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EVALUATION OF THE EGCR CATALYTIC OXIDIZER FOR OXIDATION OF HYDROGEN, CARBON MONOXIDE, AND METHANE

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ABSTRACT

The oxidizing catalyst for the EGCR helium purification system is to be a Ni-Cr-Pd ribbon catalyst manufactured by the American Metals Products Company. This catalyst has been evaluated for a range of operating parameters for the oxidation by oxygen of hydrogen, carbon monoxide, and methane in a flowing stream of helium at 300 psia. Empirical correlations suitable for design purposes were determined for the effects of temperature in the range of 400-600°C; total gas mass flow rate in the range of 0.083 to 1.00 g-moles/cm^2-min; and contaminant levels in the range of ~0.5 to 2.0 vol %. The existing oxidizer is adequate for oxidation of anticipated maximum hydrogen and carbon monoxide contamination if the allowable effluent oxygen concentration is greater than 10 ppm. If methane oxidation capacity is desired, the allowable effluent oxygen concentration must be above 100 ppm or the catalytic oxidizer must be made larger.

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1.0 INTRODUCTION

The catalyst to be used in the EGCR helium purification system for oxidation of hydrogen, carbon monoxide, and hydrocarbons is to be nickel-chromium ribbon with activated palladium on its surface. The oxidizing unit was designed to meet very restricted specifications which do not allow for hydrocarbon oxidation. There is no information available on the effects of change in operating temperature, gas mass flow rate or contaminant concentration. It was necessary to obtain kinetic information on the American Metals Products catalyst over the range of operating parameters which may occur in the EGCR purification system.

This report presents the experimental data and correlations resulting from a study of the oxidation by oxygen of hydrogen, carbon monoxide, and methane in a flowing stream of helium catalyzed by the American Metals Products catalyst at the anticipated pressure of the EGCR purification system (300 psia); in the temperature range of 400-600°C, gas mass flow rates of 0.083 - 1.00 g-moles/cm^2-min; and contaminant concentration range of ~0.5 to 2.0 vol %. Equations were derived which are suitable for predicting the effectiveness of the oxidizer.

The tests and data correlation are for a relatively narrow range of operating conditions which will be usable for the EGCR purification system and similar applications. Work was purposely limited in scope so that usable data would be available for EGCR use in a short time.

2.0 SPECIFICATIONS AND PROPERTIES OF EGCR CATALYTIC OXIDIZER

The catalytic oxidizer furnished by American Metals Products Company is a vessel 8-in.-ID by 7.5-in. deep filled with their nickel-chrome-palladium ribbon catalyst.

2.1 Properties of Catalyst

The catalyst is nickel-chrome metal ribbon coated with activated palladium. A typical gross chemical composition of the catalyst is:

Nickel - 58.3%
Chromium - 31.3%
Palladium - 1.1%

The ribbon is metallic in form and has the following dimensions:

Length - variable
Width - 0.036 - 0.037 inches
Depth - 0.005 - 0.006 inches

The packed density of the ribbon catalyst in a catalytic unit obtained from the company was 0.384 g/cc. Specific surface area was approximately equal to the exterior surface of the ribbon.

2.2 Catalytic Unit Specifications[1-3]

The design performance specifications for the catalytic unit are as follows:

Inlet gas (300 psia and 260°C to 700°C)

Component	Vol %
He	95.0
CO	2.3 max
H_2	2.3 max
CO_2	0.2
N_2	0.1
H_2O	trace
Hydrocarbons	trace
Fission Products	trace

Effluent gas (based on 650°C inlet and 300 psia)

Component	Maximum Content ppm by vol
CO	1000
H_2	1000

Gas feed rate to oxidizer:

130 lb/hr or 0.82 g-moles/cm^2-min

3.0 EXPERIMENTAL WORK

3.1 Reagents

The gases used in the tests were of the following grades:

Helium	Navy Grade A, purity ~100%
Hydrogen	99.5% purity
Carbon Monoxide	99.5% purity
Methane	99.0% purity
Oxygen	99.5% purity

3.2 Experimental Facility

All tests were made in the Gas Cooled Reactor Helium Coolant Purification Test Facility[4] (Fig. 3.1). This facility is capable of synthesizing contaminated helium with hydrogen, carbon monoxide, and methane, and oxygen addition to the contaminated gas is possible.

The 2-in.-dia oxidizers which are components of the system were used in this study. Oxidizers were fabricated from 2-in.-dia schedule 80 stainless steel pipe with high-pressure (600 psi) flanges at either end (Fig. 3.2). Catalyst bed depths of 1 to 4 in. were used in the oxidizers with thermocouple probes every 2 in. within the vessels. Each oxidizer was internally insulated at the top and bottom and externally heated and insulated by a tube furnace. In some tests a 1-in.-ID insert was used in the oxidizer to allow higher gas mass velocities. Helium contaminated with 0 - 2% hydrogen, 0 - 2% carbon monoxide, 0 - 1% methane, and 0 - 2% oxygen at 0 - 325 psig, 30 - 600°C, and gas flow rates of 0 - 120 slpm can be delivered to the oxidizer.

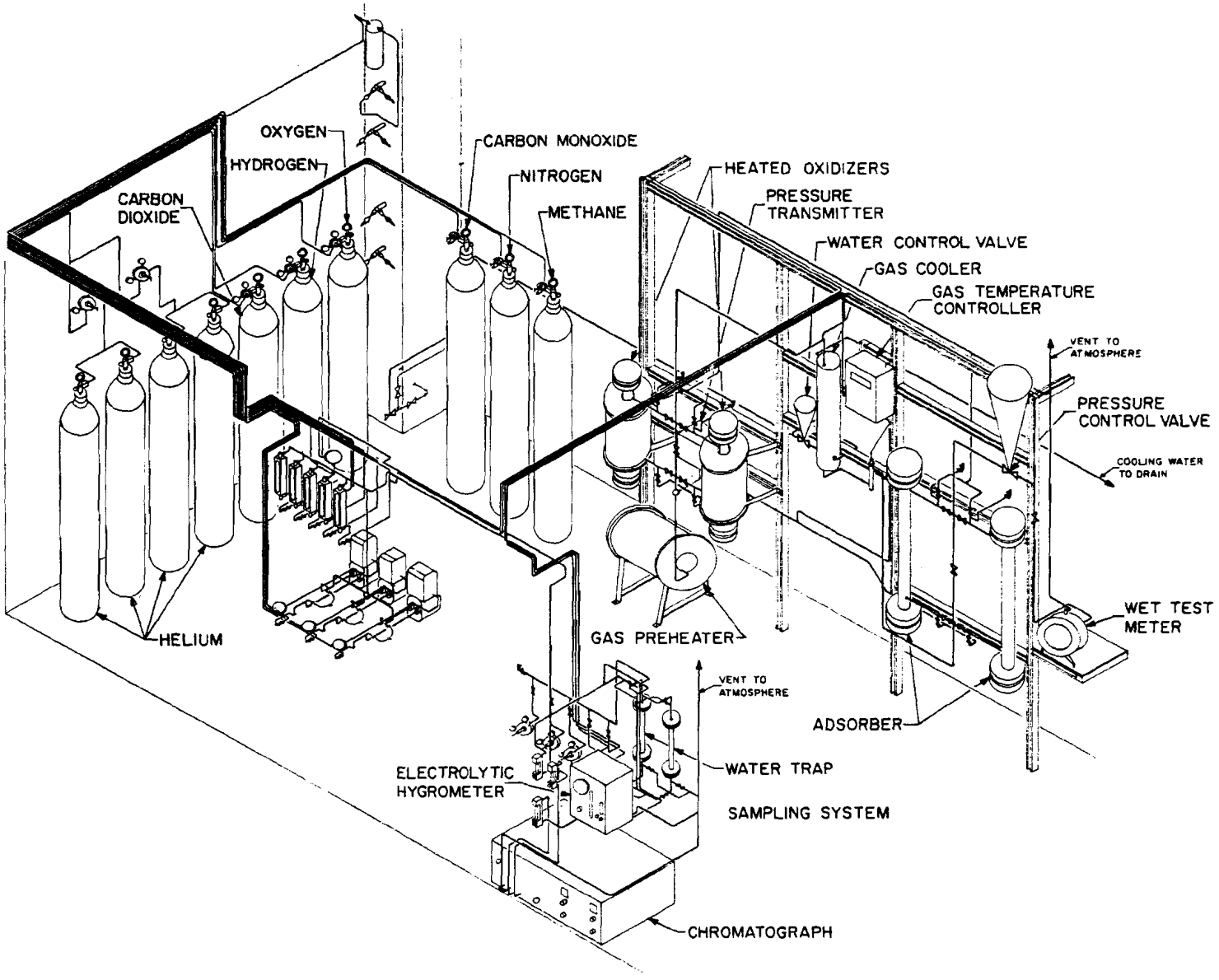

Fig. 3.1. GCR helium coolant purification test facility.

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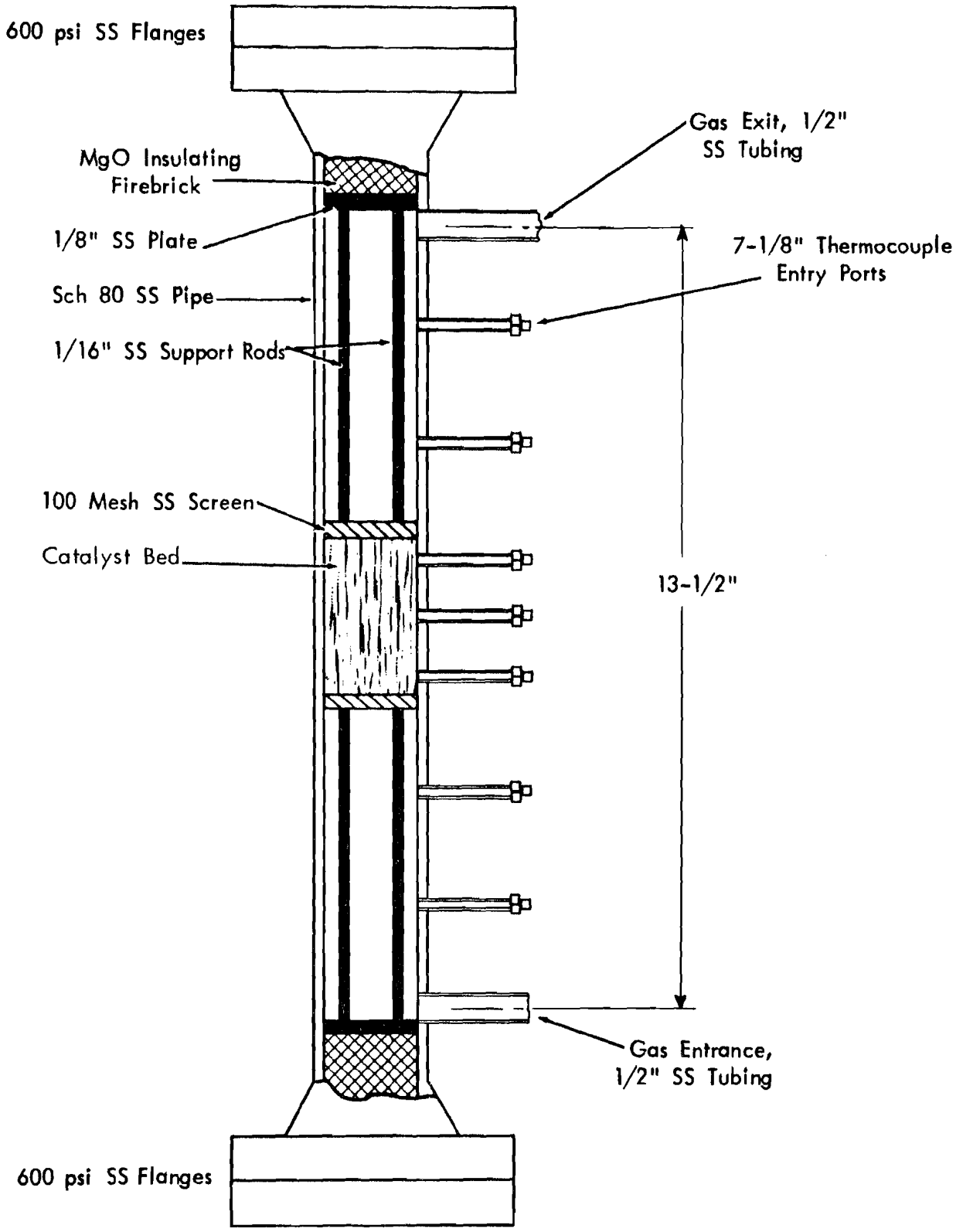

Fig. 3.2. 2-in. oxidizer in helium purification test facility without external heater.

3.3 Experimental Procedure

All tests were made by the following procedure:

1. The oxidizer was charged with the proper amount of catalyst and heated to the specified operating temperature.

2. A preheated stream of pure helium was then introduced to the oxidizer and the catalyst bed was allowed to reach thermal equilibrium.

3. A predetermined, constant rate of contaminant (hydrogen, carbon monoxide, or methane) was introduced to the gas stream.

4. Oxygen was introduced to the gas mixture just prior to its entry to the 2-in. oxidizer or to a point just below the catalyst bed at an initial, constant rate less than that required to give a stoichiometric amount.

5. The oxygen flow rate was increased as a step function periodically until there was no contaminant (H_2, CO, or CH_4) in the reactor off-gas or until the oxygen addition rate was greater than necessary to give a stoichiometric amount.

6. The oxidizer off-gas was sampled periodically by a gas adsorption chromatograph using comparative thermal conductivity measurements, and check samples were taken for analysis by mass spectrometry. The lower limit of detection of hydrogen by the chromatograph was ~10 ppm and for the oxygen, carbon monoxide and methane was ~5 ppm.

3.4 Experimental Data

From the experimental data taken it was possible to determine the oxygen and contaminant concentration in the helium gas stream prior to its entry to the oxidizer and in the oxidizer off-gas. Thus, it was possible to determine the effectiveness of a specific amount of catalyst under the various experimental conditions.

Catalytic Oxidation of Hydrogen. Fourteen tests (Table 3.1a) were made at 400 - 600°C and 300 psia with catalyst bed depths of 1 to 4 in. in a 1-in.-ID and 2-in.-ID vessel for the catalyzed reaction, $H_2 + 1/2\ O_2 = H_2O$. Gas mass flow rates of 0.083 to 1.0 g mole/cm^2-min were used; and initial hydrogen concentrations were 0.51 to 1.96 vol %.

Catalytic Oxidation of Carbon Monoxide. Twelve tests (Table 3.1b) were made at bed temperatures of 400 - 600°C and a total pressure of 300 psia for the catalyzed reaction, $CO + 1/2\ O_2 = CO_2$. Gas mass flow rates of 0.083 to 1.0 g mole/cm^2-min were used; the initial carbon monoxide concentration ranged from 0.44 to 2.47 vol %.

Catalytic Oxidation of Methane. Eight tests (Table 3.1c) were made at bed temperatures of 400 - 600°C and a pressure of 300 psia for the catalyzed reaction $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$. Gas mass flow rates of 0.083 to 1.0 g mole/

Table 3.1. Experimental Data from the Kinetic Study of the Oxidation of Hydrogen, Carbon Monoxide, and Methane by Oxygen in a Fixed Bed of American Metals Products Ni-Cr-Pd Ribbon Catalyst

Run No.	Bed Temp., °C ± 10°C	Bed Dia, cm	Bed Volume, cc	Total Gas Flow Rate, g moles/min	Contaminant Concentration, mole fraction			
					Initial		Final	
	a. Reaction $H_2 + 1/2\ O_2 = H_2O$				H_2	O_2*	H_2	O_2
1	500	5.0	100	3.28	0.010100	0.003807	0.002500	0.000007
2A	500	5.0	100	1.59	0.005100	0.002476	0.000200	0.000066
2B	500	5.0	100	1.59	0.005100	0.001860	0.001400	0.000010
3A	600	5.0	100	4.72	0.012500	0.004503	0.003500	0.000002
3B	600	5.0	100	4.72	0.012500	0.005572	0.001400	0.000022
4	600	5.0	100	3.28	0.019600	0.008911	0.001800	0.000011
5	500	5.0	100	3.28	0.018200	0.009146	0.000400	0.000246
6A	400	5.0	100	1.59	0.008000	0.003733	0.000600	0.000033
6B	400	5.0	100	1.59	0.008000	0.004243	0.000100	0.000293
7	600	5.0	100	3.28	0.010700	0.004552	0.001600	0.000002
8	500	5.0	100	4.72	0.012800	0.006380	0.000400	0.000180
9	500	2.5	56.6	4.72	0.014600	0.006642	0.001400	0.000042
10A	500	2.5	28.3	4.20	0.008100	0.003561	0.001600	0.000311
10B	500	2.5	28.3	4.20	0.008100	0.002469	0.003300	01000169
11	400	2.5	28.3	4.20	0.007900	0.004810	0.000800	0.001260
12	500	2.5	28.3	4.20	0.017000	0.008007	0.001400	0.000207
13	400	2.5	28.3	4.20	0.011000	0.002801	0.005500	0.000051
14A	400	2.5	28.3	4.20	0.014300	0.004740	0.005500	0.000090
14B	400	2.5	28.3	4.20	0.014300	0.007260	0.001700	0.000960
14C	400	2.5	28.3	4.20	0.014300	0.007684	0.001000	0.001034
	b. Reaction $CO + 1/2\ O_2 = CO_2$				CO	O_2*	CO	O_2
1A	500	5.0	100	3.28	0.010200	0.003657	0.002900	0.000007
1B	500	5.0	100	3.28	0.010200	0.004730	0.000700	0.000060
2	500	5.0	100	1.59	0.010000	0.004777	0.000500	0.000027
3	500	5.0	100	4.20	0.009600	0.004957	0.000300	0.000307
4	500	5.0	100	3.28	0.006700	0.002110	0.002500	0.000010
5	500	5.0	100	3.28	0.023000	0.010709	0.001600	0.000009
6A	400	5.0	100	3.28	0.012600	0.004706	0.003200	0.000006
6B	400	5.0	100	3.28	0.012600	0.005594	0.001500	0.000044
7	600	5.0	100	3.28	0.012300	0.004902	0.002500	0.000002
8	500	2.5	56.6	4.20	0.004400	0.002280	0.000440	0.000300

Table 3.1. (Continued)

Run No.	Bed Temp., °C ± 10°C	Bed Dia, cm	Bed Volume, cc	Total Gas Flow Rate, g moles/min	Contaminant Concentration, mole fraction			
					Initial		Final	
	b. Reaction $CO + 1/2\ O_2 = CO_2$				CO	O_2*	CO	O_2
9	400	2.5	28.3	1.59	0.011100	0.003327	0.004500	0.000027
10	400	2.5	28.3	1.59	0.024700	0.009693	0.005000	0.000043
11A	400	2.5	28.3	4.72	0.010700	0.002734	0.005000	0.000084
11B	400	2.5	28.3	4.72	0.010700	0.003734	0.003600	0.000184
11C	400	2.5	28.3	4.72	0.010700	0.005200	0.001700	0.000700
12	600	2.5	28.3	1.59	0.010100	0.005843	0.000020	0.000803
	c. $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$				CH_4	O_2*	CH_4	O_2
1	500	5.0	100	3.28	0.002900	0.001633	0.002600	0.001033
2	500	5.0	100	1.59	0.002600	0.003770	0.001520	0.001610
3	500	5.0	100	4.20	0.003400	0.002882	0.002600	0.001382
4	500	5.0	100	3.28	0.001100	0.000855	0.000970	0.000595
5	500	5.0	100	3.28	0.006700	0.002520	0.005800	0.000720
6	400	5.0	100	3.28	0.002300	0.001783	0.002100	0.001383
7	600	5.0	100	3.28	0.002100	0.001653	0.001600	0.000653
8	500	2.5	56.6	4.28	0.002000	0.002050	0.001900	0.001850

* Determined from stoichiometry.

cm^2-min were used and the initial methane concentration ranged from 0.11 to 0.67 vol %.

Simultaneous Catalytic Oxidation of Hydrogen, Carbon Monoxide, and Methane. Three tests were made in which hydrogen, carbon monoxide, and methane were co-oxidized, in two different catalyst bed sizes at 500°C (Table 3.2). In these tests a total pressure of 300 psia was used with mass flow rates of 0.171 and 0.220 g mole/cm^2-min. Initial contaminant concentrations varied from 0.44 to 1.40 vol %.

4.0 CORRELATION OF DATA

Since the purpose of this experimental study was to obtain experimental kinetic data and usable reactor design equations in a short time, no attempt was made to design the experimental program toward obtaining enough data with sufficient accuracy to permit determination of the mechanism of reaction rate control. This type of approach, as presented by Smith[5] and others, requires investigation of a considerable number of process variables and a large effort directed toward calculation and analysis of experimental results.

The approach taken was to empirically correlate the experimental data in a manner similar to that outlined by Weller[6] and used in an earlier report by the author.[7]

4.1 Apparent Reaction Rate

It was found that the apparent reaction rate for the oxidation of hydrogen, carbon monoxide, and methane at a constant mass flow rate and pressure could be expressed by

$$r = K\, y_c\, y_0 \tag{1}$$

where r = apparent reaction rate, g moles of contaminant reacter per cubic centimeter of catalyst bed per minute

K = apparent reaction rate constant at constant flow rates, g moles/cc-min

y_c, y_0 = mole fraction of contaminant and oxygen in the gas stream at any point in the reactor

The material balance around a differential volume in the reactor results in the flow reactor design equation (Sect. 6.1 for derivation).

$$\frac{V}{F} = -\int_{y_o}^{y_f} \frac{dy}{r} \tag{2}$$

where V = volume of catalyst in reactor, cc

F = gas feed rate, cc/min

y_o, y_f = mole fraction of contaminant initially and finally

Table 3.2. Experimental Results of Simultaneous Catalytic Oxidation of Hydrogen, Carbon Monoxide, and Methane at 500 ± 12°C in a Flowing Stream of Helium

Run No.	Bed Dia, cm	Bed Volume, cc	Total Gas Flow Rate, g-moles/min	Initial Contaminant Concentration, mole fraction				Final Contaminant Concentration, mole fraction			
				H_2	CO	CH_4	O_2*	H_2	CO	CH_4	O_2
1A	5.0	100	3.28	0.014000	0.008300	0.011600	0.00975	0	0.0028	0.0116	0
1B	5.0	100	3.28	0.014000	0.008300	0.011600	0.01557	0	0	0.0098	0.00082
2A	5.0	100	3.28	0.004800	0.004400	0.011500	0.01272	0	0	0.0081	0.00132
2B	5.0	100	3.28	0.004800	0.004400	0.011500	0.00705	0.0004	0.0019	0.0096	0
3A	2.5	56.6	4.20	0.013600	0.007300	0.011700	0.00335	0.0079	0.0063	0.0117	0
3B	2.5	56.6	4.20	0.013600	0.007300	0.011700	0.00740	0.0010	0.0051	0.0117	0
3C	2.5	56.6	4.20	0.013600	0.007300	0.011700	0.01125	0	0.0019	0.0112	0.00075

* Determined from stoichiometry.

Incorporation of eq. (1) individually into the flow reactor design equation with the correct stoichiometry, after integration, results in the following equations for determining the apparent reaction rate constant:

For hydrogen,

$$K_H = \frac{1}{(V/F)\left(y_{H_o} - 2y_{O_o}\right)} \ln \frac{y_{H_f}\, y_{O_o}}{y_{H_o}\, y_{O_f}} \tag{3}$$

For carbon monoxide,

$$K_C = \frac{1}{(V/F)\left(y_{C_o} - 2y_{O_o}\right)} \ln \frac{y_{H_f}\, y_{O_o}}{y_{C_o}\, y_{O_f}} \tag{4}$$

For methane,

$$K_{CH} = \frac{1}{(V/F)\left(2y_{CH_o} - y_{O_o}\right)} \ln \frac{y_{CH_f}\, y_{O_o}}{y_{CH_o}\, y_{O_f}} \tag{5}$$

where y_{H_o}, y_{C_o}, y_{CH_o}, y_{O_o} = initial mole fraction of H_2, CO, CH_4, and O_2

y_{H_f}, y_{C_f}, y_{CH_f}, y_{O_f} = final mole fraction of H_2, CO, CH_4, and O_2

All three reaction rate constants were found to be temperature and mass-flow-rate dependent (Table 4.1):

Table 4.1. Effect of Temperature and Mass Flow Rate on the Reaction Rate Constants

Contaminant	Temperature, °C	Average Reaction Rate Constant, K x 10^{-4} — Mass flow rate, g mole/cm²-min					
		0.083	0.17	0.24	0.33	0.88	1.00
H_2	400	14.3	-	-	-	22.7	-
H_2	500	21.3	22.2	34.3	-	40.4	70.1
H_2	600	-	35.2	42.8	-	-	-
CO	400	-	12.5	-	13.3	-	25.2
CO	500	22.2	24.5	28.1	-	39.4	-
CO	600	-	30.6	-	-	52.1	-
CH_4	400	-	0.59	-	-	-	-
CH_4	500	1.02	1.23	1.92	-	2.88	-
CH_4	600	-	2.98	-	-	-	-

The apparent reaction rate constant at constant mass flow rate can be incorporated into an expression for a rate constant for any flow rate which is dependent only on temperature:

$$K = kG^{\theta},\ k = K/G^{\theta} \quad \text{or} \tag{6}$$

$$\log K = \log k + \theta \log G \tag{7}$$

where k = rate constant for any mass flow rate dependent only on temperature

G = mass flow rate, g moles/cm^2-min

θ = exponent of G necessary for correlation

A plot of log K vs log G should have an intercept of k and a slope of θ for each component at each temperature. Utilizing these plots (Figures 4.1, 4.2, and 4.3), the following average values for θ were determined.

$$\theta_{H_2} - 0.37$$

$$\theta_{CO} - 0.34$$

$$\theta_{CH_4} - 0.51$$

The average values of the reaction rate constant k, determined at 400, 500, and 600°C for each contaminant from eq. (6), are plotted in as Arrhenius-type plots to obtain the temperature dependence of k (Figure 4.4). Assuming that k can be expressed with an Arrhenius-type expression results in the equation,

$$\ln k = \ln A - E/RT \tag{8}$$

Determination of the intercept and slope from these plots allow determination of the following expressions for the reaction rate constant, k,

For hydrogen,

$$k = 1.95 \times 10^{6} e^{-2200/RT} \tag{9}$$

For carbon monoxide,

$$k = 1.73 \times 10^{6} e^{-2400/RT} \tag{10}$$

For methane,

$$k = 4.08 \times 10^{5} e^{-3950/RT} \tag{11}$$

Utilizing the expressions of θ and k in eqs. (1) and (6) allows expressions for the apparent reaction rates,

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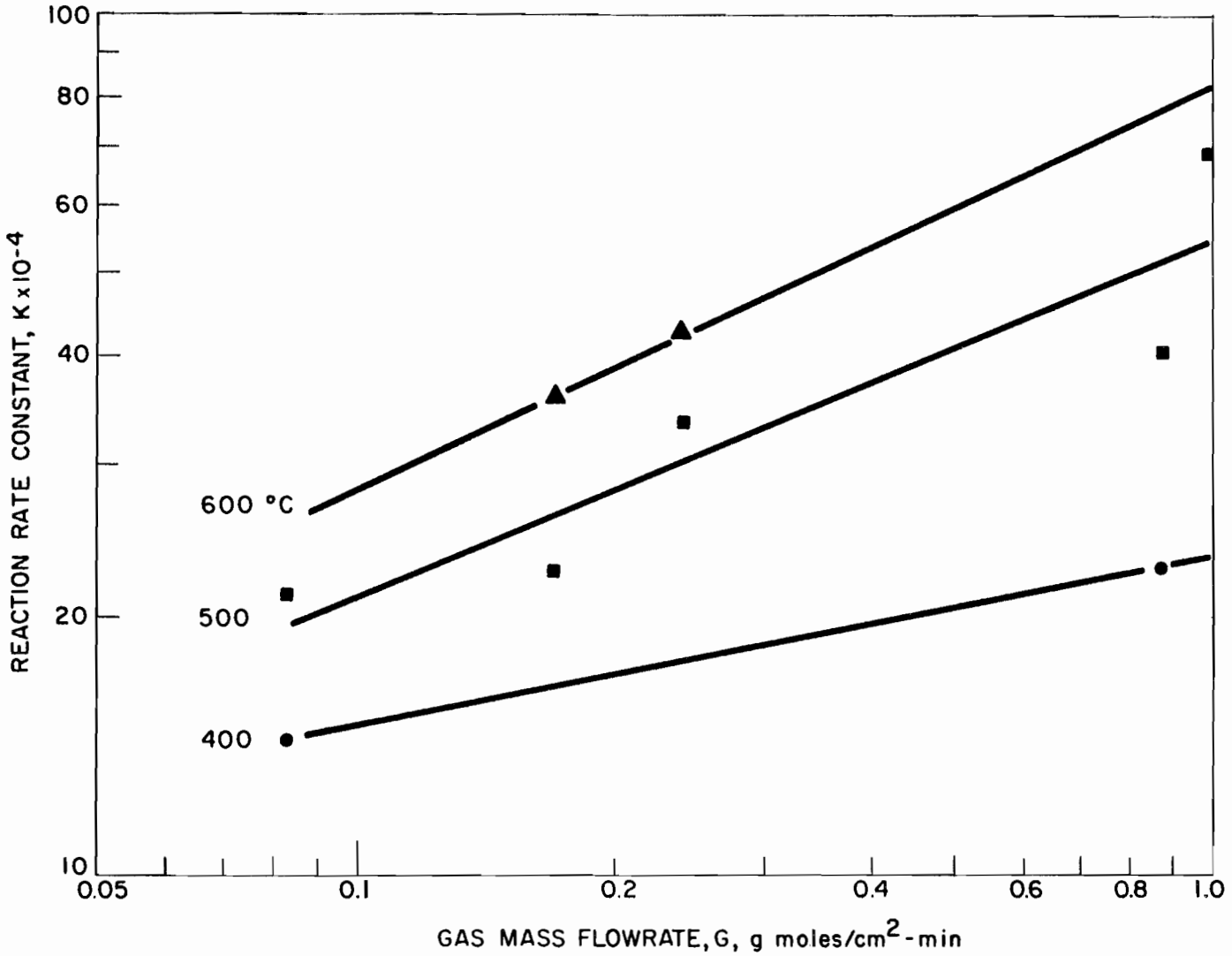

Fig. 4.1. Log reaction rate constant for catalyzed reaction, $H_2 + 1/2\ O_2 = H_2O$, vs log mass flowrate.

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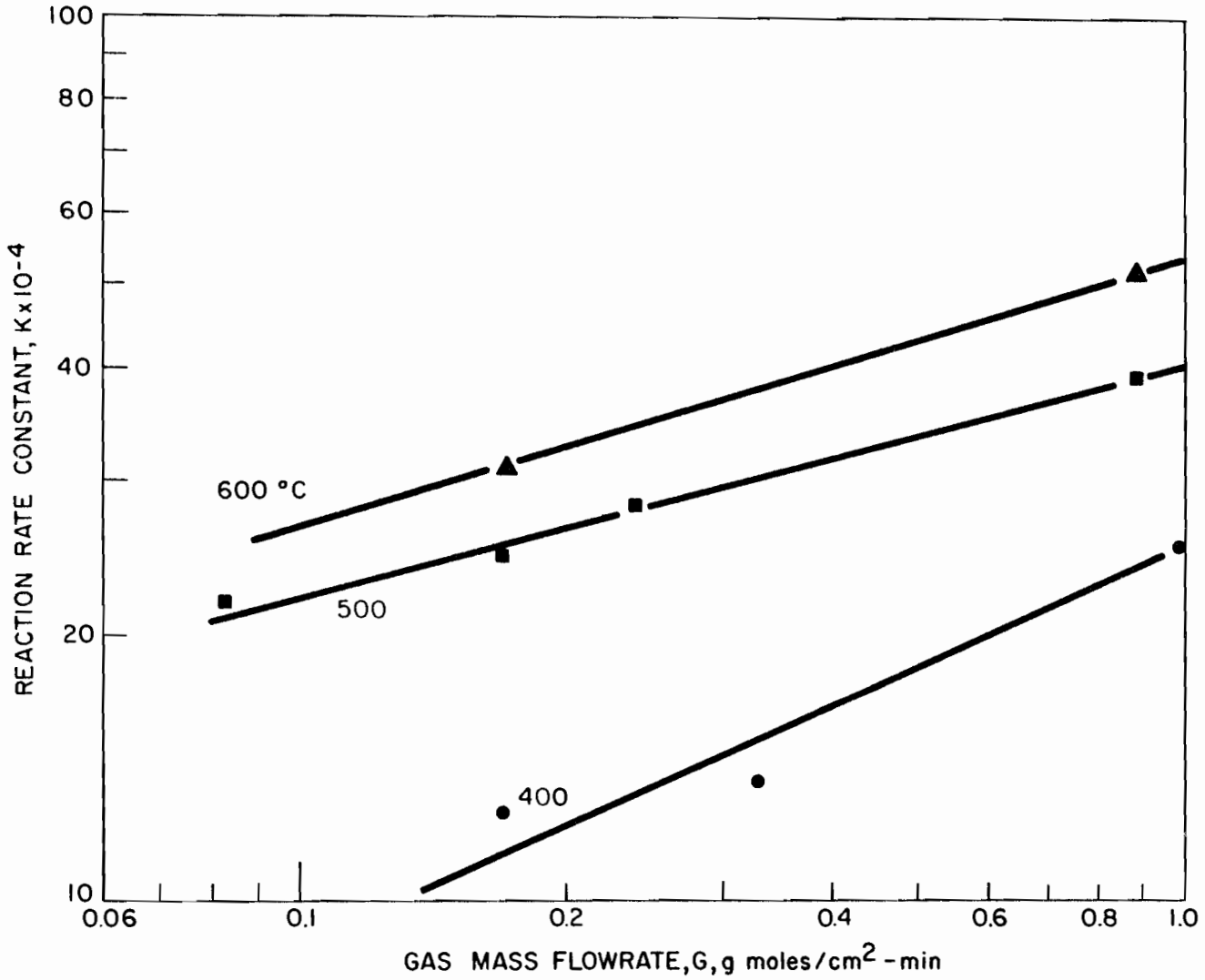

Fig. 4.2. Log reaction rate constant for catalyzed reaction, $CO + 1/2\ O_2 = CO_2$ vs log mass flowrate.

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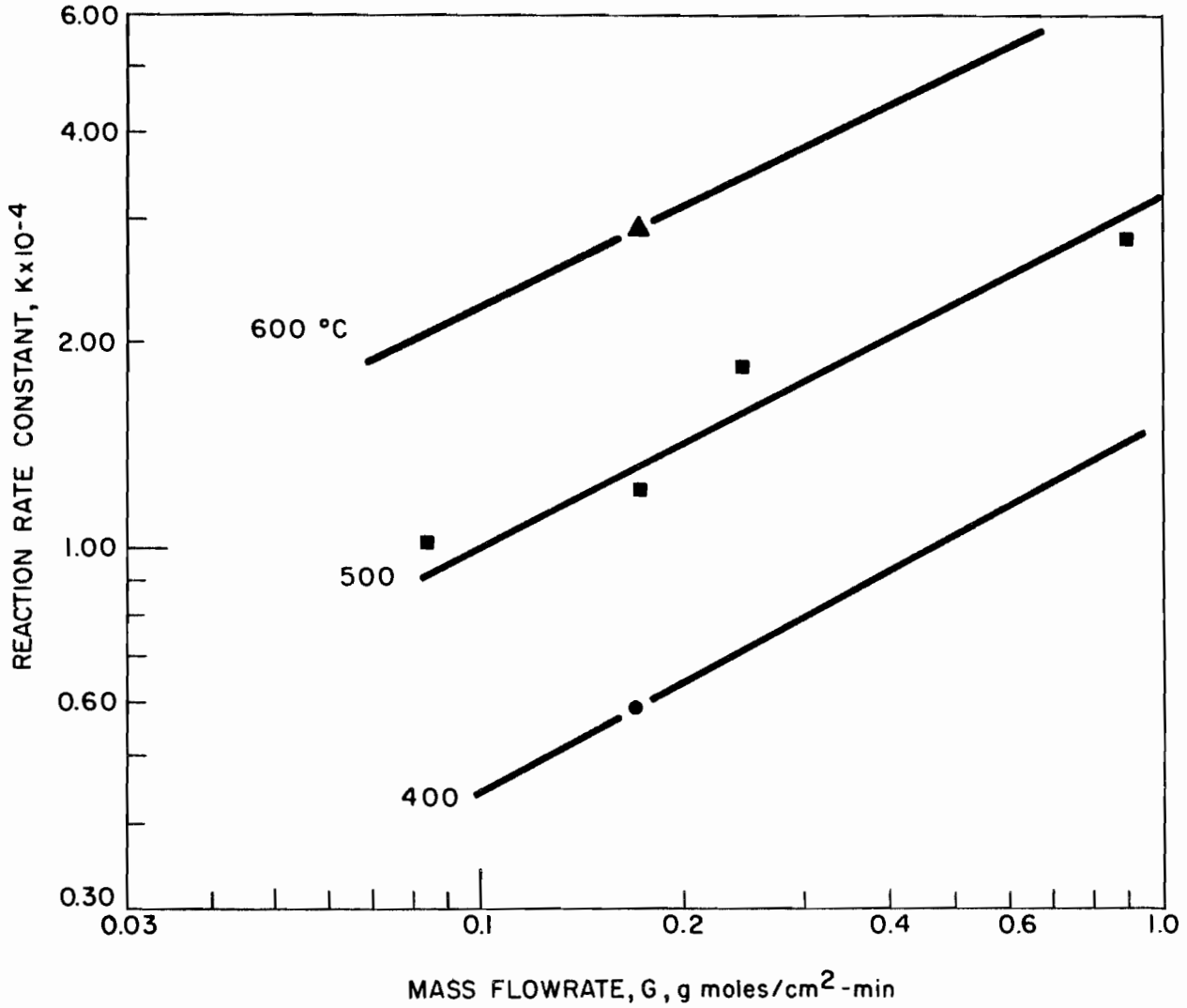

Fig. 4.3. Log reaction rate constant vs log mass flowrate for catalyzed reaction, $CH_4 + 2\ O_2 = CO_2 + 2H_2O$.

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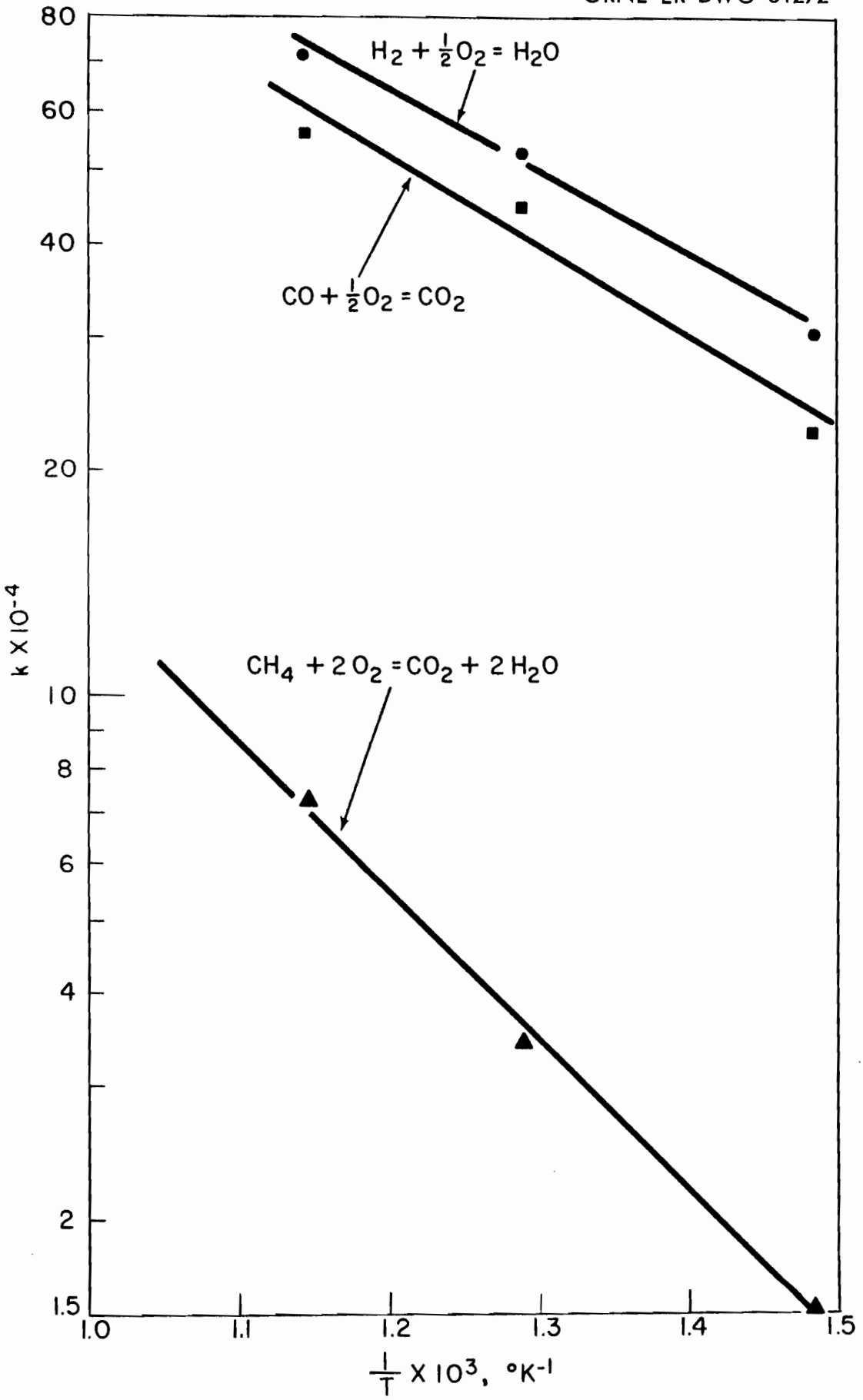


Fig. 4.4. Arrhenius plots of the rate constants for the catalyzed reactions of H_2, CO, and CH_4 with O_2 in a flowing stream of helium at 300

For hydrogen,

$$r_H = 1.95 \times 10^6 e^{-2200/RT} G^{0.37} y_H y_O \tag{12}$$

For carbon monoxide,

$$r_C = 1.73 \times 10^6 e^{-2400/RT} G^{0.34} y_C y_O \tag{13}$$

For methane,

$$r_{CH} = 4.08 \times 10^5 e^{-3950/RT} G^{0.51} y_{CH} y_O \tag{14}$$

4.2 Simultaneous Oxidation of Hydrogen, Carbon Monoxide, and Methane

The three series of tests made with simultaneous oxidation of the three contaminants showed that the preference of oxidation in the catalytic bed was hydrogen first, carbon monoxide second, and methane last. That is, the major portion of the hydrogen was oxidized prior to significant carbon monoxide or methane oxidation and the major portion of the carbon monoxide was oxidized prior to significant methane oxidation. Although these effects were not quantitative, for a conservative reactor design it should be assumed that the first portion or zone of the catalytic bed will be utilized for hydrogen oxidation by the total amount of oxygen available; the second zone for carbon monoxide oxidation by the total remaining oxygen; and the final portion of the oxidizer will oxidize the methane with the oxygen remaining after both hydrogen and carbon monoxide oxidation.

4.3 Reactor Design Equations

One of the main purposes of this work was to establish necessary design equations for evaluation of the EGCR catalytic oxidizer. The design equations can be developed by rearranging eqs. (3), (4), and (5) and incorporating eqs. (9), (10), and (11) for the apparent rate constants. The resulting design equations are:

For hydrogen,

$$V_H = \frac{5.12 \times 10^{-7} e^{2200/RT_F}}{G^{0.37}\left(y_{H_o} - 2y_{O_o}\right)} \ln \frac{y_{H_f}\, y_{O_o}}{y_{H_o}\, y_{O_f}} \tag{15}$$

For carbon monoxide,

$$V_C = \frac{5.77 \times 10^{-7} e^{2400/RT_F}}{G^{0.34}\left(y_{C_o} - 2y_{O_o}\right)} \ln \frac{y_{C_f}\, y_{O_o}}{y_{C_o}\, y_{O_f}} \tag{16}$$

For methane,

$$V_{CH} = \frac{2.45 \times 10^{-6} e^{3950/RT} F}{G^{0.51}\left(2y_{CH_o} - y_{O_o}\right)} \ln \frac{y_{CH_f}\, y_{O_o}}{y_{CH_o}\, y_{O_f}} \tag{17}$$

To evaluate an existing oxidizer, eqs. (15) and (16) can be used to establish the necessary oxidizer volume for the hydrogen and carbon monoxide oxidation and the remaining volume will be used to oxidize the methane. Equation (17) can be rearranged to give a value of the methane concentration when the catalyst volume to be used will be the remaining effective volume $\left(V_{CH} = \text{total volume} - V_H - V_C\right)$:

$$y_{CH_f} = \frac{y_{CH_o}\, y_{O_f}}{y_{O_o}} \exp\left[\frac{4.08 \times 10^5 e^{-3950/RT} V_{CH}\left(2y_{CH_o} - y_{O_o}\right)}{F}\right] \tag{18}$$

where V_{CH} = volume of catalyst remaining for the methane oxidation, cc

It should be noted that when simultaneous oxidation of two or more contaminants is contemplated, necessary reactor volumes are additive for each contaminant and the oxygen mole fraction to be used is the total unused oxygen in the gas stream (Sect. 6.2).

4.4 Reaction-rate-controlling Mechanism

Although the tests made in this study were not exhaustive enough to establish the rate-controlling mechanism, there was definite indication that mass transfer of both the contaminant and oxygen to the reaction site from the bulk gas stream contributed to the reaction rate control.

This is indicated by the dependence of reaction rate on the mass flow rate and by the low activation energies of the reaction rate constant.

4.5 EGCR Application of Oxidizer

The design criteria established for the EGCR oxidizer[1-3] plus addition of some capacity for methane oxidation would give the following gas impurity levels for the EGCR oxidizer:

Contaminant	Gas, vol % Impure	Gas, vol % Purified
H_2 (ref 1,2)	2.3	< 0.1
CO (ref 1,2)	2.3	< 0.1
CH_4	0.01	

(There are no requirements for methane oxidation in EGCR design specification, but it is felt that a realistic design should include provisions for this contaminant. There are no requirements for oxygen contamination from the oxidizer, but it should be maintained as low as possible.)

With these criteria and the reactor design equations and assuming that the mass flow rate will be 0.82 g mole/cm^2-min, and the temperature 650°C, for hydrogen and carbon monoxide only, it was determined that the oxygen concentration in the oxidizer effluent would have to be somewhat higher than 10 ppm but less than 100 ppm. If significant methane oxidation is needed, the effluent oxygen concentration would have to be greater than 100 ppm (Sect. 6.2).

If the design specifications for contaminant content are realistic, then the available catalytic oxidizer is not sufficient to oxidize all contamination, including methane, without significant oxygen contamination of the coolant.

It is recommended that the following points be considered:

1. The oxidizer should be operated at as high a temperature as possible.

2. The design specifications for contamination levels should be reinvestigated.

3. If it is necessary to maintain low oxygen content in the oxidizer effluent (less than 10 ppm), with the contamination levels specified, if capacity for methane oxidation is necessary, or if a lower operating temperature must be used (< 650°C), then a larger oxidizer should be procured with design based on the design equations given in this report.

4. If contamination levels, including oxygen contamination, must be maintained significantly lower than the above specifications, oxidation by fixed-bed CuO should be considered.[8,9]

5.0 REFERENCES

1. L. H. Landrum, American Metal Products Co., personal communication, July 6, 1961.

2. F. A. Anderson, "Proposed Helium Purification System for the Experimental Gas-Cooled Reactor (EGCR)," ORNL-2819 (1959).

3. W. L. Albreck, TVA, personal communication, July 5, 1961.

4. M. E. Whatley et al., "Unit Operations Section Monthly Progress Report, February 1960," ORNL CF 60-2-56.

5. J. M. Smith, "Chemical Engineering Kinetics," McGraw-Hill Book Co., New York, 1956.

6. S. Waller, "Analysis of Kinetic Data for Heterogeneous Reactions," J.A.I.Ch.E., 2: 39 (1956).

7. C. D. Scott, "Kinetics of the Catalyzed Oxidation of Hydrogen, Carbon Monoxide, and Methane by Oxygen in a Flowing Stream of Helium," ORNL-3043 (1961).

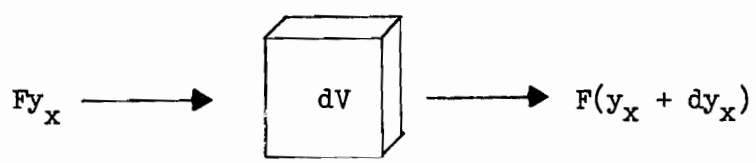
8. C. D. Scott, "Oxidation of Hydrogen and Carbon Monoxide in Helium by Use of CuO. I. Preliminary Results," ORNL CF 60-7-26.

9. C. D. Scott, "Removal of Hydrogen, Carbon Monoxide, and Methane from Gas Cooled Reactor Helium Coolants," ORNL-TM-20 (1961).

6.0 APPENDIX

6.1 Derivation of Flow Reactor Design Equation

Consider a differential volume of the fixed bed, dV. If it is assumed that the gas flow rate, F, is constant throughout the reactor, then the flow of contaminant, x, into the differential volumes is Fy_x, where y_x is the mole fraction of x in F, and the flow of contaminant out of the differential volume is $F(y_x + dy_x)$, where dy_x is the change in y_x due to the differential volume:



If the reaction rate of x is r in the differential volume, then, by the law of conservation of matter, the amount of x entering minus the amount of x leaving must be equal to the amount of x lost or reacted:

$$Fy_x - F(y_x + dy_x) = rdV \tag{19}$$

After simplifying and rearranging this becomes

$$\frac{dV}{F} = -\frac{dy_x}{r} \tag{20}$$

or

$$\int \frac{dV}{F} = -\int \frac{dy_x}{r} \tag{21}$$

Integrating over the entire volume of the reactor, V_R, and from the entering mole fraction of x, y_{x_o}, to a final mole fraction of x, y_{x_f}, the limits of integration for eq. (21) become

$$\int_{o}^{V_R} \frac{dV}{F} = -\int_{y_{x_o}}^{y_x} \frac{dy_x}{r} \tag{22}$$

Integration of the left-hand side of eq. (22) gives the flow reactor design equation:

$$\frac{V_R}{F} = -\int_{y_{x_o}}^{y_{x_f}} \frac{dy_x}{r} \tag{23}$$

The right-hand side of the equation can be integrated when the reaction rate, r, is available in terms of the mole fraction of x in the feed, y_x, at any point in the reactor.

6.2 Evaluation of Present EGCR Oxidizer for Hydrogen and Carbon Monoxide Oxidation

Assume that the contamination levels in the oxidizer gas stream will be:

Contaminant	Oxidizer Feed Gas, mole fraction	Oxidizer Off-gas, mole fraction
H_2	0.023	< 0.001
CO	0.023	< 0.001
O_2	-	0.00001

The total oxidizer volume is given as 6140 cc and the mass flow rate is 0.82 g moles/cm^2-min with a volumetric flow rate of 7.61×10^5 cc/min. The assumed operating temperature will be 650°C and the pressure will be 300 psia. It will be assumed that hydrogen at a mole fraction of 0.001 will not further oxidize and will not impede the carbon monoxide oxidation.

The initial oxygen mole fraction must be,

$$y_{O_o} = \frac{0.022}{2} + \frac{0.022}{2} + 0.00001 = 0.02201$$

Then the other oxygen mole fractions will be,

$$\left(y_{O_f}\right)_{H_2} = \left(y_{O_o}\right)_{CO} = y_{O_o} - \left(\frac{y_{H_o} - y_{H_f}}{2}\right) = 0.02201 - \frac{0.022}{2} = 0.01101$$

and

$$\left(y_{O_f}\right)_{CO} = 0.000010$$

Therefore, the necessary mole fractions of the various components are approximately:

For hydrogen oxidation

$$y_{H_o} = 0.023,\ y_{H_f} = 0.001,\ y_{O_o} = 0.02201,\ y_{O_f} = 0.01101$$

For carbon monoxide oxidation

$$y_{C_o} = 0.023,\ y_{C_f} = 0.001,\ y_{O_o} = 0.01101,\ y_{O_f} = 0.00001$$

From eq. (15), the volume of catalyst bed necessary for the hydrogen oxidation will be,

$$V_H = \frac{(5.12 \times 10^{-7})(7.61 \times 10^5)\ e^{2200/(R)(923)}}{(0.82)^{0.37}\ (0.02300 - 0.4402)} \ln \left[\frac{(0.001)(0.02201)}{(0.023)(0.01101)}\right]$$

$$V_H = -74.5 \ln 0.087 = 182 \text{ cc}$$

From eq. (16), the volume of catalyst bed necessary for the carbon monoxide oxidation will be,

$$V_C = \frac{(5.77 \times 10^{-7})(7.61 \times 10^5)\ e^{2400/(R)(923)}}{(0.82)^{0.34}\ (0.02300 - 0.02202)} \ln \left[\frac{(0.001)(0.01100)}{(0.023)(0.00001)}\right]$$

$$V_C = 1780 \ln 47.8 = 6840 \text{ cc}$$

Total volume necessary would be,

$$V_T = 182 + 6840 = 7022 \text{ cc}$$

which is somewhat greater than the amount of catalyst available. Therefore, the effluent oxygen concentration must be greater than 10 ppm.

If 100 ppm of oxygen is allowed in the effluent, then the mole fractions of the various components will be:

For hydrogen oxidation

$$y_{H_o} = 0.023,\ y_{H_f} = 0.001,\ y_{O_o} = 0.0221,\ y_{O_f} = 0.111$$

For carbon monoxide oxidation

$$y_{C_o} = 0.023,\ y_{C_f} = 0.001,\ y_{O_o} = 0.111,\ y_{O_f} = 0.0001$$

Then the necessary oxidizer volumes will be

$$V_H = \frac{(5.12 \times 10^{-7})(7.61 \times 10^5)\ e^{2200/(R)(923)}}{(0.82)^{0.37}\ (0.02300 - 0.0442)} \ln \left[\frac{(0.001)(0.0221)}{(0.023)(0.0111)}\right]$$

$$V_H = 171 \text{ cc}$$

$$V_C = \frac{(5.77 \times 10^{-7})(7.61 \times 10^5)\ e^{2400/(R)(923)}}{(0.82)^{0.34}\ (0.02300 - 0.0222)} \ln \left[\frac{(0.001)(0.0111)}{(0.023)(0.0001)}\right]$$

$$V_C = 3440 \text{ cc}$$

The necessary volume would be,

$$V_T = V_H + V_C = 171 + 3440 = 3611 \text{ cc}$$

This would allow 6140 - 3440 = 2700 cc for methane oxidation.

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