

STUDIES OF AN ALKALI IMPREGNATED COBALT-MOLYBDATE  
CATALYST FOR THE WATER-GAS SHIFT AND  
THE METHANATION REACTIONS

by

Vasfi Berispek

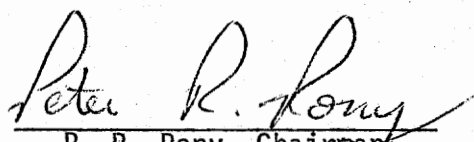
Thesis submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of

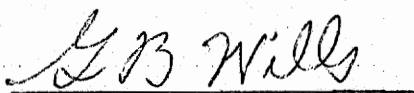
MASTER OF SCIENCE


in

Chemical Engineering

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March, 1975

Blacksburg, Virginia

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## ACKNOWLEDGEMENTS

I would like to thank Dr. Peter R. Rony, my graduate committee chairman, for his support, criticism, and helpful suggestions during the investigation and his guidance throughout the writing of this thesis. I also would like to express my appreciation to Dr. David S. Newsome, co-principal investigator of the "Supported Molten Electrolyte Catalysts" grant, for his suggestions and assistance and to Henry H. Hubble for his experimental aid. Finally, I would like to acknowledge the very useful M.S. thesis of Andrew O. Overstreet, one that helped with various phases of my work, including the writing of this thesis.

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## I. INTRODUCTION

As a consequence of the energy shortage, strict pollution controls, and an increasing dependence upon foreign sources for petroleum, there is a growing incentive for clean energy production from coal-derived fuels.<sup>1</sup> The large coal reserves and relatively moderate price for bituminous coal and lignite in the U.S. make them attractive as a source of both gas and liquid fuels. Currently, coal can be converted into high BTU gas (mainly methane) by the carbon-steam reaction followed by the water gas shift reaction and catalytic methanation. By means of the shift reaction, the hydrogen-to-carbon monoxide ratio is adjusted to a value that is slightly greater than 3:1. The shifted gas, after removal of CO<sub>2</sub> and sulfur compounds, is then methanated to provide a high BTU gaseous product.

It is likely that the U.S. coals that contain the greatest quantities of sulfur will be those that will be processed further to clean fuels. Some of the processes to accomplish such conversions will be catalytic, and a premium will be placed upon sulfur-tolerant catalysts. According to German patent number 1,959,012, cobalt molybdate catalysts impregnated with alkali salts such as cesium acetate are highly active sulfur-tolerant water-gas shift catalysts once the cobalt and molybdenum have been sulfided at high temperatures. Clyde L. Aldridge, the discoverer of this catalyst, suggested that it contained a catalytic melt dispersed within alumina under reaction conditions.<sup>2</sup> Inasmuch as the unimpregnated cobalt molybdate catalyst is the industry standard

for catalytic hydrodesulfurization of heavy oils and is also active as a sulfur-tolerant methanation catalyst, the VPI & SU catalysis group headed by Dr. Peter R. Rony decided to study it in further detail.

The most exciting aspect of this particular shift catalyst is that very few exploratory studies have been performed in industry to test its ability to activate hydrogen for a variety of hydrocarbon reactions. For example, the "Aldridge" catalyst has not been tested either for catalytic methanation or for the conversion of cellulosic materials to oil. Further, although it has been demonstrated to be a highly active commercial water-gas shift catalyst, under sulfur-tolerant conditions, the effect of a key variable, the molar ratio of the alkali salt to molybdenum and cobalt, on the rate of reaction has not been reported. The physical state of the catalyst under reactor conditions is not clear. Perhaps the molybdenum dissolves in the alkali melt, or else the melt "conditions" the surface of sulfided cobalt molybdate in some undetermined manner, such as by stabilizing a surface intermediate in a reaction pathway different from that for an unimpregnated cobalt molybdate catalyst. Such explanations rest on the correctness of Aldridge's initial suggestion that there exists a melt in his catalyst under reaction conditions. Clearly, research on the "Aldridge" catalyst could settle some of the above issues and perhaps provide new perspectives concerning high-temperature transition metal catalysis.

## A. Objectives

The objectives of our studies of the "Aldridge" catalyst in the water-gas shift, the catalytic methanation and the ethanol dehydration reactions are presented below under separate headings:

### 1. Water-Gas Shift Reaction

1. Test out a "periodic chart" catalyst and other new catalyst screening procedures that could speed up our studies.
2. Replace zinc for cobalt in the "Aldridge" catalyst and determine if the high activity characteristic of Cs-Co-Mo/Al<sub>2</sub>O<sub>3</sub> can still be obtained.
3. Add soluble Li, Na, K salts to the Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst and determine if the lower break point in the activation energy curve will appear at lower temperatures and whether such catalysts are more active than the "Aldridge" Cs-Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.
4. Test out "Aldridge" catalysts with decreased amounts of cobalt, molybdenum and cesium at the same Cs:Mo molar ratio. Compare their activities and the effect of cesium on measured rate constants to the original cesium-impregnated Nalcomo 474 catalysts.
5. Try to "see" the melt in the "Aldridge" catalyst.

### 2. Ethanol Dehydration.

Test the ability of the "Aldridge" catalyst to remove oxygen from cellulosic wastes. The deoxygenation of ethylene glycol may be a useful model reaction. However, for simplicity, study the dehydration of ethanol first.

V

### 3. Catalytic Methanation.

1. Study this reaction over the "Aldridge" catalyst and determine if it is better than any competitive sulfur-tolerant methanation catalyst.
2. Develop techniques and kinetic models for interpreting the chromatographic data so that a student that follows can analyze the data routinely.
3. Develop a gas blending station that will permit the preparation of mixtures containing different gas compositions.
4. Calibrate the new universal high pressure flow meter.

## II. DEHYDRATION AND METHANATION CATALYSIS

The dehydration of alcohol over alumina has been studied extensively. Although a substantial amount of work has been performed on the adsorption of the reactants and the reaction scheme for the surface compounds, there are conflicting views as to what happens on the catalyst surface in the catalysis of these reactions. The nature of the surface, the kinds of forces or bonds between the adsorbate and adsorbent molecules have not been clearly understood yet. The surface ethoxide ( $C_2H_5O - Al<$ )<sup>3,4,5</sup>, oxonium ( $C_2H_5O^+H_2$ ), and carbonium ions ( $C_2H_5^+$ )<sup>6,7</sup> are frequently suggested as reaction intermediates as a result of infrared spectroscopy and mass spectrometry studies. A reaction scheme for the dehydration of straight-chained and branched alcohols over alumina was proposed by Knözinger and Köhne<sup>8</sup> as a result of their studies in a differential flow reactor. Although the derivation of kinetic equations was based on suggestions for the molecular mechanism of the reaction, kinetic analysis may not be a useful tool for the elucidation of the mechanism of a reaction, or so stated Knözinger et al<sup>9</sup> by means of their statistical analysis.

Ethanol dehydration has been studied extensively because of the need to prepare olefins from alcohols. However, the interest in catalytic dehydration declined when large quantities of  $C_2H_4$  and other unsaturated hydrocarbons were prepared from petroleum. Oxide catalysts such as  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $W_2O_5$ , and  $ZrO_2$  were usually used as dehydration catalysts. Winfield<sup>10</sup> gives a good review of the catalytic dehydration reactions.

Various rate laws have been proposed for ethanol dehydration. Some of them are given in Table 1.

Catalytic methanation has been investigated over the past 70 years by many workers. The manufacture of methane from coal has suddenly become a promising method to satisfy the increasing demands for natural gas. Ruthenium, nickel, cobalt, and iron are all known as active methanation catalysts. The high cost of ruthenium and the tendency of iron and cobalt catalysts to deposit more carbon make nickel the transition metal of choice in most investigations of methane synthesis. Commercial nickel catalysts are usually supported on acid-washed kieselguler or on alumina. An excellent review of methanation catalysts is given by Mills and Steffgen.<sup>14</sup> Greyson<sup>15</sup> summarizes the work done on methanation prior to the fifties, discusses the chemistry and thermodynamics of the reaction, and reviews the catalysts used in these studies. The British Gas Research Board<sup>16</sup> has made an important contribution to methanation studies on supported-nickel and cobalt catalysts. Presently, the U.S. Bureau of Mines<sup>17,18,19,20,21,22,23,24</sup> is one of the leading research groups in this area.

To correlate experimental data, various rate expressions have been proposed for catalytic methanation. Herwijnen et al<sup>25</sup>, Nicolai et al<sup>26</sup>, Bousquet and Teichner<sup>27</sup> tested nickel catalysts. Gilkeson et al<sup>28</sup> employed a multi-metal catalyst, which was composed mainly of iron, for the synthesis of methane in a tubular reaction, whereas Frye et al<sup>29</sup> used an iron oxide catalyst in a fixed-bed reactor. A reaction mechanism was proposed by Powers<sup>30</sup> to account for observed effects of

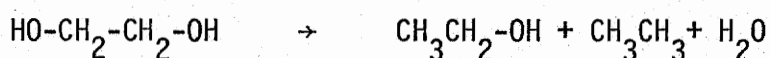
TABLE 1. VARIOUS RATE EXPRESSIONS PROPOSED FOR ETHANOL DEHYDRATION

<u>Rate Equation</u>	<u>Temperature</u>	<u>Remarks</u>
$R = \frac{KLK_a P_a}{K_a P_a + K_w P_w}$	350° - 400°C	The surface reaction on Al <sub>2</sub> O <sub>3</sub> was assumed to be the rate-determining step.
$R_{\text{overall}} = \frac{(k_{IF} S_O)^{\theta_s} A' - (k_{IR} S_O)^{\theta_c} W^1}{P_1} + \frac{k_2 F S_O^{\theta_s} E' - (k_{2R} S_O)^{\theta_c} A^1 + \frac{k_3 S_O}{P_1} C}{P_1} + \frac{(k_{4F} S_O^2)^{\theta_s} E^1 - (k_{4R} S_O^2)^{\theta_c} C^2 W^1}{P_1}$	220° - 374°C	This kinetic model is consistent with a single site interaction on the surface of gamma-alumina
$R_{\text{overall}} = k_I + (k_{II} + k_{III} P_A)^{1/3}$	307°C	k <sub>I</sub> and k <sub>II</sub> are the rate constants of ethylene and ether formation, respectively, according to the Langmuir-Hinshelwood mechanism; k <sub>III</sub> is the rate constant of ether formation according to the Rideal-Eley mechanism
$R_{\text{overall}} = k_0 + k_1 C_A \quad (a)$	200 - 420°C	k <sub>0</sub> and k <sub>1</sub> are the rate constants of ethylene and ether formation respectively.

(a) This study

pressure, temperature, and  $H_2/CO$  molar ratio on the rate of the methanation reaction in a differential reactor. Wencke<sup>31,32</sup> demonstrated the respective change in activity with increasing molybdenum compositions. He tested a molybdenum catalyst, supported on  $Al_2O_3$ , which was sulfided and reduced in the presence of  $H_2S$  and  $H_2$  at  $600^\circ C$ . The Institute of Gas Technology<sup>33</sup> tested nickel catalysts of various compositions to determine the most suitable one for the methanation step in the IGT HYGAS Process for producing pipeline gas from coal. They also provided a table of rate equations for catalytic methanation proposed by various investigators.

The reason we employed the "Aldridge" catalyst in our dehydration studies is that we thought that it might be an effective catalyst for removing oxygen from cellulosic wastes. Therefore, we chose ethylene glycol as a model compound for cellulose-to-oil conversion processes. We were quite optimistic that we could convert ethylene glycol to both ethanol and ethane according to the non-balanced equation,



Owing to its higher vapor pressure, we studied the dehydration of ethanol. We employed a catalyst bed mixture containing the "Aldridge" catalyst and  $Al_2O_3$ , which is a catalyst that is used for the dehydration of alcohols, expecting that the "Aldridge" catalyst would dominate. However, the result was that the mixed activity of the catalyst bed was lower than that of pure  $n-Al_2O_3$  catalyst used by de Boer et al.<sup>13</sup> Hence, we decided not to waste our time with the dehydration reaction.

The experimental data obtained for catalyst "VV" (Tables 6 and 8) and catalyst "ZZ" (Tables 6 and 11) was analyzed so that other investigators could benefit from our theoretical techniques and kinetic models.

Upon observing the formation of methane during preliminary studies of the water-gas shift reaction, we projected that, under suitable conditions, our "Aldridge" catalyst might be sufficiently active to compete with the commercial nickel catalyst.

We first tested catalyst "RR" (Tables 6 and 14) and then catalyst "ZO" (Tables 6 and 16) to see the effect of cesium acetate on the rate of methanation.

### III. EXPERIMENTAL

Dr. P. R. Rony, the principal investigator for the "Supported Molten Electrolyte Catalysts" grant, constructed the overall reactor system. A variety of "Aldridge" catalysts were tested for the water-gas shift reaction, methanation and ethanol dehydration with the aid of this catalytic reactor. As a result of these studies, 36 sets of data, in the form of final concentration tables and Arrhenius plots, were obtained. In all these runs, similar experimental procedures were followed. The overall reactor system and reactor operation were described in detail in the M.S. Thesis of Overstreet.<sup>2</sup> Since the same reactor was employed for our catalyst studies, we are including descriptions of the overall reactor system and operation, directly from his thesis, in Appendix II. Only the changes made in the overall reactor system for the methanation and dehydration studies, as well as catalyst preparation and pretreatment, will be described in this section.

Summaries of the overall operating conditions for the three reaction systems that we studied are provided in Tables 2, 3, and 4.

#### A. Changes

##### 1. Ethanol Dehydration.

Similar procedures were followed as in the water-gas shift reaction, except that we placed 95% ethanol and 5% water into the saturator and maintained it at 50°C. A slightly different chromatographic analysis was performed. We programmed the oven temperature to remain at 70°C for one minute, and then increase at a rate of 24°C/min, to a

TABLE 2. SUMMARY OF OVERALL OPERATING CONDITIONS  
USED FOR THE STUDY OF "ALDRIDGE" WATER  
GAS SHIFT CATALYSTS

Operating Pressure Range:	approximately 715 mm Hg
Operating Temperature Range:	150°C to 450°C
Flow Rate Range:	100 ml/min to 10 ml/min dry gas basis at STP
Length of Catalyst Bed:	less than 10 cm
Size of Reactor Tube:	Nominally 3/16-I.D. stainless steel tubing
Water Saturator Temperature:	60°C
Temperature of Gas Sampling Region:	150°C
Temperature of gas chromatographic column:	60°C
Quantity of catalyst:	from 0.1 gm to 1.5 gm
Space Velocity:	GHSV greater than 1000 at STP
Reactants:	H <sub>2</sub> , CO, COS, H <sub>2</sub> O
Products:	H <sub>2</sub> , CO, COS, H <sub>2</sub> O, CO <sub>2</sub> , H <sub>2</sub> S
Time for reactor to equilibrate for 25°C temperature change:	30 minutes
Chromatographic Analysis Time:	Approximately 5 minutes per sample
Composition of dry gas feeds:	Cylinder #1: 53.3% H <sub>2</sub> , 44.8% CO, 1.5% COS, 0.4% CO <sub>2</sub>  Cylinder #2: 59.8% H <sub>2</sub> , 37.6% CO 2.2% COS, 0.5% CO <sub>2</sub>  Cylinder #3: 49.5% H <sub>2</sub> , 48.3% CO, 1.7% COS, 0.5% CO <sub>2</sub>

TABLE 3. SUMMARY OF OVERALL OPERATING CONDITIONS  
USED FOR THE STUDY OF "ALDRIDGE" CATALYSTS  
IN ETHANOL DEHYDRATION

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Operating Pressure Range:	approximately 715 mm Hg
Operating Temperature Range:	200°C to 450°C
Flow Rate Range:	10 ml/min to 150 ml/min wet gas basis at STP
Length of Catalyst Bed:	less than 10 cm
Size of Reactor tube:	Nominally 3/16-I.D. stainless steel tubing
Saturator Temperature:	50°C
Temperature of gas sampling region:	150°C
Temperature of gas chromatographic column:	Temperature programming from 70°C to 160°C
Quantity of catalyst:	from 0.1 gm to 1.5 gm
Space Velocity:	GHSV greater than 1000 at STP
Reactants:	H <sub>2</sub> , CO, COS, C <sub>2</sub> H <sub>5</sub> OH, CO <sub>2</sub>
Products:	H <sub>2</sub> , CO, C <sub>2</sub> H <sub>5</sub> OH, CrH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O H <sub>2</sub> O, CO <sub>2</sub>
Time for reactor to equilibrate for 25°C temperature change:	30 minutes
Chromatographic Analysis Time:	Approximately 5 minutes per sample
Composition of dry gas cylinder, i.e., Cylinder #2:	59.8% H <sub>2</sub> , 37.6% CO, 2.2% COS, and 0.5% CO <sub>2</sub>

TABLE 4. SUMMARY OF OVERALL OPERATING CONDITIONS  
USED FOR THE STUDY OF "ALDRIDGE" CATALYST  
IN METHANATION

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Operating Pressure Range:	approximately 300 psig
Operating Temperature Range:	250°C to 450°C
Flow Rate Range:	100 ml/min to 1500 ml/min effluent gas basis at STP
Length of Catalyst bed:	less than 30 cm
Size of Reactor tube:	Nominally 3/16-I.D. stainless steel tubing
Temperature of gas sampling region:	150°C
Temperature of gas chromatographic column:	60°C
Quantity of catalyst:	3.0 gm to 5.0 gm
Space Velocity:	GHSV greater than 1200 at STP
Reactants:	H <sub>2</sub> , CO, CO <sub>2</sub> , COS
Products:	H <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , H <sub>2</sub> O, H <sub>2</sub> S, COS
Time for reactor to equilibrate for 25°C temperature change:	30 minutes
Chromatographic Analysis Time:	Approximately 15 minutes per sample
Composition of dry gas cylinder, i.e., Cylinder #5:	74.0% H <sub>2</sub> , 22.6% CO, 1.12% CO <sub>2</sub> and 1.96% COS

preset final temperature of 160°C. In this way the chromatographic analysis time was reduced and a good separation of the reaction products was achieved.

## 2. Methanation

To perform kinetic studies at higher pressures, it was necessary to relocate the Chatham precision valve, which was immediately upstream of the bubble meter in the water-gas shift studies, into the temperature-controlled sampling box. Thus, the single feed gas, after emerging from the gas regulator, passed through a vent line, a vacuum line, a check valve, a seven-foot reactor-gas preheater tube, a five-foot fixed bed catalytic reactor maintained between 150°C and 650°C and into the sampling region. In the sampling region, the effluent gasses passed through a Chatham precision fine-metering valve, a gas sampling valve equipped with a 0.7 ml sampling loop, a bubble meter operating at room temperature and atmospheric pressure, and finally, a vent.

A novel feature of the apparatus was the measurement of the gas flow rate at high pressures. This was achieved with a Robinson-Haalpern P60-series potentiometric pressure transducer powered by a Kepco D.C. power supply set at 18 volts. A frictionless level system within the transducer amplified the motion of the sensing element and operated a contact wiper over a precision linear potentiometer. The output resistance or voltage change was proportional to the pressure change created by periodically closing and opening an electrically operated ball valve. When the ball valve was in the open position, the pressure in the flowmeter volume,  $V_f$ , was at its maximum value. Upon closing

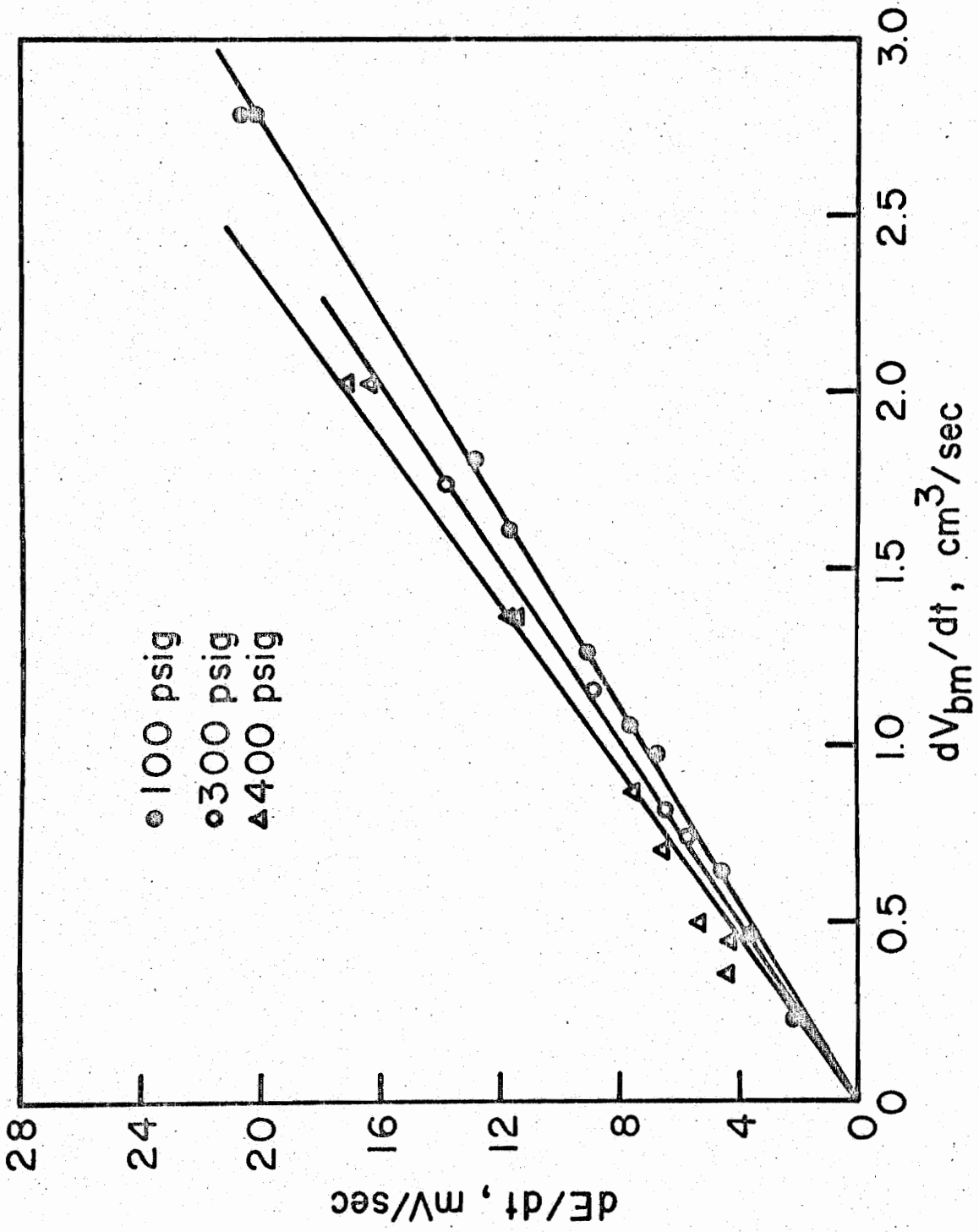


Figure 1. Calibration curve for the high pressure flowmeter

the valve, the pressure decreased linearly as a function of time until the ball valve opened again.

To calibrate the flowmeter, the upstream pressure was set at 600 psig and the downstream pressure at 100 psig. The flow rate of an inert feed gas was measured by the bubble meter at ambient conditions. For each flow rate, the electrically operated ball valve was opened and closed for a period of 60 seconds and the voltage drop, i.e., the initial voltage reading minus the reading at the end of each period, was recorded with a digital multimeter. This procedure was repeated for six different flow rates. Similar data were obtained for downstream pressures of 300 and 400 psig and the same upstream pressure. A plot of  $dE/dt$  vs  $dV_{bm}/dt$  is given in Figure 1.

One disadvantage of the pressure transducer used was the sticking of the wiper. The transducer needed to be tapped to obtain reliable readings. Several readings were taken at each flow rate to minimize errors. It was possible to produce a nice straight line when the voltage rate of change with time was plotted versus the bubble meter reading, i.e., volumetric flowrate.

#### B. Catalyst Preparation

The "Aldridge" catalysts were mainly prepared by A. D. Overstreet and H. H. Hubble, a decision made by Dr. Rony to minimize potential variations in catalyst batches. Nalcomo 474 Hydrotreating catalyst, which has the following specifications,

% MoO <sub>3</sub>	12.5
% CoO	3.5
Support	Al <sub>2</sub> O <sub>3</sub>
Surface area, m <sup>2</sup> /gm	270
Pore volume, cm <sup>3</sup> /gm	0.51
Form	1/8 - inch extrudate

was impregnated with an aqueous solution containing the desired metal ions. The water-soluble salt was typically cesium acetate, although lithium nitrate, sodium nitrate, and potassium nitrate were all tried. Cesium acetate was chosen as the principal alkali salt because of the extensive data in Clyde Aldridge's patent. The Nalcomo 474 impregnated catalysts, that is, catalysts "P", "Q", "R", "S", "T", "U", "V", "W", "Y" and "Z" were too active, so one-fifth and one-half strength catalysts, based on the cobalt and molybdenum weight percent, were prepared.

The following general procedure was used in the preparation of the "Aldridge" catalysts

1. Prepare the alkali salt solution by dissolving 0.1 gm or 1 gm salt in 1 ml of deionized water.
2. Weigh out approximately 5-7 grams of Nalcomo Hydrotreating catalyst, which was ground up with a mortar and pestle and sieved to a 20/60 standard sieve range, into a 50 ml bottle. The sieved catalyst must be free of moisture.
3. Remove the hydrotreating catalyst from the bottle and store it in a 100 ml beaker.

4. Pipet between 0.0 and 3.0 or 4.0 ml of solution into the 50 ml bottle.
5. Add some deionized water to the 50 ml bottle so that the total volume of the deionized water plus the salt solution is equal to exactly 3.0 or 4.0 ml.
6. Mix the deionized water and cesium acetate solution and pour the hydrotreating catalyst from the beaker back into the 50 ml bottle. Stir with a spatula until all particles are wet.
7. Finally, place the impregnated "Aldridge" catalyst and the bottle in the oven at approximately 150°C and let it dry for two hours.

The compositions of the catalysts prepared are given in Tables 7, 21, 33 and 53.

### C. Catalyst Pretreatment

The "Aldridge" catalysts were pretreated with a dry gas feed containing 10% Ar, 6% H<sub>2</sub>S, and 84% H<sub>2</sub> to sulfide the cobalt molybdate. First, a mixture of catalyst and 20/60 mesh inert alumina was weighed out. For the water-gas shift and ethanol dehydration studies, the mixture contained between 0.1 grams and 1.5 grams of "Aldridge" catalyst with the remainder being inert alumina (Air Products and Chemicals 200S alumina). For the methanation studies, a catalyst bed of 5.0 grams was weighed out; the fixed-bed contained between 3.0 grams to 5.0 grams of catalyst, with the rest being inert alumina particles. The mixture of catalyst and inerts was poured midway into the reactor tube.

V

A plug of quartz wool was provided at one end to prevent catalyst loss into the flowing reactant gas stream. During pretreatment the dry gas feed passed through the catalyst bed at a slow rate of 0.1 ml/sec at ambient conditions. The central portion of the reactor was heated to 550°C and the two ends to 400°C. After the desired temperatures were established, the pretreatment was continued at atmospheric pressure for 90 minutes for catalysts used in the water-gas shift and ethanol dehydration reactions. For the methanation reaction, the catalysts were pretreated for 60 minutes at the same temperatures, but at a pressure of 100 psig. The saturator was bypassed at all times during pretreatment.

#### IV. THEORETICAL

The catalytic microreactor that we used for our catalyst screening studies was an isothermal integral plug flow reactor. Thirty six runs were made in the fixed-bed microreactor in our studies of "Aldridge" catalysts of different compositions for the water-gas shift reaction, catalytic methanation and ethanol dehydration. The product compositions were measured as a function of flow rate and temperature. Reactor data were interpreted by integrating the appropriate rate expression. The integral reactor analyses that we employed is presented below.

##### A. Steady-State Plug Flow Reactor Model

We obtain the design equation for a steady-state plug flow reactor by making a material balance for a reaction component on a differential volume element,  $dV$ . The design equation that gives the relationship between space time, the rate of reaction and reactor conversion has the following form after integration,<sup>34</sup>

$$\tau = \frac{V}{F} = C_A^0 \int_{X_A^0}^{X_A} \frac{dX_A}{-r_A} \quad (1)$$

where,  $V$  = reactor volume,  $\text{cm}^3$

$\tau$  = space time, min

$F$  = volumetric feed rate at reactor conditions,  $\text{cm}^3/\text{min}$

$X_A^0$  = initial conversion of A

$X_A$  = final conversion of A

$-r_A$  = rate of loss of A, moles of A lost / unit volume per unit time

This design equation was utilized for data analysis.

### B. Determination of Overall Rate of Reaction

Typical rate laws in heterogeneous reacting systems are complicated owing to the presence of phase boundaries and the existence of both interphase and intraphase mass transport. The overall rate of reaction will be affected by mass or energy transfer between the bulk fluid and the catalyst and within the catalyst particles if there is a strong resistance to such transport. Therefore, various processes that may cause resistance to reaction must be accounted for in developing the overall rate expression. Levenspiel<sup>34</sup> cites the following typical resistances for a single porous catalyst particle.

1. Gas film resistance to the diffusion of reactant from the main body of the fluid to the exterior surface of the catalyst.
2. Pore diffusion resistance to the transport of reactants through the pores into the pellet. It may have an important effect on the rate of reaction since the reaction takes place within the particle itself.
3. Resistance to the adsorption of reactant molecules onto the surface, to the reaction of the adsorbed molecule with another molecule on an adjacent site or with one coming from the main gas stream, and to the desorption of products from the surface.
4. Pore diffusion resistance to the diffusion of products out of the pellet.

5. Gas film resistance to the transport of products into the main gas stream from the exterior surface of the catalyst.
6. Resistance to heat flow into and out of the reaction zone.

In formulating a rate law, these resistances are considered and the rate expression is developed according to the resistance that controls the rate of reaction. It is usually desirable for the resistance to the surface reaction on active sites to be the rate controlling step.

For the interpretation of the data obtained from the methanation and ethanol dehydration studies, we assumed that the resistances caused by intraparticle and interparticle diffusion were small. We developed empirical rate equations that fit the conversion data through the assumption that the surface reaction controlled the rate of reaction.

We did not search for the actual mechanisms of the reaction systems that we studied because of the nature of the research project supported under a RANN Grant and its influence upon the research objectives. Our research centered upon the development of techniques that would allow us to search for new catalyst compositions for different types of vapor-phase reactions and also yield sensible kinetic data by using a simple correlating rate law. We used this as our focal point, always keeping in mind the RANN program and its concern for technological discovery.

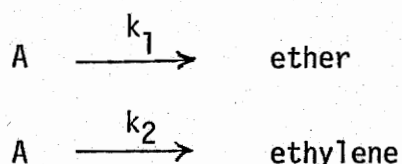
### C. Integral Analysis

In the integral method of analysis for data obtained from an integral plug-flow reactor, a rate equation is selected and equation (1) is integrated. For each experimental run, the two sides of this equation are evaluated numerically and plotted one against the other as a test for linearity. Unless a straight line is obtained, another rate expression is assumed and tested. The development of the rate laws for the ethanol dehydration and methanation reactions is described in this section. For an integral analysis of the water-gas shift reaction, please see the M.S. thesis of A. D. Overstreet.<sup>2</sup>

#### 1. Ethanol Dehydration.

Four different rate expressions were tested to fit the dehydration data. Only one expression fitted the data satisfactorily. We summarize the four rate expressions below.

Rate Expression (a). Two irreversible reactions in parallel.



where A denotes ethanol. The overall rate of disappearance of ethanol can be written as

$$-r_A = -\frac{dC_A}{dt} = (k_1 + k_2)C_A \quad (2)$$

Integration of equation (1) with this rate expression gives

$$-\ln(C_A/C_A^0) = (k_1 + k_2) \frac{V}{F} \quad (3)$$

The quantity,  $-\ln(C_A/C_A^0)$ , was plotted against  $1/F$  for the data for catalysts "VV" and "ZZ". A straight line was obtained only at the lowest temperature. (See Figures 2 and 3).

Rate Expressions (b), (c) and (d). Reactions of shifting order.

Since dehydration products comprise mainly ether at lower temperatures and ethanol, ethylene, and water at higher temperatures, we believed it more likely that rate equations describing reactions of shifting order would fit our data.

(b) Shift from zero to first order as the concentration of ethanol drops. The overall rate of reaction is<sup>34</sup>

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \quad (4)$$

At low  $C_A$ , the reaction is first order with rate constant,  $k_1$  (i.e.,  $k_2 C_A \ll 1$ ). At high  $C_A$ , the reaction is zero order with rate constant,  $k_1/k_2$  (i.e.,  $k_2 C_A \gg 1$ )

The integrated design equation is

$$\frac{\ln(C_A^0/C_A)}{C_A^0 - C_A} = -k_2 + \frac{k_1 V}{(C_A^0 - C_A)} \cdot \frac{1}{F} \quad (5)$$

Negative slopes at the temperatures, 276, 355, 378°C and positive intercepts at all temperatures were obtained. This rate expression is not acceptable since the negative rate constants at these temperatures are meaningless. (See Figure 4).

(c) Shift from second to zero order as the concentration of ethanol drops.

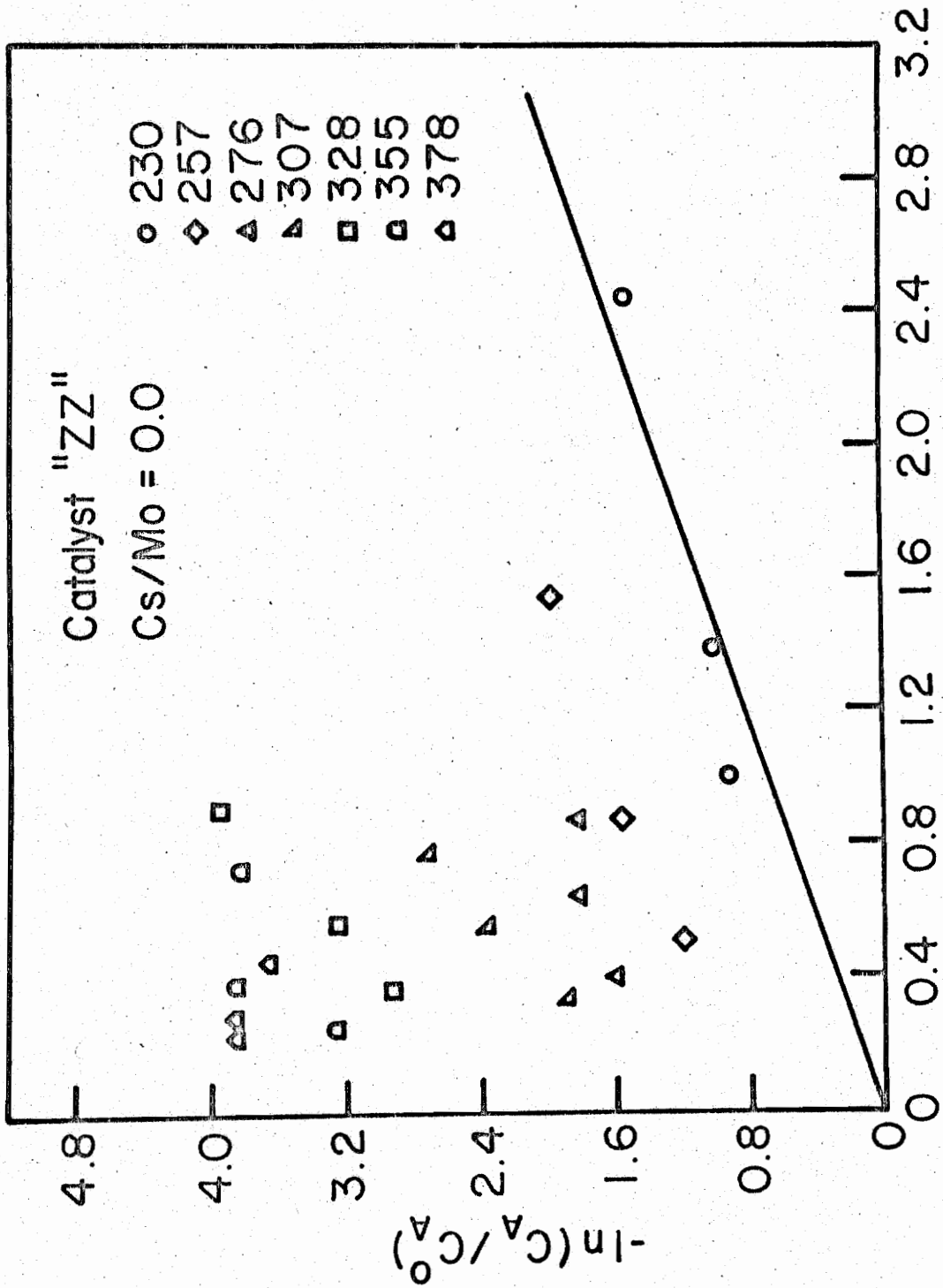
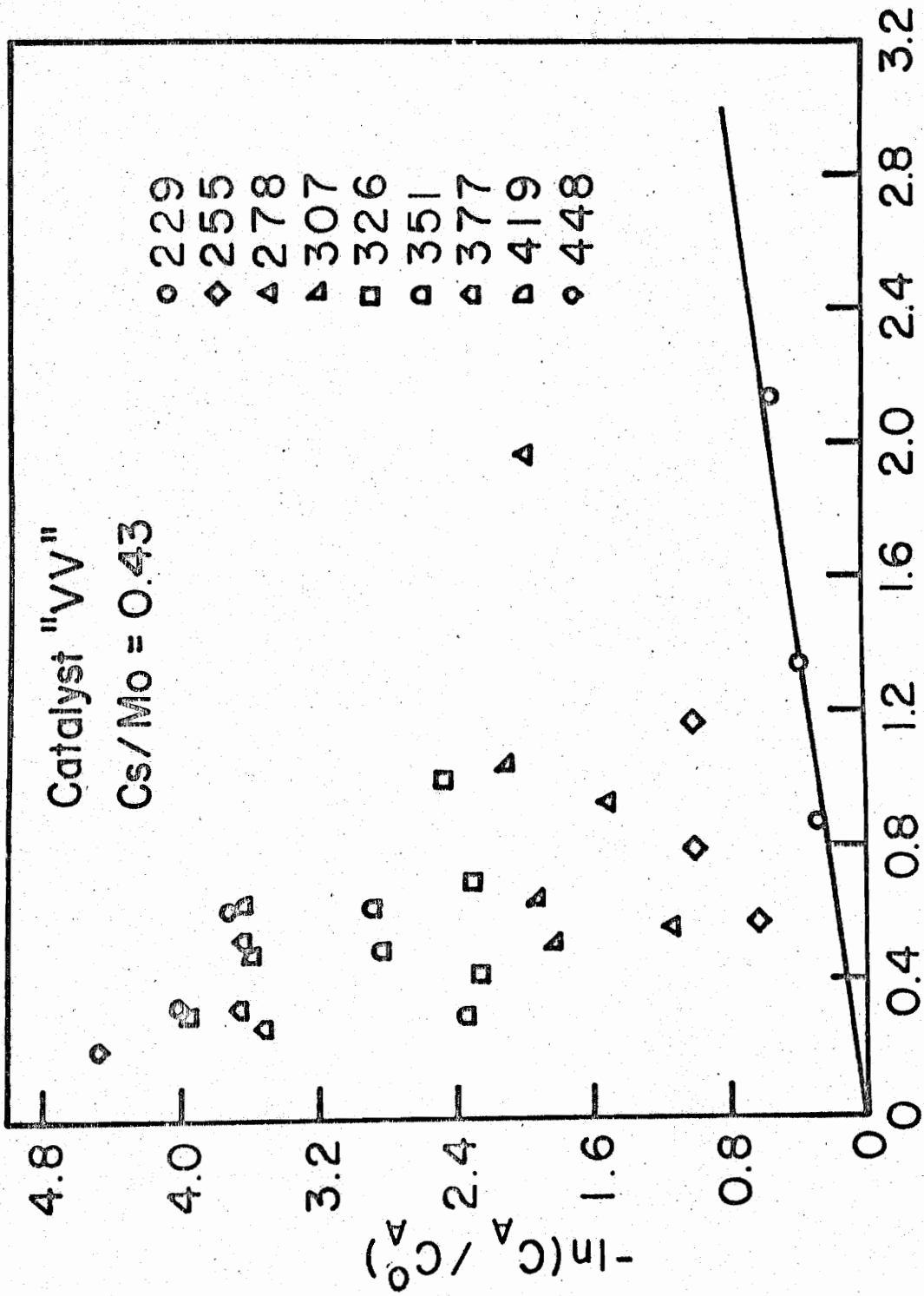


Figure 2. Test for two irreversible reactions in parallel



$1/F, \text{ sec/cc}$  at reactor conditions

Figure 3. Test for two irreversible reactions in parallel

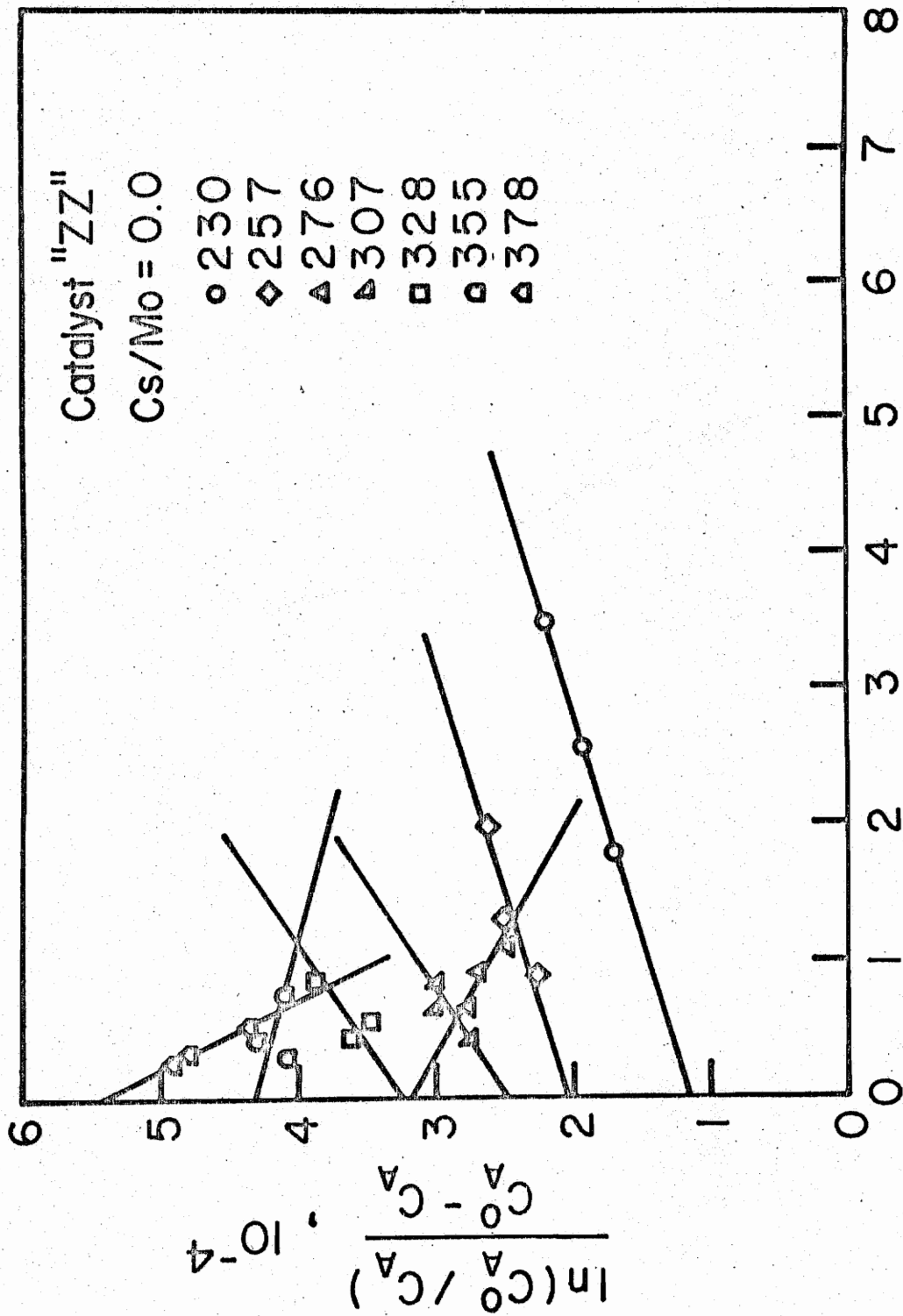


Figure 4. Test for shift from zero to first order

The overall rate for two competing reaction paths which are of different order is

$$-r_A = -\frac{dC_A}{dt} = k_1 + k_2 C_A^2 \quad (6)$$

The integrated form of the design equation is

$$\begin{aligned} \tan^{-1} \frac{C_A \sqrt{k_1 k_2}}{k_1} &= -k_1 k_2 (V/F) \\ + \tan^{-1} \frac{C_A^0 \sqrt{k_1 k_2}}{k_1} & \end{aligned} \quad (7)$$

To plot  $\tan^{-1} \frac{C_A \sqrt{k_1 k_2}}{k_1}$  vs  $1/F$ , rate constants need to be evaluated from the individual rate equations

$$(-r_A)_1 = -\frac{dC_A}{dt} = k_1$$

upon integration, we obtain

$$k_1 V = F(C_A^0 - C_A)$$

or, using the ideal gas law

$$k_1 V = \frac{F}{RT} (P_A^0 - P_A) \quad (8)$$

The quantities on the right hand side of equation (8) are known, so  $k_1 V$  can be evaluated. Similarly,  $k_2 V$  is evaluated from the following relation

$$k_2 V = \frac{RT (P_A^0 - P_A)}{P_A P_A^0} F \quad (9)$$

This form of rate equation gives a positive slope and therefore, yields a negative rate constant at 378°C. A test of the rate equation is shown in Figure 5.

(d) Shift from first order to zero order as the concentration of ethanol drops

This is the correct law. The rate expressions for ethylene and ether formation are, respectively,

$$(-r_A)_0 = k_0 \quad (10)$$

$$(-r_A)_1 = k_1 C_A \quad (11)$$

The overall reaction rate is the sum of the individual rates,

$$-(r_A)_{\text{overall}} = k_0 + k_1 C_A \quad (12)$$

The design equation can be integrated with this rate law to yield the following integrated form;

$$-\ln \frac{k_0 + k_1 C_A}{k_0 + k_1 C_A^0} = k_1 V/F \quad (13)$$

where,  $V$  = volume of catalyst bed not including inerts,  $\text{cm}^3$

$F$  = flow rate of reactant gases at reactor conditions,  $\text{cm}^3/\text{sec}$

$k_0$  = zero-order rate constant for ethylene formation, gm moles/sec  $\text{cm}^3$

$k_1$  = first-order rate constant for ether formation,  $\text{sec}^{-1}$

$C_A$  = final concentration of ethanol, gm moles/ $\text{cm}^3$

$C_A^0$  = initial concentration of ethanol, gm moles/ $\text{cm}^3$

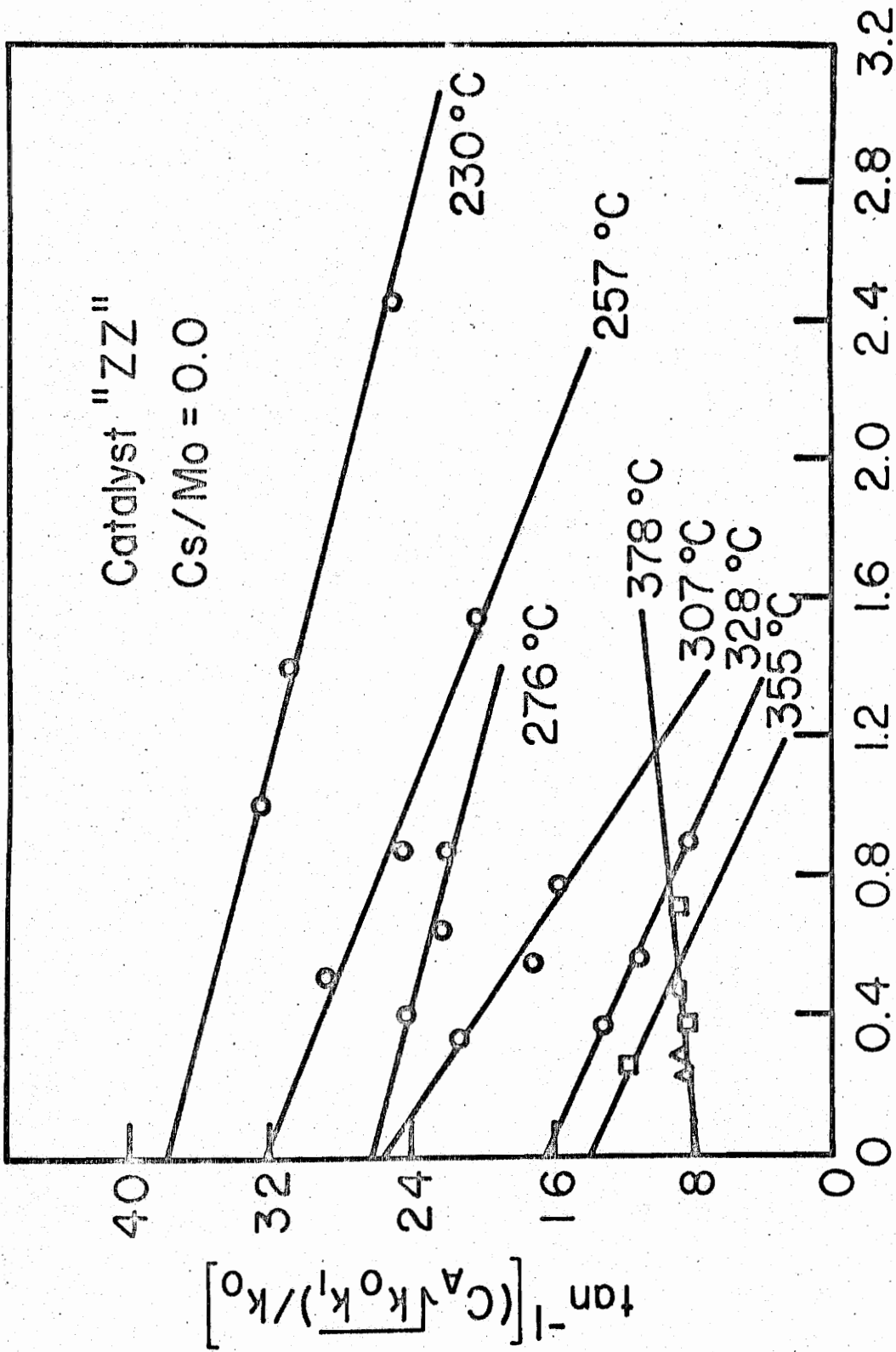


Figure 5. Test for shift from second to zero order

The rate constants,  $k_0$  and  $k_1$ , were evaluated using the integrated forms of the individual rate equations,

$$k_0 V = F (C_A^0 - C_A) \quad (\text{gm moles/sec}) \quad (14)$$

$$k_1 V = F \ln \frac{C_A^0}{C_A} \quad (\text{cm}^3/\text{sec}) \quad (15)$$

From equation (13) we note that a plot of  $\ln(k_0 V + k_1 V C_A)$  versus  $1/F$  has a slope of  $-k_2 V$  and an intercept of  $\ln(k_0 V + k_1 V C_A^0)$  as shown in Figures 6 and 9.

This rate equation acceptably fits the dehydration data obtained from catalysts "VV" and "ZZ" over the temperature range from 200° to 400°C.

## 2. Methanation.

A rate law which is pseudo-first order and reversible in carbon monoxide concentration was assumed for catalytic methanation. It has the form:

$$-r_{\text{CO}} = k(C_{\text{CO}} - C_{\text{CO}}^{\text{eq}}) \quad (16)$$

This rate equation expressed in terms of conversion of carbon monoxide is given by

$$-r_{\text{CO}} = k(x_{\text{CO}}^{\text{eq}} C_{\text{CO}}^0 - x_{\text{CO}} C_{\text{CO}}^0) \quad (17)$$

where,  $x_{\text{CO}}^{\text{eq}}$  = equilibrium conversion of CO

$C_{\text{CO}}^0$  = initial concentration of CO

$x_{\text{CO}}$  = final conversion of CO.

The equilibrium mole fraction of CO<sup>(a)</sup>,  $y_{CO}^{eq}$ , in the product gases was calculated for a temperature range of 200° to 500°C, and was found to be very small. Thus, the equilibrium conversion of CO,  $x_{CO}^{eq}$ , is essentially 1.0

Equation (1) can be integrated by substituting  $kC_{CO}^0(1-x_{CO})$  for  $-r_{CO}$  to give

$$-\ln \frac{1-x_{CO}}{1-x_{CO}^0} = \frac{kV}{F} \quad (18)$$

If we employ the ideal gas law, equation (18) has the following form for zero initial conversion of CO,

$$-\ln \frac{Y_{CO}}{Y_{CO}^0} = kV/F \quad (19)$$

where,  $F$  = flow rate of dry gas feed at reactor conditions,  $\text{cm}^3/\text{min}$

$V$  = volume of catalyst bed not including inert solids,  $\text{cm}^3$

$k$  = pseudo-first order rate constant,  $\text{min}^{-1}$

$Y_{CO}^0$  = initial carbon monoxide mole fraction

$Y_{CO}$  = final carbon monoxide mole fraction.

A plot of  $-\ln \frac{Y_{CO}}{Y_{CO}^0}$  versus the reciprocal flow rate,  $1/F$ , will yield a straight line with a slope of  $kV$  at each temperature studied.

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(a) A sample calculation of the equilibrium concentration of product gases is given on pages 48 through 50.

#### D. Arrhenius Plot

The temperature dependence of our reaction rate constants were well represented by Arrhenius plots over the temperature range of 200<sup>o</sup> to 400<sup>o</sup>C.

In the water-gas shift, methanation and ethanol dehydration studies, we normalized the measured value of kV by dividing through by W, the weight of impregnated catalyst used in grams less the alkali salt weight. The weight of the inert Al<sub>2</sub>O<sub>3</sub> solids was not included in the computation of W. Each catalyst had different amounts of alkali salt, so it was not a good choice to use the weight of the impregnated catalyst as a normalization factor.

Values of kV were divided by W, and the computed values of  $\ln \left( \frac{kV}{W} \right)$  were plotted versus reciprocal temperature for the Arrhenius equation,

$$\frac{kV}{W} = \frac{AV}{W} \exp (-E_a/RT) \quad (20)$$

where, A = frequency factor

$E_a$  = activation energy, cal/gm mole

R = gas law constant, 1.987 cal/gm mole - <sup>o</sup>K

T = temperature, <sup>o</sup>K

A plot of  $\ln(kV/W)$  vs  $1/T$  will yield a slope of  $-E_a/R$  and an intercept of  $\ln(AV/W)$ .

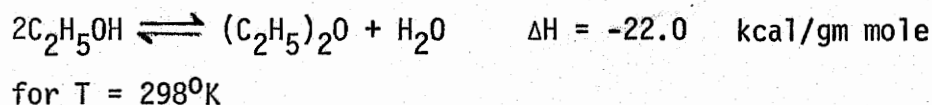
In order to compute values of k and A from the quantities, kV/W and AV/W, respectively, we need to know the bulk density of the

unimpregnated CoO-MoO<sub>3</sub> catalyst. For Nalcomo 474 unimpregnated hydrotreating catalyst in the 20/60 mesh range, W/V was found to be 0.65<sup>2</sup> grams/cm<sup>3</sup>.

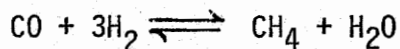
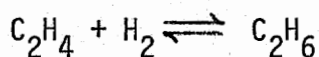
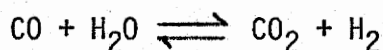
### E. Chemistry and Thermodynamics

#### 1. Ethanol Dehydration.

The chemistry of ethanol dehydration can be described by two major reactions,<sup>34,35</sup>



and the following side reactions:



The course of the reaction is displaced in favor of direct ethylene formation with increasing temperature because of the exothermicity of ether formation.

#### 2. Methanation.

The methanation of a synthesis gas mixture with a H<sub>2</sub>/CO ratio equal to or greater than 3 can be represented by the following reversible reactions:

- (a)  $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$   
 $\Delta H = 52.084 \text{ kcal/gm mole at } T = 600^\circ\text{K}$
- (b)  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$   
 $\Delta H = -9.292 \text{ kcal/gm mole at } T = 600^\circ\text{K}$
- (c)  $2\text{CO} + 5\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$   
 $\Delta H = -83.00 \text{ kcal/gm mole at } T = 298^\circ\text{K}$
- (d)  $\text{COS} + \text{H}_2 \rightleftharpoons \text{H}_2\text{S} + \text{CO}$   
 $\Delta H = +1.565 \text{ kcal/gm mole at } 700^\circ\text{F}$
- (e)  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{Cs}$   
 $\Delta H = -15.836 \text{ kcal/gm mole}$

The first two reactions are the main ones. However, reaction (e), that is, carbon deposition can become appreciable and poison the catalyst if the  $\text{H}_2/\text{CO}$  ratio is appreciably less than 3. Equilibrium methane yields are critically affected by temperature and by synthesis gas  $\text{H}_2/\text{CO}$  ratios. Pressures do not appreciably affect such equilibrium yields until a temperature of about  $425^\circ\text{C}$  is exceeded.<sup>14</sup> Lower temperatures and higher ratios favor highest theoretical methane yields.

#### F. Sample Calculations

Sample calculations used in the interpretation of the dehydration and methanation data are now presented. The two examples involve catalyst "VV" (Tables 6 and 8) for ethanol dehydration and catalyst "RR" (Tables 6 and 14) for methanation, each of which was studied at the following conditions:

Variable	Ethanol Dehydration	Methanation
	Catalyst "VV"	Catalyst "RR"
Composition of dry reactant gases	59.78% H <sub>2</sub> /37.60% CO 46% CO <sub>2</sub> /2.16% COS	74.0% H <sub>2</sub> /22.6% CO/ 1.12% CO <sub>2</sub> / 1.96% COS
Flow rate	107.20 cm <sup>3</sup> /min	122.42 cm <sup>3</sup> /min
Temperature	278°C	332°C
Pressure	1 atm	~300 psig
Saturator temperature	~50°C	---
Fluid in saturator	95% ethanol, 5% H <sub>2</sub>	---

### 1. Sensitivity factors.

To compute the initial and final mole fractions for all components from the raw chromatographic data, it was necessary to use sensitivity factors, that is, the relative response of the thermal conductivity detector to different components. Sensitivity factors on a weight percent basis were obtained from Dietz<sup>37</sup> and are shown in Table 5.

### 2. Conversion of Raw Chromatographic Data.

When a sample of product gases at a certain flow rate, temperature and fixed pressure is analyzed, the chromatographic area for each component is recorded as "peak counts" by the digital integrator. The peak count for each component is then multiplied by the sensitivity factor for that component on a mole percent basis to obtain the corrected molar peak counts. Thus, for ethanol dehydration catalyst "VV" we obtain

TABLE 5. SENSITIVITY FACTORS

Components	Sensitivity Factor <sup>(c)</sup> on a weight percent basis	Calculated Sensitivity Factor on a mole percent basis
CO	0.670	0.0239
CH <sub>4</sub>	0.450	0.0281
CO <sub>2</sub>	0.915	0.0208
C <sub>2</sub> H <sub>6</sub>	0.590	0.0197
C <sub>2</sub> H <sub>4</sub>	0.670	0.0207
H <sub>2</sub> S	0.890	0.0262
H <sub>2</sub> O	0.550	0.0306
COS	---	0.0200 <sup>(a)</sup>
C <sub>2</sub> H <sub>5</sub> OH	0.580	0.0139
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.590	0.0075
Others <sup>(b)</sup>	---	0.0180 <sup>(a)</sup>

(a) assumed

(b) mainly an unknown plus some other components present in small amounts in the effluent gases of ethanol dehydration

(c) obtained from Dietz<sup>37</sup>

$N_{CO}$	=	54142 X 0.0239	=	1295.62
$N_{CO_2}$	=	1682 X 0.0208	=	34.99
$N_{C_2H_4}$	=	6062 X 0.0207	=	125.48
$N_{C_2H_6}$	=	578 X 0.0197	=	11.39
$N_{H_2O}$	=	23236 X 0.0306	=	709.86
$N_{C_2H_5OH}$	=	32030 X 0.0139	=	445.22
$N_{(C_2H_5)_2O}$	=	42631 X 0.0075	=	319.00
$N_{others}$	=	14450 X 0.0180	=	260.00

and for methanation catalyst "RR" we obtain

$N_{CO}$	=	101761 X 0.0239	=	2432
$N_{CH_4}$	=	4026 X 0.0281	=	113
$N_{CO_2}$	=	10372 X 0.0208	=	216
$N_{C_2H_6}$	=	1267 X 0.0197	=	26.0
$N_{H_2S}$	=	0 X 0.0262	=	0.0
$N_{H_2O}$	=	5395 X 0.0306	=	165.0
$N_{COS}$	=	6813 X 0.0200	=	136.0

### 3. Back-Calculated Mass Balance.

The corrected molar counts can next be used to make a back-calculated mass balance if we use the initial composition of dry feed gas and the chemistry of the reactions. Let  $N_{H_2}$ ,  $N_{CO}$ ,  $N_{CH_4}$ ,  $N_{CO_2}$ ,  $N_{C_2H_6}$ ,  $N_{C_2H_4}$ ,  $N_{H_2S}$ ,  $N_{H_2O}$ ,  $N_{COS}$ ,  $N_{C_2H_5OH}$ ,  $N_{(C_2H_5)_2O}$  and  $N_{others}$  be the final number of moles, and  $N_{H_2}^0$ ,  $N_{CO}^0$ ,  $N_{CH_4}^0$ ,  $N_{CO_2}^0$ ,  $N_{C_2H_6}^0$ ,  $N_{C_2H_4}^0$ ,  $N_{H_2S}^0$ ,  $N_{H_2O}^0$ ,

$N_{\text{COS}}^0$ ,  $N_{\text{C}_2\text{H}_5\text{OH}}^0$ , and  $N_{(\text{C}_2\text{H}_5)_2\text{O}}^0$  be the initial number of moles for each

component. The calculations are performed as follows.

Ethanol dehydration, catalyst "Y". The final molar peak count for hydrogen must equal the final molar peak count for CO times the initial molar ratio of  $\text{H}_2/\text{CO}$  plus twice the molar peak count for  $\text{CO}_2$  less the final molar peak count for ethane, or:

$$N_{\text{H}_2} = (59.78/37.60) N_{\text{CO}} + 2N_{\text{CO}_2} - N_{\text{C}_2\text{H}_6}$$

$$\begin{aligned} N_{\text{H}_2} &= (59.78/37.60) (1295.62) + 2 \times 34.99 - 11.39 \\ &= 2118.61 \end{aligned}$$

Similarly,

$$\begin{aligned} N_{\text{CO}}^0 &= N_{\text{CO}} + N_{\text{CO}_2} \\ &= 1295.62 + 34.99 = 1330.61 \end{aligned}$$

$$\begin{aligned} N_{\text{H}_2}^0 &= N_{\text{H}_2} - N_{\text{CO}_2} - N_{\text{C}_2\text{H}_6} \\ &= 2118.61 - 34.99 - 11.39 \\ &= 2072.23 \end{aligned}$$

$$\begin{aligned} N_{\text{C}_2\text{H}_5\text{OH}}^0 &= (N_{\text{C}_2\text{H}_5\text{OH}} + N_{\text{C}_2\text{H}_4} + N_{\text{H}_2\text{O}} + N_{\text{CO}_2}) \times 0.95 \\ &= (445.22 + 125.48 + 709.86 + 34.99) \times 0.95 \\ &= 1249.77 \end{aligned}$$

$$\begin{aligned} N_{\text{H}_2\text{O}}^0 &= N_{\text{C}_2\text{H}_5\text{OH}}^0 \times 5/95 \\ &= 1249.77 \times 5/95 = 65.78 \end{aligned}$$

$$\begin{aligned} N_{\text{COS}}^0 &= (N_{\text{CO}}^0 + N_{\text{H}_2}^0) \times 2/98 \\ &= (1330.61 + 2072.23) \times 2/98 \\ &= 75.00 \end{aligned}$$

$$N_{C_2H_4}^0 = 0$$

$$N_{C_2H_6}^0 = 0$$

$$N_{(C_2H_5)_2O}^0 = 0$$

$$N_{CO_2}^0 = (1330.61 + 2072.23) \times .46/98 = 16.00$$

The initial and final molar peak count for all components are then normalized to yield mole fractions,

<u>Component</u>	<u>Initial Mole Fraction</u>	<u>Final Mole Fraction</u>
Hydrogen	0.4325	0.3866
CO	0.2765	0.2380
C <sub>2</sub> H <sub>4</sub>	0.0	0.0233
C <sub>2</sub> H <sub>6</sub>	0.0	0.0021
H <sub>2</sub> O	0.0132	0.1391
CO <sub>2</sub>	0.0048	0.0064
C <sub>2</sub> H <sub>5</sub> OH	0.2616	0.0821
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.0	0.0788
Others	0.0	0.0590
COS(a)	0.0140	---

(a) COS is included in the final mole fraction of other components

Methanation Catalyst "RR". Since a dry feed gas at a fixed composition (74% H<sub>2</sub>, 22.6% CO, 1.12% CO<sub>2</sub>, 1.96% COS) was employed, the final hydrogen mole fraction can be calculated via an atom balance. Thus, the ratio

of the free and combined hydrogen and oxygen must be the same in the initial and final gases, i.e.,

$$\frac{2N_{\text{CH}_4} + 3N_{\text{C}_2\text{H}_6} + N_{\text{H}_2\text{O}} + N_{\text{H}_2\text{S}} + N_{\text{H}_2}}{N_{\text{CO}} + 2N_{\text{CO}_2} + N_{\text{COS}} + N_{\text{H}_2\text{O}}} = \frac{0.74}{0.26} = 2.84$$

$$\begin{aligned} \text{Therefore, } N_{\text{H}_2} &= 2.84 N_{\text{CO}} + 1.84 N_{\text{H}_2\text{O}} + 5.68 N_{\text{CO}_2} + N_{\text{COS}} - 2N_{\text{CH}_4} - 3N_{\text{C}_2\text{H}_6} \\ &= 2.84 \times 2432 - 11.84 \times 165 + 5.68 \times 216 + 2 \times 136 - \\ &\quad 2 \times 113 - 3 \times 26 \qquad \qquad \qquad (21) \\ &= 8520.0 \end{aligned}$$

$$N_{\text{total}} = 11608 \text{ corrected molar counts}$$

The mole fraction for each component is computed by dividing its final molar peak count by the total molar peak counts, which is 11608 in the above example. Thus,

Component	Initial Mole Fraction	Final Mole Fractions
Hydrogen	0.740	0.7341
CO	0.226	0.2095
CH <sub>4</sub>	0.0	0.0097
CO <sub>2</sub>	0.0144	0.0186
C <sub>2</sub> H <sub>6</sub>	0.0	0.0022
H <sub>2</sub> S	0.0	0.0000
H <sub>2</sub> O	0.0	0.0142
COS	0.0196	0.0117

#### 4. Flow Rate

Ethanol Dehydration. During each run, the flow rate was measured by the bubble meter at atmospheric pressure and room temperature, which was 715 mm Hg and 24°C, respectively. For the analysis of kinetic data, the flow rate was corrected to reactor conditions.

Ethanol dehydration, catalyst "VV". The wet gas flow rate at reactor conditions was computed from the dry gas flow rate. The bubble meter reading, 10/13.9 ml/sec was multiplied by a temperature correction factor and divided by the initial mole fraction for all non-ethanol components

$$\begin{aligned} \text{Wet flow rate} \\ \text{at reactor} \\ \text{conditions} &= \frac{10 \text{ ml}}{13.9 \text{ sec}} \cdot \frac{60 \text{ sec}}{\text{min}} \cdot \frac{273^{\circ}\text{K} + 278^{\circ}\text{C}}{273^{\circ}\text{K} + 24^{\circ}\text{C}} \\ & \qquad \qquad \qquad (1. - 0.2616) \\ &= 107.20 \text{ cm}^3/\text{min} \end{aligned}$$

Methanation catalyst "RR". A novel volumetric flow meter that was independent of the nature of the flowing gas was employed to measure the flow rate at reactor pressures greater than one atm. Its operation has been discussed in detail in the experimental section. The principles behind its operation and its calibration will be presented here.

The applicable mathematics are straight forward:

$$P_f V_f = nRT \qquad \qquad \qquad [\text{pressure sensor}] \qquad (22)$$

$$\frac{dP_f}{dt} = \frac{RT}{V_f} \cdot \frac{dn}{dt} \qquad \qquad \qquad [\text{pressure sensor}] \qquad (23)$$

$$P_{bm} V_{bm} = nRT \quad [\text{bubble meter}] \quad (24)$$

$$\frac{dV_{bm}}{dt} = \frac{RT}{P_{bm}} \cdot \frac{dn}{dt} \quad [\text{bubble meter}] \quad (25)$$

Note that  $R$ ,  $T$ ,  $V_f$  for the pressure sensor, and  $P_{bm}$  for the bubble meter are all reasonably constant during a reactor run. Equating  $dn/dt$ , we obtain

$$\frac{V_f}{RT} \frac{dP_f}{dt} = \frac{P_{bm}}{RT} \cdot \frac{dV_{bm}}{dt}$$

and solving for  $V_f$ , we next obtain

$$V_f = \frac{P_{bm} \frac{dV_{bm}}{dt}}{dP_f/dt} \quad (26)$$

$\frac{dP_f}{dt}$  can be related to  $\frac{dE}{dt}$ , the slope of the voltage-vs-time curve, as follows:

$$E = CP_f \quad (27)$$

$$\frac{dE}{dt} = C \frac{dP_f}{dt} \quad (28)$$

where  $C$  is a constant [units of pressure/voltage] characteristic of the pressure sensor. The term,  $\frac{dE/dt}{C}$ , is substituted in equation (26).

Thus,

$$\frac{dE}{dt} = \frac{CP_{bm}}{V_f} \cdot \frac{dV_{bm}}{dt} \quad (29)$$

or

$$\frac{dn}{dt} = \frac{V_f}{RTC} \cdot \frac{dE}{dt} \quad (30)$$

which states that the molar flow rate can be determined.

The symbols employed are:

- $V_f$  = flowmeter volume,  $\text{cm}^3$
- $V_{bm}$  = bubble meter volume,  $\text{cm}^3$
- $P_f$  = flowmeter pressure, psia
- $P_{bm}$  = ambient pressure in bubble meter, psia
- $R$  = gas constant,  $\text{atm-cm}^3/\text{gm mole} - ^\circ\text{K}$
- $n$  = gm moles
- $T$  = temperature,  $^\circ\text{K}$
- $t$  = time, sec
- $E$  = voltage when there is no flow, mV
- $C$  = pressure sensor proportionality constant, psia/mV

To calibrate the flowmeter, the electrically operated ball valve is opened and closed periodically as the feed gas stream at about 600 psig passes through the valve and the flowmeter volume,  $V_f$ . Meanwhile the pressure in the volume,  $V_f$ , changes. Pressure change is measured as the rate of change of voltage associated with the Robinson-Halpern pressure sensor. Both the pressure and voltage are proportional to the volumetric flow rate measured by the bubble meter at atmospheric pressure and room temperature. Equation (29) describes this relationship between the voltage drop and volumetric flow rate. Thus, a plot of  $dE/dt$  versus  $dV_{bm}/dt$  will yield a straight line passing through the

origin that has a slope of  $CP_{bm}/V_f$ .  $V_f$  can be determined from the slope since  $P_{bm}$  is known and  $C$  can be calculated from equation (27). Once  $V_f$  and  $C$  are known, the number of moles of dry gas passing through the flowmeter volume is evaluated using equation (26). Finally the molar flow rate is converted to actual flowrate at the reactor conditions. A typical calculation is given below:

$$C = E/P_f = \frac{5.88 \times 10^3}{614.7} \text{ mV/psia}$$

$$C = 9.55 \text{ mV/psia}$$

Therefore, the slope of  $dE/dt$  vs  $\frac{dV_{bm}}{dt}$  from Figure 1 is  $8.0 \text{ mV/cm}^3$

$$V_f = \frac{9.55 \times (710/760) \times 44.7}{8} = 16.4 \text{ cm}^3$$

Using equation (30), where  $T$  is the ambient temperature, we can calculate

$$\begin{aligned} \frac{dn}{dt} &= \frac{16.4}{82.06 \times 297 \times 9.55} dE/dt \\ &= 7.0 \times 10^{-5} dE/dt \end{aligned} \quad (31)$$

Upon combining equations (29) and (30), we obtain

$$\begin{aligned} \frac{dn}{dt} &= 7.0 \times 10^{-5} \frac{CP_{bm}}{V_f} \frac{dV_{bm}}{dt} \\ &= 5.6 \times 10^{-4} \frac{dV_{bm}}{dt} \text{ gm moles/sec} \end{aligned}$$

For  $\frac{dV_{bm}}{dt} = 10/6.3 \text{ cm}^3/\text{sec}$

$$\frac{dn}{dt} = 5.6 \times 10^{-4} \times \frac{10}{6.3} = 8.88 \times 10^{-4} \text{ gm moles/sec}$$

Since the total number of moles of gas stream passing through the catalyst bed changes, the molar flow rate is corrected as follows;

$$\frac{dn}{dt} = 8.88 \times 10^{-4} \times \frac{Q_0}{Q} \quad (32)$$

Where,  $Q_0$  = the initial total number of corrected molar counts

$$= (N_{H_2} + 2N_{CH_4} + 3N_{C_2H_6} + N_{H_2S} + N_{H_2O}) / 0.74$$

$Q$  = the final total number of corrected molar counts

$$= N_{H_2} + N_{CO} + N_{CH_4} + N_{CO_2} + N_{C_2H_6} + N_{H_2S} + N_{H_2O} + N_{COS}$$

$$\text{Thus, } dn/dt = 8.88 \times 10^{-4} \times \frac{12150}{11608} = 9.30 \times 10^{-4} \text{ gm moles/sec}$$

Molar flow rate is finally converted to volumetric flow rate at reactor conditions,  $F$ , according to the following computation,

$$F = 9.30 \times 10^{-4} \frac{\text{gm moles}}{\text{sec}} \times 22400 \frac{\text{cm}^3}{\text{gm mole}}$$

$$\times \frac{T^{\circ}\text{K}}{273^{\circ}\text{K}} \times \frac{0.94 \text{ atm}}{21.41 \text{ atm}} \times \frac{60 \text{ sec}}{\text{min}}$$

$$\text{For } T = 332 + 273 = 605^{\circ}\text{K}$$

$$F = 122.42 \text{ cm}^3/\text{min at reactor conditions.}$$

### 5. Integral Data Analysis.

Ethanol dehydration, catalyst "VV". To compute  $\ln(k_0V + k_1VC_A)$ , values of  $k_0V$  and  $k_1V$  were calculated for each flow rate at reactor conditions using equations (14) and (15). Also, ideal gas law behavior was assumed.

At 278°C and a wet flow rate of 1.785 cm<sup>3</sup>/sec

$$k_0 V = \frac{F}{RT} (P_{A_0} - P_A)$$

$$= \frac{1.785}{820 \times 551} (0.2616 - 0.0821)$$

$$k_0 V = 1.011 \times 10^{-5} \text{ gm moles/sec}$$

$$k_1 V = F \ln \frac{C_{A_0}}{C_A}$$

$$= 1.785 \ln \frac{0.2616}{0.0821}$$

$$k_1 V = 2.09 \text{ cm}^3/\text{sec}$$

$$C_A = 1.8 \times 10^{-6} \text{ gm moles/cm}^3$$

$$\ln (k_0 V + V k_1 C_A) = \ln (1.011 \times 10^{-5} + 2.09 \times 1.80 \times 10^{-6})$$

$$= -11.093$$

Reciprocal wet flow rate,  $1/F = 0.557 \text{ sec/cm}^3$

Methanation, catalyst "RR". In obtaining the integrated form of the design equation, we assumed the equilibrium conversion of CO,  $X_{CO}^{eq}$ , to be essentially equal to unity. To justify this assumption, a sample calculation of the equilibrium compositions for the methanation reaction is given below. Because of the complexity of this reaction system, the equilibria for reactions (a), (b) and (e) were employed in our computations whereas equilibria (c) and (d) were ignored. The calculations

were performed for the temperature range 250<sup>0</sup> - 500<sup>0</sup>C, at a pressure of 300 psig by utilizing the techniques of the Gas Research Board. A H<sub>2</sub>/CO molar ratio of 3.0 was used for convenience instead of 3.27. Since the equilibrium mole fraction of CO was found to be very small, the error introduced in assuming a complete conversion of CO is small.

Let  $y_1$ ,  $y_2$ ,  $y_3$ ,  $y_4$ , and  $y_5$  be the mole fractions of CO, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and CO<sub>2</sub>, respectively, in the gas mixture in equilibrium at a given temperature and pressure. Also assume that P, in atm, is the total pressure and that  $K_1$ ,  $K_2$ , and  $K_3$  are the equilibrium constants for reactions (a), (b), and (e) respectively at the temperature in question.

The five relationships required to find the five unknowns,  $y_1$ ,  $y_2$ ,  $y_3$ ,  $y_4$ , and  $y_5$  are:

(1) The methane equilibrium, i.e.,

$$K_1 P^2 = \frac{y_3 y_4}{y_1 y_2^3}$$

(2) The water-gas equilibrium, i.e.,

$$K_2 = \frac{y_5 y_2}{y_1 y_4}$$

(3) The carbon equilibrium, i.e.,

$$K_3 P = \frac{y_5}{y_1^2}$$

(4) The sum of the mole fractions of all the constituents of the final gas must be equal to 1, i.e.,

$$y_1 + y_2 + y_3 + y_4 + y_5 = 1$$

(5) The ratio of the free and combined hydrogen to the free and combined oxygen in the initial and final gases must be the same, i.e.,

$$\frac{y_2 + 2y_3 + y_4}{y_1 + y_4 + 2y_5} = 3$$

By progressive elimination, the number of unknowns and relationships were reduced to two:

Step 1

Solve equation (5) for  $y_3$ ,

$$y_3 = 3/2 y_1 - 1/2 y_2 + y_4 + 3y_5$$

and substitute it into the other equations.

Step 2

Solve equation (4) for  $y_5$ ,

$$y_5 = 0.25 - 0.625 y_1 - 0.125 y_2 - 0.5y_4$$

and substitute it into the other 4 equations.

Step 3

Solve equation (3) for  $y_4$

$$y_4 = (-2K_3 y_1 P + 0.5 - 1.25 y_1 - 0.25)$$

and substitute it into the remaining equations. The two resulting equations have the following forms, where

$$X = y_1 \text{ and } Y = y_2$$

$$(1) \quad K_1 = \frac{(0.25X - 0.75Y + K_3 X^2 P + 0.5)(-2K_3 X^2 P + 0.5 - 1.25X - 0.25Y)}{XY^3 P^2}$$

$$(3) K_2 = \frac{K_3 X Y P}{(-2K_3 X^3 P + 0.5 - 1.25X - 0.25Y)}$$

The equilibrium constants,  $K_1$ ,  $K_2$ , and  $K_3$ , were found by a logarithmic interpolation procedure from tables of equilibrium constants.<sup>38</sup> The two unknowns,  $X$  and  $Y$ , in these two simultaneous nonlinear equations were solved by the Newton-Raphson numerical method.<sup>39,40</sup> The method of solution by the computer program is explained in Appendix III.

The computed final mole fractions for all components at equilibrium are:

<u>Component</u>	<u>Final Mole Fraction at equilibrium</u>		
CO	0.00007(a)	0.00531(b)	0.00092(c)
H <sub>2</sub>	0.01690	0.12613	0.00100
CH <sub>4</sub>	0.53148	0.47753	0.48000
H <sub>2</sub> O	0.40767	0.34016	0.01910
CO <sub>2</sub>	0.04405	0.06415	0.49900

(a)  $P = 300$  psig; H<sub>2</sub>/CO molar ratio = 3.00, and  $T = 332^\circ\text{C}$

(b)  $P = 300$  psig, H<sub>2</sub>/CO molar ratio = 3.00, and  $T = 527^\circ\text{C}$

(c)  $P = 0.0$  psig, H<sub>2</sub>/CO molar ratio = 1.00, and  $T = 327^\circ\text{C}$

## 6. Arrhenius Plot

Ethanol Dehydration, catalyst "VV". Values for the activation energy,  $E_a$ , and the preexponential factor,  $A$ , for ether formation are obtained by plotting  $\ln(k_1 V/W)$  versus  $1/T$ . The term,  $k_1 V$ , is the negative slope of the straight lines obtained when  $\ln(k_0 V + k_1 V C_A)$  is plotted versus

$1/F$  at a given temperature. The value of  $k_2V$  is normalized by dividing by the weight,  $W$ , of the unimpregnated Nalcomo catalyst.

The quantity,  $k_0V$ , is computed by subtracting  $k_1C_A^0$  from the exponential of the intercept of the above plot. This term is also normalized to yield  $\ln(k_0V/W)$ , which is then plotted versus  $1/T$  to determine the activation energy and the preexponential factor for ethylene formation.

For catalyst "VV", the straight line at  $278^\circ\text{C}$  had a slope of  $-0.758$  and intercept of  $-10.64$ . The quantities,  $\ln(k_1V/W)$  and  $\ln(k_0V/W)$ , were evaluated as follows:

$$\begin{aligned}\ln(k_1V/W) &= \ln(0.758/0.463) = 0.492 \\ \ln(k_0V/W) &= \exp(\ln(k_0V + kVC_A^0) - kVC_A^0) \\ &= \exp(-10.64) - 4.98 \times 10^{-6} \\ &= 19.0 \times 10^{-6}\end{aligned}$$

From plots of  $\ln(k_1V/W)$  vs  $1/T$  and  $\ln(k_0V/W)$  vs  $1/T$ , the following slopes and intercepts were obtained, respectively:

$$\begin{aligned}(-\text{Slope})_1 \cdot R &= (E_a)_1 = 5.1 \text{ Kcal/gm mole} \\ (-\text{Slope})_0 \cdot R &= (E_a)_0 = 6.9 \text{ Kcal/gm mole} \\ \text{where } R &= 1.987 \text{ cal/gm mole } ^\circ\text{K} \\ (\text{Intercept})_1 &= 5.24 \\ (\text{Intercept})_0 &= -3.99\end{aligned}$$

The frequency factor,  $A$ , was obtained by multiplication of the exponential of the Arrhenius plot intercept by the experimentally determined value of the bulk density of the unimpregnated hydrotreating catalyst,  $W/V$ . The value of  $W/V$  was measured and found to be  $0.65 \text{ grams/cm}^3$ .<sup>2</sup> Thus,

$$\begin{aligned}
 (A)_1 &= 0.65 \exp [5.24] \\
 &= 122.64 \text{ sec}^{-1} \\
 (A)_0 &= 0.65 \exp [-3.99] \\
 &= 1.20 \times 10^{-2} \text{ gm moles/sec-cm}^3
 \end{aligned}$$

Methanation Catalyst "RR". The raw chromatographic data was analyzed via the computer program given in Appendix III. A least square fit of the quantity,  $-\ln(y_{CO}/y_{CO}^0)$ , versus the reciprocal flow rate at reaction conditions,  $1/F$ , provides a slope, intercept, and correlation coefficient with and without (0,0) considered as a data point at each temperature. Such slopes are normalized by  $W$ , and  $\ln(kV/W)$  is then plotted versus  $1/T$ . From such an Arrhenius plot, the activation energy,  $E_a$ , and frequency factor,  $A$ , are determined.

For catalyst "RR", the slope of the line at  $332^\circ\text{C}$  equals  $kV$  and has a value of  $10.61 \text{ cm}^3/\text{min}$ . The weight of the unimpregnated catalyst used is given in Table 6 as 3.14 grams. Upon normalization by this weight, we calculate a value for  $kV/W$  of  $3.32 \text{ cm}^3/\text{gm catalyst-min}$ . The natural logarithm of 1.218 and reciprocal temperature,  $1.65 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ , provide a single point of the Arrhenius plot. Six such points fall on a straight line with a slope of  $-6.48 \times 10^3 \text{ }^\circ\text{K}$  and an intercept of 11.87. If we multiply the slope by  $-R$ , the gas constant, we obtain the activation energy, 12.9 Kcal/gm mole. The frequency factor,  $A$ , is determined by multiplying the exponential of the intercept in the Arrhenius plot by the volume-to-weight ratio of the non-impregnated catalyst,  $V/W$ . Thus,

$$\begin{aligned} A &= 0.65 \exp(\text{intercept}) \\ &= 0.65 \exp(11.87) \\ &= 9.3 \times 10^4 \text{ min}^{-1} \end{aligned}$$

The temperature dependence of the pseudo-first order rate can be expressed as follows:

$$k = 9.3 \times 10^4 \exp(-12.9/RT)$$

## V. RESULTS

In this section, we present the complete experimental and kinetic data obtained during the first twenty-two month period of the RANN NSF research grant. The results fall into the following categories:

- o Catalyst compositions, including the weights of salt and catalyst support and the calculated alkali metal:molybdenum molar ratio.
- o Raw chromatographic data, in the form of effluent gas compositions for each temperature, flow rate, and catalyst studied.
- o Analyzed rate data, in the form of space velocity plots based upon a chosen rate law. The reciprocal flow rate at reactor conditions was used in place of the space velocity.
- o Arrhenius plots.

Given are data for each "Aldridge" catalyst that we studied for the water-gas shift, ethanol dehydration, and catalytic methanation reactions. Eight of the thirty-one different "Aldridge" water-gas shift catalysts (catalysts P, Q, R, T, U, V, Y, and Z) were studied by Andrew D. Overstreet and have been reported in his M.S. thesis.<sup>2</sup> The remaining catalysts were studied by the co-principal investigator on the NSF research grant, Dr. David S. Newsome, and myself. I was in full charge of the studies of the "Aldridge" catalysts for the dehydration and

methanation reactions, and wrote all computer programs, operated the reactor, developed kinetic models, and analyzed the raw chromatographic data.

The tables and figures in this section are divided into three parts, each part corresponding to the reaction system studied:

1. The ethanol dehydration reaction, Tables 6 through 13 and Figures 6 through 11.
2. The methanation reaction, Tables 14 through 19 and Figures 12 through 15.
3. The water-gas shift reaction, Tables 20 through 90 and Figures 16 through 46.

The results for the water-gas shift reaction are further subdivided into three categories according to the amount of cobalt and molybdenum present per gram of impregnated catalyst:

- 3a. One-fifth strength catalysts having one-fifth the amount of cobalt and molybdenum as in the Nalcomo 474 cobalt-molybdate hydrotreating catalyst, Tables 21 through 32 and Figures 16 through 20.
- 3b. One-half strength catalysts having one-half the amount of cobalt and molybdenum as in the Nalcomo 474 hydrotreating catalyst, Tables 33 through 50 and Figures 21 through 28.
- 3c. Full-strength catalysts based upon the Nalcomo 474 hydroreating catalyst, Tables 52 through 90 and Figures 30 through 46.

In our water-gas shift studies, we were primarily interested in determining the relationship between the catalytic activity of the "Aldridge" catalysts and the Cs:Mo or alkali metal:Mo molar ratio. This is why the molar ratio is shown on each Arrhenius plot.

Table 93 summarizes the linear regression data for all of the water-gas shift catalysts studied. Given are the activation energy  $E_a$ , in Kcal/gm mole, pre-exponential factor,  $AV/W$ , in  $\text{cm}^3/\text{gm-min}$ , and correlation coefficient for each catalyst. With most of the full-strength catalysts, two sets of activation energies and pre-exponential factors are shown.

The computer-generated tables that summarize the raw chromatographic data require some explanation. The temperature is in  $^{\circ}\text{C}$ , the flow rate is in  $\text{cm}^3/\text{min}$  at reactor conditions, and the final gas compositions are in mole fractions. Such data can be used by other individuals to test other kinetic models for the water-gas shift reaction over the catalysts that we have studied.

TABLE 6 . AMOUNT OF FULL-STRENGTH CATALYSTS (a) USED IN ETHANOL DEHYDRATION AND METHANATION STUDIES

Catalyst Number	Metal: Molybdenum ratio	Weight Catalyst used in reactor (grams)	Weight inert-solids used in reactor (grams)	W (grams)
VV(b)	0.43	0.500	1.000	0.463
ZZ(b)	0.00	0.502	1.012	0.502
RR(c)	0.91	3.615	1.404	3.140
ZO(c)	0.00	3.652	1.342	3.652
OO(c)	$\infty$ (d)	4.992	0.000	4.760

(a) Nalcomo 474 hydrotreating catalysts were used for ETOH dehydration and methanation studies. Such catalysts consist of 35% CoO and 12.5% MoO<sub>3</sub> on the Al<sub>2</sub>O<sub>3</sub> support. The Co:Mo molar ratio is 0.538.

(b) Used for ethanol dehydration

(c) Used for methanation

(d) Catalyst contains 0.25 grams of cesium impregnated on Air Products and Chemicals Inc., hard alumina catalyst 220S. No cobalt or molybdenum is present.

TABLE 7 . COMPOSITIONS OF FULL-STRENGTH CATALYSTS USED IN ETHANOL DEHYDRATION AND METHANATION STUDIES

Catalyst Number	Salt	Weight dry catalyst (grams)	Weight salt (grams)	Weight salt per grams unimpregnated catalyst	Metal: molybdenum ratio
VV	cesium acetate	5.571	0.40	0.0670	0.43
ZZ	none	5.616	0.00	0.000	0.00
RR	cesium acetate	5.598	0.85	0.131	0.91
ZO	none	5.616	0.00	0.000	0.00
00	cesium acetate	5.980	0.25	0.042	$\infty$

TABLE 8 . MOLE FRACTIONS OF PRODUCT GASES FOR ETHANOL DEHYDRATION WITH CATALYST "VV"

Temp°C	Flow(a)	Hydrogen	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O	Others	ETOH	Ether	CO
229	69.04	.3891	.0021	.0073	.0001	.0575	.0499	.2249	.0313	.2372
229	28.35	.3812	.0057	.0119	.0007	.0948	.0519	.1689	.0576	.2267
229	44.67	.3808	.0034	.0086	.0003	.0733	.0520	.2054	.0452	.2305
255	51.50	.3739	.0083	.0173	.0019	.1358	.0542	.1027	.0782	.2274
255	75.85	.3872	.0066	.0111	.0010	.1103	.0528	.1302	.0628	.2375
255	104.89	.3892	.0058	.0088	.0007	.0980	.0538	.1485	.0550	.2396
278	107.72	.3866	.0064	.0233	.0021	.1319	.0590	.0821	.0702	.2380
278	64.51	.3696	.0091	.0386	.0037	.1616	.0505	.0627	.0788	.2248
278	30.44	.3478	.0168	.0680	.0085	.1831	.0520	.0466	.0723	.2043
307	57.80	.3522	.0088	.0716	.0082	.1848	.0620	.0394	.0557	.2169
307	93.75	.3675	.0068	.0622	.0061	.1643	.0587	.0438	.0620	.2279
307	120.96	.3764	.0063	.0566	.0049	.1535	.0605	.0458	.0619	.2336
326	141.84	.3604	.0084	.0955	.0095	.1762	.0584	.0342	.0334	.2236
326	85.34	.3332	.0115	.1147	.0140	.1906	.0665	.0374	.0264	.2052
326	59.76	.3192	.0172	.1354	.0211	.2047	.0611	.0332	.0139	.1937

TABLE 8 (cont'd)

Temp	Flow	Hydrogen	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O	Others	EtOH	Ether	CO
351	96.30	.3100	.0168	.1457	.0197	.2212	.0690	.0226	.0070	.1876
351	116.95	.3288	.0145	.1392	.0173	.2050	.0647	.0224	.0069	.2008
351	197.36	.3622	.0084	.1149	.0106	.1757	.0542	.0316	.0165	.2254
377	228.13	.3518	.0152	.1415	.0121	.2082	.0477	.0109	.0009	.2111
377	180.18	.3416	.0204	.1429	.0137	.2102	.0612	.0097	.0006	.1991
377	113.42	.3350	.0335	.1436	.0179	.2158	.0613	.0107	.0006	.1810
419	125.52	.3554	.0632	.1227	.0145	.2164	.0607	.0113	.0013	.1542
419	196.72	.3604	.0340	.1298	.0095	.2104	.0536	.0071	.0036	.1912
419	94.34	.3651	.0643	.1180	.0158	.2056	.0581	.0106	.0023	.1598
448	99.17	.3694	.0829	.1096	.0209	.1869	.0743	.0099	.0036	.1422
448	174.41	.3716	.0456	.1242	.0139	.2010	.0500	.0066	.0002	.1864
448	298.50	.3715	.0238	.1314	.0088	.1957	.0535	.0039	.0002	.2107

(a) Volumetric flow rate, cm<sup>3</sup>/min at reactor conditions.

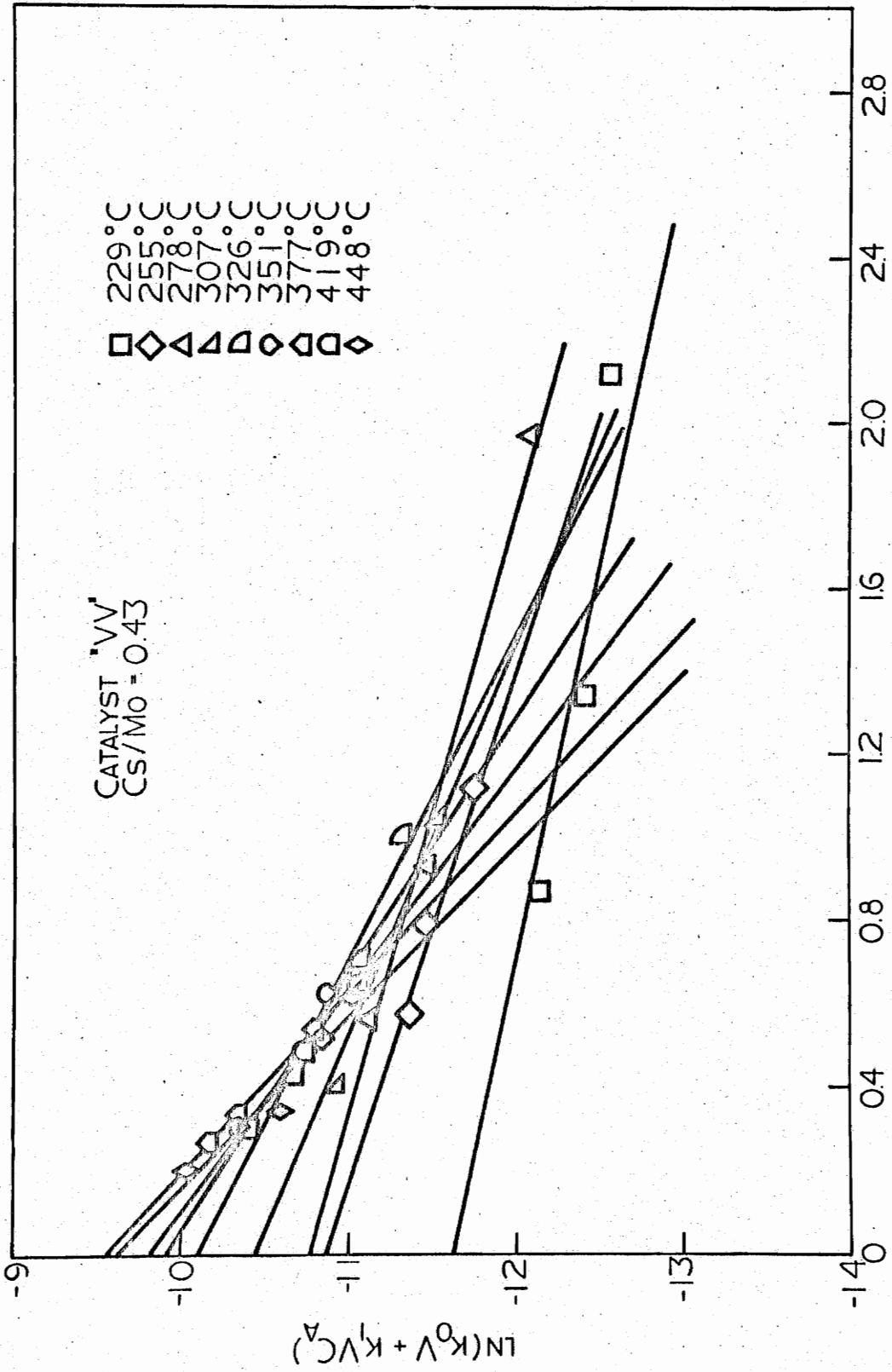


Figure 6. Conversion plot for catalyst "VV"

TABLE 9 . ARRHENIUS DATA FOR CATALYST "VV"(a)

T, °C	Intercept $\ln(Vk_0 + Vk_1 C_A^0)$	Slope, $k_1 V$ $\text{cm}^3/\text{sec}$	Normalized Slope, $k_1 V/W$ (b) $\text{cm}^3/\text{gm catalyst-sec}$	Plotted Data	
				$\ln(k_1 V/W)$	$1/T, 10^{-3} \text{ }^\circ\text{K}^{-1}$
229	-11.55	0.549	1.187	0.171	1.99
255	-10.89	0.714	1.543	0.434	1.89
278	-10.64	0.758	1.636	0.492	1.81
307	-10.38	1.064	2.298	0.832	1.72
326	-10.28	1.111	2.400	0.875	1.67
351	- 9.90	1.429	3.085	1.127	1.60
377	- 9.63	2.000	4.320	1.463	1.54
419	- 9.75	2.000	4.320	1.463	1.45
448	- 9.58	2.439	5.268	1.662	1.39

(a) Catalyst contains 0.067 grams cesium acetate per gram impregnated catalyst. The cesium: molybdenum molar ratio is 0.43.

(b)  $k_1$  = first-order rate constant,  $\text{sec}^{-1}$

V = volume of catalyst bed not including inert solids,  $\text{cm}^3$

W = weight of catalyst used less the cesium acetate weight, 0.463 grams

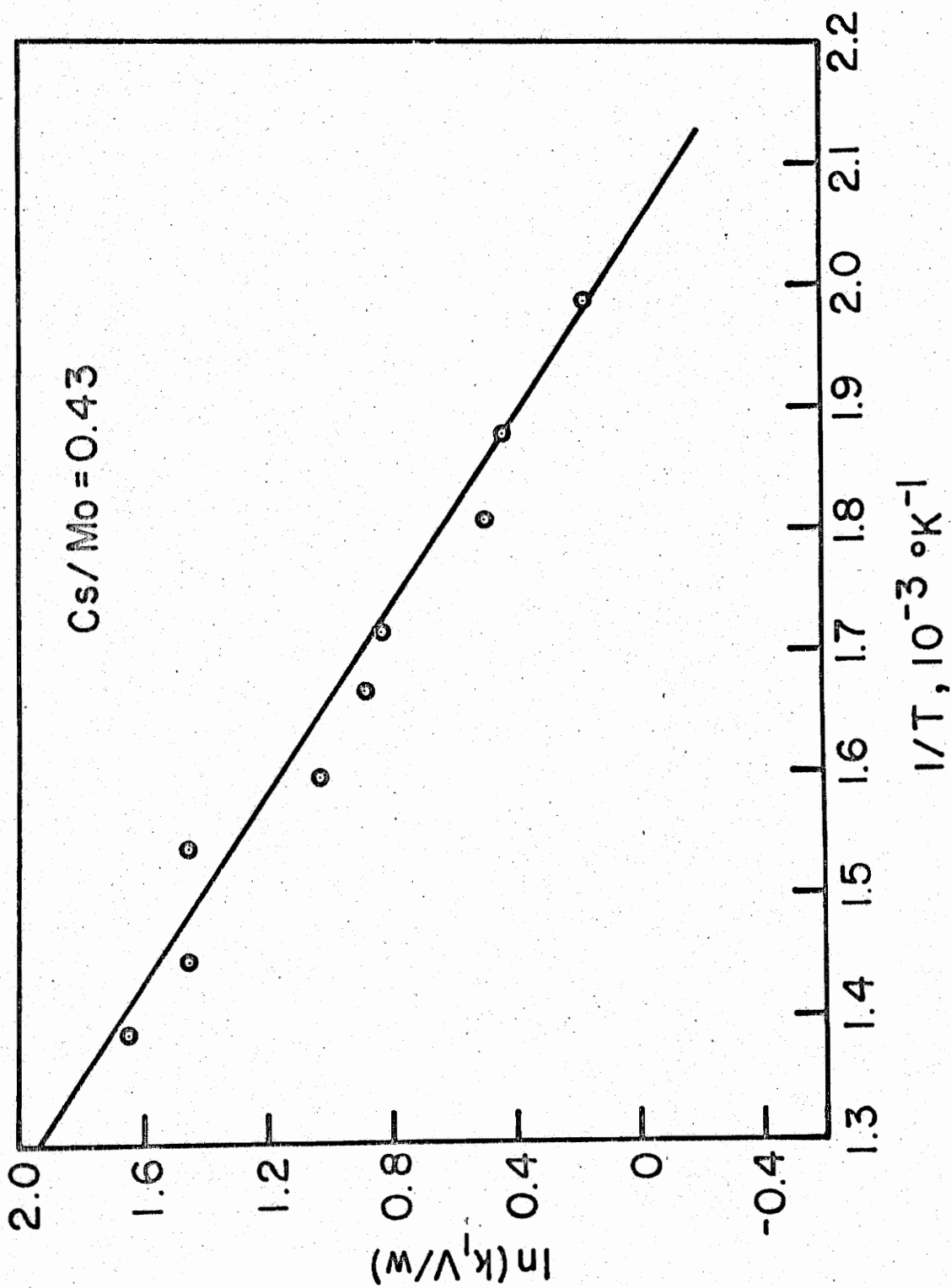


Figure 7. Arrhenius plot for catalyst "VV"

TABLE 10. ARRHENIUS DATA FOR CATALYST "VY" (a)

$T, ^\circ\text{C}$	$10^{-6}$ gm moles/sec	$k_0V$ $10^{-6}$ gm moles/sec	$k_0V/W, (b)$ $10^{-5}$ gm moles/ sec-gm catalyst	$\ln(k_0V/W)$	$1/T, 10^{-3} \text{ } ^\circ\text{K}^{-1}$
229	3.99	5.65	1.22	-11.31	1.99
255	4.59	14.05	3.03	-10.40	1.89
278	4.98	19.08	4.12	-10.10	1.81
307	6.71	24.49	5.29	- 9.85	1.72
326	8.21	26.24	5.67	- 9.78	1.67
351	10.53	39.64	8.56	- 9.37	1.60
377	13.62	52.11	11.25	- 9.09	1.54
419	14.00	44.29	9.57	- 9.25	1.45
448	15.41	53.69	11.60	- 9.06	1.39

(a) Catalyst contains 0.067 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.43.

(b)  $k_0$  = zero-order rate constant, gm moles/sec-cm<sup>3</sup>  
 $V$  = volume of catalyst bed not including inert solids, cm<sup>3</sup>  
 $W$  = weight of catalyst used less the cesium acetate weight, 0.463 grams

(c)  $C_A^0$  is the average initial ethanol concentration at three flow rates and one temperature

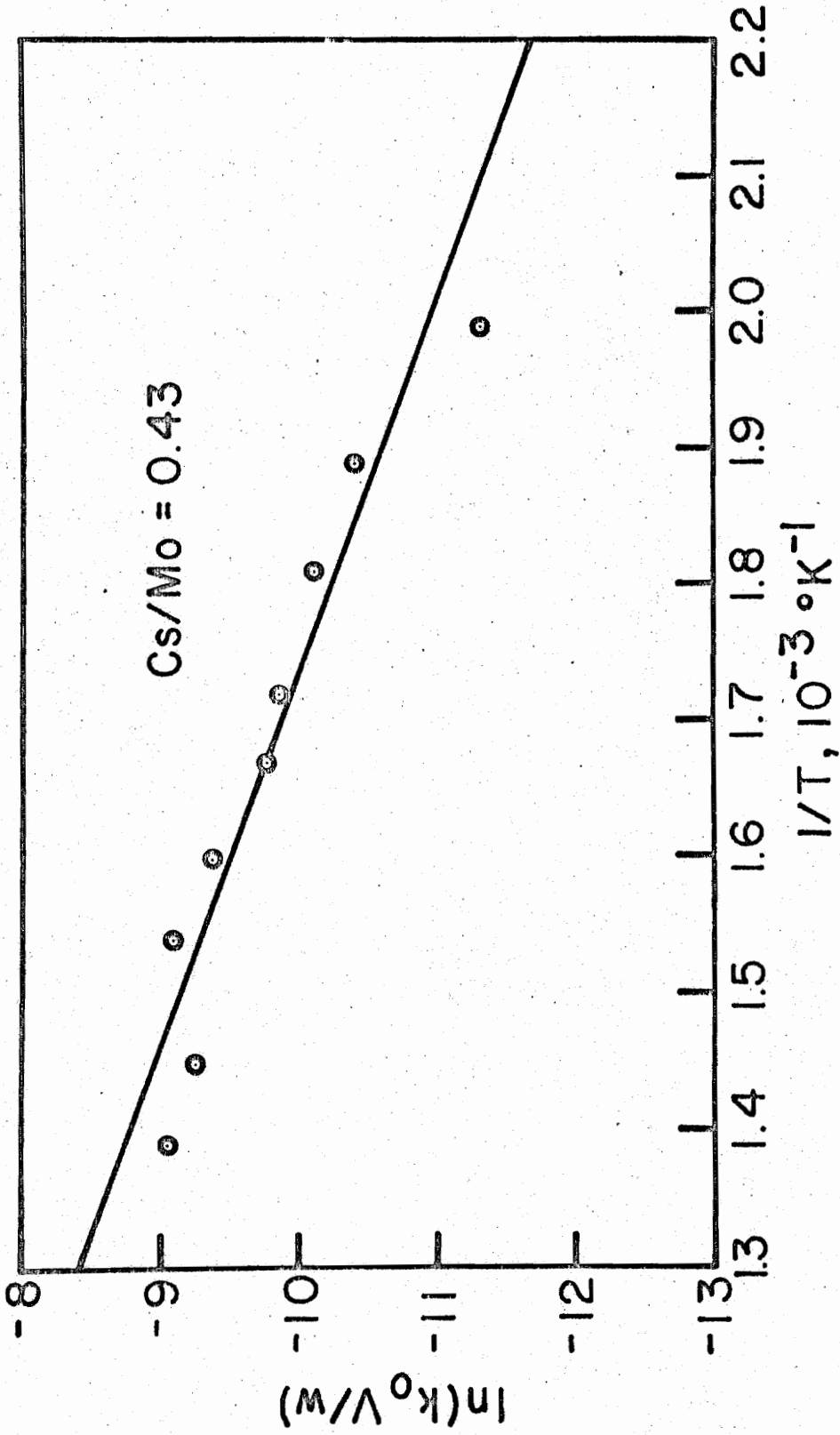


Figure 8. Arrhenius plot for catalyst "VW"

TABLE 11 . MOLE FRACTIONS OF PRODUCT GASES FOR ETHANOL DEHYDRATION WITH CATALYST "ZZ"

Temp°C	Flow <sup>(a)</sup>	Hydrogen	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O	Others	ETOH	Ether	CO
203	20.90	.3375	.0055	.0061	.0009	.1237	.0467	.1820	.0625	.2179
203	84.50	.2927	.0036	.0013	.0001	.0628	.0589	.2595	.0288	.2239
203	39.73	.3140	.0052	.0027	.0005	.0976	.0780	.2239	.0442	.2084
230	60.00	.2997	.0046	.0093	.0016	.1830	.0591	.1500	.0691	.1997
230	24.49	.2639	.0069	.0212	.0025	.2197	.0640	.0804	.0950	.1932
230	43.16	.2866	.0049	.0134	.0014	.1679	.0660	.1255	.0874	.2034
257	38.96	.2260	.0056	.0400	.0051	.2459	.0799	.0542	.0781	.1879
257	117.64	.2503	.0037	.0227	.0022	.1753	.0741	.1011	.0788	.2080
257	68.96	.2863	.0042	.0371	.0036	.1993	.0660	.0732	.0975	.1992
276	150.00	.2374	.0030	.0449	.0043	.1916	.0589	.0678	.0789	.2126
276	68.96	.2530	.0045	.0777	.0089	.2236	.0703	.0653	.0712	.1853
276	93.75	.2840	.0037	.0613	.0064	.2069	.0705	.0596	.0789	.1981
307	181.81	.2867	.0035	.0878	.0104	.2121	.0847	.0590	.0505	.1919
307	77.92	.2684	.0071	.1498	.0218	.2569	.0727	.0319	.0236	.1719
307	111.11	.2802	.0051	.1198	.0151	.2328	.0762	.0390	.0404	.1845

TABLE 11 (cont'd)

Temp	Flow	Hydrogen	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O	Others	ETOH	Ether	CO
328	66.66	.3542	.0163	.1904	.0447	.2970	.0646	.0097	0.0000	.1507
328	107.14	.3607	.0090	.1802	.0297	.2661	.0701	.0193	.0090	.1658
328	162.16	.3390	.0062	.1573	.0208	.2257	.0747	.0229	.0190	.1866
355	83.33	.3231	.0330	.1768	.0626	.2638	.0664	.0114	0.0000	.1481
355	157.89	.3165	.0182	.1894	.0414	.2525	.0721	.0097	0.0000	.1634
355	240.00	.3297	.0078	.1703	.0230	.2231	.0837	.0167	.0064	.1845
378	272.72	.3028	.0119	.1691	.0249	.2330	.0832	.0086	0.0000	.1823
378	130.43	.3336	.0302	.1682	.0410	.2422	.0797	.0123	0.0000	.1577
378	214.28	.3197	.0149	.1717	.0264	.2320	.0897	.0094	0.0000	.1752

(a) Volumetric flow rate, cm<sup>3</sup>/min at reactor conditions.

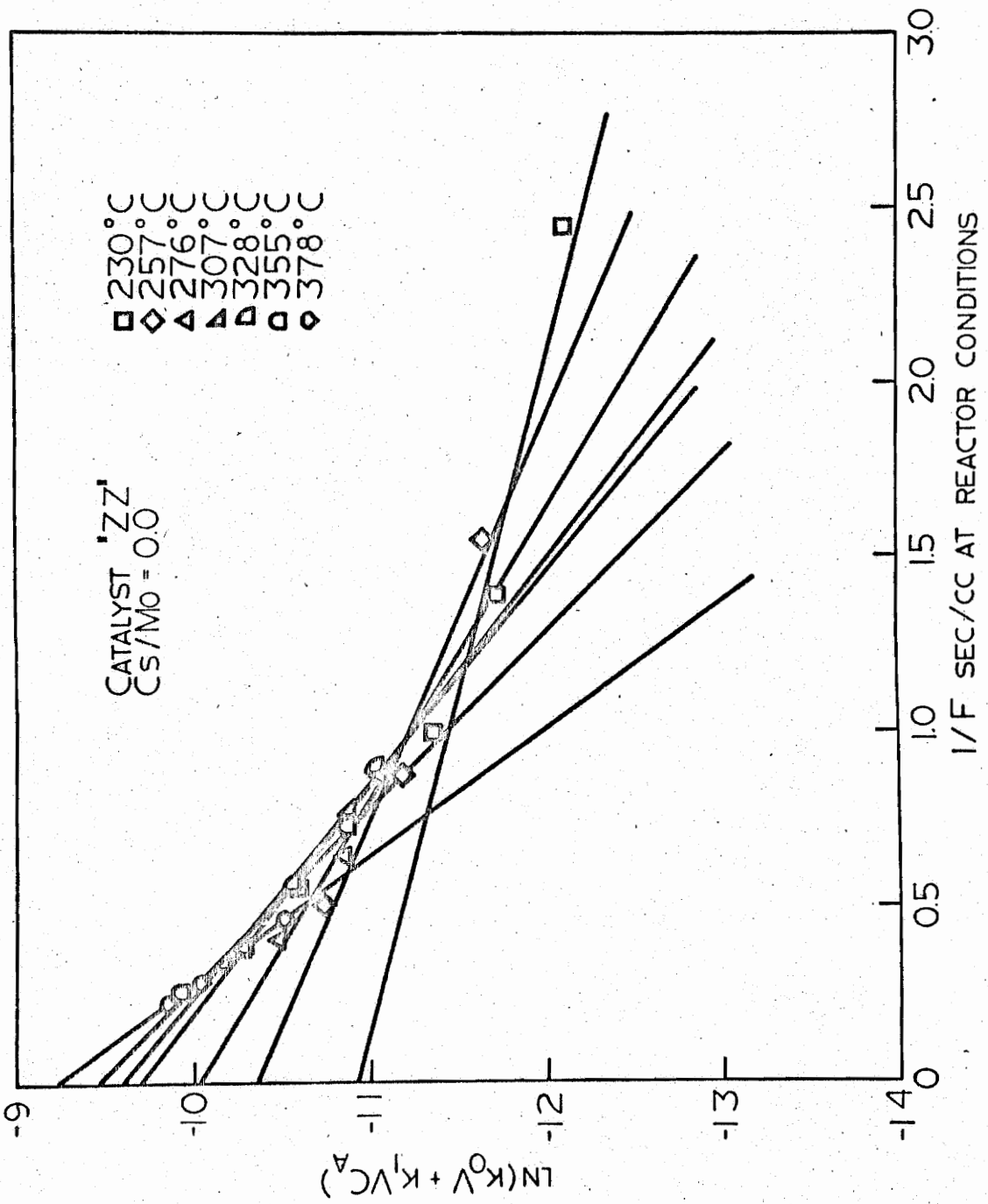


Figure 9. Conversion plot for catalyst "ZZ"

TABLE 12. ARRHENIUS DATA FOR CATALYST "ZZ" (a)

T, °C	Intercept $\ln(Vk_0 + Vk_1 C_A^0)$	-Slope, $k_1 V$ $\text{cm}^3/\text{sec}$	Normalized Slope		Plotted Data	
			$k_1 V/W^{(b)}$ $\text{cm}^3/\text{gm}$ catalyst-sec	$k_1 V/W^{(b)}$ $\text{cm}^3/\text{gm}$ catalyst-sec	$\ln(k_1 V/W)$	$1/T, 10^{-3} \text{ } ^\circ\text{K}^{-1}$
230	-10.92	0.533	1.062	0.060	1.99	
257	-10.35	0.870	1.733	0.549	1.89	
276	-10.00	1.250	2.490	0.912	1.82	
307	- 9.73	1.592	3.171	1.142	1.72	
328	- 9.77	1.515	3.018	1.105	1.66	
355	- 9.48	2.000	3.984	1.382	1.59	
378	- 9.27	2.660	5.298	1.667	1.54	

(a) Catalyst contains no cesium acetate. The catalyst is Nalcomo 474, which has 12.5% MoO<sub>3</sub> and 3.5% CoO on alumina. The cobalt: molybdenum molar ratio is 0.538.

(b)  $k_1$  = first-order rate constant,  $\text{sec}^{-1}$

V = volume of catalyst bed not including inert solids,  $\text{cm}^3$

W = weight of catalyst used, 0.502 grams

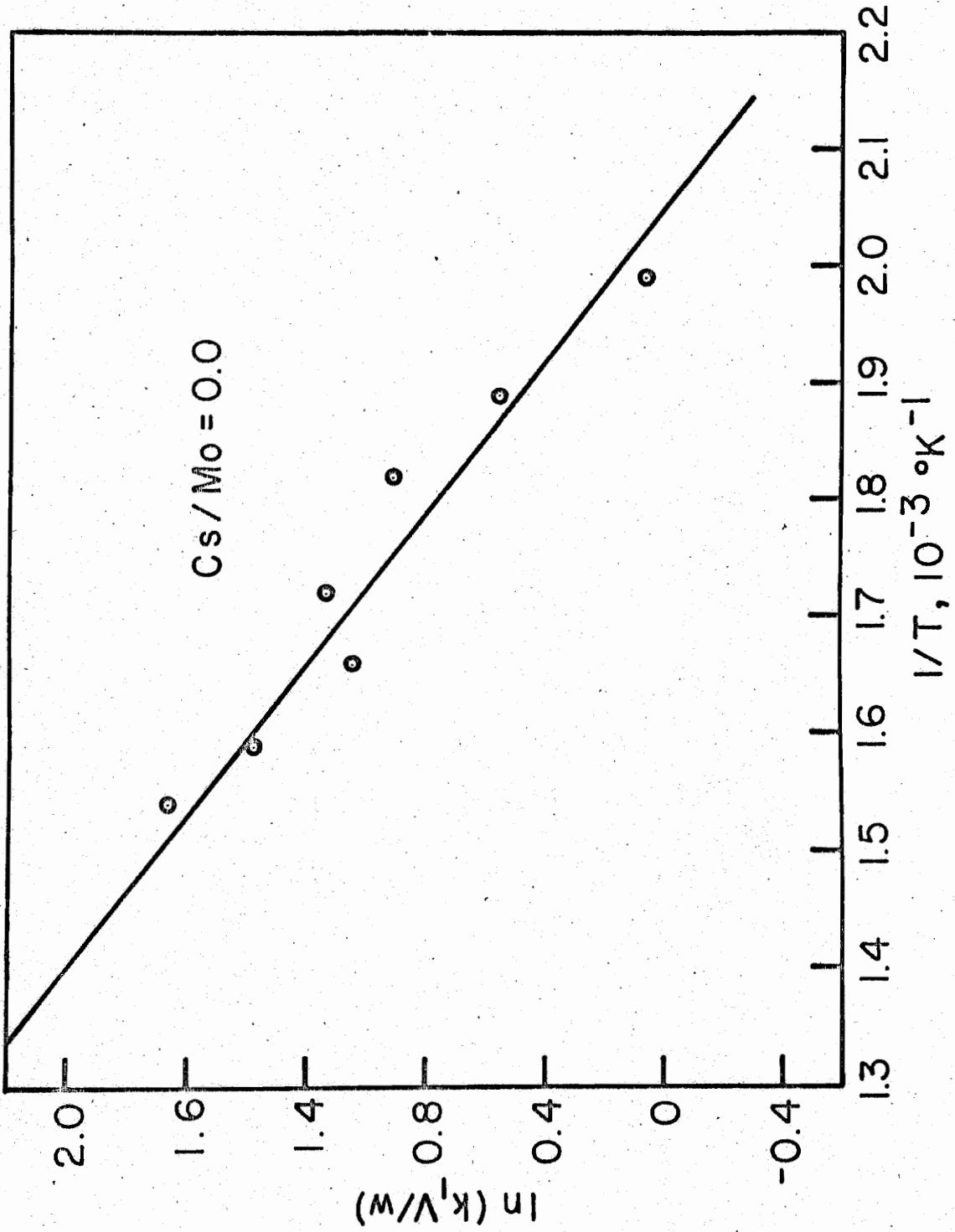


Figure 10. Arrhenius plot for catalyst "ZZ"

TABLE 13 . ARRHENIUS DATA FOR CATALYST "ZZ"(a)

T, °C	$Vk_1C_A^{0(c)}$ 10 <sup>-6</sup> gm moles/sec	$k_0V$ 10 <sup>-6</sup> gm moles/sec	$k_0V/W^{(b)}$ , 10 <sup>-5</sup> gm moles/ sec-gm catalyst	Plotted Data	
				$\ln(k_0V/W)$	$1/T$ , 10 <sup>-3</sup> °K <sup>-1</sup>
230	4.68	13.41	2.671	-10.53	1.99
257	7.16	24.83	4.946	- 9.91	1.89
276	10.25	35.15	7.002	- 9.57	1.82
307	14.12	45.35	9.034	- 9.31	1.72
328	14.67	42.76	8.518	- 9.37	1.66
355	18.10	58.65	11.683	- 9.05	1.59
378	22.22	71.99	14.341	- 8.85	1.54

(a) Catalyst contains no cesium acetate. The catalyst is NaIcomco 474, which consists of 12.5% MoO<sub>3</sub> and 3.5% CoO on alumina. The cobalt: molybdenum ratio is 0.538.

(b)  $k_0$  = zero-order rate constant, gm moles/sec-cm<sup>3</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used, 0.502 grams

(c)  $C_A^0$  is the average initial ethanol concentration at three flowrates and one temperature

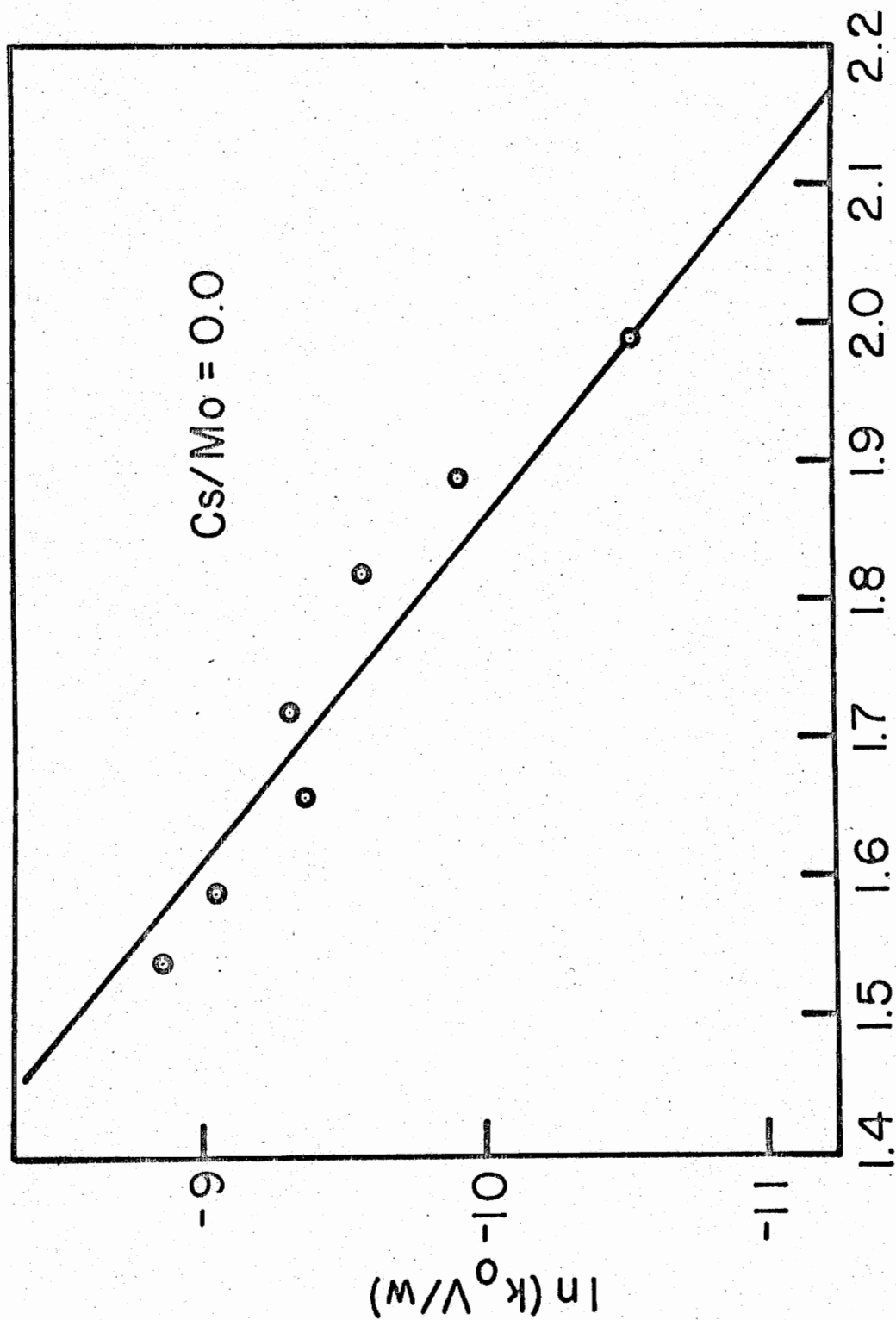


Figure 11. Arrhenius plot for catalyst "ZZ"

TABLE 14. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "RR"

TEMP	FLOW	HYDROGEN	CO	METHANE	CO2	ETHANE	H2S	WATER	CO
277.0	8.152	0.64016	0.14922	0.08006	0.05183	0.01552	0.00032	0.04961	0.01328
277.0	24.701	0.73709	0.20038	0.00826	0.02301	0.00312	0.00000	0.01674	0.01141
277.0	19.288	0.73711	0.19378	0.00991	0.02771	0.00429	0.00000	0.01515	0.01205
277.0	48.750	0.74013	0.21753	0.00439	0.01521	0.00187	0.00000	0.00891	0.01196
277.0	60.422	0.74019	0.22098	0.00400	0.01404	0.00164	0.00000	0.00860	0.01054
277.0	34.799	0.73602	0.21225	0.00682	0.01765	0.00304	0.00000	0.01303	0.01119
277.0	13.624	0.72751	0.17975	0.01553	0.03513	0.00820	0.00000	0.02309	0.01080
303.0	21.503	0.73095	0.18050	0.01840	0.03454	0.00370	0.00000	0.02061	0.01131
303.0	31.880	0.73308	0.19306	0.01428	0.02816	0.00343	0.00000	0.01582	0.01218
303.0	40.220	0.73587	0.19831	0.01100	0.02571	0.00276	0.00140	0.01251	0.01244
303.0	43.341	0.73230	0.20420	0.01037	0.02310	0.00275	0.00405	0.01174	0.01149
303.0	67.840	0.73252	0.22118	0.00715	0.01592	0.00191	0.00523	0.00651	0.00958
332.0	38.643	0.71727	0.17325	0.02788	0.03866	0.00585	0.00009	0.02603	0.01097
332.0	58.668	0.72597	0.18412	0.02060	0.03269	0.00428	0.00000	0.02040	0.01195
332.0	50.983	0.72307	0.18524	0.02249	0.03256	0.00442	0.00000	0.02123	0.01099
332.0	49.238	0.72176	0.18404	0.02293	0.03285	0.00478	0.00000	0.02283	0.01082
332.0	62.526	0.72609	0.19384	0.01885	0.02825	0.00381	0.00000	0.01853	0.01062
332.0	70.220	0.72856	0.19891	0.01561	0.02435	0.00325	0.00000	0.01693	0.01240
332.0	95.983	0.73090	0.20647	0.01347	0.02215	0.00284	0.00000	0.01447	0.00970
332.0	122.419	0.73412	0.20948	0.00971	0.01858	0.00215	0.00000	0.01422	0.01174

TABLE 14 (cont'd)

TEMP	FLOW	HYDROGEN	CO	METHANE	CO2	ETHANE	H2S	WATER	CO2S
350.0	59.382	0.71358	0.18043	0.03134	0.03587	0.00456	0.00022	0.02254	0.01145
350.0	89.972	0.71523	0.20071	0.02220	0.02686	0.00298	0.00818	0.01350	0.01032
350.0	196.011	0.72474	0.21662	0.01225	0.01795	0.00176	0.00762	0.00918	0.00989
350.0	74.137	0.71271	0.18961	0.02775	0.03241	0.00382	0.00546	0.01765	0.01060
385.0	60.180	0.68996	0.15125	0.05682	0.05103	0.00420	0.00005	0.03581	0.01089
385.0	78.526	0.70100	0.16615	0.04464	0.04184	0.00343	0.00000	0.03088	0.01207
385.0	143.190	0.71431	0.18677	0.03064	0.03137	0.00241	0.00000	0.02376	0.01074
385.0	117.410	0.70902	0.18427	0.03635	0.03517	0.00285	0.00023	0.02380	0.00831
385.0	40.332	0.66714	0.13993	0.07537	0.05771	0.00541	0.00051	0.04376	0.01017
385.0	39.123	0.66426	0.13890	0.07937	0.06122	0.00534	0.00124	0.04295	0.00672
385.0	16.443	0.60442	0.10978	0.12956	0.07708	0.00808	0.00056	0.06150	0.00902
421.0	57.376	0.64273	0.13396	0.08927	0.05933	0.00304	0.00990	0.05254	0.00922
421.0	93.873	0.66211	0.15220	0.07149	0.05031	0.00247	0.01041	0.04000	0.01101
421.0	83.239	0.65618	0.15068	0.07417	0.05207	0.00262	0.01374	0.04113	0.00941
421.0	171.766	0.68414	0.17662	0.04888	0.03869	0.00181	0.01263	0.02709	0.01013
421.0	129.278	0.67582	0.16464	0.05869	0.04480	0.00232	0.01088	0.03268	0.01016

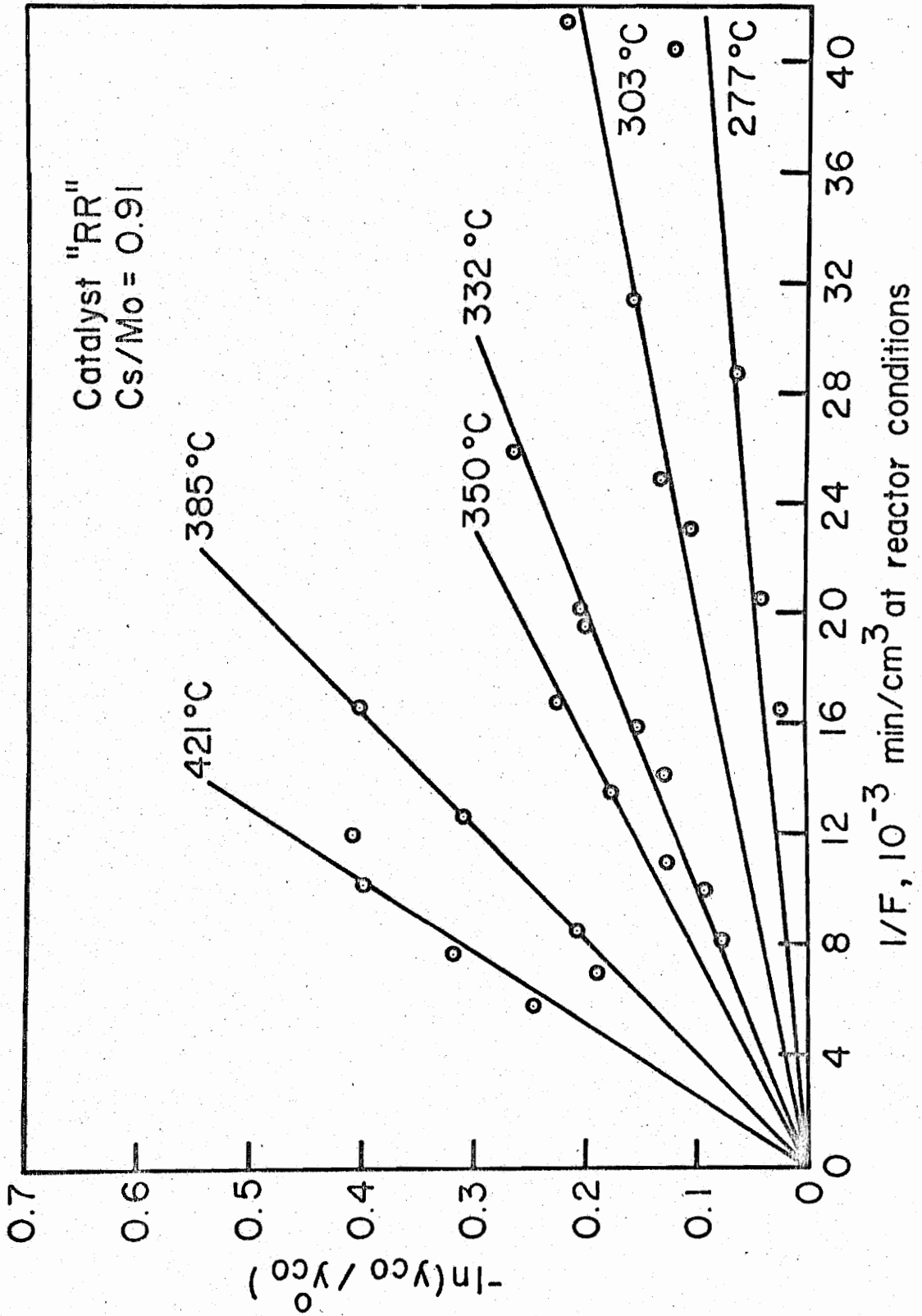


Figure 12. Conversion plot for catalyst "RR"

TABLE 15 . ARRHENIUS DATA FOR CATALYST "RR"(a)

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
277	3.53	1.12	0.117	1.82
303	15.24	1.67	0.512	1.74
332	10.61	3.38	1.218	1.65
351	13.56	4.32	1.463	1.61
385	24.50	7.80	2.054	1.52
421	38.70	12.32	2.512	1.44

(a) Catalyst contains 0.131 grams cesium acetate per gram impregnated catalyst. The cesium:molybdenum molar ratio is 0.91.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 3.140 grams

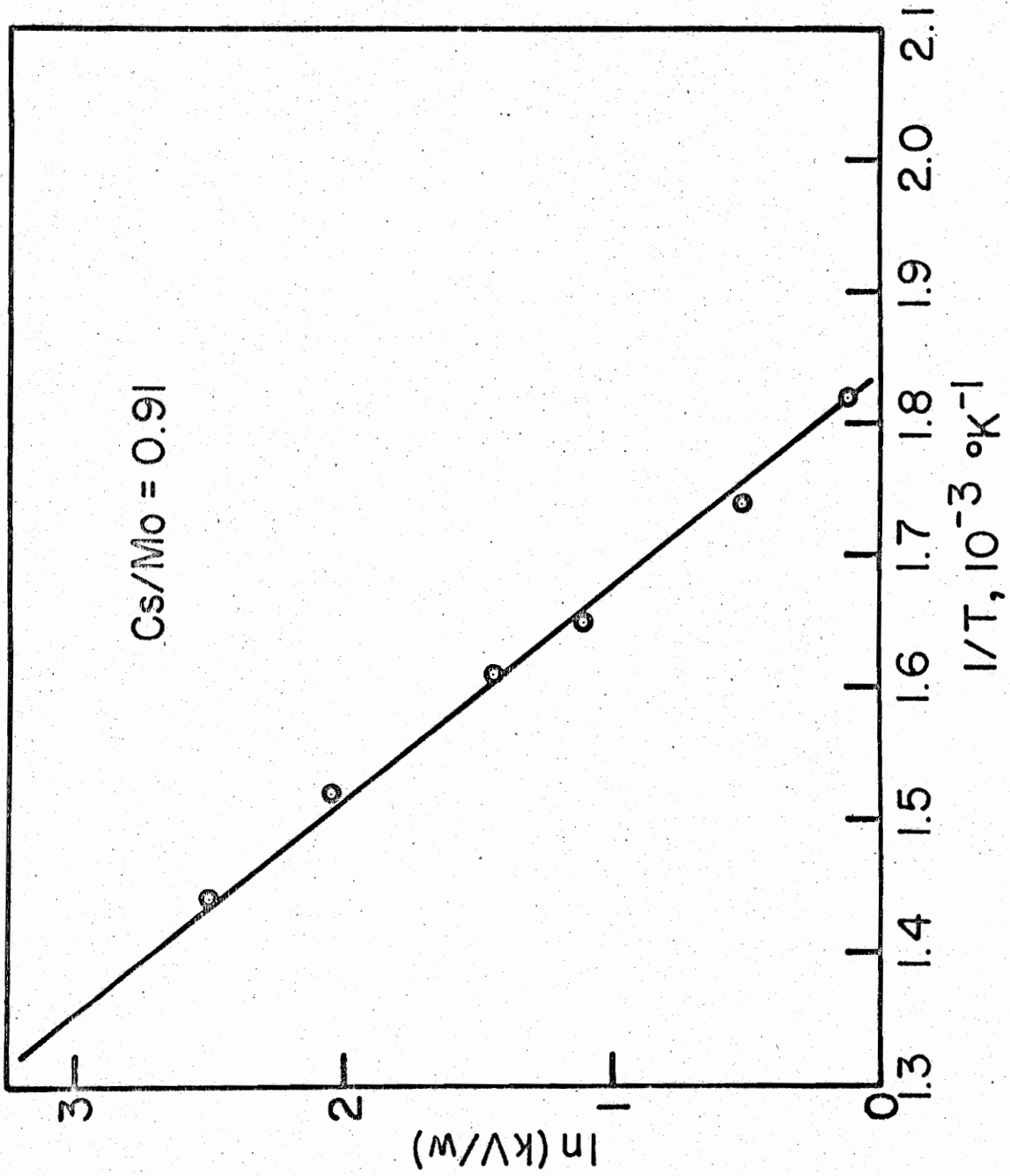


Figure 13. Arrhenius plot for catalyst "RR"

TABLE 16. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "Z0"

TEMP	FLOW	HYDROGEN	CO	METHANE	CO2	ETHANE	H2S	WATER	COS
279.0	17.135	0.73291	0.15869	0.01927	0.04712	0.00684	0.00000	0.02621	0.00895
279.0	19.675	0.72869	0.16827	0.01954	0.04299	0.00780	0.00000	0.02380	0.00891
279.0	24.342	0.73645	0.18357	0.01450	0.03856	0.00639	0.00000	0.01405	0.00649
279.0	34.314	0.73387	0.19986	0.01113	0.02729	0.00538	0.00000	0.01413	0.00833
309.0	29.682	0.70488	0.15277	0.03506	0.05133	0.00907	0.00646	0.03155	0.00888
309.0	45.737	0.71505	0.17492	0.02489	0.03975	0.00620	0.00707	0.02331	0.00881
309.0	64.782	0.71792	0.19052	0.02125	0.03258	0.00535	0.00612	0.01812	0.00814
309.0	37.961	0.70240	0.17264	0.03115	0.04446	0.00777	0.01361	0.02062	0.00734
334.0	38.763	0.69874	0.16179	0.03954	0.05259	0.01042	0.00778	0.02407	0.00507
334.0	42.760	0.70182	0.16303	0.03429	0.04901	0.00879	0.01152	0.02267	0.00888
334.0	49.523	0.70475	0.17154	0.03125	0.04555	0.00786	0.01199	0.01991	0.00715
334.0	88.487	0.71357	0.19540	0.02071	0.03171	0.00522	0.01174	0.01416	0.00750
360.0	62.040	0.67729	0.16044	0.04855	0.05170	0.00780	0.02016	0.02805	0.00600
360.0	34.764	0.65784	0.13730	0.06721	0.06613	0.01126	0.01982	0.03453	0.00591
360.0	82.454	0.69012	0.18155	0.03599	0.04096	0.00886	0.01557	0.02050	0.00644
360.0	133.301	0.70337	0.19695	0.02789	0.03261	0.00437	0.01473	0.01456	0.00551
360.0	103.861	0.69921	0.18672	0.03224	0.03734	0.00521	0.01458	0.01865	0.00604
384.0	56.836	0.65262	0.14269	0.07719	0.05939	0.00673	0.01219	0.04287	0.00632
384.0	78.551	0.66786	0.15407	0.06254	0.05157	0.00525	0.01327	0.03752	0.00791
384.0	60.431	0.65152	0.14481	0.07242	0.05826	0.00879	0.01583	0.04098	0.00738
384.0	106.186	0.67945	0.17630	0.05223	0.04510	0.00457	0.01463	0.02334	0.00438
408.0	52.419	0.64275	0.12601	0.09259	0.06434	0.00496	0.00556	0.05608	0.00769
408.0	75.800	0.64099	0.14378	0.08668	0.05885	0.00466	0.01338	0.04761	0.00405
408.0	97.099	0.65688	0.15203	0.07085	0.05387	0.00386	0.01690	0.04024	0.00537
408.0	125.179	0.66689	0.16492	0.05944	0.04563	0.00334	0.01751	0.03434	0.00794

TABLE 17. ARRHENIUS DATA FOR CATALYST "Z0" (a)

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized Slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	ln (kV/W)	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
279	6.04	1.65	0.503	1.81
309	11.30	3.09	1.130	1.72
334	13.48	3.69	1.306	1.65
360	17.61	4.82	1.573	1.58
384	26.82	7.34	7.994	1.52
408	36.80	10.08	2.31	1.47

(a) Catalyst contains no cesium acetate. The catalyst is NaIcomo 474, which has 12.5% MoO<sub>3</sub> and 3.5% CoO on alumina. The cobalt: molybdenum molar ratio is 0.538.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used, 3.652 grams

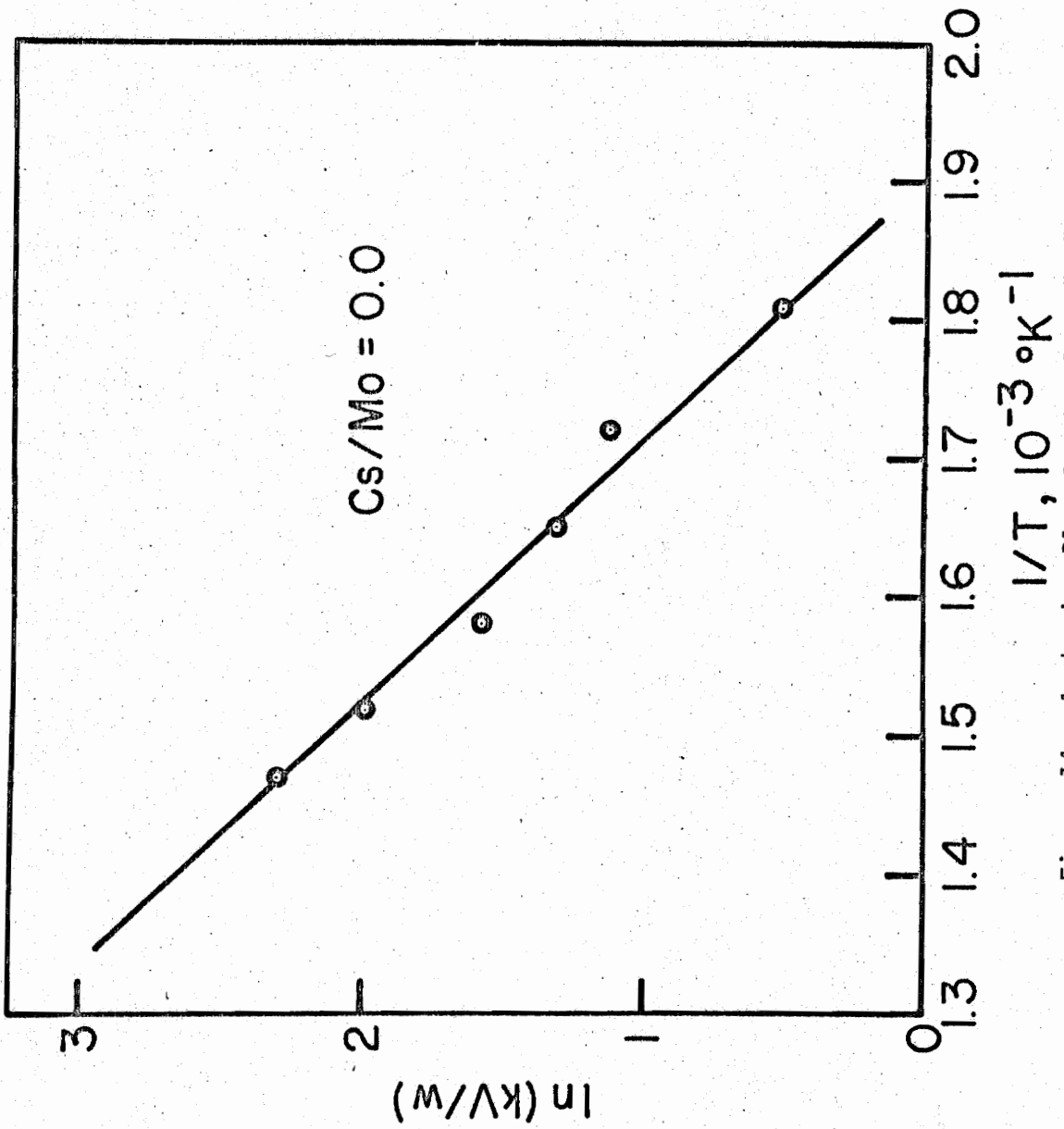


Figure 14. Arrhenius Plot for Catalyst "Z0"

TABLE 18. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "00"

TEMP	FLOW	HYDROGEN	CO	METHANE	CO2	ETHANE	H2S	WATER	CO
401.0	6.097	0.65119	0.21852	0.05443	0.02475	0.00216	0.03115	0.01404	0.00375
401.0	8.738	0.67193	0.21272	0.03693	0.02508	0.00125	0.03398	0.01448	0.00363
401.0	10.593	0.68784	0.21393	0.03039	0.02370	0.00101	0.02588	0.01364	0.00362
420.0	10.936	0.68156	0.20832	0.03839	0.02820	0.00135	0.02450	0.01516	0.00253
420.0	6.724	0.67055	0.20646	0.05045	0.03095	0.00173	0.02147	0.01628	0.00212
420.0	15.872	0.69902	0.21362	0.02855	0.02512	0.00074	0.01893	0.01190	0.00212
449.0	16.221	0.68571	0.20660	0.03841	0.03015	0.00101	0.02273	0.01345	0.00196
449.0	22.509	0.69481	0.21285	0.02975	0.02560	0.00052	0.02211	0.01266	0.00169
449.0	11.216	0.67540	0.20538	0.05132	0.03172	0.00098	0.01734	0.01584	0.00203

## INITIAL CONCENTRATIONS

0.74000 0.22600 0.00000 0.01440 0.00000 0.00000 0.00000 0.00000 0.01960

TABLE 19. ARRHENIUS DATA FOR CATALYST "00"(a)

T, °C	Slope, kV		Normalized Slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
	cm <sup>3</sup> /min	cm <sup>3</sup> /min		ln (kV/W)	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
401	0.264		0.055	-2.892	1.48
420	0.623		0.131	-2.033	1.44
449	1.133		0.238	-1.435	1.39

(a) Catalyst contains 0.042 grams cesium per gram impregnated catalyst. No cobalt or molybdenum is present. The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 2205.

(b) k = pseudo-first order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 4.760 grams

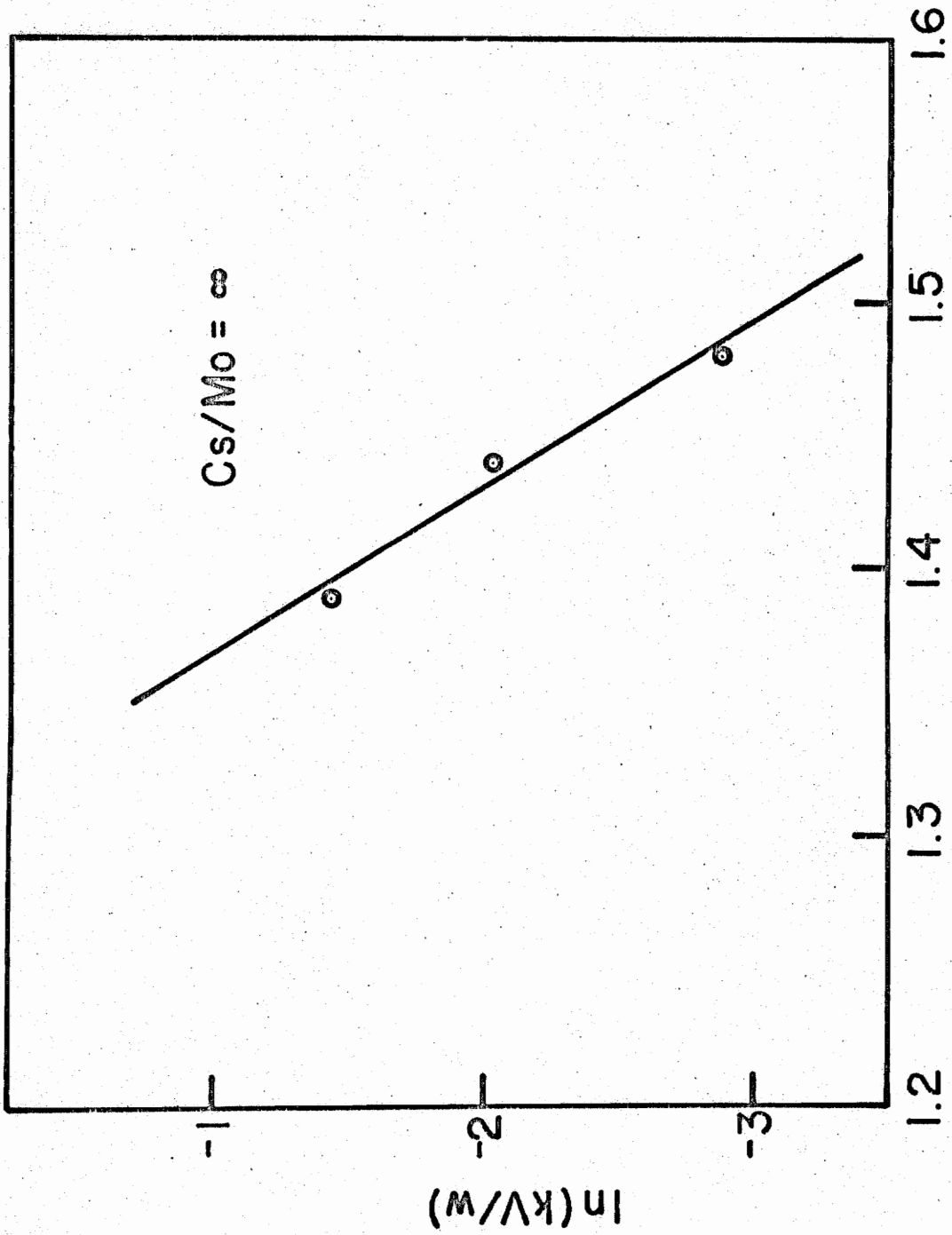


Figure 15. Arrhenius Plot for Catalyst "00"

TABLE 20. COMPOSITION OF 'UNIMPREGNATED' COBALT MOLYBDATE OR ZINC MOLYBDATE CATALYSTS

Catalyst type	Weight support, gm	Weight salts, (d) gm	Dry catalyst weight, gm	Predicted weight, gm	Moles per gram impregnated catalyst, $10^{-4}$ moles/gm
Fu11 strength (a)	---	---	---	---	4.67 Co 8.68 Mo
Fu11 strength (b)	---	---	---	---	4.67 Co 8.68 Mo
Fu11 strength (c)	10.80000	1.667 gm $Zn(NO_3)_2 \cdot 6H_2O$ 1.200 gm $MoO_3$	---	13.667	4.10 Zn
Ha1f strength (c)	30.7954	2.760 gm $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ 2.445 gm $(NO_3)_2 \cdot 6H_2O$	36.6227	36.0002	2.29 Mo
One-fifth strength (c)	36.0005	1.104 gm $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ 0.978 gm $Co(NO_3)_2 \cdot 6H_2O$	38.5328	38.0824	4.27 Co 1.62 Mo 0.872 Co

(a) Na1co Chemical Company Na1como 474 hydrotreating catalyst, which contains 3.5%  $CoO_3$  and 12.5%  $MoO_3$ . The surface area is 270  $m^2/gm$  and the mesh range is 20/60.

(b) Air Products and Chemicals, Inc. hard alumina catalyst 200S. The surface area is 200  $m^2/gm$  and the mesh range is 20/60.

TABLE 20 (con't)

- (c) Harshaw Chemical Co. Mo-1201-T-1/8, which contains 10% MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>. The surface area is 160 m<sup>2</sup>/gm and the mesh range is 20/60.
- (d) The molecular weights of the zinc, cobalt, and molybdenum hydrated salts are 297.49, 291.05, and 1235.95 gm/gm moles, respectively. The molecular weight of MoO is 143.95 gm/gm mole.

TABLE 21. COMPOSITIONS OF ONE-FIFTH STRENGTH CATALYSTS

Catalyst number	Salt	Weight dry catalyst (grams)	Weight salt (grams)	Weight salt per gram impregnated catalyst	Cesium:molybdenum ratio
A	cesium acetate	6.4193	0.2571	0.0385	1.29
B	cesium acetate	6.4191	0.2144	0.0323	1.07
C	cesium acetate	6.4193	0.0862	0.0133	0.43
D	cesium acetate	6.4190	0.0428	0.00662	0.21
E	none	6.4370	0.0000	0.0000	0.00

(a) The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate and ammonium molybdate. One gram catalyst, in the absence of cesium acetate, contains  $8.72 \cdot 10^{-5}$  moles cobalt and  $1.623 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.537. The catalyst particle mesh range is 20/60.

TABLE 22 AMOUNTS OF ONE-FIFTH STRENGTH CATALYSTS USED IN WATER GAS SHIFT STUDIES

Catalyst number	Cesium: molybdenum ratio	Weight catalyst used in reactor (grams)	Weight inert solids used in reactor (grams)	W(b) (grams)
A	1.29	0.601	0.90	0.578
B	1.07	0.600	0.90	0.581
C	0.43	0.602	0.90	0.594
D	0.21	0.602	0.90	0.598
E	0.00	0.602	0.90	0.602

(a) The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate and ammonium molybdate (MW 1235.95). One gram catalyst, in the absence of cesium acetate, contains  $8.72 \cdot 10^{-5}$  moles cobalt and  $1.623 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.537. The catalyst particle mesh range is 20/60.

(b) W = weight of catalyst used less the cesium acetate weight. This value is obtained by subtracting from one the weight salt per gram impregnated catalyst and then by multiplying the result times the weight catalyst used in the reactor.



TABLE 23. MOLE FRACTION OF PRODUCT GASES FOR CATALYST "A"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COG
202.00	39.873	0.40481	0.32052	0.03767	0.00000	0.22263	0.01437
202.00	26.853	0.41664	0.30893	0.04938	0.00000	0.21156	0.01349
202.00	69.748	0.39849	0.33843	0.02548	0.00000	0.22354	0.01406
230.00	74.048	0.42510	0.31152	0.05225	0.00000	0.19868	0.01245
230.00	30.791	0.46343	0.26345	0.09587	0.00037	0.16493	0.01190
230.00	55.081	0.43426	0.30249	0.06175	0.00041	0.18913	0.01196
254.00	59.347	0.46745	0.26973	0.09452	0.00021	0.15882	0.00928
254.00	76.181	0.45201	0.28709	0.07818	0.00028	0.17129	0.01115
254.00	37.124	0.50178	0.22488	0.13413	0.00016	0.12945	0.00959
280.00	40.477	0.54627	0.18075	0.17828	0.00000	0.08848	0.00622
280.00	54.409	0.52496	0.20674	0.15464	0.00005	0.10757	0.00604
280.00	90.654	0.47707	0.26394	0.10228	0.00029	0.14711	0.00932
306.00	97.442	0.51032	0.23129	0.13510	0.00016	0.11546	0.00766
306.00	47.743	0.56839	0.16006	0.19977	0.00010	0.06530	0.00637
306.00	74.005	0.52826	0.20945	0.15497	0.00012	0.10030	0.00691
330.00	82.463	0.54578	0.18902	0.17385	0.00000	0.08463	0.00672
330.00	116.461	0.51805	0.22508	0.14208	0.00018	0.10623	0.00839
330.00	96.818	0.53345	0.20681	0.15887	0.00012	0.09301	0.00774
355.00	115.760	0.54477	0.19812	0.16884	0.00010	0.08132	0.00685
355.00	80.141	0.56701	0.16482	0.19658	0.00000	0.06447	0.00711
355.00	151.335	0.51781	0.23466	0.13716	0.00023	0.10155	0.00859
379.00	170.727	0.53569	0.21881	0.15382	0.00004	0.08314	0.00850
379.00	94.526	0.56505	0.16864	0.19385	0.00017	0.06576	0.00653
379.00	138.209	0.54784	0.19945	0.16970	0.00012	0.07475	0.00813
403.00	142.392	0.55324	0.19383	0.17509	0.00000	0.07055	0.00730
403.00	98.228	0.56038	0.17533	0.18812	0.00014	0.06921	0.00681
403.00	204.911	0.53191	0.23422	0.14441	0.00030	0.08147	0.00770

TABLE 24. ARRHENIUS DATA FOR CATALYST "A"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	3.76	6.51	1.87	2.105
230	12.42	21.49	3.07	1.988
254	25.92	44.84	3.80	1.897
280	50.23	86.90	4.46	1.808
306	84.88	146.85	4.99	1.727
330	114.63	198.32	5.29	1.658
355	180.96	313.08	5.75	1.592
379	240.55	416.18	6.03	1.533
403	278.41	481.68	6.18	1.479

(a) Catalyst contains .0385 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.29.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.578 grams

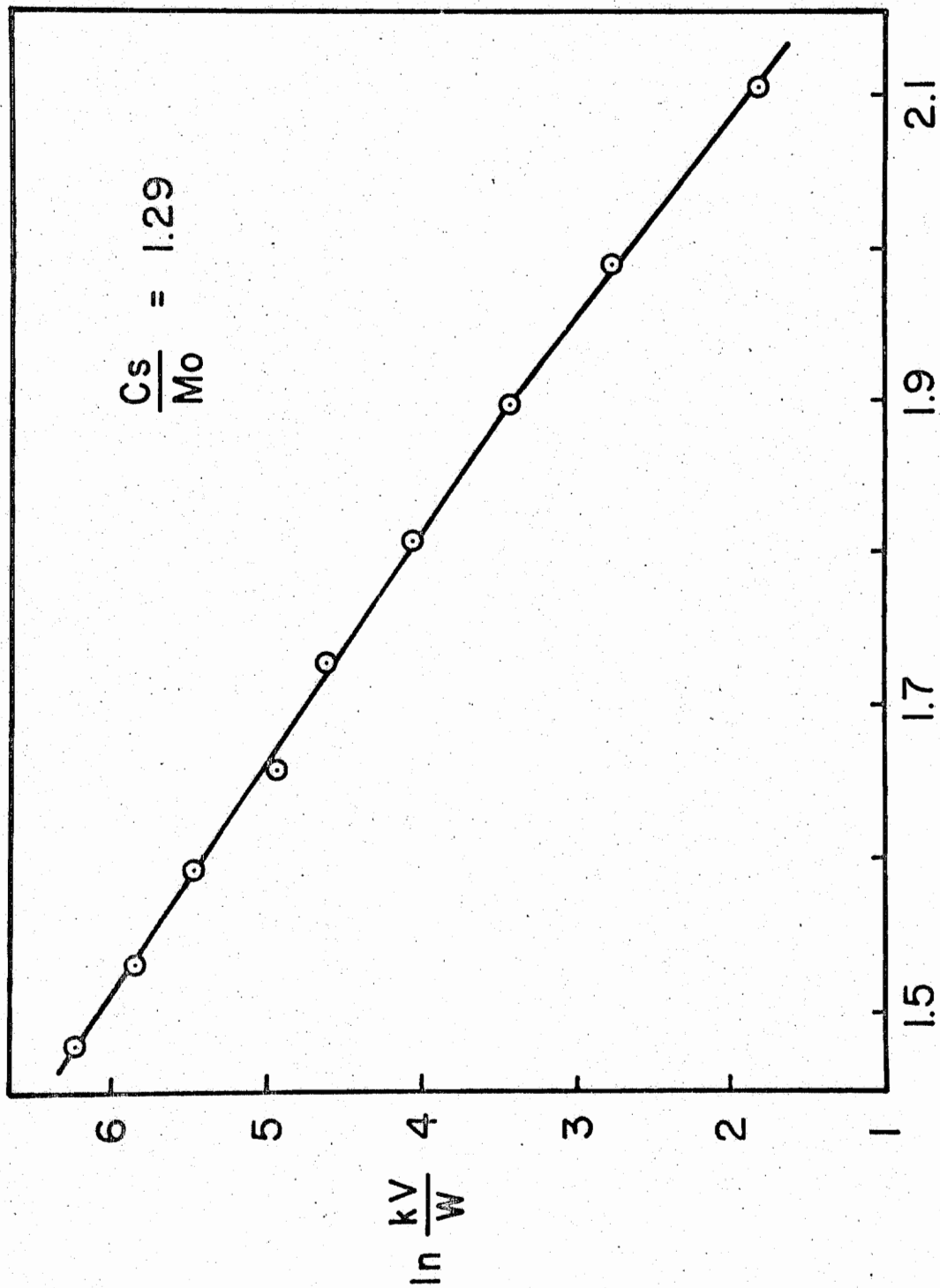


Figure 16. Arrhenius Plot for Catalyst "A"

TABLE 25. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "B"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
204.00	36.826	0.40804	0.53232	0.03384	0.00040	0.21145	0.01426
204.00	23.038	0.42315	0.31961	0.04750	0.00032	0.19740	0.01201
204.00	66.221	0.40239	0.34746	0.02308	0.00000	0.21523	0.01133
231.00	77.077	0.42326	0.33149	0.04153	0.00030	0.18976	0.01367
231.00	42.022	0.44739	0.29044	0.07415	0.00023	0.17679	0.01101
231.00	21.156	0.47684	0.25808	0.10511	0.00026	0.14931	0.00990
252.00	21.930	0.54682	0.18654	0.17460	0.00000	0.08248	0.00756
252.00	41.150	0.48125	0.26181	0.10537	0.00024	0.14249	0.00885
252.00	66.061	0.45233	0.29155	0.07580	0.00000	0.17147	0.00885
252.00	122.833	0.43134	0.31504	0.05355	0.00000	0.19054	0.00954
278.00	130.878	0.45120	0.30823	0.06705	0.00026	0.16104	0.01222
278.00	63.630	0.49763	0.24606	0.12136	0.00017	0.12619	0.00858
278.00	33.180	0.55804	0.17959	0.18467	0.00000	0.07121	0.00649
299.00	35.581	0.57955	0.14916	0.21070	0.00000	0.05412	0.00648
299.00	64.379	0.52995	0.21295	0.15399	0.00007	0.09679	0.00625
299.00	106.590	0.48548	0.26135	0.10778	0.00033	0.13695	0.00811
327.00	112.735	0.51782	0.22747	0.14064	0.00006	0.10500	0.00902
327.00	68.699	0.56569	0.17141	0.19259	0.00000	0.06466	0.00565
327.00	39.807	0.58497	0.14285	0.21657	0.00000	0.05053	0.00509
351.00	59.281	0.57557	0.15329	0.20664	0.00000	0.05780	0.00669
351.00	136.690	0.52067	0.22474	0.14359	0.00022	0.10242	0.00836
351.00	63.415	0.56258	0.17184	0.19083	0.00000	0.06906	0.00568
377.00	89.827	0.56662	0.16437	0.19636	0.00000	0.06581	0.00633
377.00	128.057	0.54879	0.18973	0.17504	0.00007	0.07907	0.00730
377.00	193.863	0.51677	0.23593	0.13606	0.00028	0.10249	0.00848
402.00	156.052	0.55085	0.19345	0.17411	0.00000	0.07420	0.00740
402.00	90.586	0.56176	0.17178	0.19046	0.00000	0.06864	0.00735
402.00	106.996	0.55874	0.17572	0.18704	0.00007	0.07131	0.00712

TABLE 26. ARRHENIUS DATA FOR CATALYST "B"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
204	3.05	5.25	1.66	2.096
231	10.21	17.57	2.87	1.984
252	25.64	44.13	3.79	1.904
278	47.17	81.19	4.40	1.814
299	75.13	129.31	4.86	1.748
327	109.26	188.06	5.24	1.666
351	160.93	276.99	5.62	1.602
377	231.72	398.83	5.99	1.538
402	266.97	459.50	6.13	1.481

(a) Catalyst contains 0.0323 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.07.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.581 grams

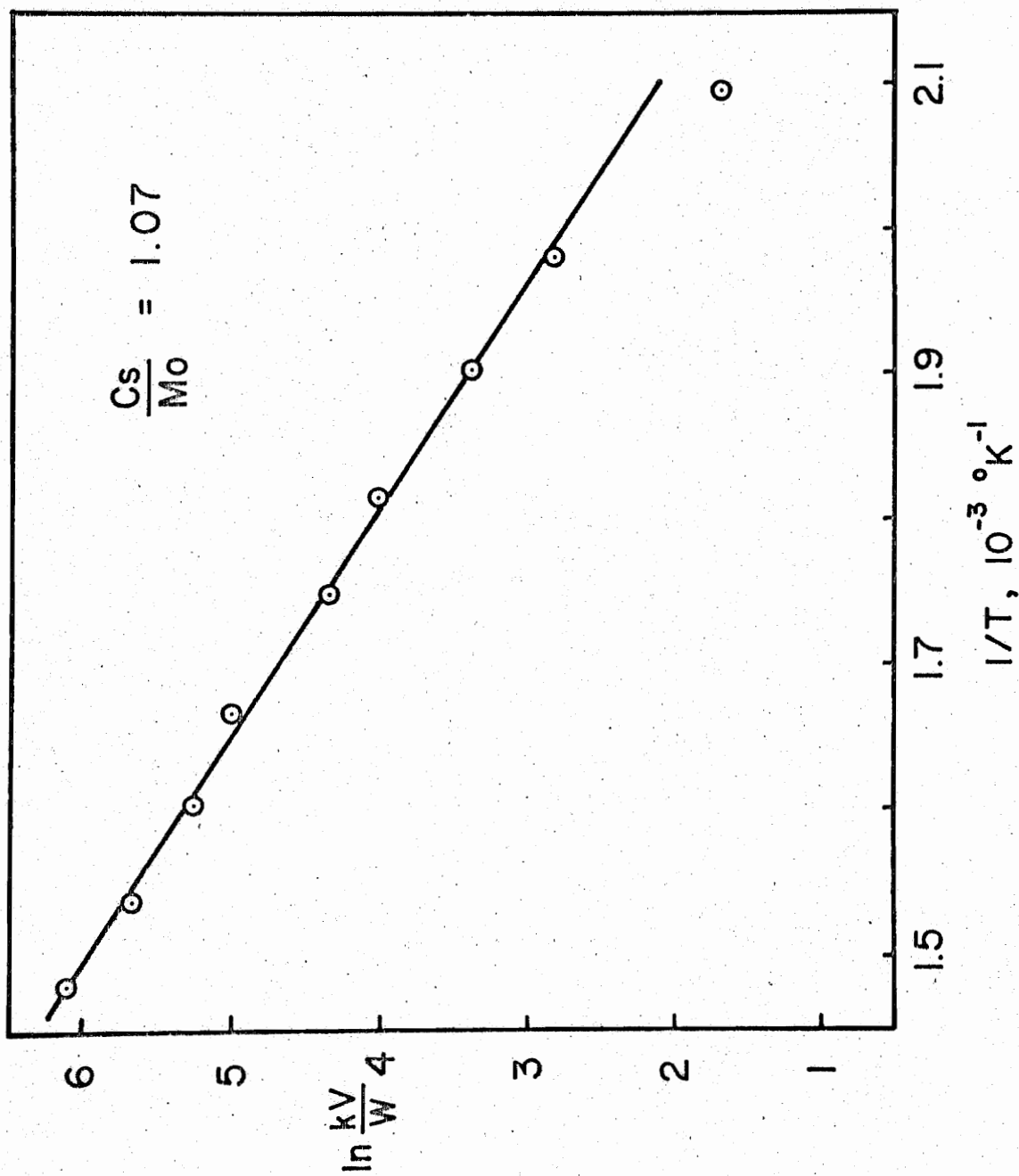


Figure 17. Arrhenius Plot for Catalyst "A"

TABLE 27. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "C"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
203.00	33.169	0.39772	0.32004	0.03441	0.00000	0.23428	0.01355
203.00	57.025	0.39152	0.33619	0.02317	0.00000	0.23477	0.01435
203.00	40.630	0.39272	0.32577	0.02904	0.00000	0.23902	0.01345
230.00	45.624	0.40651	0.29972	0.04903	0.00000	0.23095	0.01378
230.00	30.887	0.43033	0.28114	0.07020	0.00000	0.20594	0.01239
230.00	70.394	0.40594	0.32523	0.03584	0.00000	0.22088	0.01211
257.00	84.462	0.41963	0.30321	0.05375	0.00000	0.21003	0.01338
257.00	41.260	0.44484	0.25934	0.08961	0.00121	0.19432	0.01068
257.00	51.985	0.43753	0.27961	0.07571	0.00117	0.19472	0.01126
281.00	56.209	0.46628	0.24848	0.10486	0.00037	0.16925	0.01077
281.00	91.817	0.44064	0.29798	0.06750	0.00073	0.18089	0.01226
281.00	45.260	0.48022	0.23147	0.12119	0.00121	0.15656	0.00935
304.00	106.733	0.45535	0.29075	0.07811	0.00041	0.16430	0.01108
304.00	44.406	0.51390	0.20433	0.15072	0.00037	0.12092	0.00977
304.00	60.464	0.48713	0.23745	0.12137	0.00100	0.14361	0.00943
328.00	63.707	0.51128	0.20268	0.14998	0.00019	0.12616	0.00952
328.00	140.662	0.46382	0.29423	0.08064	0.00052	0.14952	0.01127
328.00	99.034	0.47937	0.26042	0.10578	0.00087	0.14291	0.01066
353.00	105.924	0.50375	0.23038	0.13241	0.00026	0.12220	0.01100
353.00	77.808	0.53041	0.19220	0.16531	0.00067	0.10335	0.00807
353.00	158.632	0.47561	0.28530	0.09166	0.00120	0.13519	0.01105
380.00	165.259	0.50416	0.26365	0.11582	0.00030	0.10564	0.01043
380.00	77.606	0.55487	0.17008	0.18859	0.00067	0.07634	0.00944
380.00	110.674	0.53016	0.20826	0.15780	0.00141	0.09335	0.00901
401.00	122.177	0.53994	0.19709	0.16795	0.00107	0.08491	0.00904
401.00	84.027	0.55181	0.17024	0.18777	0.00144	0.07979	0.00894
401.00	151.223	0.52097	0.23088	0.14168	0.00127	0.09611	0.00910

TABLE 28. ARRHENIUS DATA FOR CATALYST "C"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	2.00	3.37	1.21	2.100
230	7.31	12.31	2.51	1.988
257	14.25	23.99	3.18	1.886
281	26.62	44.81	3.80	1.805
304	40.61	68.37	4.22	1.733
328	60.19	101.33	4.62	1.664
353	99.05	166.75	5.12	1.597
380	171.40	288.55	5.66	1.531
401	209.66	352.96	5.87	1.483

(a) Catalyst contains 0.0133 grams cesium acetate per gram impregnated catalyst. The cesium:molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.594 grams

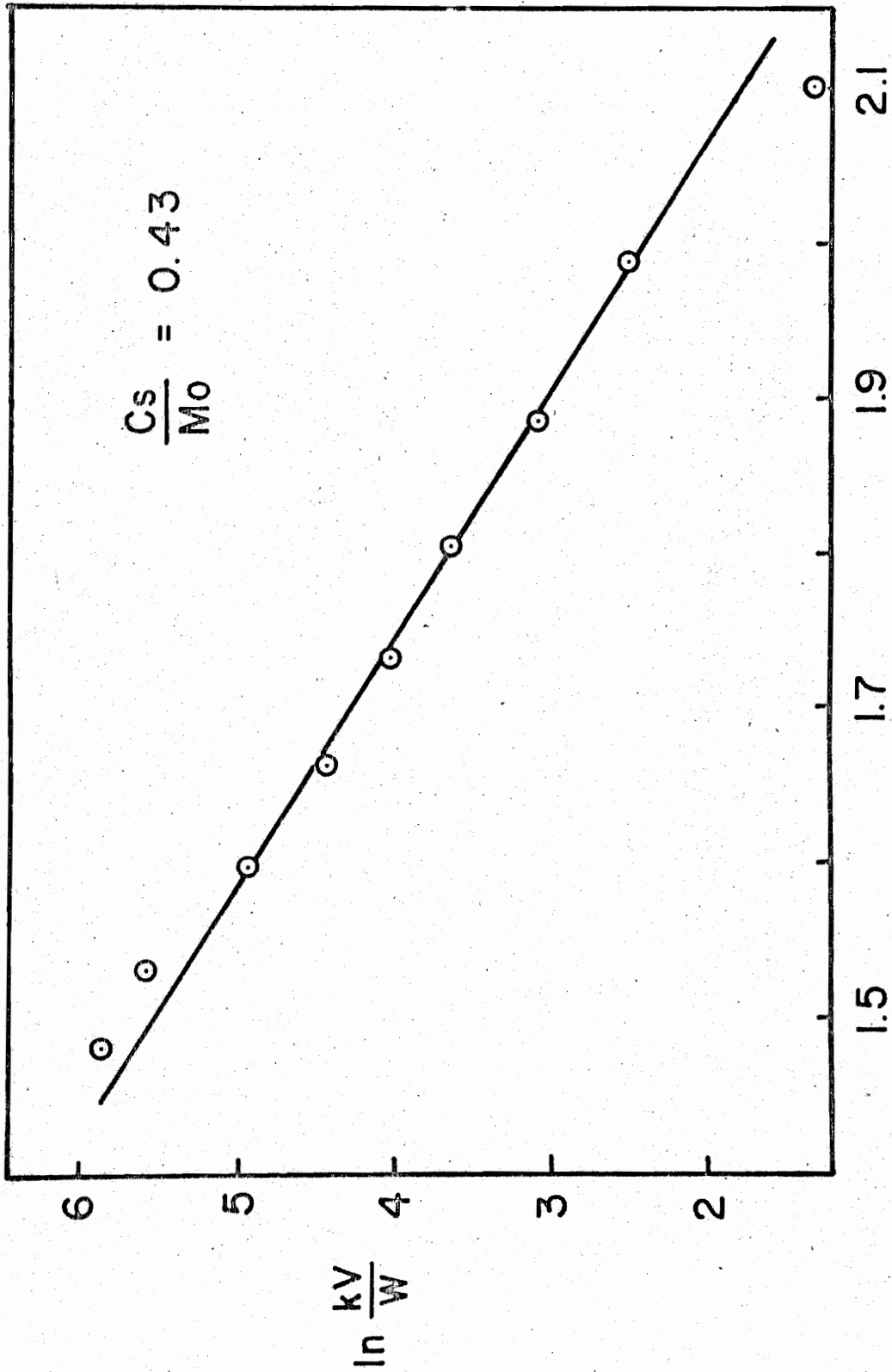


Figure 18. Arrhenius Plot for Catalyst "C"

TABLE 29. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "D"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	COS
205.00	32.672	0.39886	0.32167	0.03415	0.00000	0.23143	0.01390
205.00	39.309	0.39608	0.32999	0.02856	0.00000	0.23230	0.01307
205.00	62.291	0.39334	0.34171	0.02128	0.00000	0.23063	0.01304
234.00	75.627	0.41291	0.32437	0.03972	0.00000	0.21284	0.01016
234.00	30.632	0.43350	0.29047	0.06860	0.00155	0.19571	0.01017
234.00	49.441	0.41618	0.31050	0.05018	0.00183	0.21075	0.01056
257.00	47.465	0.45344	0.27398	0.08578	0.00054	0.17574	0.01053
257.00	70.790	0.42961	0.30877	0.05728	0.00141	0.19106	0.01188
257.00	41.828	0.45682	0.27031	0.09029	0.00153	0.17070	0.01036
282.00	45.128	0.48604	0.23247	0.12343	0.00108	0.14662	0.01035
282.00	98.398	0.43981	0.30650	0.06402	0.00197	0.17716	0.01052
282.00	51.508	0.47329	0.25106	0.10841	0.00177	0.15699	0.00848
310.00	55.146	0.50297	0.22396	0.13515	0.00013	0.12919	0.00860
310.00	75.974	0.47921	0.25512	0.10849	0.00098	0.14702	0.00918
310.00	149.575	0.45234	0.32134	0.06181	0.00108	0.15164	0.01180
333.00	154.924	0.46766	0.30224	0.07840	0.00044	0.14005	0.01119
333.00	63.203	0.51452	0.21299	0.14729	0.00102	0.11483	0.00936
333.00	52.089	0.53712	0.18512	0.17305	0.00151	0.09558	0.00763
356.00	74.584	0.53008	0.20079	0.16026	0.00013	0.09980	0.00895
356.00	92.142	0.50911	0.22485	0.13880	0.00120	0.11657	0.00948
356.00	139.713	0.48226	0.27652	0.09965	0.00146	0.13042	0.00969
382.00	153.318	0.50370	0.26238	0.11628	0.00035	0.10703	0.01026
382.00	102.363	0.53058	0.20511	0.15921	0.00101	0.09439	0.00970
382.00	82.410	0.54312	0.17869	0.17977	0.00201	0.08785	0.00856
405.00	98.751	0.54666	0.19306	0.17243	0.00019	0.07865	0.00901
405.00	169.007	0.51259	0.25533	0.12515	0.00126	0.09644	0.00924
405.00	128.753	0.53083	0.21863	0.15329	0.00182	0.08766	0.00777

TABLE 30. ARRHENIUS DATA FOR CATALYST "D"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
205	1.97	3.29	1.19	2.091
234	6.98	11.67	2.46	1.972
257	15.89	26.72	3.29	1.886
282	27.57	46.10	3.83	1.801
310	43.23	72.29	4.28	1.715
333	69.03	115.43	4.75	1.650
356	92.91	155.37	5.05	1.589
382	149.38	249.80	5.52	1.526
405	200.51	335.3	5.82	1.475

(a) Catalyst contains 0.00662 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.21.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.598 grams

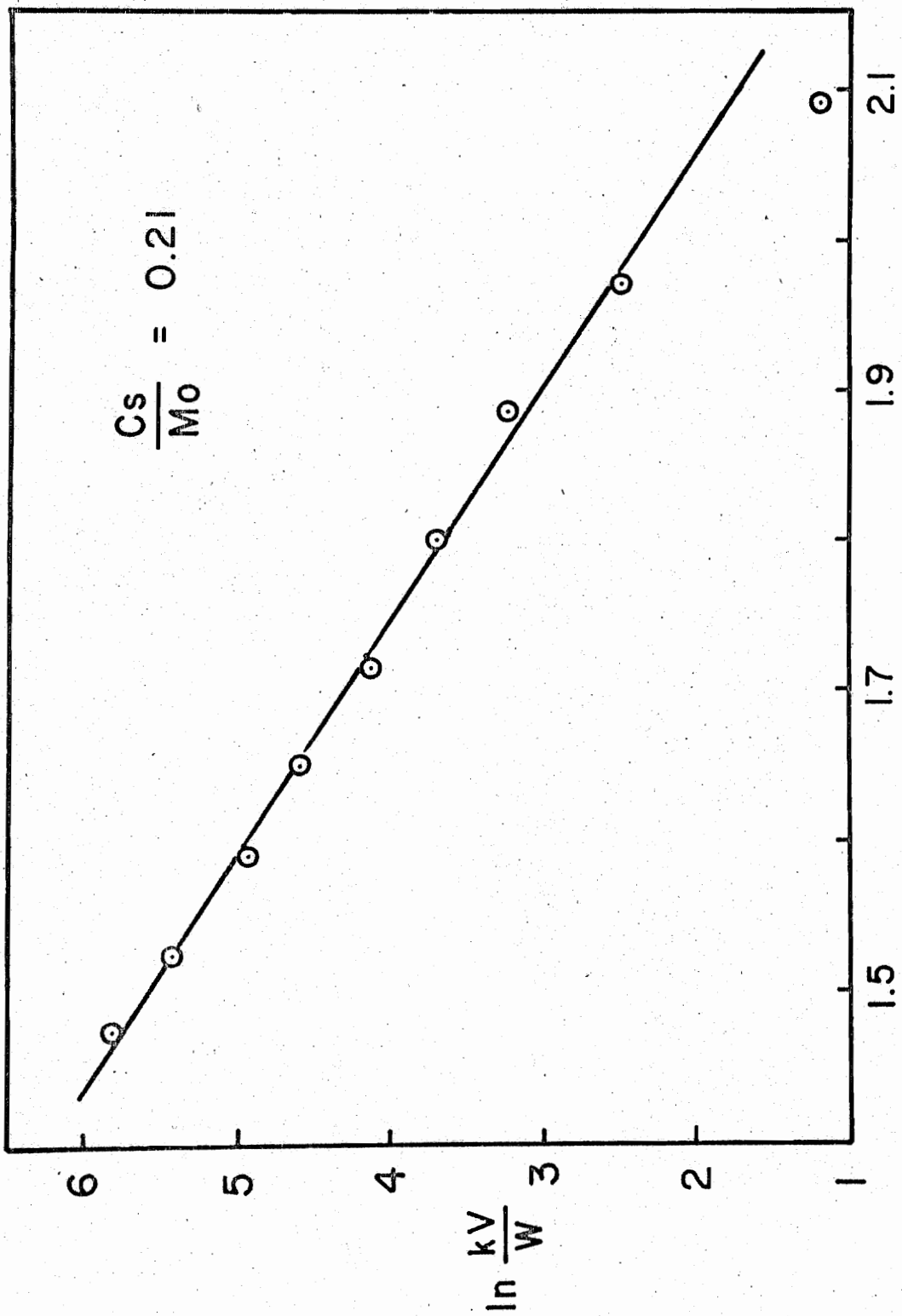


Figure 19. Arrhenius Plot for Catalyst "D"

TABLE 31. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "E"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
205.00	28.839	0.40895	0.32560	0.03714	0.00000	0.21459	0.01372
205.00	53.064	0.39309	0.33936	0.02235	0.00000	0.23152	0.01368
205.00	39.450	0.39652	0.32841	0.02958	0.00000	0.23394	0.01156
231.00	41.700	0.42328	0.30214	0.05610	0.00000	0.20257	0.01592
231.00	56.909	0.41169	0.32120	0.04072	0.00000	0.21150	0.01489
231.00	27.336	0.44340	0.28953	0.07279	0.00037	0.18308	0.01083
256.00	42.256	0.45390	0.26610	0.08579	0.00034	0.17581	0.01405
256.00	66.000	0.42843	0.30318	0.05811	0.00200	0.19652	0.01377
256.00	81.880	0.42645	0.31791	0.04958	0.00000	0.19232	0.01354
279.00	106.450	0.43414	0.31160	0.05667	0.00000	0.18504	0.01256
279.00	39.440	0.48724	0.24693	0.11607	0.00045	0.13871	0.01060
279.00	58.512	0.46213	0.28010	0.08697	0.00051	0.15886	0.01139
307.00	62.680	0.47769	0.24458	0.11266	0.00056	0.15505	0.00946
307.00	44.023	0.51382	0.21769	0.14386	0.00031	0.11556	0.00877
307.00	94.984	0.45892	0.28955	0.08069	0.00062	0.15866	0.01156
329.00	100.781	0.47171	0.27363	0.09484	0.00040	0.14704	0.01239
329.00	52.492	0.52139	0.19990	0.15661	0.00032	0.11100	0.01077
329.00	67.458	0.49943	0.23448	0.12842	0.00047	0.12742	0.00977
351.00	71.786	0.51484	0.20867	0.14909	0.00047	0.11696	0.00997
351.00	105.255	0.48474	0.26119	0.10767	0.00050	0.13514	0.01077
351.00	51.799	0.54405	0.18530	0.17510	0.00023	0.08599	0.00932
382.00	58.131	0.55369	0.16174	0.19188	0.00032	0.08398	0.00840
382.00	132.131	0.49597	0.26293	0.11245	0.00062	0.11804	0.00999
382.00	75.757	0.53996	0.19631	0.16771	0.00044	0.08665	0.00893
382.00	98.210	0.51723	0.22884	0.14014	0.00055	0.10374	0.00949
402.00	109.545	0.52640	0.21242	0.15268	0.00025	0.09825	0.01000
402.00	82.589	0.54342	0.18476	0.17536	0.00053	0.08834	0.00759
402.00	160.618	0.50062	0.26788	0.11228	0.00066	0.10963	0.00889

TABLE 32. ARRHENIUS DATA FOR CATALYST "E"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
205	2.22	3.69	1.31	2.09
231	7.33	12.18	2.50	1.98
256	15.48	25.71	3.25	1.89
279	23.47	38.99	3.66	1.81
307	38.49	63.94	4.16	1.72
329	55.83	92.74	4.53	1.66
351	79.80	132.56	4.89	1.60
382	128.17	212.91	5.36	1.53
402	158.15	262.71	5.57	1.48

(a) Catalyst contains no cesium acetate. The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate and ammonium molybdate. One gram catalyst contains  $8.72 \cdot 10^{-5}$  moles cobalt and  $1.623 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.537.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>  
 V = volume of catalyst bed not including inert solids, cm<sup>3</sup>  
 W = weight of catalyst used, 0.602 grams



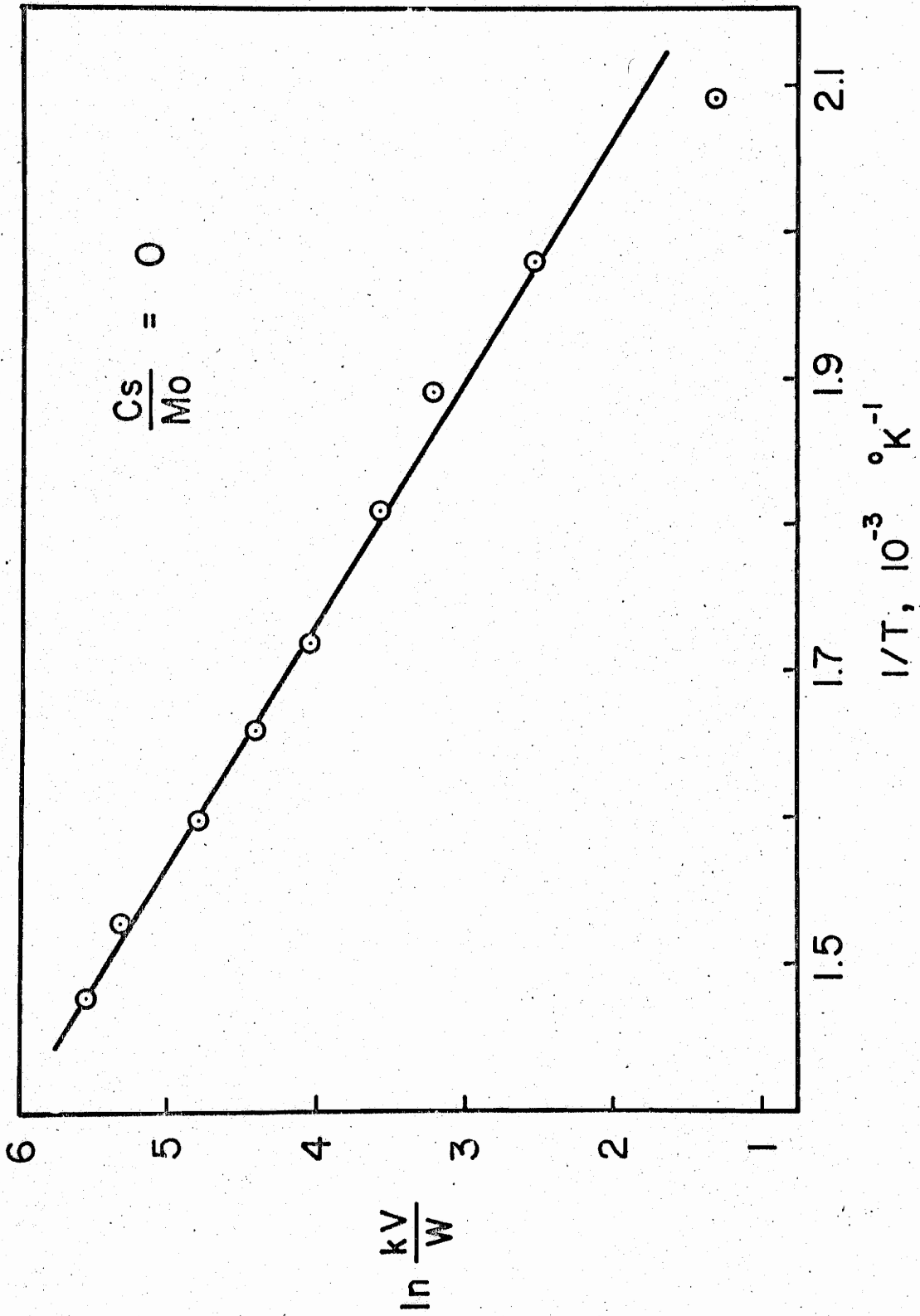


Figure 20. Arrhenius Plot for Catalyst "E"

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TABLE 33. COMPOSITIONS OF ONE-HALF STRENGTH CATALYSTS

Catalyst number	Salt	Weight dry catalyst (grams)	Weight salt (grams)	Weight salt per gram impregnated catalyst	Cesium:molybdenum ratio
F	cesium acetate	1.000	0.200	0.167	2.44
H	cesium acetate	5.2299	0.701	0.118	1.64
I	cesium acetate	5.2299	0.560	0.0967	1.31
J	cesium acetate	5.2299	0.467	0.0820	1.09
K	cesium acetate	5.2300	0.328	0.0590	0.77
L	cesium acetate	5.2299	0.1878	0.0347	0.44
M	cesium acetate	5.2302	0.0933	0.0175	0.22
N	none	5.2429	0.000	0.000	0.00
O	cesium acetate	4.3977 <sup>(b)</sup>	0.701	0.137	$\infty$

TABLE 33 (con't)

- (a) The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate (MW 291.05) and ammonium molybdate (MW 1235.95). One gram of catalyst, in the absence of cesium acetate, contains  $2.29 \cdot 10^{-4}$  moles cobalt and  $4.27 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.538. The catalyst particle mesh range is 20/60.
- (b) No cobalt or molybdenum is present.

TABLE 34. AMOUNTS OF ONE-HALF STRENGTH CATALYSTS USED IN WATER GAS SHIFT STUDIES

Catalyst number	Cesium:molybdenum ratio	Weight catalyst used in reactor (grams)	Weight inert solids used in reactor (grams)	$W^{(b)}$ (grams)
F	2.44	0.330	1.17	0.275
H	1.64	0.302	1.20	0.266
I	1.31	0.303	1.20	0.274
J	1.09	0.303	1.20	0.278
K	0.77	0.301	1.20	0.283
L	0.44	0.303	1.20	0.293
M	0.22	0.300	1.20	0.295
N	0.00	0.301	1.20	0.301
O	$\infty$ (b)	---	1.20	0.308

(a) The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate (MW 291.05) and ammonium molybdate (MW 1235.95). One gram of catalyst, in the absence of cesium acetate, contains  $2.29 \cdot 10^{-4}$  moles cobalt and  $4.27 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.538. The catalyst particle mesh range is 20/60.

(b) No cobalt or molybdenum is present.

TABLE 35. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "F"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2S
201.00	45.363	0.38977	0.33235	0.02425	0.00000	0.25362	0.00000
201.00	25.238	0.38482	0.30554	0.03538	0.00000	0.27425	0.00000
201.00	73.694	0.37482	0.32679	0.01968	0.00000	0.27871	0.00000
225.00	85.848	0.37048	0.30618	0.02797	0.00000	0.29536	0.00000
225.00	44.039	0.38279	0.29036	0.04206	0.00000	0.28473	0.00000
225.00	28.408	0.40378	0.27654	0.05942	0.00000	0.26027	0.00000
251.00	30.247	0.44372	0.22859	0.10341	0.00000	0.22428	0.00000
251.00	73.925	0.40275	0.28828	0.05297	0.00000	0.25601	0.00000
251.00	50.429	0.41216	0.26424	0.06978	0.00000	0.25381	0.00000
281.00	52.933	0.46853	0.21278	0.12367	0.00000	0.19502	0.00000
281.00	61.479	0.45756	0.22608	0.11152	0.00000	0.20484	0.00000
281.00	110.943	0.42504	0.26992	0.07327	0.00000	0.23177	0.00000
299.00	115.452	0.44943	0.24009	0.10041	0.00000	0.21007	0.00000
299.00	64.613	0.50162	0.18285	0.15516	0.00000	0.16037	0.00000
299.00	82.986	0.48330	0.21218	0.13127	0.00000	0.17325	0.00000
325.00	88.544	0.52266	0.15204	0.18114	0.00000	0.14415	0.00000
325.00	136.846	0.48692	0.20745	0.13545	0.00000	0.17019	0.00000
325.00	107.218	0.50243	0.17154	0.16128	0.00000	0.16475	0.00000
351.00	110.904	0.55569	0.13664	0.20525	0.00000	0.10241	0.00000
351.00	155.693	0.52685	0.17644	0.17086	0.00000	0.12584	0.00000
351.00	213.704	0.50123	0.21735	0.13751	0.00000	0.14391	0.00000
376.00	218.648	0.54149	0.18899	0.17174	0.00000	0.09778	0.00000
376.00	153.185	0.55248	0.15411	0.19482	0.00000	0.09859	0.00000
376.00	356.602	0.50927	0.25587	0.12198	0.00000	0.11288	0.00000
407.00	253.993	0.54628	0.17408	0.18165	0.00000	0.09799	0.00000
407.00	211.497	0.54474	0.15291	0.19161	0.00000	0.11073	0.00000
407.00	344.067	0.53549	0.21702	0.15459	0.00000	0.09291	0.00000

TABLE 36. ARRHENIUS DATA FOR CATALYST "F"

T, °C	Slope, kV		Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
	cm <sup>3</sup> /min	cm <sup>3</sup> /min		ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
201	1.64	5.96	1.79	2.11	
225	4.65	16.91	2.83	2.01	
251	11.54	41.96	3.74	1.91	
281	28.10	102.18	4.63	1.81	
299	51.80	188.36	5.24	1.75	
325	99.18	360.65	5.89	1.67	
351	195.33	710.29	6.57	1.60	
376	285.30	1037.45	6.94	1.54	
407	431.52	1569.16	7.36	1.47	

(a) Catalyst contains 0.167 grams cesium acetate per gram impregnated catalyst. The cesium: molybdenum molar ratio is 2.44.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.275 grams

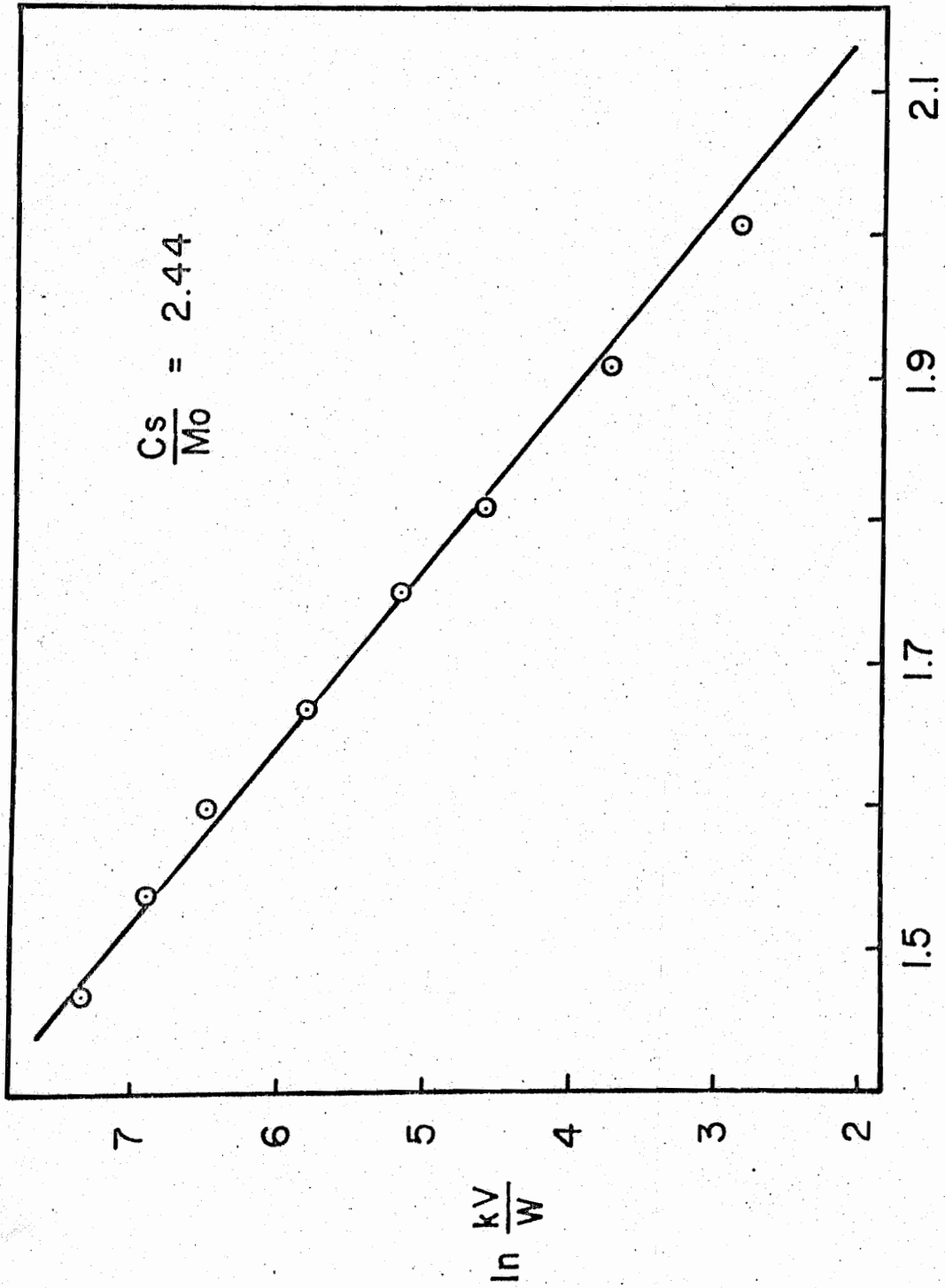


Figure 21. Arrhenius Plot for Catalyst "F"

TABLE 37. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "H"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2
203.00	41.628	0.41202	0.35973	0.02138	0.00000	0.20688	0.00000
203.00	32.312	0.41146	0.34979	0.02614	0.00000	0.20767	0.00494
203.00	24.813	0.41528	0.34529	0.03030	0.00000	0.20913	0.00000
231.00	58.652	0.42204	0.34902	0.03175	0.00000	0.19064	0.00655
231.00	39.760	0.42846	0.32824	0.04544	0.00000	0.19325	0.00461
231.00	34.437	0.43411	0.32124	0.05177	0.00000	0.19288	0.00000
259.00	86.212	0.44506	0.34249	0.04643	0.00000	0.16041	0.00562
259.00	66.666	0.44425	0.32033	0.05724	0.00000	0.17224	0.00594
259.00	43.064	0.46980	0.28566	0.08741	0.00000	0.15714	0.00000
280.00	91.950	0.46732	0.32009	0.06875	0.00000	0.13801	0.00583
280.00	57.283	0.49034	0.27586	0.10251	0.00000	0.12747	0.00382
280.00	42.588	0.51322	0.24192	0.13099	0.00000	0.11388	0.00000
307.00	97.406	0.50664	0.27399	0.11151	0.00000	0.10312	0.00474
307.00	73.846	0.52486	0.24444	0.13546	0.00000	0.09139	0.00385
307.00	61.917	0.54285	0.21328	0.16012	0.00000	0.08375	0.00000
332.00	128.025	0.53064	0.26001	0.13043	0.00000	0.07487	0.00405
332.00	100.453	0.54999	0.22631	0.15705	0.00000	0.06386	0.00279
332.00	80.674	0.56501	0.19273	0.18146	0.00000	0.05806	0.00274
359.00	157.472	0.54831	0.24990	0.14428	0.00000	0.05383	0.00368
359.00	132.090	0.56405	0.22494	0.16469	0.00000	0.04389	0.00243
359.00	92.760	0.57477	0.18643	0.18947	0.00000	0.04669	0.00264
382.00	211.935	0.54838	0.26918	0.13455	0.00000	0.04482	0.00306
382.00	121.182	0.56890	0.20171	0.17884	0.00000	0.04758	0.00297
382.00	107.365	0.57002	0.19542	0.18258	0.00000	0.04797	0.00401
404.00	220.717	0.55386	0.26771	0.13800	0.00000	0.03670	0.00373
404.00	156.801	0.56424	0.22660	0.16394	0.00000	0.04398	0.00123
404.00	125.909	0.56321	0.21391	0.16986	0.00000	0.04952	0.00350

TABLE 38. ARRHENIUS DATA FOR CATALYST "H"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/M <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	0.85	3.20	1.16	2.100
231	4.90	18.42	2.91	1.983
259	15.70	59.02	4.08	1.879
280	30.47	114.55	4.74	1.808
307	67.88	255.19	5.54	1.724
332	138.00	518.80	6.25	1.652
359	227.15	853.95	6.75	1.582
382	283.48	1065.71	6.97	1.526
404	322.99	1214.25	7.10	1.477

(a) Catalyst contains 0.118 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.64.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.266 grams

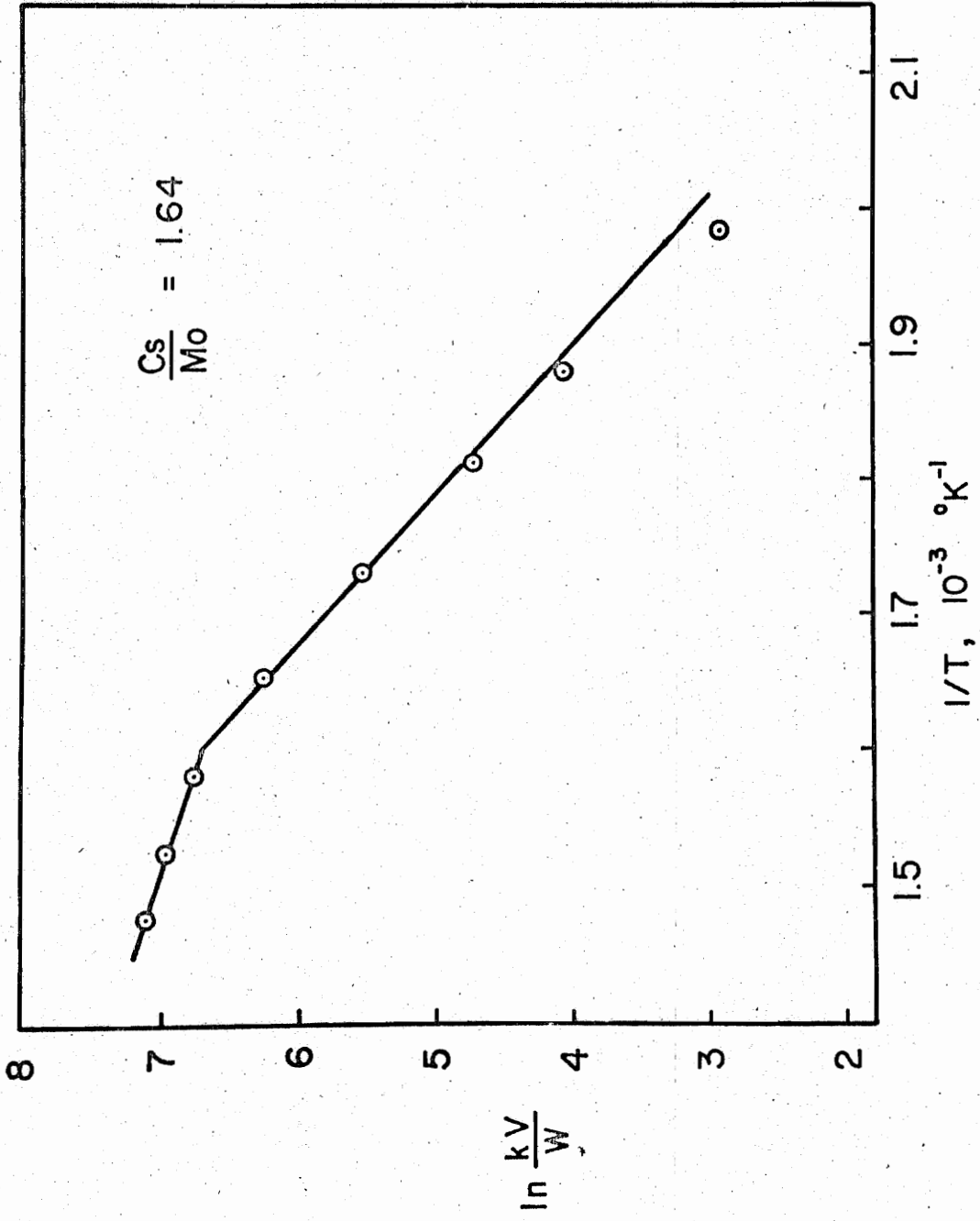


Figure 22. Arrhenius Plot for Catalyst "H"

TABLE 39. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "I"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
204.00	56.590	0.38763	0.33210	0.02333	0.00000	0.24349	0.01345
204.00	38.368	0.38993	0.32416	0.02848	0.00000	0.24851	0.00892
204.00	34.718	0.39298	0.32370	0.03022	0.00000	0.24397	0.00913
232.00	69.943	0.39967	0.31989	0.03545	0.00000	0.23604	0.00896
232.00	39.073	0.42488	0.29761	0.05918	0.00000	0.21833	0.00000
232.00	30.268	0.42626	0.28858	0.06443	0.00000	0.22074	0.00000
257.00	73.453	0.42833	0.30337	0.05796	0.00000	0.21034	0.00000
257.00	51.373	0.44221	0.27818	0.07757	0.00000	0.20204	0.00000
257.00	32.813	0.47107	0.24373	0.10926	0.00000	0.17594	0.00000
278.00	83.658	0.44874	0.27361	0.08311	0.00000	0.19455	0.00000
278.00	50.330	0.48199	0.22384	0.12472	0.00000	0.16945	0.00000
278.00	39.380	0.50722	0.20377	0.14733	0.00000	0.13784	0.00384
307.00	115.597	0.47229	0.25606	0.10362	0.00000	0.16267	0.00535
307.00	87.550	0.49423	0.22842	0.12844	0.00000	0.14891	0.00000
307.00	55.783	0.53132	0.17566	0.17347	0.00000	0.11769	0.00186
329.00	147.638	0.48919	0.24017	0.12001	0.00000	0.14531	0.00532
329.00	119.234	0.50147	0.22159	0.13548	0.00000	0.13676	0.00470
329.00	82.307	0.53460	0.16789	0.17902	0.00000	0.11478	0.00372
353.00	153.335	0.52213	0.21347	0.14979	0.00000	0.11462	0.00000
353.00	116.783	0.54259	0.17856	0.17756	0.00000	0.10129	0.00000
353.00	97.297	0.55812	0.15136	0.19900	0.00000	0.09151	0.00000
374.00	206.112	0.52274	0.21849	0.14755	0.00000	0.10720	0.00403
374.00	169.499	0.53717	0.19367	0.16724	0.00000	0.09915	0.00278
374.00	124.197	0.56100	0.15905	0.19653	0.00000	0.08343	0.00000
405.00	320.915	0.52622	0.24530	0.13569	0.00000	0.08913	0.00365
405.00	214.119	0.54640	0.20080	0.16819	0.00000	0.08005	0.00456
405.00	182.235	0.55135	0.18236	0.17997	0.00000	0.08397	0.00236

TABLE 40. ARRHENIUS DATA FOR CATALYST "I"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
204	1.49	5.44	1.69	2.096
232	6.19	22.59	3.12	1.980
257	14.70	53.65	3.98	1.887
278	29.92	109.20	4.69	1.815
307	60.06	219.20	5.39	1.724
329	100.54	366.93	5.91	1.661
353	166.89	609.09	6.41	1.597
374	243.96	890.36	6.79	1.546
405	370.70	1352.92	7.21	1.475

(a) Catalyst contains 0.0967 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.31.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.274 grams



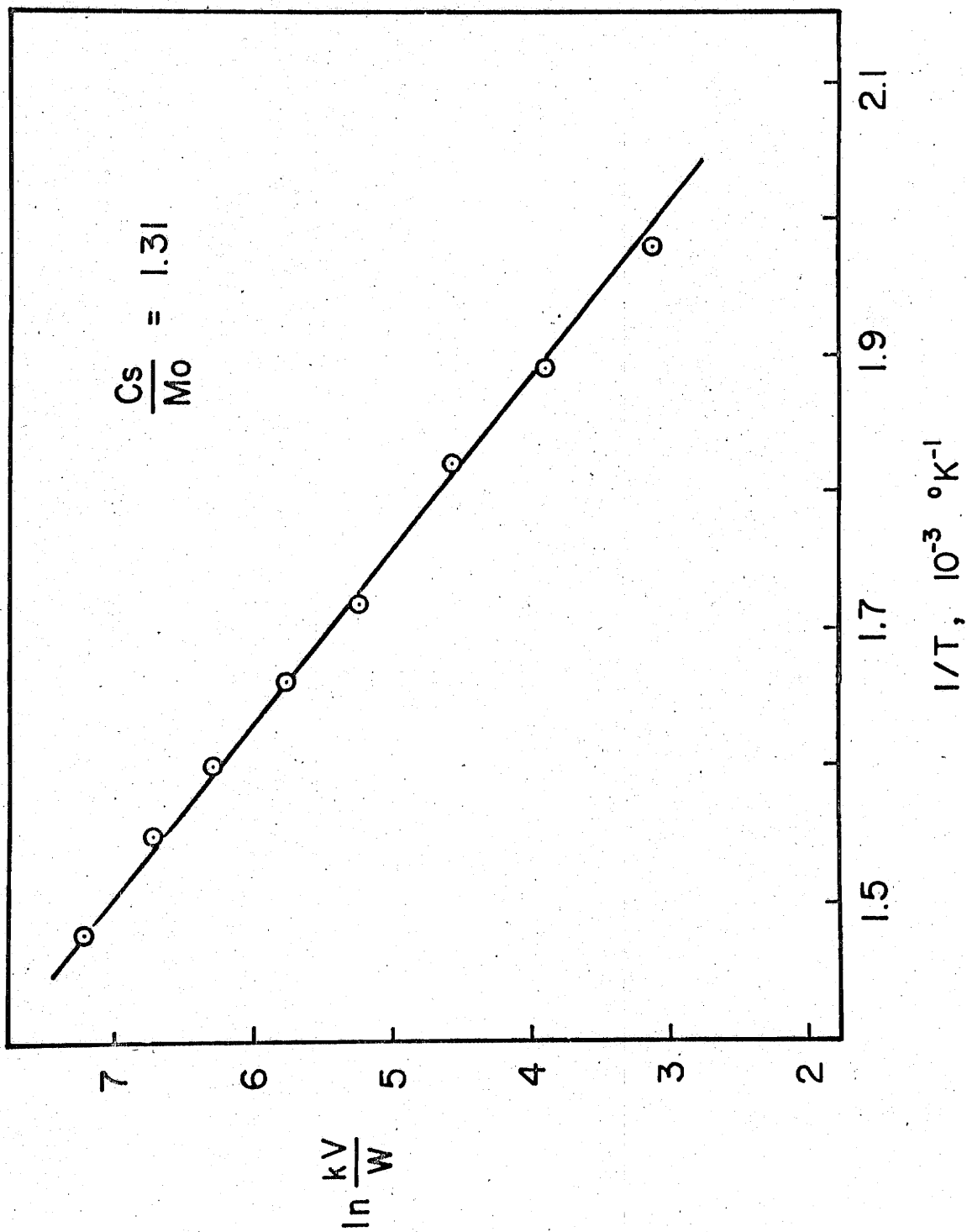


Figure 23. Arrhenius Plot for Catalyst "I"

TABLE 41. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "J"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	COS
206.00	51.676	0.41456	0.35656	0.02424	0.00000	0.19636	0.00828
206.00	35.547	0.41518	0.34443	0.03069	0.00000	0.20115	0.00855
206.00	29.887	0.41465	0.33426	0.03557	0.00000	0.20598	0.00854
233.00	76.747	0.42831	0.35559	0.03152	0.00000	0.17653	0.00805
233.00	51.214	0.43178	0.33872	0.04177	0.00000	0.17940	0.00833
233.00	32.186	0.44071	0.30431	0.06360	0.00000	0.18462	0.00676
257.00	74.345	0.44877	0.33389	0.05261	0.00000	0.15694	0.00778
257.00	42.879	0.46185	0.29202	0.08026	0.00000	0.15927	0.00660
257.00	33.124	0.48053	0.26645	0.10243	0.00000	0.14492	0.00566
277.00	78.790	0.47069	0.30557	0.07777	0.00000	0.13963	0.00634
277.00	59.499	0.48350	0.28277	0.09563	0.00000	0.13354	0.00456
277.00	45.112	0.50279	0.25234	0.12056	0.00000	0.12009	0.00422
308.00	92.383	0.50679	0.27619	0.11047	0.00000	0.10125	0.00530
308.00	74.421	0.51956	0.24770	0.13120	0.00000	0.09652	0.00502
308.00	64.182	0.53013	0.22640	0.14719	0.00000	0.09165	0.00463
332.00	118.986	0.52272	0.26759	0.12269	0.00000	0.08191	0.00510
332.00	76.148	0.55758	0.20645	0.17085	0.00000	0.06202	0.00310
332.00	61.677	0.56523	0.19030	0.18280	0.00000	0.06167	0.00000
358.00	142.957	0.54095	0.25743	0.13683	0.00000	0.06072	0.00407
358.00	103.443	0.55944	0.21583	0.16702	0.00000	0.05388	0.00383
358.00	80.384	0.57451	0.18695	0.18908	0.00000	0.04565	0.00380
381.00	165.442	0.55115	0.25024	0.14551	0.00000	0.04371	0.00438
381.00	136.691	0.55916	0.22830	0.16057	0.00000	0.04803	0.00394
381.00	97.294	0.56877	0.19752	0.18090	0.00000	0.04837	0.00444
407.00	185.980	0.61182	0.12435	0.23919	0.00000	0.02297	0.00167
407.00	118.499	0.56067	0.21809	0.16648	0.00000	0.05107	0.00369
407.00	100.614	0.56164	0.20511	0.17353	0.00000	0.05592	0.00379

TABLE 42. ARRHENIUS DATA FOR CATALYST "J"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
206	1.89	6.80	1.92	2.087
233	6.91	24.86	3.21	1.976
257	15.37	55.29	4.01	1.886
277	28.70	103.24	4.64	1.818
308	63.55	228.60	5.43	1.721
332	106.35	382.55	5.95	1.652
358	194.26	698.78	6.55	1.584
381	250.72	901.87	6.80	1.529
407	287.89	1035.57	6.94	1.470

(a) Catalyst contains 0.0820 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.09.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.278 grams



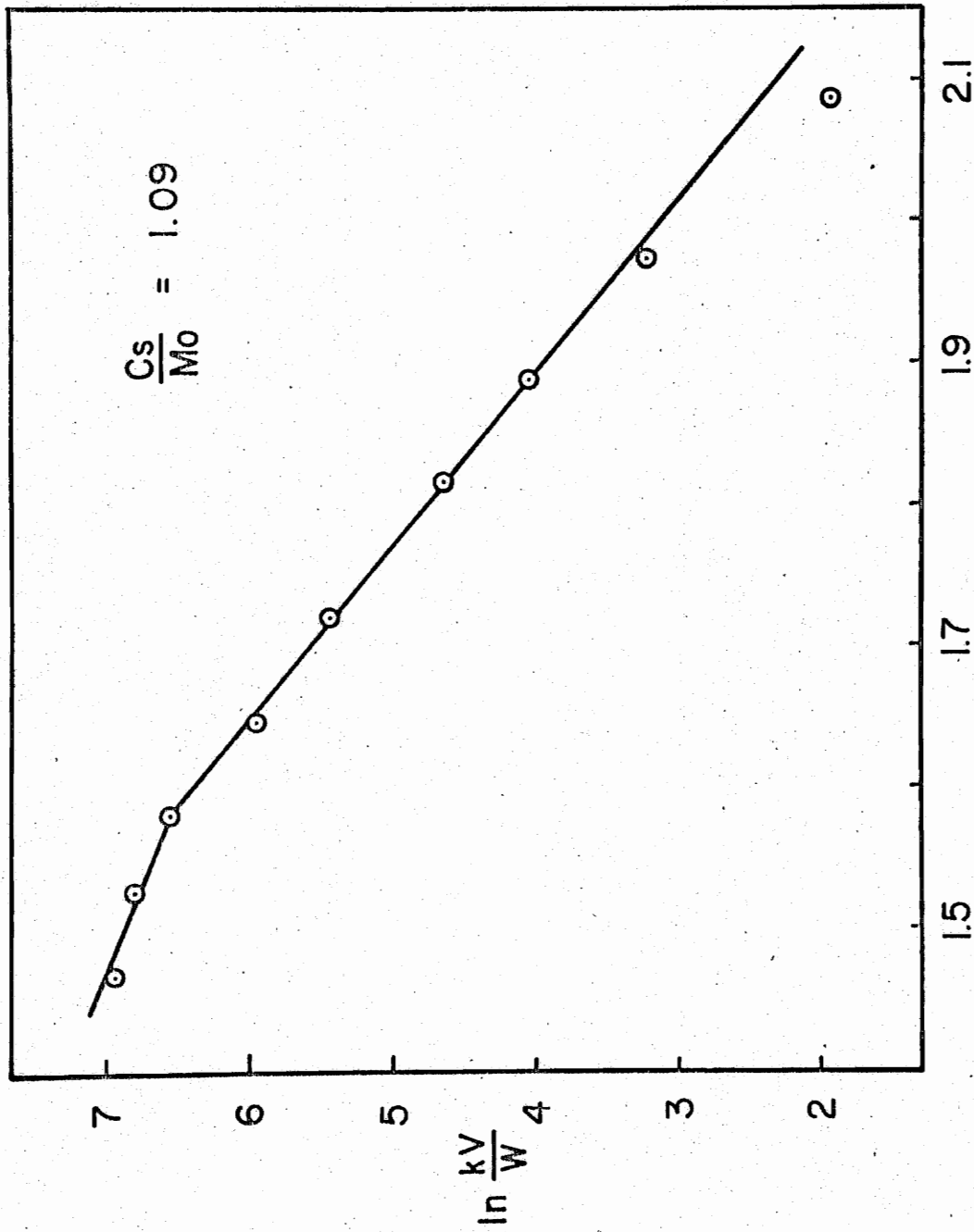


Figure 24. Arrhenius Plot for Catalyst "J"



TABLE 43. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "K"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
206.00	48.210	0.37607	0.31532	0.02610	0.00000	0.28251	0.00000
206.00	39.026	0.37585	0.30460	0.03143	0.00000	0.28812	0.00000
206.00	29.658	0.38797	0.30548	0.03696	0.00000	0.26958	0.00000
232.00	56.818	0.40023	0.30484	0.04334	0.00000	0.24772	0.00386
232.00	39.943	0.41021	0.29458	0.05347	0.00000	0.24174	0.00000
232.00	30.446	0.42104	0.28364	0.06435	0.00000	0.23097	0.00000
254.00	55.200	0.42209	0.28622	0.06356	0.00000	0.22812	0.00000
254.00	41.248	0.43802	0.26835	0.08047	0.00000	0.21316	0.00000
254.00	34.883	0.44362	0.25243	0.09130	0.00000	0.21264	0.00000
283.00	78.596	0.44039	0.26984	0.08089	0.00000	0.20887	0.00000
283.00	57.234	0.46413	0.24359	0.10590	0.00000	0.18638	0.00500
283.00	46.822	0.47417	0.23064	0.11741	0.00000	0.17778	0.00000
307.00	82.334	0.47118	0.24679	0.10776	0.00000	0.17427	0.00000
307.00	65.266	0.49541	0.20786	0.13944	0.00000	0.15730	0.00000
307.00	51.323	0.51890	0.17852	0.16588	0.00000	0.13670	0.00000
323.00	98.877	0.48925	0.22805	0.12617	0.00000	0.15653	0.00000
328.00	74.998	0.51014	0.19603	0.15270	0.00000	0.14113	0.00000
328.00	67.668	0.52716	0.17847	0.16999	0.00000	0.12438	0.00000
356.00	150.428	0.48341	0.25033	0.11201	0.00000	0.15425	0.00000
356.00	107.320	0.51219	0.20031	0.15154	0.00000	0.13596	0.00000
356.00	83.484	0.53853	0.16537	0.18224	0.00000	0.11386	0.00000
378.00	192.163	0.48548	0.24962	0.11339	0.00000	0.15150	0.00000
378.00	110.737	0.52976	0.17750	0.17177	0.00000	0.11785	0.00312
378.00	89.769	0.54917	0.15441	0.19304	0.00000	0.10338	0.00000
405.00	199.467	0.51698	0.21568	0.14613	0.00000	0.11631	0.00490
405.00	171.030	0.52474	0.19980	0.15800	0.00000	0.11475	0.00271
405.00	128.764	0.53842	0.16643	0.18164	0.00000	0.10998	0.00353

TABLE 44. ARRHENIUS DATA FOR CATALYST "K"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
206	2.01	7.10	1.96	2.09
232	5.74	20.28	3.01	1.98
254	11.39	40.25	3.70	1.89
283	24.28	85.80	4.45	1.80
307	47.80	168.90	5.13	1.72
328	69.88	246.93	5.51	1.66
356	111.90	395.41	5.98	1.59
378	158.54	560.21	6.33	1.54
405	227.97	805.55	6.69	1.47

(a) Catalyst contains 0.0590 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.77.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.283 grams



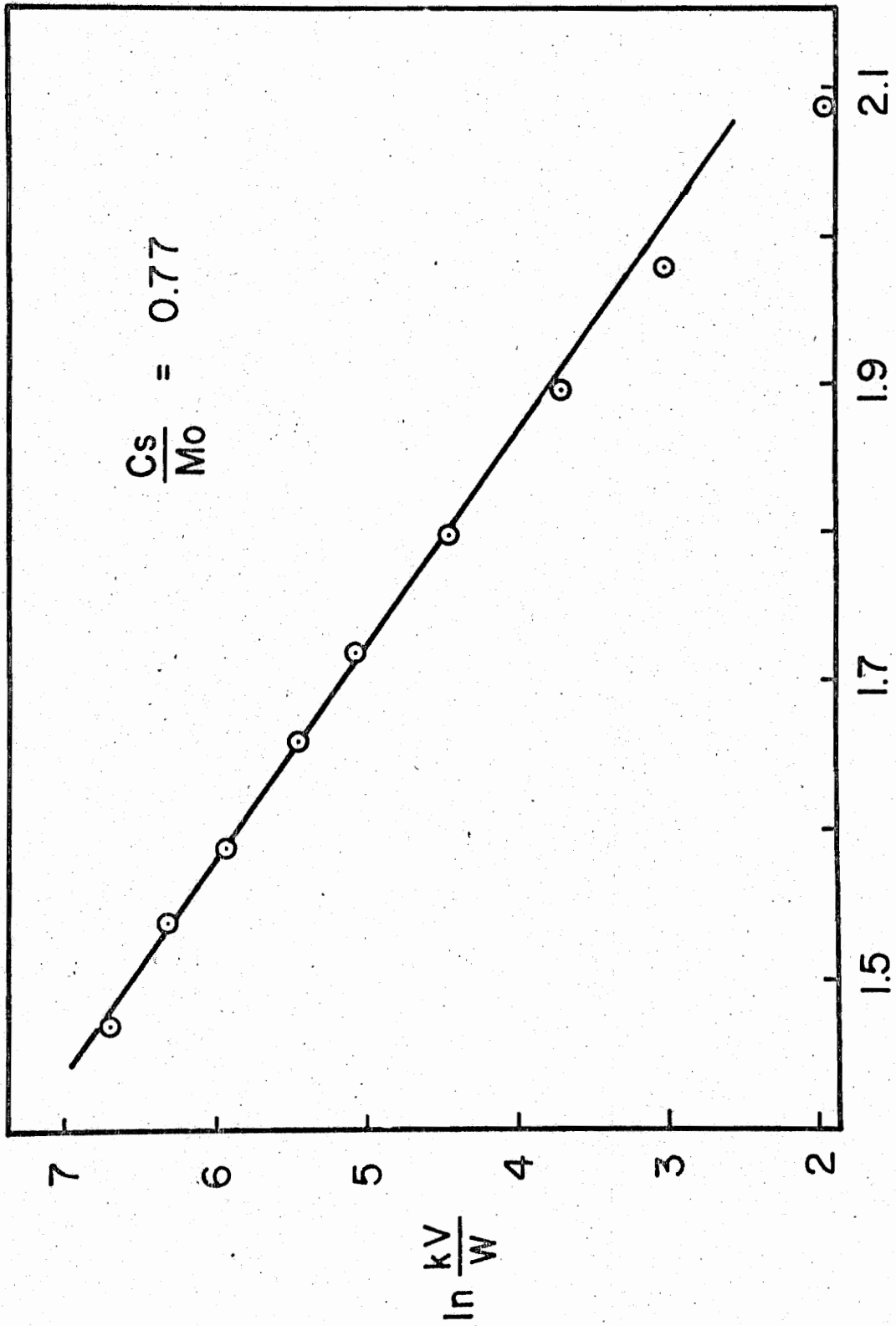


Figure 25. Arrhenius Plot for Catalyst "K"

TABLE 45. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "L"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
204.00	49.432	0.38097	0.31847	0.02694	0.00000	0.26238	0.01124
204.00	36.332	0.38193	0.31056	0.03141	0.00000	0.26582	0.01029
204.00	31.027	0.38119	0.30114	0.03581	0.00000	0.27322	0.00864
232.00	65.268	0.39992	0.31962	0.03571	0.00000	0.24475	0.00000
232.00	38.454	0.41650	0.29211	0.05782	0.00000	0.23357	0.00000
255.00	66.928	0.42394	0.30301	0.05598	0.00000	0.21707	0.00000
255.00	35.520	0.44930	0.26154	0.08949	0.00000	0.19967	0.00000
255.00	30.752	0.45721	0.24990	0.09929	0.00000	0.19361	0.00000
278.00	63.680	0.43561	0.27759	0.07461	0.00000	0.21218	0.00000
278.00	50.608	0.45253	0.25394	0.09493	0.00000	0.19860	0.00000
278.00	38.761	0.47561	0.23270	0.11708	0.00000	0.17461	0.00000
307.00	109.093	0.44119	0.28373	0.07425	0.00000	0.20083	0.00000
307.00	73.814	0.46827	0.24922	0.10510	0.00000	0.17741	0.00000
307.00	48.004	0.49608	0.20108	0.14320	0.00000	0.15212	0.00753
331.00	90.510	0.47705	0.24309	0.11253	0.00000	0.16732	0.00000
331.00	61.171	0.51770	0.18889	0.16004	0.00000	0.13337	0.00000
331.00	49.410	0.54038	0.16043	0.18565	0.00000	0.11354	0.00000
354.00	98.958	0.50222	0.20387	0.14482	0.00000	0.14484	0.00425
354.00	80.942	0.51876	0.18398	0.16306	0.00000	0.12962	0.00459
354.00	66.105	0.53958	0.15898	0.18599	0.00000	0.11545	0.00000
380.00	145.460	0.48762	0.22636	0.12622	0.00000	0.15479	0.00501
380.00	105.144	0.52386	0.18729	0.16389	0.00000	0.11995	0.00501
380.00	59.303	0.55741	0.13916	0.20483	0.00000	0.09860	0.00000
407.00	196.894	0.49606	0.23353	0.12676	0.00000	0.13962	0.00402
407.00	147.950	0.51859	0.20067	0.15452	0.00000	0.12087	0.00535

TABLE 46. ARRHENIUS DATA FOR CATALYST "L"

T, °C	Slope, kV cm <sup>3</sup> /min	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
204	2.02	6.89	1.93	2.096
232	6.05	20.65	3.03	1.980
255	11.72	40.00	3.69	1.894
278	19.43	66.31	4.19	1.815
307	37.08	126.55	4.84	1.724
331	63.21	215.73	5.37	1.656
354	91.84	313.45	5.75	1.595
380	127.24	434.27	6.07	1.531
407	185.00	631.40	6.45	1.471

(a) Catalyst contains 0.0347 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.44.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.293 grams



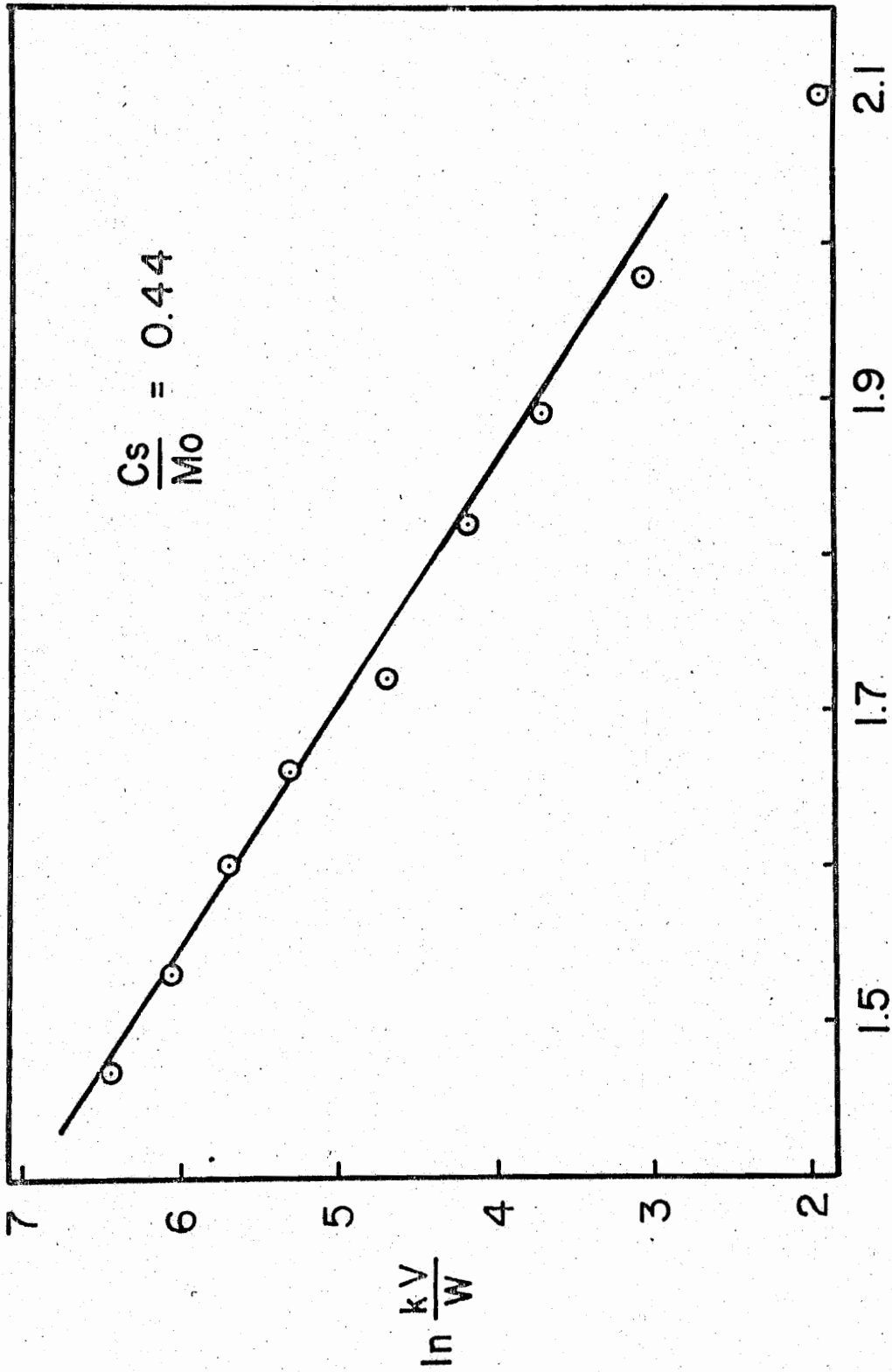


Figure 26. Arrhenius Plot for Catalyst "L"

TABLE 47. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "M"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
204.00	47.349	0.38811	0.33537	0.02190	0.00000	0.25462	0.00000
204.00	31.136	0.38998	0.32401	0.02857	0.00000	0.25744	0.00000
204.00	25.644	0.39257	0.31835	0.03272	0.00000	0.25636	0.00000
230.00	63.255	0.39246	0.32521	0.02919	0.00000	0.24797	0.00517
230.00	47.522	0.39454	0.31264	0.03658	0.00000	0.25143	0.00481
230.00	32.996	0.40727	0.29829	0.05013	0.00000	0.24431	0.00000
258.00	60.004	0.40724	0.30307	0.04770	0.00000	0.23511	0.00689
258.00	51.174	0.41839	0.29871	0.05541	0.00000	0.22748	0.00000
258.00	37.507	0.42794	0.28097	0.06911	0.00000	0.22193	0.00000
281.00	64.829	0.42391	0.29462	0.06021	0.00000	0.22125	0.00000
281.00	50.574	0.43377	0.27702	0.07399	0.00000	0.21522	0.00000
281.00	41.813	0.44726	0.26008	0.08923	0.00000	0.20344	0.00000
311.00	106.869	0.42274	0.29823	0.05780	0.00000	0.21669	0.00453
311.00	68.498	0.44878	0.26810	0.08592	0.00000	0.19721	0.00000
311.00	45.930	0.47563	0.22194	0.12254	0.00000	0.17448	0.00540
330.00	104.142	0.43981	0.28470	0.07308	0.00000	0.19663	0.00577
330.00	74.671	0.46329	0.24912	0.10269	0.00000	0.17941	0.00548
330.00	56.940	0.49540	0.21224	0.13721	0.00000	0.15515	0.00000
353.00	101.924	0.46456	0.25329	0.10120	0.00000	0.17399	0.00696
353.00	81.550	0.48378	0.21955	0.12777	0.00000	0.16165	0.00725
353.00	57.436	0.51985	0.17899	0.16612	0.00000	0.12894	0.00610
378.00	108.515	0.48640	0.22711	0.12524	0.00000	0.15414	0.00710
378.00	85.357	0.50332	0.20014	0.14725	0.00000	0.14349	0.00580
378.00	62.402	0.52582	0.17551	0.17083	0.00000	0.12271	0.00513
405.00	187.434	0.46917	0.27204	0.09399	0.00000	0.16115	0.00365
405.00	121.641	0.49594	0.21828	0.13442	0.00000	0.14456	0.00680
405.00	67.620	0.53691	0.15559	0.18639	0.00000	0.11590	0.00521

TABLE 48. ARRHENIUS DATA FOR CATALYST "M"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
204	1.30	4.41	1.48	2.096
230	4.07	13.80	2.62	1.988
258	8.18	27.73	3.32	1.883
281	13.62	46.17	3.83	1.805
311	26.98	91.46	4.52	1.712
330	40.51	137.32	4.92	1.658
353	64.96	220.20	5.39	1.597
378	83.89	284.37	5.65	1.536
405	128.34	435.05	6.08	1.475

(a) Catalyst contains 0.0175 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.22.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.295 grams



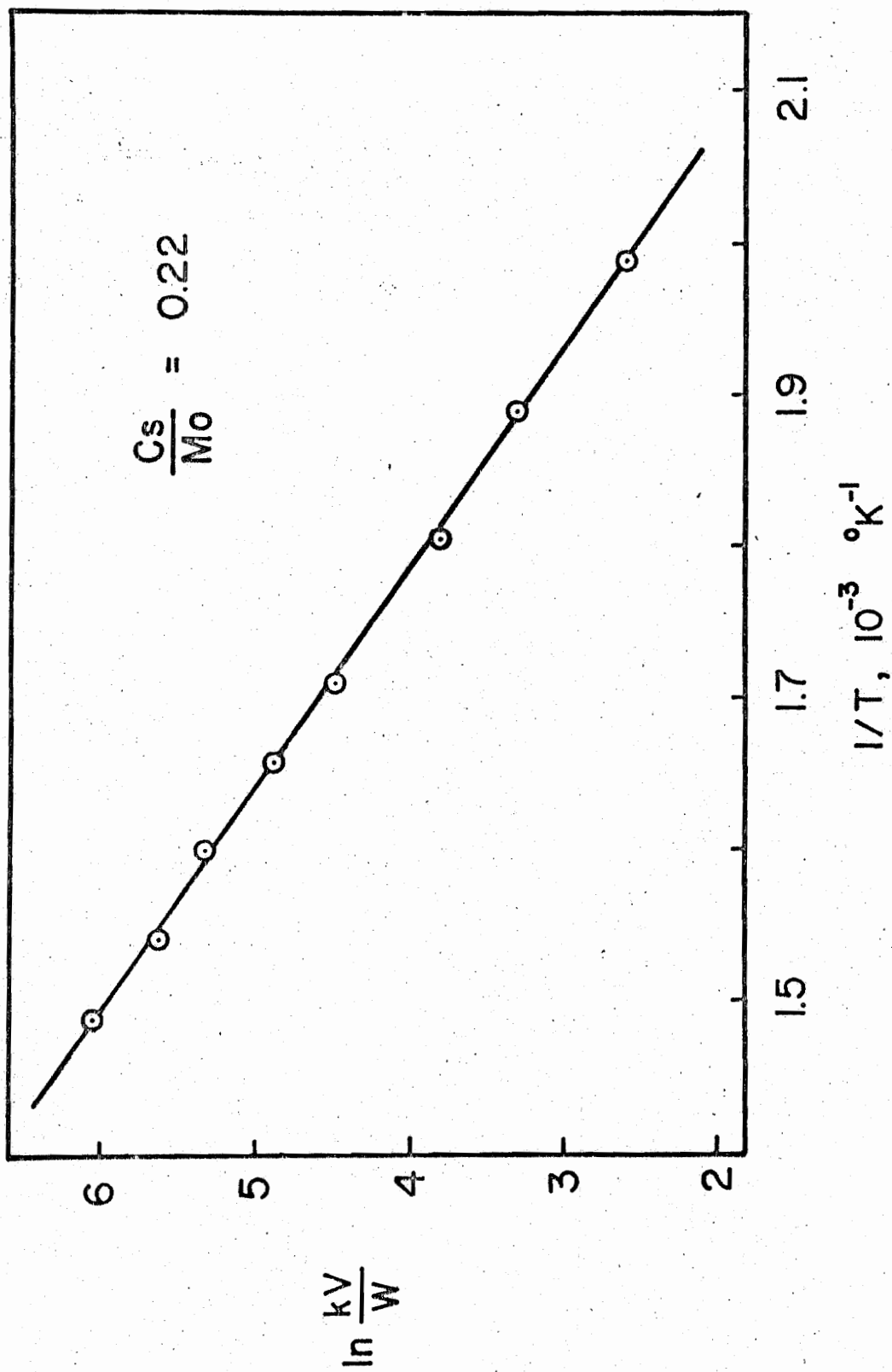


Figure 27. Arrhenius Plot for Catalyst "M"

TABLE 49. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "N"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
202.00	61.925	0.37074	0.32261	0.01979	0.00000	0.27639	0.01048
202.00	43.384	0.37916	0.32410	0.02319	0.00000	0.26638	0.00717
202.00	31.110	0.37976	0.31396	0.02861	0.00000	0.26953	0.00814
230.00	52.737	0.39359	0.31927	0.03276	0.00000	0.25437	0.00000
230.00	45.529	0.39497	0.31505	0.03558	0.00000	0.25440	0.00000
230.00	34.942	0.40145	0.30024	0.04628	0.00000	0.25203	0.00000
259.00	69.604	0.40527	0.31213	0.04215	0.00000	0.24045	0.00000
259.00	54.705	0.41123	0.29981	0.05132	0.00000	0.23764	0.00000
259.00	42.390	0.41858	0.28687	0.06150	0.00000	0.23304	0.00000
277.00	67.869	0.41397	0.30017	0.05249	0.00000	0.23337	0.00000
277.00	54.003	0.41993	0.28879	0.06120	0.00000	0.23009	0.00000
277.00	42.958	0.43210	0.27575	0.07381	0.00000	0.21834	0.00000
303.00	82.843	0.41930	0.29657	0.05695	0.00000	0.22718	0.00000 <sup>a</sup>
303.00	64.880	0.43152	0.27942	0.07166	0.00000	0.21740	0.00000
303.00	55.407	0.44220	0.26895	0.08223	0.00000	0.20662	0.00000
329.00	85.234	0.43920	0.28064	0.07484	0.00000	0.20532	0.00000
329.00	63.056	0.45753	0.24305	0.10292	0.00000	0.19650	0.00000
329.00	55.000	0.47001	0.23794	0.11167	0.00000	0.18038	0.00000
352.00	106.270	0.44086	0.27720	0.07740	0.00000	0.19892	0.00562
352.00	93.230	0.45199	0.26550	0.08882	0.00000	0.18774	0.00595
352.00	68.012	0.47905	0.22825	0.12104	0.00000	0.16571	0.00595
379.00	129.854	0.44688	0.25894	0.08961	0.00000	0.19684	0.00773
379.00	109.943	0.45923	0.25406	0.09818	0.00000	0.18089	0.00764
379.00	77.375	0.48704	0.19750	0.14055	0.00000	0.16821	0.00671
401.00	182.345	0.44597	0.27767	0.07968	0.00000	0.18903	0.00764
401.00	124.195	0.46706	0.24571	0.10844	0.00216	0.17106	0.00558
401.00	80.067	0.50684	0.18769	0.15529	0.00000	0.14276	0.00742

TABLE 50. ARRHENIUS DATA FOR CATALYST "N"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	1.15	3.83	1.34	2.10
230	3.56	11.87	2.47	1.98
259	7.66	25.53	3.24	1.88
277	10.54	35.13	3.56	1.82
303	16.74	55.80	4.02	1.74
329	28.50	95.00	4.55	1.66
352	42.58	141.93	4.96	1.60
379	65.30	217.67	5.38	1.53
401	93.37	311.23	5.74	1.48

(a) Catalyst contains no cesium acetate. The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate and ammonium molybdate. One gram catalyst contains  $2.29 \cdot 10^{-4}$  moles cobalt and  $4.27 \cdot 10^{-4}$  moles molybdenum. The cobalt:molybdenum molar ratio is 0.538.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>  
 V = volume of catalyst bed not including inert solids, cm<sup>3</sup>  
 W = weight of catalyst used, 0.301 grams

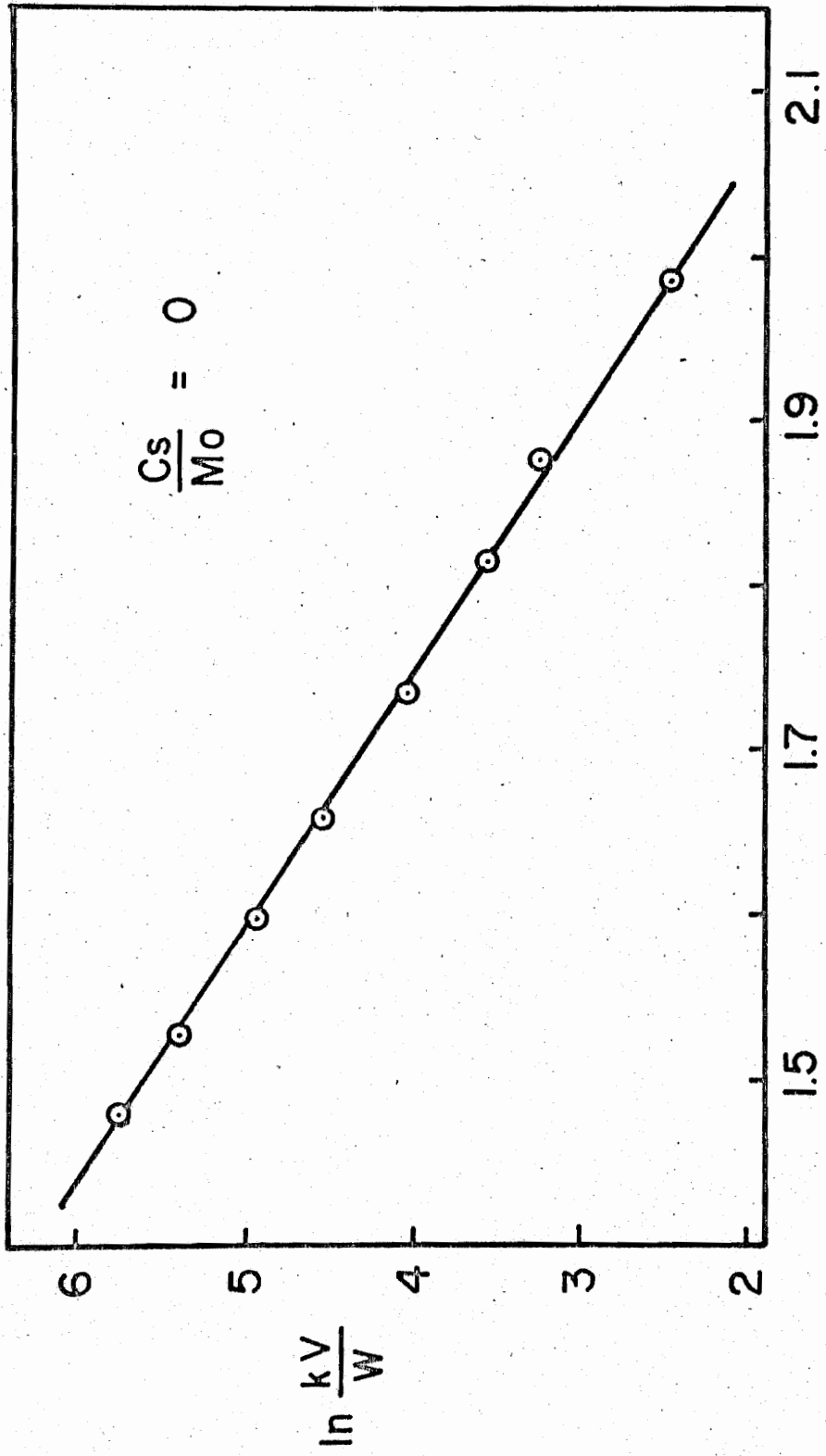


Figure 28. Arrhenius Plot for Catalyst "N"

TABLE 51. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "0"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COB
203.00	55.155	0.36354	0.33870	0.00808	0.00000	0.28967	0.00000
203.00	39.390	0.36218	0.33657	0.00849	0.00000	0.29276	0.00000
203.00	26.427	0.36011	0.33488	0.00832	0.00000	0.29663	0.00000
256.00	44.680	0.35690	0.32967	0.00938	0.00000	0.30406	0.00000
256.00	30.936	0.36236	0.33196	0.01091	0.00000	0.29476	0.00000
304.00	63.304	0.35878	0.32860	0.01085	0.00000	0.30177	0.00000
304.00	35.402	0.36273	0.32249	0.01589	0.00000	0.29889	0.00000
304.00	23.063	0.37212	0.31949	0.02204	0.00000	0.28635	0.00000
354.00	49.426	0.39162	0.32747	0.02764	0.00000	0.25327	0.00000
354.00	35.887	0.39490	0.31738	0.03436	0.00000	0.24166	0.01170
354.00	23.452	0.39840	0.29685	0.04648	0.00000	0.25826	0.00000
397.00	94.849	0.38788	0.31457	0.03232	0.00000	0.25494	0.01029
397.00	69.252	0.39755	0.30890	0.03997	0.00000	0.24224	0.01134
397.00	38.568	0.41003	0.28075	0.06038	0.00000	0.23849	0.01035

TABLE 52. ARRHENIUS DATA FOR CATALYST "0"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	-0.97	--	--	2.100
256	-0.98	--	--	1.890
304	0.46	1.49	0.40	1.733
354	3.13	10.16	2.32	1.595
397	9.28	30.13	3.41	1.492

(a) Catalyst contains 0.137 grams cesium per gram impregnated catalyst. No cobalt or molybdenum is present. The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 220S.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.308 grams



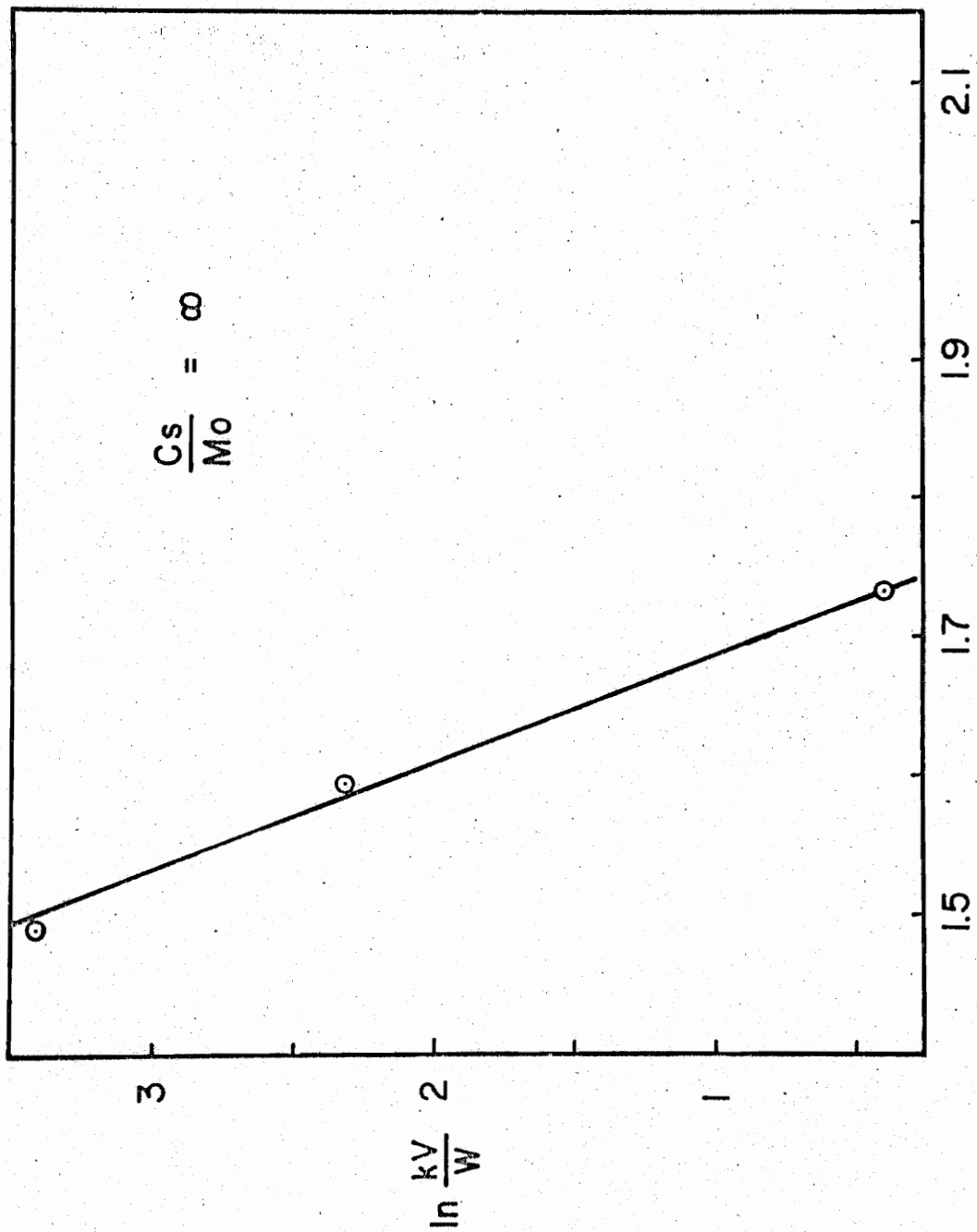


Figure 29. Arrhenius Plot for Catalyst "0"

TABLE 53. COMPOSITIONS OF FULL-STRENGTH CATALYSTS

Catalyst number	Salt	Weight dry catalyst (grams)	Weight salt (grams)	Weight salt per gram impregnated catalyst	Cesium:molybdenum ratio
P	cesium acetate	5.613	3.00	0.348	3.21
Q	cesium acetate	5.602	1.20	0.176	1.29
R,S,T	cesium acetate	5.596	1.00	0.152	1.07
U	cesium acetate	5.574	0.70	0.112	0.75
V,W,X	cesium acetate	5.571	0.40	0.0670	0.43
Y	cesium acetate	5.607	0.20	0.0344	0.21
Z	none	5.616	0.00	0.000	0.00
AA	lithium nitrate	6.001	0.155	0.0252	0.43
BB	sodium nitrate	6.000	0.191	0.0308	0.43

V

TABLE 53 (cont'd)

Catalyst number	Salt	Weight dry catalyst (grams)	Weight salt (grams)	Weight salt per gram impregnated catalyst	Metal: molybdenum ratio
CC,DD	potassium nitrate	5.999	0.227	0.0365	0.43
EE	lithium nitrate + cesium acetate	5.602	0.400	0.0651	0.43
FF	cesium acetate + zinc nitrate hexahydrate	12.000 <sup>(b)</sup>	1.667	0.115	0.67
GG	cesium acetate	--- <sup>(c)</sup>	---	0.134	1.07

(a) The unimpregnated catalyst is Nalco Chemical Company Nalcomo 474 catalyst, which is 12.5% MoO<sub>3</sub> and 3.5% CoO<sub>3</sub> supported on Al<sub>2</sub>O<sub>3</sub>. The catalyst mesh range is 20/60 and the surface area is 270 m<sup>2</sup>/gram. One gram of catalyst contains 4.67 · 10<sup>-4</sup> moles cobalt and 8.68 · 10<sup>-4</sup> moles molybdenum, in the absence of cesium acetate. The cobalt:molybdenum molar ratio is 0.538.



TABLE 53 (cont'd)

- (b) The support is Harshaw Chemical Co. Mo-1201-T-1/8, which contains 10% MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>, surface area 160 m<sup>2</sup>/gram and mesh range, 20/60.
- (c) The support is Air Products and Chemicals, Inc. hard alumina catalyst 200S, which has been impregnated with cobalt nitrate hexahydrate and ammonium molybdate to give a final catalyst that contains  $4.67 \cdot 10^{-4}$  moles cobalt and  $8.68 \cdot 10^{-4}$  moles molybdenum, in the absence of cesium acetate. The cobalt:molybdenum molar ratio is 0.538.

TABLE 54. AMOUNTS OF FULL-STRENGTH CATALYSTS USED IN WATER GAS SHIFT STUDIES

Catalyst number	Metal: molybdenum ratio	Weight catalyst used in reactor (grams)	Weight inert solids used in reactor (grams)	W <sup>(b)</sup> (grams)
P	3.21 (d)	0.112	0.000	0.073
Q	1.29 (d)	0.157	1.34	0.129
R	1.07 (d)	1.001	0.50	0.849
S	1.07 (e)	1.000	0.50	0.848
T	1.07 (d)	0.283	1.22	0.240
U	0.75 (d)	0.295	1.20	0.262
V	0.43 (d)	0.298	1.20	0.278
W	0.43 (e)	0.299	1.20	0.279
X	0.43 (f)	0.303	1.20	0.275
Y	0.21 (d)	0.349	1.15	0.337
Z	0.00 (d)	0.502	1.00	0.502
AA	0.43 (f)	0.309	1.20	0.301
BB	0.43 (f)	0.311	1.19	0.301



TABLE 54 (cont'd)

Catalyst number	Metal: molybdenum ratio	Weight catalyst used in reactor (grams)	Weight inert solids used in reactor (grams)	$W(b)$ (grams)
CC	0.43(f)	0.336	1.20	0.324
DD	0.43(f)	0.315	1.20	0.304
EE	0.42(f) 0.43	0.301	1.20	0.274
FF	0.54(f) 0.67	0.342	1.16	0.282
GG	1.07(f)	0.303	1.20	0.263

(a) The unimpregnated catalyst is Nalco Chemical Company Nalcomo 474 catalyst, which contains 12.5%  $MoO_3$  and 3.5%  $CoO_3$  supported on  $Al_2O_3$ . The catalyst mesh range is 20/60 and the surface area is  $270 m^2/gram$ . The cobalt:molybdenum molar ratio is 0.538.

(b) The support is Harshaw Chemical Company Mo-1201-I-1/8, which contains 10%  $MoO_3$  on  $Al_2O_3$ , has a surface area of  $160 m^2/gram$ , and has a catalyst mesh range of 20/60.

(c) The support is Air Products and Chemicals, Inc. hard alumina catalyst 200S which has been impregnated with cobalt and molybdenum in amounts identical to Nalcomo 474. The cobalt:molybdenum molar ratio is 0.538.

(d) These catalysts run with a gas cylinder of the following composition: 53.31%  $H_2$ , 44.77%  $CO$ , 1.48%  $CO_2$ , and 0.44%  $CO_2$  (Cylinder #1).

TABLE 54 (cont'd)

- (e) These catalysts run with a gas cylinder of the following composition: 59.78% H<sub>2</sub>, 37.60% CO, 2.16% COS, and 0.46% CO<sub>2</sub> (*Cylinder #2*).
- (f) These catalysts run with a gas cylinder of the following composition: 49.52% H<sub>2</sub>, 48.30% CO, 1.67% COS, 0.51% CO<sub>2</sub> (*Cylinder #3*).

TABLE 55. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "P"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
295.00	41.387	0.52516	0.22202	0.11900	0.00000	0.13045	0.00338
295.00	40.656	0.51729	0.22522	0.11602	0.00127	0.14009	0.00210
295.00	39.974	0.52595	0.22328	0.12207	0.00339	0.12532	0.00000
295.00	55.083	0.50474	0.25212	0.09870	0.00538	0.13906	0.00000
295.00	77.084	0.48840	0.27963	0.07734	0.00644	0.14819	0.00000
295.00	85.252	0.48369	0.28614	0.07256	0.00734	0.15026	0.00000
295.00	106.884	0.47538	0.29952	0.06203	0.00787	0.15520	0.00000
323.00	59.102	0.53947	0.20014	0.14051	0.00309	0.11679	0.00000
323.00	72.733	0.53543	0.21944	0.13227	0.00718	0.10569	0.00000
323.00	40.570	0.56249	0.18328	0.16376	0.00666	0.08381	0.00000
323.00	49.851	0.55101	0.19545	0.15273	0.00749	0.09331	0.00000
323.00	116.415	0.51010	0.26565	0.09534	0.00693	0.12198	0.00000
353.00	134.682	0.53285	0.23903	0.11656	0.00329	0.10826	0.00000
353.00	57.704	0.57368	0.16805	0.17849	0.00800	0.07178	0.00000
353.00	42.754	0.58467	0.15679	0.18819	0.00657	0.06378	0.00000
353.00	83.353	0.55131	0.20378	0.14735	0.00650	0.09106	0.00000
353.00	46.293	0.58312	0.16158	0.18331	0.00500	0.06700	0.00000
353.00	65.497	0.56563	0.18834	0.16116	0.00538	0.07949	0.00000
373.00	49.842	0.59364	0.15349	0.18981	0.00230	0.06076	0.00000
373.00	61.482	0.58543	0.16134	0.18461	0.00511	0.06350	0.00000
373.00	68.065	0.57826	0.17007	0.17720	0.00572	0.06875	0.00000
373.00	75.176	0.57680	0.17727	0.17339	0.00649	0.06604	0.00000
373.00	102.215	0.56119	0.19576	0.15648	0.00676	0.07982	0.00000
394.00	41.707	0.59328	0.15003	0.19471	0.00549	0.05650	0.00000
394.00	50.105	0.58776	0.15346	0.19193	0.00708	0.05977	0.00000
394.00	62.672	0.58500	0.16268	0.18447	0.00590	0.06195	0.00000
394.00	84.727	0.57729	0.17752	0.17229	0.00531	0.06759	0.00000
394.00	113.577	0.56522	0.19329	0.15898	0.00608	0.07643	0.00000

TABLE 56. ARRHENIUS DATA FOR CATALYST "P"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
295	30.4	416.4	6.03	1.760
323	57.2	783.6	6.66	1.677
353	101.8	1395.	7.24	1.597
373	160.5	2199.	7.70	1.548
394	278.2	3811.	8.25	1.499

(a) Catalyst contains 0.348 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 3.21.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.0730 grams

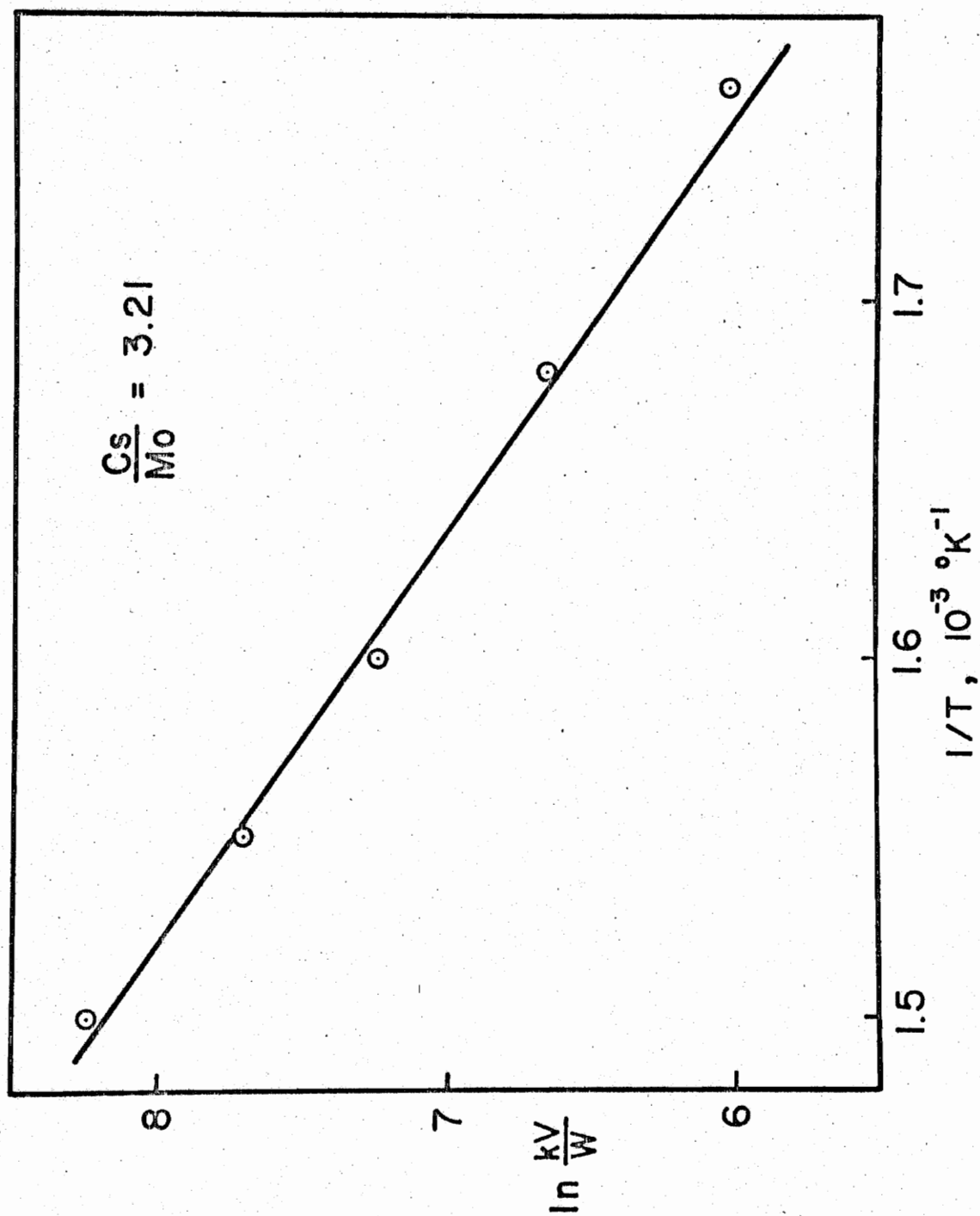


Figure 30. Arrhenius Plot for Catalyst "P"

TABLE 57. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "Q"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
203.00	27.231	0.43781	0.33709	0.02032	0.00374	0.19581	0.00524
203.00	42.415	0.43120	0.33794	0.01747	0.00436	0.20428	0.00474
203.00	74.072	0.43756	0.35249	0.01394	0.00583	0.18557	0.00461
229.00	32.757	0.44922	0.32723	0.03170	0.00455	0.18140	0.00590
229.00	46.045	0.44778	0.33626	0.02679	0.00521	0.17895	0.00501
229.00	82.575	0.44684	0.34541	0.02000	0.00381	0.17816	0.00577
255.00	33.537	0.48040	0.29813	0.06221	0.00501	0.14944	0.00481
255.00	37.005	0.47684	0.30421	0.05740	0.00512	0.15156	0.00487
255.00	49.012	0.47143	0.31296	0.04923	0.00419	0.15734	0.00485
255.00	68.212	0.46069	0.32643	0.03751	0.00469	0.16552	0.00516
281.00	41.475	0.51913	0.25082	0.10647	0.00588	0.11447	0.00324
281.00	51.066	0.49857	0.27661	0.08324	0.00604	0.13208	0.00346
281.00	63.974	0.48770	0.29366	0.06964	0.00668	0.13961	0.00271
281.00	91.542	0.47384	0.31463	0.05202	0.00678	0.14977	0.00297
308.00	52.792	0.55299	0.22072	0.13797	0.00556	0.08276	0.00000
308.00	71.321	0.52550	0.25244	0.10911	0.00648	0.10433	0.00214
308.00	112.908	0.50275	0.28743	0.07840	0.00518	0.12282	0.00343
331.00	57.972	0.58298	0.18782	0.16785	0.00387	0.05631	0.00117
331.00	80.223	0.55585	0.21481	0.14387	0.00694	0.07697	0.00156
331.00	92.611	0.54674	0.22859	0.13142	0.00614	0.08518	0.00193
331.00	125.974	0.52791	0.25636	0.10724	0.00565	0.09968	0.00316
355.00	88.037	0.57997	0.19045	0.16808	0.00690	0.05380	0.00080
355.00	110.853	0.56473	0.21113	0.14865	0.00566	0.06832	0.00152
355.00	145.602	0.54594	0.23675	0.12719	0.00671	0.08155	0.00187
382.00	121.277	0.58201	0.19657	0.16204	0.00325	0.05387	0.00226
382.00	150.227	0.56753	0.21019	0.15007	0.00530	0.06434	0.00257
382.00	226.410	0.54366	0.24581	0.12231	0.00780	0.07796	0.00246
404.00	120.614	0.58649	0.18772	0.17062	0.00498	0.04821	0.00198
404.00	166.379	0.57291	0.20732	0.15649	0.00771	0.05396	0.00161
404.00	199.287	0.56355	0.22327	0.14430	0.00845	0.05856	0.00187

TABLE 58. ARRHENIUS DATA FOR CATALYST "Q"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	2.30	17.8	2.88	2.10
229	4.77	37.0	3.61	1.99
255	11.8	91.5	4.52	1.89
281	28.8	223.3	5.41	1.81
308	60.1	465.9	6.14	1.72
331	112.8	874.	6.77	1.66
355	193.6	1501.	7.31	1.59
382	371.8	2464.	7.81	1.53
404	465.0	3605.	8.19	1.48

(a) Catalyst contains 0.176 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.29.

(b) k = pseudo-first order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.129 grams



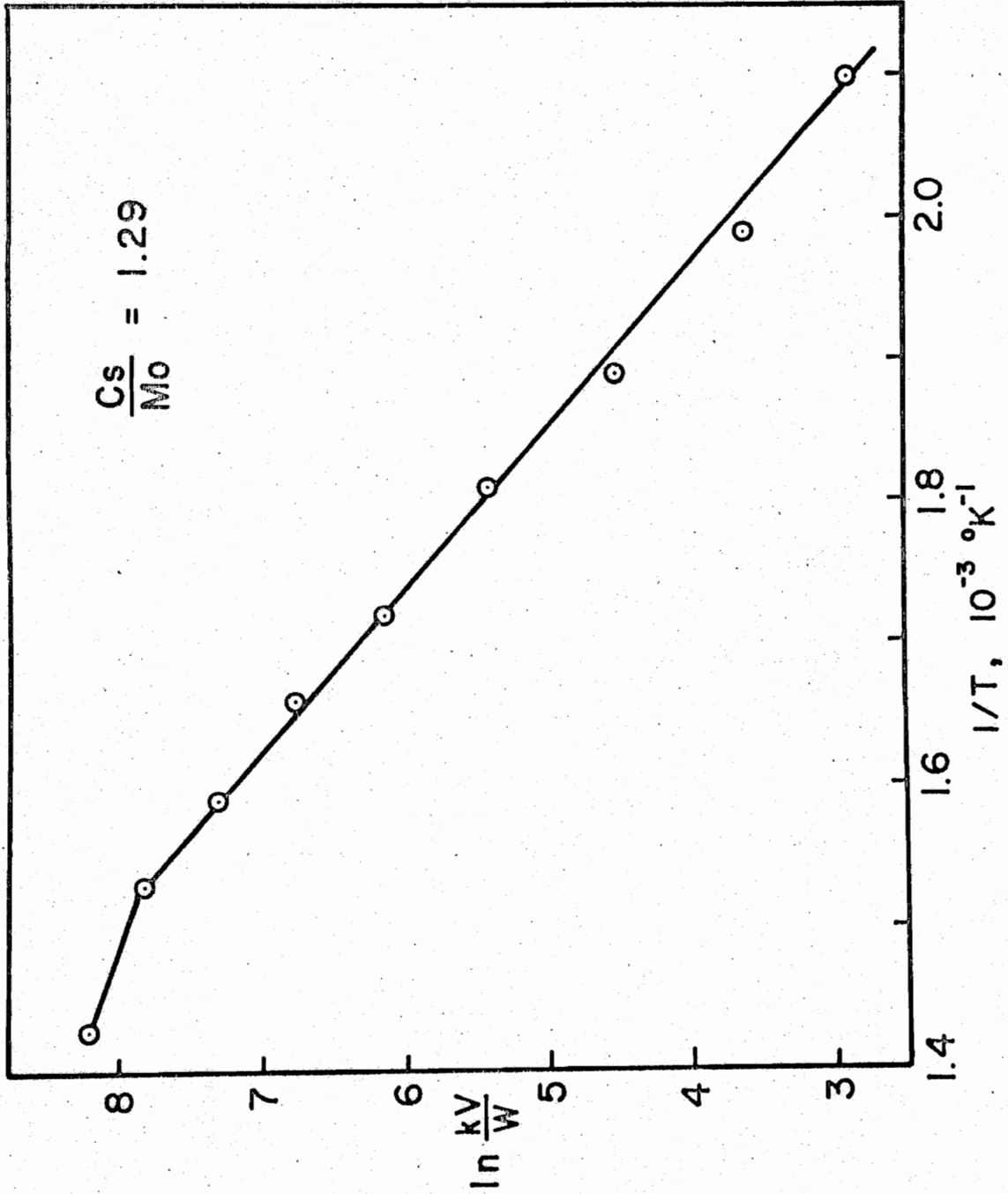


Figure 31. Arrhenius Plot for Catalyst "Q"

TABLE 59. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "R"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
132.00	7.267	0.44680	0.33497	0.02412	0.00229	0.18387	0.00795
132.00	9.670	0.44737	0.34064	0.02100	0.00199	0.18167	0.00733
132.00	14.648	0.44305	0.34007	0.01859	0.00124	0.18997	0.00709
132.00	23.122	0.43326	0.34417	0.01586	0.00520	0.19516	0.00636
142.00	8.196	0.44615	0.32249	0.03257	0.00424	0.18744	0.00712
142.00	9.668	0.43120	0.33798	0.01874	0.00566	0.20090	0.00553
142.00	14.247	0.44006	0.33281	0.02427	0.00433	0.19199	0.00654
142.00	24.839	0.44039	0.33991	0.01815	0.00192	0.19225	0.00738
159.00	9.594	0.47955	0.32189	0.04686	0.00297	0.14179	0.00695
159.00	14.811	0.45902	0.32605	0.03798	0.00571	0.16662	0.00462
159.00	19.729	0.44900	0.32943	0.03145	0.00560	0.17949	0.00504
159.00	24.106	0.45233	0.33525	0.02920	0.00499	0.17247	0.00576
159.00	44.970	0.44196	0.34789	0.01864	0.00603	0.18030	0.00520
169.00	20.726	0.45915	0.32372	0.03745	0.00386	0.16999	0.00583
169.00	24.129	0.45469	0.32947	0.03454	0.00611	0.17049	0.00470
169.00	34.489	0.45167	0.33431	0.02879	0.00436	0.17546	0.00542
169.00	39.721	0.44863	0.34002	0.02507	0.00514	0.17581	0.00532
180.00	20.027	0.47413	0.30568	0.05457	0.00433	0.15572	0.00557
180.00	28.127	0.45898	0.32366	0.03894	0.00539	0.16836	0.00466
180.00	37.602	0.45495	0.32910	0.03465	0.00590	0.17086	0.00453
180.00	42.447	0.45584	0.33514	0.02915	0.00328	0.17025	0.00635

TABLE 59 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
192.00	29.177	0.50000	0.27150	0.08530	0.00468	0.13307	0.00544
192.00	27.371	0.48424	0.28603	0.06917	0.00364	0.14990	0.00703
192.00	40.417	0.47604	0.31369	0.04785	0.00109	0.15432	0.00702
192.00	51.135	0.46165	0.32513	0.03957	0.00561	0.16257	0.00547
203.00	19.862	0.53859	0.21992	0.13267	0.00640	0.09969	0.00273
203.00	28.646	0.51193	0.24998	0.10416	0.00640	0.12497	0.00256
203.00	40.111	0.48897	0.29312	0.07021	0.00638	0.13682	0.00451
203.00	58.706	0.47742	0.31344	0.05326	0.00575	0.14467	0.00547
218.00	28.599	0.55451	0.21581	0.14189	0.00611	0.07954	0.00215
218.00	34.422	0.54224	0.20870	0.14150	0.00746	0.09899	0.00111
218.00	39.014	0.52972	0.24634	0.11160	0.00373	0.10454	0.00407
218.00	48.118	0.51742	0.26234	0.09963	0.00608	0.11140	0.00313
228.00	34.961	0.56261	0.19611	0.15419	0.00401	0.08077	0.00231
228.00	36.025	0.57452	0.18914	0.16568	0.00627	0.06333	0.00106
228.00	38.730	0.57002	0.17598	0.17076	0.00625	0.07478	0.00221
228.00	44.854	0.55429	0.21452	0.14331	0.00694	0.07944	0.00150
228.00	44.477	0.53096	0.24313	0.11695	0.00677	0.09921	0.00297

TABLE 60. ARRHENIUS DATA FOR CATALYST "R"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
132	0.85	1.00	0.001	2.468
142	1.29	1.52	0.418	2.409
159	2.67	3.15	1.15	2.314
169	3.86	4.55	1.51	2.262
180	5.73	6.75	1.91	2.207
192	10.2	12.0	2.49	2.150
203	17.3	20.4	3.01	2.100
218	30.7	36.2	3.59	2.036
228	49.6	58.4	4.07	1.995

(a) Catalyst contains 0.152 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.07.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.849 grams

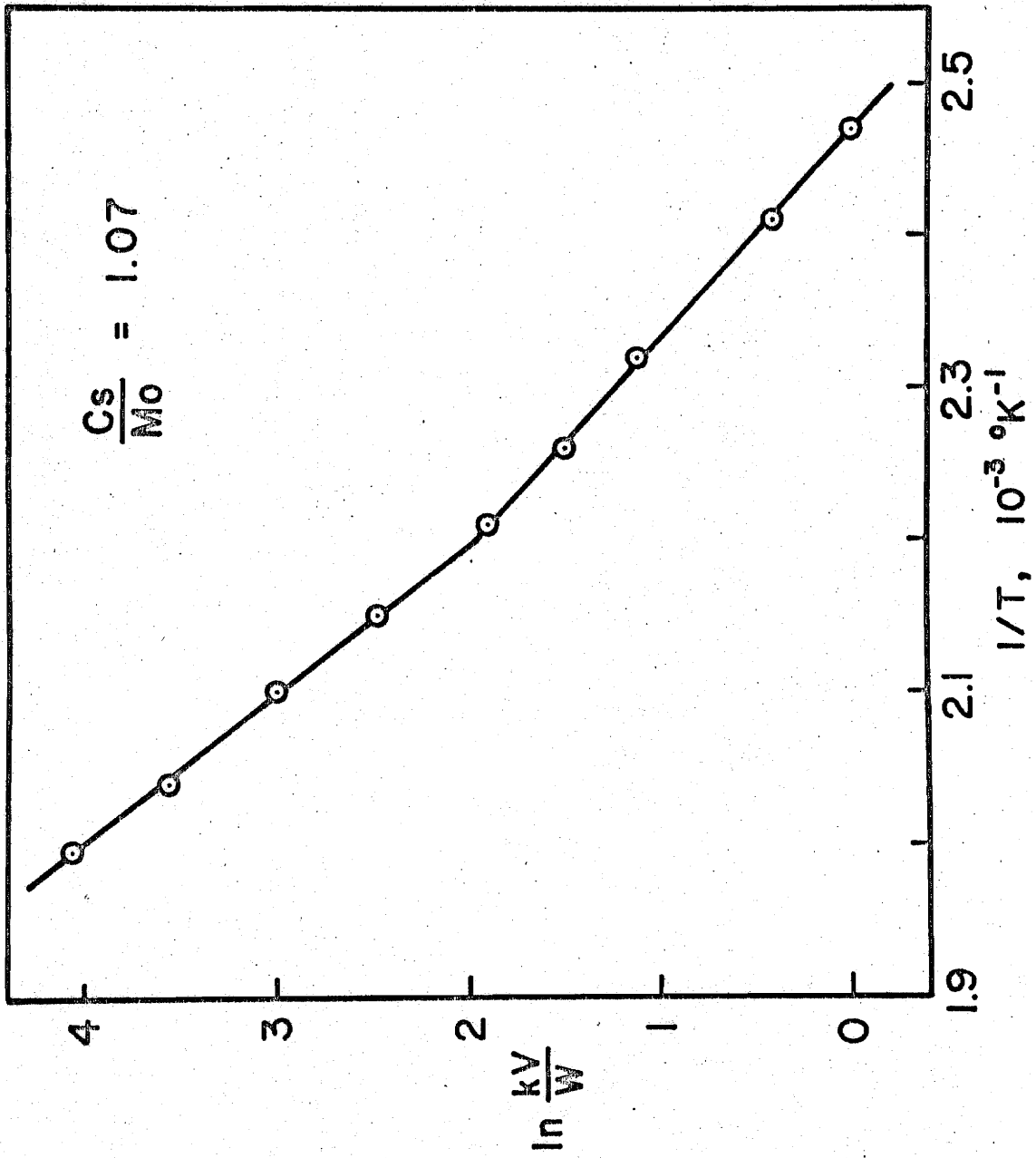


Figure 32. Arrhenius Plot for Catalyst "R"

TABLE 61. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "S"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
130.00	25.563	0.42376	0.24660	0.01458	0.00235	0.29873	0.01398
130.00	45.537	0.44561	0.26247	0.01263	0.00171	0.26438	0.01319
130.00	33.586	0.44601	0.26143	0.01341	0.00170	0.26457	0.01288
130.00	67.942	0.45215	0.26908	0.01179	0.00240	0.25250	0.01208
145.00	72.168	0.46333	0.27379	0.01334	0.00069	0.24103	0.01081
145.00	31.586	0.46397	0.26586	0.01725	0.00132	0.23919	0.01242
145.00	42.370	0.45289	0.26360	0.01498	0.00195	0.25536	0.01122
145.00	112.314	0.46585	0.27676	0.01213	0.00217	0.23089	0.01221
158.00	124.880	0.47423	0.27650	0.01405	0.00369	0.22316	0.01138
158.00	35.766	0.46107	0.25730	0.02104	0.00098	0.24735	0.01226
158.00	56.663	0.46107	0.26446	0.01698	0.00132	0.24633	0.00984
170.00	58.684	0.46667	0.26112	0.02038	0.00050	0.24130	0.01002
170.00	33.451	0.46809	0.24990	0.02795	0.00063	0.24194	0.01149
170.00	125.864	0.47555	0.27466	0.01566	0.00066	0.22263	0.01094
179.00	119.651	0.48377	0.27553	0.01807	0.00044	0.21369	0.00850
179.00	35.587	0.47830	0.23994	0.03791	0.00054	0.23450	0.00881
179.00	53.373	0.47073	0.25125	0.02818	0.00067	0.23895	0.01021
192.00	56.870	0.48720	0.24634	0.03732	0.00044	0.22038	0.00831
192.00	36.522	0.49357	0.22112	0.05541	0.00058	0.21935	0.00997
192.00	78.027	0.48545	0.25605	0.03088	0.00063	0.21640	0.01058
203.00	118.736	0.50684	0.27449	0.02763	0.00045	0.18075	0.00983
203.00	47.085	0.51233	0.21397	0.06727	0.00081	0.19576	0.00985
203.00	60.949	0.49711	0.23637	0.04808	0.00125	0.20619	0.01101
215.00	65.975	0.52173	0.22457	0.06420	0.00062	0.17993	0.00896
215.00	40.136	0.54350	0.17145	0.10566	0.00106	0.16924	0.00909
215.00	105.165	0.51132	0.24966	0.04564	0.00148	0.18087	0.01103
229.00	95.211	0.55124	0.24529	0.06291	0.00066	0.13065	0.00925
229.00	58.156	0.56393	0.18681	0.10425	0.00120	0.13559	0.00822
229.00	125.881	0.56451	0.28820	0.04210	0.00107	0.09511	0.00900

TABLE 62. ARRHENIUS DATA FOR CATALYST "S"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			In kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
130	1.21	1.43	0.358	2.480
145	1.86	2.19	0.786	2.391
158	2.70	3.18	1.16	2.319
170	3.62	4.27	1.45	2.257
179	5.44	6.42	1.86	2.212
192	9.24	10.9	2.39	2.150
203	14.9	17.6	2.87	2.100
215	22.9	27.0	3.30	2.049
229	37.8	44.5	3.80	1.991

(a) Catalyst contains 0.152 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.07.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.848 grams

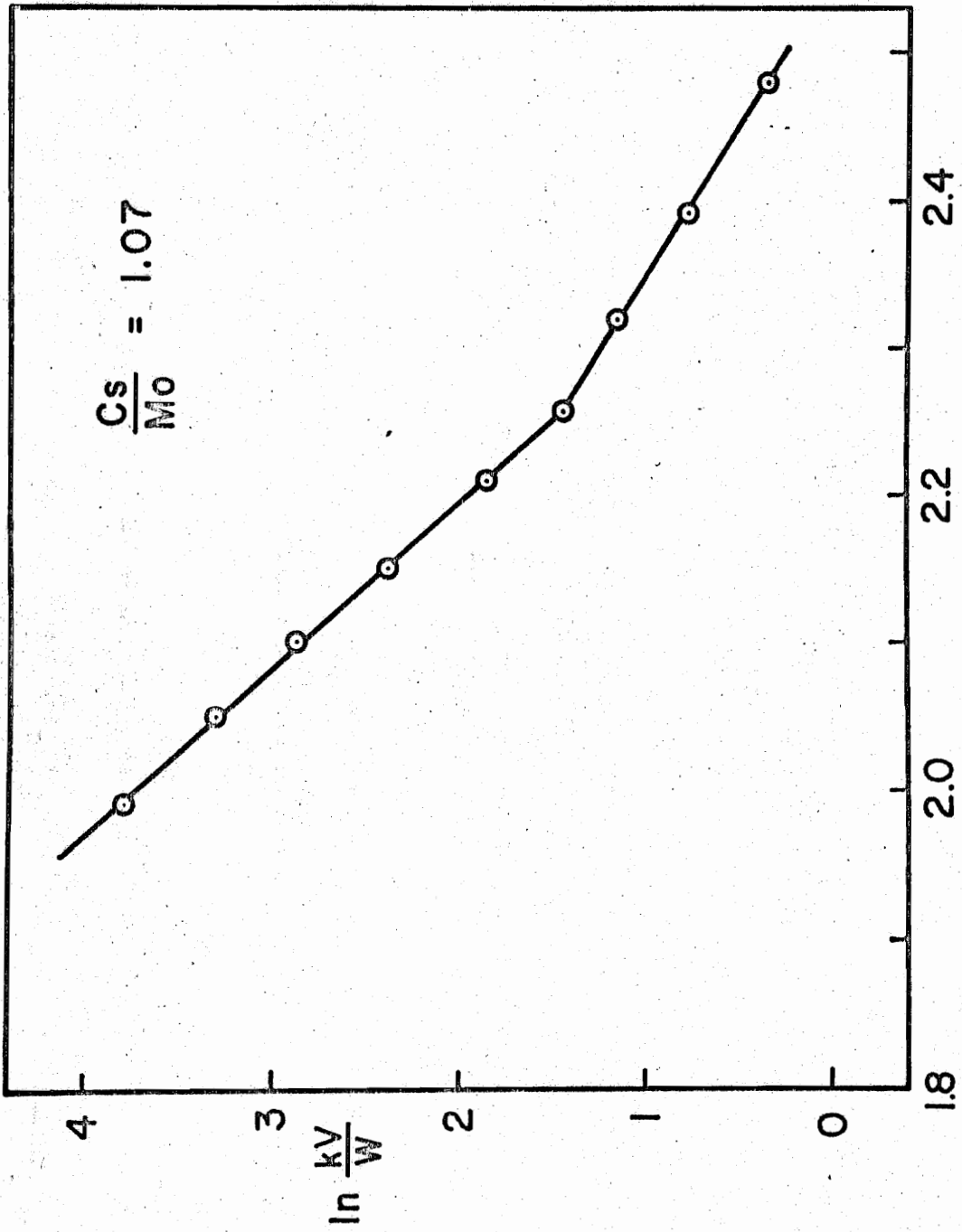


Figure 33. Arrhenius Plot for Catalyst "S"

TABLE 63. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "T"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	COS
202.00	14.043	0.47045	0.28385	0.06710	0.00667	0.17193	0.00000
202.00	17.113	0.45771	0.29129	0.05781	0.00724	0.18595	0.00000
202.00	22.522	0.45079	0.29989	0.05024	0.00751	0.18635	0.00521
228.00	14.979	0.55571	0.17559	0.16221	0.00402	0.10247	0.00000
228.00	17.181	0.54181	0.21307	0.13829	0.00682	0.10000	0.00000
228.00	19.367	0.52796	0.23352	0.12029	0.00626	0.11198	0.00000
228.00	22.755	0.52543	0.23728	0.11758	0.00675	0.11296	0.00000
228.00	26.285	0.50336	0.25910	0.09606	0.00717	0.13431	0.00000
228.00	40.060	0.48665	0.28344	0.07557	0.00754	0.14680	0.00000
255.00	18.962	0.61787	0.12126	0.22043	0.00434	0.03398	0.00212
255.00	27.396	0.60698	0.16401	0.19047	0.00259	0.03594	0.00000
255.00	33.197	0.56873	0.18908	0.16295	0.00616	0.07308	0.00000
255.00	49.890	0.53157	0.23277	0.12343	0.00734	0.10489	0.00000
255.00	91.702	0.49378	0.28651	0.07793	0.00830	0.13348	0.00000
255.00	101.538	0.48637	0.29140	0.07242	0.00883	0.14098	0.00000
275.00	37.775	0.61124	0.13669	0.21075	0.00607	0.03525	0.00000
275.00	54.281	0.57116	0.18171	0.16980	0.00789	0.06945	0.00000
275.00	96.410	0.52554	0.24450	0.11542	0.00846	0.10608	0.00000
275.00	112.763	0.51511	0.25760	0.10417	0.00909	0.11402	0.00000

TABLE 63 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
300.00	57.673	0.61243	0.13748	0.21199	0.00720	0.03091	0.00000
300.00	79.197	0.58763	0.16812	0.18491	0.00809	0.05125	0.00000
300.00	119.886	0.56918	0.19791	0.16018	0.00798	0.06476	0.00000
300.00	172.709	0.53597	0.24677	0.11893	0.00845	0.08988	0.00000
327.00	81.856	0.61002	0.14075	0.20919	0.00728	0.03275	0.00000
327.00	103.106	0.60568	0.15304	0.20050	0.00725	0.03354	0.00000
327.00	140.626	0.59053	0.17367	0.18311	0.00799	0.04469	0.00000
327.00	187.046	0.57320	0.20215	0.15978	0.00805	0.05682	0.00000
353.00	84.937	0.60519	0.14535	0.20502	0.00781	0.03663	0.00000
353.00	118.088	0.60293	0.15717	0.19719	0.00744	0.03527	0.00000
353.00	162.736	0.59837	0.16595	0.19060	0.00771	0.03738	0.00000
353.00	209.771	0.58897	0.19012	0.17196	0.00650	0.04244	0.00000
378.00	86.277	0.60159	0.15325	0.19737	0.00610	0.04169	0.00000
378.00	118.995	0.59618	0.16030	0.19327	0.00831	0.04193	0.00000
378.00	156.576	0.59662	0.16961	0.18707	0.00696	0.03973	0.00000
378.00	256.873	0.58690	0.19549	0.16953	0.00793	0.04014	0.00000
402.00	120.164	0.59000	0.16534	0.18826	0.00885	0.04755	0.00000
402.00	206.598	0.58822	0.18248	0.17773	0.00845	0.04313	0.00000
402.00	251.814	0.58487	0.19316	0.17139	0.00944	0.04114	0.00000
402.00	421.708	0.57413	0.22758	0.14776	0.00942	0.04111	0.00000

TABLE 64. ARRHENIUS DATA FOR CATALYST "T"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	3.95	16.5	2.80	2.105
228	15.1	62.9	4.14	1.995
255	40.7	169.6	5.13	1.893
275	75.9	316.3	5.76	1.824
300	164.3	685.	6.53	1.745
327	407.4	1698.	7.44	1.666
353	707.7	2949.	7.99	1.597
378	947.	3946.	8.28	1.536
402	1315.	5480.	8.61	1.481

(a) Catalyst contains 0.152 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 1.07.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.240 grams



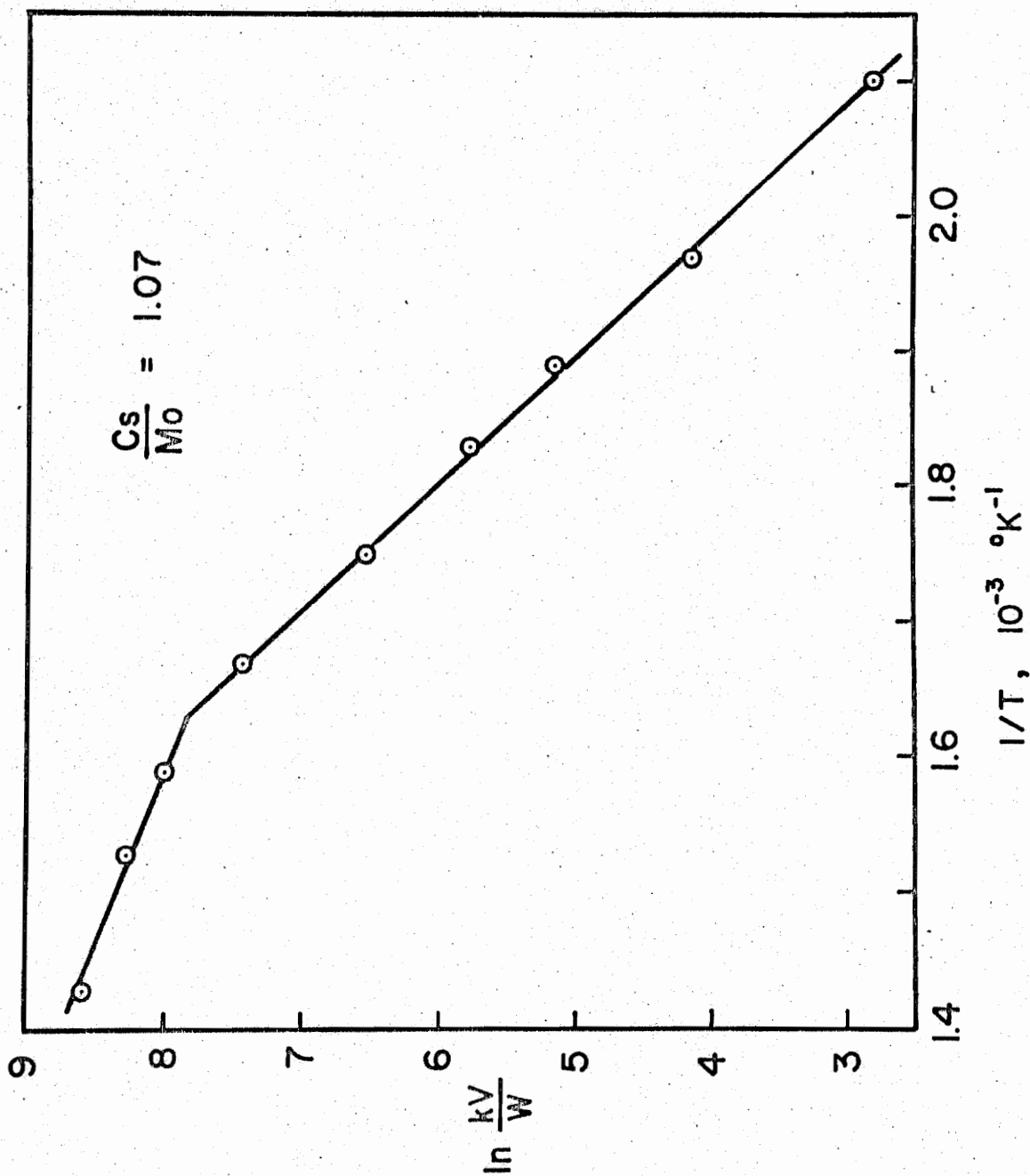


Figure 34. Arrhenius Plot for Catalyst "T"

TABLE 65. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "U"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
202.00	21.305	0.46266	0.32519	0.03482	0.00043	0.16746	0.00945
202.00	28.479	0.45658	0.33044	0.02906	0.00030	0.17309	0.01052
202.00	52.781	0.45206	0.34161	0.02101	0.00038	0.17541	0.00952
202.00	87.081	0.44951	0.34469	0.01818	0.00039	0.17835	0.00888
232.00	25.806	0.49824	0.29008	0.06997	0.00025	0.13223	0.00923
232.00	39.857	0.47561	0.31309	0.04814	0.00126	0.15285	0.00905
232.00	49.761	0.46852	0.32425	0.03818	0.00060	0.15870	0.00976
232.00	73.408	0.46446	0.33211	0.03244	0.00098	0.16044	0.00957
256.00	32.510	0.51633	0.26614	0.09198	0.00099	0.11678	0.00779
256.00	33.917	0.51673	0.26977	0.09095	0.00175	0.11425	0.00656
256.00	41.332	0.51319	0.27714	0.08390	0.00032	0.11647	0.00898
256.00	63.781	0.48530	0.30584	0.05646	0.00122	0.14271	0.00847
256.00	73.160	0.48139	0.31388	0.05015	0.00106	0.14368	0.00985
256.00	104.411	0.47416	0.32692	0.04047	0.00177	0.14808	0.00860
283.00	34.022	0.58152	0.20234	0.15578	0.00035	0.05901	0.00100
283.00	104.301	0.50141	0.29091	0.07325	0.00254	0.12396	0.00794

TABLE 65 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
309.00	44.710	0.60051	0.17288	0.18063	0.00052	0.03989	0.00556
309.00	63.420	0.57232	0.20806	0.14965	0.00153	0.06231	0.00612
309.00	96.408	0.54362	0.24424	0.11627	0.00092	0.08750	0.00745
309.00	109.452	0.53164	0.25923	0.10459	0.00285	0.09463	0.00706
331.00	59.971	0.60485	0.16836	0.18596	0.00142	0.03533	0.00408
331.00	95.227	0.57511	0.20702	0.15245	0.00250	0.05746	0.00547
331.00	118.438	0.56060	0.22947	0.13252	0.00139	0.06971	0.00631
353.00	67.314	0.60319	0.16840	0.18808	0.00432	0.03322	0.00279
353.00	100.215	0.59583	0.18729	0.17190	0.00176	0.04026	0.00297
353.00	117.116	0.58803	0.19243	0.16678	0.00300	0.04589	0.00386
353.00	209.169	0.55212	0.24359	0.12398	0.00440	0.07075	0.00516
375.00	66.466	0.60034	0.17110	0.18358	0.00259	0.03878	0.00361
375.00	66.530	0.60295	0.17529	0.18095	0.00104	0.03597	0.00381
375.00	94.117	0.59714	0.18049	0.17840	0.00397	0.03662	0.00337
375.00	106.695	0.59523	0.18327	0.17569	0.00365	0.03866	0.00350
375.00	128.300	0.59034	0.19262	0.16887	0.00414	0.04103	0.00299
398.00	93.872	0.59103	0.18404	0.17603	0.00632	0.04002	0.00256
398.00	97.345	0.59413	0.18481	0.17428	0.00357	0.03984	0.00337
398.00	122.373	0.59159	0.19144	0.17024	0.00430	0.03939	0.00304
398.00	216.246	0.57867	0.21594	0.15182	0.00509	0.04539	0.00308

TABLE 66. ARRHENIUS DATA FOR CATALYST "U"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	3.92	15.0	2.71	2.105
232	11.8	45.0	3.81	1.980
256	21.5	82.1	4.41	1.890
283	52.7	201.1	5.30	1.798
309	101.2	386.3	5.96	1.718
331	175.0	667.9	6.50	1.655
353	330.9	1263.	7.14	1.597
375	538.9	2057.	7.63	1.543
398	725.2	2768.	7.93	1.490

(a) Catalyst contains 0.112 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.75.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.262 grams

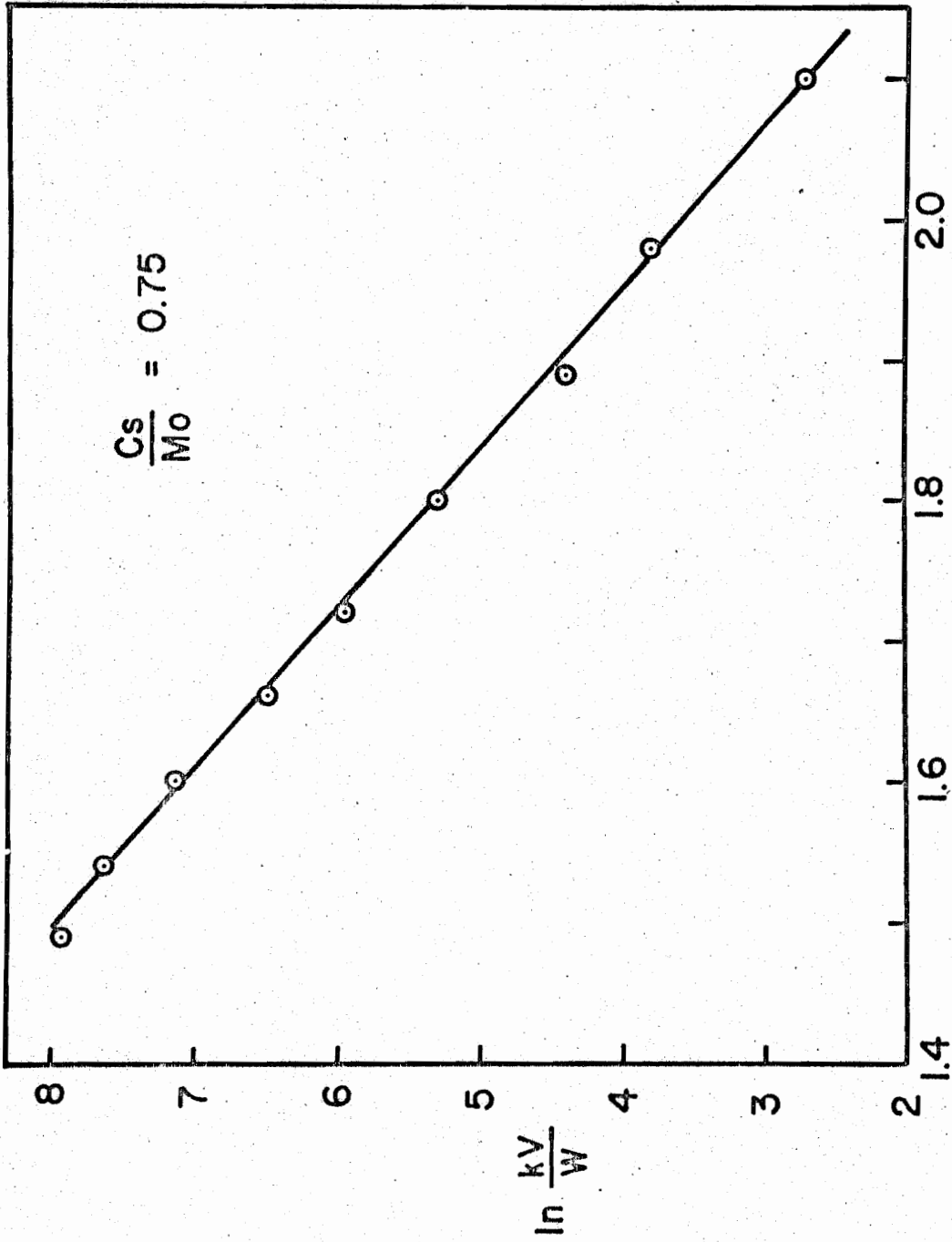


Figure 35. Arrhenius Plot for Catalyst "U"

TABLE 67. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "V"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
202.00	27.463	0.44591	0.35136	0.01445	0.00193	0.17774	0.00860
202.00	34.964	0.44159	0.35310	0.01360	0.00399	0.18120	0.00652
202.00	49.419	0.44297	0.35782	0.01280	0.00513	0.17541	0.00587
227.50	32.081	0.44963	0.34860	0.02054	0.00482	0.17066	0.00575
227.50	38.130	0.44975	0.34839	0.02055	0.00466	0.17072	0.00593
227.50	55.350	0.44861	0.35534	0.01522	0.00363	0.17014	0.00706
257.00	29.771	0.46495	0.33005	0.03545	0.00265	0.15905	0.00786
257.00	33.286	0.46616	0.33249	0.03302	0.00100	0.15806	0.00927
257.00	49.284	0.45818	0.34067	0.02607	0.00213	0.16358	0.00937
257.00	59.274	0.45592	0.34528	0.02343	0.00304	0.16379	0.00854
281.00	31.501	0.48783	0.30452	0.05820	0.00109	0.14070	0.00766
281.00	49.930	0.47055	0.32500	0.04236	0.00426	0.15152	0.00631
281.00	60.478	0.46791	0.32886	0.03760	0.00281	0.15507	0.00775
281.00	77.388	0.46201	0.33767	0.03142	0.00410	0.15791	0.00688
307.00	35.598	0.51987	0.26467	0.09661	0.00320	0.10948	0.00616
307.00	43.890	0.50487	0.28242	0.08098	0.00407	0.12161	0.00605
307.00	54.319	0.49766	0.29447	0.06859	0.00152	0.12979	0.00798
307.00	94.793	0.47683	0.32308	0.04527	0.00326	0.14411	0.00745
332.00	47.129	0.54905	0.23627	0.12506	0.00290	0.08161	0.00510
332.00	65.056	0.52469	0.26509	0.09913	0.00376	0.10211	0.00522
332.00	100.631	0.49854	0.29803	0.07018	0.00465	0.12276	0.00584
357.00	50.325	0.58739	0.19303	0.16403	0.00087	0.05034	0.00434
357.00	71.265	0.56222	0.22311	0.13805	0.00273	0.06905	0.00484
357.00	102.134	0.53415	0.25757	0.10856	0.00478	0.08994	0.00501
357.00	140.886	0.51585	0.28341	0.08581	0.00443	0.10488	0.00562
383.00	69.394	0.59287	0.18687	0.17048	0.00147	0.04420	0.00412
383.00	99.209	0.57356	0.21186	0.15078	0.00417	0.05612	0.00351
383.00	114.314	0.56856	0.21415	0.14902	0.00593	0.05967	0.00266
383.00	154.592	0.54503	0.25007	0.11641	0.00359	0.07970	0.00519
405.00	119.458	0.58205	0.20418	0.15829	0.00363	0.04828	0.00356
405.00	130.823	0.57645	0.21205	0.15288	0.00505	0.05127	0.00230
405.00	162.220	0.56372	0.22741	0.13839	0.00472	0.06236	0.00338
405.00	217.580	0.54929	0.25130	0.11981	0.00571	0.07039	0.00348

TABLE 68. ARRHENIUS DATA FOR CATALYST "V"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			In kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	1.95	7.01	1.95	2.105
228	3.17	11.4	2.43	1.995
257	6.29	22.6	3.12	1.886
281	12.1	43.5	3.77	1.805
307	25.8	92.8	4.53	1.724
332	55.9	201.1	5.30	1.653
357	128.4	461.9	6.14	1.587
383	222.2	799.3	6.68	1.524
405	366.7	1319.	7.19	1.475

(a) Catalyst contains 0.0670 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.278 grams



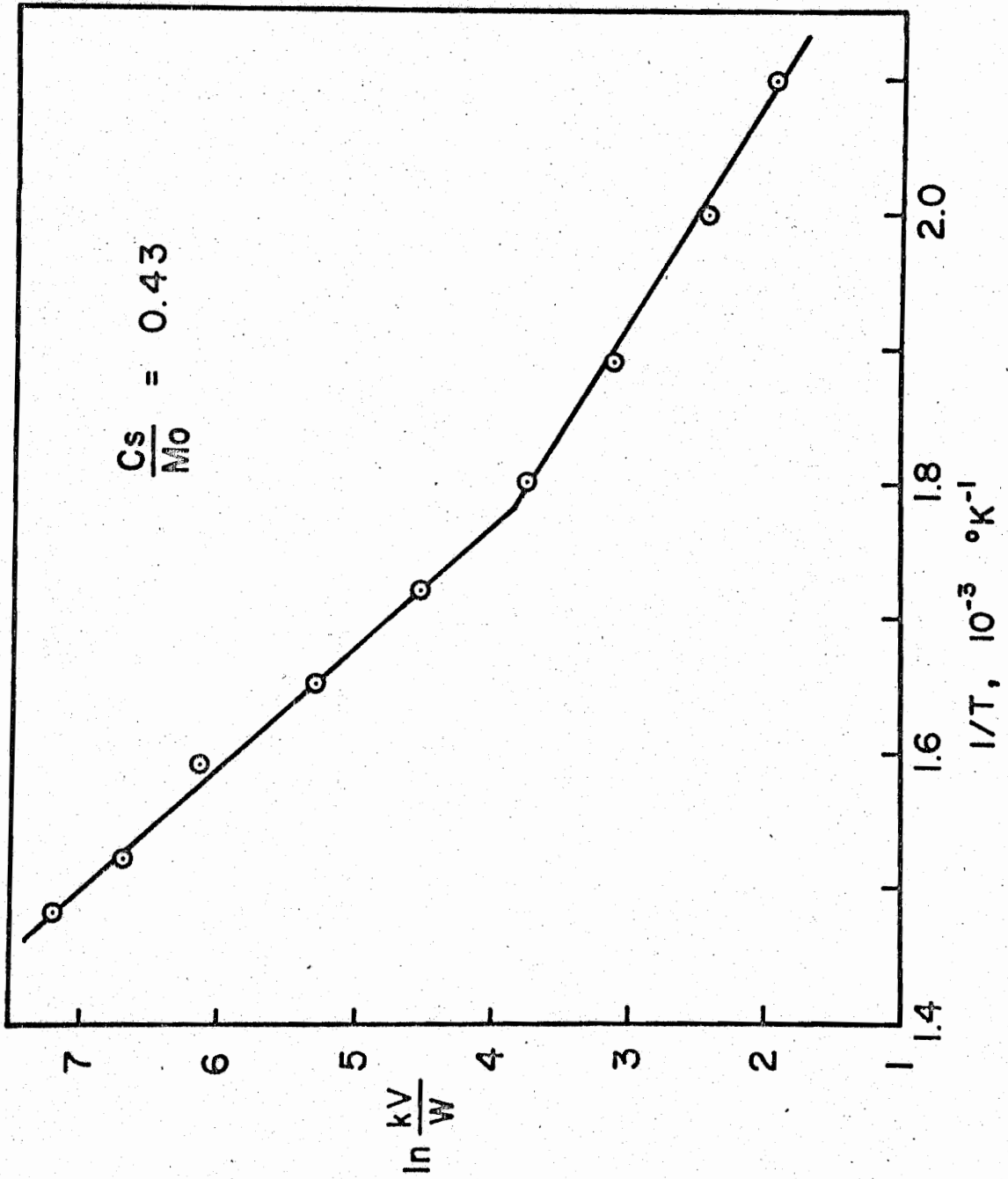


Figure 36. Arrhenius Plot for Catalyst "V"

TABLE 69. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "W"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
209.00	35.792	0.48023	0.23493	0.04178	0.00059	0.23152	0.01093
209.00	57.749	0.47394	0.24881	0.03083	0.00058	0.23402	0.01101
209.00	28.367	0.49280	0.23050	0.04936	0.00060	0.21593	0.01081
230.00	30.072	0.52146	0.20478	0.07620	0.00057	0.18796	0.00903
230.00	42.089	0.50409	0.22647	0.05612	0.00052	0.20430	0.00850
230.00	82.143	0.49036	0.25361	0.03443	0.00079	0.20998	0.01082
257.00	92.048	0.50356	0.24139	0.04678	0.00055	0.19661	0.01111
257.00	40.017	0.53159	0.19674	0.08512	0.00065	0.17655	0.00935
257.00	69.204	0.50900	0.22911	0.05673	0.00086	0.19459	0.00971
282.00	72.428	0.52645	0.20963	0.07514	0.00055	0.17936	0.00886
282.00	102.479	0.51304	0.23325	0.05551	0.00062	0.18867	0.00891
282.00	42.374	0.55401	0.17263	0.10892	0.00100	0.15485	0.00859
304.00	45.403	0.57088	0.15110	0.12815	0.00050	0.14126	0.00811
304.00	65.055	0.54517	0.18409	0.09835	0.00087	0.16305	0.00846
304.00	123.746	0.51862	0.23134	0.05953	0.00130	0.17954	0.00967
327.00	132.242	0.53555	0.21324	0.07653	0.00066	0.16468	0.00934
327.00	49.682	0.60055	0.12403	0.15674	0.00100	0.11158	0.00610
327.00	81.831	0.55492	0.17744	0.10718	0.00186	0.15095	0.00764
352.00	87.881	0.57723	0.15607	0.12783	0.00077	0.13033	0.00777
352.00	58.301	0.60420	0.11957	0.15095	0.00107	0.10863	0.00557
352.00	130.544	0.55038	0.19806	0.09271	0.00180	0.15039	0.00666
375.00	143.837	0.56940	0.18192	0.10881	0.00064	0.13148	0.00774
375.00	51.279	0.61978	0.10073	0.17871	0.00124	0.09482	0.00472
375.00	86.541	0.59458	0.13592	0.14800	0.00187	0.11286	0.00677
398.00	95.227	0.60715	0.12916	0.15584	0.00071	0.10150	0.00564
398.00	154.094	0.58568	0.16681	0.12520	0.00147	0.11517	0.00567
398.00	58.634	0.61351	0.10897	0.17264	0.00260	0.09683	0.00555

TABLE 70. ARRHENIUS DATA FOR CATALYST "W"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln k/V/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
209	6.58	23.8	3.17	2.074
230	11.8	42.6	3.75	1.988
257	19.4	70.0	4.25	1.886
282	30.1	108.8	4.69	1.801
304	43.0	155.3	5.05	1.733
327	74.2	268.3	5.59	1.666
352	105.7	381.8	5.94	1.600
375	168.6	609.3	6.41	1.543
398	237.3	857.2	6.75	1.490

(a) Catalyst contains 0.0670 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed no including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.279 grams

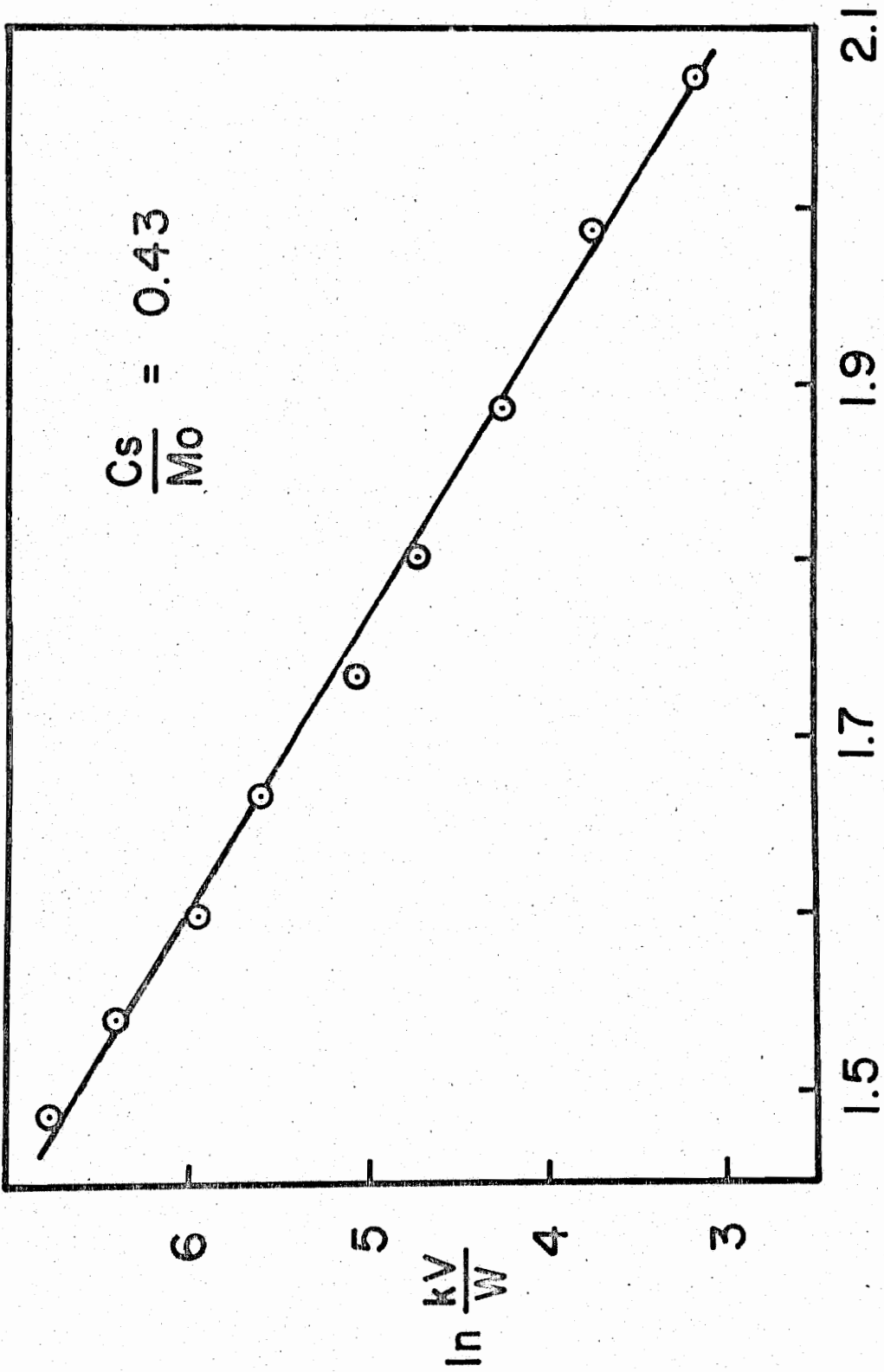


Figure 37. Arrhenius Plot for Catalyst "W"

TABLE 71. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "X"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
203.00	100.597	0.58757	0.33496	0.02185	0.00000	0.25560	0.00002
203.00	19.699	0.41308	0.29669	0.05381	0.00000	0.23534	0.00107
203.00	29.695	0.39533	0.30997	0.03833	0.00000	0.25537	0.00101
231.00	47.454	0.40474	0.31290	0.04149	0.00000	0.21839	0.02248
231.00	16.430	0.45813	0.25546	0.09693	0.00000	0.17269	0.01678
231.00	31.527	0.41778	0.29402	0.05749	0.00000	0.21586	0.01486
231.00	91.123	0.39486	0.33128	0.02731	0.00000	0.22526	0.02129
254.00	25.089	0.45941	0.24691	0.10189	0.00000	0.17364	0.01815
254.00	77.335	0.40771	0.31349	0.04266	0.00000	0.22049	0.01565
254.00	35.903	0.43586	0.27536	0.07687	0.00000	0.19633	0.01758
276.00	44.342	0.43884	0.26829	0.08091	0.00000	0.19293	0.01903
276.00	124.073	0.41204	0.32293	0.04002	0.00000	0.21001	0.01500
276.00	56.756	0.43160	0.28109	0.07085	0.00000	0.19911	0.01735
309.00	64.086	0.44701	0.26440	0.08692	0.00000	0.18364	0.01804
309.00	48.559	0.46850	0.24015	0.10980	0.00000	0.17035	0.01120
309.00	110.039	0.41976	0.29777	0.05657	0.00000	0.20885	0.01705
328.00	102.931	0.43996	0.28303	0.07400	0.00000	0.18703	0.01597
328.00	75.495	0.46051	0.24507	0.10336	0.00000	0.17632	0.01473
328.00	136.145	0.42660	0.29819	0.05973	0.00000	0.19847	0.01701
357.00	115.177	0.46335	0.24505	0.10478	0.00000	0.17074	0.01609
357.00	190.268	0.43792	0.29243	0.06824	0.00000	0.18769	0.01372
357.00	76.022	0.50159	0.19521	0.14889	0.00000	0.13978	0.01453
378.00	83.366	0.53422	0.16291	0.18135	0.00000	0.10874	0.01278
378.00	163.802	0.47981	0.25148	0.10965	0.00000	0.14749	0.01158
378.00	101.734	0.52267	0.20013	0.15681	0.00000	0.10766	0.01273
407.00	69.293	0.55546	0.15836	0.19415	0.00000	0.08161	0.01042
407.00	210.623	0.50049	0.24681	0.12223	0.00000	0.11812	0.01235
407.00	116.543	0.53936	0.18810	0.17114	0.00000	0.09028	0.01112

TABLE 72. ARRHENIUS DATA FOR CATALYST "X"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	ln kV/W	Plotted Data 1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	2.79	10.15	2.32	2.100
231	6.91	25.13	3.22	1.984
254	11.34	41.24	3.72	1.897
276	14.90	54.18	3.99	1.821
309	25.64	93.24	4.54	1.718
328	37.01	134.58	4.90	1.664
357	79.91	290.58	5.67	1.587
378	140.87	512.25	6.24	1.536
407	213.80	777.45	6.66	1.470

(a) Catalyst contains 0.0670 grams cesium acetate per gram impregnated catalyst. The cesium molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate weight, 0.275 grams

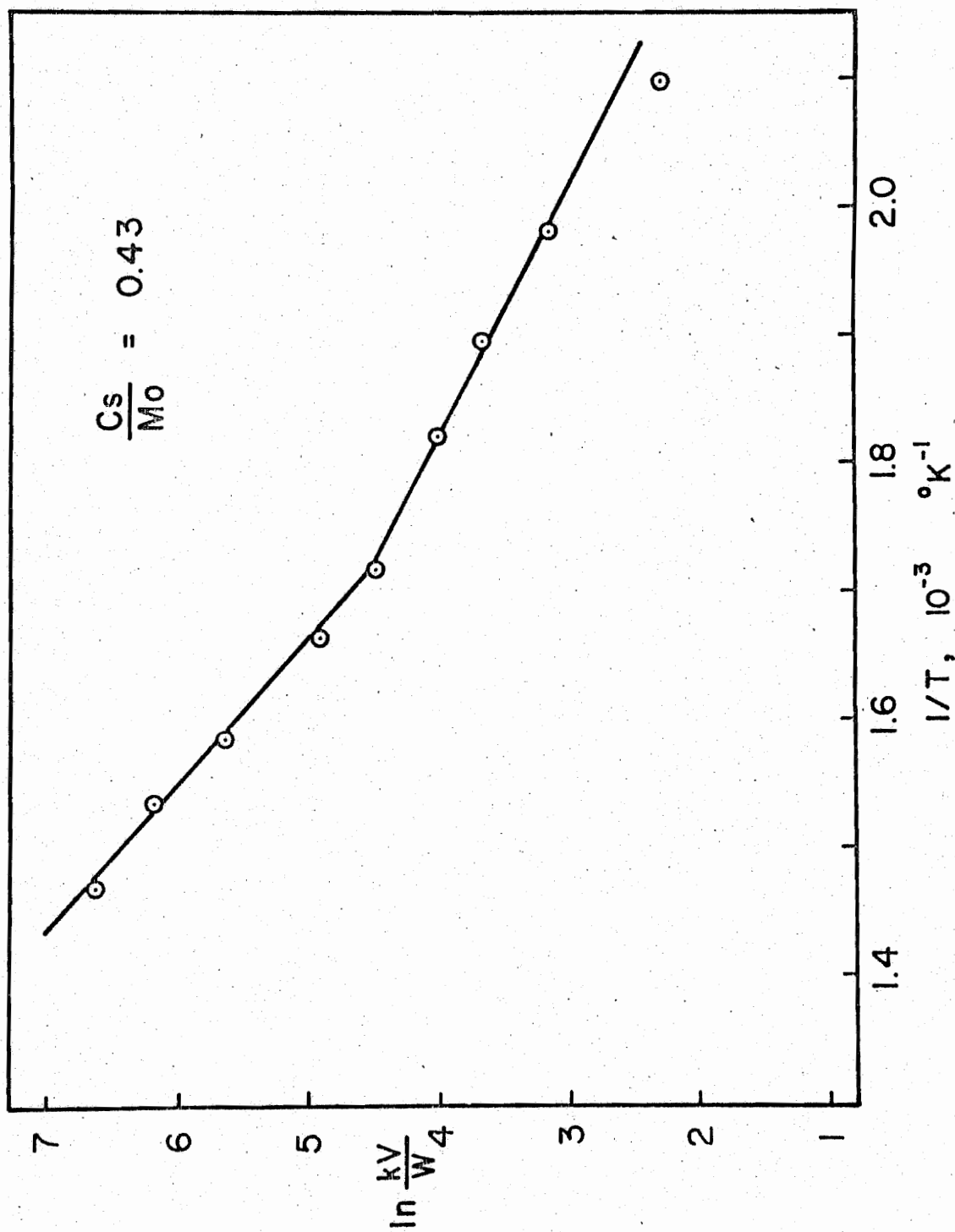


Figure 38. Arrhenius Plot for Catalyst "X"

TABLE 73. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "Y"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
200.00	23.968	0.45638	0.33319	0.03318	0.00600	0.16714	0.00410
200.00	36.633	0.45125	0.34235	0.02594	0.00608	0.16986	0.00453
200.00	46.535	0.44906	0.34696	0.02268	0.00633	0.16977	0.00519
200.00	68.083	0.44478	0.34921	0.02018	0.00700	0.17409	0.00475
229.00	29.144	0.47404	0.31706	0.04867	0.00466	0.15043	0.00514
229.00	40.219	0.46370	0.32735	0.03911	0.00541	0.15873	0.00569
229.00	51.904	0.46402	0.33516	0.03270	0.00310	0.15744	0.00758
229.00	79.720	0.45412	0.34387	0.02555	0.00521	0.16506	0.00619
257.00	43.818	0.48054	0.31197	0.05471	0.00496	0.14237	0.00545
257.00	52.423	0.47254	0.32010	0.04720	0.00553	0.14957	0.00506
257.00	69.617	0.46651	0.33127	0.03877	0.00592	0.15264	0.00490
257.00	96.115	0.46069	0.34012	0.03134	0.00596	0.15641	0.00548
277.00	48.036	0.48867	0.30003	0.06505	0.00511	0.13545	0.00570
277.00	76.141	0.47432	0.32046	0.04664	0.00436	0.14800	0.00622
277.00	92.061	0.46922	0.32851	0.04065	0.00507	0.15022	0.00634
277.00	116.508	0.46743	0.33637	0.03412	0.00362	0.15166	0.00680
308.00	55.198	0.50750	0.28164	0.08363	0.00510	0.11783	0.00429
308.00	73.584	0.49363	0.29664	0.06751	0.00346	0.13181	0.00695
308.00	99.665	0.48146	0.31326	0.05484	0.00538	0.13941	0.00566
308.00	125.288	0.48061	0.32360	0.04572	0.00226	0.14054	0.00727

TABLE 73 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2S
331.00	59.551	0.52530	0.26233	0.09980	0.00264	0.10379	0.00613
331.00	73.085	0.51299	0.27514	0.08882	0.00425	0.11321	0.00558
331.00	102.616	0.49430	0.29766	0.06953	0.00573	0.12790	0.00488
331.00	129.404	0.48886	0.31212	0.05772	0.00426	0.13028	0.00675
355.00	72.686	0.53802	0.24532	0.11676	0.00456	0.09073	0.00461
355.00	112.276	0.51361	0.28340	0.08325	0.00293	0.11051	0.00641
355.00	140.482	0.49947	0.29523	0.07391	0.00643	0.12064	0.00433
383.00	100.701	0.54265	0.23971	0.12326	0.00589	0.08482	0.00366
383.00	158.274	0.52305	0.27172	0.09602	0.00499	0.09975	0.00447
383.00	174.148	0.50963	0.28853	0.08176	0.00600	0.10956	0.00452
402.00	111.948	0.56084	0.22652	0.13577	0.00293	0.06896	0.00499
402.00	148.169	0.54033	0.24888	0.11842	0.00709	0.08217	0.00311
402.00	212.683	0.51922	0.28117	0.09960	0.00546	0.09969	0.00486
424.00	131.913	0.56639	0.21595	0.14453	0.00341	0.06564	0.00408
424.00	171.910	0.55102	0.23391	0.13078	0.00644	0.07487	0.00299
424.00	197.111	0.53686	0.25527	0.11129	0.00493	0.08702	0.00471
449.00	120.314	0.57380	0.20866	0.15523	0.00676	0.05327	0.00228
449.00	173.368	0.56530	0.22749	0.13866	0.00430	0.06052	0.00374
449.00	217.780	0.55069	0.24619	0.12297	0.00546	0.07098	0.00372

TABLE 74. ARRHENIUS DATA FOR CATALYST "Y"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
200	3.72	11.0	2.40	2.114
229	7.91	23.5	3.16	1.991
257	14.1	41.8	3.73	1.886
277	19.7	58.5	4.07	1.818
308	32.9	97.6	4.58	1.721
331	49.6	147.2	4.99	1.655
355	79.6	236.2	5.47	1.592
383	131.7	390.8	5.97	1.524
402	211.5	627.6	6.44	1.481
424	323.4	959.6	6.87	1.434
449	534.6	1586.	7.37	1.385

(a) Catalyst contains 0.0344 grams cesium acetate per gram impregnated catalyst. The cesium: molybdenum molar ratio is 0.21.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>  
 V = volume of catalyst bed not including inert solids, min<sup>-1</sup>  
 W = weight of catalyst used less the cesium acetate weight, 0.337 grams



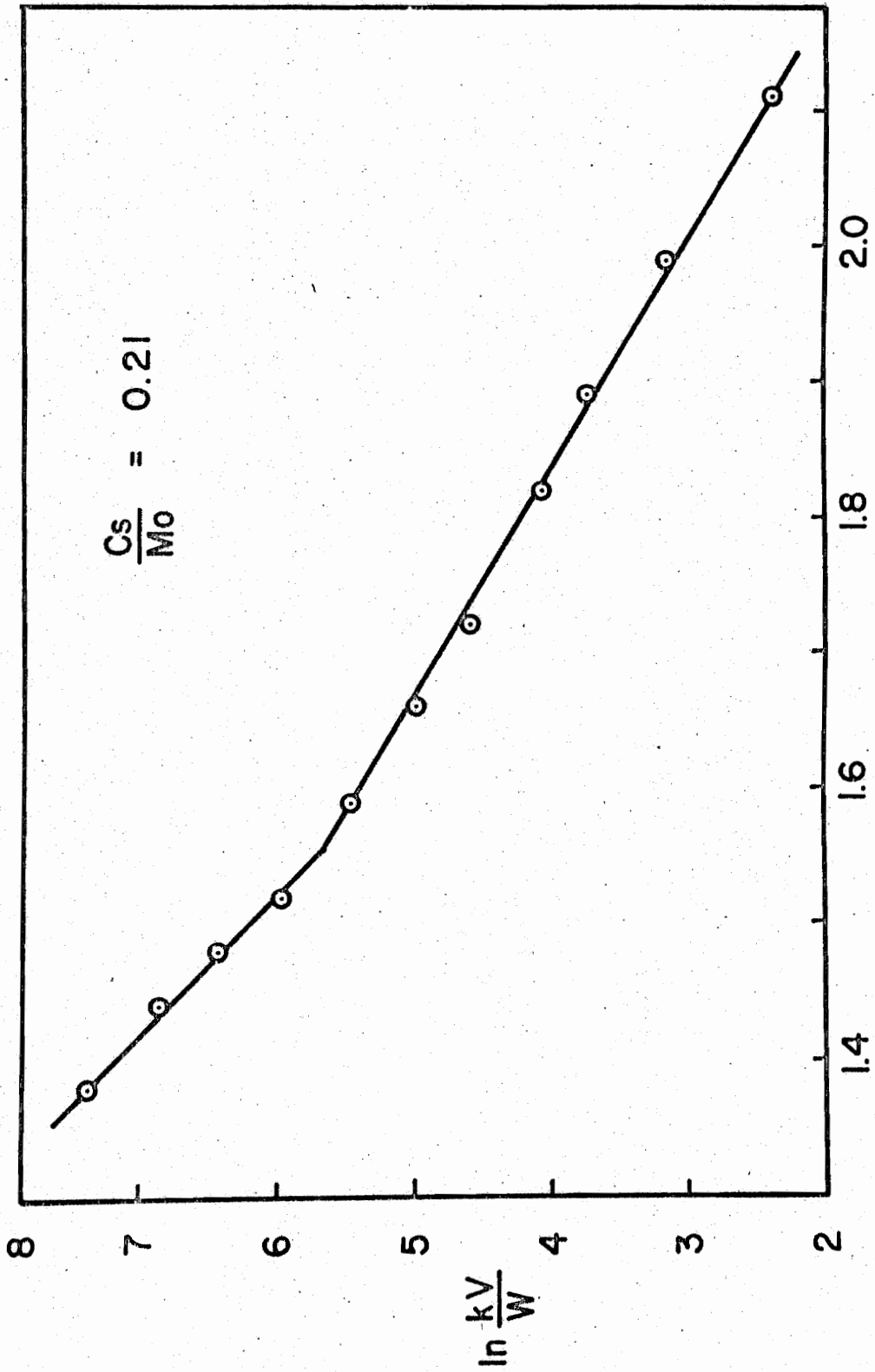


Figure 39. Arrhenius Plot for Catalyst "γ"

TABLE 75. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "Z"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2S
205.00	30.961	0.46282	0.30547	0.04907	0.00389	0.17204	0.00671
205.00	40.077	0.45472	0.31765	0.04067	0.00580	0.17532	0.00583
205.00	54.070	0.44757	0.32624	0.03289	0.00596	0.18121	0.00613
205.00	114.803	0.44347	0.34425	0.02121	0.00593	0.17858	0.00656
230.00	31.911	0.49323	0.26960	0.08424	0.00567	0.14183	0.00543
230.00	42.554	0.48635	0.28528	0.07099	0.00409	0.14693	0.00635
230.00	58.993	0.46806	0.30509	0.05355	0.00576	0.16078	0.00675
230.00	108.020	0.45342	0.33041	0.03338	0.00604	0.17027	0.00648
257.00	34.972	0.52929	0.23820	0.11590	0.00381	0.10788	0.00491
257.00	43.116	0.51260	0.25729	0.09955	0.00545	0.12033	0.00473
257.00	60.674	0.49546	0.27709	0.08091	0.00539	0.13564	0.00552
257.00	82.865	0.48094	0.29872	0.06377	0.00665	0.14439	0.00553
279.00	41.259	0.55077	0.22354	0.13314	0.00328	0.08430	0.00497
279.00	50.297	0.52765	0.23854	0.11714	0.00598	0.10576	0.00493
279.00	59.912	0.51734	0.25277	0.10434	0.00562	0.11444	0.00549
279.00	92.442	0.49497	0.28586	0.07683	0.00631	0.13039	0.00563

TABLE 75 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
307.00	53.675	0.55870	0.20913	0.14530	0.00398	0.07868	0.00421
307.00	64.963	0.53796	0.22814	0.12814	0.00662	0.09526	0.00388
307.00	91.194	0.51702	0.25525	0.10323	0.00600	0.11417	0.00432
307.00	106.145	0.50767	0.26796	0.09318	0.00713	0.11919	0.00485
330.00	68.892	0.56193	0.23823	0.14728	0.00400	0.07460	0.00396
330.00	89.779	0.53552	0.23280	0.12380	0.00593	0.09724	0.00471
330.00	131.532	0.51492	0.26520	0.09724	0.00638	0.11204	0.00422
357.00	82.757	0.56409	0.19896	0.15513	0.00582	0.07289	0.00311
357.00	102.193	0.55090	0.21741	0.13865	0.00539	0.08382	0.00384
357.00	155.361	0.52698	0.25661	0.10750	0.00647	0.09802	0.00443
382.00	95.634	0.57509	0.19407	0.16009	0.00311	0.06342	0.00421
382.00	106.249	0.56659	0.19683	0.15738	0.00577	0.06992	0.00350
382.00	143.324	0.55197	0.22027	0.13638	0.00419	0.08206	0.00512
399.00	117.047	0.57788	0.18480	0.16998	0.00669	0.05762	0.00302
399.00	144.905	0.56071	0.20887	0.14975	0.00738	0.07037	0.00292
399.00	215.278	0.53883	0.24709	0.11952	0.00791	0.08310	0.00355

TABLE 76. ARRHENIUS DATA FOR CATALYST "Z"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
205	7.40	14.7	2.69	2.09
230	15.5	30.9	3.43	1.99
257	27.6	55.0	4.01	1.87
279	43.9	87.5	4.47	1.81
307	68.5	136.5	4.92	1.72
330	98.2	195.6	5.28	1.66
357	140.2	279.3	5.63	1.59
382	220.5	439.2	6.09	1.53
399	287.5	572.8	6.35	1.49

(a) Catalyst contains no cesium acetate. The catalyst base is NaIcomco 474, which has 12.5% MoO<sub>3</sub> and 3.5% CoO on alumina. The cobalt:molybdenum molar ratio is 0.538.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used, 0.502 grams

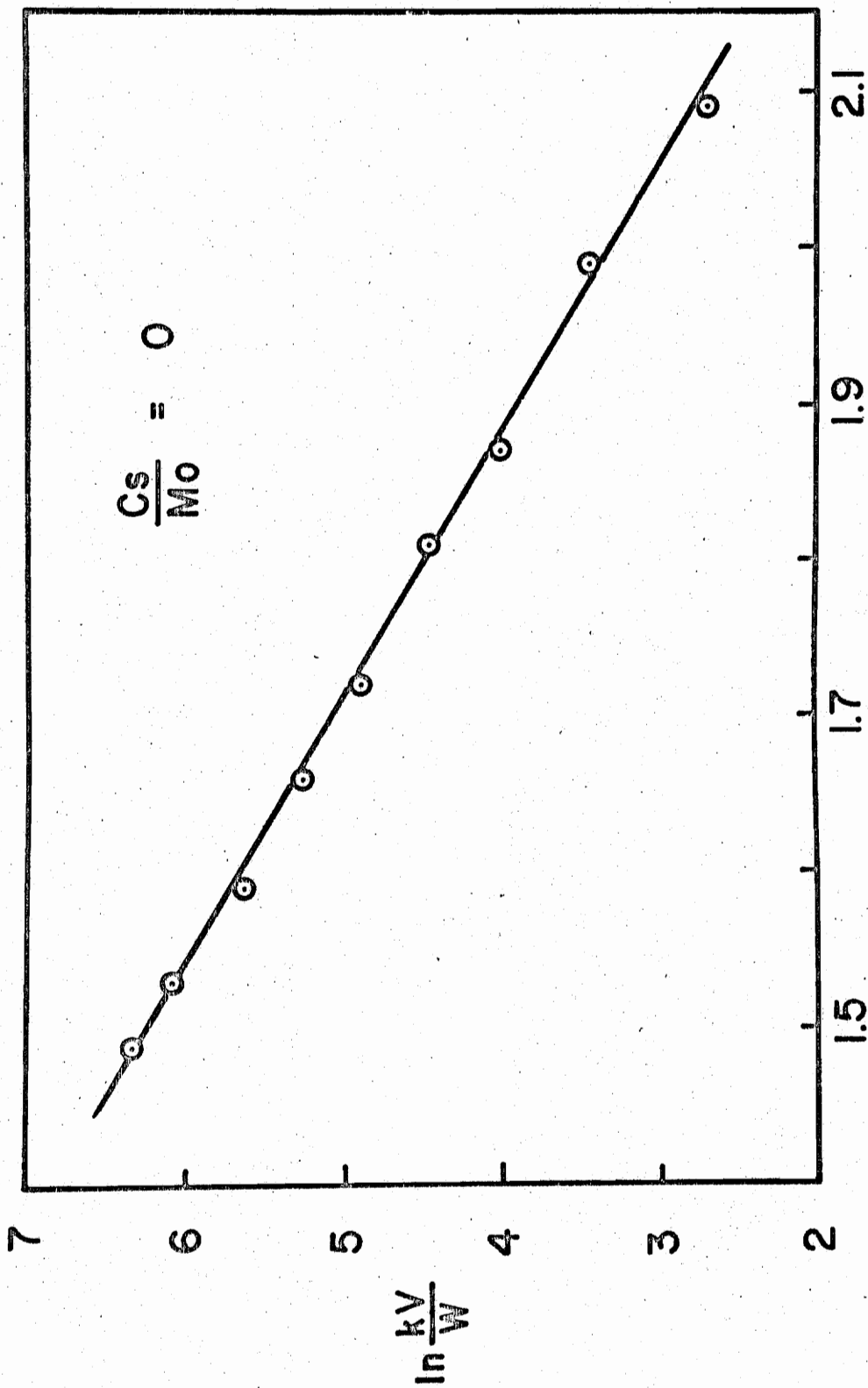


Figure 40. Arrhenius Plot for Catalyst "Z"

TABLE 77. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "AA"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CDS
203.00	56.017	0.41468	0.34656	0.02936	0.00000	0.20426	0.00515
203.00	29.064	0.42850	0.53213	0.04349	0.00000	0.19583	0.00000
203.00	39.160	0.41581	0.34028	0.03310	0.00000	0.20635	0.00446
230.00	41.986	0.42443	0.31965	0.04780	0.00000	0.20027	0.00786
230.00	55.448	0.42310	0.53375	0.04000	0.00000	0.19684	0.00630
230.00	29.315	0.43728	0.50832	0.05988	0.00000	0.18837	0.00616
256.00	31.052	0.46005	0.28026	0.08533	0.00000	0.16664	0.00772
256.00	50.146	0.43990	0.51670	0.05693	0.00000	0.18056	0.00592
256.00	70.113	0.42914	0.32743	0.04619	0.00000	0.19085	0.00640
277.00	71.659	0.44345	0.31517	0.05946	0.00000	0.17216	0.00975
277.00	36.720	0.46952	0.27621	0.09205	0.00000	0.15444	0.00778
277.00	68.150	0.43533	0.32549	0.05022	0.00000	0.18336	0.00550
304.00	106.761	0.44174	0.31569	0.05835	0.00000	0.17419	0.01003
304.00	50.480	0.47872	0.27313	0.09816	0.00000	0.14404	0.00595
304.00	85.917	0.44775	0.30501	0.06672	0.00000	0.17044	0.01008
329.00	86.592	0.46663	0.28348	0.08695	0.00000	0.15241	0.01054
329.00	57.799	0.49277	0.24915	0.11723	0.00000	0.13262	0.00823
329.00	50.304	0.50392	0.23404	0.13038	0.00000	0.12316	0.00849
353.00	54.189	0.52605	0.20631	0.15535	0.00000	0.10351	0.00899
353.00	78.792	0.49105	0.25069	0.11560	0.00000	0.13404	0.00862
353.00	107.455	0.47456	0.28341	0.09090	0.00000	0.14171	0.00943
379.00	115.771	0.49153	0.25394	0.11419	0.00000	0.12903	0.01132
379.00	64.508	0.53725	0.19586	0.16617	0.00000	0.09254	0.00817
379.00	94.738	0.50336	0.24052	0.12683	0.00000	0.12019	0.00910
403.00	109.045	0.51459	0.22286	0.14131	0.00000	0.11095	0.01028
403.00	63.189	0.54976	0.18167	0.17953	0.00000	0.08185	0.00720
403.00	87.652	0.52823	0.20908	0.15502	0.00000	0.09900	0.00667

TABLE 78. ARRHENIUS DATA FOR CATALYST "AA"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
203	2.76	9.17	2.22	2.10
230	5.56	18.47	2.92	1.99
256	10.70	35.55	3.57	1.89
277	15.13	50.27	3.92	1.82
304	23.90	79.40	4.37	1.73
329	39.19	130.20	4.87	1.66
353	62.04	206.11	5.33	1.60
379	94.60	314.29	5.75	1.53
403	131.57	437.11	6.08	1.48

(a) Catalyst contains 0.0252 grams lithium nitrate per gram impregnated catalyst. The lithium molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the lithium nitrate, 0.301 grams



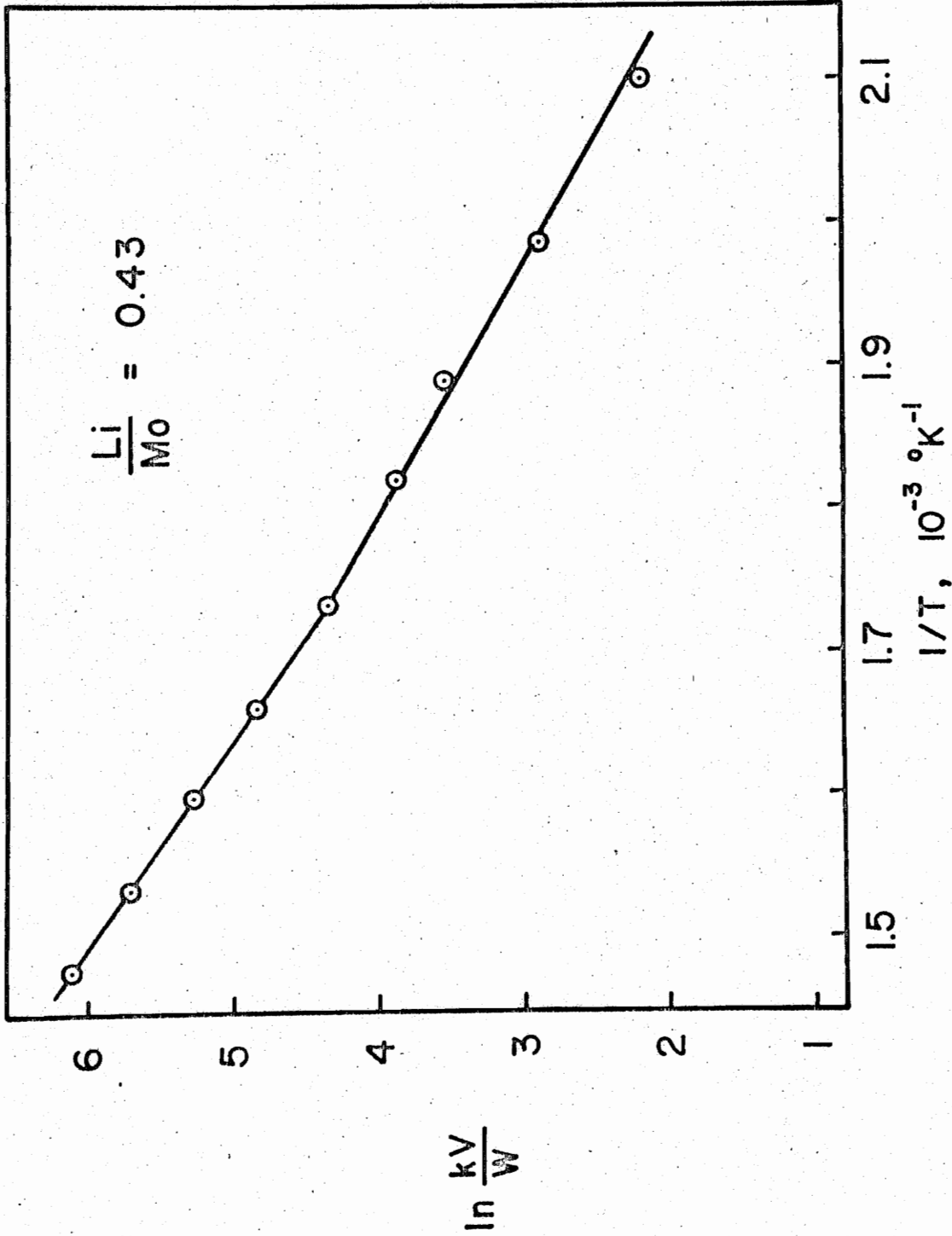


Figure 41. Arrhenius Plot for Catalyst "AA"

TABLE 79. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "BB"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
206.00	31.746	0.42639	0.34400	0.03644	0.00000	0.18082	0.01235
206.00	62.921	0.42576	0.36771	0.02413	0.00000	0.17156	0.01085
206.00	49.469	0.42422	0.36175	0.02638	0.00000	0.17606	0.01158
230.00	50.497	0.43657	0.35238	0.03722	0.00000	0.16193	0.01190
230.00	30.379	0.44368	0.32774	0.05321	0.00000	0.16428	0.01109
230.00	32.562	0.45266	0.34104	0.05091	0.00000	0.14566	0.00973
260.00	48.041	0.44682	0.32419	0.05655	0.00000	0.16334	0.00909
260.00	36.996	0.45362	0.30706	0.06859	0.00000	0.16228	0.00846
260.00	58.023	0.44336	0.33234	0.05072	0.00000	0.16711	0.00647
282.00	60.153	0.45934	0.31702	0.06637	0.00000	0.14816	0.00911
282.00	42.143	0.46963	0.29334	0.08343	0.00000	0.14624	0.00735
282.00	85.704	0.45053	0.34343	0.04865	0.00000	0.14963	0.00777
311.00	89.987	0.46800	0.32712	0.06553	0.00000	0.13101	0.00835
311.00	50.310	0.49065	0.27802	0.10157	0.00000	0.12277	0.00699
311.00	43.387	0.50596	0.25441	0.12108	0.00000	0.11161	0.00695
334.00	39.207	0.55123	0.19964	0.17116	0.00000	0.07236	0.00561
334.00	76.287	0.48800	0.29139	0.09349	0.00000	0.11941	0.00770
334.00	102.524	0.47416	0.32563	0.06933	0.00000	0.12340	0.00748
348.00	72.730	0.51823	0.25878	0.12493	0.00000	0.09187	0.00620
348.00	52.527	0.54191	0.21689	0.15783	0.00000	0.07749	0.00588
348.00	134.919	0.47935	0.33643	0.06643	0.00000	0.11160	0.00619
370.00	61.273	0.55143	0.20827	0.16689	0.00000	0.06860	0.00481
370.00	77.209	0.53569	0.23659	0.14479	0.00000	0.07715	0.00578
370.00	157.025	0.49099	0.32932	0.07577	0.00000	0.09788	0.00604
400.00	176.667	0.50980	0.31930	0.09013	0.00000	0.07428	0.00649
400.00	73.504	0.55261	0.21918	0.16195	0.00000	0.06172	0.00455
400.00	114.700	0.53376	0.25054	0.13677	0.00000	0.07386	0.00507

TABLE 80. ARRHENIUS DATA FOR CATALYST "BB"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
206	2.25	7.5	2.01	2.09
230	5.45	18.7	2.90	1.99
260	9.69	32.3	3.48	1.88
282	16.05	53.5	3.98	1.80
311	30.51	101.7	4.62	1.71
334	58.84	196.3	5.28	1.65
348	71.20	237.33	5.47	1.61
370	103.31	344.37	5.84	1.56
400	142.57	475.23	6.16	1.49

(a) Catalyst contains 0.0308 grams of sodium nitrate per gram impregnated catalyst. The sodium molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the sodium nitrate, 0.301 grams



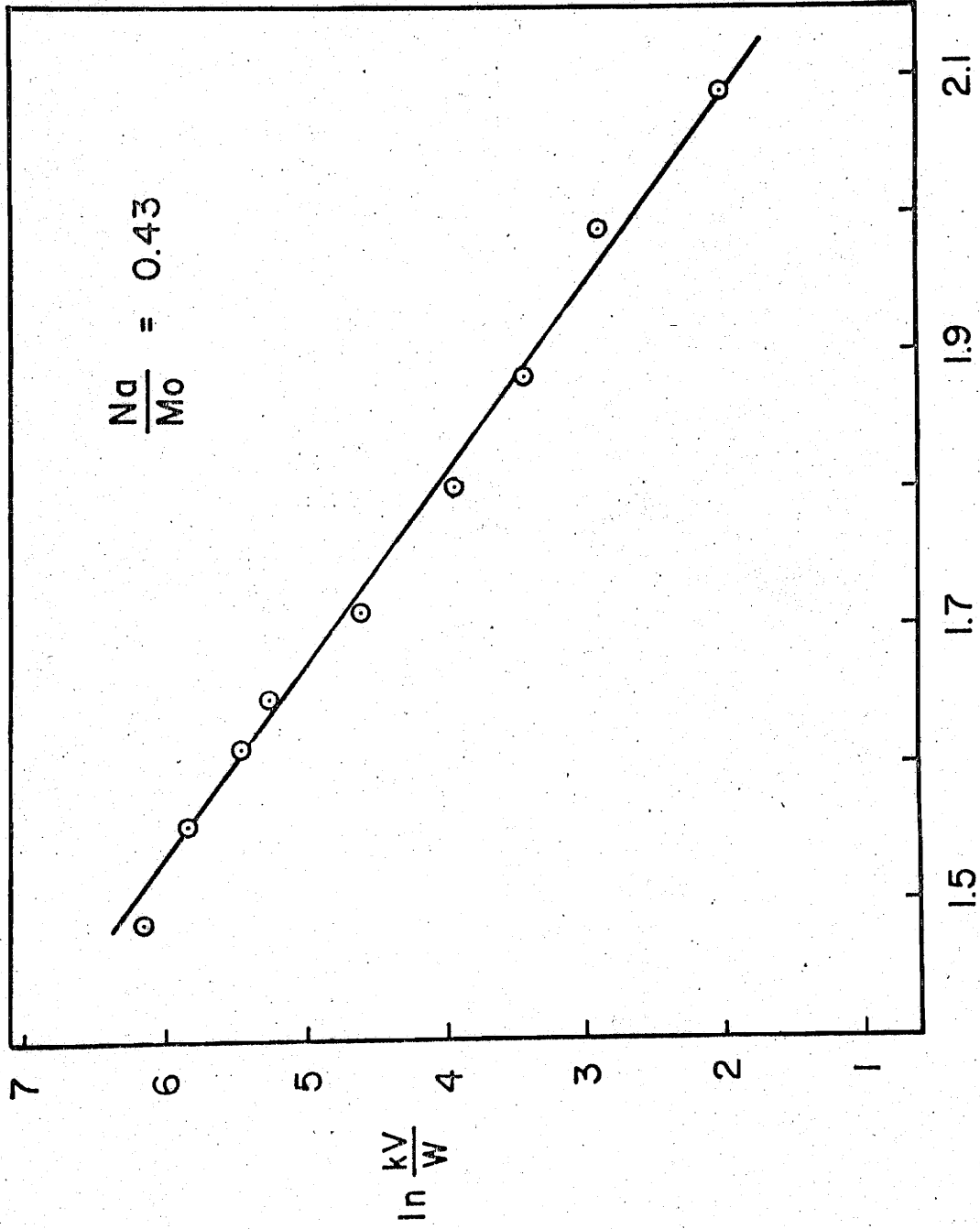


Figure 42. Arrhenius Plot for Catalyst "BB"

TABLE 81. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "CC"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2S
205.00	64.508	0.42034	0.35793	0.02640	0.00000	0.18659	0.00874
205.00	43.849	0.41584	0.33860	0.03397	0.00000	0.20220	0.00940
205.00	26.830	0.42494	0.31882	0.04847	0.00000	0.19940	0.00837
233.00	66.275	0.43690	0.34014	0.04358	0.00000	0.17034	0.00904
233.00	37.373	0.44757	0.30774	0.06525	0.00000	0.17157	0.00787
233.00	33.173	0.44608	0.30195	0.06745	0.00000	0.17625	0.00828
260.00	79.036	0.45580	0.33270	0.05668	0.00000	0.14748	0.00733
260.00	56.085	0.45956	0.30301	0.07357	0.00000	0.15623	0.00763
260.00	38.615	0.48455	0.27014	0.10255	0.00000	0.13641	0.00635
280.00	81.593	0.46977	0.31864	0.07070	0.00000	0.13413	0.00677
280.00	58.716	0.48523	0.28498	0.09537	0.00000	0.12888	0.00554
280.00	40.482	0.49737	0.26050	0.11376	0.00000	0.12262	0.00575
309.00	104.242	0.49350	0.31117	0.08620	0.00000	0.10324	0.00590
309.00	34.008	0.50191	0.28622	0.10298	0.00000	0.10268	0.00621
309.00	60.930	0.52164	0.24736	0.13239	0.00000	0.09348	0.00512
309.00	46.018	0.54558	0.20700	0.16464	0.00000	0.07802	0.00475
327.00	112.806	0.50803	0.30028	0.09888	0.00000	0.08798	0.00483
327.00	88.187	0.52129	0.26690	0.12233	0.00000	0.08403	0.00545
327.00	70.316	0.53629	0.23421	0.14628	0.00000	0.07806	0.00514
356.00	181.849	0.52107	0.34612	0.08212	0.00000	0.04537	0.00532
356.00	116.492	0.54193	0.26612	0.13292	0.00000	0.05393	0.00510
356.00	73.443	0.56233	0.20662	0.17311	0.00000	0.05187	0.00608
378.00	177.805	0.53908	0.32636	0.10102	0.00000	0.02974	0.00380
378.00	113.637	0.55846	0.24015	0.15423	0.00000	0.04295	0.00421
378.00	82.826	0.56399	0.23283	0.16066	0.00000	0.03827	0.00424
399.00	125.392	0.55687	0.23441	0.15634	0.00000	0.04844	0.00392
399.00	78.876	0.56363	0.20822	0.17294	0.00000	0.05261	0.00259

TABLE 82. ARRHENIUS DATA FOR CATALYST "CC"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
205	3.58	11.05	2.40	2.091
233	8.31	25.65	3.24	1.976
260	18.69	57.69	4.06	1.875
280	25.01	77.19	4.35	1.808
309	56.71	175.03	5.16	1.718
327	78.28	241.60	5.49	1.666
356	145.75	449.85	6.11	1.589
378	187.41	578.43	6.36	1.536

(a) Catalyst contains 0.0365 grams of potassium nitrate per gram impregnated catalyst. The potassium:molybdenum molar ratio is 0.43.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the potassium nitrate, 0.324 grams



TABLE 83. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "DD"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
198.00	35.071	0.37958	0.28787	0.04174	0.00000	0.28073	0.01008
198.00	23.299	0.39207	0.27670	0.05355	0.00000	0.27768	0.00000
198.00	51.454	0.37601	0.30264	0.03250	0.00000	0.28334	0.00553
250.00	61.402	0.40789	0.27966	0.05987	0.00000	0.25258	0.00000
250.00	30.745	0.44345	0.23449	0.10030	0.00000	0.21994	0.00182
250.00	42.904	0.42110	0.25920	0.07675	0.00000	0.23612	0.00683
301.00	49.891	0.48246	0.19640	0.13884	0.00000	0.18230	0.00000
301.00	79.915	0.44426	0.24596	0.09489	0.00000	0.21489	0.00000
301.00	59.269	0.46076	0.21909	0.11664	0.00000	0.19520	0.00830
352.00	66.857	0.53540	0.14811	0.18943	0.00000	0.12706	0.00000
352.00	128.684	0.47074	0.22934	0.11638	0.00000	0.18354	0.00000
352.00	110.881	0.48047	0.21737	0.12724	0.00000	0.17492	0.00000
397.00	117.614	0.53376	0.16295	0.18110	0.00000	0.12219	0.00000
397.00	136.698	0.51522	0.17538	0.16566	0.00000	0.13781	0.00594
397.00	222.738	0.48121	0.23783	0.11723	0.00000	0.16013	0.00355
347.00	91.413	0.47045	0.21049	0.12578	0.00000	0.19329	0.00000
347.00	225.644	0.42434	0.29577	0.05984	0.00000	0.22005	0.00000
347.00	117.619	0.45646	0.23879	0.10454	0.00000	0.20021	0.00000
302.00	109.816	0.40159	0.28453	0.05430	0.00000	0.25958	0.00000
302.00	50.036	0.44931	0.23275	0.10407	0.00000	0.21386	0.00000
302.00	70.204	0.43390	0.25477	0.08532	0.00000	0.22601	0.00000
251.00	34.392	0.41545	0.26780	0.06961	0.00000	0.24713	0.00000
251.00	69.421	0.38949	0.30287	0.03904	0.00000	0.26860	0.00000
251.00	45.952	0.39901	0.27780	0.05643	0.00000	0.26677	0.00000
218.00	44.628	0.37316	0.29760	0.03364	0.00000	0.29560	0.00000
218.00	34.957	0.38917	0.29219	0.04428	0.00000	0.27436	0.00000
218.00	22.561	0.39421	0.28147	0.05220	0.00000	0.27212	0.00000

TABLE 84. ARRHENIUS DATA FOR CATALYST "DD"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
198	3.16	10.39	2.34	2.123
250	11.31	37.20	3.62	1.912
301	32.45	106.74	4.67	1.742
352	92.17	303.19	5.71	1.600
397	183.87	604.84	6.40	1.492
347	58.17	191.35	5.25	1.613
302	21.78	71.64	4.27	1.739
251	7.42	24.41	3.19	1.908
218	3.04	10.00	2.30	2.036

(a) Catalyst contains 0.0365 grams of potassium nitrate per gram impregnated catalyst. The potassium:molybdenum molar ratio is 0.43. The runs were conducted in the following order: 198°C, 250°C, 301°C, 352°C, 397°C, 347°C, 302°C, 251°C, and 218°C.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the potassium nitrate weight, 0.304 grams

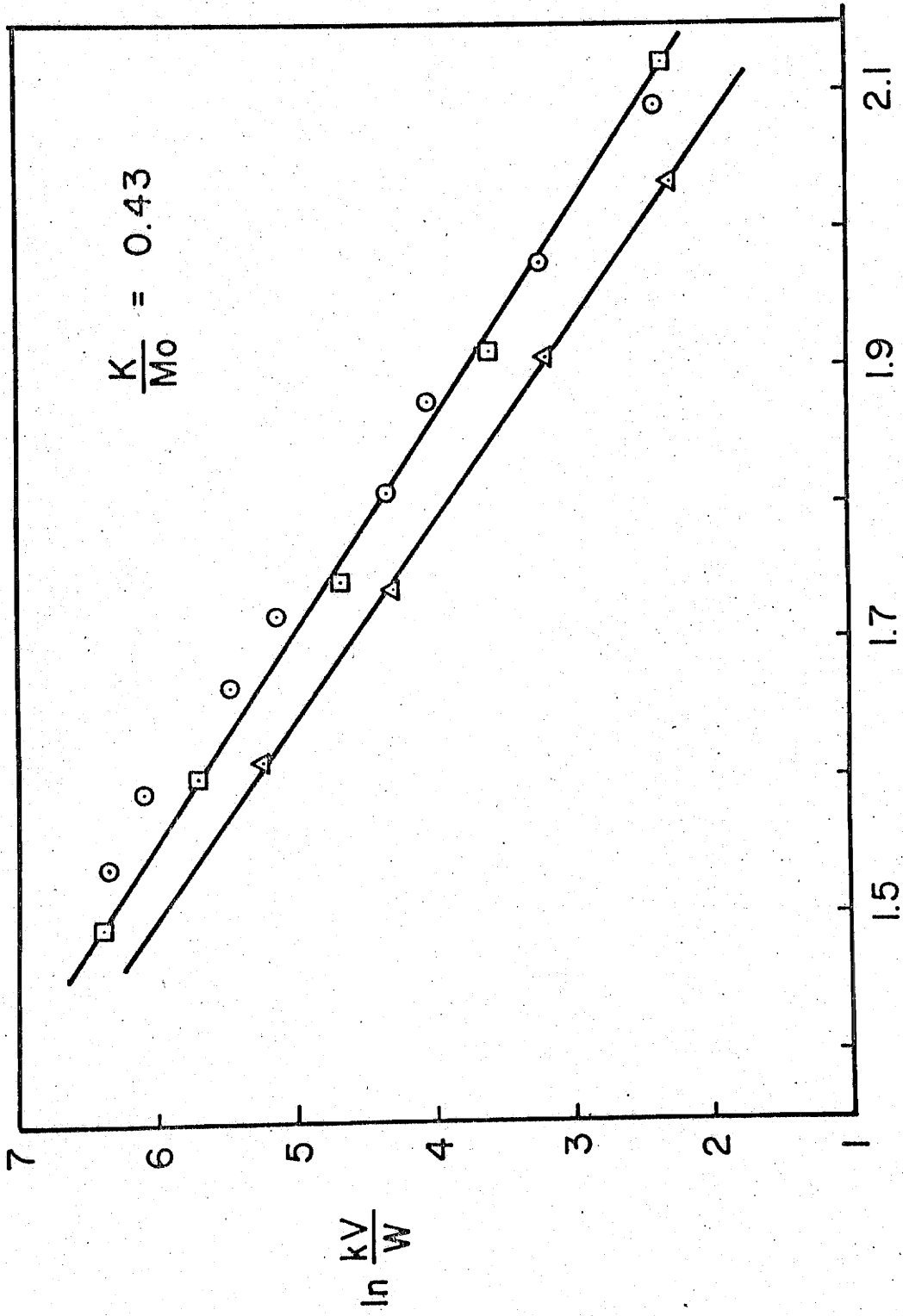


Figure 43. Arrhenius Plot for Catalysts "CC" and "DD"

TABLE 85. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "EE"

TEMP	FLOW	HYDROGEN	CO	CO <sub>2</sub>	H <sub>2</sub> S	WATER	CO <sub>S</sub>
158.00	30.290	0.45670	0.26552	0.01677	0.00344	0.25757	0.00000
158.00	20.003	0.46818	0.27127	0.01757	0.00334	0.23964	0.00000
177.00	20.653	0.49057	0.25854	0.03309	0.00240	0.21197	0.00343
177.00	35.989	0.46570	0.27563	0.01495	0.00435	0.23548	0.00389
177.00	45.181	0.47466	0.27432	0.02036	0.00550	0.22094	0.00422
209.00	23.813	0.50609	0.24178	0.04850	0.00152	0.19611	0.00601
209.00	43.927	0.49323	0.25619	0.03283	0.00352	0.21827	0.00596
209.00	88.479	0.49477	0.27437	0.02234	0.00361	0.20322	0.00668
227.00	48.993	0.49588	0.24501	0.04377	0.00272	0.20688	0.00574
227.00	94.107	0.48915	0.26701	0.02873	0.00379	0.20486	0.00645
227.00	25.956	0.51935	0.21873	0.06994	0.00370	0.18380	0.00448
254.00	27.192	0.55169	0.17936	0.10463	0.00173	0.15856	0.00433
254.00	48.723	0.51768	0.22393	0.06631	0.00390	0.18288	0.00529
254.00	98.473	0.50069	0.25522	0.04094	0.00430	0.19252	0.00632
272.00	98.981	0.50786	0.24363	0.04865	0.00213	0.18952	0.00821
272.00	55.047	0.53040	0.20907	0.07937	0.00293	0.17205	0.00618
272.00	27.960	0.56661	0.16196	0.12239	0.00305	0.14070	0.00529
272.00	98.797	0.50519	0.24308	0.04981	0.00399	0.19210	0.00584

TABLE 85 (cont'd)

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2
305.00	109.784	0.52593	0.22481	0.06660	0.00155	0.17395	0.00716
305.00	56.832	0.56339	0.17058	0.11562	0.00281	0.14297	0.00463
305.00	30.695	0.60321	0.11787	0.16428	0.00374	0.10760	0.00331
326.00	30.732	0.61966	0.10206	0.17916	0.00256	0.09293	0.00363
326.00	58.950	0.57934	0.15378	0.13244	0.00316	0.12681	0.00446
326.00	101.197	0.54673	0.20146	0.09059	0.00318	0.15225	0.00579
349.00	106.342	0.56821	0.17793	0.11124	0.00109	0.13582	0.00571
349.00	61.926	0.60602	0.12234	0.16180	0.00292	0.10334	0.00357
349.00	33.096	0.62406	0.09074	0.19051	0.00526	0.08690	0.00253
374.00	33.774	0.62106	0.09689	0.18451	0.00420	0.08993	0.00341
374.00	74.860	0.60444	0.12666	0.16022	0.00460	0.10119	0.00289
374.00	137.035	0.56907	0.17805	0.11529	0.00487	0.12858	0.00415
400.00	126.330	0.59615	0.14873	0.14225	0.00338	0.10531	0.00418
400.00	67.196	0.60827	0.11522	0.17041	0.00628	0.09684	0.00299
400.00	36.611	0.60736	0.11011	0.17526	0.00836	0.09592	0.00299

TABLE 86. ARRHENIUS DATA FOR CATALYST "EE"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
158	1.33	4.85	1.58	2.32
177	3.03	11.0	2.40	2.22
209	5.71	20.8	3.04	2.07
227	9.32	34.0	3.53	2.00
254	17.2	62.6	4.14	1.90
272	23.0	83.7	4.43	1.83
305	45.0	164.1	5.10	1.73
326	60.9	222.2	5.40	1.67
349	97.2	354.2	5.87	1.61
374	138.1	503.3	6.22	1.55
400	212.0	773.0	6.65	1.49

(a) Catalyst contains 0.0651 grams of cesium acetate and 0.0228 grams of lithium nitrate per gram impregnated catalyst. The cesium:molybdenum molar ratio is 0.43 and the lithium:molybdenum molar ratio is 0.42.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate and lithium nitrate weight, 0.274 grams



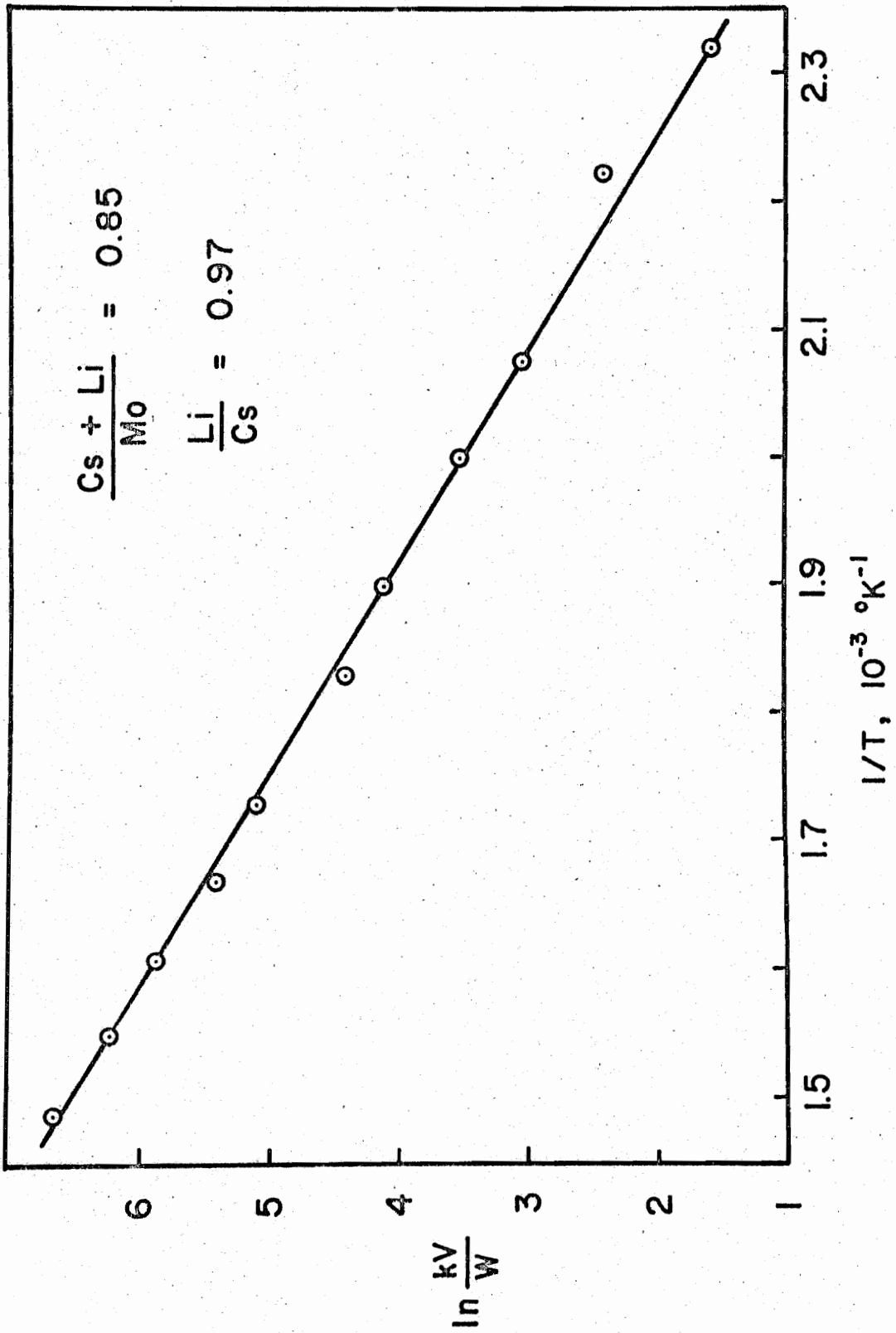


Figure 44. Arrhenius Plot for Catalyst "EE"

TABLE 87. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "FF"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	COS
205.00	28.416	0.38073	0.32605	0.02389	0.00092	0.25829	0.01021
205.00	68.281	0.37499	0.33918	0.01517	0.00167	0.25620	0.01280
205.00	37.805	0.37853	0.33377	0.01972	0.00174	0.25571	0.01053
257.00	41.710	0.40031	0.30980	0.04215	0.00127	0.23577	0.01071
257.00	32.470	0.41156	0.30224	0.05099	0.00073	0.22511	0.00936
257.00	65.878	0.39370	0.32644	0.03048	0.00129	0.24009	0.00801
308.00	82.628	0.40753	0.31202	0.04384	0.00053	0.22800	0.00809
308.00	37.510	0.44007	0.26812	0.08222	0.00062	0.19962	0.00934
308.00	50.094	0.42288	0.28818	0.06370	0.00074	0.21494	0.00956
350.00	53.513	0.46302	0.24398	0.10542	0.00027	0.17921	0.00810
350.00	90.316	0.42832	0.29067	0.06490	0.00051	0.20597	0.00964
350.00	35.731	0.49008	0.20703	0.13771	0.00049	0.15655	0.00815
405.00	40.334	0.53804	0.15887	0.18551	0.00023	0.11177	0.00557
405.00	69.908	0.49437	0.21311	0.13711	0.00085	0.14603	0.00853
405.00	114.500	0.45686	0.26558	0.09261	0.00143	0.17527	0.00825

TABLE 88. ARRHENIUS DATA FOR CATALYST "FF"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
205	0.45	1.59	0.46	2.09
257	4.49	15.87	2.76	1.89
308	12.10	42.76	3.76	1.72
350	28.95	102.30	4.63	1.61
405	76.62	270.74	5.60	1.47

(a) Catalyst contains 0.0590 grams of cesium acetate and 0.115 grams of zinc nitrate hexahydrate per gram impregnated catalyst. The cesium:molybdenum molar ratio is 0.54 and the zinc:molybdenum molar ratio of 0.67.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>

V = volume of catalyst bed not including inert solids, cm<sup>3</sup>

W = weight of catalyst used less the cesium acetate and zinc nitrate hexahydrate weight, 0.283 grams



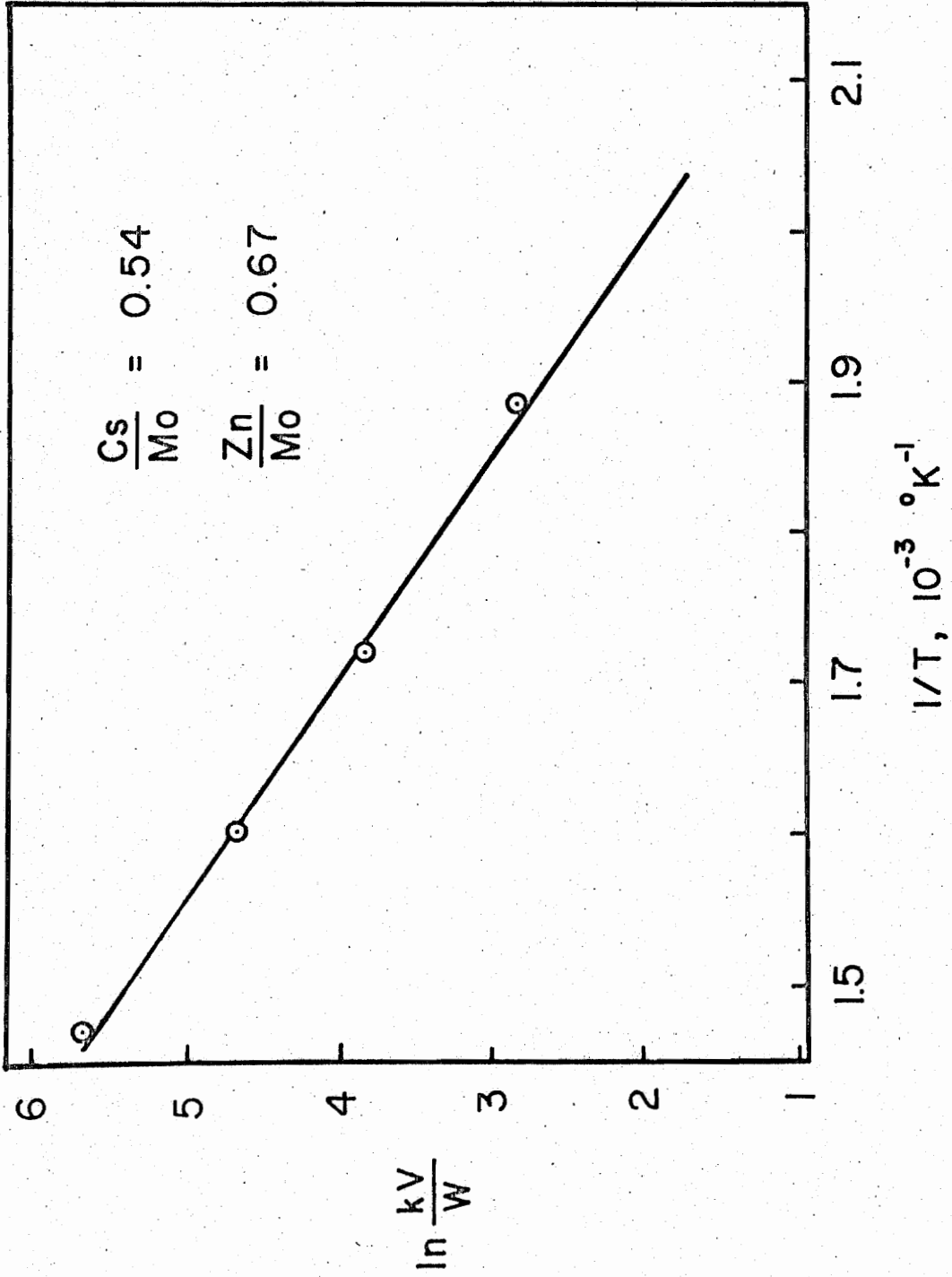


Figure 45. Arrhenius Plot for Catalyst "FF"

TABLE 89. MOLE FRACTIONS OF PRODUCT GASES FOR CATALYST "GG"

TEMP	FLOW	HYDROGEN	CO	CO2	H2S	WATER	CO2
202.00	75.808	0.36865	0.33381	0.01308	0.00000	0.28445	0.00000
202.00	42.056	0.37163	0.32325	0.01990	0.00000	0.28522	0.00000
202.00	29.749	0.36970	0.32027	0.02046	0.00000	0.28957	0.00000
230.00	60.590	0.38766	0.32522	0.02682	0.00000	0.26030	0.00000
230.00	44.392	0.38447	0.30634	0.03480	0.00000	0.27439	0.00000
230.00	32.132	0.37819	0.30411	0.03283	0.00000	0.28487	0.00000
230.00	19.329	0.39145	0.28182	0.05066	0.00000	0.27607	0.00000
253.00	65.302	0.38813	0.30356	0.03802	0.00000	0.27029	0.00000
253.00	42.096	0.39790	0.28176	0.05387	0.00000	0.26647	0.00000
253.00	30.475	0.41577	0.27124	0.06802	0.00000	0.24497	0.00000
278.00	63.774	0.41419	0.27223	0.06674	0.00000	0.24633	0.00000
278.00	53.216	0.42194	0.25866	0.07744	0.00000	0.24196	0.00000
278.00	44.337	0.43052	0.25098	0.08556	0.00000	0.23295	0.00000
303.00	117.792	0.43401	0.29157	0.06674	0.00000	0.20767	0.00000
303.00	66.453	0.46408	0.23280	0.11134	0.00000	0.19178	0.00000
303.00	51.179	0.48243	0.20372	0.13512	0.00000	0.17872	0.00000
330.00	124.159	0.46417	0.25122	0.10206	0.00000	0.18256	0.00000
330.00	102.743	0.48166	0.22755	0.12268	0.00000	0.16812	0.00000
330.00	83.737	0.49906	0.20296	0.14372	0.00000	0.15426	0.00000
349.00	192.571	0.47342	0.27579	0.09419	0.00000	0.15660	0.00000
349.00	138.517	0.49664	0.23414	0.12674	0.00000	0.14248	0.00000
349.00	109.578	0.52301	0.19292	0.16062	0.00000	0.12345	0.00000
377.00	211.099	0.50306	0.24927	0.12225	0.00000	0.11999	0.00544
377.00	196.444	0.51103	0.23922	0.13127	0.00000	0.11848	0.00000
377.00	144.807	0.53737	0.19314	0.16761	0.00000	0.10189	0.00000
404.00	304.873	0.51442	0.26582	0.11948	0.00000	0.09435	0.00593
404.00	239.666	0.51917	0.23488	0.13749	0.00000	0.10246	0.00601
404.00	200.940	0.53575	0.21139	0.15756	0.00000	0.09530	0.00000

TABLE 90. ARRHENIUS DATA FOR CATALYST "GG"

T, °C	Slope, kV cm <sup>3</sup> /min.	Normalized slope, kV/W <sup>(b)</sup> cm <sup>3</sup> /gm catalyst-min.	Plotted Data	
			ln kV/W	1/T, 10 <sup>-3</sup> °K <sup>-1</sup>
202	0.40	1.52	0.42	2.105
230	2.41	9.16	2.22	1.988
253	6.38	24.26	3.19	1.901
278	13.60	51.71	3.95	1.814
303	33.17	126.12	4.84	1.736
330	64.19	244.07	5.50	1.658
349	111.30	423.19	6.05	1.607
377	188.07	715.10	6.57	1.538
404	276.70	1052.09	6.96	1.477

(a) Catalyst contains 0.134 grams cesium acetate per gram impregnated catalyst. The catalyst base is Air Products and Chemicals, Inc. hard alumina catalyst 200S impregnated with cobalt nitrate hexahydrate and ammonium molybdate in an amount comparable to Naicom 474. The cesium:molybdenum ratio is 1.07.

(b) k = pseudo-first-order rate constant, min<sup>-1</sup>  
 V = volume of catalyst bed not including inert solids, cm<sup>3</sup>  
 W = weight of catalyst used less the cesium acetate weight, 0.263 grams

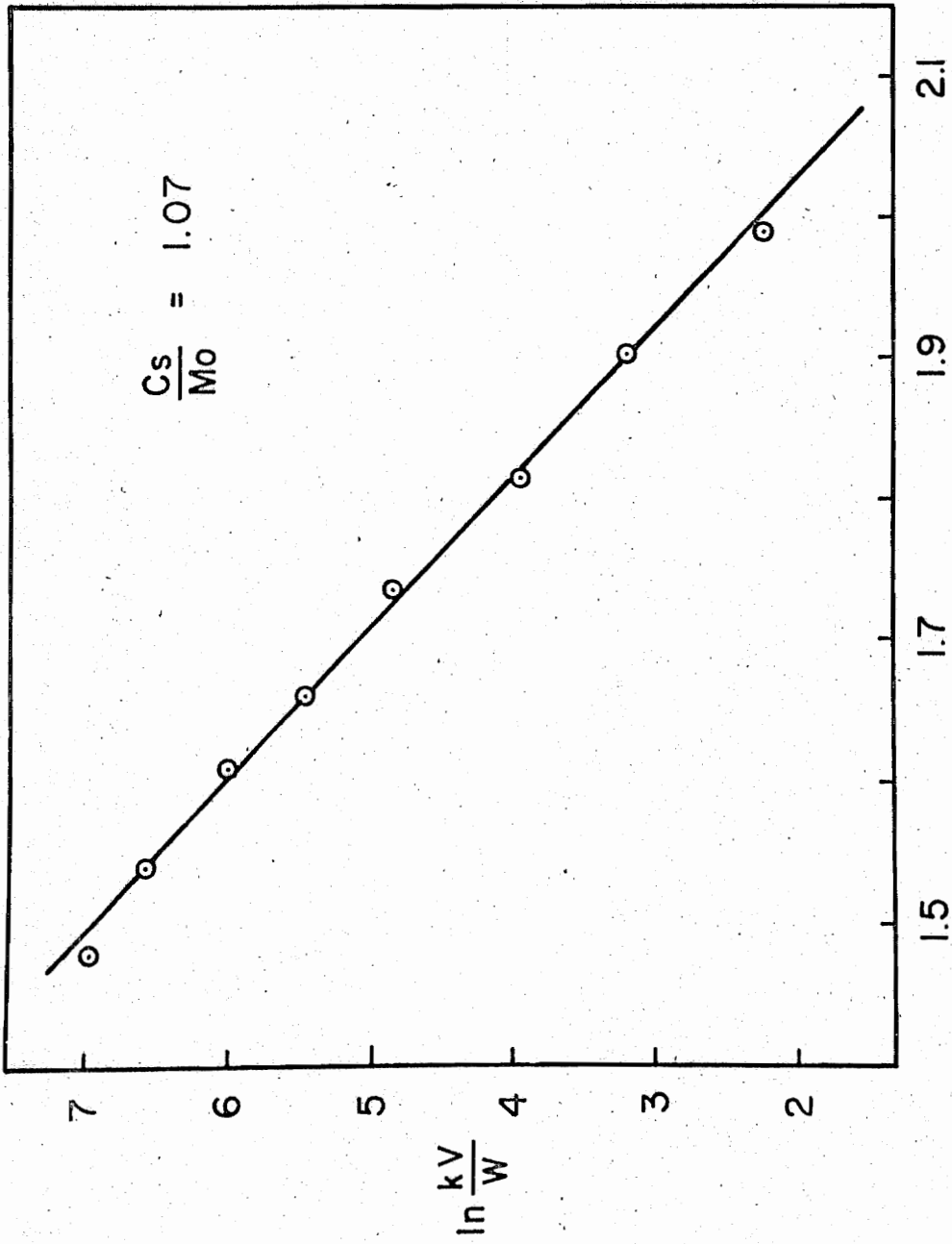


Figure 46. Arrhenius Plot for Catalyst "GG"

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## VI. DISCUSSION

In this section, we shall discuss the results obtained from our water-gas shift, methanation, and ethanol dehydration studies and provide recommendations for further work. The five important reaction variables and the implications of the data presented in the results sections are also discussed.

### A. Gas Composition

Three slightly different gas compositions (Tables 2, 3, and 4) were employed for the water-gas shift studies. Only one catalyst was tested with the three different cylinders. Upon examination of the results for catalysts "V", "W", and "X", all of the same composition (Cs:Mo = 0.43), catalyst "V" was found to be slightly more active than the others. Catalysts "R" and "S", each with Cs:Mo = 1.07, were tested with cylinder #1 and cylinder #2, respectively. Catalyst "R" was more active. The differences in catalytic activity of these catalysts may be within experimental error, so we will make no attempt to correlate the data with the compositions of the different gas cylinders.

For catalytic methanation, preliminary studies indicated that carbon deposition occurred with a dry gas feed of composition 37.2% H<sub>2</sub>, 59.1% CO, 1.49% CO<sub>2</sub>, and 2.22% COS. In addition, the water-gas shift reaction dominated the methanation reaction. We were able to obtain higher methane yields with a gas feed that had a H<sub>2</sub>/CO molar ratio equal to 3.27.

### B. Catalyst Loading

The activity of the "Aldridge" catalyst is markedly dependent upon catalyst loading. As can be seen from Figures 50 through 52 at 400°C, a pressure of 715 mm Hg, and a Cs:Mo molar ratio of 1.0, full strength catalysts are much more active than the one-half and one-fifth strength catalysts. The rate constants for the full, one-half, and one-fifth strength catalysts at these conditions are 3400, 1810, and 460 min<sup>-1</sup>, respectively. Transition temperatures were frequently observed with high catalyst loadings but not with low catalyst loadings. The difference in gas cylinder composition (cylinder #1 versus cylinder #3) might have obscured or eliminated such effects in the one-fifth and one-half strength catalysts.

### C. Cesium:Molybdenum Ratio

The Cs:Mo molar ratio is the most important experimental variable in our water-gas shift studies. The activities, kV/W, of one-fifth, one-half, and full strength catalysts, respectively, are plotted versus this ratio at 260°C. As can be seen from Figures 47, 48, and 49, the data are not sufficient for the one-fifth strength catalysts, and some points do not fall on the correlation curve for the one-half strength catalysts at this temperature. For the full strength catalysts, the activity appears to be a maximum at a Cs:Mo molar ratio of 1.07.

The activity is correlated better at 400°C. The one-half and full strength catalysts apparently have maximum activity at a Cs:Mo molar ratio of 1.8 and 1.07, respectively. For the one-fifth strength catalysts, the relationship is linear, and maximum activity probably occurs

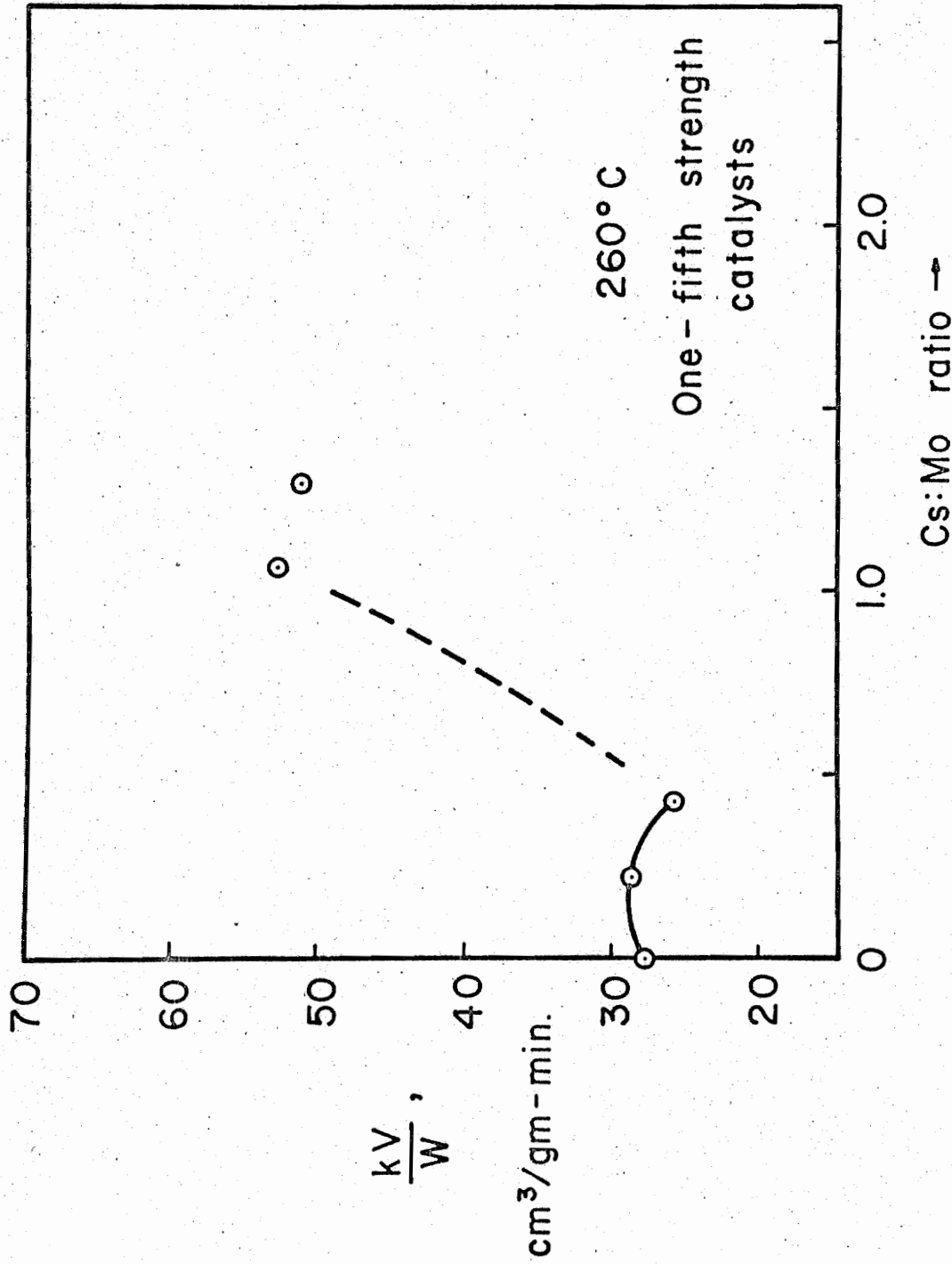


Figure 47. Catalyst Activity vs Cs:Mo Molar Ratio at 260°C

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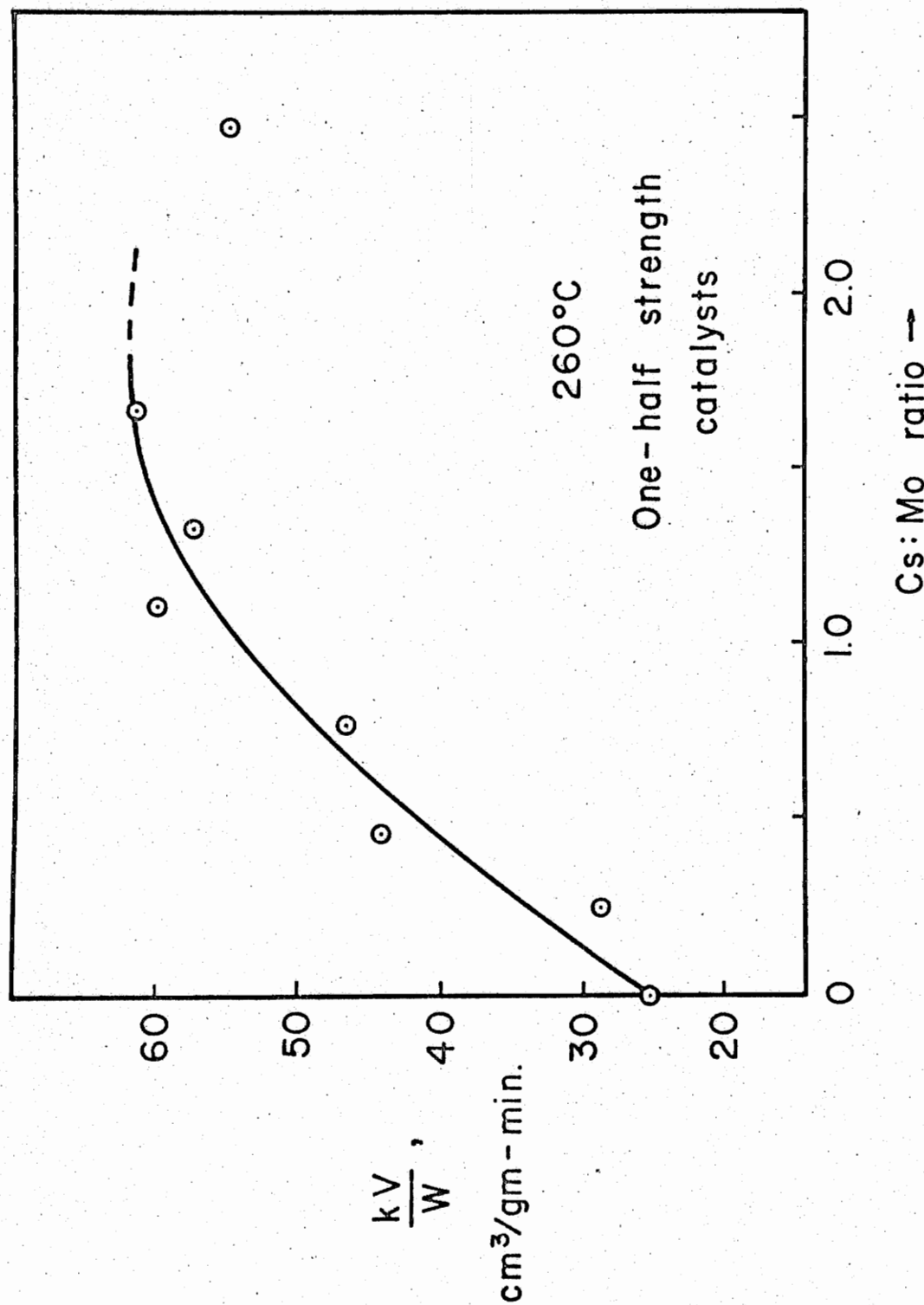


Figure 48. Catalyst Activity vs Cs:Mo Molar Ratio at 260°C

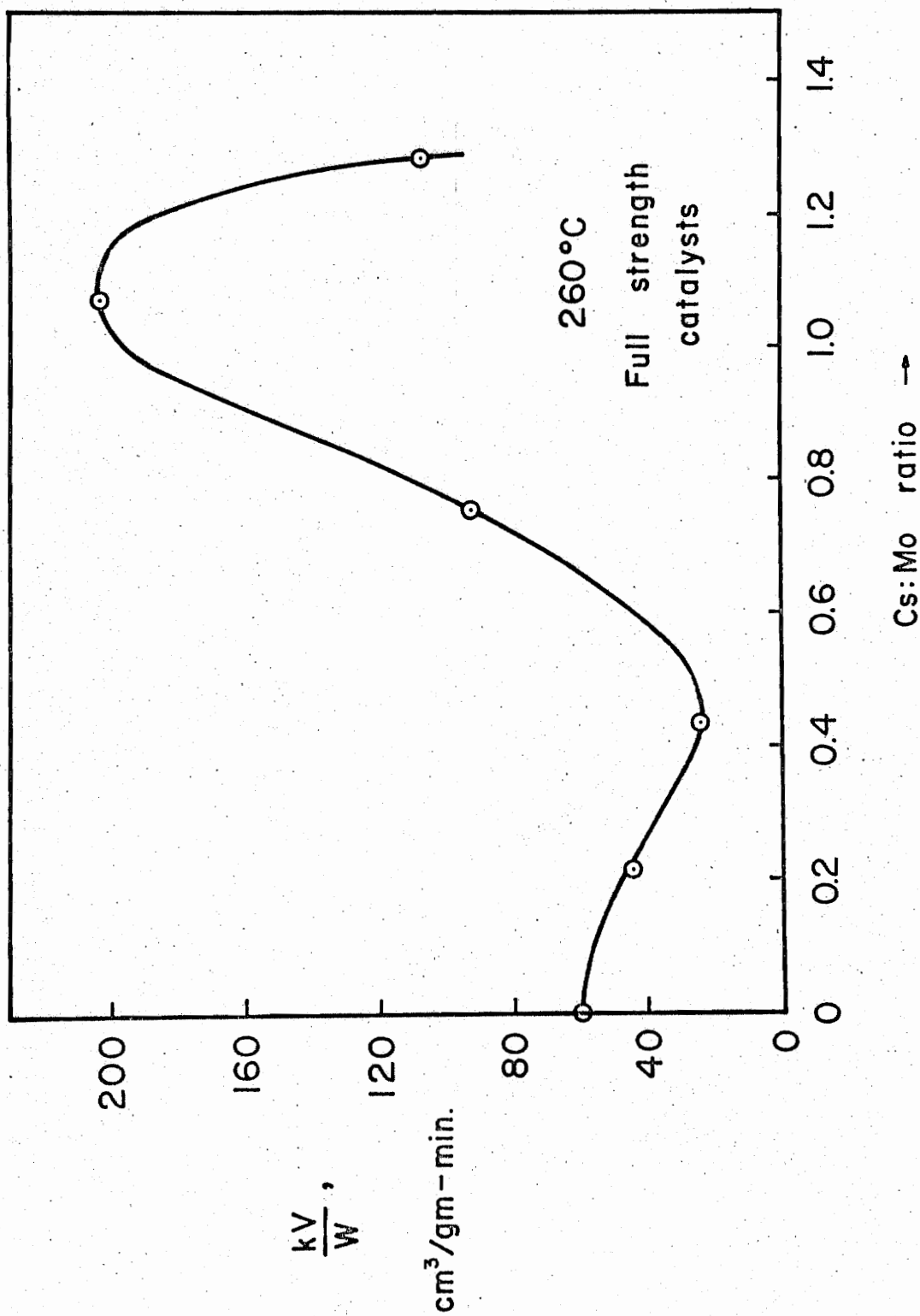


Figure 49. Catalyst Activity vs Cs:Mo Molar Ratio at 260°C

at higher Cs:Mo molar ratios. The existence of smooth curves in Figures 50, 51, and 52 supports the validity of our data.

The decrease of activity at higher Cs:Mo molar ratios such as in Figures 48, 49, 51, and 52 may be an indication of pore blockage. The presence of an excess of cobalt, molybdenum, and cesium causes the pores to block, thus diminishing the catalyst surface area. This interpretation accounts for the fact that the full strength catalysts have the maximum activity at the same Cs:Mo molar ratio for both temperatures.

For the methanation and ethanol dehydration reactions, the Cs:Mo molar ratio had a small effect on the activity, i.e., the addition of cesium acetate did not appreciably influence the activity of the unimpregnated cobalt molybdate catalyst.

#### D. Temperature

Temperature is clearly an important experimental variable. The temperature dependence of the experimentally measured rate constants is discussed in connection with the Arrhenius plots.

#### E. Total Pressure

The water-gas shift and ethanol dehydration studies were performed at one atmosphere pressure. We made some preliminary water-gas shift runs at 100 psig and observed a reasonable amount of methane formation at temperatures greater than 325°C. The water-gas shift reaction should be studied at higher pressures because in some coal gasification processes the synthesis gas will be shifted at pressures as high as 1000 psig.

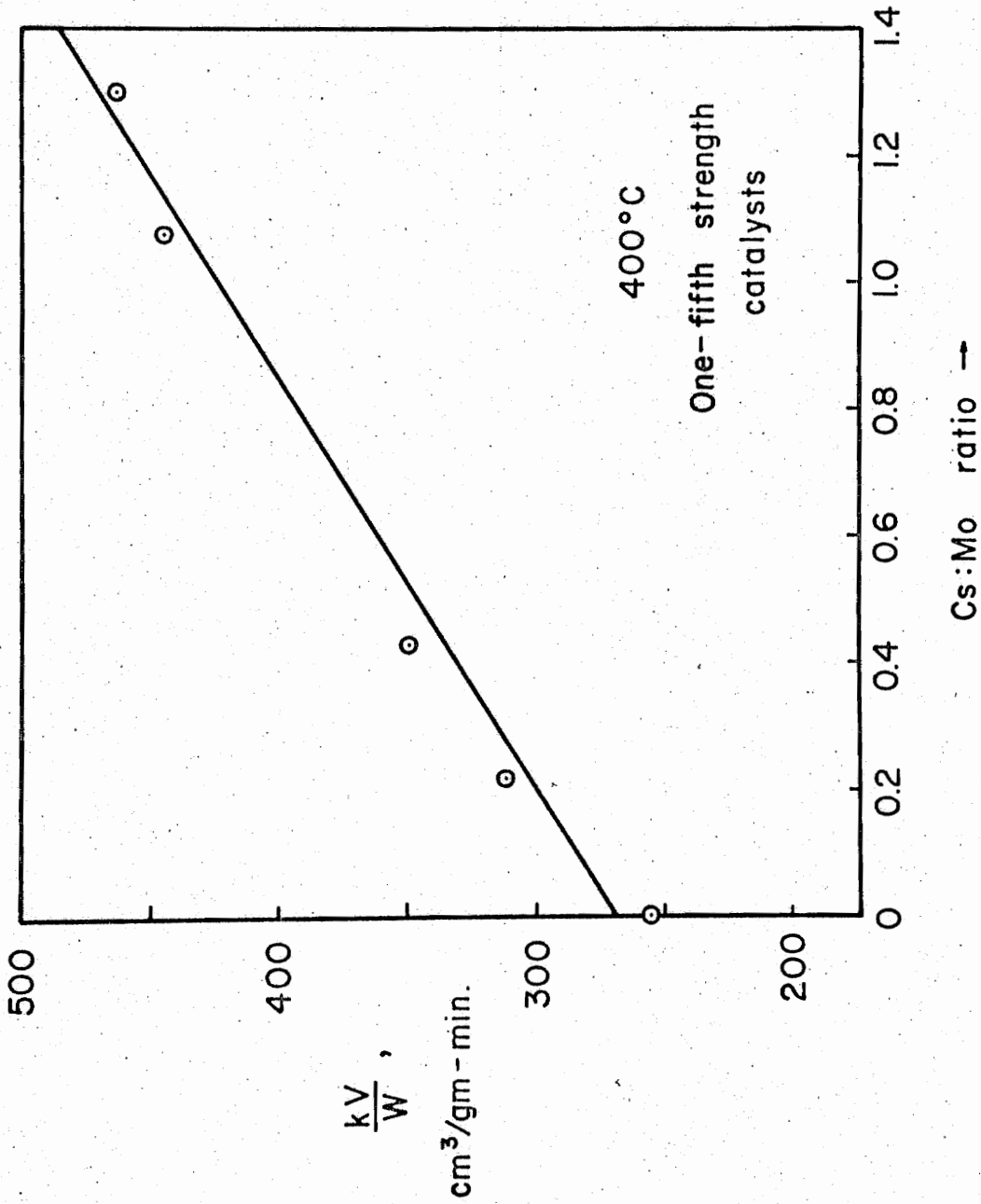


Figure 50. Catalyst Activity vs Cs:Mo Molar Ratio at 400°C

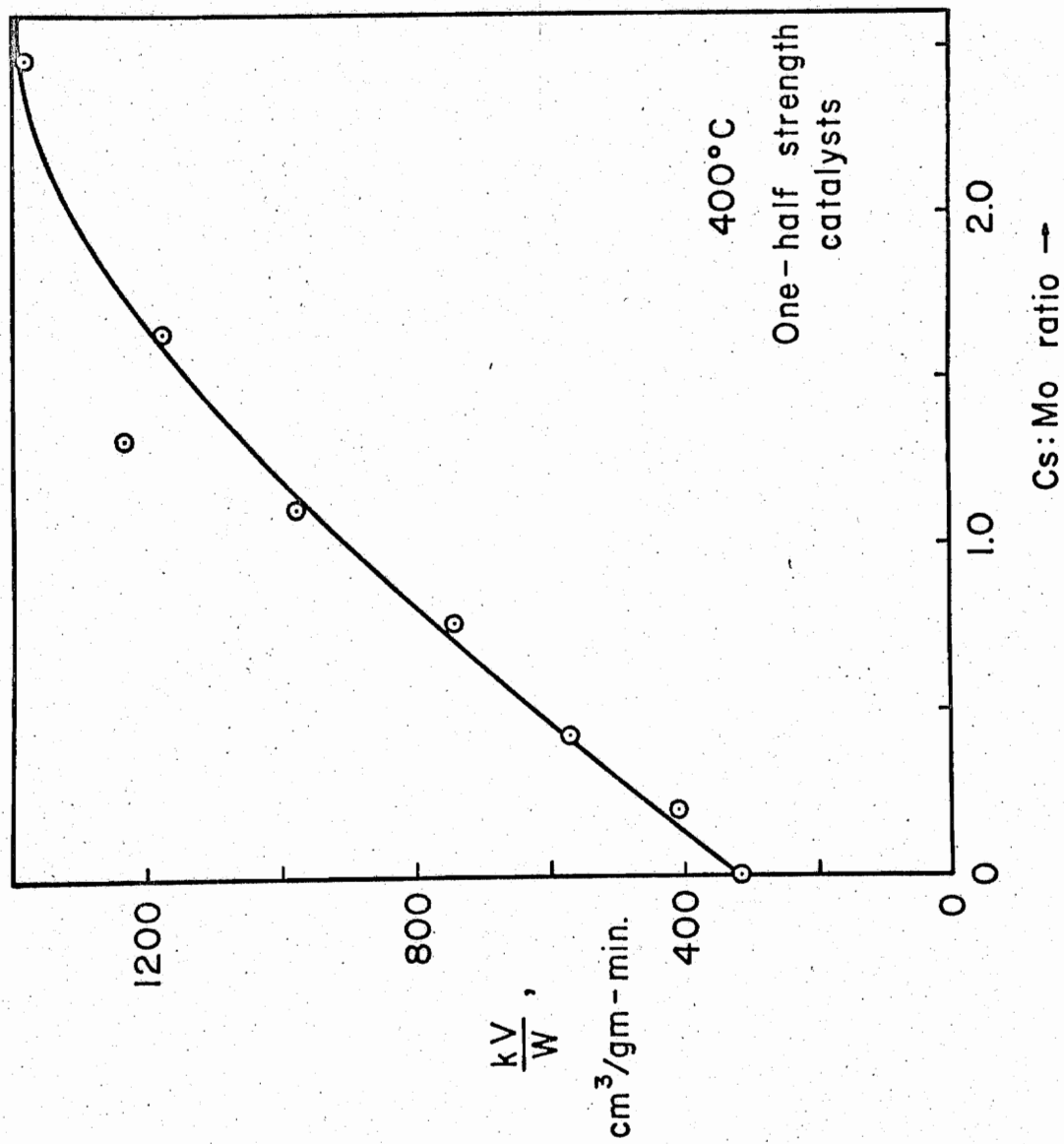


Figure 51. Catalyst Activity vs Cs:Mo Ratio at 400°C

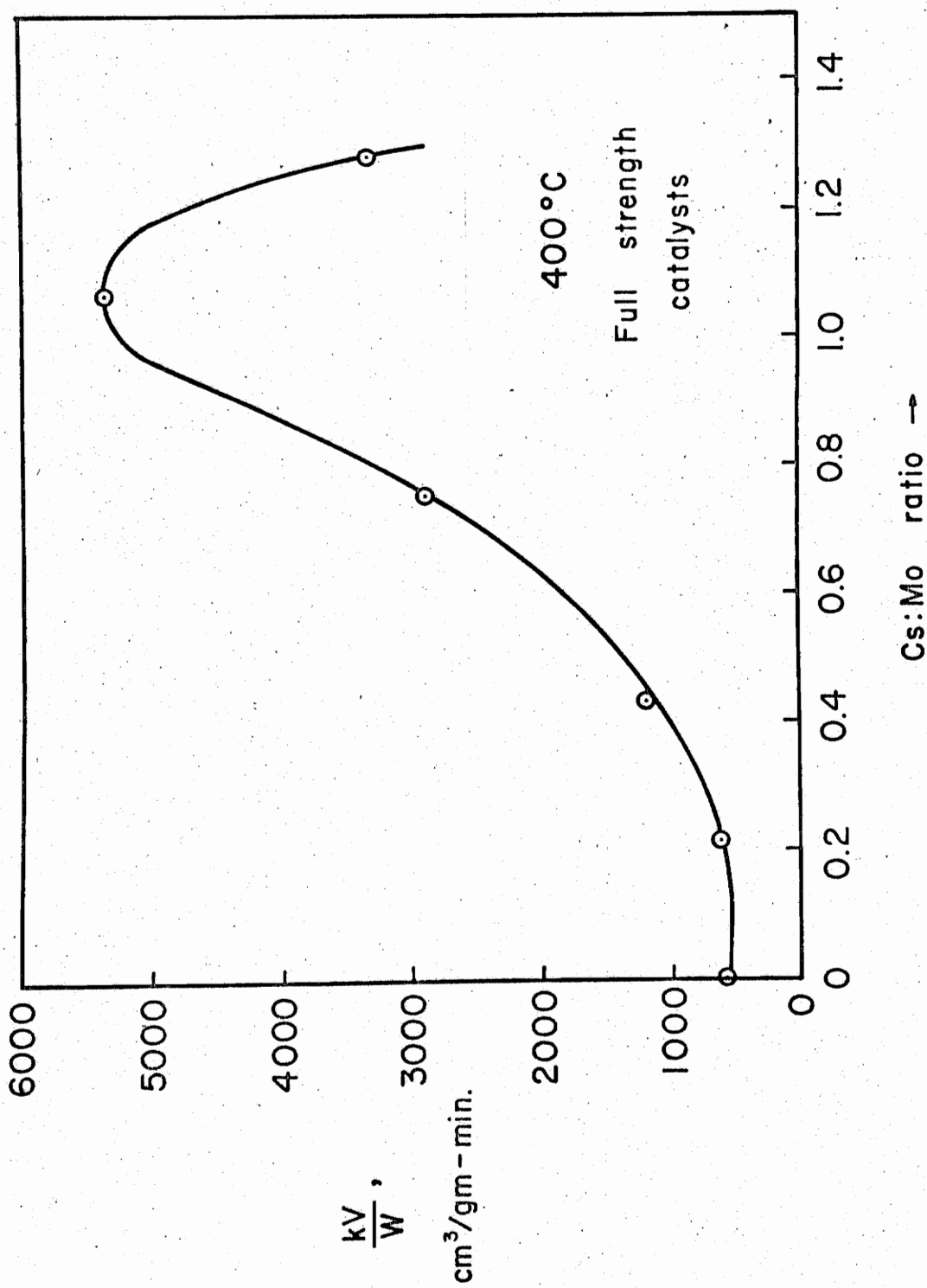


Figure 52. Catalyst Activity vs Cs:Mo Molar Ratio at 400°C

Preliminary studies of methanation at 100, 200, 300, and 400 psig and temperatures of 300 and 400°C with a H<sub>2</sub>/CO molar ratio of 0.63 indicated an increase in methane yield at higher pressures.

#### F. Rate Law

The water-gas shift and methanation reactions are first order in carbon monoxide at temperatures ranging between 200 and 400°C, and between 275°C and 450°C, respectively. This relationship is linear up to conversion levels of 90% and 40% for the water-gas shift reaction and catalytic methanation, respectively. The heterogeneous catalysis of these reactions is complex. It will require considerable experimental work to obtain the true dependence of the rate on the partial pressures of the reactant gases.

The rate law obtained for the ethanol dehydration reaction correlates the experimental data up to 98 percent conversion of ethanol, as can be seen from Figures 6 and 9.

#### G. Rates and Their Comparisons With Other Commercial Catalysts

The activities of catalyst "ZZ" and catalyst "RR", which were employed for the ethanol dehydration and the methanation reactions, respectively, have been compared with the activities of the existing commercial catalysts. The former are considerably less active. The "Aldridge" catalysts for the water-gas shift reaction were very active when compared to the competitive Fe/Cr and Zn/Cr/Cu water-gas shift catalysts, the latter being sulfur intolerant.<sup>2</sup>

Although the kinetics of ethanol dehydration and catalytic methanation have been investigated by many workers, the number of comparisons

that can be made is limited owing to difficulties in finding conditions similar to the ones that we employed. Such conditions include temperature, pressure, and reactant gas composition. For example, The Bureau of Mines<sup>22</sup> has performed an extensive study of methane synthesis in fixed-bed, conventional fluidized-bed, and multiple feed, fluidized-bed reactors. However, no rate equation was reported. Neither were the equilibrium concentrations of CO and the product gas compositions obtained from the fixed-bed reactor reported. In evaluating their data, The Bureau of Mines employed the calorific-conversion efficiency to determine the activity of the nickel catalysts that they studied.

In comparing their nickel catalyst No. L-6025, which was used in a conventional fluidized-bed reactor, with our "Aldridge" catalyst, we were aware of the fact that their conversion data would be misleading owing to back-mixing in their fluidized-bed reactor. The percent conversion of CO for their space velocity should be lower in a fixed bed reactor since the average residence time for CO molecules would be shorter.

#### 1. Ethanol dehydration catalysts.

After having tested catalyst "VV" and catalyst "ZZ" for their ethanol dehydration activities, we fitted the data satisfactorily by equation (13) and obtained rate constants.

The first order rate constant for ether formation for catalyst "VV" was then compared to the pseudo-first-order rate constant for the water-gas shift reaction with catalyst "W" (Table 70) at the following conditions:

$$T = 377^{\circ}\text{C}$$

$$P = 1 \text{ atm}$$

Both catalysts had the same composition and cylinder No. 2 was used for both reactions.

The rate constants were found to be

$$k_{\text{cat "VV"}} = 168 \text{ min}^{-1}$$

$$k_{\text{cat "W"}} = 414 \text{ min}^{-1}$$

We next compared the initial rate of ethanol dehydration for catalyst "ZZ" to that for the  $\eta\text{-Al}_2\text{O}_3$  catalyst used by de Boer et al.<sup>31</sup> The comparison is summarized below:

At saturation of the surface with adsorbed alcohol and water molecules, they represented the rate of ethylene production as

$$\begin{aligned} v_{\text{ethylene}} &= k_1 (1-\theta_w) \\ &= k_I \end{aligned} \quad (33)$$

and the rate of ether formation as

$$\begin{aligned} v_{\text{ether}} &= \frac{k_2 n}{2} (1-\theta_w)^2 + k_3 (1-\theta_w) P_A \\ &= k_{II} + k_{III} P_A \end{aligned} \quad (34)$$

where,  $k_I$  = rate constant for ethylene formation according to the Langmuir-Hinshelwood mechanism

$k_{II}$  and  $k_{III}$  = rate constants for ether production according to the Langmuir-Hinshelwood and the Rideal-Eley mechanisms respectively.

$n$  = number of available sites

$P_A$  = average alcohol pressure, mm Hg

$\theta_w$  = the degree of coverage with water molecules

Values of the rate constants for ethyl alcohol dehydration on  $n\text{-Al}_2\text{O}_3$  at a temperature of  $307^\circ\text{C}$  were reported to be

$$k_I = 0.93 \text{ cm}^3 \text{ (STP)/m}^2\text{-min}$$

$$k_{II} = 0.101 \text{ cm}^3 \text{ (STP)/m}^2\text{-min}$$

$$k_{III} = 0.014 \text{ cm}^3 \text{ (STP)/m}^2\text{-min-mm Hg}$$

The above rates can be evaluated at standard conditions for an initial ethanol pressure of 325 mm Hg, and the above units can be converted to gm moles/ $\text{m}^2\text{-min}$ , as shown below:

$$(\text{v}_{\text{ethylene}})_{\text{initial}} = k_I$$

$$= 0.93 \text{ cm}^3 \text{ (STP)/min-m}^2$$

$$= 0.93 \times 22400 \text{ gm mole/min-m}^2$$

$$= 4.15 \times 10^{-5} \text{ gm mole/min-m}^2$$

$$(\text{v}_{\text{ether}})_{\text{initial}} = k_{II} + k_{III} P_A^0, \text{ where } P_A^0 = 325 \text{ mm Hg}$$

$$= 0.4267 \text{ atm}$$

$$= 0.101 + 0.014 P_A^0 \text{ cm}^3 \text{ (STP)/min-m}^2$$

$$= (0.101 + \frac{0.0104}{\text{mm Hg}} \times 325 \text{ mm Hg})/22400$$

$$\text{gm mole/min-m}^2$$

$$= 2.08 \times 10^{-4} \text{ gm mole/min-m}^2$$

The data obtained for ethanol dehydration on "Aldridge" catalyst "ZZ" were fitted by the following rate equation.

$$(-r_A)_{\text{overall}} = (-r_0) + (-r_1) \quad (35)$$

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where, A = ethanol

$$-r_0 = k_0 = \text{rate of ethylene formation}$$

$$-r_1 = k_1 C_A = \text{rate of ether formation}$$

At 307°C, the values of  $k_0V$  and  $k_1V$ , respectively, are  $45.35 \times 10^{-6}$  gm moles/sec and  $1.592 \text{ cm}^3/\text{sec}$ , both at reactor conditions. The initial rates for ethylene and ether formation can be calculated separately.

The reactor volume,  $V$ , is given by

$$\begin{aligned} V &= 0.502 \text{ gm} \times \frac{1}{0.65 \text{ gm/cm}^3} \\ &= 0.773 \text{ cm}^3 \end{aligned}$$

The value of  $k_0V$  can be divided by the reactor volume to give the initial rate of ethylene formation

$$k_0 = \frac{45.35 \times 10^{-6}}{0.773} = 58.5 \times 10^{-6} \text{ gm moles/sec-cm}^3$$

and its units can be converted to  $\text{gm moles/min-m}^2$  through the use of values for the bulk density,  $\text{gm/cm}^3$ , and surface area,  $\text{m}^2/\text{gm}$ , for unimpregnated catalyst "ZZ".

$$\begin{aligned} k_0 &= 58.5 \times 10^{-6} \frac{\text{gm moles}}{\text{sec-cm}^3} \times \frac{1}{0.65} \frac{\text{cm}^3}{\text{gm}} \times \frac{1}{270} \frac{\text{gm}}{\text{m}^2} \\ &\quad \times 60 \text{ sec/min} \\ &= 2.0 \times 10^{-5} \text{ gm moles/min-m}^2 \end{aligned}$$

The initial rate of ether formation can be evaluated in the same way.

Thus,

$$\begin{aligned}
 k_1 &= 1.592 \text{ cm}^3/\text{sec} \times \frac{1}{0.773 \text{ cm}^3} \\
 &= 2.06 \text{ sec}^{-1} = 123.5 \text{ min}^{-1}
 \end{aligned}$$

Therefore,

$$\begin{aligned}
 (-r_1)_{\text{initial}} &= k_1 C_A^0 \\
 &= 123.5 \left( 0.4267 \text{ atm} / 82.06 \frac{\text{atm-cm}^3}{\text{gm mole } ^\circ\text{K}} \right) \\
 &\quad \times \frac{1}{273 \text{ } ^\circ\text{K}} \\
 &= 2.35 \times 10^{-3} \text{ gm moles/min-cm}^3 \\
 &= 2.35 \times 10^{-3} \frac{1}{0.65} \frac{\text{cm}^3}{\text{gm}} \times \frac{1}{270} \frac{\text{gm}}{\text{m}^2} \\
 &= 1.34 \times 10^{-5} \text{ gm moles/min-m}^2
 \end{aligned}$$

In the above calculations,  $C_A^0$  is the initial concentration of ethanol, in units of gm-moles/cm<sup>3</sup>.

The comparisons of the initial rates can be summarized as shown below:

	<u>Initial rates, gm mole/min-cm<sup>2</sup></u>	
	Ether Production	Ethylene Production
$\eta$ -Al <sub>2</sub> O <sub>3</sub> catalyst	$20.8 \times 10^{-5}$	$4.15 \times 10^{-5}$
Catalyst "ZZ"	$1.34 \times 10^{-5}$	$2.0 \times 10^{-5}$
Ratio, $\eta$ -Al <sub>2</sub> O <sub>3</sub> / catalyst "ZZ"	15.5	2.08

The "Aldridge" catalyst "ZZ" is not as active as the  $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst; however, it may be preferable in a commercial process since it is tolerant to sulfur. The selectivity toward the production of ethylene for catalyst "ZZ" is better than that for the  $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

## 2. Methanation Catalysts

Catalyst "RR" (Tables 6 and 14) was compared with the nickel catalyst employed by the U.S. Bureau of Mines<sup>22</sup> in their fluidized-bed reactor studies at the following conditions:

Catalyst composition: NiO-Al<sub>2</sub>O<sub>3</sub>-kaolin; 100:159:97

Pretreatment: Reduced with H<sub>2</sub> at 400°C and 100 psig for 60 hrs.

H<sub>2</sub>/CO, molar ratio 2.5

Fresh feed space velocity, hr.<sup>-1</sup> 5530

Catalyst age (end of period), hrs. 32

Reactor temperature, °C 304

Reactor pressure, psig 300

Conversion of CO 96

Product gas analysis, (dry basis),

percent by volume:

CH<sub>4</sub> 80.8

CO<sub>2</sub> 11.9

H<sub>2</sub> 5.96

CO 1.38

Calorific efficiency, percent 99.9

We can calculate the conversion of CO that would be obtained for our "Aldridge" catalyst at 303°C and 300 psig by using equation (18) and the value of their space velocity, 5530 hr<sup>-1</sup>, used in their fluidized bed studies. The first order rate constant for catalyst "R" at 303°C is 65 hr<sup>-1</sup>.

For  $X_{CO}^0 = 0$ , the final conversion of CO is calculated to be

$$\begin{aligned}
 -\ln(1-X_{CO}) &= k(V/F) \\
 &= 65 \text{ hr}^{-1} \left( \frac{1}{5530 \text{ hr}^{-1}} \right) \\
 &= 1.175 \times 10^{-2} \\
 1 - X_{CO} &= 0.988 \\
 X_{CO} &= 0.012 = 1.2\%
 \end{aligned}$$

It is clear that the activity of our sulfur-tolerant catalyst is relatively low when compared to that of nickel. We emphasize that the comparison of the activities of an impregnated cobalt molybdate catalyst in a fixed-bed reactor and a nickel catalyst in a fluidized bed reactor will introduce some errors owing to the operation characteristics of the two reactors. The above calculation is the best that we can do with the information available to us.

Catalyst "RR" was also compared to the commercial nickel non-alumina catalyst used for the fixed-bed methanation of a synthesis gas mixture by IGT<sup>33</sup>. The 1/4-inch nickel pellets supported on alumina and crushed to -12 + 18 USS were used for the initial tests. The feed gas contained a CO mole of 4 to 13 percent. The rate expression,

$$r = \frac{k P_{CO} P_{H_2}^{0.5}}{1 + K_2 P_{H_2} + K_3 P_{CH_4}}$$

correlated their data satisfactorily.

At 302°C, the rate equation can be expressed with the computed values of the constants as follows:

$$r = \frac{(2 \times 10^{-5}) P_{CO} P_{H_2}^{0.5}}{1 + 0.1 P_{H_2} + 0.05 P_{CH_4}} \quad (37)$$

✓

We can make a rough comparison of our catalyst to theirs by employing the initial partial pressures of CO, H<sub>2</sub>, and CH<sub>4</sub> in our reactor at 303°C and 300 psig to evaluate the rate of reaction for their catalyst. At 303°C and  $F = 43.34 \text{ cm}^3/\text{min}$  at reactor conditions,

$$P_{\text{CO}} = 0.226 \times 314.7$$

$$= 71.2 \text{ psia}$$

$$P_{\text{H}_2} = 0.740 \times 314.7$$

$$= 233.0 \text{ psia}$$

$$P_{\text{CH}_4} = 0 \text{ psia}$$

Thus,

$$r = 8.92 \times 10^{-4} \text{ lb moles/hr-gm cat.}$$

At these conditions, our rate constant,  $k$ , was evaluated to be  $1.085 \text{ min}^{-1}$ , as shown below,

$$kV = 5.24 \text{ cm}^3/\text{min}$$

$$k = 5.24 \text{ cm}^3/\text{min} / 4.83 \text{ cm}^3 = 1.085 \text{ min}^{-1}$$

The rate of reaction with our catalyst is calculated with the aid of a pseudo-first order rate law in CO,

$$-r_{\text{CO}} = k (C_{\text{CO}} - C_{\text{CO}}^{\text{eq}}) \quad (38)$$

where,  $C_{\text{CO}}^{\text{eq}}$  is negligible when compared to  $C_{\text{CO}}$ . Therefore,

$$\begin{aligned} -r_{\text{CO}} &= 1.085 \text{ min}^{-1} \frac{21.41 \times 0.226}{82.06 \times 576} \text{ gm moles/cm}^3 \\ &\quad \times 60 \frac{\text{min}}{\text{hr}} \times \frac{1}{0.65} \frac{\text{cm}^3}{\text{gm}} \end{aligned}$$

$$\begin{aligned}
 &= 1.025 \times 10^{-2} \text{ gm moles/gm cat.-hr} \\
 &= 2.28 \times 10^{-5} \text{ lb moles/gm cat.-hr}
 \end{aligned}$$

Therefore,

$$\frac{r_{\text{nickel}}}{(-r_{\text{CO}})_{\text{catalyst "RR"}}} = \frac{89.2 \times 10^{-5}}{2.28 \times 10^{-5}} = 39$$

This comparison again shows that the "Aldridge" catalyst is not competitive with the commercial nickel catalyst.

#### H. The Effect of Physical Processes on the Observed Rate of the Methanation Reaction

A reaction that occurs in a fixed-bed of porous catalysts occasionally is accompanied by mass transfer and/or heat transfer limitations. If the effective diffusion coefficient and thermal conductivity are low, there will be both concentration and temperature gradients across the gas film and within the catalyst particles. The effect of temperature gradients within the porous catalysts may be more serious than that of concentration gradients when the heat of reaction is large. In the presence of such gradients, the observed rate may differ appreciably from the actual rate at an assumed constant bed temperature,  $T$ .

To determine the combined effect of mass and heat transfer, we can calculate an effectiveness factor. For exothermic reactions, this will be the nonisothermal effectiveness factor, which is defined by Smith<sup>41</sup> as

$$\eta = \frac{\text{actual rate for the whole pellet}}{\text{rate evaluated for the outer surface conditions}}$$

A solution for the combined energy and mass balance is required to evaluate the nonisothermal effectiveness factor.

Weisz and Hicks<sup>43</sup> solved the differential mass and energy balances numerically to obtain the concentration profile within the porous catalysts. They expressed the nonisothermal effectiveness factor for first-order reactions in spherical catalyst pellets as a function of a Thiele-type modulus, Arrhenius number, and heat-reaction parameter.

Our rate expression has the same form as a first-order irreversible rate equation since the equilibrium concentration of CO is very low. The Arrhenius number,  $E/RT_s$ , can be evaluated if we assume the temperature and concentration gradients are small across the gas film  $T_s$  can be taken as the temperature of the bulk fluid. Thus,

$$\begin{aligned} E/RT_s &= \frac{12500 \text{ cal/gm mole}}{(1.987 \text{ cal/gm mole } ^\circ\text{K})(643^\circ\text{K})} \\ &= 9.8 \end{aligned}$$

In this case, we can use Figure 3.4 given by Satterfield.<sup>44</sup> It is a plot of the effectiveness factor  $\eta$  as a function of  $\phi_s$ , the Thiele type modulus, for  $E/RT_s = 10$ .

To calculate  $\phi_s$ , we need to know the value of the effective diffusivity,  $D_e$ , for gases diffusing in the porous "Aldridge" catalyst. Since the pores are quite small (the average pore diameter is  $38 \text{ \AA}$ ), the molecules collide with the pore wall much more frequently than with each other.<sup>44</sup> This is known as Knudsen diffusion. The Knudsen diffusion coefficient for gases in a straight round pore can be calculated from the following equation:

$$D_K = 9700 r_e \sqrt{T/M} \quad (38)$$

where,  $D_K$  = Knudsen diffusion coefficient,  $\text{cm}^2/\text{sec}$   
 $r_e$  = the pore radius, cm  
 $T$  = the temperature,  $^\circ\text{K}$   
 $M$  = the molecular weight of a typical component

In evaluating  $D_K$ , it is assumed that each component of a mixture behaves as though it alone were present. We can determine the Knudsen diffusion coefficient for CO in the porous catalyst particles because it is the limiting reactant and diffuses more slowly than  $\text{H}_2$ . The pore radius is calculated from the following relation,<sup>44</sup>

$$r_e = \frac{2V_p}{S} = \frac{2\theta}{S\rho_b} \quad (39)$$

where,  $V_p$  = the pore volume,  $\text{cm}^3/\text{gm}$   
 $S$  = the catalyst surface, area,  $\text{cm}^2/\text{gm}$   
 $\theta$  = the total void fraction  
 $\rho_b$  = the bulk density of the catalyst,  $\text{gm}/\text{cm}^3$

Therefore,

$$r_e = \frac{2 \times 0.51}{270 \times 10^4} = 3.77 \times 10^{-7} \text{ cm}$$

and

$$\begin{aligned} \theta &= \frac{3.77 \times 10^{-7} \times 270 \times 10^4 \times 0.65}{2} \\ &= 0.331 \end{aligned}$$

We can determine the effective Knudsen diffusion coefficient for CO by using equation 1.33 in Satterfield,<sup>44</sup>

$$\begin{aligned}
 D_{K,eff} &= \frac{D_K \theta}{\tau_m} & (40) \\
 &= 9700 r_e \sqrt{T/M} \theta / \tau_m \\
 &= 9700 \times 3.77 \times 10^{-7} \frac{643}{28} 0.331/0.53 \\
 &= 10.9 \times 10^{-3} \text{ cm}^2/\text{sec}
 \end{aligned}$$

The value of  $\tau_m$ , the tortuosity factor, was obtained from Table 1.13.<sup>44</sup> It is for a cobalt molybdenum catalyst with a total void fraction of 0.354 and a pore radius of  $22.4 \times 10^{-8}$  cm. For this same catalyst, we calculated the effective Knudsen diffusion coefficient of hydrogen through nitrogen at room temperature and one atm to make comparison with the value given by Satterfield.<sup>44</sup> The reported value of the effective diffusivity was  $17.5 \text{ cm}^2/\text{sec}$ , whereas our computed value  $17.7 \text{ cm}^2/\text{sec}$ . This comparison shows that the Knudsen diffusion regime assumption for the calculation of the effective diffusivity of CO is reasonable.

We employed the value,  $10.9 \times 10^{-3} \text{ cm}^2/\text{sec}$ , for the effective diffusivity to calculate the Thiele-type modulus with the aid of equation (11-78) given in Smith.<sup>41</sup>

$$(\phi_s)_s = \frac{r_s}{3} \sqrt{\frac{(k_1)_s \rho_p}{D_e}} \quad (41)$$

N

- where,  $r_s$  = radius of a spherical catalyst pellet, cm  
 $(k_1)_s$  = the rate constant at the surface temperature,  $\text{min}^{-1}$   
 $\rho_p$  = pellet density,  $\text{gm/cm}^3$   
 $D_e$  = effective diffusivity of CO at  $370^\circ\text{C}$ ,  $\text{cm}^2/\text{sec}$

Thus,

$$\begin{aligned}
 (\phi_s)_s &= \frac{5.45 \times 10^{-2} \text{ cm}}{2 \times 3} \sqrt{\frac{(3.87 \times \frac{1}{0.65} \frac{\text{cm}^3}{\text{min-gm}})(0.97 \frac{\text{gm}}{\text{cm}^3})}{1.09 \times 10^{-2} \text{ cm}^2/\text{sec} \times 60 \text{ sec/min}}} \\
 &= \frac{5.45 \times 10^{-2}}{2 \times 3} \times 2.96 \\
 &= 0.027
 \end{aligned}$$

With this small value for  $\phi_s$  and  $E/RT_s \approx 10$ , the nonisothermal effectiveness factor can be determined from the Weisz and Hicks chart in Figure 3.4 given by Satterfield.<sup>44</sup> Since the curves for different values of the heat-reaction parameter,  $\beta$ , approach an effectiveness factor of unity for values of  $\phi_s$  less than 0.2, we can conclude that there is neither diffusion control nor resistance to heat flow for the methanation reaction for a Thiele-type modulus of 0.027.

### I. Transition Temperatures

The reason for the occurrence of transition temperatures for the full and one-half strength cesium impregnated catalysts, but not for the one-fifth catalysts, is not clear. It is difficult to explain such behaviour. The identity of the anion in the cesium salt that is formed during the course of the reaction is not known at present. Such an anion might be carbonate, bicarbonate, formate, hydroxide or some combination of these. Most likely, it is carbonate.

We initially thought that the transition temperature was an indication of a phase change, that is, the melting point of the "Aldridge" catalyst. We performed an experiment to determine whether a salt mixture consisting of cesium acetate, cobalt nitrate, and ammonium molybdate at Cs:Mo and Co:Mo molar ratios of 1.07 and 0.538, respectively, would melt. A one gram solid sample of such a mixture was pretreated in 6% H<sub>2</sub>S in H<sub>2</sub> at one atm and 550°C in a small glass tube wrapped with heating tube. We then passed a reaction gas mixture through the tube and watched the physical state of the catalyst through a small hole as we increased the temperature from 200°C to approximately 350°C. We did not observe any melting but did see some sintering. This experiment demonstrated the absence of bulk melting in our "Aldridge" catalysts. Consequently we do not believe that the "Aldridge" catalyst is a supported catalytic melt. Transition temperatures obtained from Arrhenius plots are given in Table 91.

#### J. Effect of Alkali Salt

The activities of Nalcomo 474 catalysts which are impregnated with alkali salts of potassium, sodium, lithium, cesium, and a mixture of cesium and lithium are compared at 260°C and 400°C in Table 92. The difference in activities is more pronounced at 400°C. The potassium-impregnated catalysts are quite active. Potassium may be the alkali salt of choice in commercial processes because it is cheaper than cesium. Transition temperature is observed only for the lithium impregnated catalyst.



TABLE 91. TRANSITION TEMPERATURES

Catalyst number	Alkali metal	Metal: molybdenum ratio	Transition temperature, °C
H(c)	cesium	1.64	351(d)
J(c)	cesium	1.09	358(d)
R(a)	cesium	1.07	180
S(b)	cesium	1.07	170
T(a)	cesium	1.07	341(d)
V(a)	cesium	0.43	268
X(c)	cesium	0.43	315
Y(a)	cesium	0.21	362
AA(c)	lithium	0.43	292

(a) Cylinder #1.

(b) Cylinder #2.

(c) Cylinder #3.

(d) Diffusion-controlled transition.

TABLE 92. COMPARISON OF ACTIVITIES OF NALCOMO 474 CATALYSTS IMPREGNATED WITH VARIOUS ALKALI SALTS. (b)

Catalyst number	Alkali Metal	Catalyst activity, kV/W	
		260°C	400°C
		cm <sup>3</sup> /gm catalyst-min.	
AA	Li	38.6	418.
BB	Na	32.5	473.
CC	K	58.0	832.
DD	K	47.1	628.
X	Cs	46.6	681.
EEE	Li + Cs	71.2	773.

(a) Extrapolated from 378°C with  $E_a = 14.4$  Kcal/gm mole.

(b) Cylinder #3.



V

### K. Arrhenius Plots

Arrhenius plots for 31 water-gas shift catalysts and three methanation catalysts provide a clear indication of the quality of our data. The temperature dependence of the first order rate constant for each catalyst is correlated very well, as can be seen from the nice straight lines.

In the water-gas shift reaction, the activation energies and frequency factors don't follow any trend with respect to the Cs:Mo ratio. For the one-fifth strength catalysts, the activation energy does not change appreciably, whereas the frequency factor decreases with decreasing Cs:Mo ratio.

For the one-half strength catalysts and the full strength catalysts with cylinder #1, correlations of activation energy and frequency factor with the Cs:Mo ratio make little sense. Linear regression data for the Arrhenius plots for the water-gas shift catalysts are given in Table

For the methanation reaction, catalysts "RR" and "ZO" have approximately the same activation energies (12.9 and 9.9 Kcal/gm mole) and frequency factors ( $9.3 \times 10^4$  and  $9.6 \times 10^3$  cm<sup>3</sup>/gm min). Catalyst "00", a cesium impregnated Al<sub>2</sub>O<sub>3</sub> catalyst, has high activation energy of 31.8 Kcal/gm mole and a frequency factor of  $7.68 \times 10^8$  cm<sup>3</sup>/gm min. Linear regression data for the Arrhenius plots for catalysts "RR", "ZO", "00", and the catalysts used for the ethanol dehydration reaction are presented in Table 94.

TABLE 93. LINEAR REGRESSION DATA FOR ARRHENIUS PLOTS FOR CATALYSTS A THROUGH GG

Catalyst number	Cesium: molybdenum ratio	Activation energy, Kcal/gm mole	AV/W, $10^7$ cm <sup>3</sup> /gm-min.	Correlation coefficient, r	Number of points
A	1.29(c)	12.2	0.51	-0.9938	Last 8
B	1.07(c)	12.5	0.63	-0.9877	Last 8
C	0.43(c)	13.3	0.77	-0.9992	Last 8
D	0.21(c)	12.9	0.51	-0.9971	Last 8
E	0.00(c)	11.9	0.20	-0.9986	Last 8
F	2.44(c)	17.1	56.9	-0.9979	Last 8
H	1.64(c)	19.8	76.7	-0.9993	2 through 6
		6.7	0.02	-0.9945	Last 3
I	1.31(c)	16.2	26.1	-0.9979	Last 8
J	1.09(c)	16.8	46.2	-0.9996	2 through 6
		6.8	0.02	-0.9835	Last 3
K	0.77(c)	14.6	4.5	-0.9977	Last 8
L	0.44(c)	13.4	1.4	-0.9988	Last 8
M	0.22(c)	13.6	1.1	-0.9990	Last 8

TABLE 93 (cont'd)

Catalyst number	Cesium: molybdenum ratio	Activation energy, Kcal/gm mole	AV/W, $10^7$ cm <sup>3</sup> /gm-min.	Correlation coefficient, r	Number of points
N	0.00(c)	12.7	0.4	-0.9993	Last 8
O	$\infty$ (c)	25.0	456.0	-0.9972	All 3
P	3.21(a)	16.5	85.	-0.9961	All 5
Q	1.29(a)	17.6	200.	-0.9991	First 8
R	1.07(a)	14.6	7.4	-0.9999	First 5
		20.0	3100.	-0.9994	Last 5
S	1.07(b)	9.8	0.029	-0.9999	First 4
		17.5	200.	-0.9999	Last 6
T	1.07(a)	20.5	4800.	-0.9988	First 6
		10.6	1.5	-0.9976	Last 3
U	0.75(a)	17.2	120.	-0.9992	All 9
V	0.43(a)	10.7	0.054	-0.9952	First 3
		20.9	740.	-0.9990	Last 6

TABLE 93 (cont'd)

Catalyst number	Cesium: molybdenum ratio	Activation energy, Kcal/gm mole	AV/W, $10^7 \text{ cm}^3/\text{gm-min.}$	Correlation coefficient, r	Number of points
W	0.43(b)	12.0	0.63	-0.9976	A11 9
X	0.43(c)	11.3	0.17	-0.9909	1 through 5
Y	0.21(a)	17.8	42.6	-0.9961	Last 5
Z	0.00(a)	11.3	190.	-0.9988	First 7
AA	$\frac{\text{Li}}{\text{Mo}} = 0.43(c)$	19.8	160.	-0.9994	Last 4
BB	$\frac{\text{Na}}{\text{Mo}} = 0.43(c)$	11.7	0.34	-0.9989	A11 9
CC	$\frac{\text{K}}{\text{Mo}} = 0.43(c)$	11.6	0.21	-0.9979	First 5
		13.6	1.1	-0.9991	Last 5
		13.9	1.8	-0.9974	A11 9
		14.4	17.54	-0.9989	A11 8

TABLE 93 (cont'd)

Catalyst number	Cesium: molybdenum ratio	Activation energy, Kcal/gm mole	AV/W, $10^7$ cm <sup>3</sup> /gm-min.	Correlation coefficient, r	Number of points
DD	$\frac{K}{Mo} = 0.43$ (c)	12.9	16.02	-0.9994	First 5
		13.7	16.33	-0.9993	Last 4
EE	$\frac{Li + Cs}{Mo} = 0.85$ (b)	11.7	0.45	-0.9989	All 11
FF	$\frac{Cs}{Mo} = 0.54$ , (c)				
	$\frac{Zn}{Mo} = 0.67$ (c)	13.6	0.6	-0.9983	Last 4
GG	1.07(c)	18.7	136.0	-0.9978	Last 8

(a) These catalysts run with cylinder #1.

(b) These catalysts run with cylinder #2.

(c) These catalysts run with cylinder #3.

TABLE 94. LINEAR REGRESSION DATA FOR ARRHENIUS PLOTS FOR CATALYSTS USED IN  
ETHANOL DEHYDRATION AND METHANATION STUDIES

Catalyst number	Cesium: molybdenum ratio	Activation energy, Kcal/gm mole	AV/W, $\text{cm}^3/\text{gm-min.}$	Correlation coefficient, r	Number of points
VV ( $k_1$ )	0.43	5.1	$1.89 \times 10^2$	-0.9870	A11 9
ZZ ( $k_1$ )	0.0	6.3	$6.79 \times 10^2$	-0.9743	A11 7
VV ( $k_0$ )	0.43	6.9	$1.85 \times 10^{-2}$	-0.9462	A11 9
ZZ ( $k_0$ )	0.0	6.7	$2.50 \times 10^{-2}$	-0.9675	A11 7
RR	0.91	12.9	$1.43 \times 10^5$	-0.9985	A11 6
ZO	0.0	9.9	$1.48 \times 10^4$	-0.9901	A11 6
00	$\infty$	31.8	$1.18 \times 10^9$	-0.9861	A11 3

## VII. CONCLUSIONS

On the basis of our investigation of the "Aldridge" catalyst, an alkali impregnated cobalt-molybdate on an  $\text{Al}_2\text{O}_3$  support, for the water-gas shift, methanation, and ethanol dehydration reactions, we can make the following conclusions:

1. The cesium-impregnated "Aldridge" catalyst is highly active for the water-gas shift reaction under sulfur tolerant conditions.
2. The activity of this catalyst is strongly dependent upon the cesium:molybdenum molar ratio. The normalized first order rate constant increases with this ratio until an optimum is reached for the full strength and half strength catalyst.
3. The transition temperatures appeared only with the cesium-impregnated full and half strength catalysts, but not with the one-fifth catalysts.
4. The potassium-impregnated cobalt-molybdate catalyst is quite active, in comparison to lithium- and sodium-impregnated versions.
5. The cesium-impregnated zinc-molybdate catalyst is not as active as the unimpregnated cobalt-molybdate. Its activity is approximately half of that of catalyst "Z" at  $400^\circ\text{C}$ .
6. We don't believe that the "Aldridge" catalyst is a catalytic melt.

7. A rate expression of shifting order, which shifts from zero to first order as the concentration of ethanol drops, fits the experimental data obtained for our ethanol dehydration studies.
8. The "Aldridge" catalyst is not as active as the commercial  $\eta\text{-Al}_2\text{O}_3$  catalyst for the ethanol dehydration reaction, but may have the potential to catalyze it better under sulfur tolerant conditions.
9. The cesium:molybdenum ratio has little effect on the rate of ethanol dehydration reaction.
10. The sulfur-tolerant "Aldridge" catalyst is a fair methanation catalyst. Its activity is considerably lower than the best existing nickel catalyst.
11. The experimental data for the methanation reaction are correlated satisfactorily by a pseudo-first order rate law at temperatures between 275 and 450°C and a pressure of 300 psig up to a 40% conversion of CO.
12. The diffusion and exothermic heat of reaction effects on the rate of methanation are small.
13. The difference between the activities of the cesium-impregnated "Aldridge" catalyst and the unimpregnated catalyst is not appreciable for the catalytic methanation reaction.

## VIII. RECOMMENDATIONS

We recommend the following steps to be taken as a continuation of the study of the "Aldridge" catalyst for the water-gas shift, ethanol dehydration, and methanation reactions:

1. Various compositions of the potassium impregnated "Aldridge" catalyst should be tested for the water-gas shift reaction to see whether it is as active as the cesium impregnated one. This is important in view of the fact that the potassium salt may be preferred for commercial processes owing to its low cost.
2. In some coal gasification processes the water-gas shift reaction will be performed at pressures as high as 1000 psig. The activity and stability of the "Aldridge" catalyst should be investigated at such pressures.
3. An independent method for observing of the melting point of the "Aldridge" catalyst at reactor conditions should be developed.
4. The ethanol dehydration reaction should be studied with a catalyst bed consisting of only the cobalt-molybdate catalyst to determine whether the "inert"  $Al_2O_3$  particles used with catalysts "VV" and "ZZ" contribute to the activity.
5. The reaction of ethylene glycol with the synthesis gas should be investigated next. We expect the "Aldridge" catalyst to

- be quite active for this reaction as well. A different gas chromatographic column will be needed for such a study.
6. Other "Aldridge" catalysts, such as those based on nickel molybdate should be tested next for the catalytic methanation reaction.
  7. Other means for controlling the flow rate should be employed for the above reaction system. The Chatham precision valve positioned in the sampling box does not stand up very long to corrosive gases such as COS and H<sub>2</sub>S at high pressures. The potentiometer of the Robinson-Halpern pressure transducer sticks and must be tapped continuously in order to obtain reliable readings. The replacement of this pressure transducer would enable to measure the flow rate more accurately.
  8. To determine the temperature and pressure dependences of the overall rate of methation, the catalytic microreactor should be operated differentially. This can be achieved through the use of less catalyst and consequently lower conversions of the synthesis gas. For effluent gas analysis, a flame ionization detector, which is quite sensitive to organic substances, will be needed in conjunction with the hot wire detector.
  9. The catalyst particle size should be kept at 20/60 mesh or smaller to avoid heat and mass transfer limitations in the methanation reaction.

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## APPENDIX I

A summary of the materials and apparatus used in this work is taken from Overstreet<sup>2</sup> and presented here with several additions.

### Materials and Apparatus

This section contains a description of the various materials and apparatus used.

#### Materials Used for Catalytic Microreactor

##### Nitrogen

Obtained from Airco, New York, New York. Used for detecting leaks in the reactor.

94% H<sub>2</sub>/6% H<sub>2</sub>S. Matheson Gas Products, Division of Will Ross, Inc., East Rutherford, N. J. Used in pretreating catalysts.

49% H<sub>2</sub>/49% CO/2% COS. 1000 psig delivery pressure. Obtained from Matheson Gas Products, Division of Will Ross, Inc., East Rutherford N. J. Used as feed for study of water gas shift reaction.

CoO-MoO<sub>3</sub> Catalyst. 12.5% CoO<sub>3</sub>/3.5% MoO<sub>3</sub> Nalcomo 474 hydrotreating catalyst supported on Al<sub>2</sub>O<sub>3</sub>. Surface Area = 270 m<sup>2</sup>/gm. Nalco Chemical Company, Houston, Texas. Used as hydrogenation/dehydrogenation component of "Aldridge" catalysts.

Al<sub>2</sub>O<sub>3</sub>. Hard Alumina Catalyst 200S, code #520-CP-45, Air Products and Chemicals, Inc., Paulsboro, N. J. Used for diluting catalyst beds.



Cesium Acetate. CsOAc, Research Organic/Inorganic Chemical Corporation, Belleville, N. J. Used as the alkali metal component of the "Aldridge" catalyst.

Apparatus Used for Overall Reactor System.

Regulator. Matheson Model 8-H two stage regulator, delivery pressure from 0 to 650 psig, Matheson Gas Products, Division of Will Ross, Inc., East Rutherford, N. J. Used to regulate tank pressure.

Regulator. Airco, 2 stage, delivery pressure 0 to 50 psig, Airco, New York, New York. Used for regulation of gas pressure before precision valve.

4-way, 5-port Ball Valve. Whitey Company, Oakland, California. Used for selection of feed gas.

Safety Valve. Hoke Model 6564L4Y Stainless Steel adjustable Safety Valve, Hoke Inc., Cresskill, N. J. Used to prevent excess pressure inside the reactor.

On/off Valves. Whitey Company, Oakland, California. Used for connecting reactant line to exhaust system when flushing system.

Fittings. Fittings are either brass or stainless steel, several types, exclusively Swagelock, Crawford Fitting Company, Solon, Ohio. Used for connecting tubing throughout entire reactor system.



Pressure Gauge. Matheson 0 to 1000 psig, 6-inch dial, Division of Will Ross, Inc., East Rutherford, N. J. Used to monitor reactant gas pressure before entering precision metering valve.

Water Saturator. Obtained locally [of unspecified origin]. An appropriate substitute would be the 1000- to 500- ml stubby stainless steel bombs sold by Whitey, with one end welded closed and the other end welded to a stainless steel Swagelock tee. Used for saturating dry gas feed with water vapor.

Temperature Controller. Love Model 72-1, 0 to 800°C with type J thermocouples. Love Controls Corp., Wheeling, Ill. Used to control temperature of central portion of catalytic microreactor.

Temperature Controllers. Love Model 72-1, 0 to 200°C with type J thermocouples. Love Controls Corp., Wheeling, Ill. Used for controlling temperatures of water saturator, sampling valve, and exit tube.

Temperature Controller. Southland Chemitronics Model A solid state temperature controller, 0 to 800°C, Southland Chemitronics, Newport, Va. Used for controlling temperature of reactor ends.

Heating Tapes. Arthur H. Thomas 5954-H50 heating tapes of various dimensions, Hotwatt, Inc., Danvers, Mass. Used for heating reactor and for heat-tapping lines.



Glassrope Heaters. Hotwatt, Inc., Danvers, Mass. Used for heat tapping various lines.

Insulation. Johns-Manville 4-lb density Cerafelt. Used to insulate reactor tube and various lines. Johns-Manville Co., New York.

Insulation. Cerakote 5" by 1-1/2" thermo 12 pipe covering. Used to enclose reactor insulated with Cerafelt. Porter Hayden Co., Baltimore, Md.

Sampling Valve. Valco Model ACMV5V-10-HPx C-20 valve, 10 port, multifunctional with 1.16" zero volume fittings, carpenter 20 steel, with UA-1 air operator and 0.7 ml loop. Used for obtaining gas samples from reactor exit. Valco Instruments Co., Houston, Texas.

Gas Sampling Region. Made by VPI&SU Chemical Engineering Shop. Box made of pressed asbestos, insulated with cerafelt, heated with 150 watt light bulb. Contains a fan to circulate air. Used to maintain the sampling valve at a constant temperature and to minimize water condensation.

Chromatograph. Perkin-Elmer model 900 with thermal conductivity detector, Perkin Elmer Corporation, Norwalk, Conn. Used for analysis of exit gas stream.

Chromatographic Columns. 1/8" stainless steel columns, 6' long, packed with 80/100 mesh chromosorb 102.

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Digital Integrator. Autolab Model 6300-02 with parallel BCD output available at back, area and retention time output, Autolab Company, Mountain View, Calif. Used to analyze chromatographic areas.

Recorder. Beckman 10-inch recorder equipped with linear-log button, Beckman Instruments, Fullerton, Calif. Used for obtaining analog representation of chromatograph output.

Sifter. Allen-Bradley #3 Sonic Sifter, with No. 20 and 60 sieves, Fisher Scientific Company, Pittsburgh, Pa. Used to obtain 20/60 mesh catalyst for use in reactor.

Chatham Precision Metering Valve. Model 5G SST, 0.0005 Cv, Viton O-Ring. Chatham Precision, Inc., 9 Commerce Street, Chatham, N. J. Used to control the flow rate.

Power Supply. Kepco D.C. power supply, Model ABC 40 -0.5 M, Kepco Co. New York. Used as power source for the pressure transducer.

Pressure Transducer. Robinson-Halpern, Potentiometer Pressure Transducer Model No. P6D-320-31N, 0-3000 psig, 100052. Robinson-Halpern Company, Plymouth Meeting, Pa. Used to measure the pressure or the pressure change in the volume,  $V_f$ .

Digital Multimeter. Keithley Model 171. Used to measure reactor temperature with a thermocouple.

Repeat-cycle Timer. Eagle Signal Company, Davenport, Iowa.

Maximum time range is 5 minutes.

## APPENDIX II

The detailed experimental description of the overall reactor system and the reactor operation procedure are presented here directly from Overstreet's M.S. thesis.<sup>2</sup> The reactor system is subdivided into three parts. Photographs are provided in Figures 53 through 56.

### A. Overall Reactor System

#### 1. Gas Handling System.

A single feed gas passes through a four-way ball valve, an on/off valve, a two-stage gas regulator, a check valve, a relief valve set at 500 psig, a pressure gauge, a vent line, a vacuum line, a precision fine-metering valve, and a bubble meter in the order given. With the aid of the four-way ball valve, different feed gases may be readily selected: nitrogen for preliminary studies and leak checks; CO and CO<sub>2</sub> for calibration of the gas chromatograph; 6% H<sub>2</sub>S/94% H<sub>2</sub> for pretreating the "Aldridge" catalyst; and 2% COS/49% CO/49% H<sub>2</sub> for studying the water gas shift reaction. A bubble meter is used to measure dry gas flow rates.

#### 2. Reactor and Water Saturator

After the precision metering valve, the feed gas passes through a high pressure water saturator [equipped with a 1/8-inch stainless steel bypass valve] maintained at approximately 60°C, a heat-tapped stainless-steel line, a seven-foot reactor-gas preheater tube, and a five foot fixed-bed catalytic reactor maintained between 150°C and 650°C and packed with 20/60 mesh catalyst. Four inches of insulation

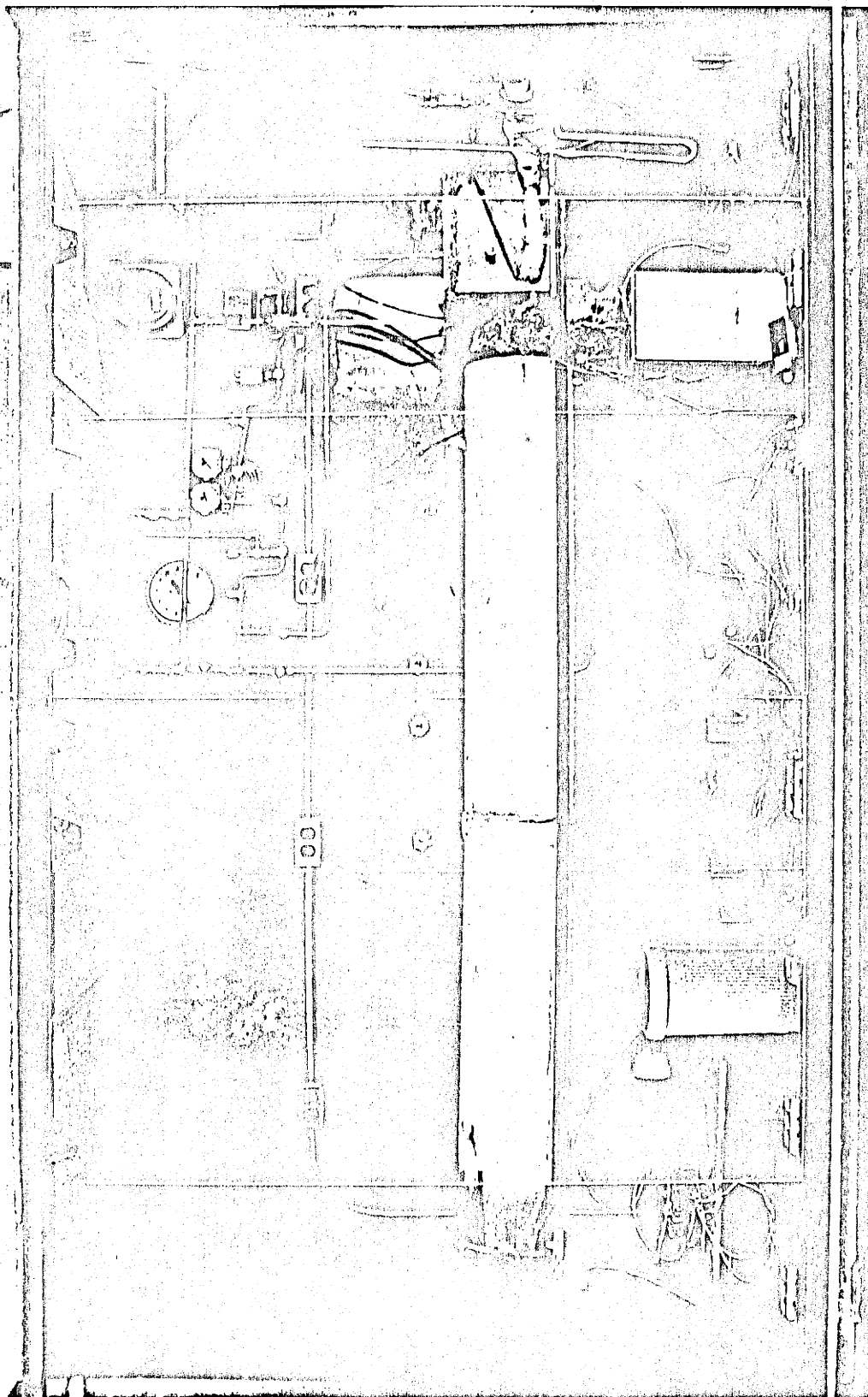


Figure 53. Catalytic Reactor in Aluminum Hood

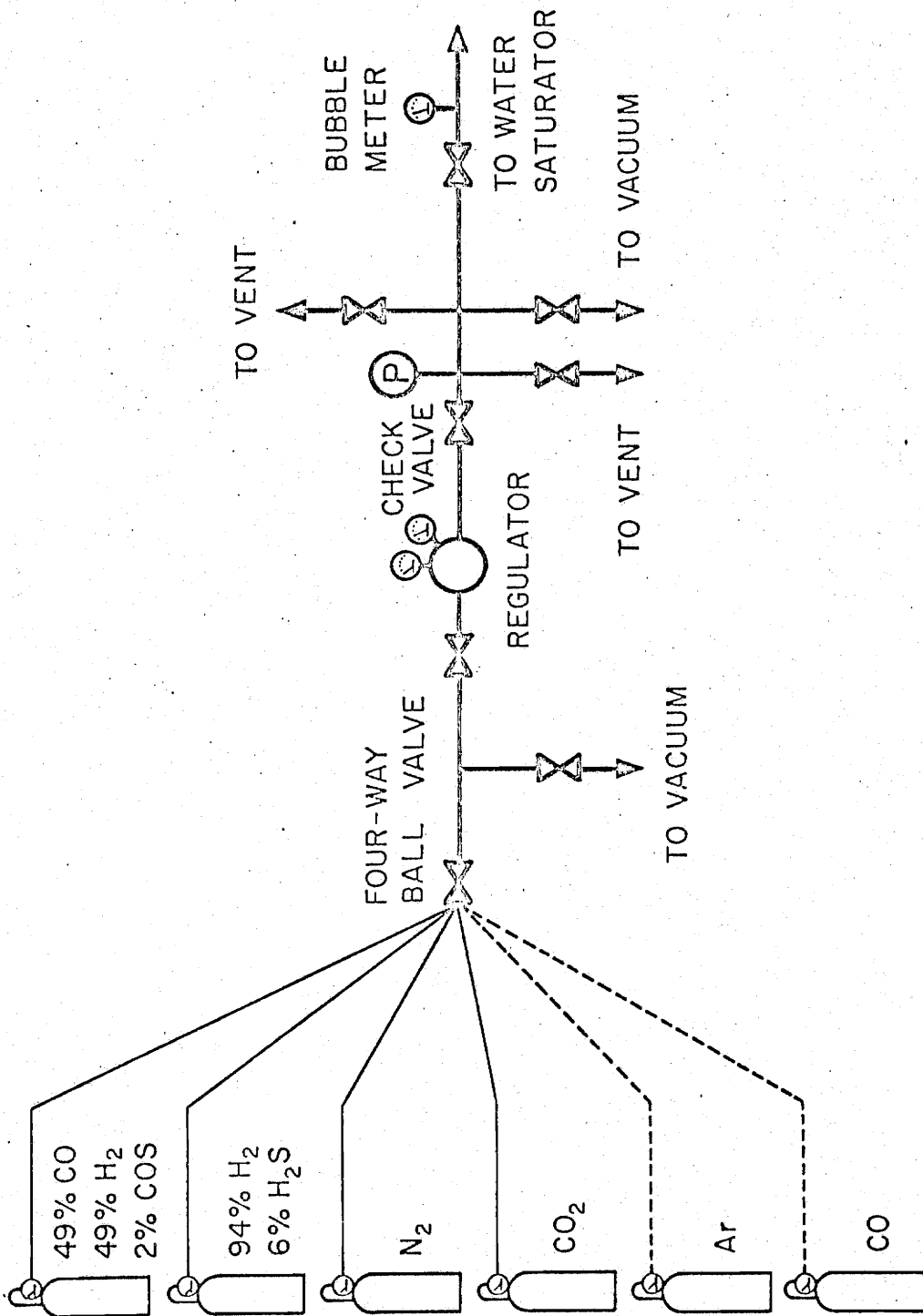


Figure 54. Gas Handling System

surround a 3/4-inch I.D. steel tube which contains the 1/8-inch I.D. preheater tube and 3/16 inch I.D. reactor tube.

Heating of the reactor is accomplished by a one-inch-by-six-foot length of heating tape stretched adjacent to the 3/4-inch I.D. steel tube. Additional short lengths of heating tape are wound at each end of the steel tube to reflect heat back into the center of the furnace and to minimize axial temperature profiles.

Figures and demonstrate the temperature profiles actually established over the length of the reactor. It is clear that 120 cm is usable at 250°C with  $\pm 2^\circ\text{C}$  precision or at 500°C with  $\pm 4^\circ\text{C}$  precision.

A water saturator is employed as the method for metering water into the flowing reactant gas stream of COS, CO, and H<sub>2</sub>. Gases enter at the top of a stainless steel bomb and pass through a fritted glass tube through approximately 200 ml of water. The saturated gas passes out through a heat-tapped side arm and into the catalytic reactor via an additional segment of heat tapped line.

Alternative approaches to the metering of water into the feed gas, such as a liquid metering pump or steam generator/needle valve, were rejected. The important advantage of a water saturator is that the fixed gas feed rate can be varied without significantly changing the percent water in the feed stream entering the catalytic reactor. With the saturator, only one flow rate adjustment needs to be made to adjust the flow rate at constant composition. With the metering pump and

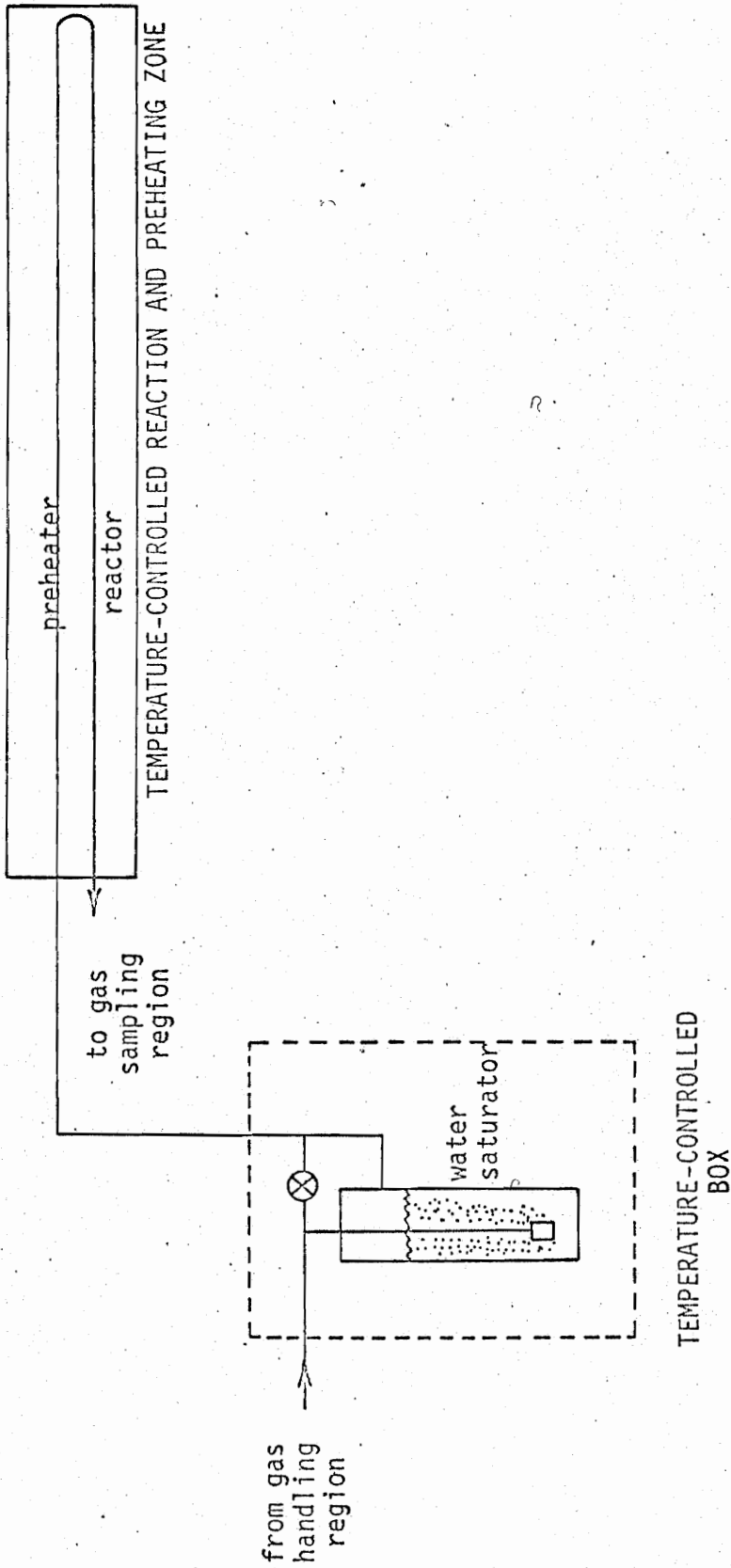


Figure 55. Catalytic Reactor and Water Saturator

✓

steam generator, two flow rate adjustments need to be made in order to change the gas flow rate while maintaining constant gas composition.

### 3. Gas Sampling and Analysis System.

After the fixed bed catalytic reactor, the effluent gases pass through a heat-tapped line, a gas sampling valve equipped with a 0.7 ml sampling loop, a trap for water vapor, and finally, a vent. The sampled gas passes through a heat-tapped line to a nearby gas chromatograph, where it is analyzed for low molecular weight organic and inorganic gases. The peripheral equipment associated with the gas chromatograph include a digital integrator, a homemade digital interface to a minicomputer located five laboratories away, and a recorder.

#### B. Reactor Operation

A dry gas feed of 49% H<sub>2</sub>/49% CO/2% COS was used in this study. An equimolar ratio of hydrogen and carbon monoxide is called "synthesis gas"; such a gas composition is frequently found as an intermediate stage in hydrogen production. A substantial amount of carbonyl sulfide was added both to demonstrate the sulfur tolerance of the "Aldridge" catalysts studied and to maintain the sulfide level within the catalysts.

By choosing a water saturator temperature of 60°C, a steam-to-dry-gas ratio of one to 3.35 was established. Higher temperatures led to problems of varying water composition with changing feed gas flow rates.

#### 1. Startup.

The startup of the reactor system proceeds as follows:

1. Ready the chromatograph by setting the column heater to 60°C, the hot wire detector to a temperature of 250°C, and the hot

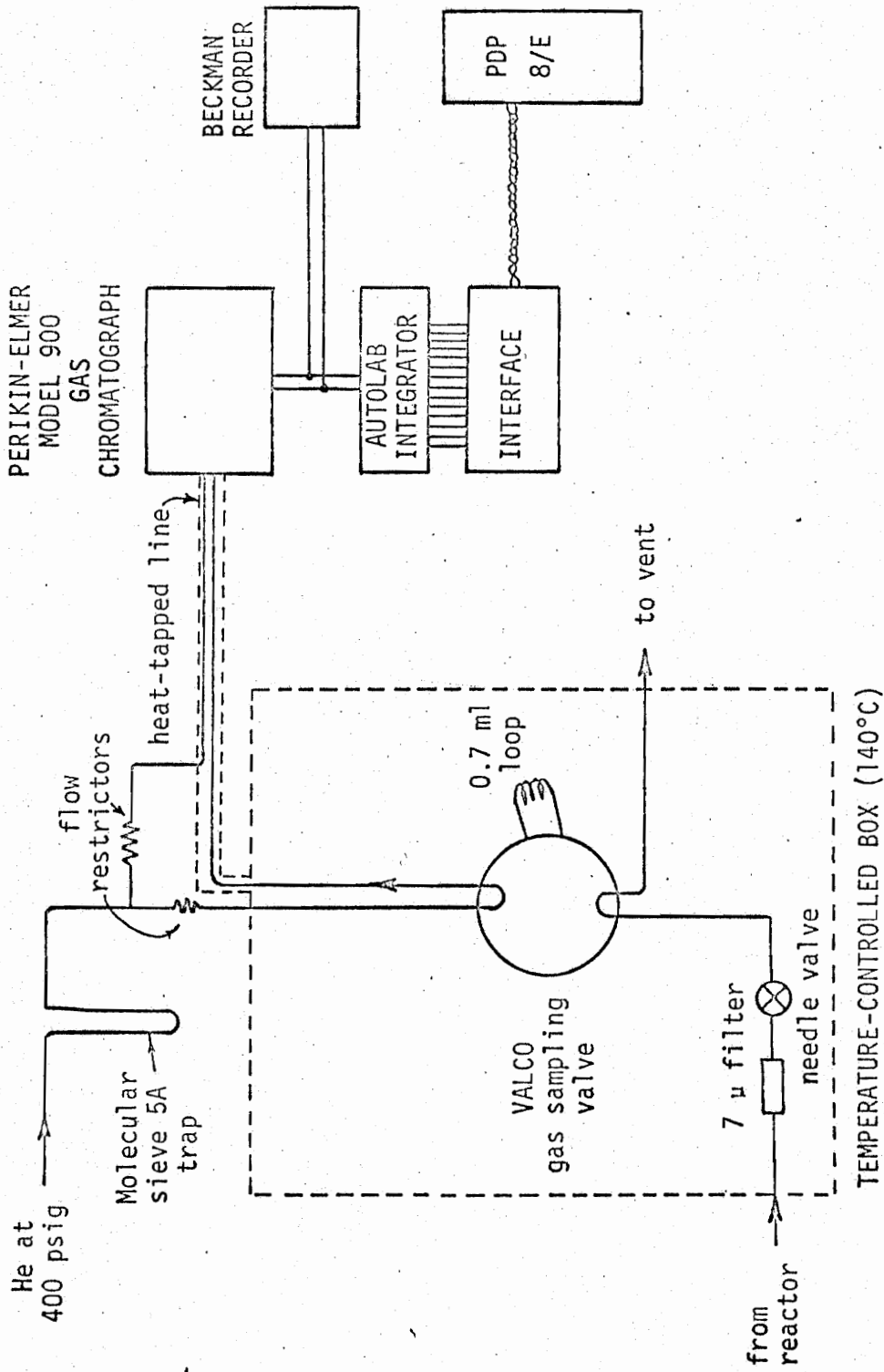


Figure 56. Gas Sampling and Analysis System

- wire current to 125 milliamps. Crimped flow restrictors permanently establish the helium carrier gas flow to the chromatograph at 24 milliliters per minute.
2. Turn on the digital integrator and recorder.
  3. Adjust the regulator on the reactant gas tank to achieve maximum delivery pressure and open the regulator valve to establish flow.
  4. Adjust the regulator inside the hood to achieve maximum delivery pressure and then open the regulator valve.
  5. Adjust the precision metering valve to establish flow to the reactor itself. By setting high delivery pressures using the regulators, very steady flows can be observed past the precision metering valve. The water saturator is initially bypassed.
  6. After flow through the reactor has been observed, turn on the two reactor temperature controllers to the lowest experimental temperature of interest.
  7. Set the temperature controllers for the water saturator, the sampling valve region, and the region between the reactor exit and sampling valve at 60°C, 150°C, and 150°C, respectively.
  8. Switch on autotransformers controlling the heat-tapped exit lines and carrier lines between the sampling valve and chromatograph.

9. After a period of ten minutes, close the water saturator bypass valve, thus causing the dry reactant gas stream to become saturated with water vapor.

## 2. Run Procedure.

Data were taken after the initial steady state temperature profile was established in the reactor, a warm-up time that took approximately 45 minutes. The initial temperature used was generally 200°C which was then increased to 400°C in 25°C increments. Data for a single "Aldridge" catalyst could be obtained in one 8-hour day.

For any given "Aldridge" catalyst, the following procedure was used for obtaining data:

1. Establish a dry-gas flow rate using the precision metering valve. Determine the actual dry gas flow rate using a bubble meter. Flow rates generally range from 15 ml/min to 75 ml/min at ambient temperature and pressure. Allow two or three minutes for equilibration of the reactor system.
2. Switch the sampling valve to the fill position. Allow 30 seconds for the sample loop to fill.
3. Switch the sample valve to the sample position while simultaneously pressing the injection reset/totalize button on the digital integrator.
4. Observe the output for the five detected components in the order: CO, CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O, and COS. The gas chromatograph output for each component is given in analog fashion by the recorder and in digital form by the digital integrator.

5. Repeat steps (1) through (4) between three and five times.
6. Disconnect the thermocouple attached to the central reactor temperature controller. Connect it to a digital voltmeter and record the actual temperature at the center of the reactor.
7. After all desired flows at a given temperature are run, raise the reactor temperature 25°C by adjusting the two reactor temperature controllers.
8. Allow thirty minutes for the reactor to come to equilibrium at the new temperature.
9. Repeat steps (1) through (6).
10. Repeat steps (7) through (9) as often as desired or until an upper temperature limit is reached.

The flow rates chosen for a given catalyst depend upon (a) the reactor temperature, (b) the type of catalyst, and (c) the amount of catalyst in the microreactor. For example, flows were maintained in the faster flow regime for a "hot" catalyst at higher temperatures. For such a catalyst, slower flow rates led to equilibrium conversions.

### 3. Shutdown.

Shutdown procedures are similar to startup procedures:

1. Shut down the gas chromatograph by turning off the column heater, the hot wire detector heater, and the hot wire current.
2. Turn off the recorder and digital integrator detector.
3. Disconnect the power to the temperature controller for the two reactor zones, the water saturator, the sampling valve

region, and the region between the reactor exit and sampling valve.

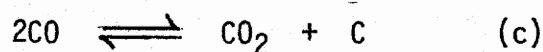
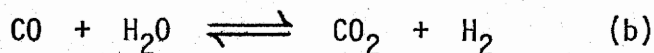
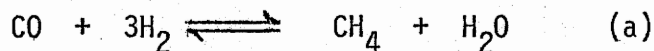
4. Switch off autotransformers controlling the heat-tapped exit lines and carrier lines between the sampling valve and chromatograph.
5. Open the water saturator bypass.
6. Allow fifteen minutes for cooling before shutting off dry reactant gas flow; then close the flow valves for the two regulators. Finally, close the precision metering valve.

APPENDIX III  
COMPUTER PROGRAMS

The computer programs that we wrote to analyze the kinetic data and to calculate the equilibrium composition for the feed gases at a given temperature and pressure are described and the listings of the both programs are presented in this appendix.

1. Data Analysis.

The computer program receives the data for the initial gas composition, chromatographic sensitivity factors, reaction equilibrium constants for a temperature range of 300-1200<sup>0</sup>F, reactor temperatures, the time (in seconds) needed for the product gases to pass through a 10 cm<sup>3</sup> volume of the bubble meter, and finally component peak areas. The variables, AIN, BIN, CIN, DIN, EIN, FIN, GIN, and HIN, are the initial mole fractions of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>S, H<sub>2</sub>O, and COS, respectively. SFCO, SFCH<sub>4</sub>, SFCO<sub>2</sub>, SFETN, SFH<sub>2</sub>S, SFH<sub>2</sub>O, and SFCOS are the sensitivity factors<sup>37</sup> on a mole percent basis, and A1, A2, A3, A4, A5, A6, and A7 are the final chromatographic peak areas in total counts, for CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>S, H<sub>2</sub>O and COS, respectively. The variables, KC1, KC2, and KC3, are the equilibrium constants at the given temperatures for the following reactions:



The flow rates at reactor conditions, the mole fractions of the product gases and the conversion parameters are computed at each temperature in the loop that covers the statements 11 and 12. The data points for the plot of the conversion parameter,  $-\ln(y_{CO}/y_{CO}^0)$ , versus the reciprocal flow rate for a set of flow rates are fitted by subroutine STSQM<sup>2</sup>, which employs a least squares method. Slopes, intercepts and correlation coefficients are evaluated and printed at each temperature both with and without the assumption that (0.0) is a valid data point. The flow rates are calculated by using the following two equations:

$$\text{FLOW} = 1.285 * (T + 273)/\text{SECS} \quad (1)$$

$$\text{FLOW} = \text{FLOW} * ((A8/0.74)/Q) \quad (2)$$

where,  $T$  = reactor temperature, °C

SECS = time, in seconds it takes the product gases to pass through a volume of 10 cm<sup>3</sup> at ambient conditions.

A8 = the final corrected molar counts for hydrogen

Q = the total number of molar counts

1.285 = unit conversion factor, cm<sup>3</sup>-sec/min-°K

0.74 = initial mole fraction of H<sub>2</sub>

A sample input to and output from the program at 332°C is given with the listing below.

## 2. Equilibrium compositions.

We can calculate the equilibrium mole fractions for the product gases by assuming equilibria for reactions (a), (b), and (e) are

```

REAL KC1(25), KC2(25), KC3(25), T1(25), T2(25), T3(25), CONP(25), INFLOW(
125), K1, K2, K3
READ(5, 7) AIN, BIN, CIN, DIN, EIN, FIN, GIN, HIN
READ(5, 8) SFCD, SFCH4, SFCD2, SFETN, SFH2S, SFH20, SFCOS
P=21.41
READ(5, 1) J, L, N
DO 2 I=1, J
  READ(5, 3) T1(I), KC1(I)
2 CONTINUE
  DO 4 I=1, L
    READ(5, 29) T2(I), KC2(I)
    DO 6 I=1, N
      READ(5, 39) T3(I), KC3(I)
6 WRITE(6, 10)
10 FORMAT(IH1)
  IP=0
11 REAC, T, SECS
  IF(T.EQ.0.0) GO TO 12
  IF(T.LT.0.0) STOP
  FLCH=1.285*(T+273)/SECS
  T=1.8*T+32.
  READ, A1, A2, A3, A4, A5, A6, A7
  A1=A1*SFCO
  A2=A2*SFCH4
  A3=A3*SFCO2
  A4=A4*SFETN
  A5=A5*SFH2S
  A6=A6*SFH20
  A7=A7*SFCOS
  A8=2.84*A1+1.84*A6+5.68*A3+2.84*A7-2*A2-3*A4-A5
  Q=A1+A2+A3+A4+A5+A6+A7+A8

```

```

FLCW=FLOW#((A8/.74)/Q)
A1=A1/Q
A2=A2/Q
A3=A3/Q
A4=A4/Q
A5=A5/C
A6=A6/Q
A7=A7/Q
A8=A8/Q
IP=IP+1
INFLOW(IP)=1/FLOW.
K1=EQCST(T1,KC1,T,J)
K2=EQCST(T2,KC2,T,L)
K3=EQCST(T3,KC3,T,N)
T=(T-32.)/1.8
WRITE(6,13) T,K1,K2,K3,FLOW,INFLOW(IP)
WRITE(6,14) AIN,BIN,CIN,DIN,EIN,FIN,GIN,HIN
WRITE(6,16) A8,A1,A2,A3,A4,A5,A6,A7
SAV=A1/BIN
IF(SAV.LE.0.0) GO TO 21
COMP(IP)=-ALOG(SAV)
WRITE(6,17) COMP(IP)
GO TO 11
21 WRITE(6,18)
IP=IP-1
GO TO 11
12 CALL LSTSQM(COMP,INFLOW,SLOPE,XCEPT,IP,SLOPEP,XCEPT,CORCO,CORCOP)
WRITE(6,119) SLOPE,XCEPT,SLOPEP,XCEPT

```

```

WRITE(6,120) CORCO,CORCOP
GO TO 36
1  FORMAT(I2,2X,I2,2X,I2)
7  FORMAT(8F8.5)
3  FORMAT(F10.2,6X,E9.4)
29 FORMAT(F10.2,5X,F11.4)
39 FORMAT(F10.2,6X,E8.3)
8  FCRMAT(7F10.6)
13 FORMAT(IH ,//,2X, TEMPERATURE=,F7.2,1X, DEG C,5X, 'K1=',E11.5,5X
2, 'K2=',E11.5,5X, 'K3=',E11.5,/,10X, FLOW=,F10.5,5X, '1/FLOW=',F10.7
3)
14 FORMAT(IH0,10X, HYDROGEN',4X, 'CO',4X, 'METHANE',4X, 'CO2',5X, 'ETHANE
3',4X, 'H2S',5X, 'WATER',5X, 'COS',/,2X,
'INI CONC:',8(F8.5,1X))
16 FORMAT(IH ,1X, 'FIN CONC:',8(F8.5,1X))
17 FORMAT(IH ,31X, 'CONVERSION PARAMETER=',F15.8)
18 FORMAT(IH ,5X, 'NC CONVERGENCE')
119 FORMAT (IH0,10(//),5X, 'SLOPE =',F10.5,5X, 'INTERCEPT =',F10.5,
15X, 'SLOPE WITH 0,0=',F10.5,5X, 'INTERCEPT WITH 0,0=',F10.5)
120 FORMAT (IH0,5X, 'CORRELATION COEFFICIENT =',F10.5,5X, 'CORRELATION C
5OEFFICIENT WITH 0,C =', F10.5)
END

FUNCTION EQCST(T,K,TIQ,N)
REAL K(25),T(25)
NMI=N-1
DO 3 I=1,NMI
IF ( TIQ.LT. T(I+1) .OR. I.EQ. NMI ) GO TO 5
3 CONTINUE
5 EQCST=EXP(((ALOG(K(I)))*(T(I)+460.))+(TIQ-T(I))/(T(I+1)-T(I)))*
1(ALOG(K(I+1)))+(T(I+1)+460.)-(ALOG(K(I)))+(T(I)+460.))/(TIQ+460.)
2)
RETURN
END

```

```

SUBROUTINE LSTSQM(CONP, INFLOW, SLOPE, XCEPT, IP, SLOPEP, XCEPT, CORCO, C
10RCOP)
REAL CONP(25), INFLOW(25)
IPP=IP+1
X2=0.
X=0.
Y=0.
Y1=0.
Y2=0.
DO 3 I=1, IP
X2=X2+(INFLOW(I))**2
X=X+INFLOW(I)
Y=Y+CONP(I)
Y1=Y1+(CONP(I))*(INFLOW(I))
Y2=Y2+(CONP(I))**2
3 CONTINUE
D=X2#FLOAT(IP)-X**2
A=Y1#FLOAT(IP)-Y#X
B=X2#Y-X#Y1
SXY=Y1#FLOAT(IP)-X#Y
SYY=Y2#FLOAT(IP)-Y**2
SXX=X2#FLOAT(IP)-X**2
SLCPE=A/D
XCEPT=B/D

```

```
CORCO=SXY/SQRT(SXX#SYY)
AP=Y1#FLCAT(IPP)-Y#X
DP =X2#FLOAT(IPP)-X#2
SXP= Y1#FLOAT(IPP)-X#Y
SYYP=Y2#FLOAT(IPP)-Y#2
SXXP=X2#FLOAT(IPP)-X#2
SLOPEP=AP/DP
XCEPT=B/DP
CORCOP=SXP/SQRT(SXXP#SYYP)
RETURN
ENC
```



500.	.421E8								
600.	.104E07								
700.	.491E05								
800.	.377E04								
900.	.425E03								
1000.	.648E02								
1100.	.126E02								
1200.	.300E01								
332.,19.5									
82013.	21030.	11265.	3362.	39.	9625.	6207.			
332.,13.									
87412.	17831.	8348.	2466.	0.	7564.	6779.			
332.,14.9									
86616.	17491.	8974.	2506.	0.	7753.	6143.			
332.,15.4									
86245.	17688.	9171.	2718.	0.	8355.	6057.			
332.,12.2									
90369.	15133.	7501.	2156.	0.	6747.	5916.			
332.,10.9									
94030.	13224.	6299.	1866.	0.	6251.	7004.			
332.,8.									
96863.	11941.	5396.	1615.	0.	5302.	5438.			
332.,6.3									
101761.	10372.	4026.	1267.	0.	5395.	6818.			
0.			0.	0.					
-50.			0.	0.					

TEMPERATURE= 332.00 DEG C      K1=0.13612E 07      K2=0.25357E 02      K3=0.39737E 06  
 FLOW= 122.41940      1/FLOW= 0.0081686

	HYDROGEN	CO	METHANE	CO2	ETHANE	H2S	WATER	COS
INI CONC:	0.74000	0.22600	0.00000	0.01440	0.00000	0.00000	0.00000	0.01960
FIN CONC:	0.73412	0.20948	0.00971	0.01858	0.00215	0.00000	0.01422	0.01174

CONVERSION PARAMETER= 0.07590997

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Figure 57. Sample Output of the Computer Program for Analysis of Methanation Data

satisfied. The equilibria for reactions (c) and (d) are ignored for simplicity. The details of the reduction of the number of unknowns and relationships to two by progressive elimination are given in section IV.

The solution of the last two nonlinear equations by a Newton-Raphson technique will be described in this section. Those two equations form the following system of nonlinear equations when expressed as  $F(x,y)$  and  $G(x,y)$ :

$$F(x,y) = K_1 XY^3 P^2 - (K_3 X^2 P - 0.75 Y + 0.25 X + 0.5) \\ (-2K_3 X^2 P - 0.25 Y + 0.5) = 0 \quad (3)$$

$$G(x,y) = K_2 (-2K_3 X^2 P + 0.5 - 1.25 X - 0.25 Y) - K_3 XYP = 0 \quad (4)$$

By expanding each function in a Taylor series and dropping the higher order terms a linear system of equations with respect to the increments,  $XONE$  and  $YONE$  can be obtained. Beginning with initial estimates for  $X$  and  $Y$ , the increments are calculated and compared with the values of  $x$  and  $y$ . This iteration is continued until the absolute value of the difference between  $X$  and  $XONE$  and that between  $Y$  and  $YONE$  are smaller than a given error,  $EPS$ . When this condition is satisfied, the calculated values of  $XONE$  and  $YONE$  are printed out as  $X$  and  $Y$  respectively. The mole fractions of  $CH_4$ ,  $H_2O$ , and  $CO_2$ , which are, respectively,  $X_3$ ,  $X_4$ , and  $X_5$ , can be found from the relationships obtained during the progressive elimination procedure.

We tried to calculate the equilibrium compositions by a direct approach, but could not obtain reasonable results owing to the divergence

of the Newton-Raphson method as applied to the following three nonlinear equations:

$$K_1 = \frac{X_1(X_1 - X_2)(A + B - 2X_1 - X_2 - 2X_3)^2}{(A - X_1 - X_2 - 2X_3)(B - 3X_1 + X_2)^3 P^2} \quad (5)$$

$$K_2 = \frac{(X_2 + X_3)(B - 3X_1 + X_2)}{(A - X_1 - X_2 - 2X_3)(X_1 - X_2)} \quad (6)$$

$$K_3 = \frac{(X_2 + X_3)(A - X_1 - X_3)}{(A - X_1 - X_2 - 2X_3)^2 P} \quad (7)$$

where, A = initial number of moles of CO

B = initial number of moles of H<sub>2</sub>

X<sub>1</sub> = moles of CH<sub>4</sub> formed at equilibrium

X<sub>1</sub> - X<sub>2</sub> = moles of H<sub>2</sub>O present at equilibrium

X<sub>2</sub> + X<sub>3</sub> = moles of CO<sub>2</sub> present at equilibrium

A - X<sub>1</sub> - X<sub>2</sub> - 2X<sub>3</sub> = moles of CO present at equilibrium

B - 3X<sub>1</sub> + X<sub>2</sub> = moles of H<sub>2</sub> present at equilibrium

The listing of the program with a sample output is given below.

```

LOGICAL FLAG
REAL K1,K2,K3
READ(5,2) X,Y
2 FORMAT(2F10.5)
WRITE(6,15)
15 FORMAT(22X,67HHYDROGEN      CO      METHANE      CO2
      WATER//)
P=21.41
K1=1.361*(10**6)
K2=25.357
K3=3.974*(10**5)
EPS=.0008
IU=100
FLAG = .FALSE.
JOB=1
3 F=K1*X*(Y**3)*(P**2)-(K3*(X**2)*P-.75*Y+.25*X+.5)*(-2*K3*(X**2)*P-
1.25*Y+.5)
G=K2*(-2*K3*(X**2)*P+.5-1.25*X-.25*Y)-K3*X*Y*P
FPX=K1*(Y**3)*(P**2)-(2*K3*X*P+.25)*(-2*K3*(X**2)*P+.5-1.25*X-.25
1*Y)+(K3*(X**2)*P+.25*X-.75*Y+.5)*(-4*K3*X*P-1.25)
FPY=3*K1*X*(Y**2)*(P**2)-(-.75)*(-2*K3*(X**2)*P+.5-1.25*X-.25*Y)+
1(K3*(X**2)*P+.25*X-.75*Y+.5)*(-.25)
GPX=K2*(-4*K3*X*P-1.25)-K3*Y*P
GPY=K2*(-.25)-K3*X*P
DENOM=(FPX)*(GPY)-(FPY)*(GPX)
TOPX=(F)*(GPY)-(G)*(FPY)
TOPY=(G)*(FPX)-(F)*(GPX)
XONE=X-TOPX/DENOM
YONE=Y-TOPY/DENOM

```

```

IF ((ABS(XONE-X)).GT.EPS) GO TO 5
IF ((ABS(YONE-Y)).GT.EPS) GO TO 5
X=XONE
Y=YONE
X4=-2*K3*(X**2)*P+.5-1.25*X-.25*Y
X5=.25-(5/8)*X-.125*Y-.5*X4
X3=1.5*X-.5*Y+X4+3*X5
WRITE(6,6) Y,X,X3,X5,X4
WRITE(6,10)
10 FORMAT(1H1)
6 FORMAT(19X,5F15.10)
GO TO 8
5 IF (JOB.LT.IU) GO TO 7
FLAG = .TRUE.
GO TO 8
7 X=XONE
Y=YONE
JOB=JOB+1
GO TO 3
8 STCP
END

```


	HYDROGEN	CO	METHANE	CO2	WATER
	0.0169005400	0.0000719183	0.5314845000	0.0440521200	0.4076706000

## VITA

The author was born on May 8, 1949, in Beypazarı -Ankara, Turkey. A 1969 graduate of Robert Academy, Istanbul, the author went on to Bosphorus University (formerly Robert College) in Istanbul, Turkey to complete his B.S. degree in Chemical Engineering. While an undergraduate, he was the president of the Athletic Association of the University as well as captain of the soccer team. As a member of the Turkish Folklore Club, he represented the country in International Folk festivals.

His related career employment before entering graduate study at Virginia Polytechnic Institute and State University in September 1973 included practical training in the Projects and Engineering Department at ICI, Agricultural Division in England and in a cement factory in Turkey. He completed his requirements for a Master of Science degree in Chemical Engineering in March 1975.

The author plans to go back to Turkey and seek employment in that country.

  
Vasfi Berispek

STUDIES OF AN ALKALI IMPREGNATED COBALT-MOLYBDATE  
CATALYST FOR THE WATER-GAS SHIFT AND  
THE METHANATION REACTIONS

by

Vasfi Berispek

(ABSTRACT)

An alkali impregnated cobalt molybdate on  $Al_2O_3$  support was tested under sulfur-tolerant conditions for the water-gas shift, methanation, and ethanol dehydration reactions in an isothermal integral plug flow reactor. Experimental data were obtained for 31 catalysts of different compositions for the water-gas shift reaction and two catalysts for the ethanol dehydration reaction over a temperature range of  $200^{\circ}C$  to  $400^{\circ}C$  and atmospheric pressure. The catalytic methanation reaction was performed at temperatures ranging between  $275^{\circ}C$  to  $450^{\circ}C$ , a pressure of 300 psig, and a space velocity of greater than  $2000\text{ hr}^{-1}$  at STP. The synthesis gas used for the above experiments contained 2% COS and had a  $H_2/CO$  molar ratio of 3.27 for the methanation reaction and approximately 1.0 for the remaining two reactions.

A table of the mole fraction of the product gases and a plot of the activity,  $\ln(kV/W)$ , versus  $1/T$  are presented for each catalyst for each reaction system. A change in the activation energy was observed at higher temperatures for some of the full strength water-gas shift catalysts, but not for the half strength and one-fifth strength catalysts. The reason for the occurrence of the "break" points in the Arrhenius plots is not known. The catalyst does not appear to melt at reactor conditions.

The most important variable in the water-gas shift studies is the cesium:molybdenum ratio. The activity,  $\ln(kV/W)$ , is critically affected by this ratio. A maximum in activity appears to exist for the one-half and full strength catalysts as a function of such a ratio.

In the ethanol dehydration and methanation studies, the addition of cesium acetate to sulfided cobalt molybdate on alumina didn't enhance the catalyst's activity. The 'Aldridge' cesium-cobalt-molybdate catalyst thus appears to be uniquely effective for the water-gas shift reaction.