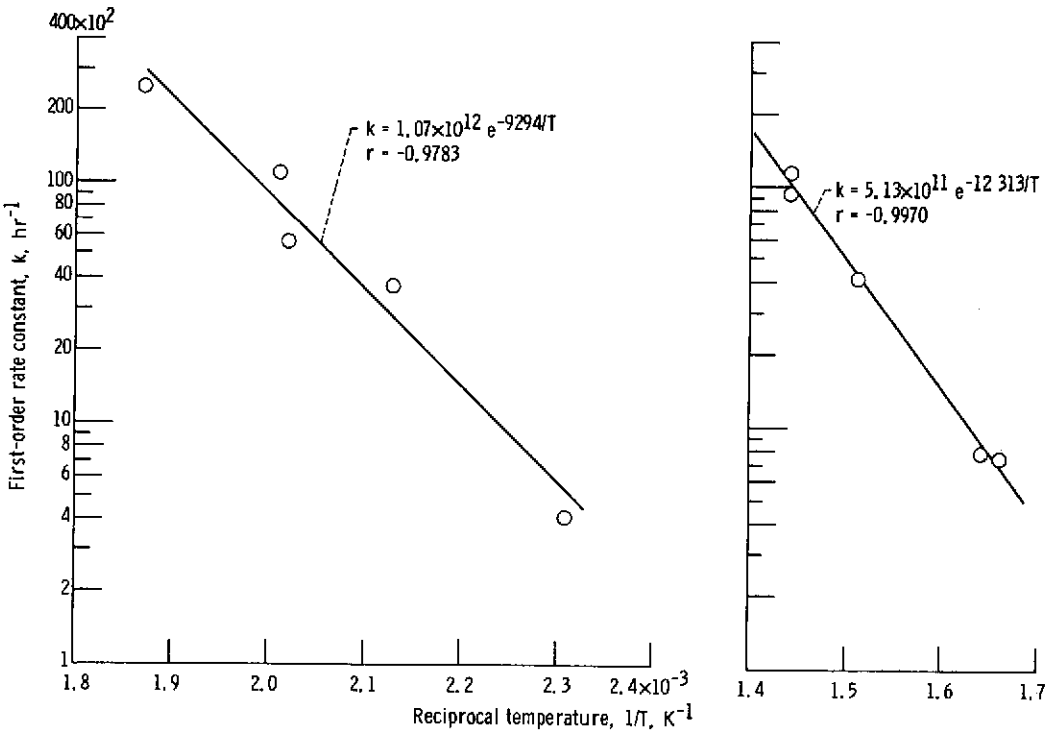


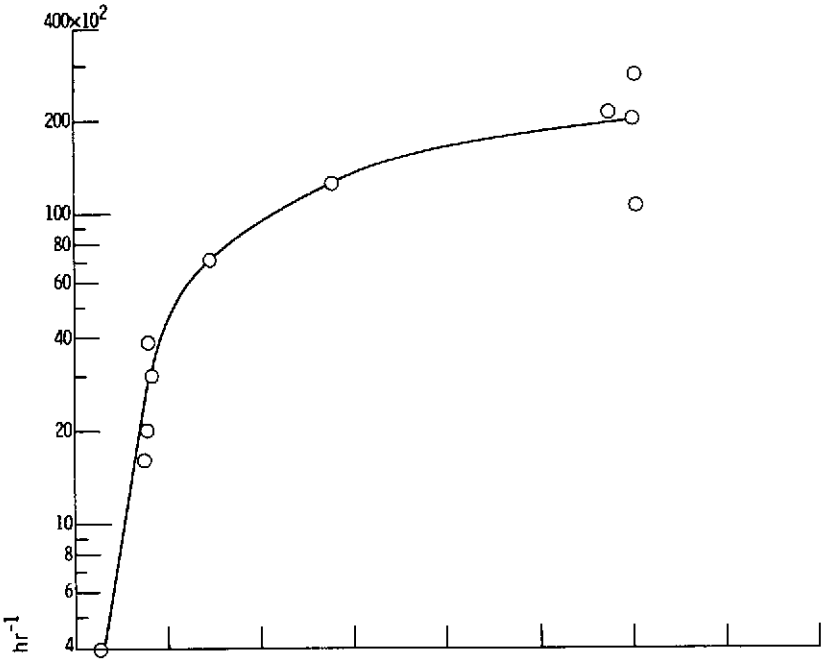

Figure 1. - Tabular catalytic reactor (not to scale).



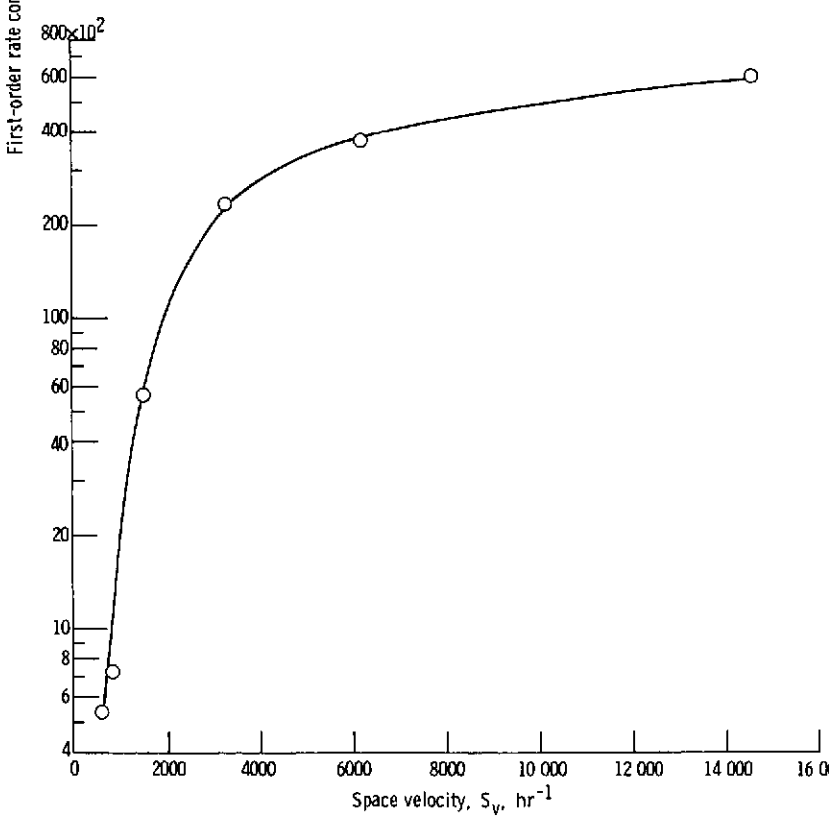

(a) 0.5 Percent rhodium on gamma alumina; bed length, 22.9 centimeters; concentration of methane in oxygen, 14.5 to 18.8 ppm; pressure, 441 kilonewtons per square meter (49.5 psig); space velocity, 6065 reciprocal hours.

(b) 1 Percent platinum on gamma alumina; bed length, 20.3 centimeters; concentration of methane in oxygen, 5.8 to 6.0 ppm; pressure, 442 kilonewtons per square meter (49.7 psig); space velocity, 6020 reciprocal hours.

Figure 2. - Effect of temperature on first-order rate constant for two noble-metal catalysts.

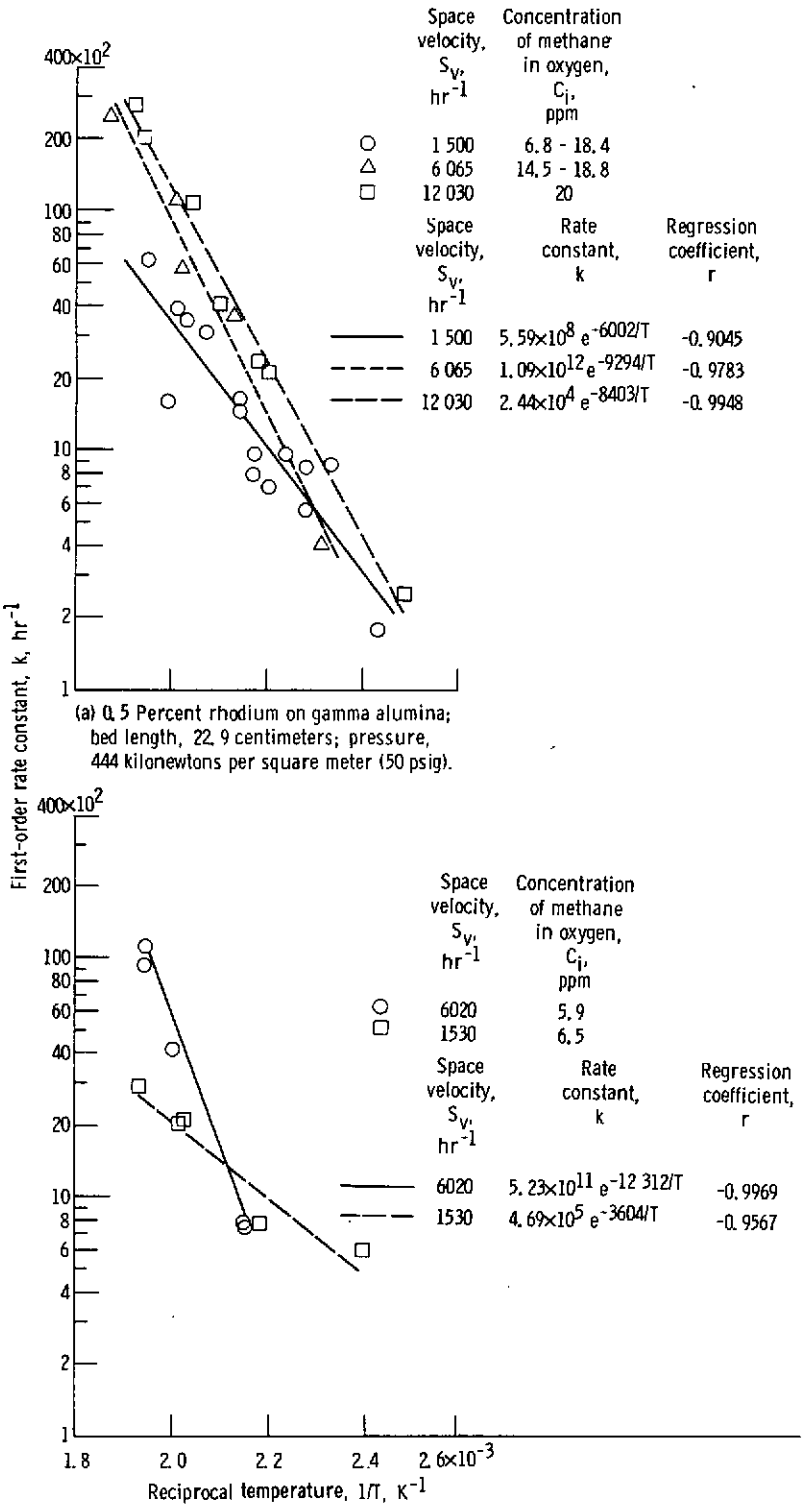



(a) 0.5 Percent rhodium on gamma alumina; bed length, 22.9 centimeters; concentration of methane in oxygen, 7.7 to 20 ppm; temperature, 500 K; pressure, 441 kilonewtons per square meter (49.5 psig).




(b) 1 Percent platinum on gamma alumina; bed length, 5.24 centimeters; concentration of methane in oxygen, 9 to 17.3 ppm; temperature, 703 K; pressure, 442 kilonewtons per square meter (49.7 psig).

Figure 3. - Effect of space velocity on first-order rate constant for two noble-metal catalysts.




(a) 0.5 Percent rhodium on gamma alumina; bed length, 22.9 centimeters; pressure, 444 kilonewtons per square meter (50 psig).

(b) 1 Percent platinum on gamma alumina; bed length, 20.3 centimeters; pressure, 442 kilonewtons per square meter (49.7 psig).

Figure 4. - Effect of space velocity on first-order rate constant at various temperatures for two noble-metal catalysts.

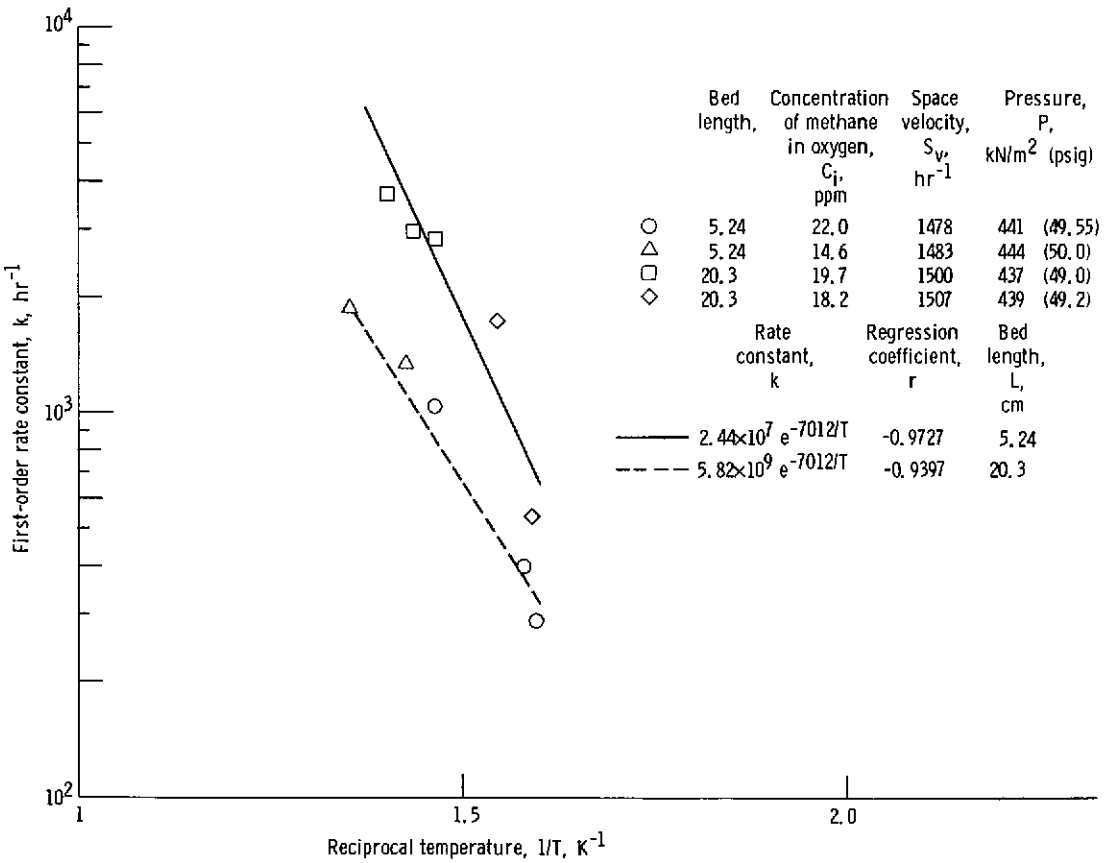
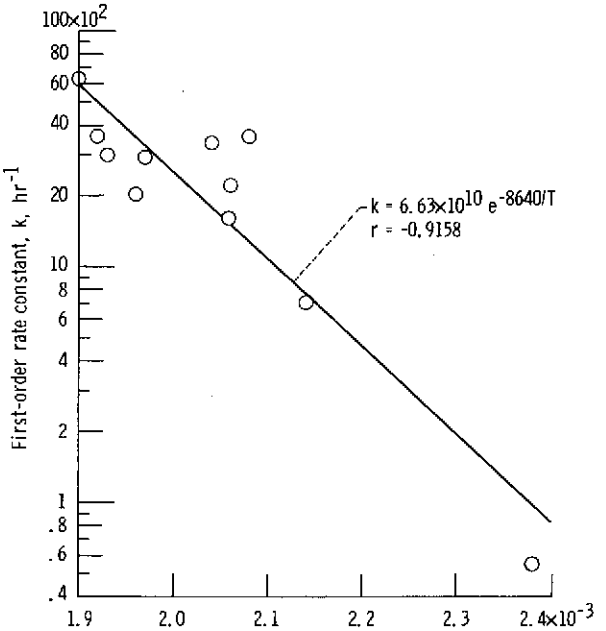
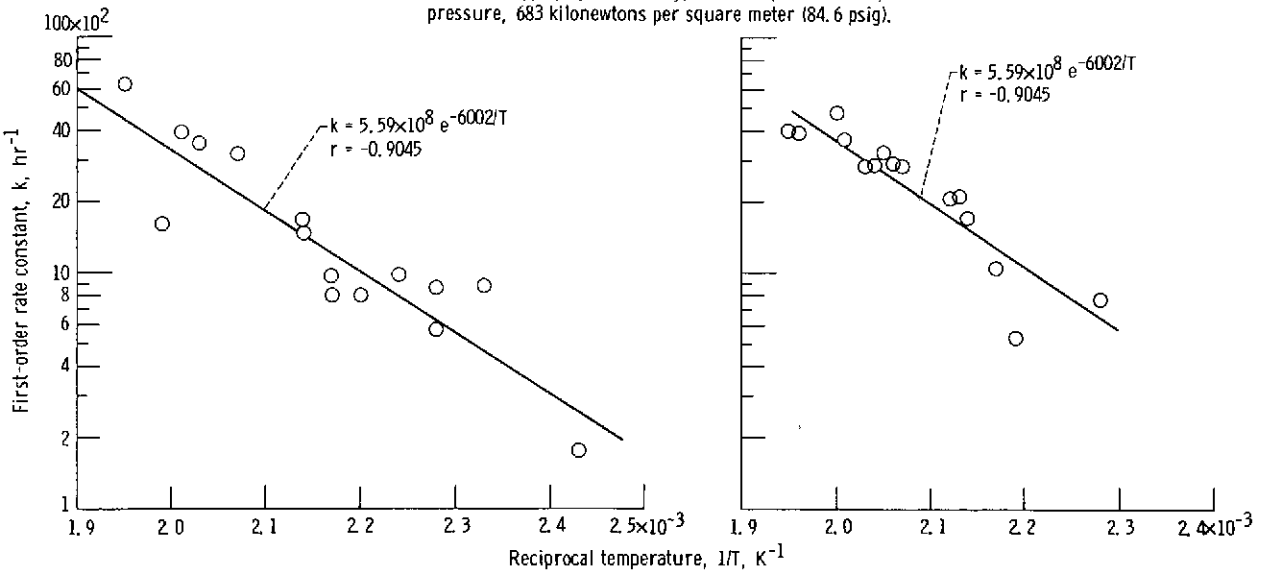



Figure 5. - Effect of bed length on first-order rate constant for platinum catalyst (10 percent Pt on gamma alumina).



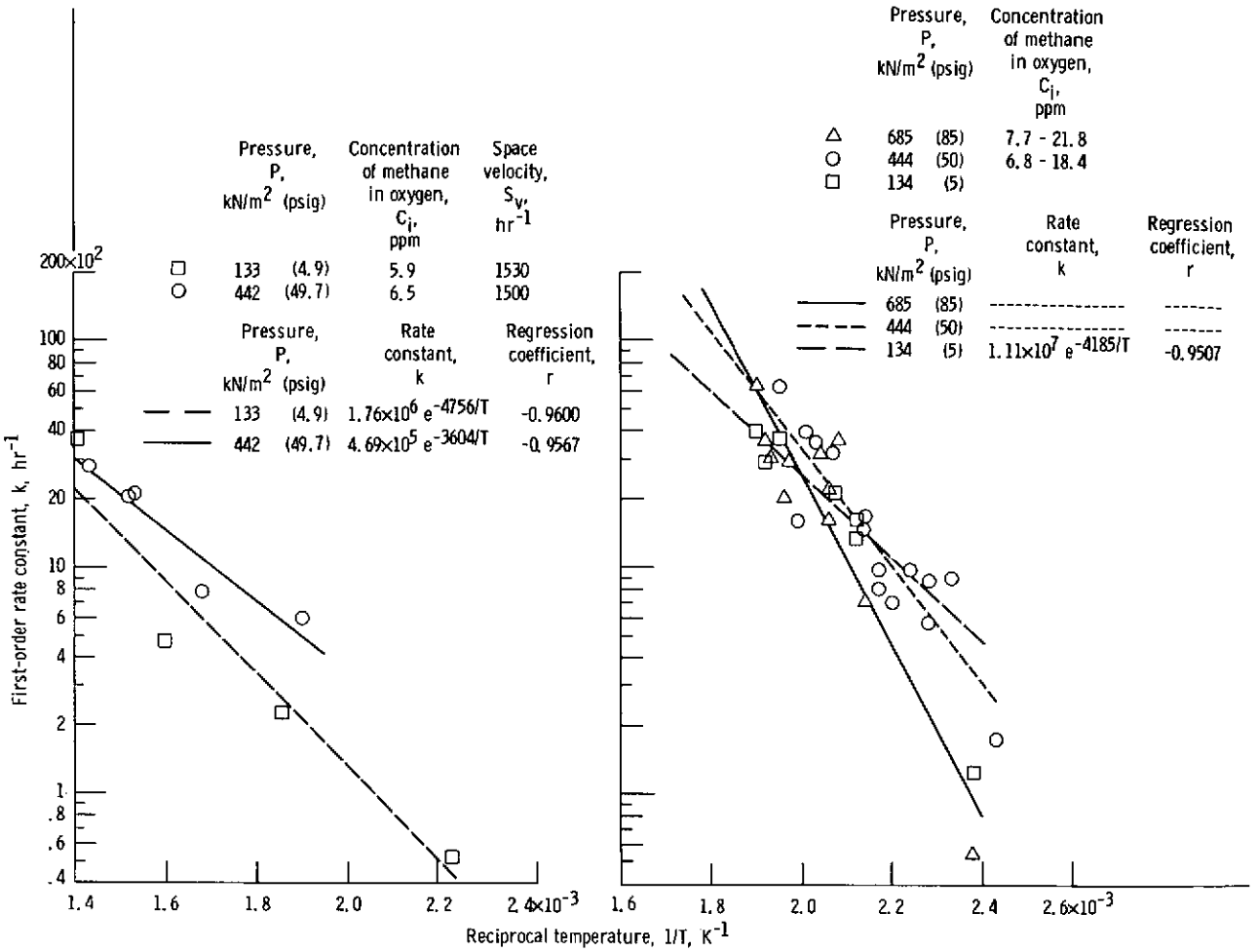

(a) 0.5 Percent rhodium on gamma alumina; bed length, 22.9 centimeters; concentration of methane in oxygen, 7.7 to 21.8 ppm; space velocity, 1500 reciprocal hours; pressure, 683 kilonewtons per square meter (84.6 psig).




(b) 0.5 Percent rhodium on gamma alumina; bed length, 22.9 centimeters; concentration of methane in oxygen, 6.8 to 18.4 ppm; space velocity, 1490 reciprocal hours; pressure, 444 kilonewtons per square meter (50 psig).

(c) 1 Percent platinum on gamma alumina; bed length, 20.3 centimeters; concentration of methane in oxygen, 5.8 to 19.4; space velocity, 1490 reciprocal hours; pressure, 437 kilonewtons per square meter (49 psi).

Figure 6. - Effect of concentration on first-order rate constant at various temperatures for two noble-metal catalyst.




(a) 1 Percent platinum on gamma alumina; bed length, 20.3 centimeters.

(b) 0.5 Percent rhodium on gamma alumina, bed length, 22.9 centimeters.

Figure 7. - Effect of pressure on first-order rate constant at various temperatures and for two noble-metal catalyst.