

FOREWORD

The work described herein was conducted as Part I of an in-house research effort concerning the investigation of catalysts for the reduction of carbon dioxide for space vehicle atmospheric control. This effort is being conducted by the Air Force Flight Dynamics Laboratory of the Research and Technology Division, AFSC, WPAFB, Ohio, under Project 6146, Flight Vehicle Environmental Control, Task 614603, Atmosphere Generation and Control. The chief investigator is Mr. E. B. Thompson, Jr., with assistance from Messrs. A. Civetz and J. Brennan Gisclard; and Mr. E. Bryan of the Harshaw Chemical Company. The first phase of the continuing program was initiated in June 1963 and completed in October 1963. Since this is a continuing program, this report is designated as Part I.

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ABSTRACT

A nickel-kieselguhr methanation catalyst was selected as the initial catalyst of this program for promoting the catalytic reduction of carbon dioxide by hydrogen to methane and water. A catalytic reactor was designed, fabricated, and evaluated utilizing the nickel-kieselguhr methanation catalyst. The reactor processed 2.2 pounds of CO<sub>2</sub> per day, equivalent to a one-man daily output.

The minimum temperature required to achieve the maximum CO<sub>2</sub> conversion rate of 98% for this catalyst was determined to be 575°F at a pressure of 1 atmosphere. The total weight of hydrogen required to reduce the 2.20 pounds of CO<sub>2</sub> under these conditions is 0.397 pounds. The same batch of catalyst, weighing 300 grams, was used during this entire phase of the experimental program. The catalyst was periodically examined for possible carbon deposition and physical deterioration. While neither of these effects was perceptible, it eventually became necessary to purge the catalyst with hydrogen before each experiment to offset the increasing effect of sulfur poisoning. The report includes a discussion of theory of catalysis and is concluded by recommendations for altering the reactor design and selecting other catalysts for the future phases of this program.

Publication of this technical documentary report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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## 1. Introduction

### 1.1. Program Objectives

This report summarizes the work conducted as the first phase of a continuing in-house research program concerning the Sabatier methanation reaction or the reduction of carbon dioxide by hydrogen catalysis. The scope of the entire program provides for accomplishing the two-fold objective of, first, determining a practical technique for an experimental evaluation of Sabatier reaction catalysts and, second, to pinpoint that catalyst or family of catalysts which are most effective in promoting this reaction to maximum water yield and at minimum temperature conditions. The general approach to be taken is to evaluate the effectiveness of a common nickel catalyst for promoting the Sabatier reaction as the first phase. The resulting data on the performance of this catalyst would then serve as reference criteria for evaluating additional catalysts.

The particular catalysts selected for experimental evaluation and considered most feasible for the Sabatier Reactor must satisfy the following general conditions:

- (1) The physicochemical properties of the catalyst must be identifiable for correlation with its effectiveness in promoting the reaction.
- (2) The catalyst must be capable of initiating and sustaining the reaction at a temperature of 300°F and a pressure of 1 atmosphere.
- (3) The catalyst must be capable of sustaining the reaction at maximum CO<sub>2</sub> conversion at the reaction conditions specified in (2) above.
- (4) The catalyst must be resistant to "poisoning" by sulfur compounds and halogen compounds, etc., or be easily regenerable by heating and/or purging with hydrogen.
- (5) The catalytic reactor containing the catalyst in question must be capable of converting a minimum of 2.20 pounds of CO<sub>2</sub> per day to water and methane.

## 2. Analytical Program

### 2.1. Theory of Catalysis

#### 2.1.1. Sabatier Reaction

The Sabatier methanation reaction is considered to be one of the more feasible chemical approaches to recovering oxygen by reducing carbon dioxide with hydrogen over a catalyst to form methane and water with subsequent electrolysis of the water. The present state-of-the-art concerning the mechanics and necessary conditions for this reaction to occur states that nickel-kieselguhr catalysts will effect the maximum reduction of carbon dioxide at a temperature of 560°F-580°F and a pressure of 1 atmosphere. It is possible to obtain a 98% conversion rate of carbon dioxide through this process provided that the exotherm of 41 kilocalories per mole of CO<sub>2</sub> converted is removed from the catalyst bed or catalytic reactor so as to prevent the internal temperature of the catalyst bed from increasing to a temperature level where the chemical equilibrium would be reversed therefore reducing the yield of water. It is also necessary that the nickel-kieselguhr catalyst remain uncontaminated by sulphur and halogen compounds, etc. so that the catalyst does not become poisoned by the adsorption of these contaminants on its surface. Assuming then that the gas stream into the catalytic reactor remains relatively free of potential poisons such as hydrogen sulfide and that the exotherm is removed at a rate which maintains the catalyst bed temperature at 560°F to 580°F, the Sabatier reaction utilizing a nickel catalyst is quite satisfactory. However, since CO<sub>2</sub> reduction to methane and water now appears as a probable method for recovering oxygen in long duration space vehicles, it is imperative that the activation energy necessary to initiate the reaction be reduced or that the reaction proceeds at minimum temperature with a corresponding increase in product yield and decrease of power required from the vehicle auxiliary power unit.

Nearly all of the experimental work conducted to date on the Sabatier reaction has centered on the nickel catalyst which would initiate the reaction at a low temperature while still effecting the maximum conversion of carbon dioxide. The onset of space vehicle atmosphere control has established a premium on power and weight and so has changed this complexion considerably. The performance of nickel catalysts, when well established and documented, serves as an excellent reference basis for evaluating the effectiveness of potentially new and more effective types of catalysts for this reaction. Furthermore, the well known physicochemical properties of the nickel catalysts make it possible to correlate these properties with the



ability of the catalyst to promote the reaction in question. In any event, it is best to have a firm understanding of how a catalyst functions as such before beginning any program concerning an experimental evaluation of catalyst characteristics.

## 2.1.2. Fundamentals of Catalysis

Solid catalysts which increase the rates of reactions whose reactants and products are liquids or gases play an important part in any chemical regenerating process for recovering oxygen from carbon dioxide. The catalyst in many instances not only makes the chemical reaction possible but also serves to accelerate the reaction to equilibrium as well as to increase the yield of the desired product. Of course in any reacting system, only certain "active" molecules possessing a minimum energy,  $q$ , actually take part in the reaction and the velocity of the change is directly proportional to the concentration of these active molecules. If it is assumed that the total energy in the system is distributed by collisions between the constituent molecules, the following relation holds for the velocity of the reaction:

$$k = Ze^{-q/RT} \quad (1)$$

Where

$q$  = activation energy

$R$  = universal gas constant

$k$  = velocity constant

$Z$  = number of collisions in unit time

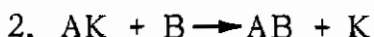
$T$  = absolute temperature.

It can be seen that as  $q$  (which is the activation energy necessary for the uncatalyzed reaction to proceed) becomes smaller the reaction proceeds faster at a given temperature. The function of the catalyst then is to activate the reaction at a lower energy level than  $q$ , and since the time required for the reactants to reach a lower energy level is less, the reaction proceeds at a faster rate.

In the present state-of-technology, a catalyst is defined as an element, compound, or mixture which initiates and/or accelerates the rate of a chemical reaction through the occurrence of intermediate reactions on its surface without the catalyst, itself, incurring any change of state or properties.

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(Negative catalysts, for decreasing reaction rates, also exist.) In actuality, the catalyst does enter into the reaction as an intermediate compound but is regenerated when the final step of the reaction is completed. So when catalyst K changes the velocity of a reaction or accelerates it, it does so by creating a new path through which the reaction can proceed. This is illustrated by the following example of A converting to B:



Result:  $A + B \longrightarrow AB$  catalyzed by K.

This is an example of catalysis as an "intermediate compound". The intermediate compound, AK in step 1 above, is formed by electron bonding or "hydrogen" bonding (sometimes termed "electrovalent adsorption) between atoms at the catalyst surface and atoms of one of the reactants. (The reactant "A" for purposes of this experimental program is considered to be hydrogen). While the electrovalent adsorption characteristics of the catalyst are primarily responsible for determining its effectiveness as a catalyst for a specific reaction, it is also desired that the catalyst should have a large available surface area on which the reacting gases/liquids can be adsorbed and that the chemical nature of this surface selectively adsorbs only the reactants for the reaction desired. This adsorption, termed "electrovalent", occurs because of the chemical structure of the catalyst surface or the type of electron bonding which results between the atoms of the catalyst surface and the reacting gas/liquid molecules.

The activity of any heterogeneous catalyst chiefly resides at the interface between the solid and the less dense phase, and that the reactant (or at least one of the reactants if there are more than one) must be adsorbed at this interface. An atom on the surface is joined by chemical forces to other atoms in the same plane and also below it, but there are, of course, no atoms above it. There is therefore a net resultant force on each surface atom acting towards the bulk. This is represented diagrammatically in Figure 1. It is assumed that a surface atom is capable of forming the same number of bonds as a bulk atom, and therefore that surface atom must necessarily have one or more unused valences directed outwards from the surface. The same conclusion is reached by considering the formation of a surface by the fracture of a crystal. In this process, chemical bonds (whose nature depends on the kind of binding in the solid) are broken, and the free valences thus created remain the property of the surface atoms. To a first approximation it is visualized that a free valency exists at a metal surface as an unpaired electron associated with a particular atom.

There is, then, a certain energy associated with the surface of solids, similar to the surface energy of liquids. In the adsorption process the unused valences interact with the adsorbing molecules to an extent which depends on the nature of the adsorption: the adsorbing molecule loses entropy because its motion on the surface is more restricted than in the gas phase, and the free energy of the system also decreases as the surface valences become saturated. Remembering that for an isothermal process

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

it is concluded that adsorption processes will always be exothermic.

For efficient catalysis, the strength of adsorption of the reactant(s) must lie within certain fairly wide limits. If a reactant is too strongly adsorbed it will be correspondingly difficult to remove, and it may then constitute a poison such as hydrogen sulfide; if it is too weakly adsorbed, it has little chance of remaining on the surface long enough to react. For a given reaction occurring on a series of related catalysts, it is therefore expected to find an inverse relationship between strengths of adsorption of reactants and the catalytic efficiency.

## 2.2. Techniques of Catalyst Preparation

The amount of surface area possessed by a given catalyst and thereby available for a reaction to proceed is determined largely by the particular technique utilized in preparing the catalyst. Some of the more common methods for preparing catalysts are as follows:

1. Decomposition of a thermally unstable chemical compound to give a finely divided compound such as a pure metal or metal oxide from a metal salt.
2. Impregnation of a carrier or support material with a solution of the catalyst salt followed by ignition of the mixture, leaving pure metals or metal oxides deposited on materials with high surface area to volume ratios.
3. Precipitation of a catalyst material from a solution with subsequent washing of extraneous ions, and final conversion usually by heating or drying.
4. Application of films of active metal catalysts to surfaces by actual evaporation of the metal with condensation up the support surface, under vacuum or the presence of very low pressure gases such as argon or nitrogen.

Any of these methods (in addition to numerous others) are satisfactory for catalyst preparation provided that the largest surface area can be attained for a given mass/volume of catalyst material without altering the electrovalent properties of the material itself. It is possible to attain surface areas of a 1,000 sq. meters per gram of material for some catalytic materials, however an area of 10 sq. meters is closer to the rule. Catalysts such as nickel-kieselguhr and its variations considered for the Sabatier reaction are known to have surface areas ranging from 150 to 250 sq. meters per gram, depending on technique of preparation. Any research concerning more effective catalysts for the Sabatier reaction must therefore center on a material possessing larger surface areas than that available from nickel-kieselguhr catalysts while possessing at least the same or greater electrovalent adsorptivity.

Following is a list of catalysts considered favorable for the Sabatier Reaction:

- Cobalt
- Iron
- Iron with copper and cobalt
- Nickel
- Cobalt sulfate with cupric oxide and manganese oxide
- Nickel on magnesium oxide granules
- Nickel on porcelain
- Nickel on porcelain with ceria
- Nickel on kieselguhr
- Nickel on pumice
- Nickel plus promoters on pumice
- Nickel with thoria and ceria on carbon
- Ruthenium on asbestos
- Ruthenium-thorium on asbestos.

This list serves as a partial guide to selecting catalysts for an experimental evaluation in comparison to nickel-kieselguhr. At least some of these catalysts, e.g., ruthenium on asbestos, have demonstrated ability to promote the Sabatier reaction at relatively low temperatures. Investigations concerning base metal oxides and precious metal catalysts will be the subject of reports subsequent to this one.

## 2.3. Analysis of the Nickel-Kieselguhr Catalyst

### 2.3.1. General Description

Harshaw catalyst, N-0104, is a methanation catalyst composed of two parts, (1) the carrier and (2) the catalyzing coating itself. The carrier for N-0104 which comprises 20% of the mass is "kieselguhr" or a calcined silicon dioxide ( $\text{SiO}_2$ ), while the coating is 55%-60% nickel (Ni) and 45%-40% nickel oxide (NiO). The kieselguhr is interstitial and skeletal structured. So the coating which is a heterogenous mixture of Ni and NiO makes up 80% of the entire catalyst mass and the carrier, kieselguhr, is the remaining 20%. It is practical to assume that water is also present in concentrations of 0.5% to 1% in the coating material. Water present in this amount has a negligible effect on the effectiveness of the catalyst. While the specific process for preparing N-0104 is proprietary to the Harshaw Chemical Company, the general method employed is to deposit a thin coating of nickel oxide on the kieselguhr and then reduce the nickel oxide in a hydrogen atmosphere. As stated previously, 55%-60% of the nickel oxide is reduced to pure nickel for this catalyst. Further reduction of the nickel oxide might serve to increase the susceptibility of the catalyst to poisoning while negligibly increasing the effectiveness of the catalyst.

A total of 6600 pellets were used for this phase of the experimental program; 22 pellets weighing one gram. The total weight of the catalyst used equalled 300 grams.

### 2.3.2. Catalyst Properties

#### 2.3.2.1. Densities

In chemical reactions catalyzed by solid surfaces the reaction rate per unit mass of catalyst is influenced by the size and shape of the catalyst particle. Since the nickel-kieselguhr catalyst is extremely porous, the reaction occurs not only on the external available surface of the catalyst pellets but also on the interior surfaces. The external area is sometimes only a fraction of the total effective area. The availability of the interior of the catalyst pellets for catalysis depends on the size, shape and permeability of the pore structure. Generally, it is required that the pores and capillaries be of large and uniform cross section and be interconnected with the external surface of the pellet.

In considering the properties of the catalyst bed the external void space must be distinguished from the internal void space within the particles. This distinction is marked from the experimental determination

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of three densities; bulk density,  $\rho_B$ , expressed as mass per unit volume of bed; particle density,  $\rho_P$ , mass per unit volume of particle; and solid density,  $\rho_C$ , mass per unit volume of solid free from all voids, external and internal. The measured values of these densities for catalyst N-0104 are as follows:

Bulk density,  $\rho_B$ , = 1.43 gms/cc

Particle density,  $\rho_P$ , = 2.60 gms/cc

Solid density,  $\rho_C$ , = 5.78 gms/cc.

The external void fraction of the bed is determined by the following relation:

$$F_e = 1 - \frac{\rho_B}{\rho_P} \quad (3)$$

then

$$F_e = 0.45$$

The internal void fraction of the bed is determined by the relation:

$$F_i = 1 - \frac{\rho_P}{\rho_C} \quad (4)$$

then

$$F_i = 0.55$$

## 2.3.2.2. Surface Area

The total surface area available then from 300 grams of the nickel-kieselguhr can be calculated from the following general relations:

$$A_T = A_E + A_I \quad (5)$$

where

$A_T$  = total area in  $\text{cm}^2$

$A_E$  = external gross area in  $\text{cm}^2$

$A_I$  = internal area in  $\text{cm}^2$

calculating  $A_E$  from:

$A_E$  = area per particle  $\times$  particles per gram  $\times$  number of grams

$$A_E (\text{cm}^2) = 0.330 \frac{\text{cm}^2}{\text{particle}} \times 22 \frac{\text{particles}}{\text{gram}} \times 300 \text{ grams}$$

$$A_E = 2200 \text{ cm}^2.$$

Calculating  $A_I$  from:

$$V_O = V_T - V_S \quad (6)$$

where

$V_O$  = volume of open space, internal plus external

$V_T$  = total volume occupied by 300 grams of catalyst material = 210 cubic centimeters

$V_S$  = volume of solid material

and

$$V_S = 300 \text{ grams} \times \frac{1 \text{ cc}}{5.78 \text{ grams}} = 52 \text{ cubic centimeters}$$

so

$$V_O = 210 - 52 = 158 \text{ cubic centimeters.}$$

Open space, both external and internal to the catalyst pellets, occupies 158 cc for a batch of 300 grams of the catalyst at a bulk density of 1.43 gms/cc and a solid density of 5.78. Since 45% of this volume is external

to the pellets as previously determined, 55% is internal or 87 cc total pore volume for a catalyst batch weighing 300 grams. Treating this volume as representative of a single pore, cylindrically shaped, with a diameter of  $5.75 \times 10^{-5}$  centimeters, all that remains is to calculate the length of the single pore cylinder by solving the simultaneous equations for the formulae of the area and volume of a cylinder.

Solution of the equations shows the total area of the cylinder to be 46,200  $\text{cm}^2$  which is also the total available internal area of the 300 gram catalyst batch on which the hydrogen and carbon dioxide reactants can react. The total area, external and internal, available is then 46,200 plus 2200 = 48,400  $\text{cm}^2$ .

### 2.3.2.3. Effective Particle Size

The effective particle size for the nickel-kieselguhr catalyst can next be calculated from the relation:

$$D_P' = \frac{6V_P}{A_P} = \frac{6(1 - F_e)}{A_V} = \frac{6}{A_m \rho_P} \quad (7)$$

where

$V_P$  = average volume per particle

$A_P$  = average gross exterior area per particle

$F_e$  = fraction external void volume

$A_V$  = surface area of particles per unit volume of bed

$A_m$  = surface area per unit mass of particles

$\rho_P$  = density of particles, mass per volume.

Using the form:

$$D_P' = \frac{6V_P}{A_P} = \frac{6(0.026)}{(0.482)} = 0.324 \text{ centimeters.}$$



### 2.3.2.4. Effectiveness Factor

It is evident from the discussion of internal and external void fractions that in a fluid reaction catalyzed by a porous solid the concentration of the fluid reactant at the interface will be lower at the interior surfaces than at the gross external surface of the particle and that the rate of reaction per unit interfacial area will be lower at the interior surface. This is also recognized from the calculations on total available area of the catalyst where the gross exterior area comprises only 4.5% of the total area. The ratio of the actual rate of reaction per unit mass of solid to the rate which would exist if the concentration at all interior interfaces were the same as those at the gross exterior surface has been termed the effectiveness factor of the catalyst. The general equation for the rate of a reaction catalyzed by a porous solid is as follows:

$$\gamma A = C \Delta_{a_i} = E_A J \Delta_{a_i} \quad (8)$$

where

- $\gamma \Delta$  = reaction rate per unit mass
- $C$  = observed overall rate factor of the reaction
- $\Delta_{a_i}$  = driving force of the reaction in terms of activities at the external surface of the particle
- $E_A$  = effectiveness factor
- $J$  = the rate factor of the catalytic reaction which when multiplied by the driving force  $\Delta_{a_i}$  gives the rate of reaction per unit mass of catalyst if the driving force is uniform throughout.

An effectiveness factor of 1.0 indicates that the reaction rate at all interior surfaces is the same as that at the exterior surfaces. This is particularly true when (1) the particle size is small, (2) the pores are large and well interconnected, (3) the rate factor of the reaction is relatively low, (4) the diffusion coefficients of reactants and products are high. It has been proven for reactions in which the rate is proportional to the first power of the concentration at the interface. The effectiveness factor is a function of a modulus which is defined as follows:

$$M = \frac{D'p}{2} \sqrt{\frac{K}{cD_v}} \quad (9)$$

where

- M = Thiele's Modulus
- D'p = effective particle diameter
- c = average radius of pores in the particle
- D<sub>v</sub> = diffusion coefficient
- K = reaction velocity constant.

The modulus may also be expressed in the form:

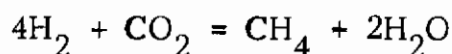
$$M = \frac{D'p a' e^{\frac{b'}{T}}}{F_i^{\frac{1}{4}}} \quad (10)$$

where a' and b' are empirical constants, characteristic of the reaction process and F<sub>i</sub> is the internal void fraction.

By calculating the modulus for a number of temperature values it is possible to determine the effectiveness factor for the catalyst from standard reference graphs depicting effectiveness factor vs. Thiele's Modulus. However, it is impossible at this early point in the experimental program to calculate the modulus, M, without knowing the values for a' and b' which are dependent on the type of catalytic process rather than the catalyst itself. a' and b' can be determined by simultaneous equations based on data collected for two (2) different catalysts used in the same reactor for the methanation process. Since this report concerns the evaluation of only one catalyst, N-0104 nickel-kieselguhr, it would be necessary to conduct a similar evaluation of another catalyst in order to set up the necessary simultaneous equations. Other catalysts will be investigated in follow-on phases to this work, and the resulting data will be shown in the next report for the calculation of the modulus, M, and the corresponding effectiveness factors.

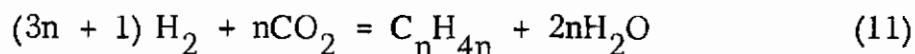
## 2.4. CO<sub>2</sub> Reduction Reactions and Equilibrium

All carbon dioxide reduction reactions and specifically the Sabatier reaction, behave as any other chemical reaction in that when hydrogen and carbon dioxide react with each other to yield water and methane, the reaction will proceed until each of the initial reactants has decreased to a certain concentration and each of the products formed has increased from zero to a certain concentration. This phenomenon occurs for all chemical reactions if a sufficient length of time for a specific batch of reactants is allowed; however, the length of time varies greatly from one reaction to another. (This time is usually referred to as "space velocity"\* when a continuous process is involved.) It also holds true for a continuous-flow process in which the space velocity is relatively low. Concerning the Sabatier reaction which is stoichiometrically represented as follows:

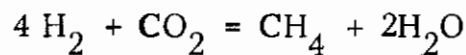


The concentrations of the reactants and products at this point are referred to as equilibrium concentrations, and gases reacting to form other gases may be measured as percentages by volume. These volume percentages are mathematically related to each other in a definite manner which is dependent upon the chemical equation written for the reaction, and upon a constant, K, which is determined from the thermodynamic properties of the initial components and final products.

For example, the general form equation which can be written for any CO<sub>2</sub> reduction reaction is as follows:



Where N = 1 for the Sabatier reaction, or



The equilibrium equation relating gas volume percentages, represented by the term "X", with  $\pi$  representing reaction total pressure, is:

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\* Defined as the volume of feed measured at standard conditions per unit time per unit volume of reactor.

$$K = \frac{(x_{H_2O})^2 (x_{CH_4})}{(x_{CO_2}) (x_{H_2})^4} \pi^{(2+1)-(1+4)}$$

$$K = \frac{(x_{H_2O})^2 (x_{CH_4})}{(x_{CO_2}) (x_{H_2})^4 \pi^3} \quad (12)$$

The equilibrium constant, K, is related to the Gibb's free energy change in the standard state,  $\Delta G^\circ$ , according to the following formula:

$$\frac{-\Delta G^\circ}{T} = R \ln K \quad (13)$$

Where T is the reaction temperature, and R is the universal gas constant.

The quantity  $\frac{\Delta G^\circ}{T}$  may be evaluated from the following:

$$\frac{G^\circ}{T_T} = \left( \sum \frac{G^\circ_T - H^\circ_O + \frac{H^\circ_{fo}}{T}}{T} \right)_{\text{Prod.}} - \left( \sum \frac{G^\circ_T - \Delta H^\circ_O + \frac{\Delta H^\circ_{fo}}{T}}{T} \right)_{\text{React.}}$$

Where,

$G^\circ_T$  = standard Gibbs' free energy at temperature T.

$H^\circ$  = enthalpy of the compound or element at 0°K.

$\Delta H^\circ_{fo}$  = standard heat of formation at 0°K.

	$\frac{G^\circ_T - H^\circ_O/T}{(\text{cal}) / (\text{g-mole}) (^\circ\text{K})}$	$\frac{\Delta H^\circ_{fo}}{(\text{cal}) / (\text{g-mole})}$
CO <sub>2</sub>	-51.060	-94,052
H <sub>2</sub>	-31.204	-0.0
H <sub>2</sub> O	-45.106	-57,798
CH <sub>4</sub>	-44.500	-17,889

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For example, using the Gibbs' free energy relationship to calculate the equilibrium constant, K, for five arbitrary temperatures of 500°F, 550°F, 575°F, 600°F, and 625°F, yields the following values:

$$K = 2.09 \times 10^7 \text{ for } 500^\circ\text{F}$$

$$K = 2.4 \times 10^6 \text{ for } 550^\circ\text{F}$$

$$K = 9.8 \times 10^5 \text{ for } 575^\circ\text{F}$$

$$K = 4.9 \times 10^5 \text{ for } 600^\circ\text{F}$$

$$K = 2.2 \times 10^5 \text{ for } 625^\circ\text{F}.$$

These calculated values for K illustrate that as the temperature of the reaction decreases the product yield increases. Theoretically, the yield would be relatively higher than at still lower temperatures for a catalyzed reaction. An additional factor is that as the temperature decreases the reaction tends to be more irreversible. In conclusion, the important point illustrated here is that a low temperature catalyzed reaction is not only desired from the standpoint of lesser power required to preheat the catalytic reactor but also that the product yield is increased as the reaction temperature is lowered.

## 3. Experimental Program

### 3.1. General Plan

The experimental program was directed towards determining the optimum catalyst(s) for catalyzing the reduction of  $\text{CO}_2$  with hydrogen to maximum yields of water and methane at minimum temperature; and by accomplishing this, to provide a set of technical criteria and procedures for evaluating the effectiveness of all such catalysts considered for this reaction. A standard and straight forward technique for accomplishing this was adopted. A catalytic reactor, somewhat similar to those used in other  $\text{CO}_2$  reduction work, was designed and fabricated. A unique feature incorporated in this reactor was the readily removable cap which permits quick exchange of catalysts for examination which lends greater flexibility to the program. A common  $\text{CO}_2$  methanation catalyst, nickel-kieselguhr manufactured by the Harshaw Chemical Company as N-0104 was selected as the catalyst for the first phase of investigation. The procedure then was to subject this catalyst to a set number of variables for the conditions of  $\text{CO}_2$  reduction and to determine the yield of water for each condition of variables.

The fundamental theory of catalysis and, particularly, for this reaction discussed in the previous section of this report entitled "Analytical Program" served as the criteria for setting process variables such as catalyst bed temperature and  $\text{H}_2/\text{CO}_2$  flowrate ratio during the experimental program. The theory was helpful in estimating the actual effect on the  $\text{CO}_2$  reduction rate due to the preheated catalyst bed temperature.

As the number of experimental runs were increased, the process variables were continually and experimentally altered on the basis of their individual effects on the  $\text{CO}_2$  conversion rate, rather than on the basis of theoretical prediction. This is necessary because although definite and reliable mathematical calculations can be made of equilibrium constants, theoretical reaction rates cannot be predicted according to the present development of rate theory without some error factor.

### 3.2. Apparatus

The initial phase of the experimental program was intended as familiarization with the use of system apparatus and operating procedures as well as to correct the design deficiencies of the catalytic reactor by alteration.

The catalytic reduction system was arranged as shown in Figure 7. The major components of this system were the (1) H<sub>2</sub> and CO<sub>2</sub> gas sources comprised of two cylindrical tanks complete with gauges, regulators, and valves; (2) two dessicator columns containing CaSO<sub>4</sub>; (3) two rotameters for precise metering of the H<sub>2</sub> and CO<sub>2</sub> gas flow rates; (4) the reactor containing the nickel-kieselguhr catalyst; (5) a Weston potentiometer for thermocouple temperature recording, and (6) the condenser coil and graduated cylinder for water collection and measurement.

The catalytic reactor, shown diagrammatically in Figure 6, includes an outer shell acting as a dead air space or containing glass wool insulation, the center cylinder for the entering H<sub>2</sub> and CO<sub>2</sub> gases complete with gas flow reverser, and the peripheral annule to the center cylinder which acts as the catalyst bed. The center cylinder also serves as a counter flow heat exchanger by using the exotherm of 41 K cal./mole CO<sub>2</sub> converted to preheat the incoming H<sub>2</sub> and CO<sub>2</sub> gases. All heat in excess of that required to preheat the incoming gases was removed by air cooling the outer shell of the reactor after first removing the insulation. The incoming gases enter the center cylinder at the bottom of the reactor after premixing in the main inlet line and then rise to the top of the center cylinder before leaving through a number of exit ports at the top. The flow direction is then reversed and the gases pass down over the catalyst in the peripheral section. The catalyst consisted of 300 grams of nickel-kieselguhr, cylindrical pellets. The catalyst bed was heated through the outer cylindrical wall by a 12.7 cm high × 10.2 cm diameter ceramic enveloped nichrome wire electrical resistance heater. The nichrome wire coils were separated by approximately 1/16 inch from the wall. The nichrome wire resistance heater required 290 watts at 57.5 volts, 5.05 amps, to heat the catalyst bed in twenty minutes to a nominal temperature of 575°F, which is the temperature shown later in this report to be ideal for this type of catalyst. The H<sub>2</sub> and CO<sub>2</sub> gases diffuse and react in the catalyst bed with the water vapor and methane products leaving through an exit port at the bottom of the reactor.

The water condenser consisted of a cylindrically wound copper tubing coil (8 inches long × 6 inches diameter) and a graduated cylinder of 100 milliliter capacity. Water vapor leaving the reactor was condensed in the coil and collected in the graduated cylinder, thus providing direct measurement of yield. The products were not recycled through the reactor and therefore the apparatus did not include a recycling pump.

Two (2) Brooks-Perkins gas flow rotameters were used for metering of the H<sub>2</sub> and CO<sub>2</sub> gases to the reactor inlet manifold. The rotameter for hydrogen flow measurement (Brooks Model 1110) has a stainless steel ball float for

# Contrails

metering hydrogen in a range of 200-2800 cc/min; specific gravity at 0.069, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is  $\pm 2\%$  of maximum flow. The rotameter for CO<sub>2</sub> flow measurement (Brooks Model 1110) has a sapphire float for metering CO<sub>2</sub> in a range of 50-500 cc/min, specific gravity at 1.529, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is also  $\pm 2\%$  of maximum flow.

The feed gases of H<sub>2</sub> and CO<sub>2</sub> were stored in two (2) separate cylindrical tanks and metered individually through high pressure regulators to a lower pressure of 4 psig. The pressure level of 4 psig was maintained with precise accuracy since both rotameters were calibrated for this pressure and the flow rate is a direct indication of the CO<sub>2</sub> reduction rate. The high pressure regulators were also equipped with feed throttle valves for manual adjustment of the feed flow rates to meet the H<sub>2</sub>/CO<sub>2</sub> flow rate ratio requirement set for any particular experiment. Two (2) dessicator drying columns containing CaSO<sub>4</sub> were installed in parallel in both outlet lines from the high pressure regulators to remove any residual water vapor in the gas feed lines.

Foxboro potentiometer, Model Nr. 8106, Serial Nr. D74155, was equipped with four (4) iron-constantan thermocouples (installed at equal intervals along the longitudinal wall of the catalyst bed) for direct continuous readings of temperature in the catalyst bed.

The potentiometer has two (2) scales; one scale for low temperature readings in the range of 0 - 1000°F, and the second for high temperature readings in the range of 1000°F - 2000°F. The tolerance of accuracy on the low and high ranges is 0.5% and 0.1%, respectively. Since the catalyst bed temperatures encountered in this experimental program were on the order of 400°F - 700°F, a practical tolerance of 0.3% can be assumed. The iron - constantan thermocouple was used instead of copper-constantan because of its high reliability for readings in the medium temperature range.

It is worth noting that after thermocouples have been used for some time at high temperatures, it is difficult if not impossible to determine how much the calibrations are in error except by removing them from an installation and testing in a laboratory furnace. The thermocouples are usually heterogeneous after such use and in such a condition that the EMF developed by the couples depends upon the temperature distribution along the wires.



## 3.3. Experiments

### Results - Preliminary Tests

Approximately twenty-four preliminary test runs were conducted initially on the reactor to check out the operation of all components and the workability of the total system, to locate and eliminate leaks in the apparatus, and to gain familiarization with the sequence of operations for all steps of each experimental run. As a result of these preliminary tests it was decided to use a total quantity of catalyst pellets weighing 300 grams. An excess of catalyst insures the reaction of most amounts of  $H_2$  and  $CO_2$  present in the catalyst bed at any given instant considering the very low gas flow rates involved and the high porosity of the catalyst, itself. In addition, experimental programs conducted prior to this one pointed out that an excess of catalyst in the bed would serve to remove "poisons" from the incoming gas stream without impairing the efficiency of the bed. Since the cross section of the bed nearest the gas inlet port is cooler than the remainder of the bed, this would assist in "trapping" the poisons. It was also decided to place the catalyst pellets loosely in the reactor as opposed to "packaging" them in a cylindrical fine mesh metal "basket". While the "basket" arrangement did facilitate the removal of the catalyst pellets whenever desired, this advantage was out weighed by the fact that random packaging would insure a more even distribution of the reacting gases on the catalyst. This set of preliminary tests also confirmed that this catalyst for reducing the  $CO_2$  requires a purge with  $H_2$  gas at a temperature of  $500^\circ F$  before initiating the reduction of  $CO_2$ . The purging time depends on the degree of poisons present in the catalyst.

### Results - No. 1 to 3

Three test runs were then conducted as the next group of experiments to determine if carbon monoxide would be generated in the reactor if the  $H_2/CO_2$  flowrate ratio was kept at less than 4/1, stoichiometric reactant conditions.

Each of the three runs were made at different temperatures of  $590^\circ F$ ,  $530^\circ F$ , and  $560^\circ F$ . The  $H_2$  gas flowrate was maintained at 1675 cc/min, 1600 cc/min and 1600 cc/min, respectively, for those temperatures. The  $CO_2$  gas flowrate was kept at 425 cc/min, for all three runs, as well as for all ensuing runs.

The gases were metered from storage at 4 psig and "dried" in the  $CaSO_4$  dessicator columns prior to entering the reactor.

# Contrails

During these first three runs, it was indicated that the thermocouple (one of four) nearest the inlet ports to the catalyst bed recorded a temperature 55°F lower than the next three in sequence which recorded a uniform and equal temperature. This was expected since a "full" reaction would not occur at this initial point in the catalyst bed. It was decided at this time to rely on the temperature indicated by the other three thermocouples for a "true" catalyst bed temperature reading.

A partial reduction of CO<sub>2</sub> to CO was evident during these three runs. The experimenters developed headaches soon after initiation of each run and the process was immediately shut down. There was also no water condensate in evidence.

A slight fluctuation of approximately 10% of each of the two rotameter ball floats was indicated periodically during these runs which was due to back pressure in the reactor from CO<sub>2</sub> to CO conversion. This was expected and it was considered negligible for follow-on experiments provided it would occur very infrequently and the floats would readily stabilize themselves.

The catalytic reactor was disassembled and the catalyst pellets were inspected. There was no evidence of carbon deposition and/or structure deformation.

## Results - No. 4 to 7

This set of runs was made to determine if a stoichiometric reactant quantity of H<sub>2</sub>/CO<sub>2</sub> equal to 4/1 or slightly higher would serve to activate the reduction of CO<sub>2</sub>. It was also decided that if reduction of CO<sub>2</sub> to H<sub>2</sub>O occurred, that the temperature of the catalyst bed would be varied over a range of 565°F to 625°F. This range, according to previous literature surveys, indicated maximum yield condition for the Sabatier reaction.

The CO<sub>2</sub> gas flowrate was maintained at 425 cc/min for all four runs; the H<sub>2</sub> flowrate was set at 1700 cc/min, 1750 cc/min, 1800 cc/min and 1800 cc/min for runs 4, 5, 6, and 7, respectively. The temperature of the catalyst bed was set at 565°F, 575°F, 580°F, and 625°F for the four runs in that order. The gases were metered at 4 psig and pre-dried. The CaSO<sub>4</sub> dessicator columns had been first purged by heating to 300°F for two hours in an oven. This practice was followed after completion of each set of runs.

During each of these four runs there was a sharp increase in temperature indicated soon after initiation of each run. Subsequently, a water condensate formed in the collection graduate. Upon noting the temperature rise which

indicated the reaction was in progress, the heating element was shut off and the reaction allowed to sustain itself. The reactor shell did not contain insulation and, in due course, the reactor cooled below the temperature set for that particular run. The rate of water condensation immediately decreased and the heating element was turned on again. Upon reaching the temperature previously determined for each run the reaction rate increased as did the rate of water condensation. The heating element was, subsequently, observed continuously to insure that the catalyst bed temperature remained constant.

In each of these four runs a good water yield was obtained and no CO was detected. Run 5, conducted at 575°F, provided a water condensate of 65 mil. or 98% of the maximum theoretical yield. During run 7, a small H<sub>2</sub> fire occurred at the cap to the reactor due to leakage. This terminated the run before the pre-set run time of two hours has elapsed. The leak was corrected by an exchange of cap gaskets.

The reactor was disassembled at the completion of this set of runs and the catalyst pellets were examined for possible carbon deposition and/or structure deformation. No unusual effects were noticeable although it became necessary at this point to increase the time of pre-reaction hydrogen purging of the catalyst bed for each succeeding set of experimental runs. This was apparently due to the fact that the surface of the catalyst pellets was being increasingly "poisoned" by sulfur (from the laboratory air) with each successive run.

## Results - No. 8 to 13

This set of runs was intended to discern if the rate of CO<sub>2</sub> conversion decreased when the catalyst bed temperature increased to the range of 650°F to 750°F. Such an occurrence would confirm the work of other experimenters.

It was also planned to insulate the reactor shell during this set of runs to determine if the reaction would be self-sustaining due to the exotherm.

The H<sub>2</sub> and CO<sub>2</sub> gas flowrates were set at 1850 cc/min., and 425 cc/min., respectively, for all six runs, and metered from storage at 4 psig. The gases were pre-dried before entering the reactor. The catalyst bed temperature was set at 650°F, 675°F, 750°F, 725°F, 700°F, and 650°F, respectively, for runs 8, 9, 10, 11, 12, and 13. The CaSO<sub>4</sub> dessicator columns had previously been purged as well as the catalyst bed itself. The H<sub>2</sub>/CO<sub>2</sub> flow-rate ratio was maintained at 4.36, slightly in excess of stoichiometric as this value had previously effected the maximum rate of CO<sub>2</sub> conversion.

# Contrails

The water yield successively decreased throughout this set of runs as the catalyst bed temperature was increased from 650°F to 750°F. At 750°F the water yield was less than half of that previously attained at the temperature of 575°F and the total water condensate collected was only 40% of the theoretical maximum. During run 12 a small hydrogen fire occurred at the cap of the reactor due to leakage. This occurred near the end of the run and did not affect the validity of data obtained. The leak was corrected by an exchange of gaskets after disassembling the reactor.

During each run the heating element was shut off when it became evident the reaction was in progress. Without exception the catalyst bed temperature remained constant within  $\pm$  three degrees and the reaction continued until termination of each run. Each of the three thermocouples used for the temperature recording showed the same temperature (See Results - No. 1 to 3) indicating that no "hot spots" were developing in the catalyst bed. The reactor was disassembled at the termination of this set of runs and the condition of the catalyst examined.

There appeared to be a small precipitate of carbon formed irregularly on the pellets. It was surmised that the increase in temperature to 750°F caused a slight side reaction of reducing  $\text{CO}_2$  to water and carbon. Accordingly, it was planned to conduct the remainder of the tests at temperatures not exceeding 600°F.

## Results - No. 14 to 18

It was planned for these five runs to confirm the data obtained on water yield in the temperature range from 600°F down to 525°F.

The catalyst bed was first purged with  $\text{H}_2$  for 1 hour at a catalyst bed temperature of 500°F. The  $\text{CaSO}_4$  dessicator columns had also been "dried" at 300°F for two hours. The catalyst bed temperatures were set at 600°F, 575°F, 550°F, 525°F, and 575°F, respectively, for runs 14, 15, 16, 17, and 18.

The water yield obtained at 575°F for runs 15 and 18 again proved to confirm existing data at this temperature or 98% of the theoretical maximum. Water condensate for both runs amounted to 65 milliliters. The water yield at 600°F and 550°F, runs 14 and 16, was slightly less, proving to be 60 milliliters (90% theoretical) and 50 milliliters (75% theoretical). The yield then decreased sharply at 525°F to 24 milliliters or 36% theoretical. It was then planned to conduct the remainder of the experimental runs for this phase of the program at 575°F, varying only the  $\text{H}_2/\text{CO}_2$  flowrate ratio.

The catalytic reactor was disassembled at completion of the runs and the catalyst examined. No evidence of carbon deposition or structure deformation was found.

## Results - No. 19 to 25

This remaining group of experimental runs was intended to determine the effect of CO<sub>2</sub> conversion rate at 575°F due to wide variations of the H<sub>2</sub>/CO<sub>2</sub> flowrate ratio.

The catalyst bed and CaSO<sub>4</sub> columns were first purged as previously described. The catalyst bed temperature set at 575°F and the H<sub>2</sub> and CO<sub>2</sub> gases metered at 4 psig from storage. Flowrate ratios for H<sub>2</sub>/CO<sub>2</sub> were set at 4.36, 4.12, 3.82, 3.77, 4.36, 4.48, 4.59, 4.71, respectively for runs 18, 19, 20, 21, 22, 23, 24 and 25. The CO<sub>2</sub> flowrate was held at 425 cc/min. and only the H<sub>2</sub> flowrate was varied.

A maximum water yield of 65 milliliters (98% theoretical) was obtained when the H<sub>2</sub>/CO<sub>2</sub> flowrate ratio equaled or exceeded a value of 4.36. This was the case for runs 22, 23, 24, and 25. Run 19 involved a ratio of 4.12 which effected a conversion rate of 95% theoretical and a water condensate of 63 milliliters was collected. During runs 20 and 21, the flowrate ratio was held at 3.82 and 3.77 and no water yield resulted. CO was again detected and served to confirm the data obtained during runs 1 to 3.

TABULATION OF EXPERIMENTS

Experiment	Reactor Temp (°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (hr-1)	Water Yield (cc)	Remarks
1	590	1675	425	3.96	492	None	1. CO generated. No water yield.
2	530	1600	425	3.77	475	None	2. CO generated. No conversion of CO <sub>2</sub> detected. No water yield.
3	560	1600	425	3.55	475	None	3. CO generated. No conversion of CO <sub>2</sub> detected.
4	565	1700	425	4.00	498	50	4. Good water yield. No CO detected.
5	575	1750	425	4.12	510	65	5. Water yield improved. CO <sub>2</sub> conversion seemed high.
6	580	1800	425	4.25	521	63	6. Good water yield. Small fire at reactor due to H <sub>2</sub> excess and leakage.
7	625	1800	425	4.25	521	58	7. Good water yield. Small fire at reactor due to H <sub>2</sub> excess and leakage
8	650	1850	425	4.36	533	52	8. Water yield decreased. Several fires occurred due to leakage. Gasket replaced in reactor cap. No leakage detected.

TABULATION OF EXPERIMENTS (Cont'd)

Experiment	Reactor Temp (° F)	H <sub>2</sub> Flowrate (cc/Min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (hr-1)	Water Yield (cc)	Remarks
9	675	1850	425	4.36	533	40	9. Water yield decreased still more. Decided to increase temperature at next run.
10	750	1850	425	4.36	533	27	10. Temperature was too high. Planned future work at lower temperature range. H <sub>2</sub> /CO <sub>2</sub> to be held constant.
11	725	1850	425	4.36	533	31	11. Water yield improved but still low. Planned to further reduce temperature.
12	700	1850	425	4.36	533	36	12. Water yield better but still low. Planned to further reduce temperature.
13	650	1850	425	4.36	533	53	13. Water yield improved. Planned to further reduce temperature.
14	600	1850	425	4.36	533	60	14. Water yield approaching previous high established at 570° F.

TABULATION OF EXPERIMENTS (Cont'd)

Experiment	Reactor Temp (°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (hr-1)	Water Yield (cc)	Remarks
15	575	1850	425	4.36	533	65	15. Water yield identical to that obtained on 5th experimental "run".
16	550	1850	425	4.36	533	50	16. Water yield appears slightly less. Further temperature reduction planned.
17	525	1850	425	4.36	533	24	17. Water yield considerably off. Plan to return to 575° F operating temperature.
18	575	1850	425	4.36	533	65	18. Water yield again at maximum. Planned to reduce H <sub>2</sub> /CO <sub>2</sub> ratio.
19	575	1750	425	4.12	510	63	19. Water yield appeared at maximum planned to reduce H <sub>2</sub> /CO <sub>2</sub> ratio.
20	575	1650	425	3.82	487	38	20. No water yield. CO detected. Planned to reduce H <sub>2</sub> /CO <sub>2</sub> still further.



TABULATION OF EXPERIMENTS (Cont'd)

Experiment	Reactor Temp (°F)	H <sub>2</sub> Flowrate (cc/min)	CO <sub>2</sub> Flowrate (cc/min)	H <sub>2</sub> /CO <sub>2</sub> Flowrate Ratio	Space Velocity (hr <sup>-1</sup> )	Water Yield (cc)	Remarks
21	575	1600	425	3.77	475	37	21. CO strongly detected. No water yield. Planned to increase H <sub>2</sub> /CO <sub>2</sub> ratio to 4.36.
22	575	1850	425	4.36	533	65	22. Maximum water yield. Planned to increase H <sub>2</sub> /CO <sub>2</sub> ratio still further.
23	575	1900	425	4.48	545	65	23. Same water yield as obtained with H <sub>2</sub> /CO <sub>2</sub> ratio of 4.36. Small fire occurred due to leakage.
24	575	1950	425	4.59	557	65	24. Same water yield as previous run. Small fire occurred due to leakage.
25	575	2000	425	4.71	569	65	25. Same water yield as previous run. Explosion occurred, no damage to reactor.

425 cc/min (CO<sub>2</sub>) corresponds to 2.20 lbs/day.

#### 4. Conclusions and Recommendations

##### 4.1. Conclusions

The following conclusions were reached based on the experimental investigation of a nickel-kieselguhr catalyst for promoting the Sabatier reaction:

(a) The nickel-kieselguhr (80:20) will promote a 98% conversion of  $\text{CO}_2$  to water and methane at a catalyst bed temperature of  $575 \pm 5^\circ\text{F}$  in a single pass reactor containing 300 grams of the catalyst.

(b) The conversion rate of 98% can be attained in a single pass reactor without the necessity of recycling provided an excess of catalyst is used and that the space velocity be on the order of  $500 \text{ hr}^{-1}$  to  $550 \text{ hr}^{-1}$ .

(c) The nickel-kieselguhr catalyst should be purged with  $\text{H}_2$  for a period of 1 hour with the bed at  $500^\circ\text{F}$  to remove residual poisons such as hydrogen sulfide, before initiating the reduction reaction.

(d) Efficient operation of the reactor for reducing 2.2 pounds of  $\text{CO}_2$  / day stipulates  $\text{H}_2$  and  $\text{CO}_2$  gas flowrates of 1850 cc/min. and 425 cc/min. for a ratio of 4.36 or greater.

(e) An electrical resistance heater of the coiled nichrome wire type can heat the catalyst bed to  $575^\circ\text{F}$  in 20 minutes, then be shut off, and the exotherm will sustain the reaction. A nominal amount of insulation must be used to retard the rate of convective heat transfer from the reactor.

(f) Raising the temperature of the catalyst bed above  $575^\circ\text{F}$  appears to decrease the rate of  $\text{CO}_2$  conversion and at temperatures above  $625^\circ\text{F}$  there is a slight side reaction to form carbon.

(g) The integrated counter-flow type heat exchanger serves very efficiently to pre-heat the incoming gases to reaction temperatures.

(h) Two ball type float rotameters calibrated at 4 psig and  $70^\circ\text{F}$  equipped with high pressure regulators and throttle valves are accurate within  $\pm 2\%$  for metering the  $\text{H}_2$  and  $\text{CO}_2$  feed gases to the reactor.

(i) Lowering the  $H_2/CO_2$  flowrate ratio below the value of 4/1 serves to generate carbon monoxide thereby preventing the reduction of carbon dioxide to methane and water. (This experimental result confirmed existing literature.)

(j) A cylindrical annular reactor, 5 inches (long) ~~x 3 inches~~ (o.d.) ~~x 1 inch~~ (i.d.) provides sufficient catalyst volume for converting 2.2 pounds  $CO_2$ /day.

## 4.2. Recommendations

The following recommendations are made concerning future investigations for evaluating catalysts for  $CO_2$  reduction by the Sabatier methanation reaction:

(a) Harshaw catalyst, N-0104, should be investigated for its effectiveness in catalytic reactors having larger length/diameter ratios.

(b) Base metal oxide and precious metal catalysts should be experimentally evaluated in comparison to nickel catalyst N-0104 in reactors of larger length/diameter ratios.

(c) Varying heat exchanger designs should be implemented in different reactors to determine the effect on pre-heating the hydrogen and carbon dioxide inlet gases.

(d) Chemical methods of heating the catalyst bed to reaction initiation temperature should be investigated instead of using any electrical resistance type heater.

(e) Based on completion of experimental evaluations of other catalysts, an index of catalyst effectiveness should be established for correlating activation energies with electrovalent adsorptivities.

(f) Hydrogen purging of the catalyst bed to remove residual poisons should be eliminated because of its undesirability as a step process in an actual space vehicle atmosphere regeneration process.

(g) It is imperative that a poison resistant catalyst be found to insure high reliability for eventual space vehicle application.

(h) Gas chromatographic techniques should be used for a more accurate quantitative analysis of the reactor exit gas composition.

## 5. References

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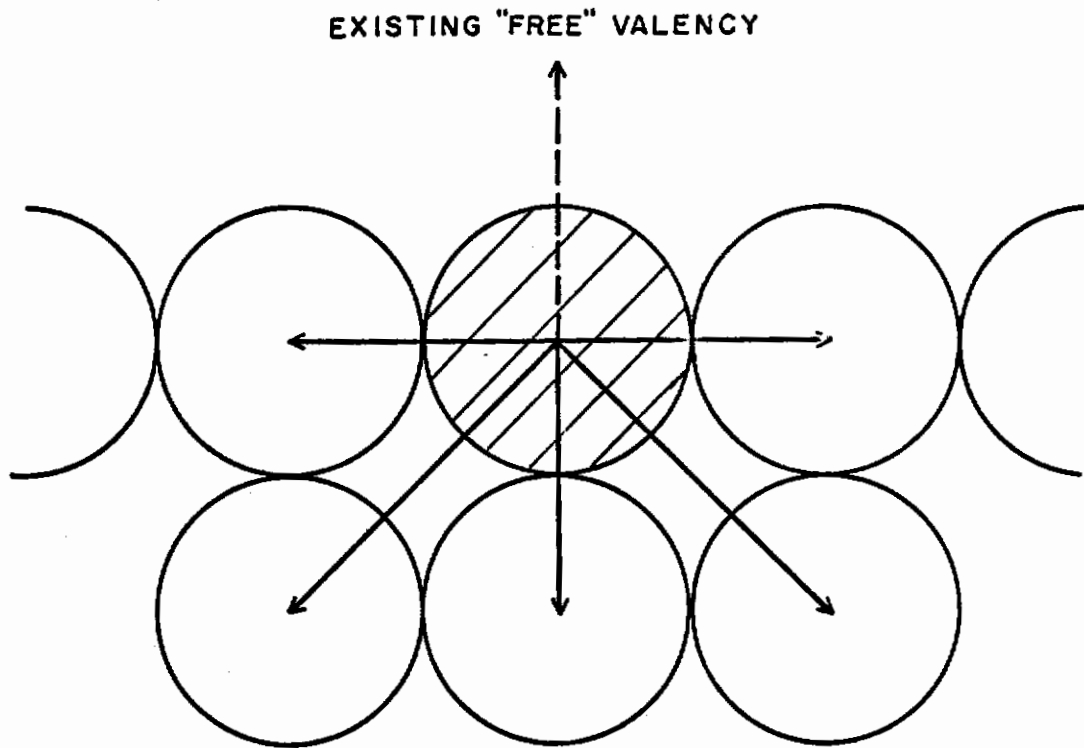


FIGURE 1. DIAGRAMMATIC REPRESENTATION OF THE SURFACE ENERGY OF A SOLID

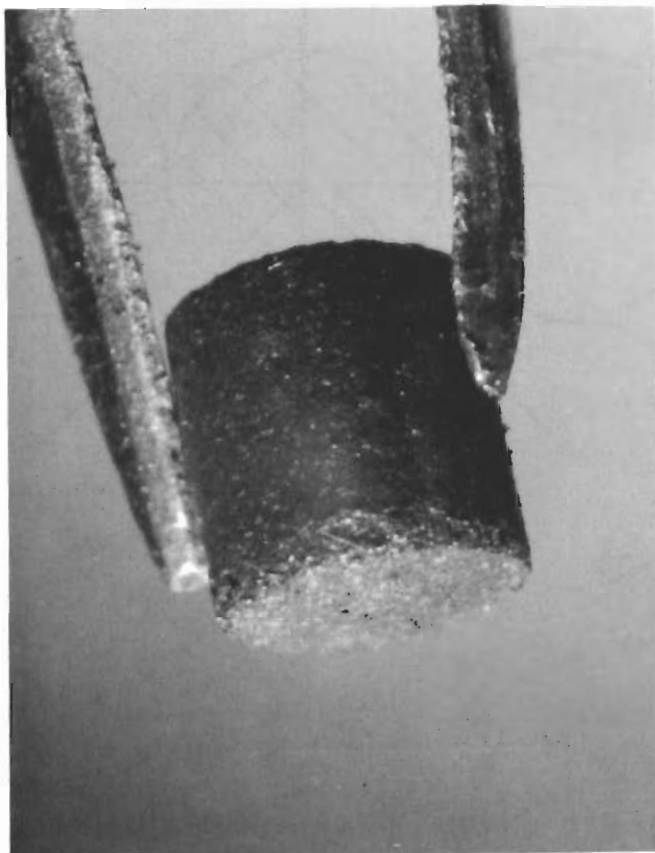


FIGURE 2. PHOTOGRAPH OF A SINGLE  
CATALYST PELLETT

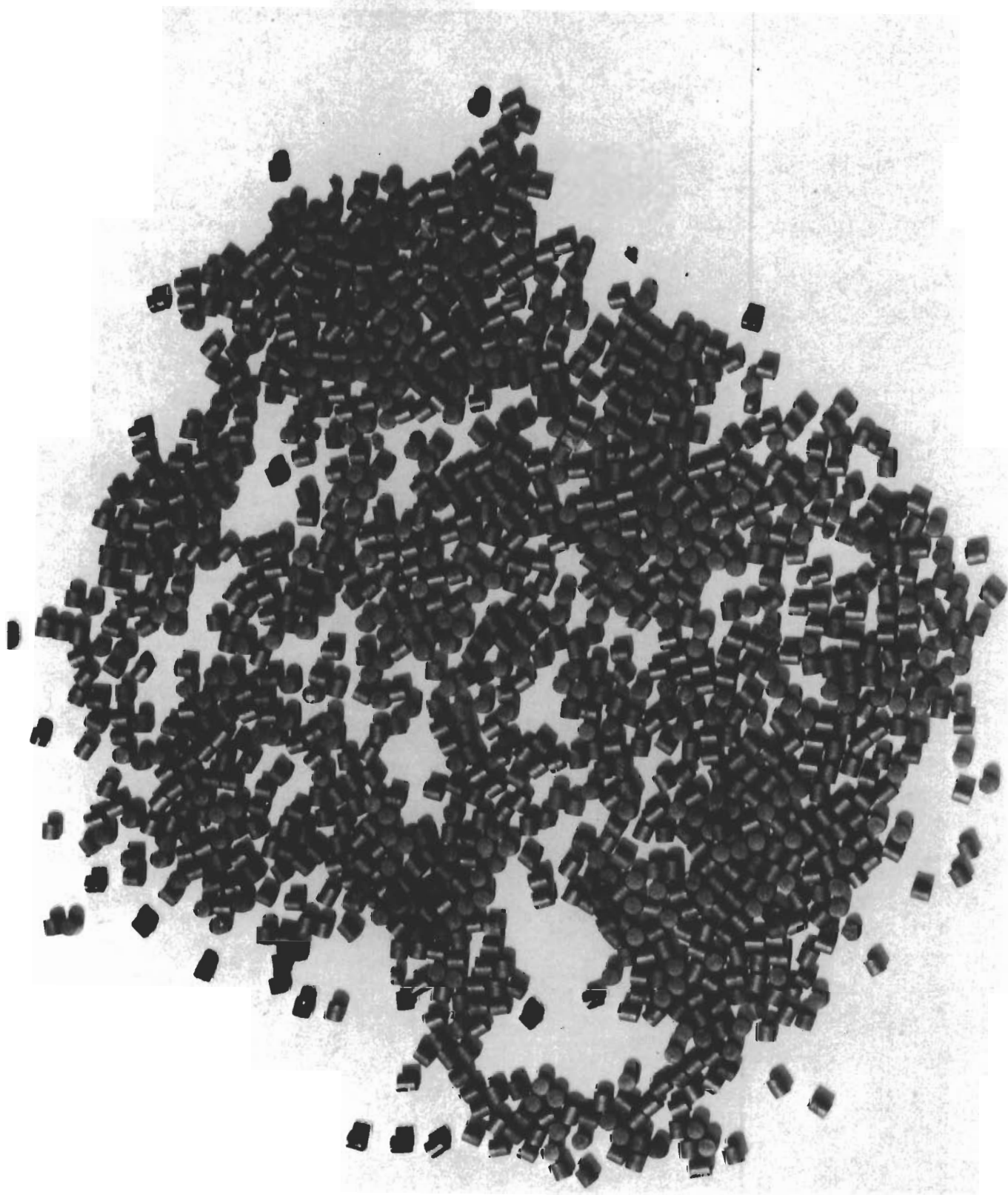


FIGURE 3. PHOTOGRAPH OF CATALYST PELLETS

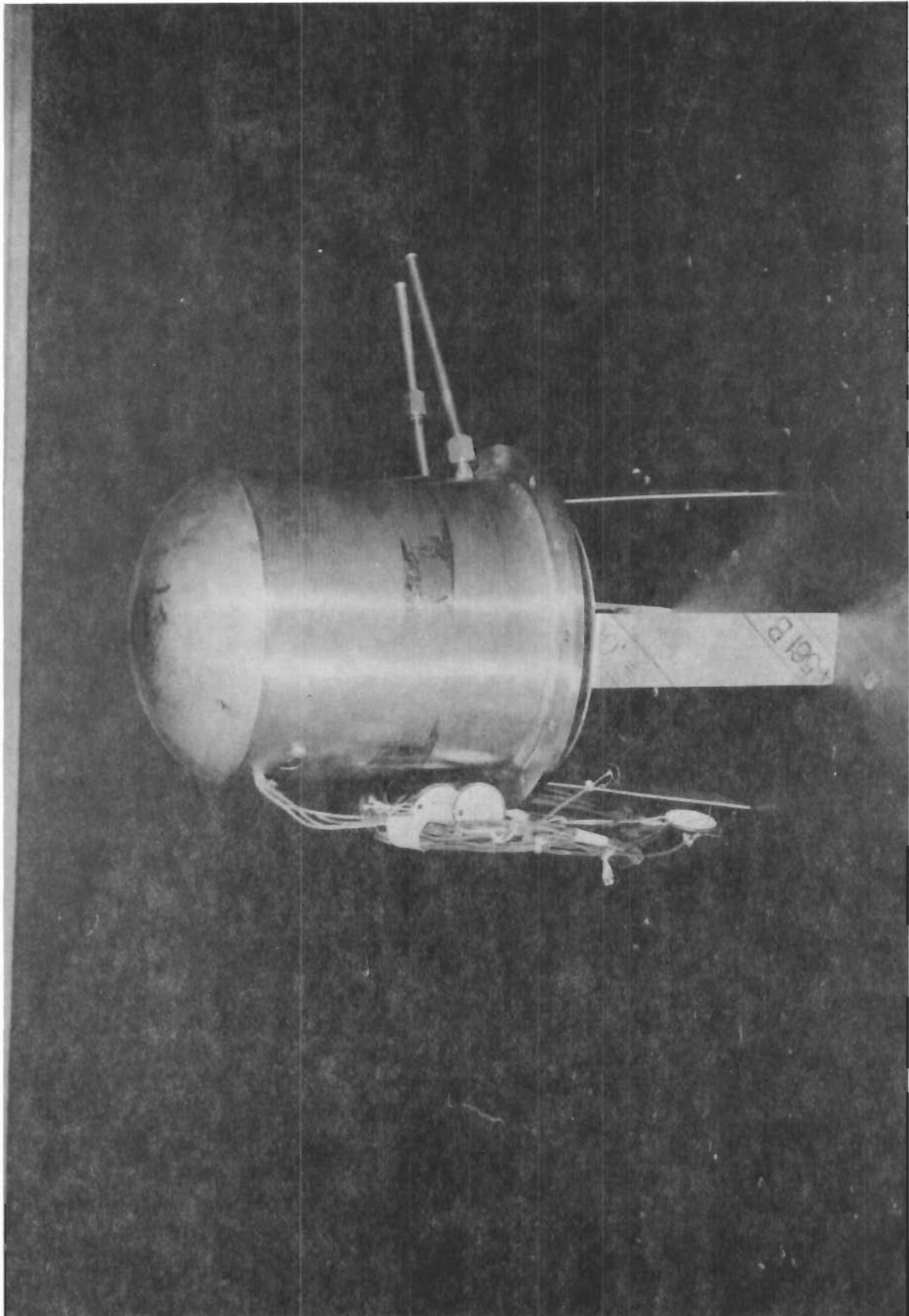


FIGURE 4. PHOTOGRAPH OF CATALYTIC REACTOR



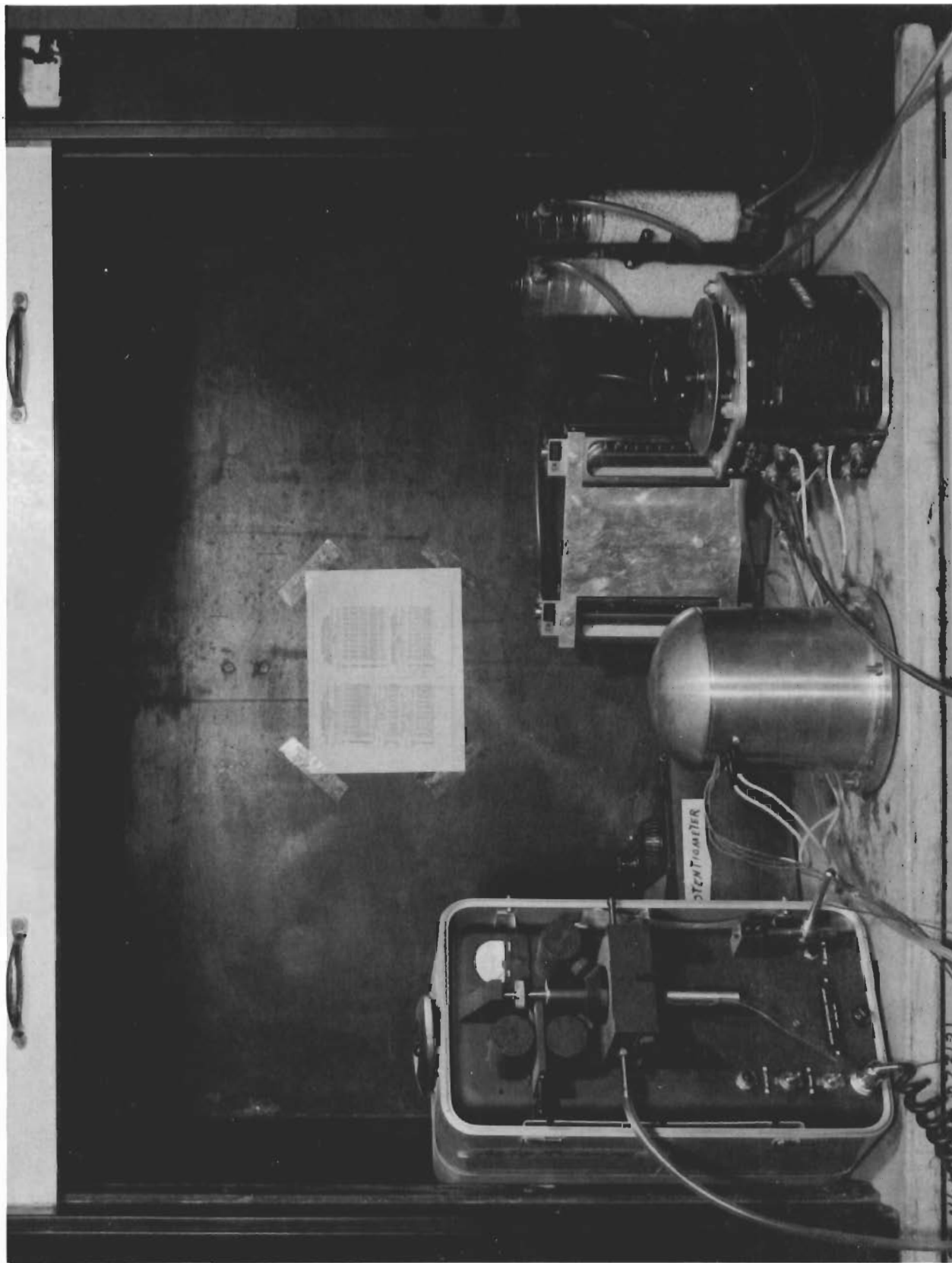


FIGURE 5. PHOTOGRAPH OF CO<sub>2</sub> REDUCTION SYSTEM

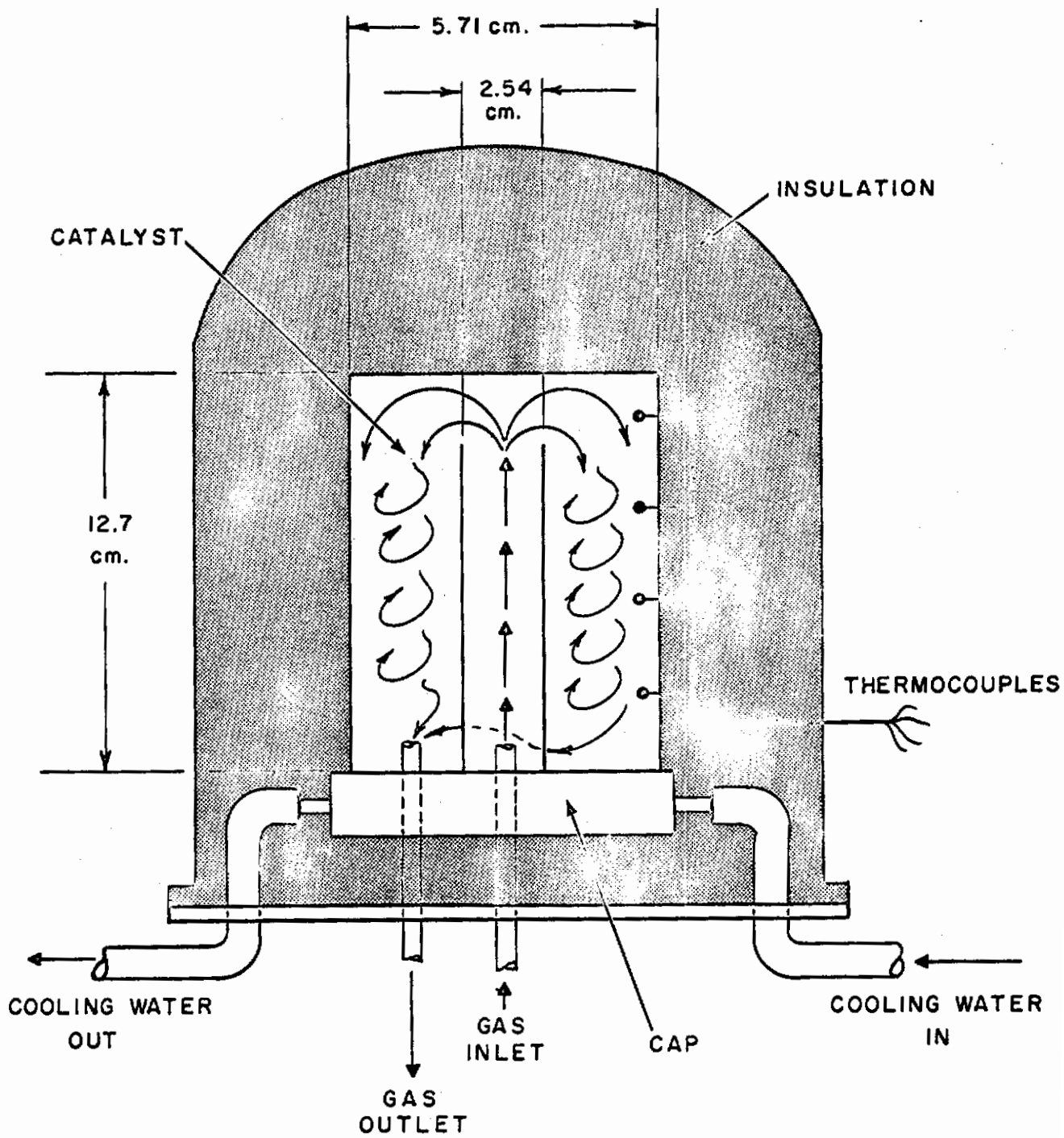


FIGURE 6. CATALYTIC REACTOR FLOW DIAGRAM

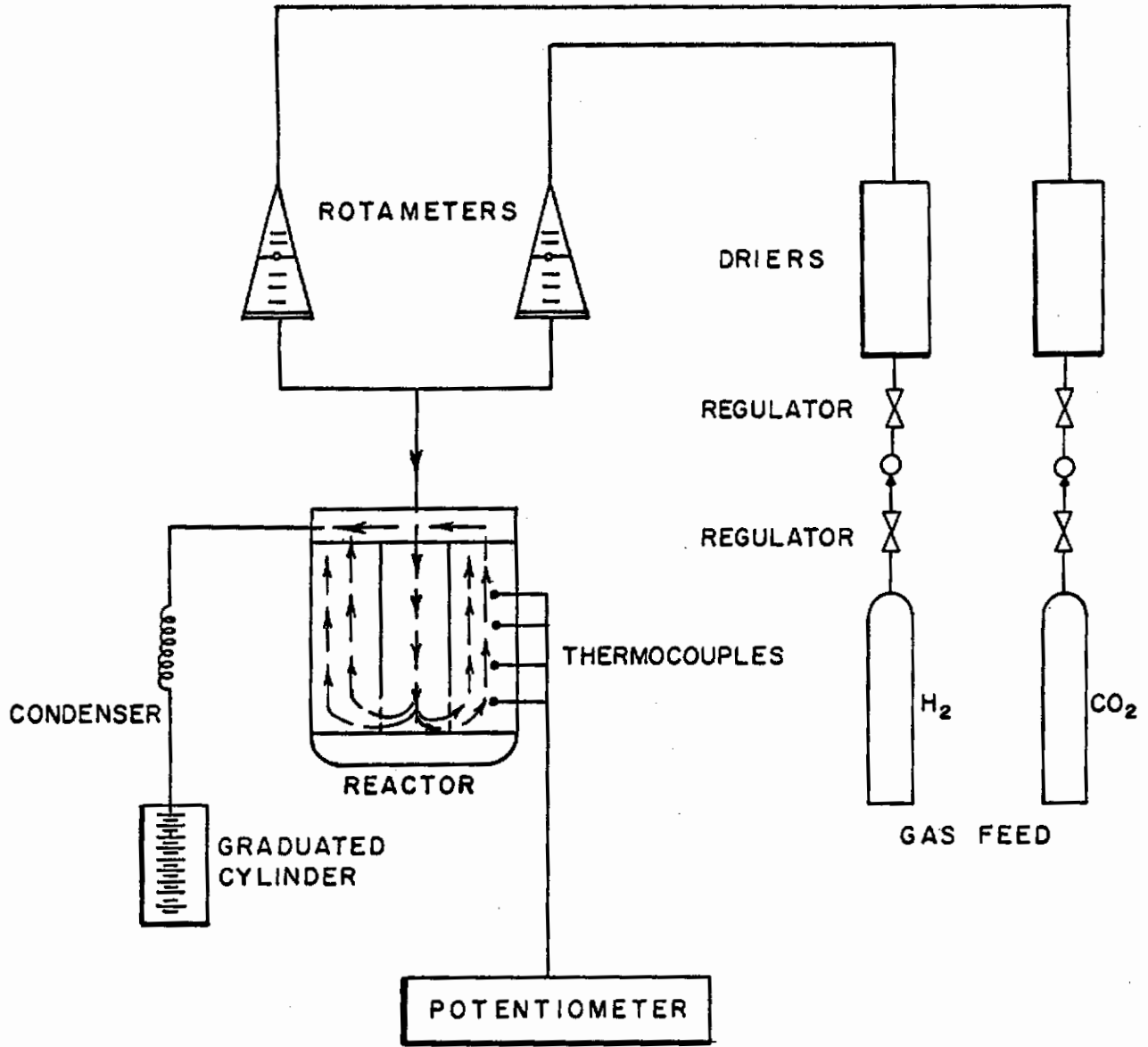


FIGURE 7. CO<sub>2</sub> REDUCTION SYSTEM FLOW DIAGRAM

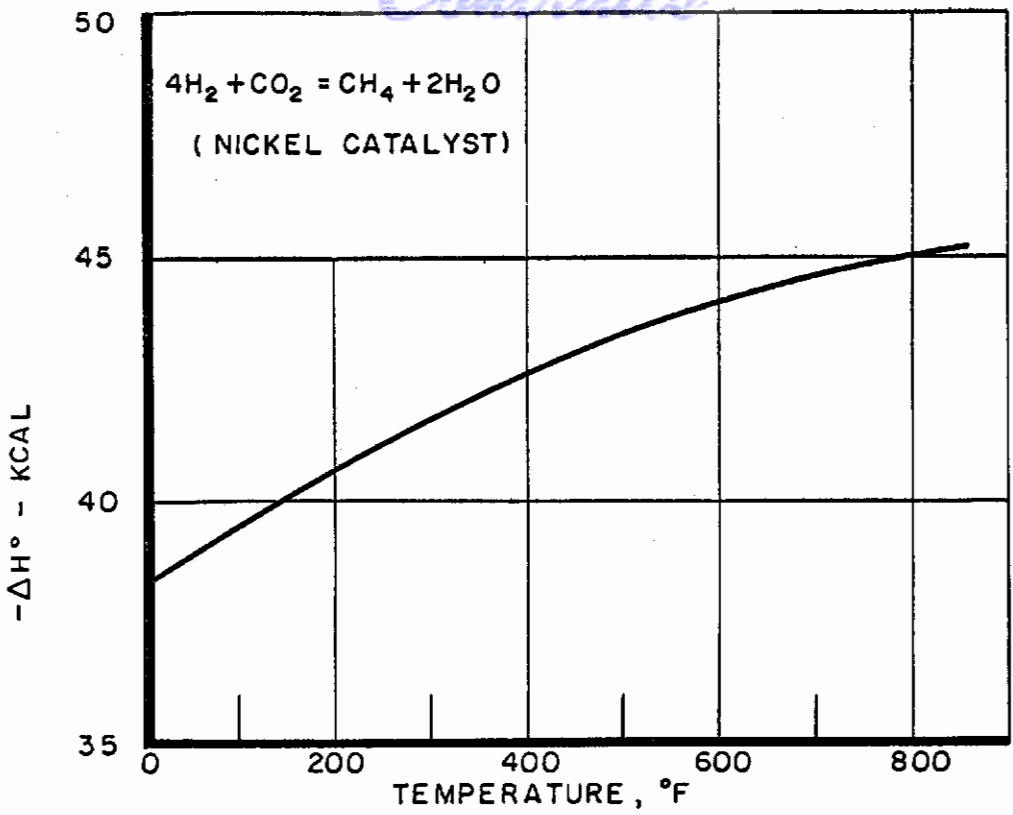


FIGURE 8. SABATIER REACTION-HEATS OF REACTIONS AS FUNCTIONS OF TEMPERATURE

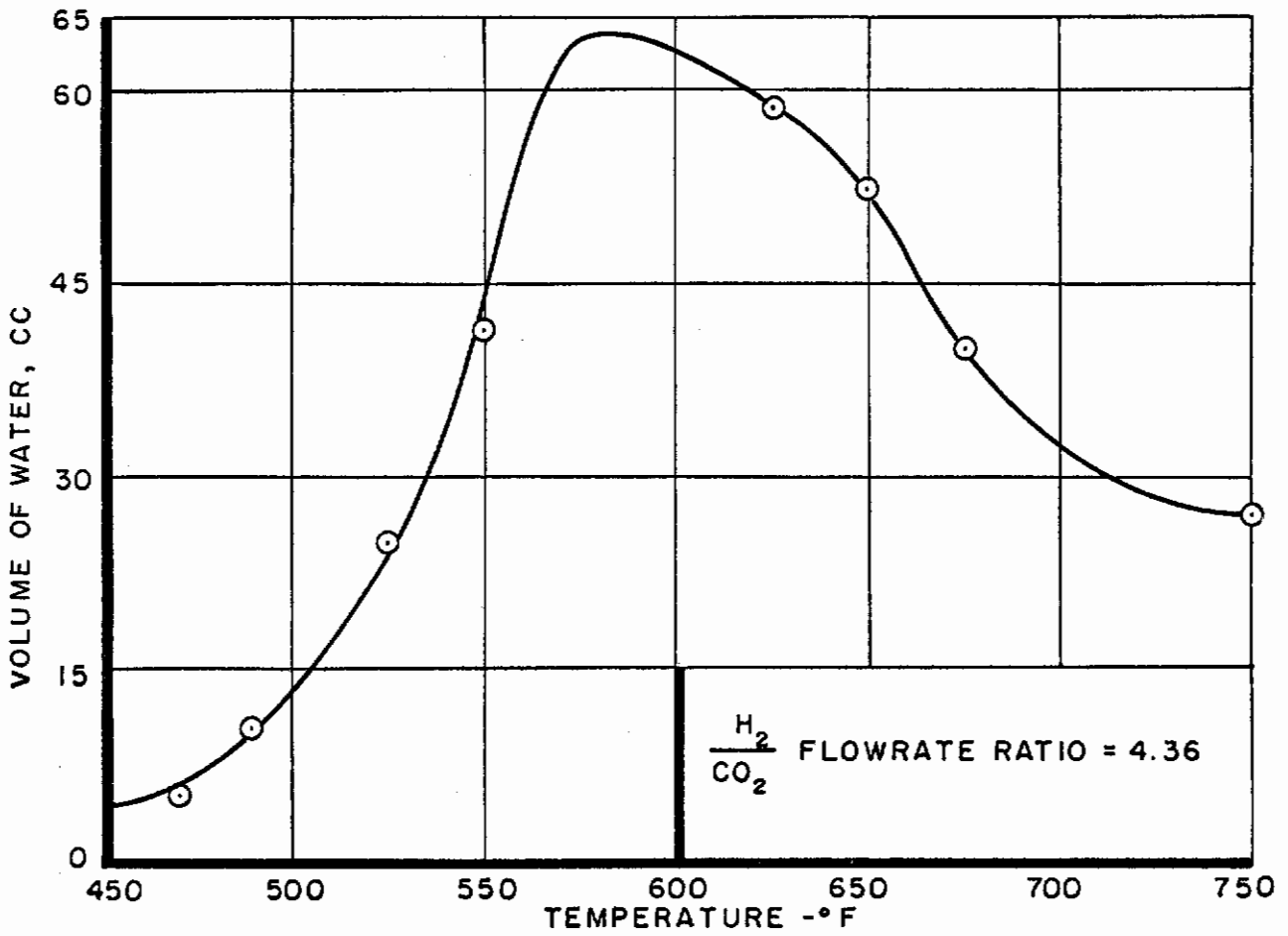


FIGURE 9. SABATIER REACTION-WATER YIELD VS. TEMPERATURE

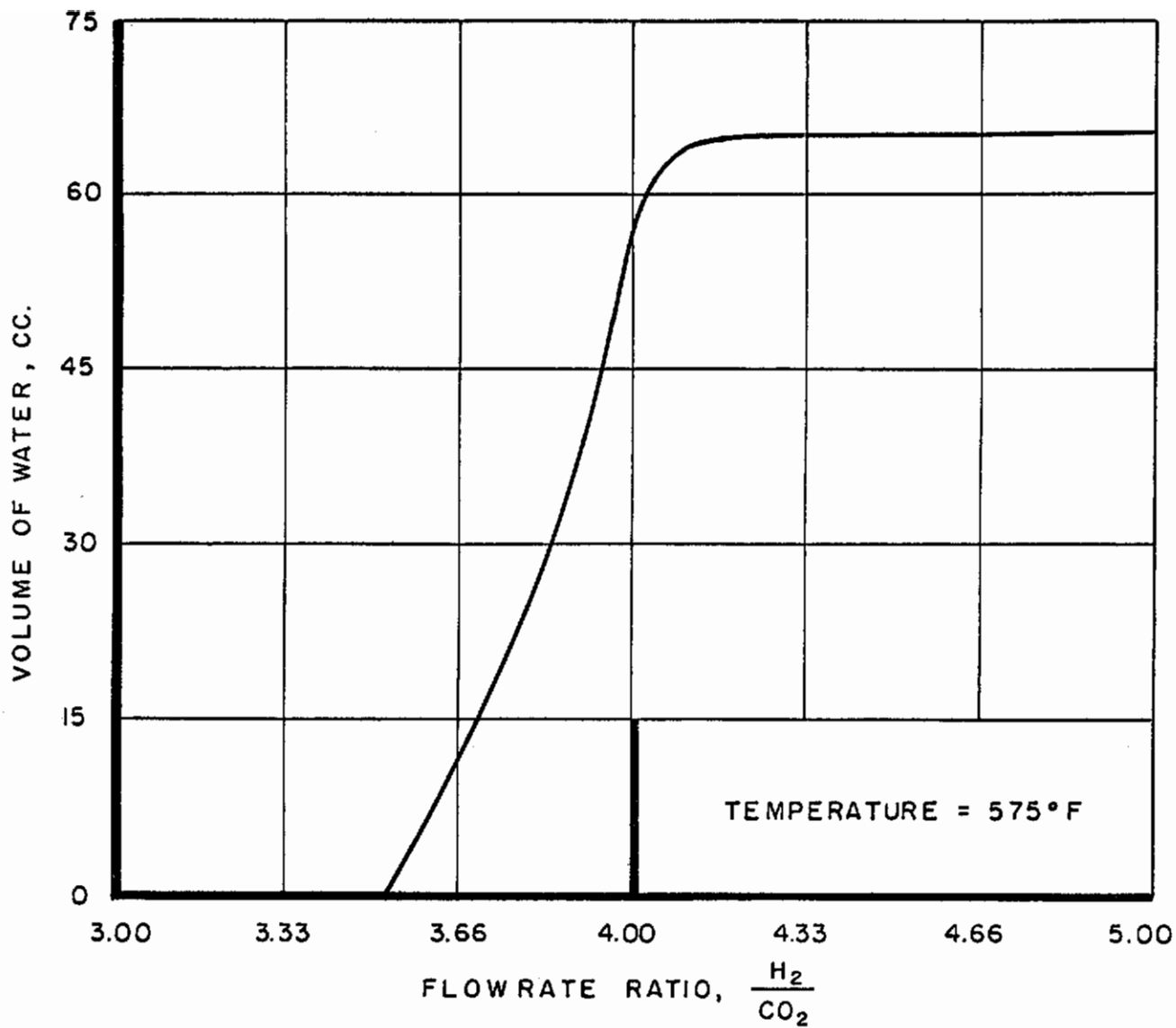


FIGURE 10. SABATIER REACTION - WATER YIELD VS. H<sub>2</sub> / CO<sub>2</sub>  
VOLUMETRIC FLOWRATE RATIO

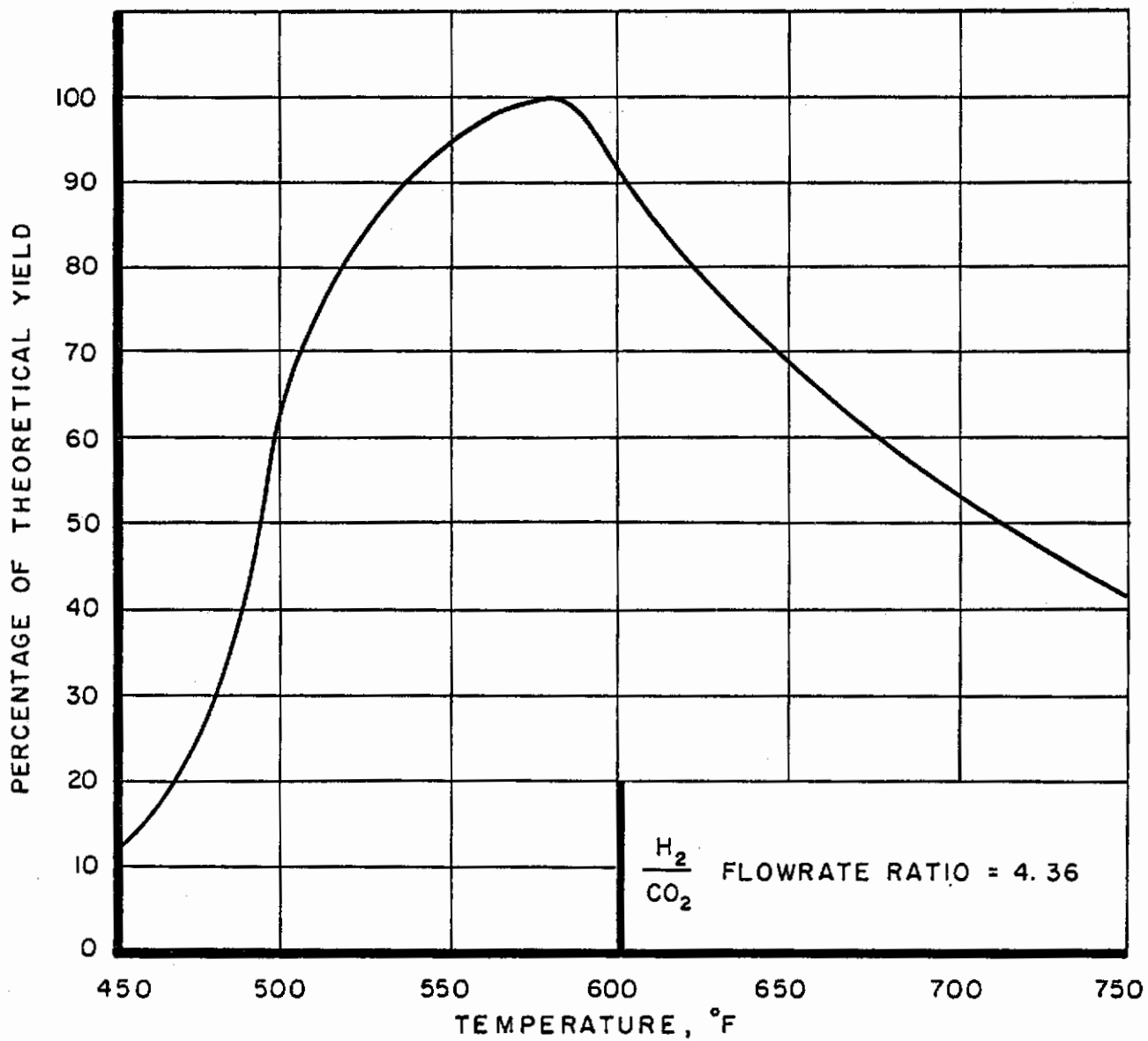


FIGURE II. SABATIER REACTION - PERCENTAGE OF THEORETICAL YIELD VS. TEMPERATURE