ACKNOWLEDGEMENT

The author is deeply indebted to his supervisor, Professor R. S. Mann, for the advice, guidance, encouragement and unfailing interest during the course of this investigation. He also wishes to acknowledge other faculty members of the department, particularly Dr. B. C.-Y. Lu for their interest in this work.

The author wishes to express his gratitude to Dr. K. C. Yao and Mr. A. M. Shah for their helpful suggestions and discussions and to Mr. C. P. Khulbe and Mr. P. S. Puri for their ready help in making the graphs and drawings.

The author is also, sincerely thankful to Miss F. Lemieux for typing the manuscript and indebted to Mr. and Mrs. B. K. Bhargava for their assistance from time to time.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figures | Page

ABSTRACT

The vapor phase air oxidation of methanol to formaldehyde over molybdenum trioxide, vanadium pentoxide and their mixtures has been investigated in an integral fixed bed tubular reactor, at atmospheric pressure. A preliminary study of the effects of the composition of the mixed oxide catalyst on the yield and conversion, at temperatures 300° - 460° C indicated that maximum yield was obtained with a catalyst containing 20% vanadium pentoxide and 80% molybdenum trioxide at 460° C. A detailed kinetic study was hence made for methanol oxidation over vanadium - molybdenum oxide (20:80 weight ratio) catalyst.

The effect of various process variables, viz. the feed ratio of methanol to air, ratio of the catalyst weight to methanol feed rate and reaction temperature on the conversion of the methanol and the product distribution was determined by gas chromatography. The liquid products; formaldehyde, methanol and water, were separated by a chromatographic column packed with 15% (wt.) sucrose octa-acetate on columpak T and analyzed quantitatively by Gow Mac Thermal conductivity cell. The gaseous products, carbon monoxide, carbon dioxide, nitrogen and unreacted oxygen were analyzed by a Fisher Gas Partitioner using HMPA (Hexamethylphosphoramide), DEHS (di-2, ethylhexyl sebacate) and molecular sieve columns.

The vanadium-molybdenum oxide (20:80 wt. ratio) catalyst was found to be highly active. However, the reaction at temperatures above 466°, with higher methanol content in the reactant feed mixture

resulted in the formation of carbon oxides along with formaldehyde. The maximum yield with one hundred percent selectivity and 99% conversion was obtained at 466° C with a W/F ratio of 31.7 gm-hr/mole and 8 mole percent methanol in air.

The kinetic analysis of the experimental data was restricted to the range of the process variables when no carbon oxides were formed. The kinetic expression derived by Mars and van Krevelen on the basis of two-stage oxidation-reduction mechanism was tested to fit the experimental data. According to this mechanism:

$$CH_3OH\ (g) + s_{ox} \xrightarrow{k_1} HCHO\ (g) + s_{red} \qquad (1)$$

$$s_{red} + O_2\ (g) \xrightarrow{k_2} s_{ox} \qquad (2)$$

where s_{ox} was an active site of lattice or adsorbed oxygen, and s_{red}, the reduced site of lattice oxygen or the empty site. The rate of reaction is expressed by:

$$r = \frac{k_1 p_M^m}{1 + \left(k_1 p_M^m \mid 2k_2 p^n{}_{O_2} \right)} \qquad (3)$$

where k_1 and k_2 are temperature - dependent rate constants of the two processes (1) and (2) respectively, and m and n, are the reaction orders with respect to methanol and oxygen respectively.

The rate equation (3) with $m = 1.0$ and $n = 0.5$ was found to give the best possible fit to the experimental data.

I. INTRODUCTION

A. Importance of Chemical Kinetics

Chemical Kinetics is a study of the rate at which the chemical reaction occurs and the variables affecting this rate. A kinetic study is of both theoretical and practical importance in chemical engineering. It is a valuable tool for understanding how chemical bonds are broken and formed, for estimating their energies and stability, to identify the molecular structure of compounds and to gather greater insight into the nature of the reacting system.

From a practical viewpoint it permits considerable freedom of choice in chemical reactor design, in selection of batch or continuous process, in the specification of the size of the equipment and the process operating conditions of temperature, flow rate and reactant concentrations, and in making controlled adjustments in these variables during the plant operations. Thus a correlation between the reaction rate and process variables is necessary for an economic or optimum process design. By making a systematic kinetic study, one can investigate several proposed reaction mechanisms and attempt to select the proper mechanism from an analysis of the experimental data. A rate equation can be evaluated to represent the mechanism of the reaction.

It is also fairly common in practice to simply select the operating conditions under which the best yield of product can occur. This practice has the disadvantage that the reaction rate can not be predicted if the operating conditions are changed in the process. Another way is to develop an empirical rate equation. The mechanistic approach of ascertaining the rate equation is desirable if any extrapolation outside the range of the data becomes necessary.

Furthermore, while evaluating overall rate of reaction for the design of industrial reactors, other physical processes, such as mass transfer and heat transfer which greatly affect the reaction rate, are also taken into account.

B. Nature of Catalytic Reactions

The term catalysis describes all the processes in which the rate of reaction is influenced by a substance that remains chemically unaffected. From the kinetic studies of Bodenstein and Ostwald and the thermodynamic principles enunciated by van't Hoff [1] it is concluded that, a catalyst can increase the rate of thermodynamically feasible processes only, and it facilitates the approach to equilibrium of a given chemical change. Also, that for a given group of reactants there may be several reaction paths and by the appropriate choice of catalyst any one of these paths may be "selected".

A catalyst is effective in increasing the rate of reaction because it provides an alternate mechanism, each step of which has a lower free energy of activation than that for the uncatalysed reaction [2]. This concept suggests that an intermediate substance is formed by one or more of the reactants and the catalytic surface. The alternate mechanism can be postulated in terms of an activated molecule adsorbed on the surface of the catalyst. Because of the high heat of adsorption, the energy possessed by strongly adsorbed or chemisorbed molecules can be considerably different from that of the molecules by themselves. Hence the energy of activation for reaction involving chemisorbed molecules can be considerably less than that for reaction involving the molecules alone.

Catalytic reactions can be classified according to whether they occur homogeneously (in a single phase) or heterogeneously (at an interface between two phases). An important group of heterogeneous reactions, the vapor phase oxidation of oxygenated hydrocarbons catalyzed by a solid surface, is the subject of the present study.

C. Method of Study

Although several methods [3] are available for measuring the reaction rates using different types of reactors, differential or integral, batch or continuous flow, there is no entirely satisfactory method by which the reaction rate can be measured directly. The differential method consists in operating the reactor with a small conversion so that the reaction rate may be assumed constant. Rate determinations in a differential reactor can be made in a straight-forward manner. However, the main drawback is the difficulty in a precise analysis because of the low concentration of products in the gas stream. On the other hand, the integral method is not restricted to a small conversion and analytical accuracy is not as important. However it is much more difficult to integrate the rate equations since there are several hidden parameters which may diminish the value of the experimental data [4].

From industrial viewpoint, one is more interested in yield and selectivity using a mixture of methanol and air over a heated stationary catalyst at approximately atmospheric pressure. Such studies are generally carried in flow reactors. A fixed bed integral flow reactor operating at approximately atmospheric pressure is most suitable for studying oxidation reactions.

II. LITERATURE SURVEY

Formaldehyde was first prepared by the Russian chemist A. M. Butlerov [5, 6] in 1859 as the product of an attempted synthesis of methylene glycol by the hydrolysis of methylene diacetate. Since then it has become an industrial chemical of outstanding importance. With improved methods of manufacture and new uses, formaldehyde production from methanol oxidation has tremendously increased in the last decade. It is only in the recent years that some attempts have been made on the kinetic study and mechanism of the reaction.

A large number of patents and publications related to formaldehyde are available in the literature. A comprehensive bibliography on formaldehyde research was published in 1964 by J. W. Walker as part of the American Chemical Society's chemical monograph series [7]. The present review is limited to studies on heterogeneous oxidation of methanol to formaldehyde on metal and metal oxide catalysts.

A. Metal Catalysts

The classical way of manufacturing formaldehyde by methanol oxidation over metal catalyst employs a rich mixture of methanol and high temperature in the range of 500° - 800° C. Off-gases from this process contains 18 - 20% hydrogen, less than one percent oxygen and minor amounts of carbon oxides and methane.

In 1868, Hofmann [8], who prepared formaldehyde by passing a mixture of methanol vapor and air over a heated platinum spiral, definitely established its chemical identity. Practical methods of

manufacture developed with Loew's [9] use of a copper catalyst around 1886, and commercial production was initiated in 1889 in Germany [10]. Improvements in operations and equipment were also reported by Klar and Schulze [11], Brochet [12] and Orlov [13]. In 1910, O. Blank [14] patented the use of a silver catalyst in Germany. Le Blanc and Plaschke [15] in 1911 reported that formaldehyde yields obtained with silver catalysts were higher than those with copper. The silver catalyst was patented in U. S. by Kuznezow [16] in 1913. Thomos [17] reported laboratory-scale results of methanol oxidation in the presence of copper, silver and gold. For a silver catalyst using gaseous mixtures containing 0.5 to 0.3 gm oxygen per gm of methanol, 83-92 percent net yields of formaldehyde were obtained. Homer [18] in 1941, reported net yields of around 90 percent in commercial practice.

Numerous modifications in the classical silver catalyzed formaldehyde process are covered by patents. These include a special reactor design by Schideler and Richardson [19] and Meath [20]. Methods of controlling temperature include Marullo and Maffezoni's [21] use of a silver or copper plug inserted through the center of a silver gauze packing in a cylinder reactor tube. Eguchi, Yamamoto and Yamauchi [22] cooled the catalyst by an upward directed spray of water, methanol or formaldehyde solution contacting the bottom surface of the bed through which the reactants descended. Polyakov, Shalya and Vysotskiy [23] obtained higher yields with the use of supported copper catalyst in a fluidized bed at temperature 540° to 580°C than that with a stationary copper catalyst. Polyakov et al studied the effect of reactant flow rate through fluidized catalyst beds on conversion [24] and correlated grain size of silver and copper catalysts

to aldehyde yield [25]. They also studied the influence of reactor diameter on yield at various operating conditions [26].

In 1960 Punderson [27] discovered a selective dehydrogenation catalyst for methanol consisting of 97.8% silver, 2% copper and 0.2% silicon and obtained good yields of formaldehyde at 600 to 700° C. Kushnarenko and Atroshchenko [28, 29] studied kinetics of methanol oxidation over silver catalyst with a pumice carrier at 450-600° C and 1 to 3 atmospheric pressure. They observed that at gas velocities above a critical level, conversion is increased with temperature and pressure, and below the critical level formation of carbon monoxide increased.

Wolfren [30] and Vitvitskii et al [31] investigated the kinetics of methanol oxidation over silver catalyst with aluminium silicate carrier. The activation energies of methanol oxidation to formaldehyde and formaldehyde oxidation to carbon dioxide were 18 and 79.2 kilojoules/mole respectively.

The reaction mechanism for the formation of formaldehyde from methanol and air using a metal catalyst may be either a dehydrogenation, followed by oxidation of hydrogen to the extent that the oxygen is present in the gaseous mixture:

$$CH_3OH \rightleftharpoons HCHO + H_2 \qquad - 20 \text{ kcal}$$

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O \qquad + 58 \text{ kcal}$$

or, a combination of the dehydrogenation and oxidation reaction. A German study [32] indicated that silver catalyzed process may depend exclusively on dehydrogenation, the combustion of hydrogen offsetting the endothermic nature of this reaction. Le Blanc and

Plaschke [15] and Thomos [17] concluded the reaction mechanism to be a combination of the two reactions. The function of oxygen, aside from maintaining the necessary temperature, was to keep the catalyst active by oxidizing and removing any "poisons" or to keep the surface of the metal in the proper physical and chemical state. The kinetics of the reaction over copper and gold were similar to silver, but these metals were found to be much less active and to cause more decomposition of formaldehyde. Formation of undesirable products by pyrolytic oxidation of formaldehyde to carbon oxides can be avoided by proper control of temperature and other factors and by proper catalyst selection.

More recent work [33–36] on methanol oxidation over silver catalyst has been carried out to improve the industrial processes, to obtain high concentration aqueous formaldehyde solution, to study the effect of diluting the reaction mixture with inert gas and to obtain optimum process conditions for maximum yield. The presence of water in reaction mixture has been found to improve the formaldehyde yield over silver based catalyst at 600°-800° C [37, 38, 17].

B. Metal Oxide Catalysts

The oxide catalyst process for formaldehyde production has assumed increasing importance in recent years. A process of this type differs from the classical procedure in that it employs a metal oxide or a mixture of one or more metal oxides as catalyst, operates with a feed gas containing methanol with a large excess of air and yields a formaldehyde product solution containing from zero

to one percent of methanol. A general survey of literature related to formaldehyde production indicates that the methanol - air mixture favored for use with metal oxide catalyst contains 5 to 10 percent methanol by volume. Reaction temperatures apparently fall in approximate range of 300° to 450°C. Manufacturing yields are said to be higher than those obtained with silver and other pure metal catalysts. The oxide catalyst process converts methanol to formaldehyde by an oxidation process as follows:

$$CH_3\,OH + \tfrac{1}{2}\,O_2 \longrightarrow HCHO + H_2O \quad + 38\ \text{kcal}$$

In 1926, a catalyst containing equal amounts of iron and molybdenum oxide was first found to be very efficient for methanol oxidation. Adkins and Peterson [39] initiated their investigation to correlate the characteristics of iron-molybdenum oxide catalyst with those of containing only iron or molybdenum oxide. Most of the studies were made using a catalyst bed 15 cm. in length with a cross-sectional area of 3 sq. cm. and feed rate of 10 gm of methanol in 93 litres of air per hour. The molybdenum oxide catalyst was found to be highly selective in the formation of formaldehyde with about 36% yield. The conversion was a linear function of the rate of passage of methanol over catalyst but did not increase the rate of formation of formaldehyde. However, the percentage conversion of methanol to formaldehyde rose with decrease in the rate of passage of methanol over catalyst. With 9.5 gm. of methanol in 93 litres of air passing over the catalyst at 361°, 373°, 390° and 400°C, yields of 23.8, 31.5, 32.1 and 32.4% respectively, were obtained in the steady state.

On the other hand iron oxide was found to be a very active catalyst and oxidized methanol almost wholly to carbon dioxide. The maximum activity was obtained when equimolar proportions of iron and molybdenum oxides were present in the oxide mixture. A high percentage of iron oxide in the catalyst showed more of the carbon dioxide forming property of an iron oxide catalyst, while a high percentage of molybdenum oxide in the catalyst showed properties intermediate between those of an iron-molybdenum oxide catalyst and a molybdenum oxide catalyst. 91% conversion of methanol to formaldehyde were obtained with equimolar mixture of Iron and molybdenum oxides at 373°C. Decreasing the length of the bed from 15 cm. to 5 cm. gave the same conversion but the yield of formaldehyde increased slightly. Decreasing the feed rate, at constant methanol to air ratio resulted in a loss in formaldehyde yield due to further oxidation. Similarly at temperatures of 353°, 373° and 400° conversions of 85. 2, 91. 8 and 91. 9% respectively, were obtained. However, at 400°C some loss in yield due to the continued oxidation of formaldehyde was observed.

Jiru et al [40, 41] taking into consideration the work of Adkins and Peterson together with a number of patents, [42-47] carried out an extensive study on the oxidation of methanol to formaldehyde over a catalyst composed of 17. 5% ferric trioxide and 82. 5% molybdenum trioxide. The reaction rate was measured in a through-flow integral reactor at atmospheric pressure. They deduced a rate expression based on the mechanism which was originally suggested by Mars and van Krevelen [48] for the vapor phase oxidation of aromatic hydrocarbons on vanadium pentoxide. According to this mechanism:

$$\text{Reactant} + (\text{Catalyst})_{OX} \xrightarrow{k_1} \text{Product} + (\text{Catalyst})_{Red}$$

$$(\text{Catalyst})_{Red} + O_2 \xrightarrow{k_2} (\text{Catalyst})_{OX}$$

The rate of oxidation of methanol at temperature of 270° C is given by the expression:

$$r = \frac{k_1 p_M^m}{1 + k_1 p_M^m \mid k_2 p_{O_2}^n} \qquad (2.1)$$

where $m = 1$ and $n = 1$ or 0.5

The ideas on oxidation-reduction mechanism were confirmed by the results of the investigations on: (a) the rate of interaction between methanol and catalyst without the participation of oxygen in gaseous phase. (b) the rate of interaction between oxygen and partially reduced catalyst without participation of methanol in the gaseous phase. These studies of interaction between methanol or oxygen and the catalyst were carried out in a static sorption apparatus with a McLeod manometer, by means of a microcatalytic chromatographic pulse method.

Friedlander and Bennet [49] and Cotter [50] studied the kinetics of methanol oxidation and obtained the rate expression:

$$r = k p_M^m \qquad (2.2)$$

Friedlander and Bennett employed a flow-recycling differential reactor between 402° and 452° C and a lean methanol air mixture containing 0.4 to 3.0% methanol. Cotter used a fixed bed integral reactor between temperatures 260° and 330° C, methanol concentration of 1-3 mole per cent and a gas flow rate of 0.3 to 0.9 cu. ft/min. Jiru et al [51], also made kinetic studies in a differential reactor with recycle at 370° C and deduced the same rate equation (2-1) with m = 0.5 or 1 and n = 1.0.

Dente et al [52-54] studied the kinetics of methanol oxidation over iron and molybdenum oxides at temperatures 220° to 330° C. The two step redox mechanism was used to correlate the data with the same rate equation (2.1) as obtained by Jiru et al, with m = 0.5 and n = 0.5. In another investigation [55], they found that for particle diameter of 0.6mm heat and mass transfer have no effect on the reaction velocity at temperatures below 300° C. For particle diameter of 3 mm., these effects become important in the whole temperature range. Boreskov et al [56] studied the nature and phase composition of iron-molybdenum oxide catalyst for methanol oxidation by means of x-ray, E.P.R., infrared and thermographic analysis. Normal iron molybdate proved to be the active component. The highest activity was found for the catalyst with the atomic ratio (Mo - Fe) of 1.7 [57, 58, 59]. Jiru et al [60] obtained 90% conversion of methanol to formaldehyde by using a 2.1 mixture of iron molybdate - iron oxide catalyst having specific surface of 2.5 m^2/gm. at 525° C and confirmed iron molybdate to be the active component of the oxidation catalyst.

Bliznakov et al [61, 62] studied the catalytic action of tungstate of Period IV metals. All tungstate studied showed medium catalytic

activity, the highest being that of Iron tungstate. The catalytic properties of tungsten oxide were analogous to those of molybdenum oxide with respect to the methanol oxidation. At 450° C [63] the tungsten oxide, molybdenum oxide and their equimolar mixture gave 54, 80 and 84 percent conversion respectively.

Field [64] patented a catalyst, consisting of manganese dioxide - molybdenum trioxide for methanol oxidation at temperature 250° to 450° C. Almost complete conversion of methanol to formaldehyde with small amounts of carbon monoxide was obtained. Klissourski and Bliznakov [65] studied catalytic activity of manganese-molybdenum oxide catalyst on a mixture of 4.5% methanol and 20% oxygen (by volume) diluted with Nitrogen. Maximum yield of 92% was reached at 440° C with a 20:80 proportion of MnO_2 - MO_3 catalyst. Bliznakov et al [66] also carried out kinetic study at 370° C in a differential reactor with recycle. The best fit was obtained with the value m = 0.5, n = 1.0 and m = n = 1.0, in rate equation (2.1). Mann and Hahn [67] studied kinetics of methanol oxidation to formaldehyde over catalyst containing 20% manganese dioxide and 80% molybdenum oxide. On the basis of a two stage irreversible oxidation-reduction mechanism, they found that the rate expression (2.1) with m = 1 and n = 0.5 fitted the experimental data best. Maximum conversion with 100% selectivity to formaldehyde was found to be 84% at 365° C.

C. Vanadium Pentoxide Catalyst

Vanadium oxide is known as an excellent oxidation catalyst in various manufacturing processes. Its use in oxidation of sulphur

dioxide and in the oxidation of naphthalene to phthalic anhydride is well established. A literature survey has shown that there are but a few reports on the methanol oxidation over vanadium catalysts. Craver and Bailey [68] patented the use of vanadium oxide at 225-400°C, Craver [69] and Jaeger [70] used vanadium oxide with other metal oxides such as potassium oxide and manganese oxides. Hahn [71] reported Vanadium oxide catalyst to be highly active but selectivity to formaldehyde in high conversion range drops down due to further oxidation to carbon oxides.

Bhattacharya et al [72] recently carried out a kinetic study of methanol oxidation at low conversion using Vanadium pentoxide catalyst at 246-281°C. Based on two stage redox mechanism their experimental data were found to fit the rate expression (2.1) with $m = 1$ and $n = 1$.

Tarama et al [73] studied the structures of the catalysts of V_2O_5 - MoO_3 system and of V_2O_5 - K_2SO_4 system by x-ray, infrared, ESR and magnetic susceptibility measurements and correlated these physico-chemical properties with the catalytic activities for oxidation reaction. Both potassium sulphate and molybdenum oxide were found to have promotive action on V_2O_5. Kurina and Maidanovskaya [74] have recently reported the use of a catalyst containing V_2O_5 and K_2SO_4 for methanol oxidation in a flow system at 200-370°C. It was observed that an increase of K_2SO_4 decreased the activity of V_2O_5 and increased its selectivity to formaldehyde. The catalytic activity was further increased with temperature. In 1968 Kurina et al [75] patented the preparation of vanadium - molybdenum oxide catalyst. However, no kinetic or catalytic studies

have yet been published. Hence a detailed kinetic study of methanol oxidation over vanadium oxide-molybdenum oxide catalyst was undertaken.

D. OBJECTIVES OF THE PRESENT WORK

A systematic study was undertaken on the oxidation of methanol to formaldehyde over oxides of vanadium and molybdenum with the purpose of:

1) confirming and extending the previous work on molybdenum - vanadium oxide catalyst with a view to reconcile the apparent differences.

2) investigating the kinetics of the reaction in detail.

3) investigating the effect of catalyst composition on yield and selectivity at several temperatures.

4) investigating the effect of process variables, temperature, reactant ratio and space velocity on conversion and product distribution over the oxide catalyst, and

5) developing a suitable rate expression and propose a plausible reaction mechanism, which might satisfactorily represent the experimental data.

III. EXPERIMENTAL

A. APPARATUS

The oxidation of methanol to formaldehyde by air was investigated in a flow system. The experimental set up, constructed in the department, was designed to study the kinetics of oxidation reactions over a catalyst at controlled temperatures and pressures. A schematic diagram of the experimental apparatus is shown in Figure 3-1.

The apparatus may be divided in three sections: (i) Feed of reactants and auxiliary gases, (ii) Reactor assembly and, (iii) Product separation unit.

(i) FEED SECTION

This section consisted of five gas streams and a methanol feed system. Two gas streams supplied helium as carrier gas, to gas chromatograph and to gas partitioner. The third stream carried air to the reactor through methanol vaporising unit during the reaction. The fourth stream along with the third one was used to prepare synthetic mixtures of carbon dioxide, carbon monoxide, oxygen and nitrogen for calibration of the gas partitioner. The fifth stream carried compressed air from the air compressor to the fluidized sand which was used for heating the reactor.

The calibrating gases, air and helium were obtained from high pressure cylinders through two-stage pressure regulators (model B, Matheson of Canada Ltd. Whitby, Ontario). In addition to the two-stage pressure regulators, two Edward pressure controllers

Figure 3 - 1

Schematic Diagram of Experimental Apparatus

Symbol	Item
C	Water condenser
CG	Calibrating gas cylinder (CO, CO_2, O_2 or N_2)
D_1, D_2, D_3, D_4, D_5	Drying tubes
GC	Gow Mac Cell
GP	Gas Partitioner
HI	Hot Inlet
LT	Liquid trap
P	Pressure regulator
PS	Power supply control unit
R	Reactor and fluidized sand bed
R_1, R_2, R_3, R_4, R_5	Rotameters
$\overline{R}_1$, $\overline{R}_2$	Chart recorders
S	Sample injection block
SC	Separating column (chromatographic)
SP	Syringe pump
SV	Sample valve
TC_1, TC_2, TC_3, TC_4	Temperature Controllers
ZS	Zero suppressor

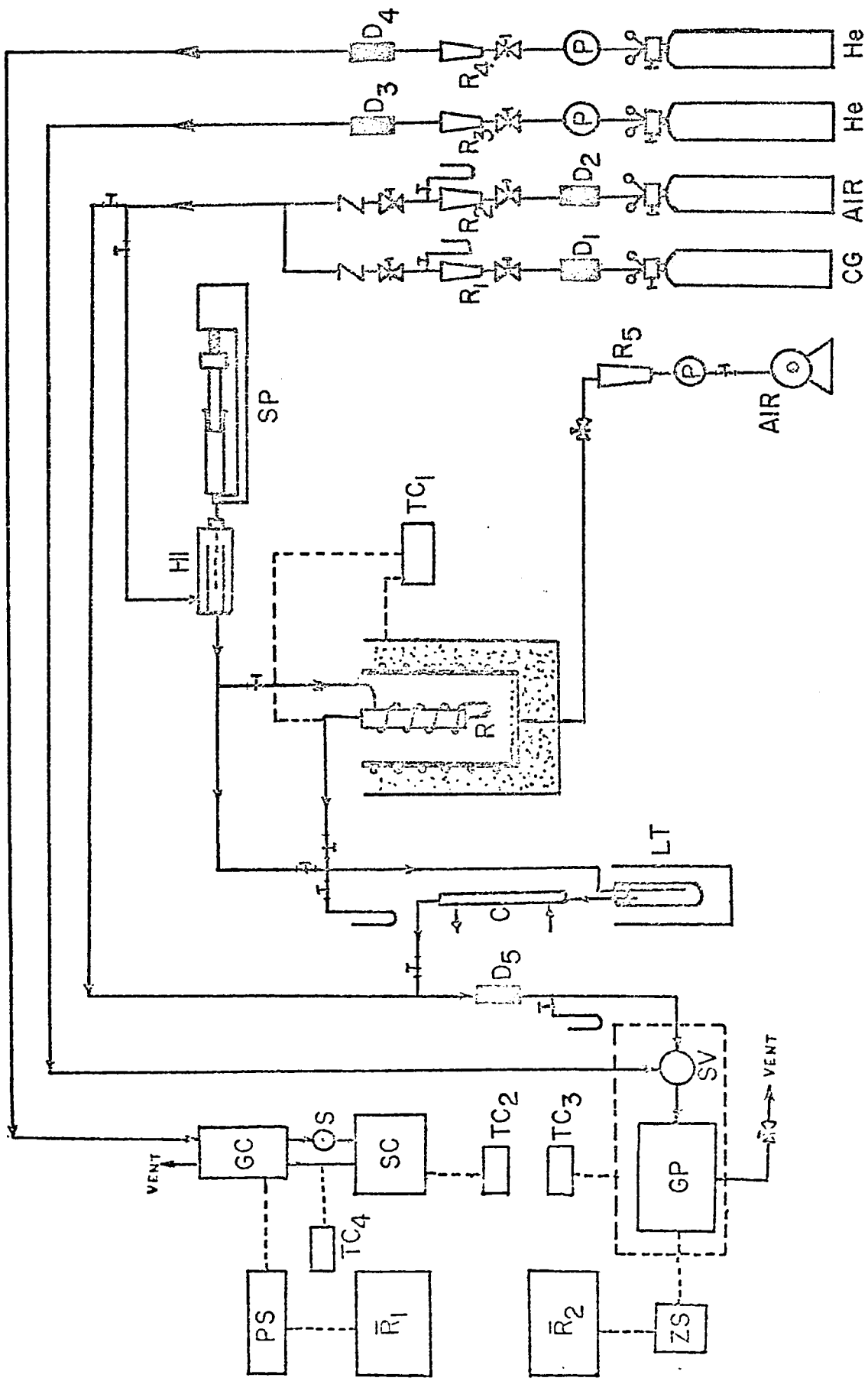

Fig. 3-1 Schematic Diagram of Experimental Apparatus

(model VPC1 code no. D8301, Edward High Vacuum Ltd, Sussex, England) were used to maintain a constant pressure in the helium lines. Traces of moisture were removed by passing the gases through the drying tube packed with indicating "drierite", the gas lines used for air and calibrating gases were made of $\frac{1}{8}$" O. D. stainless steel tubing and those used for helium were made of $\frac{1}{4}$" O. D. copper tubings. Fine metering valves and unidirectional check valves, supplied by Nupro Co. Cleveland, Ohio, were used to regulate the gas flow rates. All other valves and fittings were made by Autoclave Engineering Inc., Erie, Pa., and were capable to withstand pressure up to 5000 psi. Flow rates of each gas stream was measured by a Brooks rotameter with needle valve (body series 620, flowmeter tube and float series 600-602, Matheson Co.). The air and calibrating gas rotameters were connected with mercury manometers so that the pressure effect on the flow rate could be corrected.

The methanol feed system consisted of an infusion pump (S. M. 21350, catalogue no. 1100, Harvard Apparatus Co. Inc., Millis, Mass.) and a hot inlet (No. 186800 Hamilton Co., Whitby, California). The flow rate of methanol could be varied by using different combinations of syringe sizes and motor speeds. From the syringe driven by motorized infusion pump, methanol was continuously and precisely introduced into the hot inlet. The hot inlet was designed to vaporise the liquid continuously and uniformly. The outer body was made of heavy aluminium which evenly distributed the heat from the cartridge heater and eliminated cold spots. The high velocity preheated air stream continuously washed the septum and restricted flushback. The methanol introduced

into the 1 mm. I. D. glass vaporiser at a constant speed was thus continuously vaporised and carried away by hot air to the reaction system. $\frac{1}{8}$ x 1/16" stainless steel tubing transporting the methanol-air mixture to the reaction system was heated externally by means of a heating tape to keep the methanol in vapor form. The heating tape (supplied by the Chemical Rubber Co. of Cleveland, Ohio, catalog no. 37-278) was also used to cover the last two feet of the air line immediately preceding the hot inlet.

(ii) REACTOR ASSEMBLY

The reactant stream from the hot inlet was bifurcated, one branch leading to the reactor through a preheater and the other bypassing the reactor and preheater. The preheater was made of 10 feet long $\frac{1}{8}$ " O. D. 316 stainless steel tubing which was wound round the reactor. The preheated reactants entered the reactor from the bottom of the reactor. The reactor was 6" x $\frac{1}{2}$ " O. D. 316 stainless steel tube. A porous stainless steel plate supplied by Pall Trinity Micro Corp., Cortland, New York, was fixed at the bottom of the reactor tube. The grade D plate had mean pore size of 65 microns, a normal thickness of 1/16 inch and produced a pressure drop of approximately 0.1 psig per 180 cfm / sq. ft. of air. An autoclave reducer was welded below the porous plate and connected to the feed line from the hot inlet through the preheater.

The top of the reactor was connected to swagelok "T" connection (810-3-2-316) through a $\frac{1}{2}$ " to $\frac{1}{2}$ " reducer union. The upper opening of the "T" was further connected to a $\frac{1}{2}$ " to 1/16 " reducing unit through which a stainless steel tube 1/16 " O. D. containing two

iron constantan thermocouples was inserted. The lower end of the thermocouple tube was kept just above the porous plate in contact with the catalyst bed. The first thermocouple in the protection tube was connected to the temperature controller TC1 for controlling the catalyst bed temperature and the second was connected to a potentiometer (Honeywell, model 2745) for measuring the temperature during the reaction. The two ends of the thermocouple inside the protection tube were one inch apart. The temperature at both levels in the reactor were checked periodically, and the difference between two ends was found to be negligible. The thermocouples were supplied by Thermoelectric Canada Ltd., Brampton, Ontario.

The temperature of the reactor was controlled by a Honeywell Pyr-O-vane temperature controller. It was used with transducers such as thermocouples that generated a millivolt signal. The output signal of the thermocouple was measured by the controller which activated the relay to maintain the temperature constant at the set point. The controller when coupled with an energy regulator (Fisher catalogue no. 28-4-50) could maintain the reaction temperature to $\pm$ 2° C.

The reactor and the preheater were kept immersed in a constant temperature fluidized bed furnace. The container for the fluidized bed was made from an 8 inch O.D. steel cylinder. A porous stainless steel plate (Pall Trinity Micro Corp., Cartland, New York) was inserted at the bottom and further welded to a reducing cone with $\frac{1}{2}$" pipe. Clean Ottawa sand 40-60 mesh size was used as the heating medium of the fluidized bed, and was placed in the container on top of the porous plate. The reactor was held upright in the center of the bed. During operation, sufficient air was passed to

keep the sand fluidised and to obtain uniform temperatures around the reactor. The compressed air was supplied from the Departmental air compressor and the pressure was adjusted to 8 psig by a pressure regulator (supplied by Matheson Co., model 73) and its flow rate was adjusted by a Brooks flowmeter.

For heating the reactor, two layers of Ceram-A-Flex beaded heating wire (Chemical Rubber Co., Cleveland, Ohio) were wrapped around the steel cylinder. A paste of Asbestos powder with water was applied in $\frac{3}{4}$" thick layers to the heating wires for insulation and to fix the wires in position. Before supplying power to the heating wires, the asbestos was dried slowly to prevent it from cracking. The inner heating wire was connected to a 7.5 ampere powerstat (Fisher catalogue no. 0-521-120-V2) and then to the temperature controller TC1. The external heating wire was connected to another 10 ampere powerstat (Fisher catalogue no. 9-521) and was left on all the time. The powerstat was set in such a way that it supplied just sufficient power to maintain the reactor temperature slightly below the required temperature set on the temperature controller TC1. This reduced the heating load in the controller circuit (inner heating wire) and a more precise control of the reaction temperature could be made possible.

The reactor and fluidized sand bed were then placed in an outer steel cylinder 15 inches in diameter, resting on a piece of asbestos plate, in the center of which a hole was provided for a compressed air line to the fluidized bed. The annular space between the steel cylinder and the "bed" was packed with "vermiculite".

The surface of the outer cylinder was coated with a layer of one inch thick asbestos powder and then covered by a 4" thick fibre glass insulation.

(iii) PRODUCT SEPARATION UNIT

This section of the apparatus consisted of a liquid trap, a condenser, a drying tube, a gas chromatograph for the liquid product analysis, a gas partitioner for gaseous product analysis. Two chart recorders for recording the chromatographic analysis of the products, a constant temperature oil bath, and a wet test meter were also used. The gaseous products were analysed "on stream" and samples of liquid reactants and products were injected by means of a Hamilton microliter syringe.

The products from the reactor entered into a liquid trap which was kept cooled in an ice bath. The heavier reaction products formaldehyde, water and unreacted methanol were condensed and the lighter gaseous products carbon dioxide, carbon monoxide, unreacted oxygen and nitrogen were passed through a water-jacketed condenser and a drying tube. The liquid trap was made of a 7" x 7/8 " O. D. glass tube fitted with a two-hole rubber stopper, for insertion of the product line and the tube to the condenser. The condenser was made of two feet long and one inch O. D. copper tube surrounding a central condensing tube of $\frac{1}{8}$" O. D. stainless steel. Cold water was used as a condensing medium between the two tubes. The drying unit was made of a 6" x 2" O.D. acrylic tube packed with indicating "drierite".

All traces of moisture from the gaseous reaction products were removed prior to their analysis in the Fisher gas partitioner by the condenser and the drying tube.

The product stream after the removal of formaldehyde, methanol and water was led to the Fisher gas partitioner through a six-way linear gas sampling valve supplied by Aerograph Co.. This gas was passed through a sampling loop (0. 25 ml) and then vented to the atmosphere. A stream of helium gas was passed through the other leg of the sampling valve on its way to the separating columns in the gas partitioner. When the sampling valve was turned on, the sampling loop was taken out of the product stream and connected with the carrier gas stream instantaneously. The sampling valve was shut off swiftly after a couple of seconds. Using this scheme, it was possible to flush reproducible sample volumes into separating column of the gas partitioner. To ensure consistency in the amounts of samples introduced, the temperature and pressure of the gas stream in the sample loop had to be controlled. The temperature was maintained constant at 35°C by a Fisher Thermal stabli zer (model 27). The pressure was controlled at 830 mm.Hg by adjusting the needle valve in the exit line.

The Fisher gas partitioner with suitable chromatographic columns could separate and analyze oxygen, nitrogen, methane, carbon dioxide, and carbon monoxide present in the gaseous product stream. Output signal in millivolts from the partitioner was transferred to a chart recorder (Texas Instrument Inc., Texas model servo/ritter II), through a zero suppressor (supplied by Fisher Scientific Co., 0-10 mv), which could suppress the recorder input signal in discrete

steps of 1 mv. and the remaining signal between 0-1 mv. was recorded. This enabled the use of higher sensitivity in the partitioner for more precise analysis.

The gas chromatograph, assembled in the department, consisted of a separating column, sample injection block, a thermal conductivity cell and a direct current power supply. The column immersed in a liquid bath (Fisher bath oil no. 2) was heated by a "variac" regulated immersion heater (Fisher catalogue no. 11-463-5V4). The temperature of the oil bath was maintained constant within $\pm$ 0.01°C by a Yellow Spring Thermistor temperature controller (model 71). A 2" thick layer of glass wool around and below the liquid bath (Pyrex-Corning Glass work, Corning, New York) and an asbestos plate (Fisher catalogue no. 1-435), placed on top of the bath reduced heat losses to the surroundings.

The liquid sample, injected by means of a Hamilton microliter syringe into an evaporating block, was carried by an incoming helium stream to the separating column. The evaporating block, supplied by Wilkens Instrument and Research Inc., California was maintained at approximately 200°C.

A Gow Mac W-2X hot wire, 333 mount, made of rhenium-tungsten, in a temperature regulated four-element macro cell (model TRIIIA, 4W2) was used to analyse the product separated by the column. Since water, one of the products of the reaction could condense at temperatures less than 100°C, the cell temperature was constantly maintained at 120°C. The detector temperature was controlled by a Fenwal Thermo switch with an

adjustable range from ambient to 205° C. Two cartridge heaters were connected in series with a thermoswitch and the temperature of the unit could be varied by turning an adjustible screw at the bottom of the case, one revolution clockwise for every 32° C rise in temperature and vice-versa.

Direct current for the detector was supplied by a Gow Mac model 405-C:1 solid state DC power supply with input power 115 volts A. C. at 60 cycles per seconds and output power from 0 to 40 volts A. C. Regulated output ranged from 0 to 500 ma with a four-step voltage control starting at 6-10 volts.

A Phillips recorder PR2210V, with various multistage units connected to the Gow Mac Cell, recorded the peak heights representing the composition of the effluent stream.

The $\frac{1}{8}$" O. D. stainless steel tubing carrying the separated products with helium was wrapped with a heating tape and stream temperature was controlled at 100° C by a Yellow Spring Thermistor temperature controller, model 63.

B. PREPARATION AND PROPERTIES OF CATALYSTS

(i) Vanadium Pentoxide - Molybdenum Trioxide

Ammonium molybdate and Ammonium meta vanadate were weighed according to a desired ratio of the molybdenum trioxide and vanadium pentoxide. Ammonium molybdate, dissolved in distilled water was mixed with ammonium vanadate to make a paste. The paste was dried for 12 hours at 40° C and for 6 hours at 150° C. The temperature was increased stepwise and maintained successively for 2 hours at 200°, 300°, and 400° C. The catalyst was calcined at temperature 500° C for 6 hours and activated at 600° C for 2 hours.

(ii) Molybdenum Trioxide and Vanadium Pentoxide

Molybdenum trioxide catalyst and Vanadium pentoxide catalyst were obtained by thermal decomposition of Ammonium molybdate and purified ammonium meta vanadate. The catalysts were calcined and activated at same temperature similar to their mixtures.

A 40-60 mesh size of catalyst (20% V_2O_5: 80% MoO_3) was used and the surface area per unit gm. of catalyst, as determined by the Department of Energy, Mines and Resources, Ottawa, Ontario, was 3.87 m^2/gm.

The catalyst was reactivated when charged into the reactor at 500° C for about 8 hours. The color of the fresh catalyst was greenish yellow but turned black after the use.

C. EXPERIMENTAL PROCEDURE

(1) Calibration of Equipment

Flow rates of the gas streams were measured by calibrated rotameters. The volumetric flow rates were checked by both the soap bubble method and the wet test gas meter supplied by the American Instrument Co.. The pressure was maintained at 1360 mm.Hg by adjusting the metering valves on the exit side of rotameters. A correction for fluctuation in the room temperature was necessary, so as to maintain a constant molar flow rate of the gaseous streams.

The feed rate of methanol was controlled by the speed of pump and the syringe size. For a particular combination of the pump speed and syringe size, the feed rate was calibrated by weighing distilled water, pumped for a certain time.

The thermocouples were calibrated by inserting them into a fluidized bed furnace and direct temperatures were noted by an ASTM thermometer attached to the thermocouple. A calibration curve of temperature against millivolts is shown in Figure 8-D-3.

For the calibration of Gas Partitioner and gas chromatograph, synthetic mixtures similar to the actual samples were used, with the time and order of elution of the components based on previous injections of the pure compounds. Mixtures of oxygen, carbon dioxide, carbon monoxide with nitrogen or air in varying proportions were accordingly made for separation by the Gas Partitioner. Mixtures of water, methanol and formaldehyde of

a known composition were injected into the chromatographic column through the evaporating block. The calibration curves for both the Gas Partitioner and gas chromatograph are given in Appendix (8-D-1).

The widths of each of the component peaks in the samples tested were found nearly unchanged. A quantitative analysis could thus be based on either peak height or on the relative peak height ratio versus percentage composition or mole ratios. The peak height ratio method (internal normalisation method) was preferred due to its simplicity and greater accuracy over the method of measuring the areas under the peaks with an integrator, especially when the sample quantities were small.

(2) Analysis Procedure

(i) Gases

Two 1/4" O. D. copper tubing columns in series were used to analyse gas samples containing oxygen, nitrogen, carbon monoxide and carbon dioxide. The first column was packed with a 6 feet long, 30% HMPA (hexamethylphosphoramide) coated on celite diatomaceous silica followed by a foot long 30% DEHS (di-2, ethyhexyl sebacate) coated on celite diatomaceous silica which could separate carbon dioxide from other gases. The second column packed with a 7 feet long molecular sieve 5A followed by a 5 feet long uncoated celite diatomaceous silica could separate oxygen, nitrogen and carbon monoxide. A typical analysis of the products from the Gas Partitioner is shown in the Figure 3-2.

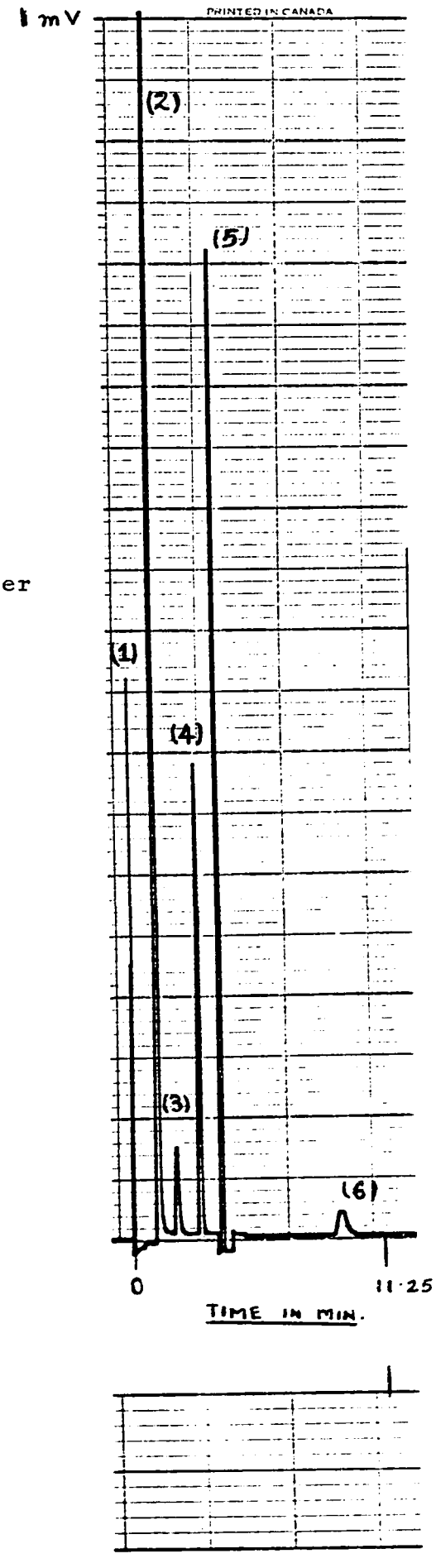

Fig. 3-2

A typical analysis of gaseous products from Fisher Gas Partitioner

(1) Sample injection
(2) Composit peak of the mixture
(3) Peak for carbon dioxide
(4) Peak for oxygen
(5) Peak for nitrogen (with zero suppressor set to suppress the signal by 1.0 mv.)
(6) Peak for carbon monoxide

(ii) Liquid Products

Samples withdrawn from the liquid trap after every run were introduced into the separating column by means of a microliter syringe. 15% (wt.) sucrose octa-acetate coated on Columpak T (Teflon powder) was packed in a 14 feet long - 1/4 " O.D. copper tube. Methyl chloride was used as a solvent for sucrose octa-acetate. The column was dried at 195° C for one hour prior to use. During analysis, the column temperature was constantly maintained at 100° C ($\pm$ 0.1) in the oil bath. This column separated water, methanol and formaldehyde very efficiently. A current of 250 ma was kept in the thermal conductivity cell.

The quantitative analysis of formaldehyde proved to be difficult because of its rapid polymerisation. This polymerisation was probably caused by the presence of water in the formaldehyde solution at room temperature. The temperature was therefore maintained at 100° C to prevent polymerisation of formaldehyde in the air stream. The presence of methanol in the mixture of water and formaldehyde in the liquid trap effectively prevented the polymerisation. However, at high conversion of methanol the product samples were freshly analyzed immediately after the withdrawal from the liquid trap.

The total acid content of the liquid products was determined by titration with a standard potassium hydroxide solution. Phenolphthalein was used as the indicator for titration. However, no acid was found in the liquid products. A typical gas chromatogram is shown in Figure 3-3.

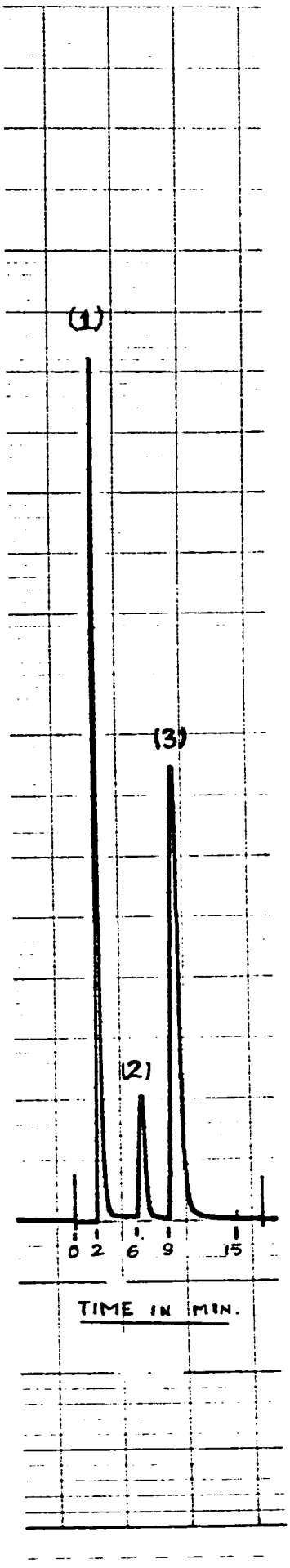

Fig. 3-3

A typical analysis of liquid products.

Chromatographic separation with
15 wt. % sucrose octa-acetate on
Columpak T at 100° C.
Sample size: 1 microliter commercial
solution of formaldehyde containing
37. 2% formaldehyde, 11. 9% methanol
and 50. 9% water.
Bridge current: 250 ma
Sensitivity setting: 32

(1) Peak for formaldehyde
(2) Peak for methanol
(3) Peak for water

(3) Leakage

The system was tested at 30 psig for any possible leaks in the following way:

(i) Every accessible connection part was tested with snoop.

(ii) No indication of the gas flow through the rotameter as the valves in the downstream were closed.

(iii) There was no indication of a pressure drop in the system, even after two hours, when the inlet and outlet valves were closed.

(4) Operating Procedure

The operating procedure can be divided into two parts - one for start up and preparation and second for making the actual run.

(a) Start Up

(i) Check all the connections and tighten the loose ones. Test the system for any leaks.

(ii) Purge the feed line and the reactor with compressed air at 20 psig.

(iii) Charge the reactor with the weighted amount of fresh catalyst and cover it with a layer of glass wool to prevent the catalyst escape from the reactor.

(iv) Reassemble the reactor and check for any leaks. A careful attention is needed while handling the thermocouples.

(v) Clamp the reactor to place it upright in the center of the fluidized bed furnace and cover the top of the furnace to prevent the out flow of fluidizing sand.

(vi) Turn on the air stream for activation of the catalyst and later for the oxidation of methanol.

(vii) Turn on the power to the reactor heating elements and adjust the two "variac" transformed periodically until the desired temperature is attained. Approximately 36 hours will be required for the system to reach equilibrium from ambient temperature.

(viii) Switch on the various heating tapes for preheating the air, warming the feed line leading to the reactor, and the transport line for sampling gas from the separating column to the Gow Mac Cell.

(ix) Switch on the power for the hot inlet, sample injection block, oil bath, temperature controller in the Gow Mac Cell, and Fisher thermal stabilizer and set the required temperature.

(x) Turn on the departmental compressed air to fluidize the furnace bed at 8 psig and a flow rate of about 2 liters per minute.

(xi) Turn on the helium gas for Gas partitioner and Gas Chromatograph and adjust the helium flow rate at 60 c. c./min. and 80 c. c./min. respectively.

(xii) After the temperature and helium gas flow are stabilized, switch on detectors and recorders for the gas partitioner and gas chromatographs in order to check the base lines to be straight and stable.

(b) Run

(i) Clean the syringe and fill with methanol. Fix it on the infusion pump and insert the needle into the hot inlet. Check for the leakage around the rubber septum.

(ii) Place the liquid trap in position in an ice bath and turn on the water for condenser above the liquid trap.

(iii) Adjust the air flow rate in the rotameter. In case there is appreciable change in the atmospheric conditions, measure the air flow rate at the exit of the system by means of a wet test gas meter or a bubble meter and adjust the volumetric flow rate so as to give a required constant molal flow rate. Similar corrections are applied to helium gas flow rates as well.

(iv) Check the temperatures of the oil bath, and Gow Mac Cell in order to verify they are stablised at the required temperatures.

(v) Switch on the infusion pump and start feeding methanol to the reactor with the incoming air to the hot inlet.

(vi) Maintain the feed of air and methanol at their specified flow rates for one to two hours to obtain steady state conditions at the desired temperature.

(vii) Steady state conditions are checked firstly by observing the constant reactor temperature and secondly by analyzing the product gases in the Gas Partitioner periodically.

(viii) Replace a clean tube in the liquid trap quickly and collect the liquid products for 45 to 60 minutes. During this time introduce the gaseous products into the Gas Partitioner through the sampling valve to analyse the products 3 - 4 times.

(ix) Inject the liquid samples from the liquid trap into the Gas Chromatograph to analyze the liquid products.

(x) Continue the steady state run for another hour and analyze both the liquid and gaseous products again in the similar way.

(xi) During the run, rotameter reading, temperature and pressure setting are checked and noted.

(xii) Shut off the methanol feed pump and keep air flowing through the reactor for about 30 minutes, before making the next run.

(xiii) At the end of each day's operation, the preceding steps are reversed. In general, any change in the reactor temperature was made at this time, by adjusting the "variacs" controlling the power to the fluidized bed furnace.

(xiv) Periodically the gas chromatographic calibrations are checked to assure the stability of the columns.

D. REACTANTS AND CHEMICALS

Certified A. C. S. Spectranalyzed Methanol (Lot no. 795409-105, catalogue no. A-408) supplied by Fisher Scientific Company was used in the present study.

Compressed air supplied by Liquid Carbonic Canadian Corp. Ltd., in cylinders at a pressure of 2500 psig was used as the source of oxygen. The gas chromatograms of air showed air composition to be 20.95% oxygen, 79.00% nitrogen and 0.05% carbon dioxide. The moisture was removed by passing it through a drying tube containing indicating drierite.

The chemicals used in the preparation of the Gas Chromatographic column were: sucrose octa-acetate $C_{28}H_{38}O_{19}$, m.w. 678.59 (Eastman Kodak grade, Lot no. P4024, Canlab catalogue no. V-134), 40-60 mesh Columpak T (catalogue no. 587, Lot no. 724875) and methylene chloride(reagent grade) from Fisher Scientific Co. Ltd. Columns for the Gas Partitioner were made from 40-60 mesh molecular sieve 13X (Lot no. 62688), molecular sieve 5A (Lot no. 122369) supplied by Coast Engineering Laboratory, Redondo Beach, California; 30% DEHS on 60-80 mesh Columpak, (Fisher catalog no. 11-134-63A), 30% HMPA on 60-80 mesh Columpak (Fisher 11-130-57) and 60-80 mesh uncoated chromosorb made by Johns-Manville Products Corp.

The chemicals used for the preparation of the catalysts were: ammonium molybdate, $(NH_4)_6 MO_7O_{24} \cdot 4H_2O$ supplied by BDH Chemical Ltd, Poole England (Anala R grade), purified Ammonium meta-vanadate (NH_4VO_3), (Fisher catalog no. A-714) and Vanadium Pentoxide (Fisher catalog no. V-7, lot no. 7 65287).

The chemicals used in the qualitative tests for the products were sodium bisulphite $NaHSO_3$ (BDH Canada Ltd, lot no. 35531), Hydrochloric acid (Fisher catalog 50-A-55, lot no. 786486) phenolphthein, $C_{20}H_{30}O_4$ (Fisher catalog no. P-79), thymolphthalein, $C_{28}H_{30}O_4$ (Fisher catalog no. T-119) and potassium hydroxide, KOH, (analytical reagent, B.D.G., catalog no. 280-P).

Helium used as carrier gas was supplied by Canadian Liquid Air Ltd.. Nitrogen was supplied by Linde Co. Carbon monoxide and carbon dioxide for calibration of the Gas Partitioner were supplied by Matheson Co.

IV. RESULTS

The experimental data was obtained by means of a quasi-isothermal fixed bed reactor at atmospheric pressure. The steady state was inferred from the operating conditions and the product analysis. The effects of various variables, namely, methanol to air ratio in the feed mixture, $\bar{R}$, reaction temperature , T, and the ratio of the catalyst weight to methanol feed rate, W/F, on the conversion of methanol X, yield of formaldehyde, y and the selectivity, s of the catalyst for formaldehyde formation were studied.

The conversion (x) is defined as the ratio of moles of methanol reacted per hour to the moles of methanol fed per hour into the reactor. The yield is defined as the ratio of the moles of formaldehyde formed per hour to the methanol feed rate in moles per hour. The ratio of formaldehyde formed to the sum of formaldehyde and carbon oxides formed has been defined as selectivity (s).

During the experiments, though the methanol feed rate was maintained constant through a syringe pump, different feed ratios were obtained by adjusting the air flow rate. The W/F ratio was varied by changing the amount of catalyst in the reactor.

The effect of different compositions of the vanadium-molybdenum oxide catalyst on the conversion and yield was first studied, to select a suitable catalyst composition for a detailed kinetic study. The W/F ratio and methanol to air ratio were kept constant at 27.5 gm-hr/mole and 8 percent respectively. Figures 4-1 to 4-4 show the

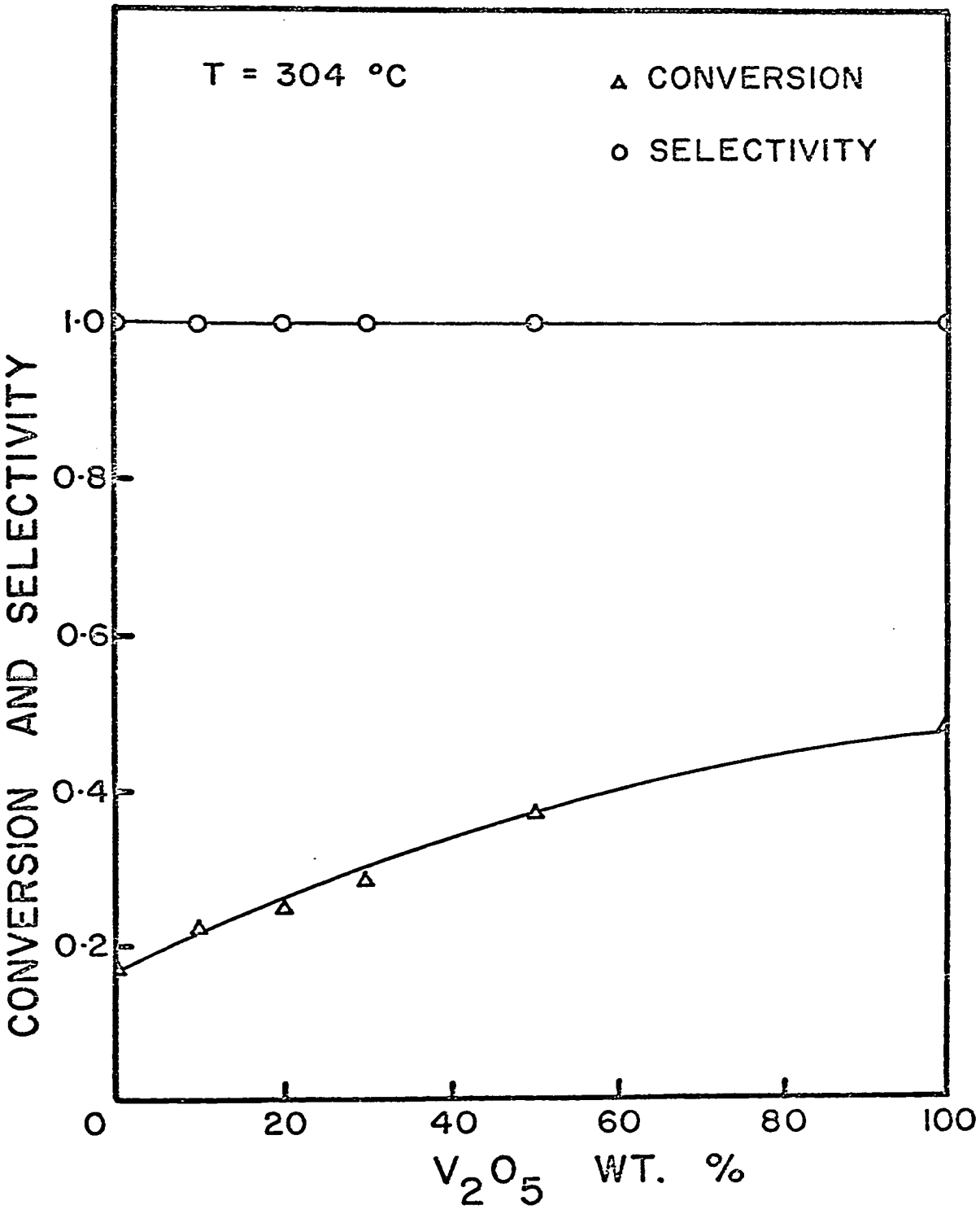

Fig. 4-1 Effect of Catalyst Composition on conversion and selectivity at 304° C

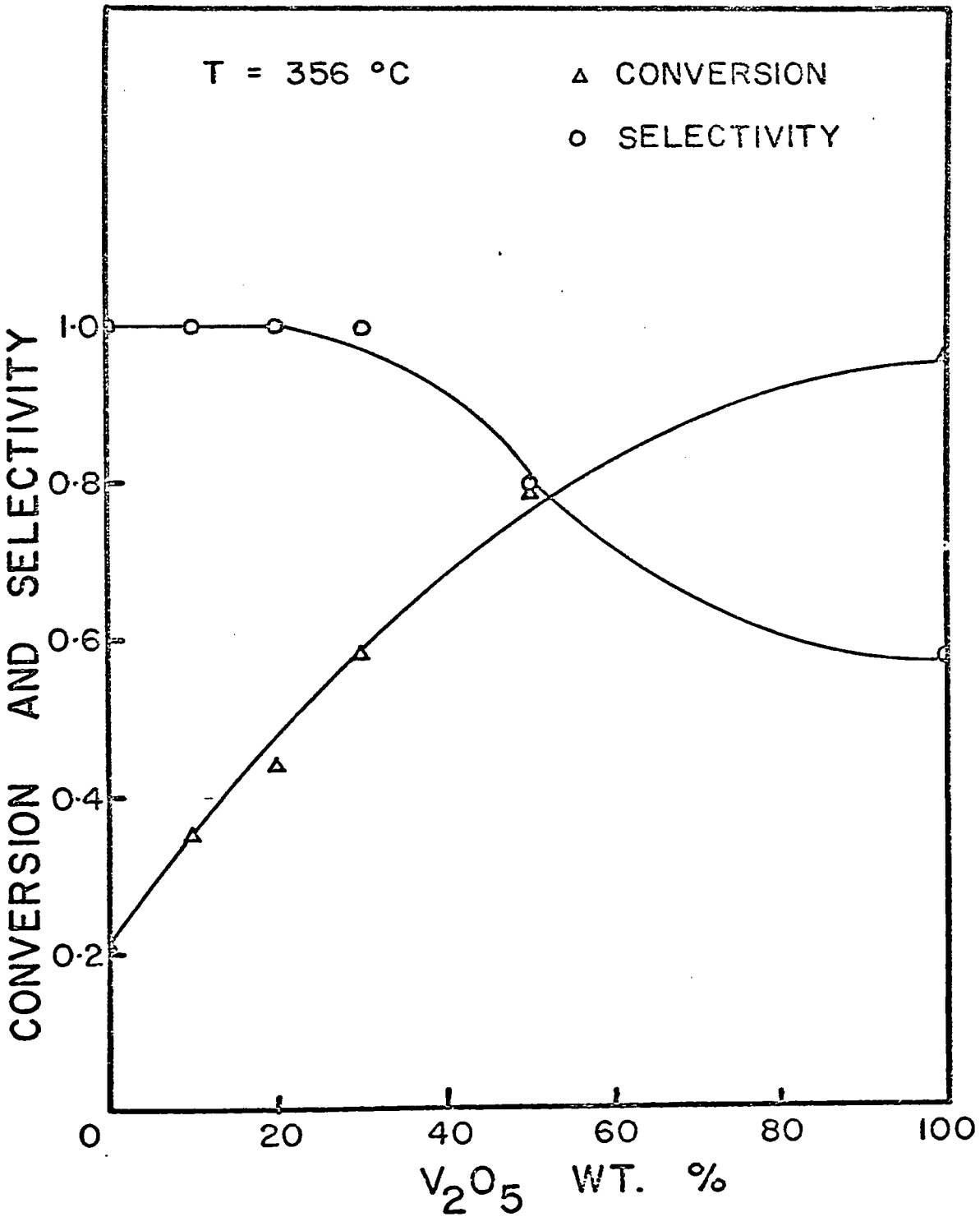

Fig. 4 2 Effect of Catalyst Composition on conversion and selectivity at 356 C

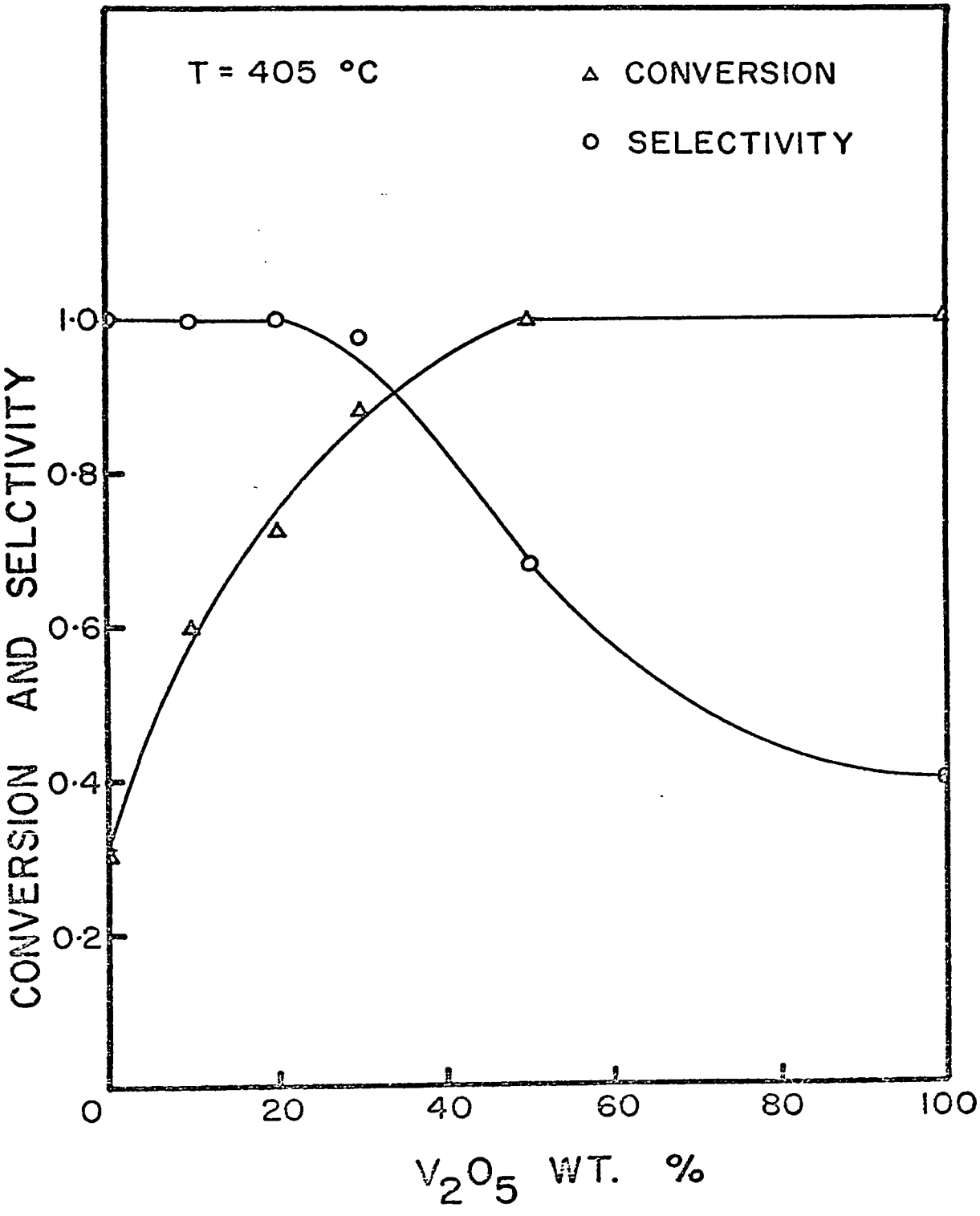

Fig. 4-3 Effect of Catalyst Composition on Conversion and Selectivity at 405° C

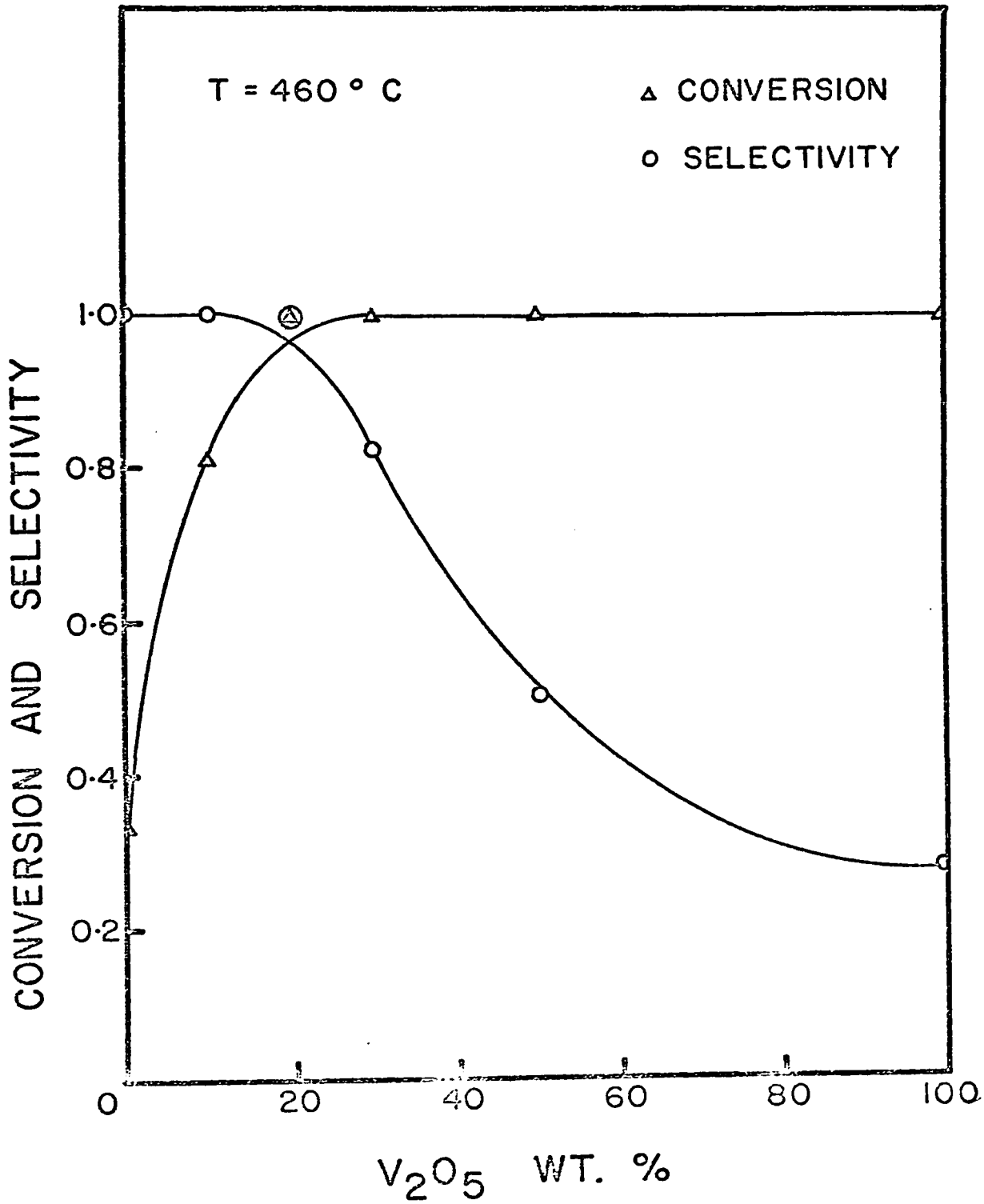

Fig. 4.4 Effect of Catalyst Composition on Conversion and Selectivity at 460° C

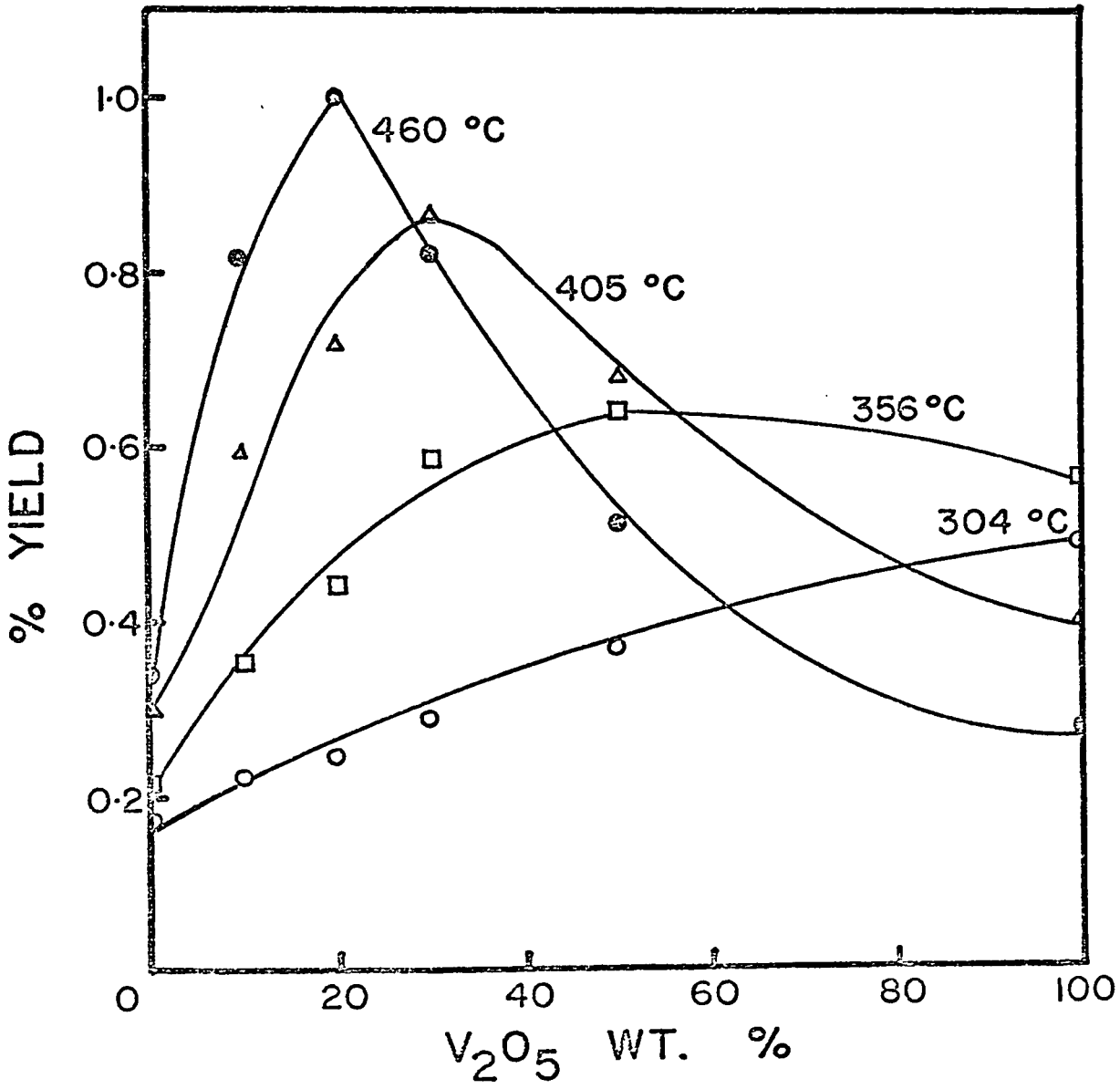

Fig. 4-5 Effect of Catalyst Composition on Yield of Formaldehyde

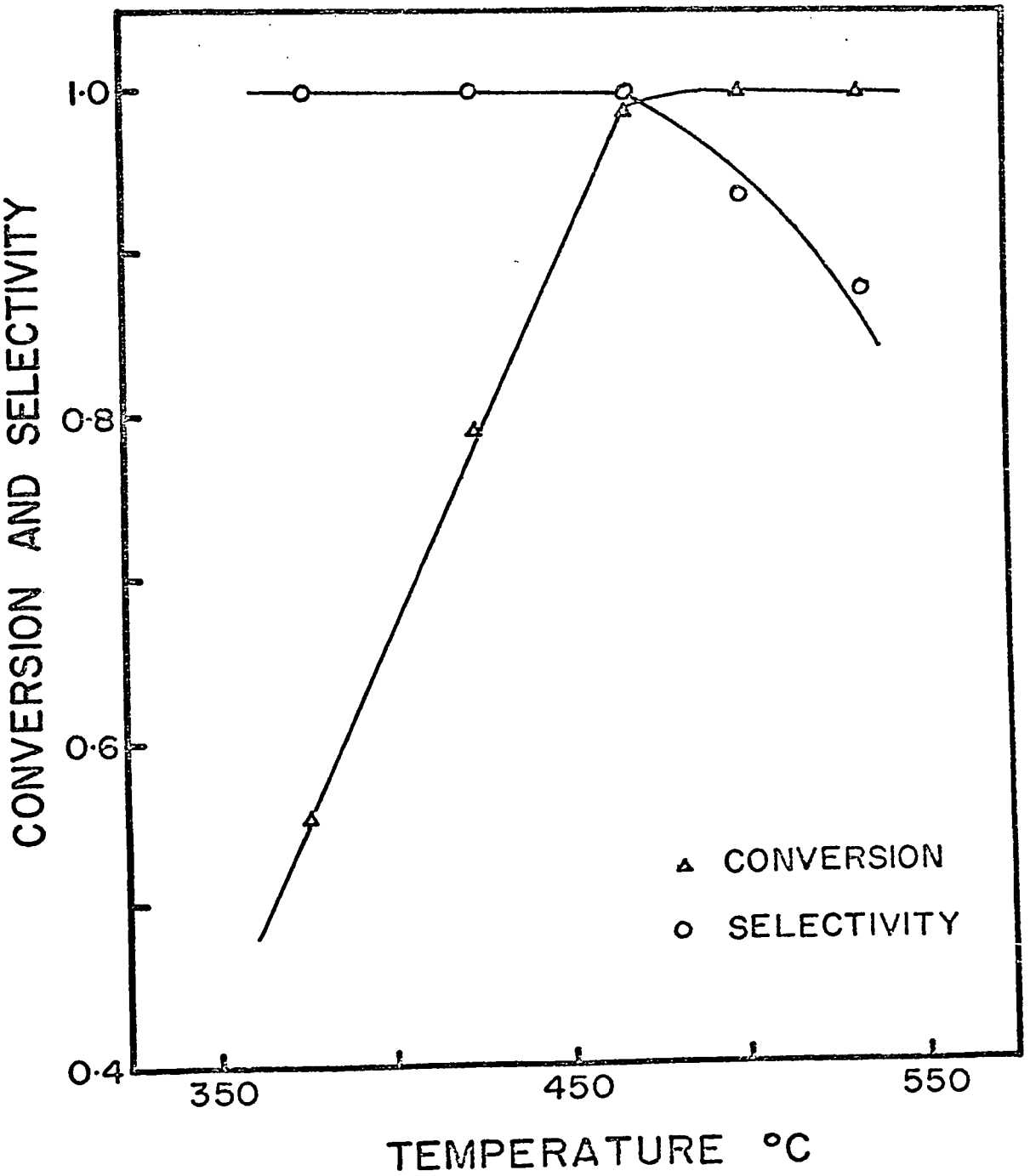

Fig. 4 6 Effect of Temperature on Conversion and Selectivity for W/F = 31.7 gm.hr./mole and 8% methanol in air

effect of catalyst composition on conversion, and selectivity at different temperatures. Though the selectivities for molybdenum trioxide, vanadium pentoxide and for their various mixtures was found to be hundred percent at 304° C, the conversions were always low. However, as the V_2O_5 content increased, the conversion also increased. The activity of all the catalysts increased with the rise in reaction temperature. At high temperatures, the activity of catalyst sharply increased with the increased amount of V_2O_5 up to 20% without any loss in the selectivity. For catalyst containing more than 20% V_2O_5 very high conversions were always obtained though the selectivity of the catalyst steeply decreased with the formation of undesired carbon oxides in the products. Figure 4-5 shows the effect of catalyst composition and temperature on the yield of formaldehyde. The maximum yield of nearly 100% was obtained at 460° C with a catalyst containing 20% vanadium pentoxide and 80% molybdenum trioxide by weight. Detailed kinetic studies were hence, carried with vanadium-molybdenum oxide (20:80) catalyst.

The effect of temperature on the conversion, yield and selectivity was investigated in the temperature range of 375-531° C and the results are given in Appendices B and C. Figure 4-6 shows the effect of temperature at a W/F ratio of 31.70 and methanol to air ratio of 8 percent. Both conversion and yield increased with increasing temperature up to 466° C and selectivity remained one hundred percent. At temperatures above 466° C, the conversion increased to 100% but the yield of formaldehyde decreased due to decreased selectivity of the catalyst.

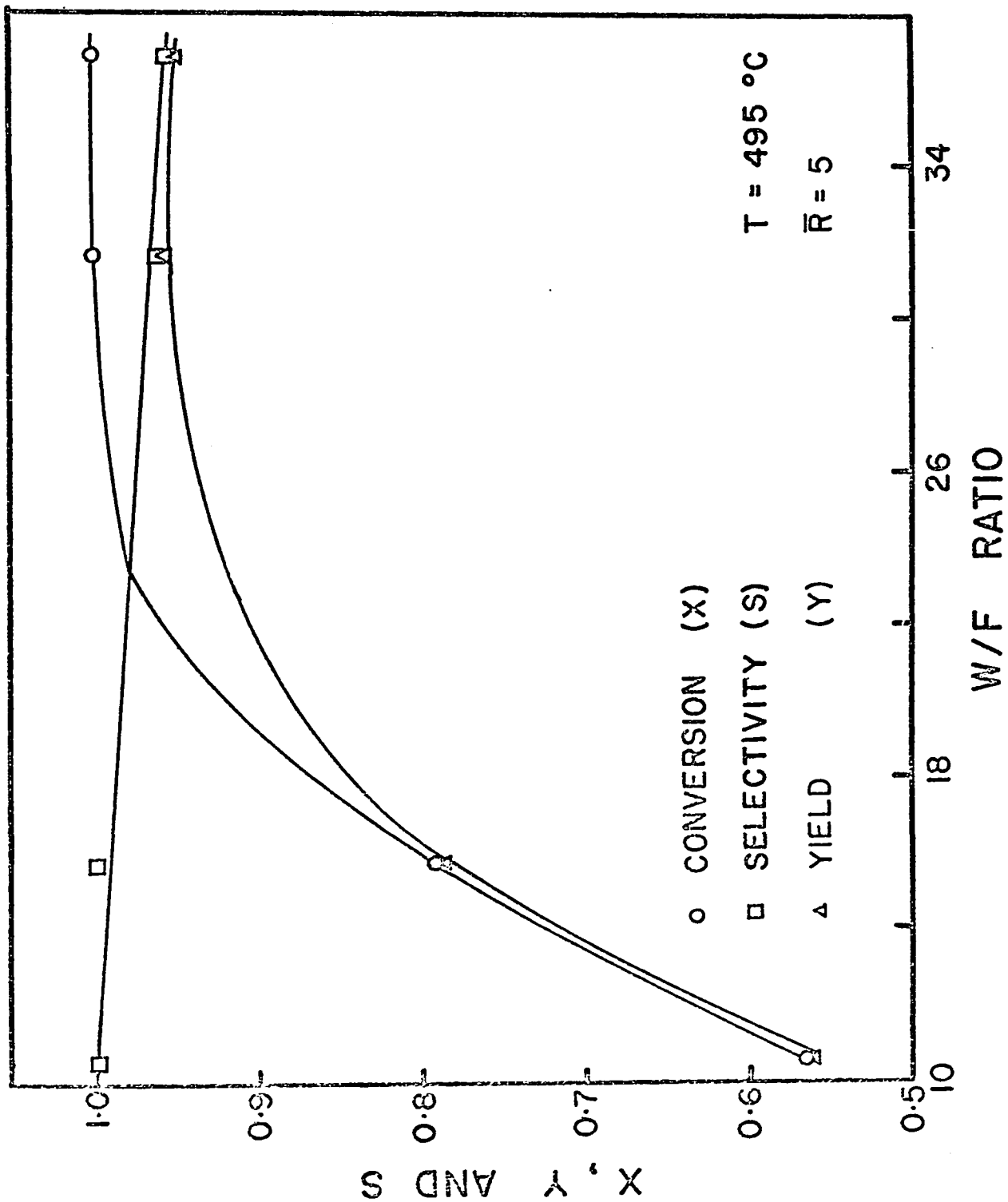

Fig. 4-7 Effect of W/F (gm. hr. /mole) on Conversion, Selectivity and Yield of formaldehyde at 495° C for R̄ = 5.0

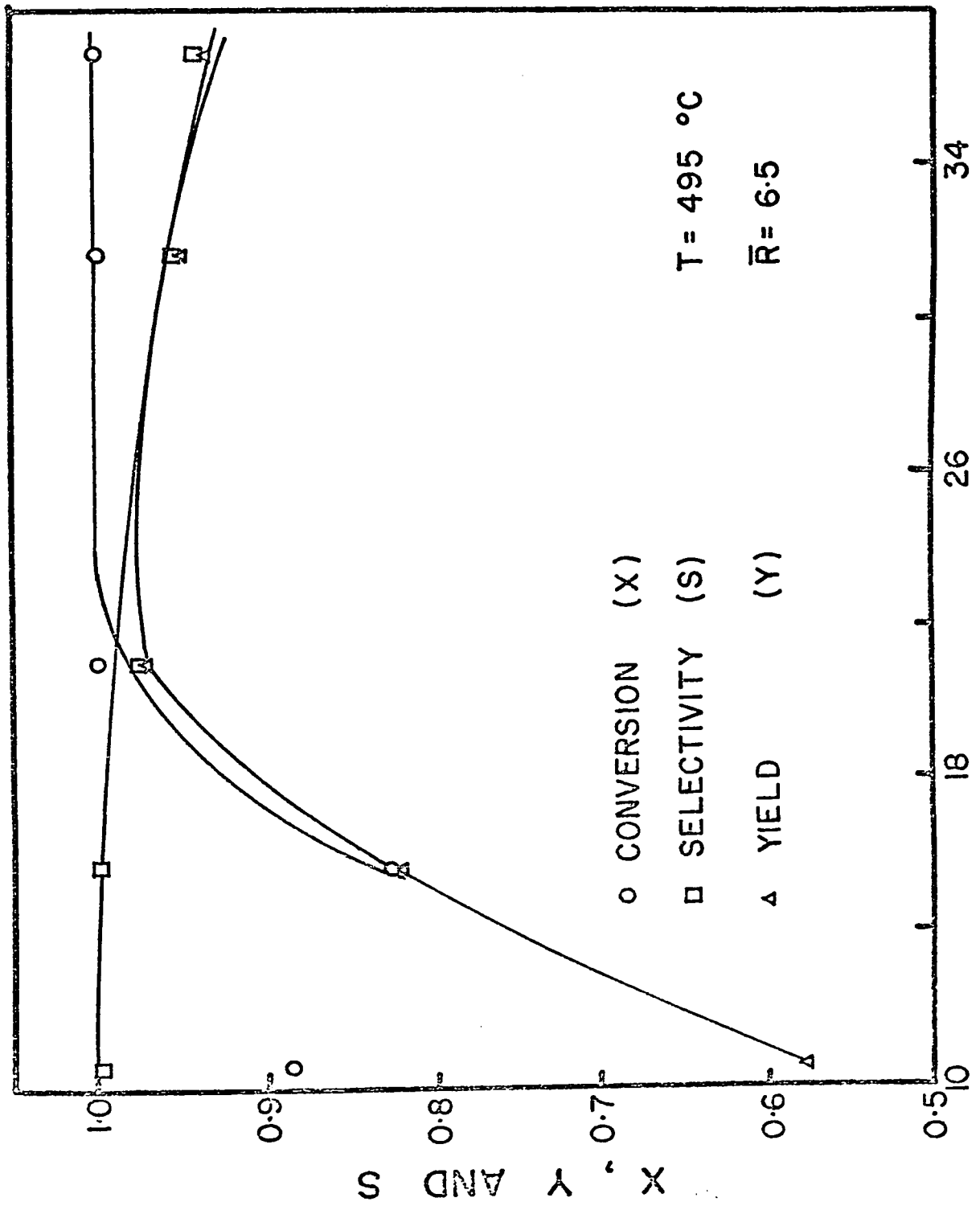

Fig. 4-8 Effect of W/F (gm.hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 495° C, for $\bar{R}$ = 6.5

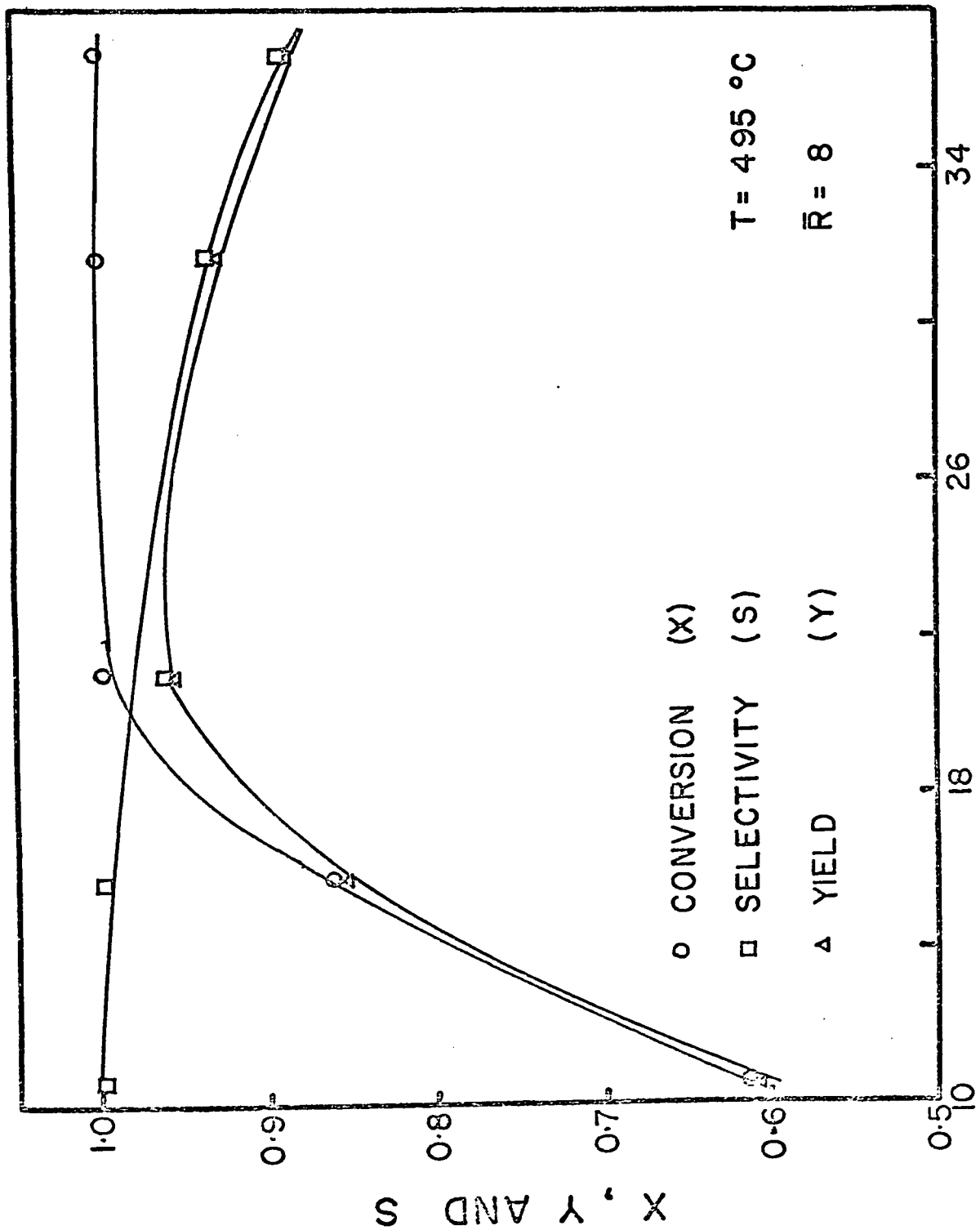

Fig. 4-9 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 495° C for $\bar{R}$ = 8.0

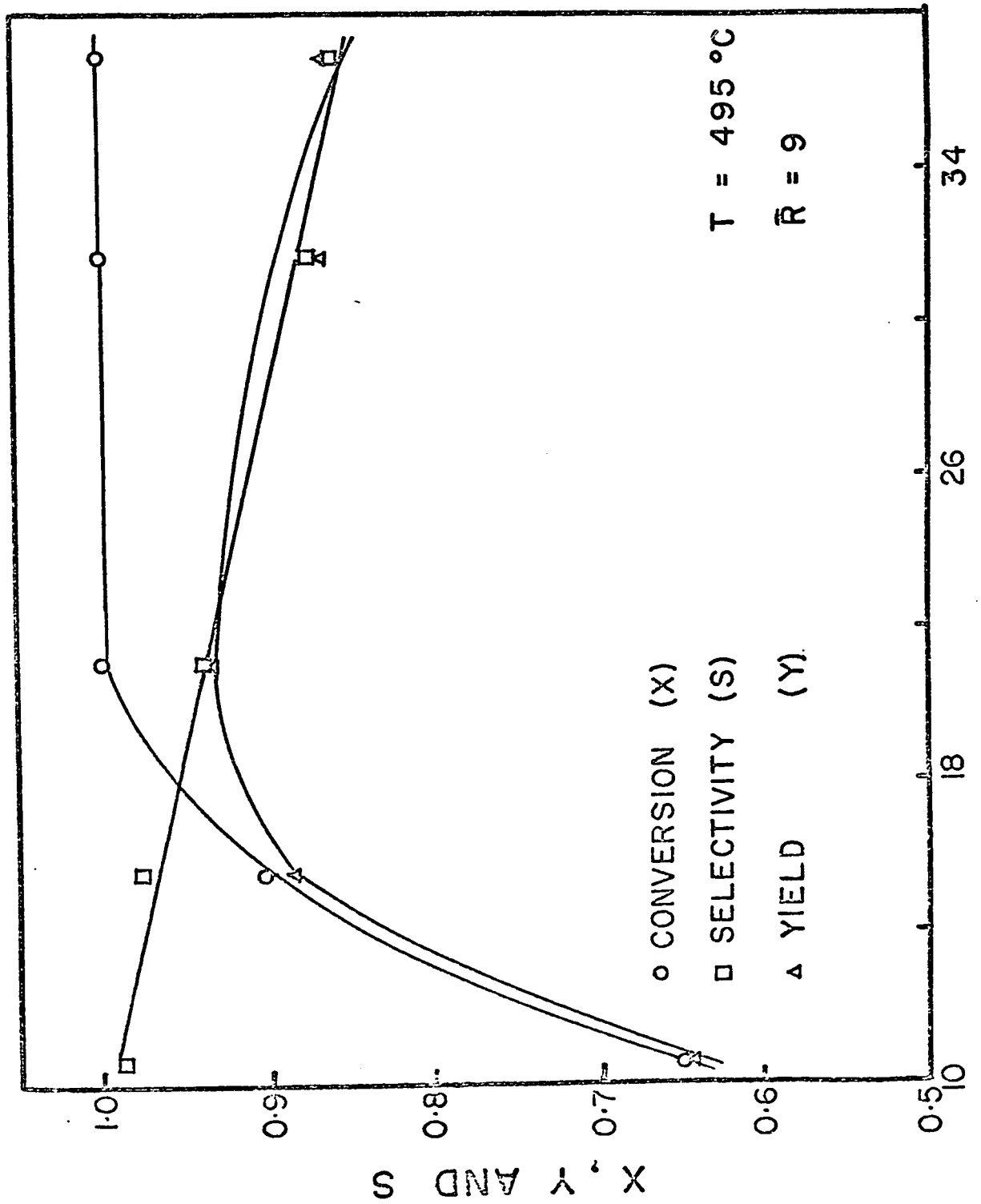

Fig. 4-10 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 495 C for $\bar{R}$ = 9 0

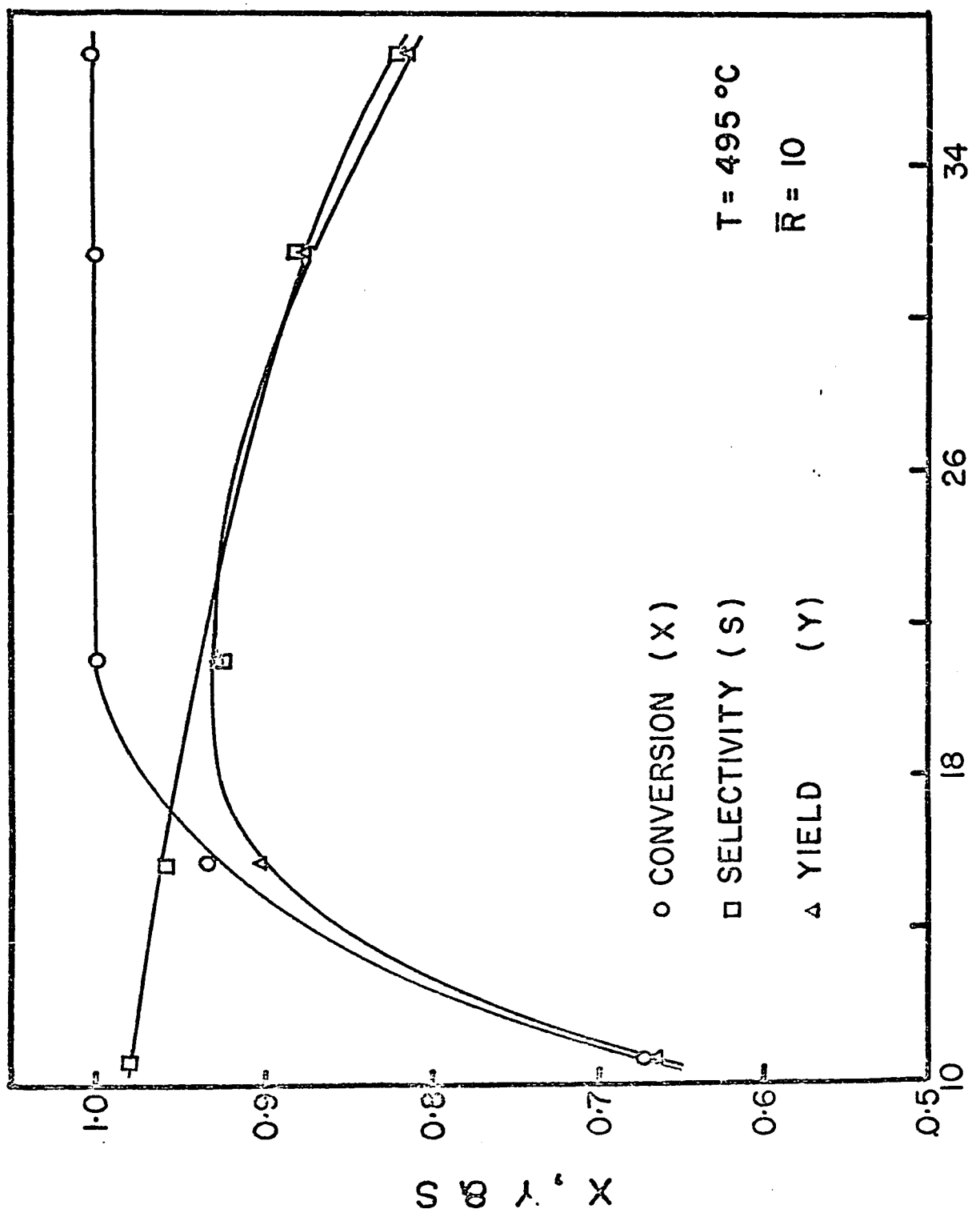

Fig. 4-11 Effect of W/F (gm. hr. /mole) on Conversion, Selectivity and Yield of Formaldehyde at 495°C for $\bar{R}$ = 10.0

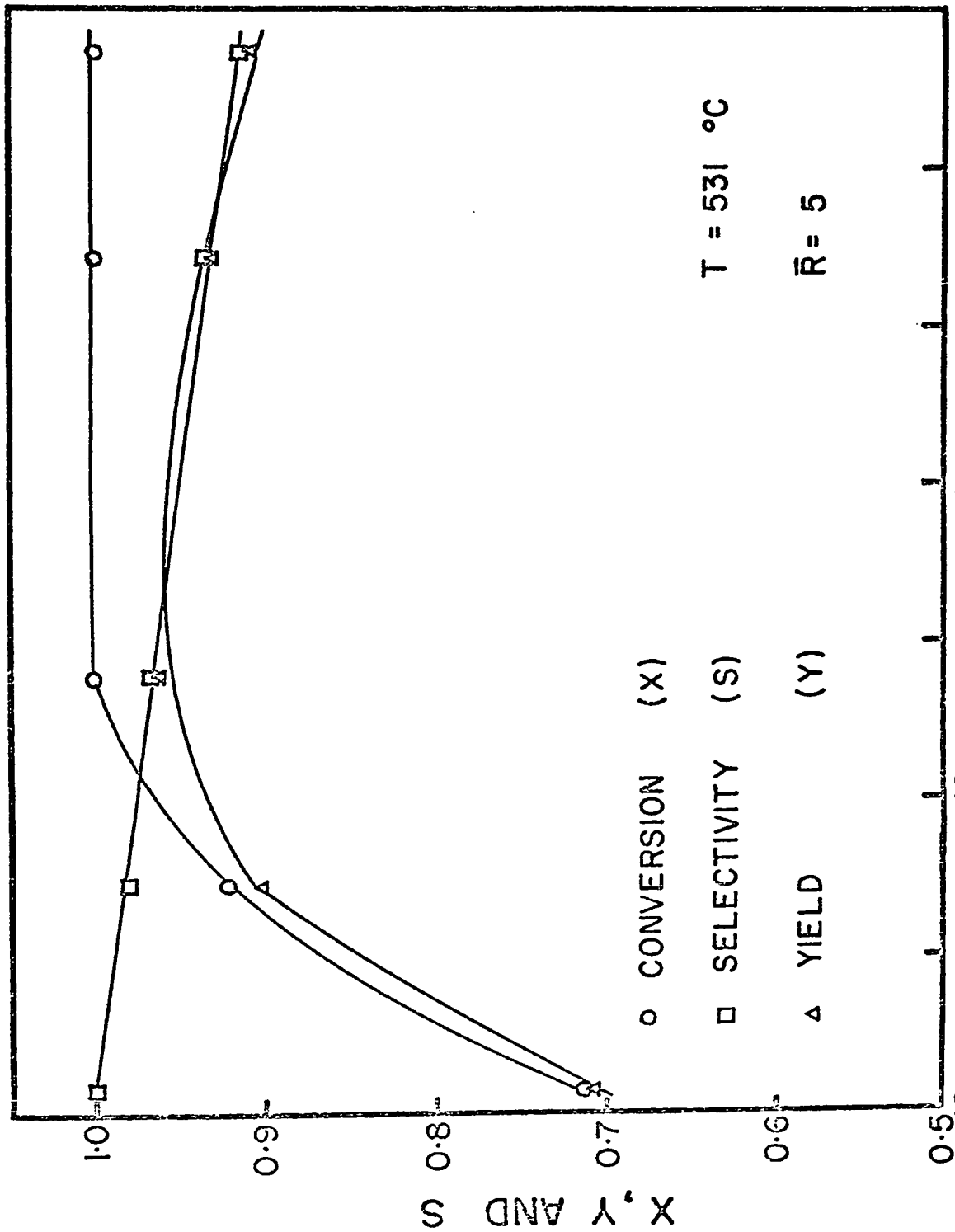

Fig. 4-12 Effect of W/F (gm. hr. /mole) on Conversion, Selectivity and Yield of Formaldehyde at 531° C for $\bar{R}$ = 5.0

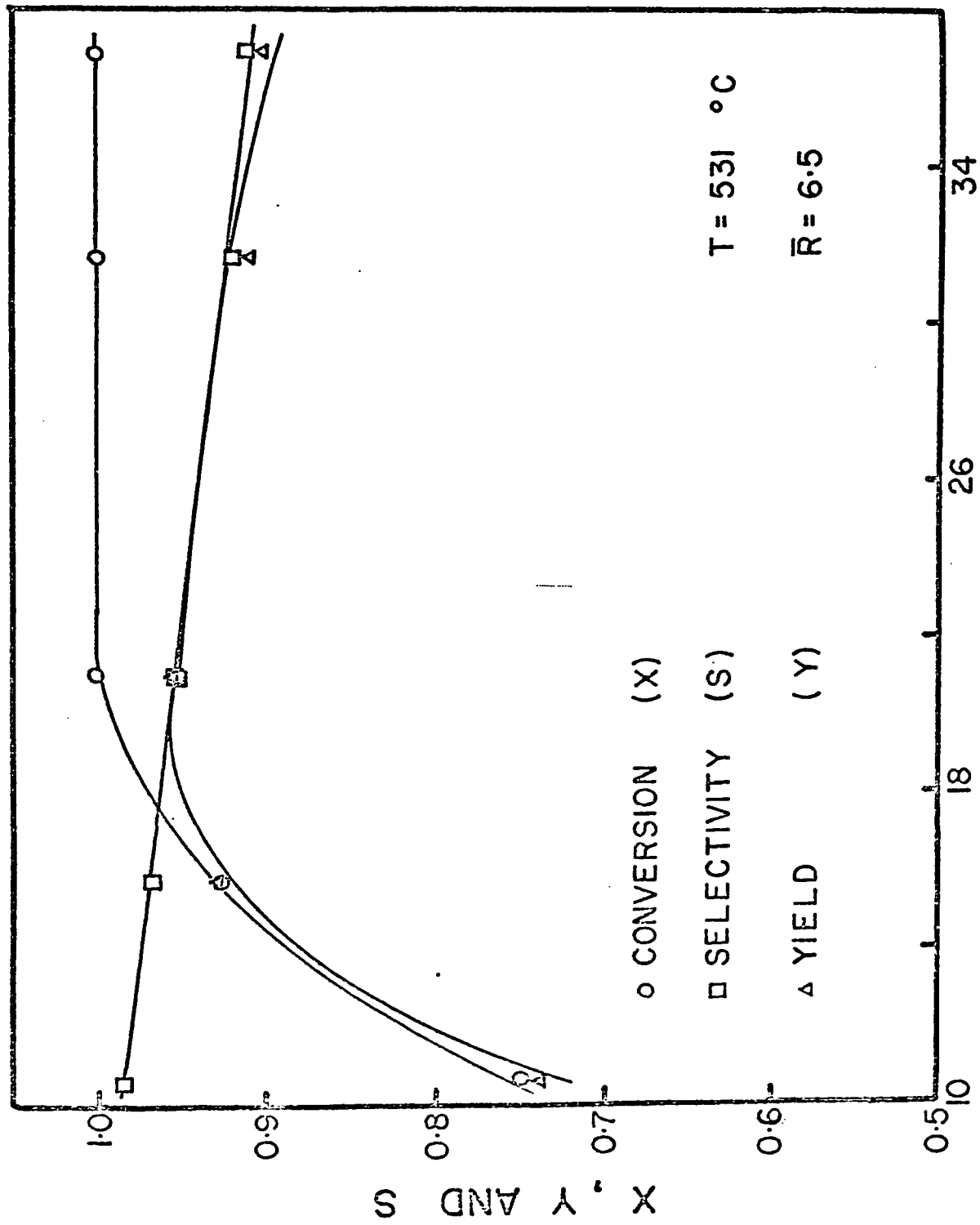

Fig. 4-13 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at T = 531 C for R̄ = 6.5

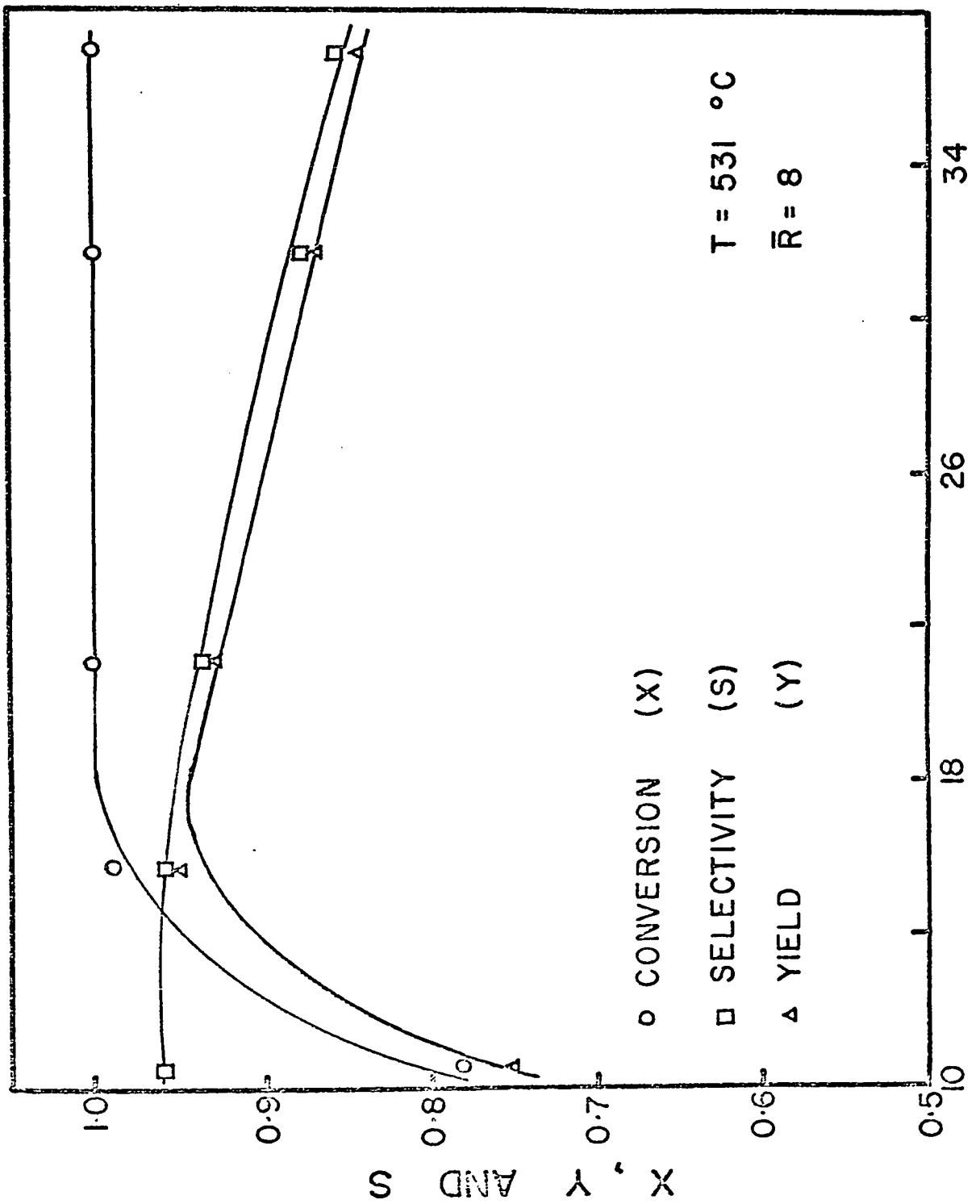

Fig. 4-14 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 531°C for $\bar{R}$ = 8.0

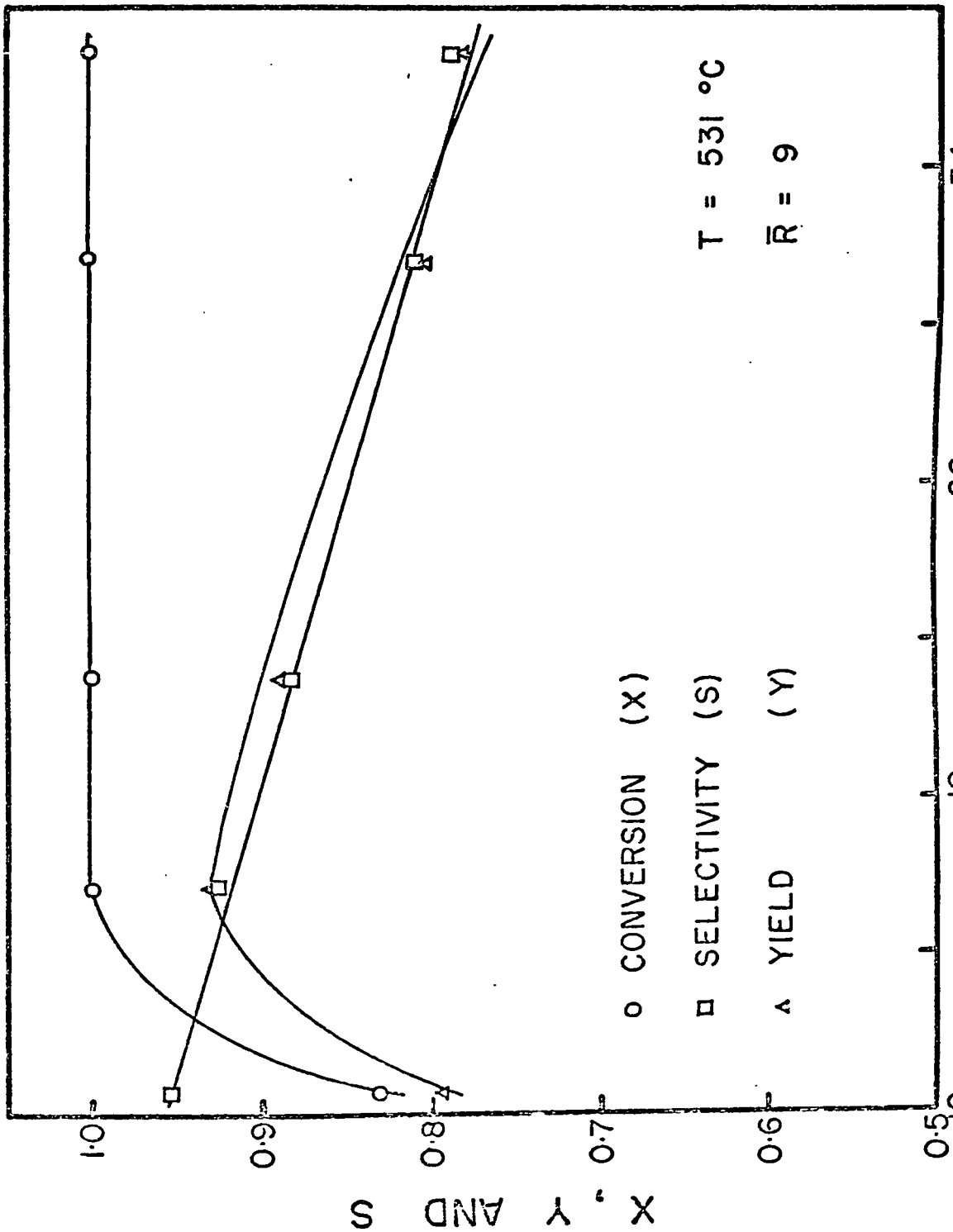

Fig. 4-15 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 531 °C for $\bar{R}$ = 9.0

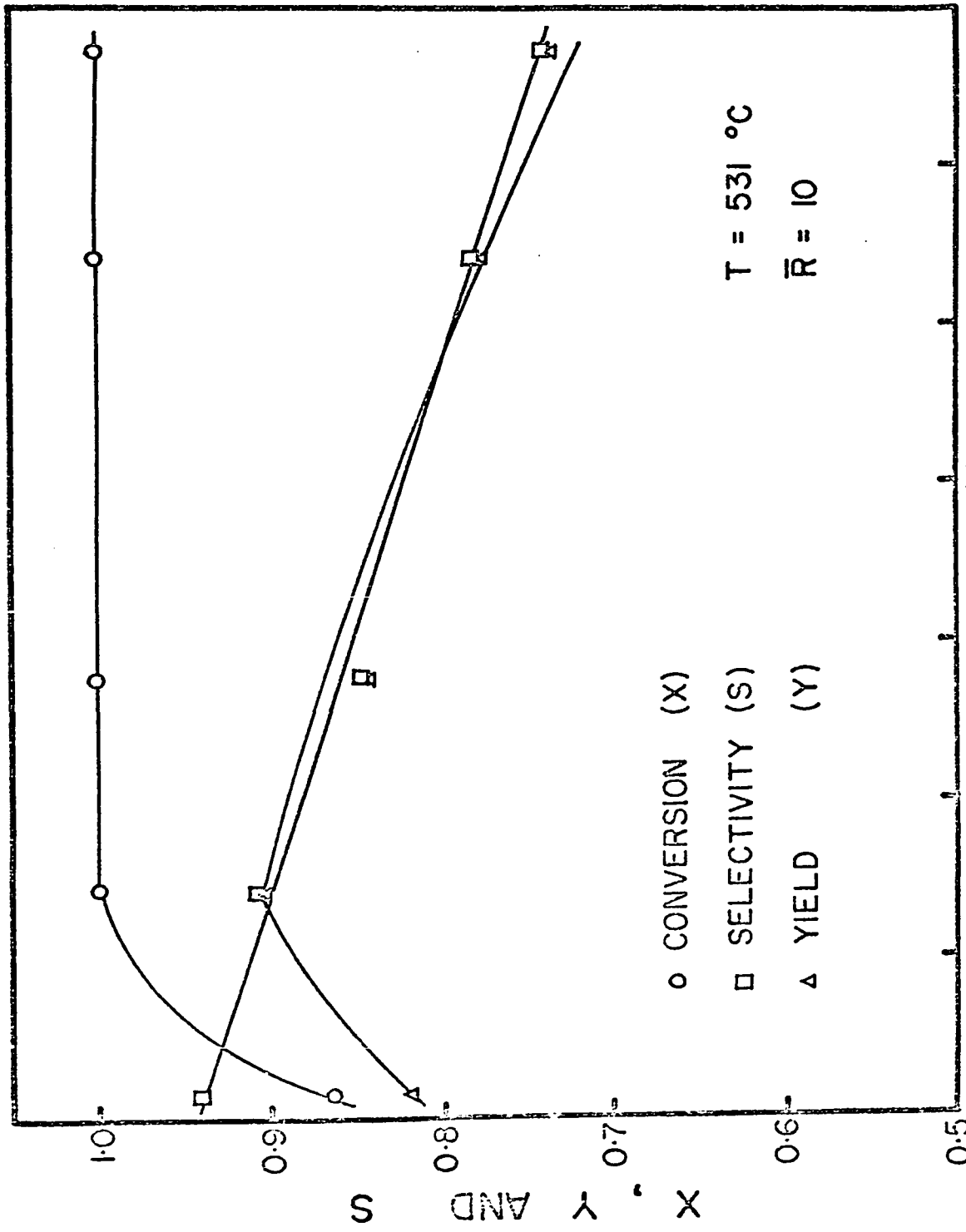

Fig. 4-16 Effect of W/F (gm. hr./mole) on Conversion, Selectivity and Yield of Formaldehyde at 531° C for $\bar{R}$ = 10.0

The effect of various W/F ratios on the conversion of methanol and the yield of formaldehyde was investigated in the range 10.6 to 36.9. Experimental results of the effect of W/F ratio on the conversion at temperatures 375°, 422° and 466° are shown by circles in the Figures 5-1 to 5-3, where the selectivity of the catalyst remained 100%. The effects of W/F ratio on conversion, selectivity and yield for various feed ratio at 495° C and 531° C are shown in Figures (4-7 to 4-16). In general, with the increase of W/F ratio, though the conversion increased up to 100%, the selectivity of the catalyst and the yield of formaldehyde decreased. It was also observed that the conversion increased with increased amounts of methanol in the reactant feed mixture. The selectivity was also found to decrease with the increased methanol content in the feed at temperatures higher than 466° C. At 466° C, for W/F ratios grater than 21.12 the selectivity of the catalyst dropped below 100%.

V. KINETIC ANALYSIS OF DATA

The determination of the relationship between the reaction rate and the operating variables is an important aspect in the design of a catalytic process. The theoretical development of the reaction mechanism requires a number of postulates due to the complex nature of gas-solid catalytic system. It is customary to correlate and derive a rate expression in terms of partial pressure of the reactants and the products based on the well known Langmuir-Hinshelwood Theory (76).

(A) Steps in heterogeneous catalytic reactions:

A logical starting point for the development of Langmuir-Hinshelwood approach is to consider the sequence of physical and chemical steps which occur in a heterogeneous reaction system. The over-all process involving a non-porous catalyst can be broken into five steps:

(1) Transport of the reactants from the bulk-fluid phase to the solid-fluid interface.

(2) Adsorption of reactants (one or more) on the solid surface.

(3) A surface reaction between the adsorbed reactants or one of the gaseous reactants and an adsorbed reactants on the catalyst surface.

(4) Desorption of products (one or more) from the surface to the fluid-solid interface.

(5) Transport of the products from the interface to the bulk-fluid stream.

With porous catalysts,internal diffusion through the pores of the catalyst may also be involved along with external diffusion (step 1 and 5) in the fluid phase surrounding the catalyst particle. In this event, two additional steps should be added to the list : (1a) internal diffusion of reactants along the pores; (5a) internal diffusion of products along the pores to the outer surface. Normally, these steps are eliminated by designing the catalyst so that all active centers are easily accessible.

If the main velocity is sufficiently high so that the main gas stream becomes a highly turbulent phase, then the laminar sublayer tends to disappear and the partial pressure in the main gas stream becomes equal to that at the interface. Under these conditions, step (1) and (5) do not exist. However, the chemical steps 2, 3 and 4 contribute significant resistances, which can not be reduced by altering physical conditions and hence are the most important ones to be considered. Inclusion of only these three steps results in equations of high complexity. Usually only one of these three steps offers a much higher resistance than the other two, and is therefore considered to be rate controlling or rate determining step, while the other two are considered to be at equilibrium.

(B) Factors affecting the Rate Mechanism

In a chemical kinetic study, several experimental errors might be encountered. Hougen has pointed out the following sources of errors which could seriously affect the evaluation of rate equation and the interpretation of rate data:

(1) Variation in catalyst activity.
(2) Neglect of external resistance to mass and heat transfer.
(3) Use of catalyst particles with effectiveness factor differing from unity (internal diffusion).
(4) Appreciable departure from plug flow.
(5) Neglect of pressure drop due to flow.
(6) Side reactions.
(7) Homogeneous reactions and reactions catalyzed by the reactor wall.

In this section, the sources of these errors, their evaluation and elimination are discussed in detail.

(1) Variation in catalytic activity

The activity of a catalyst refers to its behavior in terms of degree of conversion or reaction rate under given conditions of temperature, feed rate of reactant and concentration. In this study, the activity of the catalyst remained fairly constant during the entire run of experiments. This was confirmed by repeating a standard run after every 5 or 10 runs in each of the experimental sets. Every set of experiments was carried out with different amounts of catalyst.

(2) External resistance to heat and mass transfer

The partial pressure and temperature at the gas-solid interface are usually assumed same as those in the ambient stream to simplify the correlation of experimental data with the reaction rate. However, these values in the bulk stream and at the interface may appreciably differ because of the resistances imposed by heat and mass transfer. It is therefore necessary to evaluate and eliminate these resistances. The effect of heat and mass transfer can be visualised from the following:

$$r_{m_A} = k_{G_A} a_m \phi (P_A - P_{A_i}) \qquad (5\text{-}1)$$

and

$$g_{m_A} = r_{m_A} \Delta H_A = h_G a_m \phi (T - T_i) \qquad (5\text{-}2)$$

where

r_{m_A} = rate of reaction or mass transfer of A per unit mass of catalyst.

g_{m_A} = heat transfer due to heat of reaction per unit mass of catalyst.

k_{G_A} = mass transfer coefficient for component A.

h_G = heat transfer coefficient per unit exterior surface of catalyst particle.

a_m = external surface area of catalyst per unit mass.

ϕ = shape factor, equal to 1.0 for spheres, 0.90 for irregular granules.

P_A = partial pressure of component A in the ambient stream.

P_{A_i} = partial pressure of component A at the catalyst surface.

T = temperature of the ambient stream.

T_i = temperature of the catalyst.

The transfer coefficients h_G and k_{G_A} can be calculated from the dimensionless Chilton-Colburn[77] j - factors.

$$j_d = \left(\frac{k_G p_{f_A}}{G_m}\right)\left(\frac{\mu}{p D_{AM}}\right)_f^{2/3} \qquad (5\text{-}3)$$

$$j_h = \left(\frac{h_G}{C_p G_m}\right)\left(\frac{C_p \mu}{K}\right)_f^{2/3} \qquad (5\text{-}4)$$

where,

p_{f_A} = film pressure factor, defined by equation (5-10)

μ = viscosity of the gas.

ρ = density of the gas.

D_{AM} average diffusion coefficient of component A.

C_p = specific heat of the gas.

G_m = the molal velocity of gas flowing based upon the total cross-sectional area.

K = thermal conductivity of the gas.

$\frac{C_p \mu}{K}$ = the dimensionless Prandtl number.

$\frac{\mu}{\rho D_{AM}}$ = the dimension Schmidt number.

subscript f = properties at average condition of the gas film.

Gausson, Thodes and Hougen [78] developed expressions for j_h and j_d in the range of Reynolds numbers above 350 and Wilke and Hougen[79] recomended equations for Reynolds numbers less than 350.

for $\frac{D_p G}{\mu} < 350$

$$j_h = 1.06 \left(\frac{D_p G}{\mu} \right)^{-0.41} \quad (5\text{-}5)$$

$$j_d = 0.09 \left(\frac{D_p G}{\mu} \right)^{-0.41} \quad (5\text{-}6)$$

for $\frac{D_p G}{\mu} > 350$

$$j_h = 1.95 \left(\frac{D_p G}{\mu} \right)^{-0.51} \quad (5\text{-}7)$$

$$j_d = 1.82 \left(\frac{D_p G}{\mu} \right)^{-0.51} \quad (5\text{-}8)$$

where,

$\frac{D_p G}{\mu}$ = modified Reynolds number.

G = mass velocity of flow based on the total crossectional area of the bed, mass per unit time per unit area.

D_p = effective particle diameter = $\frac{a_p}{\pi}$

π = total pressure.

a_p = average surface per particle.

The film pressure factor in equation (5-3), is defined as follows:

for reaction

$$aA + bB = rR + sS \tag{5-9}$$

$$P_{f_A} = \frac{(\pi + \delta_A P_A) - (\pi + \delta_A P_{A_i})}{\ln\left(\frac{\pi + \delta_A P_A}{\pi + \delta_A P_{A_i}}\right)} \tag{5-10}$$

where

$$\delta_A = \frac{r + s + a + b}{a} \tag{5-11}$$

If the ratio $(\pi + \delta_A P_A) \mid (\pi + \delta_A P_{A_i})$ is less than 1.2, the arithmatic mean is sufficiently accurate for practical purposes.

The mathematical procedure for calculating the temperatures and partial pressures of gases at the surface of catalyst particles for flow reactions taking place in fixed bed has been described by Yoshida et al. [78]. This procedure includes the effect of gradients of temperature and pressure inside catalyst paticles.

The temperature drop (ΔT) and the partial pressure drop of component A (Δp_A) from the catalyst surface to the ambient stream may be obtained from the following relations:

$$\Delta T = \mathcal{Q} \, (j_h)^{-1} \, (P_r)_f^{2/3} \tag{5-12}$$

$$\frac{\Delta p_A}{p_A} = \frac{\Delta Y_A}{} = R \, (j_d)^{-1} \, Y_{f_A} \, (Sc)^{2/3} \tag{5-13}$$

where,

$$\mathcal{Q} = \frac{r_{m_A} \, \Delta H_A}{a_m \, \Phi \, C_p \, G_m} \tag{5-14}$$

ΔH_A = molal heat of reaction of component A.

P_r = Prandtl number = $\frac{C_p \mu}{K}$

$$R = \frac{r_{m_A}}{a_m \, \Phi \, G_m} \tag{5-15}$$

Sc = Schmidt number = $\frac{\mu}{\rho \, D_{AM}}$

$$Y_{f_A} = \frac{P_{f_A}}{\pi}$$

The values of j - factors to be used in this procedure were recorrelated with Reynolds number $\left(\frac{G}{a_v \Phi \mu}\right)$ as follows:

for $0.01 < Re < 50$

$$j_d = 0.84 \ Re^{-0.51} \tag{5-16}$$

for $50 < Re < 1,000$

$$j_d = 0.57 \ Re^{-0.41} \tag{5-17}$$

and

$$j_h = 0.076 \ j_d \tag{5-18}$$

The terms Θ and ΔT have the dimensions of temperature and all other terms are dimensionless. From the data of many investigators, Yoshida et al [78] concluded that R and Θ are the most significant factors in controlling the pressure drop ratio and the temperature drop respectively.

It can be also seen that both the temperature and partial pressure differences across the gas film are proportional to $r_A D_p^{n+1} G_m^{n-1}$. Since n is a fraction (0.51 or 0.41), it is possible to eliminate the heat and mass transfer resistance effectively by decreasing the particles size and increasing the gas flow rate.

A sample calculation based on the method of Yoshida et al is shown in Appendix (G). The partial pressure gradient was found to be of the order of 0.001 and temperature difference across the gas film was found to be less than 1° C. Hence, these effects could be neglected.

(3) Internal Diffusion and Effectiveness Factor:

As most of the catalysts are porous, their external surface area constitutes a small fraction of the total surface area on which the reaction takes place. Most of the reaction occurs on the inner surface of the porous structure. The diffusion of reactant into and of the product out of them could be important factors in controlling reaction rate. Two kinds of diffusion in pores are possible - bulk or molecular diffusion, and Knudsen diffusion, depending on whether the mean free path between intermolecular collisions is small or large compared with the pore radius. For most conditions of operation of catalytic reactors, the pore diffusion is of the Knudsen type. Molecular diffusion predominates only at high pressure or at atmospheric pressure with catalyst having very large pore (> 5000 °A radius). Furthermore, the effect of molecular diffusion in this investigation was minimised by using high gas velocity stream passing through the catalyst bed.

The effect of Knudsen diffusion is evaluated from the knowledge of effectiveness factor of the catalyst. This factor is defined as the ratio of the actual reaction rate per unit mass of catalyst to

the rate which would exist if the concentration at all interior interfaces were same as those at the gross exterior surface [79]. Although much efforts have been made to correlate the effectiveness factor with the physical properties of the system, its value can be estimated for only relatively simple cases, by a method [79] developed by Thiele. It is desirable to obtain kinetic data under such conditions, that the value of effectiveness factor approaches unity, when the reaction rate at all interior surfaces is the same as that at the exterior surfaces. This is generally accomplished by decreasing the particle size and using catalyst with large and well interconnected pores. The use of small particle size (40-60 mesh) thus eliminated the possibility of the Knudsen diffusion in the pores controlling the reaction rate.

(4) Appreciable Departure from Plug Flow

In a steady-state flow system the following relationship between the space velocity and conversion is obtained assuming a flat velocity profile (plug flow) in the reactor tube:

$$\frac{W}{F} = \int_o^x \frac{dx}{r} \qquad (5\text{-}19)$$

where,

r = reaction rate moles/(mass of catalyst)(time)

x = conversion, moles per unit mole of feed.

W = mass of catalyst in the reactor

F = feed rate, moles per unit time.

In an investigation made by Smith et al [80, 81], the flow patterns in the packed beds were found to be affected by the packing shape, packing depth, the position of flow, the packing size and the tube size. According to their experimental results, the divergence from a flat profile increased as the packing size increased and tube size decreased. It was reported that the deviation from a uniform velocity profile is very insignificant if the ratio of tube to pellet diameter is greater than 30. In the present study, ratio of reactor to catalyst diameter is about 35. In addition, a porous stainless steel plate was inserted at the entrance of the reactor to brake the velocity pattern of the incoming gases. It appears that no appreciable errors were produced by assuming plug flow even though it rarely exists.

(5) Neglect of Pressure Drop due to flow:

If the pressure drop through the catalyst bed is large in an experiment, the assumption of constant total pressure is not correct. In this investigation the pressure drop was measured experimentally and the maximum pressure drop did not exceed 10 mm. Hg. Therefore the outlet pressure of the reactor (840 mm Hg) was employed for the computation of total pressure.

(6) Side Reactions

The formation of carbon monoxide is believed [82] to be caused by the thermal decomposition of formaldehyde and carbon dioxide is formed by oxidation of carbon monoxide. These side reactions cause tremendous complexity in the correlation of kinetic data. Therefore the present kinetic study is limited up to the range of process variable, where no side reactions were observed.

(7) Homogeneous Reactions and Reactions Catalyzed by the Reactor Wall:

To determine if there was any homogeneous reaction or a reaction catalyzed by the Reactor wall, 0.0949 moles/hr of methanol was passed through the empty reactor in a 8% methanol - air mixture. No reaction between methanol and air was observed to take place, in the absence of catalyst even after 3 hours at 460° C.

(C) Correlation of Rate Equations

(1) Langmuir-Hinshelwood Mechanism

The classical Langmuir-Hinshelwood theory of catalysis on solid surfaces is founded primarily on the concept of monolayer chemisorption on the surface of the catalyst and the assumption of an equilibrium between the adsorption and desorption processes under isothermal conditions. On the basis of this theory, the

Hougen-Watson type rate equation is derived by assuming a definite reaction mechanism and selecting one of the reaction steps as the rate-determining step. The mechanism formally states that the reaction takes place between:

a) an adsorbed reactant molecule and a gaseous reactant molecule.

b) two chemisorbed molecules on adjacent sites,

or by

c) adsorption and desorption of the reactants.

Since all five reaction steps occur in series, the slowest step will control the overall reaction rate, while all other steps will be at equilibrium.

As an example, a rate equation is developed for a bimolecular reaction, $A + B \rightarrow C$, as given by Smith [82]. Surface reaction between adsorbed A and adsorbed B is first assumed and this process may be represented by the expression:

$$A.s + B.s = C.s + s \qquad (5\text{-}20)$$

where A.s, B.s , and C.s represent an adsorbed molecule and s represents a site available for reaction. Selecting step 3, the rate of chemical reaction on the catalyst surface, as the slow step, a rate expression is written in the form:

$$r = k\,(\text{driving force}) \,/\, (\text{resistance forces}) \qquad (5\text{-}21)$$

where, k represents adsorption and other coefficients combined.

The final expression in terms of the interfacial partial pressures for coadsorbed reactants, can be written as:

$$r = k_s C_t K_A K_B \frac{p_{Ai} p_{Bi} - (1/K) p_{Ci}}{(1 + K_A p_{Ai} + K_B p_{Bi} + K_C p_{Ci})^2} \qquad (5\text{-}22)$$

where,

k_s = reaction-rate constant on surface of catalyst

C_t = total concentration of active centers

K_A, K_B, K_c = adsorption equilibrium constants

p_{Ai}, p_{Bi}, p_{Ci} = interfacial partial pressures

K = equilibrium constant for homogeneous reaction

Similar rate equations have been systematically developed and compiled by Hougen-Watson [83] and Yang and Hougen [84] for various reaction mechanisms with different rate controlling steps.

(2) Redox Mechanism (Modified Langmuir-Hinshelwood Mechanism)

When the rate of adsorption of the reactants is of the same order of magnitude as the rate of chemical reaction, the assumption of adsorption equilibrium in the classical Langmuir -

Hinshelwood theory remains no longer valid. The modified Hinshelwood theory considers that the amount of reactant A on the surface increases by adsorption and decreases by reaction and a stationary condition is established when the two rates are equal. Shelstad et al [85, 86] who studied the kinetics of oxidation of naphthalene and toluene supported this theory.

A rate equation exactly similar [72], to the one developed according to the modified Hinshelwood theory is deduced by Jiru et al [40, 41]. The latter is based on a two stage redox mechanism which was originally suggested by Mars and van Krevelen [48] for the vapor phase oxidation of aromatic hydrocarbon on vanadium pentoxide. According to this mechanism, a steady state is assumed between the following two steps:

$$m \left[CH_3OH\,(g) + s_{o_x} \xrightarrow{k_1} HCHO\,(g) + H_2O + s_{red} \right] \quad (5\text{-}23)$$

$$n \left[O_2\,(g) + s_{red} \xrightarrow{k_2} s_{ox} \right] \quad (5\text{-}24)$$

Since the equilibrium in both stages is shifted to the right sides of the above equations, only the reaction rates from left to right is considered in the kinetic equation. The rate of the process (5-23) is given by

$$r_1 = k_1 p_M^m \Theta \quad (5\text{-}25)$$

where Θ is the fraction of the catalyst surface covered by the adsorbed or lattice oxygen. The rate of process (5-24) is given by:

$$r_2 = k_2 p_{O_2}^{n} (1-\Theta) \tag{5-26}$$

At steady state

$$\alpha r_1 = r_2 \tag{5-27}$$

where α is the number of oxygen molecules required to oxidize one molecule of methanol. In the present case, the value of α is 0.5.

From equations 5-25, 5-26, 5-27:

$$\Theta = \frac{1}{1 + \alpha k_1 p_M^{m} \mid k_2 p_{O_2}^{n}} \tag{5-28}$$

Thus, the rate of oxidation of methanol (r) to formaldehyde is

$$r = r_1 = k_1 p_M^{m} \Theta = \frac{k_1 p_M^{m}}{1 + (\alpha k_1 p_M^{m} \mid k_2 p_{O_2}^{n})} \tag{5-29}$$

The integrated forms of rate equation (5-29) with different values of m and n are listed in Table 5-1, where

$$p_M = {}_o p_M (1-x) \tag{5-30}$$

$$p_{O_2} = {}_o p_{O_2} - \tfrac{1}{2} {}_o p_M x \tag{5-31}$$

p_M = partial pressure of methanol at time t.

$_op_M$ = partial pressure of methanol in the feed.

p_{O_2} = partial pressure of oxygen at time t.

$_op_{O_2}$ = partial pressure of oxygen in the feed.

x = fractional conversion of methanol to formaldehyde

Table 5-1

Two-Stage Redox Mechanisms

No	Reaction Order m (CH_3OH)	Reaction Order n (O_2)	Integrated Rate Equation
1	1	0.5	$\frac{W}{F}\frac{{}_oP_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{4\alpha}{k_2}\frac{\left[{}_oP_{O_2}^{\frac{1}{2}} - \left({}_oP_{O_2} - \frac{1}{2}x\,{}_oP_M\right)^{\frac{1}{2}}\right]}{\ln(1-x)}$
2	1	0	$\frac{W}{F}\frac{1}{x} = -\frac{1}{k_1}\frac{\ln(1-x)}{{}_oP_M x} + \frac{\alpha}{k_2}$
3	0.5	0	$\frac{W}{F}\frac{1}{x} = \frac{2}{k_1}\frac{\left[1-(1-x)^{\frac{1}{2}}\right]}{{}_oP_M^{\frac{1}{2}} x} + \frac{\alpha}{k_2}$
4	1	1	$\frac{W}{F}\frac{{}_oP_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{2\alpha}{k_2}\frac{\ln\left[{}_oP_{O_2} / \left({}_oP_{O_2} - \frac{1}{2}\,{}_oP_M x\right)\right]}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F}\frac{{}_oP_M^{\frac{1}{2}}}{\left[1-(1-x)^{\frac{1}{2}}\right]} = \frac{2}{k_1} + \frac{4\alpha}{k_2}\frac{{}_oP_{O_2}^{\frac{1}{2}} - \left({}_oP_{O_2} - \frac{1}{2}\,{}_oP_M x\right)^{\frac{1}{2}}}{{}_oP_M^{\frac{1}{2}}\left[1-(1-x)^{\frac{1}{2}}\right]}$

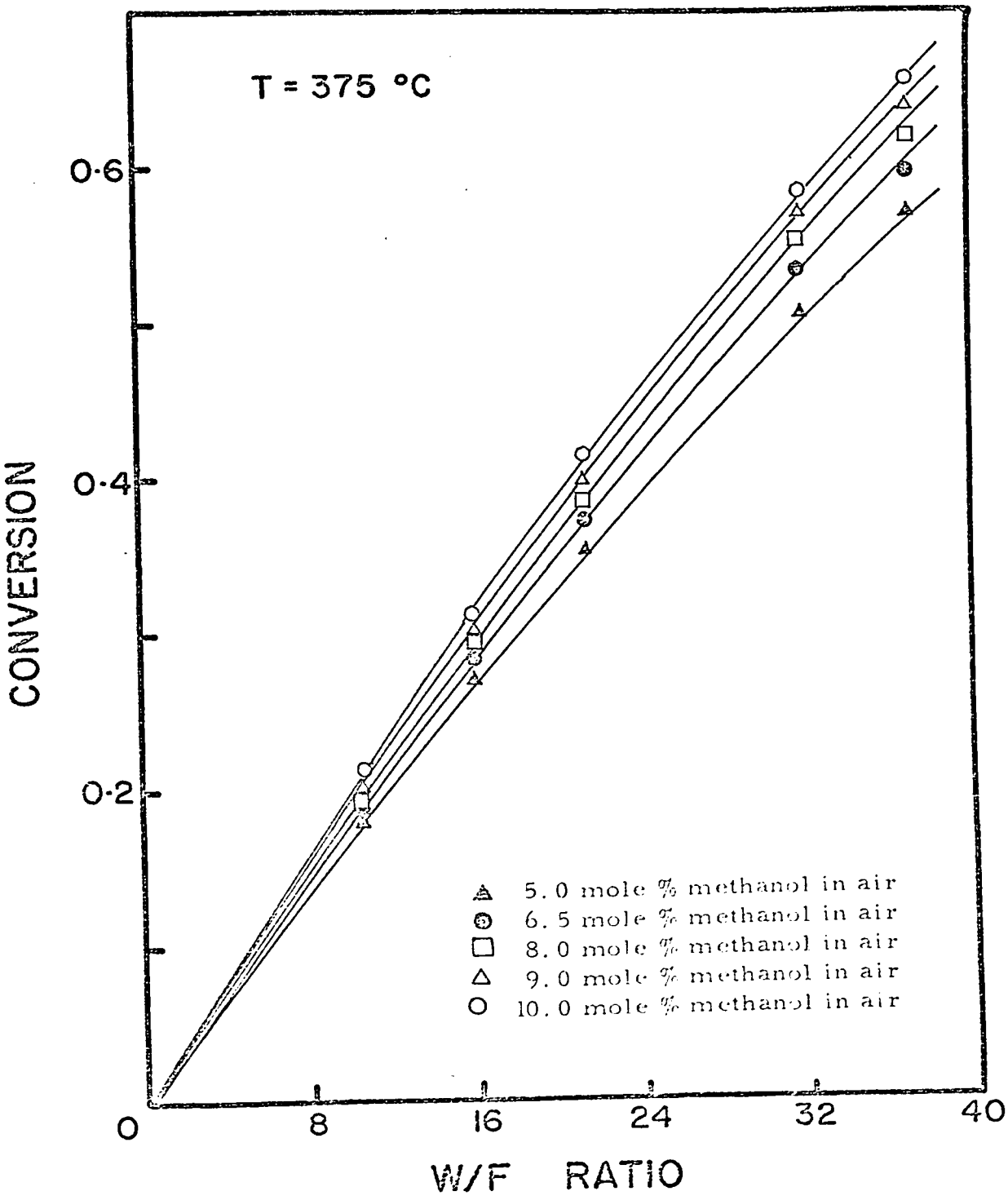

Fig. 5-1 Effect of W/F (gm. hr./mole) on Conversion of methanol to formaldehyde at 375° C

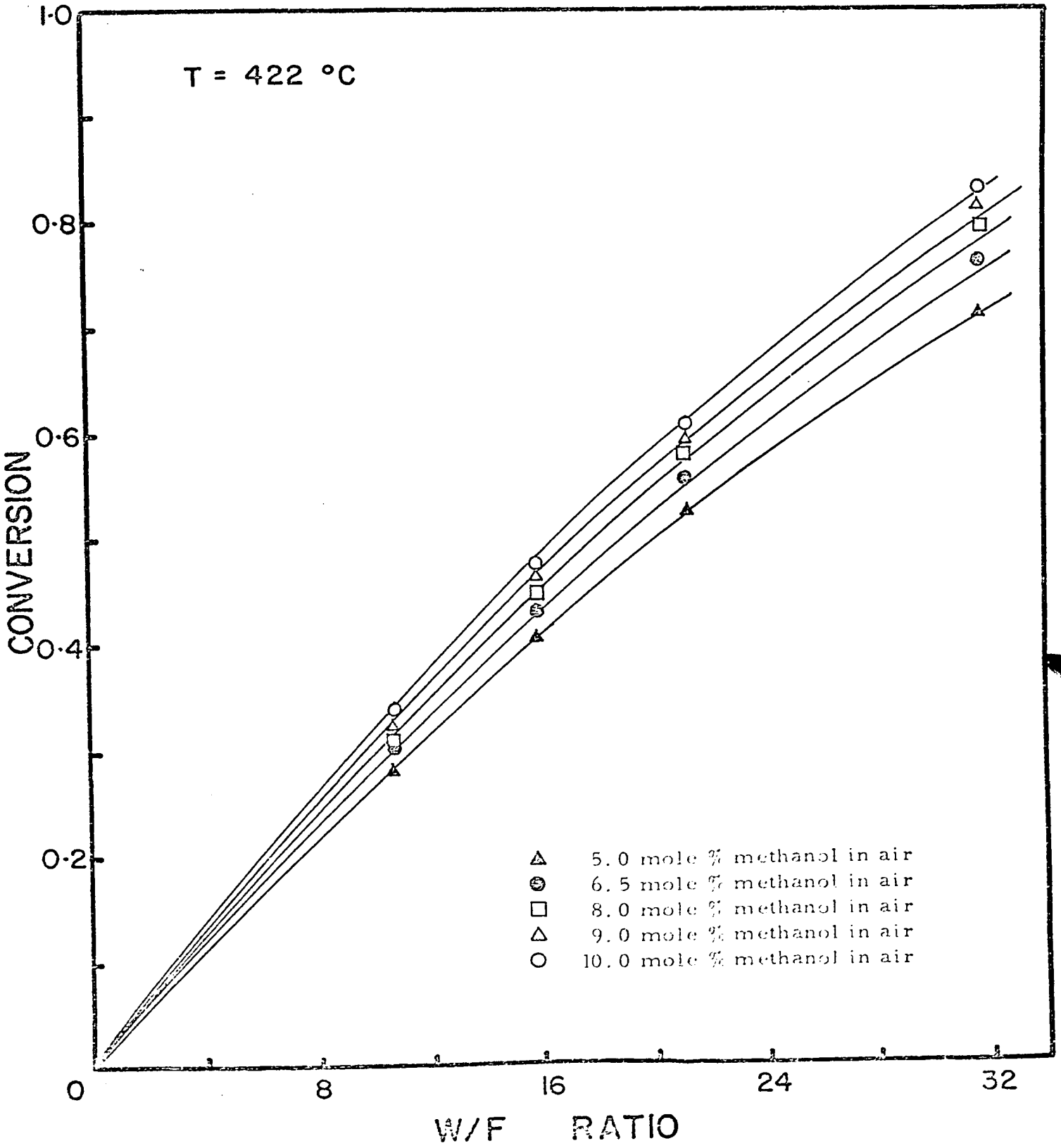

Fig. 5-2 Effect of W/F (gm. hr. /mole) on Conversion of methanol to formaldehyde at 422° C

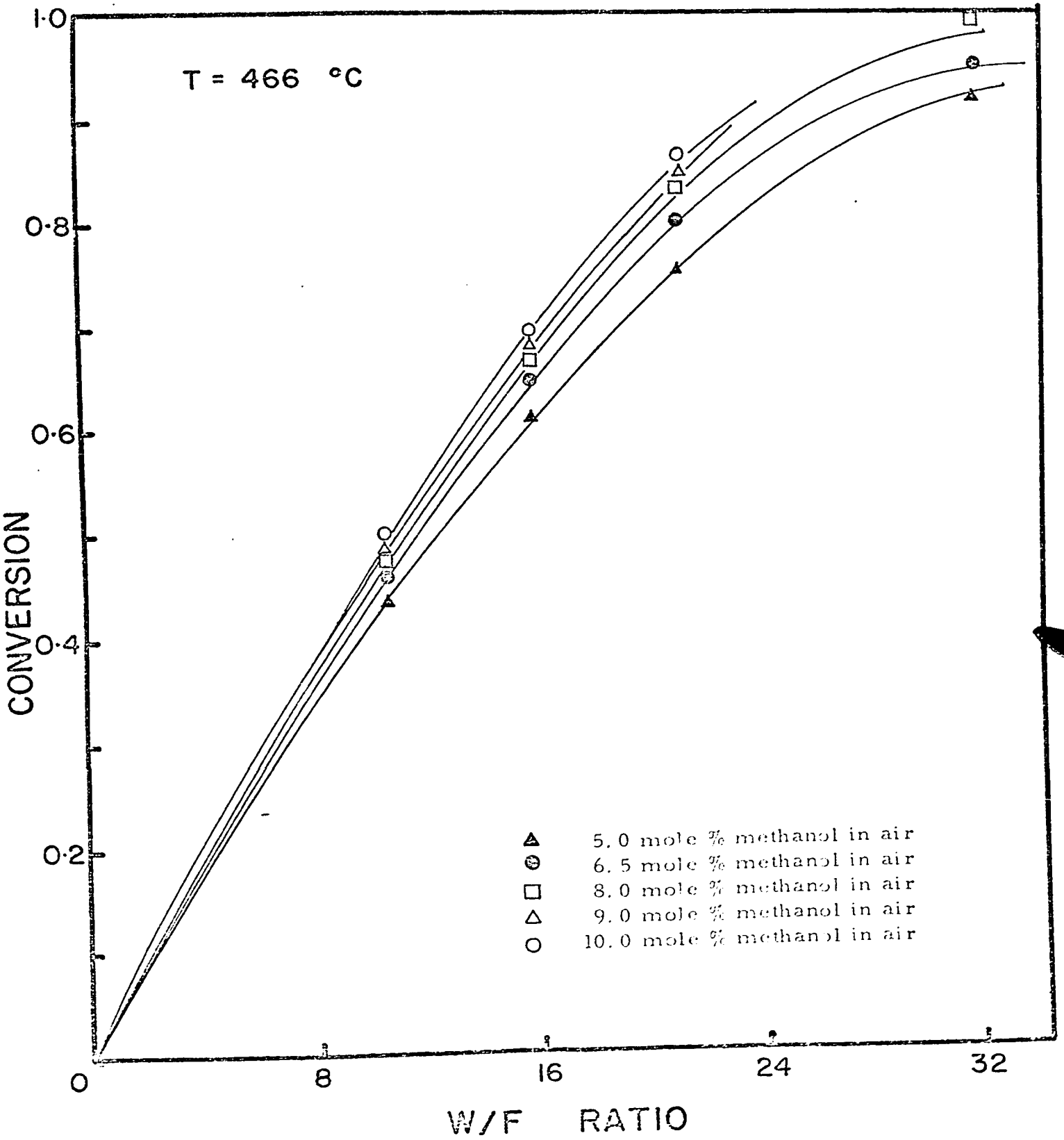

Fig. 5-3 Effect of W/F (gm.hr./mole) on Conversion of methanol to formaldehyde at 466° C

(3) Correlation of Initial Rate data

The rate of reaction at zero conversion is defined as the initial rate. Its value is determined by plotting the experimental data (conversion versus W/F) and finding the slope of the curve at W/F equals to zero. The initial-rate approach, as a modification of the integration method, is frequently used to simplify the kinetic study, Yang and Hougen [87] considered several reactions and showed that by considering the effect of pressure on initial rate (x = 0), it is possible to reduce the number of reaction mechanisms and finally test some of them for their suitability in representing the data.

The advantage of the initial rate method is that a more simple rate equation can be derived, since the partial pressure of the products are neglected. However, the disadvantage is the necessity of estimating the slopes at low conversion by use of extrapolation.

The initial rates were obtained by finding the slopes of the curves shown in the Figures 5-1 to 5-3 (x vs. W/F) at x = 0, for various feed ratios. The plots of mole percent methanol in the feed versus the initial rates (r_o) for 375°, 422° and 466° C are given in figure 5-4.

The initial rate curves in figure 5-4 were compared with the type of curves used by Yang and Hougen [87] for identifying various mechanisms and concluded that controlling step in the reaction was either the adsorption of the reactants or a surface reaction between the reactants.

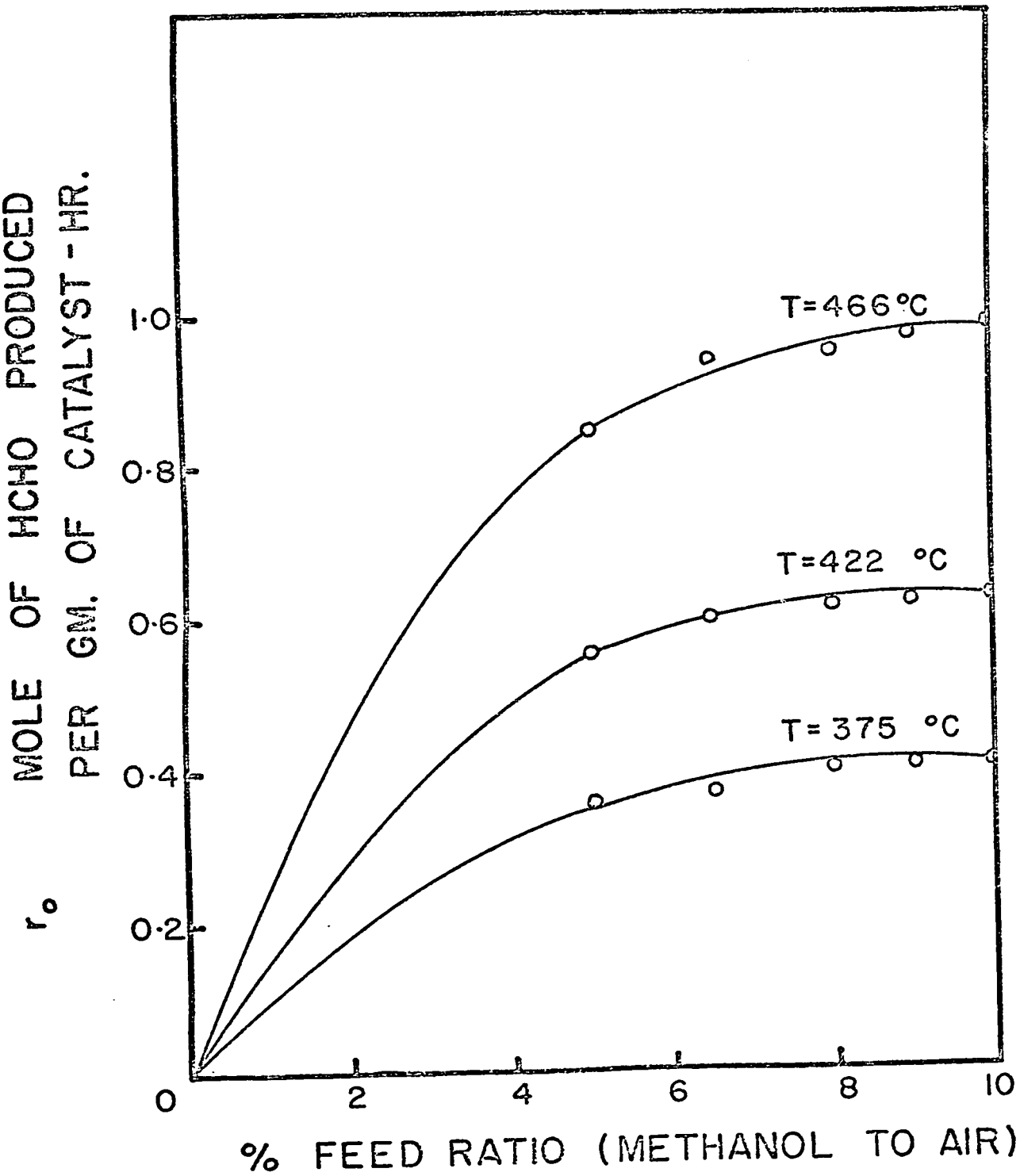

Fig. 5-4 Initial Rates (r_o) vs. mole % methanol in air

D. Correlation of Conversion Data

The integrated rate equations in Table 5-1 are rearranged into the form of $y = a_o + a_1 x$ as shown in Table 5-2. The values of y and x in columns six and seven of the table are calculated from the experimental data by substituting the values of W/F, conversion and respective partial pressures. A linear equation correlating y and x values is obtained by using the method of least-square error. The values of a_o and a_1 (intercept and slope) can be expressed by this method as:

$$a_o = \frac{\sum_{i=1}^{n} y_i - a_1 \sum_{i=1}^{n} x_i}{n} \qquad (5\text{-}32)$$

$$a_1 = \frac{\sum_{i=1}^{n} x_i y_i - \left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_i\right)/n}{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2 /n} \qquad (5\text{-}33)$$

Where, n is the total number of experimental data.

Table 5-2

Correlated y and x Relations

No.	Reaction Order m (CH_3OH)	Reaction Order n (O_2)	a_o	a_1	y	x
1	1	0.5	$1/k_1$	$1/k_2$	$(-W/F)\left[{}_oP_M/\ln(1-x)\right]$	$\left[4\alpha/\ln(1-x)\right]\left[({}_oP_{O_2} - x\,{}_oP_M/2)^{\frac{1}{2}} - {}_oP_{O_2}^{\frac{1}{2}}\right]$
2	1	0	$1/k_2$	$1/k_1$	$W/Fx\alpha$	$-\ln(1-x)/{}_oP_M x\alpha$
3	0.5	0	$1/k_2$	$1/k_1$	$W/Fx\alpha$	$2\left[1-(1-x)^{\frac{1}{2}}\right]/{}_oP_M^{\frac{1}{2}} x\alpha$
4	1	1	$1/k_1$	$1/k_2$	$-W\,{}_oP_M/F\ln(1-x)$	$\dfrac{-2\alpha\ln\left[{}_oP_{O_2}/({}_oP_{O_2} - \frac{1}{2}\,{}_oP_M x)\right]}{\ln(1-x)}$
5	0.5	0.5	$1/k_1$	$1/k_2$	$W\,{}_oP_M^{\frac{1}{2}}/2F\left[1-(1-x)^{\frac{1}{2}}\right]$	$2\alpha\left[{}_oP_{O_2}^{\frac{1}{2}} - ({}_oP_{O_2} - \frac{1}{2}\,{}_oP_M x)^{\frac{1}{2}}\right]/{}_oP_M^{\frac{1}{2}}\left[1-(1-x)^{\frac{1}{2}}\right]$

The values of k_1 and k_2 obtained from a_o and a_i were substituted in the corresponding integrated rate equations to determine the W/F versus x relation. These calculated W/F values were compared with their experimental values and the rate equation with m = 0.1 and n = 0.5 was found to give best possible fit to the experimental data. The rate equation is:

$$r = \frac{k_1 p_M}{1 + k_1 p_M \mid 2k_2 p_{O_2}^{0.5}} \qquad (5\text{-}34)$$

The values of k_1 and k_2 at temperatures 375°, 422° and 460° C for m = 1.0 and n = 0.5 are given in table 5-3. For other values of m and n, k_1 and k_2 values are given in Appendix (J). Figures 5-1 to 5-3 show the comparison between the experimental and calculated values for the relation with m = 1.0 and n = 0.5 at various temperatures and methanol to air ratio. The solid lines in the figures refer to the curves predicted by substituting appropriate values of k_1 and k_2 in the relation and the points represent the experimental data. A sample calculation is given in Appendix (E-4).

E. Temperature effect on Rate Constants

The temperature dependence of the rate constants k_1 and k_2 was determined for temperatures between 375° and 460° C. The reaction appears (Figure 5-5) to follow the Arrhenius Law in the temperature range studied. The mathematical relations obtained from reaction constant versus temperature plot, are:

Table 5-3

Temperature Effect on Rate Constants

for m = 1, n = 0.5

Temp. °C	1/Temp. 1/°K	$\bar{R}$ %	k_1 $\frac{\text{moles}}{\text{gm-mm Hg-hr}}$ $\times 10^3$	k_2 $\frac{\text{moles}}{\text{gm-mm Hg.}^{\frac{1}{2}}\text{-hr}}$ $\times 10^3$
375		5.0	1.383	1.056
		6.5	1.496	0.970
		8.0	1.647	0.929
		9.0	1.311	1.024
		10.0	1.106	1.123
	overall K values at 375° C		1.42	1.003
422		5.0	2.082	1.695
		6.5	2.073	1.661
		8.0	2.283	1.563
		9.0	2.128	1.644
		10.0	1.825	1.777
	overall K values at 422° C		2.090	1.660
466		5.0	3.407	2.693
		6.5	3.643	2.502
		8.0	5.353	2.194
		9.0	3.943	2.435
		10.0	3.793	2.497
	overall K values at 466° C		3.970	2.430

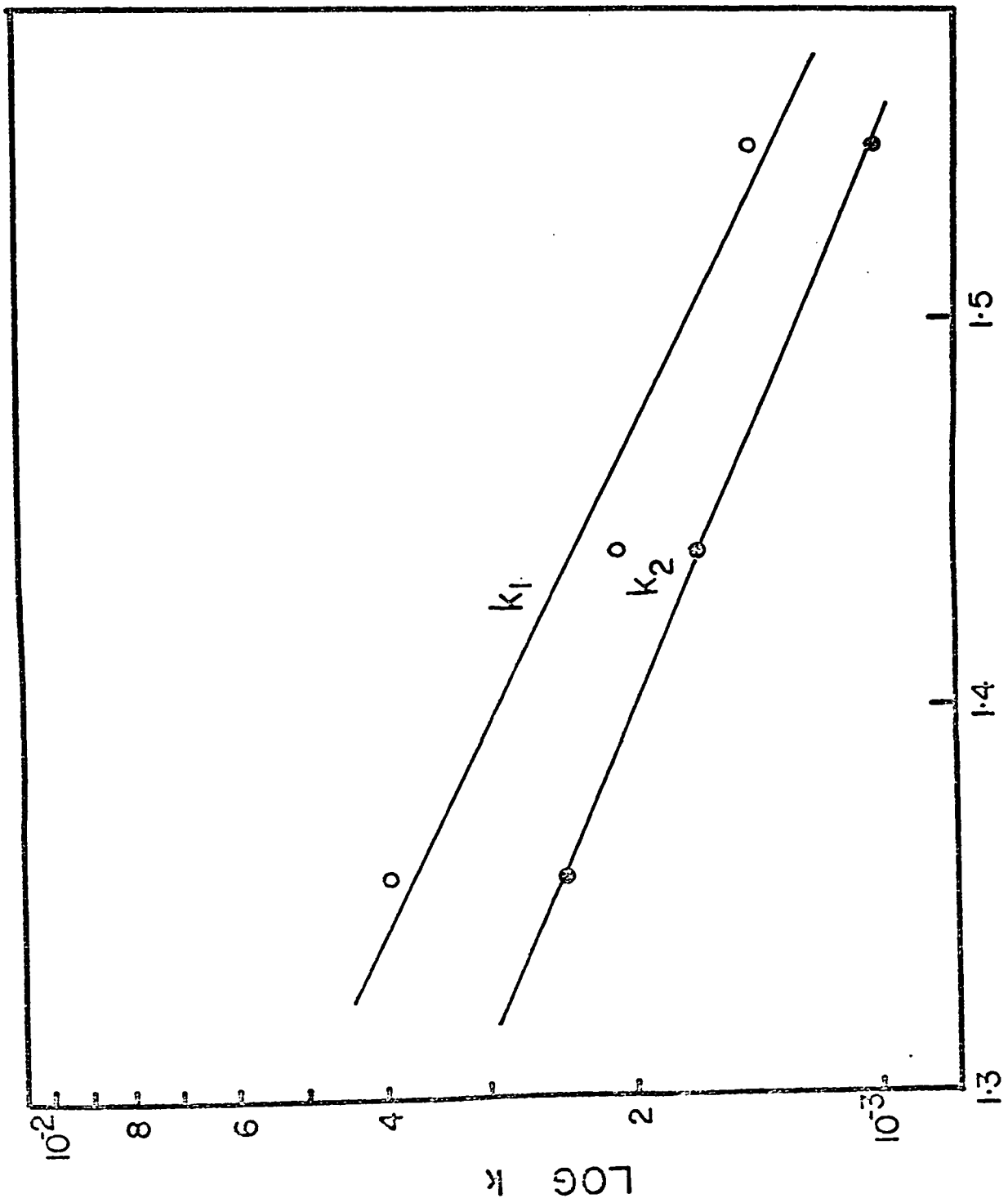

Fig. 5-5 Temperature Effect on Rate Constants

$$\log k_1 = 0.773 - \frac{2.358 \times 10^3}{T} \qquad (5\text{-}35)$$

$$\log k_2 = 0.157 - \frac{2.04 \times 10^3}{T} \qquad (5\text{-}36)$$

The activation energies of the two steps (5-23) and (5-24), evaluated from the relations (5-35) and (5-36), are 10.8 and 9.3 kcal./mole, respectively.

VI. DISCUSSION

The kinetics for the air oxidation of methanol to formaldehyde have been investigated between temperatures 375° and 531° C, over vanadium pentoxide-molybdenum trioxide catalyst. In 1968, the preparation of a similar catalyst was patented by Kurina et al [75], but no kinetic work with vanadium-molybdenum oxide catalyst has yet been published in the literature. The molybdenum trioxide as a catalyst for methanol oxidation is very well established [39] to be highly selective to formaldehyde formation, but gives low conversion of methanol. On the other hand the vanadium pentoxide catalyst is well known for the oxidation of sulphur dioxide and naphthalene. The use of vanadium pentoxide catalyst has also been reported [68-71] for methanol oxidation, and is said to be highly active but its selectivity to formaldehyde formation decreased due to further oxidation to carbon oxide. Bhattacharya et al [72] carried out kinetic study of methanol oxidation over vanadium pentoxide 100% with conversion up to 24.2%. Similar results with the use of molybdenum trioxide and vanadium pentoxide have been obtained in the present work.

Tarama et al [73] studied the structures of catalysts of V_2O_5 - MoO_3 system and of V_2O_5 - K_2SO_4 system by x-ray, infrared, E.S.R. and magnetic susceptibility measurements. Both potassium sulphate and molybdenum trioxide were found to have promotive action on vanadium pentoxide for oxidation processes. They elucidated that the strength of V = O bond was a controlling factor for the activity of the catalytic oxidation and the promotive action of MoO_3 on V_2O_5 was due to the weakening of this bond by the formation of solid solution of

substituted type. In case of V_2O_5 - K_2SO_4 system the catalytic activity were mainly attributed to two factors, the one, weakening of V = O bond due to the formation of $VOSO_4$ or a compound formed by doping of K_2SO_4 and the other, an increase in the concentration of active centers, caused by the lowering of the melting point. Kurina and Maidanovskaya [74] carried out methanol oxidation in a flow system at 200-370° C over a catalyst containing V_2O_5 and K_2SO_4. They reported that an increase in the concentration of K_2SO_4 decreased the activity of V_2O_5 and increased its selectivity to the formaldehyde formation, thus increasing the overall yield of formaldehyde. In the case of catalyst containing more than 50 mole % MoO_3, Tarama et al observed a new crystal phase which was formed from the about-equimolar mixture of V_2O_5 and MoO_3. From the studies of Tarama et al [73] and Kurina et al [74] and keeping the high selectivity of molybdenum trioxide in mind, it was visualised that molybdenum trioxide - vanadium pentoxide catalyst may give high conversions of methanol without much loss in its selectivity to formaldehyde formation. The results of present investigation of the kinetic study of methanol oxidation largely confirmed the expected behaviour of the MoO_3 - V_2O_5 oxide catalyst. The conversion increased with increasing V_2O_5 content in catalyst but the selectivity of the catalyst to formaldehyde formation decreased for more than 20% V_2O_5 at 466° C.

The Hougen-Watson method based on Langmuir-Hinshelwood isotherm, and the initial rate technique were used for the kinetic analysis of the data.

The oxidation reaction of methanol to formaldehyde was considered highly irreversible, since the values of equilibrium constant K_p (Table 8-F1) for the reaction in vapor phase are very large, in the order of 10^{18} at 250° C and 10^{12} at 450° C. The rate equation derived on the basis of a two-stage irreversible redox mechanism fitted the experimental data best in the temperature range of 375° - 466° C, at atmospheric pressure.

The mechanism and the general kinetics of the reaction over the vanadium-molybdenum oxide catalyst investigated in the present study have been found similar to those obtained by Jiru, Witchterlova and Tichy [40], Mars and van Krevelen [48], Bhattacharya et al [72] and Mann and Hahn [67].

Jiru et al carried kinetic studies of methanol oxidation over iron-molybdenum oxide at 270° C using a micro catalytic pulse technique. The two stage oxidation - reduction mechanism was confirmed by determining the rate of interaction between methyl alcohol and catalyst without participation of oxygen in the gaseous phase and the rate of interaction between oxygen and partially reduced catalyst without participation of methyl alcohol in the gaseous phase.

Mars and van Krevelen [48] studied the mechanism of oxidation of several aromatic hydrocarbons like, benzene, naphthalene and anthracene over a vanadium pentoxide catalyst. They suggest, however, that since a maximum rate does not occur with changes in the partial pressures of oxygen and aromatics, a reaction must take

place between the aromatic compound and oxygen present on the underlying catalyst surface. They also noted a color change in the vanadium catalyst from yellowish brown in the oxidized state to greenish-blue in the reduced. This color change was completely reversible and on analysis of the reduced catalyst, a high concentration of tetravalent vanadium was found. Vanadium pentoxide contains two kinds of oxygen ions in the lattice - three fifths existing in about the same plane as the vanadium ions and two fifths arranged in planes parallel and alternating with the first. Mars and Krevelen believe the alternating lattice oxygen ions to be those which interact with aromatic molecules at the surface of the catalyst.

Jiru et al have also found a remarkable equality between the amount of oxygen removed by methanol (in the absence of oxygen in the gaseous phase) and the oxygen taken up subsequently by the reduced catalyst and believed that the lattice oxygen atoms in the surface participates in the oxidation process. This was further supported by Bhattacharya et al who investigated kinetics of methanol oxidation over vanadium pentoxide between temperatures 246° and 281° C.

Shelstad, Downie and Graydon [85, 86] studied the kinetics of the oxidation of naphthalene and toluene. They suggest a two-stage redox mechanism whereby adsorbed oxygen reacts with the other reactant remaining in the gaseous phase and the rate of removal of adsorbed oxygen by the reaction equals the rate of adsorption of oxygen. Ioffe et al [87] also favored this mechanism.

Though both the mechanisms outlined above lead to the same rate expression, a point of difference exists between them. The first mechanism proposes the removal of actual lattice oxygen atoms by direct interaction with the reactant, which must hence be chemisorbed, while the latter ignores such a catalyst-reductant interaction and instead, it suggests that only adsorbed molecules or atoms and not the lattice oxygen, are removed by reacting with the reductant molecules, which remain exclusively in the gas phase.

However, Tarama et al [73] by x-ray diffraction established that certain V-O distance in V_2O_5 lattice (exposed on 001 face) are comparable in length with those in $VOCL_3$, having a double bond between oxygen and vanadium. According to them these oxygen atoms are more reactive (especially in the presence of easily oxidizable compounds), since they are linked with bonds having appreciable,"double bond characteristic ". The presence of MoO_3, which forms a nearly equimolar solid solution with V_2O_5 further weakens V = O bond. This weakening is seemed to be caused by increase of V^{4+} (E. S. R. and magnetic susceptibility measurements) resulted from substitution of V^{5+} with Mo^{6+} (x-ray measurements).

Several other workers [88, 89, 90] have also suggested that the lattice oxygen from V_2O_5 is removed during the oxidation of organic compounds and that a lower oxide of vanadium is the actual composition of V_2O_5.

In the present investigation, it has been observed that the conversion of methanol and hence the activity of the catalyst increased

with increasing V_2O_5 content in the catalyst. This could probably be attributed to the increased amount of lattice oxygen available from V_2O_5.

It is, of course, true that inspite of all these observations, one can not make an absolute choice between the above mechanisms, and that the catalysed methanol oxidation could possibly take place with adsorbed oxygen being responsible for the oxidation only when the lattice oxygen is lacking.

The proposed rate equation does not exclude the possibility that the reoxidation of partially reduced catalyst is realized by means of adsorbed oxygen. The rate equation can also represent a modified Langmuir-Hinshelwood mechanism for the catalyst surface sparsely covered by one or both reactants, where one or both the rate constants represent the product of a rate constant and an adsorption constant.

VII. CONCLUSIONS AND RECOMMENDATIONS

On the basis of a preliminary study of the effect of catalyst compositions on the yield of formaldehyde, at temperatures 304° C to 460° C, a catalyst containing 20% vanadium pentoxide and 80% molybdenum trioxide (by weight) was selected, for the detailed kinetic study of the oxidation of methanol to formaldehyde reaction.

Experiments were carried out for W/F ratios between 10.57 and 36.89 gm.hr/moles, containing 5.0 to 10.0% methanol in air at temperatures between 375° and 531° C, in order to establish maximum conversion and yield, and to derive a plausible reaction mechanism, which might satisfactorily represent the experimental data.

The 20:80 vanadium-molybdenum oxide catalyst proved to be highly active and selective for the formaldehyde formation and gave nearly 99% conversion of methanol to formaldehyde for a W/F ratio of 31.70 gm.hr/moles and 8% methanol in air at temperature 466° C. The conversion further increased to 100% with the increase of methanol content in air over 8% and also with the increase in temperature and W/F ratio, however, the overall yield of formaldehyde decreased due to the formation of carbon oxides.

The rate equation for the oxidation of methanol to formaldehyde was derived on the basis of a "two-stage oxidation-reduction mechanism. According to this mechanism:

$$CH_3OH\ (g) + s_{ox} \xrightarrow{k_1} HCHO\ (g) + H_2O\ (g) + s_{red} \qquad (7\text{-}1)$$

$$O_2\ (g) + s_{red} \xrightarrow{k_2} s_{ox} \qquad (7\text{-}2)$$

Where, s_{ox} is an active site of lattice or adsorbed oxygen, and s_{red} is the reduced site of lattice oxygen or the empty site.

The rate equation for the temperature range of 375° to 466° C, which correlated the experimental data most satisfactorily is:

$$r = \frac{k_1 p_M}{1 + k_1 p_M \mid 2k_2 p_{O_2}^{0.5}} \qquad (7\text{-}3)$$

where, k_1 and k_2 are the temperature-dependent rate constants of the two processes, (7-1) and (7-2), respectively.

The equations relating k_1 and k_2 with temperature are:

$$\log k_1 = 0.773 - \frac{2.358 \times 10^3}{T} \qquad (7\text{-}4)$$

$$\log k_2 = 0.157 - \frac{2.04 \times 10^3}{T} \qquad (7\text{-}5)$$

The activation energies of the two steps, evaluated by comparing Equations (7-4) and (7-5) with the Arrhenius equation, are 10.8 and 9.3 kcal/mole, respectively.

It is recommended that in order to obtain a better understanding of the nature of the oxygen (lattice or adsorbed) participating in the reaction, further work should be carried out at molecular level. This includes:

(a) the isolated studies on the interaction between the methyl alcohol and the catalyst and between the reduced catalyst and the oxygen.

(b) the study of the crystallographic structure of the mixed catalyst.

(c) kinetic studies of the reaction and isotope exchange with a specially prepared catalyst, containing a sufficient concentration of O^{18} in the lattice.

Low pressure studies with a mass spectrometer may also be carried out to obtain more information regarding the reaction intermediates.

It is also recommended that further work on the oxidation of methanol should be carried out to study the effect of diluting the reaction mixture with water and nitrogen, to approach more realistic process conditions as encountered in the industry.

VIII. APPENDIX

(A) Effect of Catalyst Composition

The effect of catalyst composition on the conversion, yield and selectivity was studied in the temperature range of 304° - 460°C. The following running condition were used:

Methanol feed rate (F) = 0.0949 moles/hr
Weight of catalyst (W) = 2.60 gms.
W/F ratio = 27.40 gm-hr/moles
% methanol in air = 8.0%
Moles of air in feed = 1.1863 moles/hr
Moles of O_2 in feed = 0.2491 moles/hr
Moles of N_2 in feed = 0.9372 moles/hr

The experimental data for molybdenum trioxide, 10% V_2O_5 - 90% MoO_3, 20% V_2O_5 - 80% MoO_3, 30% V_2O_5 - 70% MoO_3, 50% V_2O_5 - 50% MoO_3 (all weight%) and vanadium pentoxide catalysts are summarized in Table 8-A-1 to 8-A-6, respectively.

Table 8-A-1

Experimental Data for Molybdenum Trioxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
21	304	17.29	100.00	0.2564	0.0	0.0	0.2403	0
22	356	21.32	100.00	0.2542	0.0	0.0	0.2382	0
23	405	30.06	100.00	0.2515	0.0	0.0	0.2357	0
24	460	33.58	100.00	0.2496	0.0	0.0	0.2340	0

Run No.	Yield y%	F_{CO} moles/hr	$\overline{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
21	17.29	0	0.1474	0.1474	0.7052	0.01641	0.07849	0.1113
22	21.32	0	0.1757	0.1757	0.6485	0.02023	0.07466	0.1151
23	30.06	0	0.2311	0.2311	0.5377	0.02853	0.06637	0.1234
24	33.58	0	0.2514	0.2514	0.4972	0.03187	0.0630	0.1268

Table 8-A-2

Experimental Data for 10% Vanadium Pentoxide - 90% Molybdenum Trioxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
17	304	22.56	100.00	0.2536	0.0	0.0	0.2377	0
18	356	35.74	100.00	0.2480	0.0	0.0	0.2325	0
19	405	59.77	100.00	0.2360	0.0	0.0	0.2212	0
20	460	81.47	100.00	0.2251	0.0	0.0	0.2110	0

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
17	22.56	0	0.1841	0.1841	0.6318	0.02141	0.07349	0.1163
18	35.74	0	0.2633	0.2633	0.4734	0.03392	0.06098	0.1288
19	59.77	0	0.3741	0.3741	0.2518	0.05670	0.03818	0.1516
20	81.47	0	0.4489	0.4489	0.1021	0.07732	0.01758	0.1722

Table 8-A-3

Experimental Data for 20% Vanadium Pentoxide - 80% Molybdenum Trioxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
13	304	24.83	100.00	0.2536	0.0	0.0	0.2377	0
14	356	44.37	100.00	0.2424	0.0	0.0	0.2272	0
15	405	72.68	100.00	0.2276	0.0	0.0	0.2133	0
16	460	100.00	100.00	0.2158	0.0	0.0	0.2023	0

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
13	24.82	0	0.1989	0.1989	0.6022	0.02356	0.07133	0.1185
14	44.37	0	0.3073	0.3073	0.3853	0.04211	0.05279	0.1370
15	72.68	0	0.4209	0.4209	0.1582	0.06897	0.02592	0.1639
16	100.00	0	0.5000	0.5000	0	0.0949	0	0.1898

Table 8-A-4

Experimental Data for 30% Vanadium Pentoxide - 70% Molybdenum Trioxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
9	304	28.78	100.00	0.2536	0.0	0.0	0.2377	0
10	356	58.71	100.00	0.2353	0.0	0.0	0.2205	0
11	405	88.44	97.64	0.2187	0.0	0.00213	0.2050	0
12	460	100.00	82.48	0.2048	0.0	0.01761	0.1919	0

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
9	28.77	0	0.2235	0.2235	0.5530	0.02731	0.06758	0.1222
10	58.71	0	0.3699	0.3699	0.2601	0.05572	0.03918	0.1506
11	87.14	0.0020	0.4785	0.4604	0.0610	0.08270	0.01096	0.1796
12	81.86	0.0165	0.5891	0.4108	0.0	0.07769	0.0	0.1891

Table 8-A-5

Experimental Data for 50% Vanadium Pentoxide - 50% Molybdenum Trioxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
5	304	37.18	100.00	0.2482	0.0	0.0	0.2326	0
6	356	79.48	80.83	0.2116	0.0544	0.00992	0.1983	0.0510
7	405	100.00	68.12	0.1888	0.1408	0.01846	0.1769	0.01320
8	460	100.00	51.18	0.1770	0.0228	0.02646	0.1659	0.02140

Run No.	Yield y%	F_{CO} moles/hr	$\overline{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 Moles/hr
5	37.18	0	0.2710	0.2710	0.4579	0.03529	0.05961	0.1302
6	63.98	0.0093	0.5283	0.3571	0.1145	0.06072	0.01947	0.1700
7	68.68	0.0173	0.6580	0.3420	0.0	0.06518	0	0.1906
8	51.03	0.0248	0.7444	0.2555	0	0.04843	0	0.1895

Table 8-A-6

Experimental Data for Vanadium Pentoxide

Run No.	Temp. °C	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
1	304	48.55	100.00	0.24041	0.0	0.0	0.2253	0
2	356	96.56	57.66	0.18161	0.0171	0.02443	0.1702	0.01610
3	405	100.00	39.88	0.16743	0.0259	0.03511	0.1569	0.02430
4	460	100.00	27.73	0.15525	0.0404	0.03788	0.1455	0.03260

Run No.	Yield y%	F_{CO} moles/hr	$\overline{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
1	48.54	0	0.3268	0.3268	0.3463	0.04607	0.04882	0.1410
2	55.96	0.02290	0.6985	0.2840	0.0174	0.05311	0.00326	0.1870
3	39.99	0.03290	0.8003	0.1996	0	0.03795	0	0.1900
4	27.53	0.03550	0.8618	0.1382	0	0.02613	0	0.1891

(B) Effect of W/F ratio at 375°, 422° and 466° C

The effect of W/F ratio on conversion, yield and selectivity was studied in the temperature range of 375° - 531° C. The methanol feed rate (F) was kept constant at 0.0949 moles/hr. The running conditions for the various feed ratios and the weight of the catalyst used are mentioned below in a tabular form:

% Methanol In air	Air moles/hr	Oxygen moles/hr	Nitrogen moles/hr	Wt. of catalyst W. gm.	W/F ratio gm-hr/moles
5.0	1.8980	0.3986	1.4994	1.0029	10.57
6.5	1.4601	0.3066	1.1535	1.5010	15.82
8.0	1.1863	0.2491	0.9372	2.0040	21.12
9.0	1.0544	0.2214	0.8330	3.0080	31.70
10.0	0.9490	0.1993	0.7497	3.5001	36.89

The experimental data obtained at 375°, 422°, and 466° C for various feed ratio are summarized in table 8-B-1, 8-B-2, and 8-B-3 respectively, where selectivity of the catalyst remains 100%. The experimental data where the selectivity of the catalyst is less than 100% are given in Table 8-B-4.

Table 8-B-1

Effect of W/F on conversion at 375° C for 5 % methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\bar{W}/T_1$)	M/T_1	W gm
25	10.57	18.51	0.1562	0.6876	1.0029
26	15.82	27.48	0.2155	0.5689	1.5010
27	21.12	35.67	0.2629	0.4742	2.0040
28	31.70	50.82	0.3369	0.3261	3.0080
29	36.89	57.45	0.3649	0.2702	3.5001

Run No.	O_2N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
25	0.2591	0.01756	0.07733	0.3885	100.0
26	0.2563	0.02608	0.06882	0.3842	100.0
27	0.2537	0.03385	0.06105	0.3804	100.0
28	0.2482	0.04823	0.04667	0.3721	100.0
29	0.2469	0.05452	0.04038	0.3702	100.0

Table 8-B-1 (cont'd)

Effect of W/F on conversion at 375° C for 6.5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\bar{W}/T_1$)	M/T_1	W gm
30	10.57	19.02	0.1598	0.6804	1.0029
31	15.82	28.54	0.2220	0.5559	1.5010
32	21.12	37.53	0.2729	0.4542	2.0040
33	31.70	53.49	0.3485	0.3030	3.0080
34	36.89	59.82	0.3743	0.2514	3.5001

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
30	0.2554	0.01805	0.07685	0.2946	100.0
31	0.2517	0.02708	0.06782	0.2904	100.0
32	0.2480	0.03562	0.05928	0.2861	100.0
33	0.2423	0.05076	0.04414	0.2795	100.0
34	0.2379	0.05677	0.03813	0.2744	100.0

Table 8-B-1 (cont'd)

Effect of W/F on conversion at 375° C for 8% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\overline{W}/T_1$)	M/T_1	W gm
35	10.57	19.54	0.1635	0.6731	1.0029
36	15.82	29.45	0.2275	0.5450	1.5001
37	21.12	38.61	0.2785	0.4429	2.0040
38	31.70	55.32	0.3562	0.2877	3.0080
39	36.89	62.23	0.3836	0.2328	3.5001

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
35	0.2576	0.01854	0.07636	0.2414	100.0
36	0.2530	0.02795	0.06695	0.2371	100.0
37	0.2485	0.03664	0.05826	0.2329	100.0
38	0.2403	0.05250	0.04240	0.2252	100.0
39	0.2329	0.05906	0.03584	0.2183	100.0

Table 8-B-1 (cont. D)
Effect of W/F on conversion at 375° C for 9% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\bar{W}/T_1$)	M/T_1	W gm
40	10.57	20.37	0.1692	0.6615	1.0029
41	15.82	30.68	0.2348	0.5304	1.5010
42	21.12	40.10	0.2862	0.4275	2.0040
43	31.70	56.83	0.3624	0.2752	3.0080
44	36.89	63.76	0.3893	0.2213	3.5001

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
40	0.2555	0.01933	0.07557	0.2128	100.0
41	0.2451	0.02911	0.06578	0.2041	100.0
42	0.2406	0.03805	0.05684	0.2004	100.0
43	0.2299	0.05393	0.04097	0.1915	100.0
44	0.2260	0.06051	0.03439	0.1882	100.0

Table 8-B-1 (cont'd)

Effect of W/F on conversion at 375° C for 10% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\bar{W}/T_1$)	M/T_1	W gm
45	10.57	21.46	0.1767	0.6467	1.0029
46	15.82	31.50	0.2395	0.5209	1.5010
47	21.12	41.72	0.2944	0.4112	2.0040
48	31.70	58.49	0.3690	0.2619	3.0080
49	36.89	65.50	0.3958	0.2085	3.5001

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
45	0.2471	0.02037	0.07453	0.1852	100.0
46	0.2403	0.02989	0.06500	0.1801	100.0
47	0.2318	0.03959	0.05531	0.1738	100.0
48	0.2219	0.05551	0.63939	0.1663	100.0
49	0.2164	0.06216	0.03274	0.1623	100.0

Table 8-B-2

Effect of W/F on conversion at 422° C for 5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\bar{W}/T_1$)	M/T_1	W gm
50	10.57	28.52	0.2219	0.5562	1.0029
51	15.82	41.01	0.2908	0.4183	1.5010
52	21.12	52.61	0.3447	0.3105	2.0040
53	31.70	71.49	0.4169	0.1662	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
50	0.2566	0.02706	0.06783	0.3848	100.0
51	0.2549	0.03892	0.05598	0.3822	100.0
52	0.2509	0.04993	0.04497	0.3763	100.0
53	0.2447	0.06784	0.02706	0.3669	100.0

Table 8-B-2 (cont'd)

Effect of W/F on conversion at 422° C for 6.5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 $(=\overline{W}/T_1)$	M/T_1	W gm
55	10.57	30.73	0.2351	0.5299	1.0029
56	15.82	43.20	0.3017	0.3966	1.5010
57	21,12	55.46	0.3567	0.2865	2.0040
58	31.12	76.42	0.4332	0.1336	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
55	0.2541	0.02916	0.06574	0.2931	100.0
56	0.2500	0.04100	0.05390	0.2883	100.0
57	0.2469	0.05263	0.04227	0.2848	100.0
58	0.2386	0.07252	0.02238	0.2752	100.0

Table 8-B-2 (cont'd)

Effect of W/F on conversion at 422° C for 8% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\overline{W}/T_1$)	M/T_1	W gm
60	10.57	31.32	0.2385	0.5230	1.0029
61	15.82	45.11	0.3109	0.3783	1.5010
62	21.12	58.03	0.3672	0.2656	2.0040
63	31.70	79.35	0.4424	0.1151	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
60	0.2482	0.02972	0.06518	0.2326	100.0
61	0.2404	0.04281	0.05209	0.2253	100.0
62	0.2297	0.05517	0.03980	0.2152	100.0
63	0.2242	0.07536	0.01960	0.2102	100.0

Table 8-B-2 (cont'd)

Effect of W/F on conversion at 422° C for 9% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\overline{W}/T_1$)	M/T_1	W gm
65	10.57	32.87	0.2474	0.5052	1.0029
66	15.82	46.52	0.3175	0.3650	1.5010
67	21.12	59.64	0.3736	0.2528	2.0040
68	31.70	81.74	0.4498	0.1005	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
65	0.2500	0.03119	0.06370	0.2082	100.0
66	0.2366	0.04415	0.05075	0.1971	100.0
67	0.2270	0.05660	0.03830	0.1891	100.0
68	0.2225	0.07757	0.01733	0.1853	100.0

Table 8-B-2 (cont'd)

Effect of W/F on conversion at 422° C for 10% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\overline{W}/T_1$)	M/T_1	W gm
70	10.57	34.18	0.2547	0.4905	1.0029
71	15.82	47.89	0.3238	0.3524	1.5010
72	21.12	60.62	0.3774	0.2452	2.0040
73	31.70	83.02	0.4536	0.0978	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
70	0.2511	0.03244	0.06246	0.1882	100.0
71	0.2409	0.04545	0.04945	0.1806	100.0
72	0.2351	0.05773	0.03737	0.1763	100.0
73	0.2221	0.07879	0.01611	0.1665	100.0

Table 8-B-3
Effect of W/R on conversion at 466° C for 5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\overline{W}/T_1$)	M/T_1	W gm
75	10.57	43.62	0.3037	0.3925	1.0029
76	15.82	61.13	0.3794	0.2412	1.5010
77	21.12	75.04	0.4287	0.1426	2.0040
78	31.70	91.52	0.4779	0.0443	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
75	0.2523	0.04139	0.05350	0.3783	100.0
76	0.2476	0.05801	0.03689	0.3713	100.0
77	0.2440	0.07121	0.02369	0.3658	100.0
78	0.2382	0.08685	0.00805	0.3572	100.0

Table 8-B-3 (cont'd)
Effect of W/F on conversion at 466° C for 6.5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 $(=\bar{W}/T_1)$	M/T_1	W gm
80	10.57	45.89	0.3145	0.3709	1.0029
81	15.82	64.25	0.3912	0.2176	1.5010
82	21.12	79.95	0.4443	0.1114	2.0040
83	31.70	95.03	0.4872	0.0255	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
80	0.2457	0.04355	0.05135	0.2835	100.0
81	0.2412	0.06097	0.03393	0.2782	100.0
82	0.2359	0.07587	0.01903	0.2721	100.0
83	0.2316	0.09018	0.00472	0.2671	100.0

Table 8-B-3 (cont'd)

Effect of W/F on conversion at 466° C for 8% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\overline{W}/T_1$)	M/T_1	W gm
85	10.57	47.78	0.3233	0.3534	1.0029
86	15.82	67.02	0.4013	0.1975	1.5010
87	21.12	83.22	0.4542	0.0916	2.0040
88	31.70	98.93	0.4973	0.0054	3.0080

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
85	0.2432	0.04534	0.04956	0.2279	100.0
86	0.2287	0.06360	0.03130	0.2143	100.0
87	0.2210	0.07898	0.01592	0.2071	100.0
88	0.2128	0.09388	0.00101	0.1997	100.0

Table 8-B-3 (cont'd)

Effect of W/F on conversion of 466° C for 9% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 ($=\overline{W}/F_1$)	M/T_1	W gm
90	10.57	49.01	0.3289	0.3422	1.0029
91	15.82	68.53	0.4066	0.1867	1.5010
92	21.12	84.61	0.4583	0.0834	2.0040

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
90	0.2416	0.04651	0.04839	0.2012	100.0
91	0.2290	0.06503	0.02986	0.1908	100.0
92	0.2131	0.08029	0.01460	0.1775	100.0

Table 8-B-3 (cont'd)

Effect on W/F on conversion at 466° C for 10% methanol

Run No.	W/F gm-hr/moles	Conv. x%	F_f/T_1 (= $\overline{W}/T_1$)	M/T_1	W gm
95	10.57	50.23	0.3343	0.3313	1.0029
96	15.82	69.87	0.4113	0.1774	1.5010
97	21.12	86.11	0.4627	0.0746	2.0040

Run No.	O_2/N_2	F_f moles/hr	F_m moles/hr	F_{O_2} moles/hr	Selectivity s%
95	0.2319	0.04767	0.04723	0.1739	100.0
96	0.2244	0.06631	0.02859	0.1682	100.0
97	0.2151	0.08172	0.01318	0.1612	100.0

Table 8-B-4

Effect of W/F on conversion

Run No.	% Methanol	Conv. x%	Selecti-vity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	Yield y%
54	5.0	80.21	99.21	0.2395	0	0.00040	0.3591	79.65
59	6.5	84.09	97.77	0.2291	0	0.00154	0.2643	82.26
64	8.0	87.20	95.36	0.2182	0	0.00409	0.2045	83.03
69	9.0	89.22	91.25	0.2091	0	0.00892	0.1742	81.62
74	10.0	92.13	89.79	0.1995	0	0.01194	0.1496	82.94
79	5.0	98.13	97.31	0.2351	0	0.00167	0.3525	95.30

Run No.	Temp °C	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	W/F gm-hr/moles
54	422	0.00060	0.4484	0.4418	0.1098	0.07559	0.01878	31.70
59	422	0.00178	0.4668	0.4467	0.0864	0.07807	0.01510	31.70
64	422	0.00383	0.4877	0.4439	0.0684	0.07880	0.01214	31.70
69	422	0.00743	0.5123	0.4308	0.0569	0.07746	0.01023	31.70
74	422	0.00895	0.5280	0.4311	0.0409	0.07871	0.00746	31.70
79	466	0.00250	0.5091	0.4815	0.0094	0.09044	0.00177	31.70

Table 8-B-4 (cont'd)

Effect W/F on conversion

Run No.	% Methanol	Conv. x%	Selecti-vity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	Yield y%
84	6.5	100.0	95.86	0.2242	0	0.00340	0.2586	95.73
89	8.0	100.0	93.27	0.2133	0	0.00683	0.1999	93.53
93	9.0	100.0	95.05	0.2044	0	0.00564	0.1703	95.04
94	10.0	100.0	89.31	0.1974	0	0.01360	0.1480	89.84
98	9.0	100.0	92.47	0.2031	0	0.00864	0.1692	93.19
99	10.0	100.0	86.40	0.1963	0	0.01707	0.1471	85.72

Run No.	Temp. °C	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	W/F gm-hr/moles
84	466	0.00392	0.5210	0.4790	0	0.09085	0	31.70
89	466	0.00640	0.5330	0.4670	0	0.08876	0	31.70
93	466	0.00470	0.5248	0.4752	0	0.09019	0	21.12
94	466	0.01020	0.5521	0.4479	0	0.08526	0	31.70
98	466	0.00720	0.5358	0.4641	0	0.08844	0	21.12
99	466	0.01280	0.5697	0.4303	0	0.08135	0	31.70

(C) Effect of W/F ratio at 495° and 531° C

The experimental data for the study of the effect of W/F ratio on conversion, selectivity and yield at temperatures 495° C and 531° C are summarized in Tables 8-C-1 and 8-C-2 respectively. The running conditions for feed ratios and the weight of the catalyst used were same as that are given in Appendix (B).

Table 8-C-1

Effect of W/F on conversion and yield at 495° C for 5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selecti-vity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
100	10.57	56.67	100.00	0.2482	0.0	0.0	0.3722	0
101	15.82	79.12	100.00	0.2401	0.0	0.0	0.3560	0
102	21.12	97.35	98.90	0.2328	0	0.00075	0.3491	0
103	31.70	100.00	95.98	0.2325	0.0	0.00255	0.3486	0
104	36.89	100.00	95.38	0.2321	0.0	0.00291	0.3480	0

Run No.	Yield y%	F_{CO} moles/hr	$\overline{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
100	56.66	0	0.3617	0.3617	0.2766	0.05377	0.04112	0.1487
101	79.11	0	0.4417	0.4417	0.1166	0.07508	0.01981	0.1700
102	96.51	0.01120	0.4988	0.4878	0.0134	0.0915	0.00251	0.1875
103	96.20	0.00382	0.5195	0.4805	0	0.09130	0.0	0.1900
104	95.20	0.00437	0.5235	0.4765	0	0.09035	0.0	0.1896

Table 8-C-1 (cont'd)

Effect of W/F on conversion and yield at 495° C for 6.5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
105	10.57	88.76	100.00	0.24229	0.0	0.0	0.2795	0
106	15.82	82.76	100.00	0.23230	0.0	0.0	0.2680	0
107	21.12	100.00	97.51	0.22411	0.0	0.002046	0.2585	0
108	31.70	100.00	95.25	0.22176	0.0	0.003893	0.2558	0
109	36.89	100.00	94.31	0.22149	0.0	0.004673	0.2555	0

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
105	58.11	0	0.3675	0.3675	0.2649	0.05515	0.03975	0.1500
106	82.76	0	0.4528	0.4528	0.0943	0.07854	0.01636	0.1734
107	97.68	0.00236	0.5120	0.4880	0.0	0.09270	0.0	0.1899
108	94.93	0.00449	0.5245	0.4754	0	0.09009	0	0.1895
109	94.08	0.00539	0.5290	0.4709	0	0.08928	0	0.1896

Table 8-C-1 (cont'd)

Effect of W/F on conversion and yield at 495° C for 8% methanol

Run No.	W/F gm-hr/mole	Conv. x%	Selecti-vity y%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
110	10.57	61.40	100.00	0.23426	0.0	0.0	0.21950	0
111	15.82	86.17	100.00	0.22181	0.0	0.0	0.20780	0
112	21.12	100.00	95.94	0.21165	0.001387	0.002732	0.19835	0.00130
113	31.70	100.00	93.53	0.21232	0.002796	0.003745	0.19898	0.00262
114	36.89	100.00	89.25	0.20836	0.004450	0.006434	0.19527	0.00417

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
110	61.39	0	0.3804	0.3804	0.2392	0.05826	0.03663	0.1532
111	86.16	0	0.4629	0.4629	0.0743	0.08177	0.01310	0.1767
112	96.08	0.00256	0.5199	0.4800	0	0.09118	0	0.1899
113	93.35	0.00351	0.5328	0.4672	0	0.08859	0	0.1896
114	89.28	0.00603	0.5536	0.4463	0	0.08473	0	0.1898

Table 8-C-1 (cont'd)

Effect of W/F on conversion and yield at 495° C for 9% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selecti-vity x%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
115	10.57	64.92	98.55	0.2288	0.0	0.001080	0.1906	0
116	15.82	96.21	97.87	0.2139	0.0	0.002197	0.1782	0
117	21.12	100.00	93.73	0.2050	0.002761	0.004370	0.1708	0.0023
118	31.70	100.00	87.49	0.1981	0.006243	0.007923	0.1650	0.0052
119	36.89	100.00	86.00	0.1953	0.007371	0.008716	0.1627	0.0061

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
115	64.57	0.00090	0.3979	0.3901	0.21190	0.06128	0.03329	0.1571
116	88.73	0.00183	0.4832	0.4654	0.05135	0.08421	0.00929	0.1809
117	93.59	0.00364	0.5317	0.4683	0	0.08882	0	0.1896
118	86.97	0.00660	0.5638	0.4362	0	0.08254	0	0.1892
119	86.73	0.00726	0.5682	0.4318	0	0.08231	0	0.1906

Table 8-C-1 (cont'd)

Effect of W/F on conversion and yield at 495° C for 10% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
120	10.57	67.40	98.12	0.22215	0.0	0.001618	0.16615	0
121	15.82	93.65	95.97	0.20387	0.002019	0.002808	0.15247	0.00151
122	21.12	100.00	92.34	0.19679	0.004573	0.005201	0.14718	0.00342
123	31.70	100.00	88.17	0.18996	0.007982	0.006993	0.14207	0.00597
124	36.89	100.00	81.90	0.17499	0.012515	0.010349	0.13088	0.00936

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
120	66.65	0.00121	0.4090	0.3969	0.1941	0.06325	0.03093	0.1594
121	90.67	0.00210	0.5011	0.4663	0.0326	0.08605	0.00602	0.1845
122	92.84	0.00389	0.5370	0.4630	0	0.08811	0	0.1903
123	87.96	0.00523	0.5597	0.4403	0	0.08348	0	0.1896
124	81.54	0.00774	0.5914	0.4086	0	0.07738	0	0.1894

Table 8-C-2

Effect of W/F on conversion and yield at 531° C for 5% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
125	10.57	71.29	100.00	0.24274	0.0	0.0	0.36397	0
126	15.82	92.08	97.95	0.23640	0.0	0.001200	0.35446	0
127	21.12	100.00	96.64	0.23265	0.0	0.002134	0.34844	0
128	31.70	100.00	93.63	0.23070	0.001434	0.002581	0.34591	0.00215
129	36.89	100.00	91.44	0.23060	0.001834	0.003560	0.34577	0.00275

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
125	71.28	0	0.4162	0.4162	0.16760	0.06765	0.02725	0.1625
126	90.50	0.00180	0.4884	0.4704	0.04115	0.08589	0.00751	0.1826
127	96.90	0.00320	0.5161	0.4838	0	0.09196	0	0.1900
128	93.27	0.00387	0.5327	0.4673	0	0.08852	0	0.1894
129	91.10	0.00534	0.5436	0.4564	0	0.08645	0	0.1899

Table 8-C-2 (cont'd)

Effect of W/F on conversion and yield at 531° C for 6.5 methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
130	10.57	75.07	98.51	0.23416	0.0	0.000919	0.27010	0
131	15.82	95.04	96.60	0.22430	0.0	0.002688	0.25873	0
132	21.12	100.00	95.17	0.22316	0.001214	0.002774	0.25741	0.00140
133	31.70	100.00	91.83	0.22149	0.002956	0.003737	0.25548	0.00341
134	36.89	100.00	91.27	0.21837	0.003408	0.003711	0.25189	0.00393

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
130	74.10	0.00106	0.4338	0.4229	0.1423	0.07033	0.02366	0.1663
131	92.92	0.00310	0.5011	0.4736	0.0253	0.08818	0.00471	0.1862
132	95.57	0.00320	0.5231	0.4768	0	0.09070	0	0.1902
133	91.14	0.00431	0.5419	0.4581	0	0.08670	0	0.1893
134	90.47	0.00428	0.5456	0.4544	0	0.08590	0	0.1890

Table 8-C-2 (cont'd)

Effect of W/F on conversion and yield at 531° C for 8.0 methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selecti-vity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
135	10.57	78.29	95.92	0.22438	0.001280	0.001974	0.21028	0.00120
136	15.82	99.16	95.75	0.21113	0.001814	0.002476	0.19787	0.00170
137	21.12	100.00	93.53	0.21005	0.003041	0.003468	0.19685	0.00285
138	31.70	100.00	87.69	0.21014	0.005260	0.007118	0.19694	0.00493
139	36.89	100.00	85.70	0.20267	0.007896	0.006402	0.18994	0.00740

Run No.	Yield y%	F_{CO} moles/hr	$\overline{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
135	75.50	0.00185	0.4561	0.4224	0.1215	0.07164	0.02060	0.1696
136	95.46	0.00232	0.5177	0.4780	0.0042	0.09060	0.00080	0.1895
137	92.91	0.00325	0.5339	0.4661	0	0.08817	0	0.1892
138	87.04	0.00667	0.5631	0.4369	0	0.08264	0	0.1891
139	84.62	0.006	0.5742	0.4258	0	0.08030	0	0.1886

Table 8-C-2 (cont'd)

Effect of W/F on conversion and yield at 531° C for 9.0% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selectivity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
140	10.57	83.31	95.09	0.21351	0.0	0.004682	0.17785	0
141	15.82	100.00	92.59	0.20145	0.002761	0.005726	0.16780	0.00230
142	21.12	100.00	88.62	0.20101	0.006891	0.006075	0.16744	0.00574
143	31.70	100.00	81.00	0.19529	0.012245	0.009244	0.16267	0.01020
144	36.89	100.00	78.73	0.19188	0.014046	0.010120	0.15983	0.01170

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
140	79.66	0.00390	0.4757	0.4335	0.0908	0.07560	0.01584	0.1744
141	93.15	0.00477	0.5356	0.4644	0	0.08840	0	0.1904
142	88.63	0.00506	0.5568	0.4431	0	0.08411	0	0.1898
143	80.48	0.00770	0.5963	0.4037	0	0.07638	0	0.1892
144	78.51	0.00843	0.6069	0.3931	0	0.07451	0	0.1895

Table 8-C-2 (cont'd)

Effect of W/F on conversion and yield at 531° C for 10% methanol

Run No.	W/F gm-hr/moles	Conv. x%	Selecti-vity s%	O_2/N_2	CO_2/N_2	CO/N_2	F_{O_2} moles/hr	F_{CO_2} moles/hr
145	10.57	86.46	94.17	0.20473	0.003557	0.002888	0.15312	0.00266
146	15.82	100.00	90.74	0.19141	0.006298	0.005415	0.14316	0.00471
147	21.12	100.00	84.51	0.18998	0.012595	0.007020	0.14209	0.00942
148	31.70	100.00	77.94	0.18466	0.017836	0.009974	0.13811	0.01334
149	36.89	100.00	74.39	0.17156	0.022543	0.009827	0.12831	0.01686

Run No.	Yield y%	F_{CO} moles/hr	$\bar{W}/T_1$	F/T_1	M/T_1	F_f moles/hr	F_m moles/hr	T_1 moles/hr
145	82.04	0.00216	0.4892	0.4384	0.0723	0.07786	0.01284	0.1776
146	90.43	0.00405	0.5471	0.4529	0	0.08582	0	0.1895
147	84.36	0.00525	0.5778	0.4222	0	0.08006	0	0.1896
148	77.42	0.00746	0.6116	0.3884	0	0.07347	0	0.1892
149	74.11	0.00735	0.6288	0.3712	0	0.07033	0	0.1894

(D) Calibration of Equipment

1. Calibration of Gas Chromatographs:

The calibration curves for the analysis of liquid products, formaldehyde, methanol and water and for the analysis of gaseous products, carbon dioxide, carbon monoxide, and unreacted nitrogen and oxygen are shown in Figures 8-D-1 and 8-D-2, respectively.

2. Calibration of Syringe pump

Methanol was fed to the reactor at a constant flow rate. The syringe pump, used with a 1/5 r.p.m. speed motor and 20 ml capacity syringe, was calibrated by collecting methanol for a known period of time and weighing it.

Mass flow rate of methanol = 3.0370 gm/hr

Molal flow rate of methanol = 0.0949 mole/hr

3. Calibration of Thermocouple:

The calibration curve, temperature in °C versus millibolts, is shown in Figure 8-D-3.

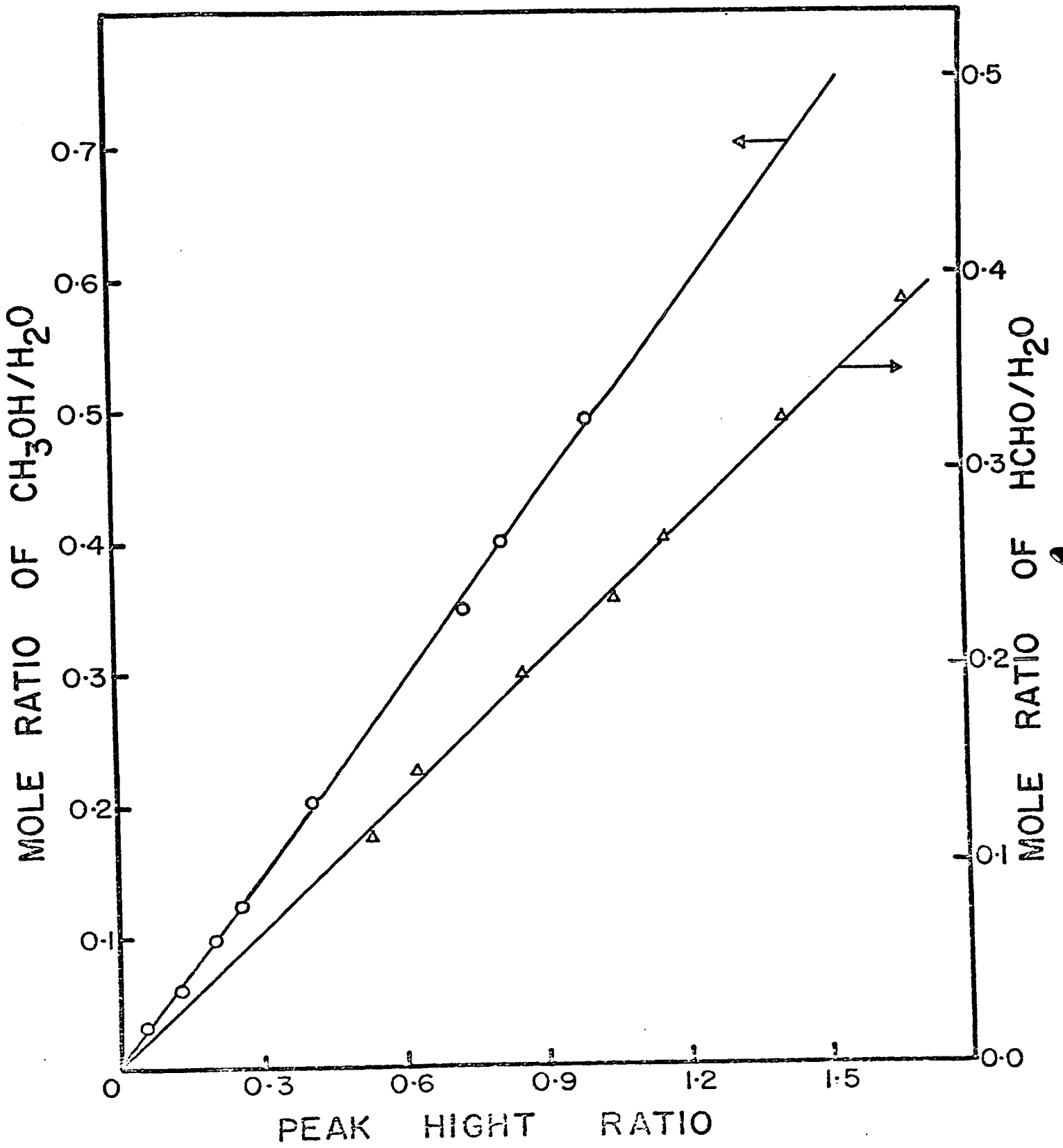

Fig. 8-D-1 Calibration of Gas Chromatograph for liquid products

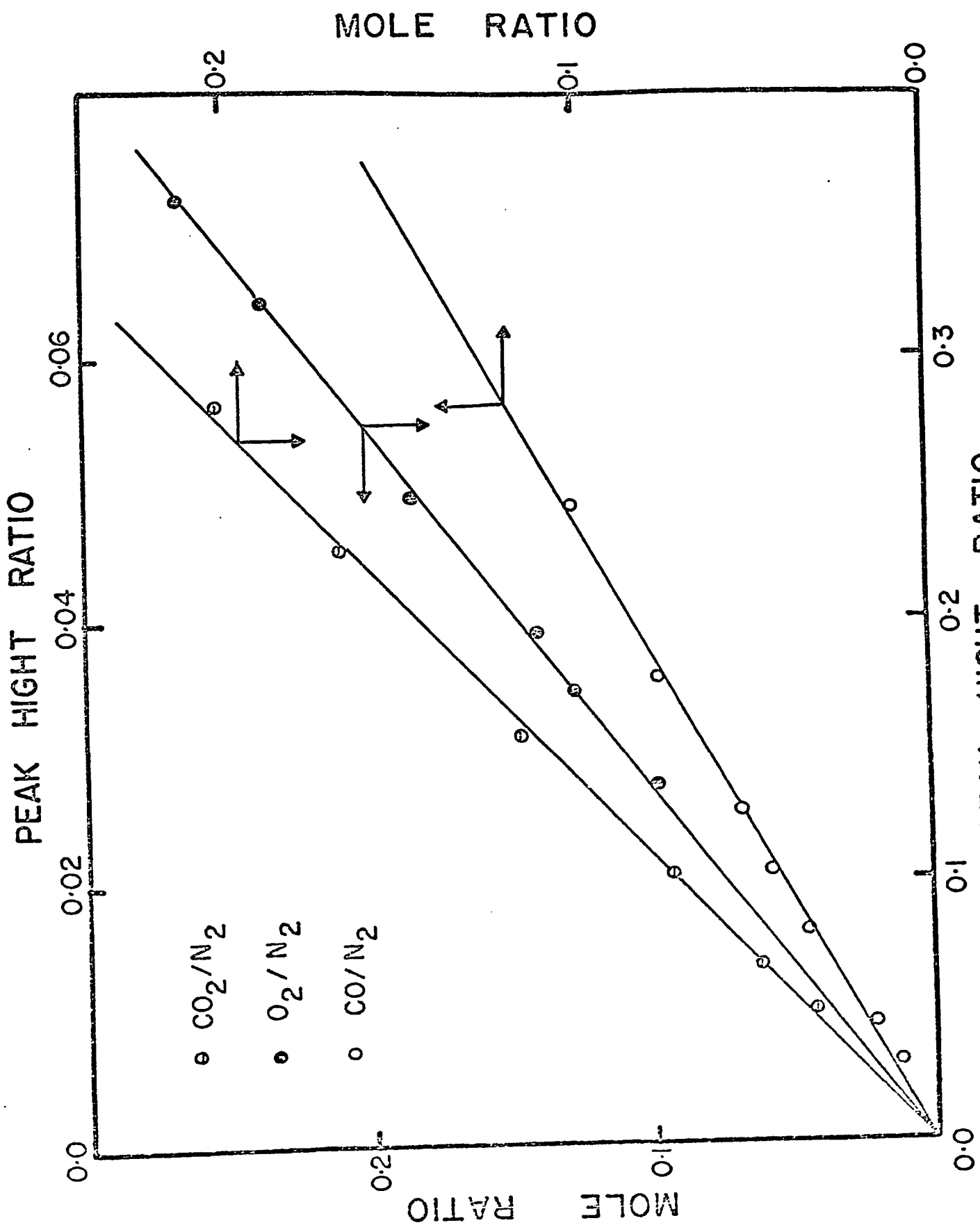

Fig. 8-D-2 Calibration of the Fisher Gas Partitioner

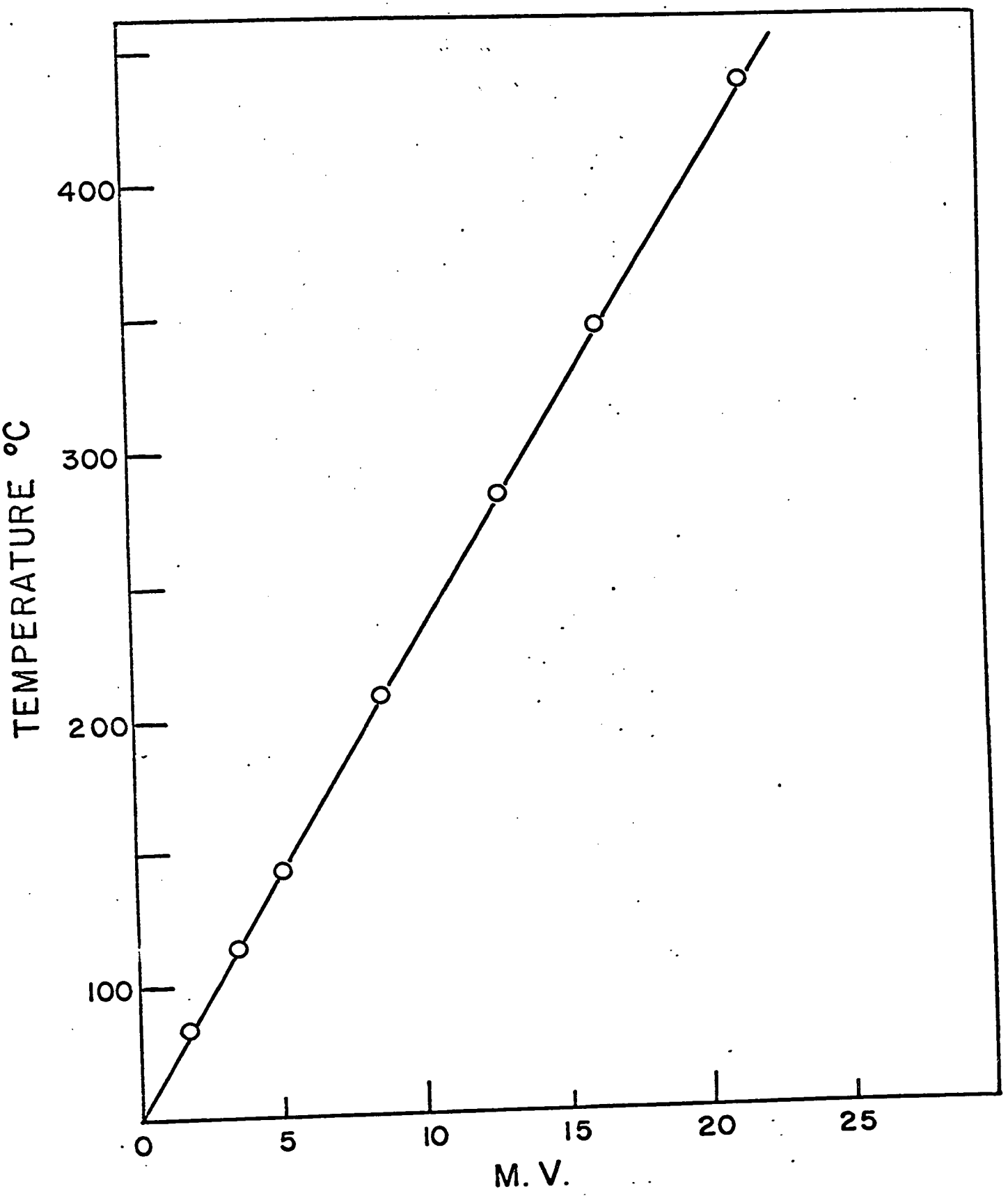

Fig. 8-D-3 Calibration of Thermocouples

(E) Sample Calculations and Material Balance

1. A sample calculation is shown below on the basis of the experimental data of Run No. 149, where the catalyst selectivity to formaldehyde formation is less than 100%:

Gas Analysis:

Peak height ratio:

$$(CO_2/N_2)_h = .02834$$

$$(CO/N_2)_h = .00459$$

$$(O_2/N_2)_h = 0.234$$

Mole ratio:

$$(CO_2/N_2)_m = 0.795\ (CO_2/N_2)_h \qquad (8\text{-}1)$$

$$= 0.795 \times 0.02834 = 0.02254$$

$$(CO/N_2)_m = 2.14\ (CO/N_2)_h \qquad (8\text{-}2)$$

$$= 2.14 \times 0.00459 = 0.00983$$

$$(O_2/N_2)_m = 0.733\ (O_2/N_2)_h \qquad (8\text{-}3)$$

$$= 0.733 \times 0.234 = 0.17156$$

As nitrogen remains unreacted,

moles of N_2 in product = moles of N_2 in feed

moles of N_2 in feed = 0.7497 moles /hr

Thus,

F_{CO_2}, moles of CO_2 in the product

$= 0.02254 \times 0.7497$

$= 0.01686$ moles/hr

F_{CO}, moles of CO in the product

$= 0.00983 \times 0.7497$

$= 0.00735$ moles/hr

F_{O_2}, moles of O_2 in the product

$= 0.17156 \times 0.7497$

$= 0.12831$ moles/hr

Liquid Analysis

Peak height ratio:

$(F/\overline{W})_h = 2.556$

$(M/\overline{W})_h = 0$

Mole ratio

$(F/\overline{W}) = 0.231\,(F/\overline{W})_h$

or $\dfrac{(F/T_l)}{(\overline{W}/T_l)} = 0.231\,(F/W)_h$

$(F/T_l) = 0.231\,(F/\overline{W})_h\,(\overline{W}/T_l)$ (8-4)

and $(M/T_l) = 0.487\,(M/\overline{W})_h\,(\overline{W}/T_l)$ (8-5)

Adding (8-4) and (8-5)

$$\left(\frac{F}{T_1}\right) + \left(\frac{M}{T_1}\right) = 0.231\left(\frac{F}{W}\right)_h\left(\frac{W}{T_1}\right) + 0.487\left(\frac{M}{W}\right)\left(\frac{W}{T_1}\right)$$

$$1 - \left(\frac{W}{T_1}\right) = \left(\frac{W}{T_1}\right)\left[0.231\left(\frac{F}{W}\right) + 0.487\left(\frac{M}{W}\right)_h\right]$$

$$\text{or } \left(\frac{W}{T_1}\right) = \frac{1}{1 + 0.231\left(\frac{F}{W}\right)_h + 0.487\left(\frac{M}{W}\right)_h} \qquad (8\text{-}6)$$

$$= \frac{1}{1 + 0.231\,(2.556) + 0.487\,(0)}$$

$$= 0.62876$$

$$\left(\frac{F}{T_1}\right) = 0.231 \times (2.256)\,(0.6288)$$

$$= 0.3712$$

$$\left(\frac{M}{T_1}\right) = 0.487\,(0)\,(0.6288)$$

$$= 0$$

From material balance:

$$M_O = M + F_f + F_{CO} + F_{CO_2}$$

$$M = M_O - (F_f + F_{CO} + F_{CO_2})$$

also, $\overline{W} = F_f + 2(F_{CO} + F_{CO_2})$

therefore,

$$T_1 = M + W + F_f$$

$$= M_O - (F_f + F_{CO} + F_{CO_2}) + F_f + 2(F_{CO} + F_{CO_2}) + F_f$$

$$= M_O + F_f + F_{CO} + F_{CO_2} \qquad (8\text{-}7)$$

$$F_f / T_1 = \frac{F_f}{F_f + M_O + F_{CO} + F_{CO_2}}$$

or $$F_f = \frac{(M_o + F_{CO} + F_{CO_2})(F_f/T_1)}{1 - (F_f/T_1)} \qquad (8\text{-}8)$$

$$= \frac{(0.0949 + 0.01686 + 0.00735)(0.3712)}{1 - (0.3712)}$$

$$= 0.07033 \text{ moles/hr}$$

$$\left(\frac{M}{T_1}\right) = \frac{M}{F_f + M_O + F_{CO} + F_{CO_2}}$$

or $$M = (M/T_1)(F_f + M_O + F_{CO} + F_{CO_2}) \qquad (8\text{-}9)$$

$$= 0$$

Moles of methanol reacted $= M_r$

$$= M_O - M$$

$$= 0.0949 \text{ moles/hr}$$

$$T_1 = M_O + F_f + F_{CO_2} + F_{CO}$$

$$= (0.0949 + 0.07033 + 0.01686 + 0.00735)$$

$$= 0.18944 \text{ moles/hr}$$

$$x\% = \frac{M_r}{M_O} \times 100 \qquad (8\text{-}10)$$

$$= \frac{0.0949}{0.0949} \times 100$$

$$= 100\%$$

$$s\% = \frac{F_f}{F_f + F_{CO_2} + F_{CO}} \qquad (8\text{-}11)$$

$$= \frac{0.07033 \times 100}{0.07033 + 0.1686 + 0.00735}$$

$$= \frac{.07033}{.09454} \times 100$$

$$= 74.39\ \%$$

$$y\% = \frac{F_f}{M_O} \qquad (8\text{-}12)$$

$$= \frac{0.07033}{0.0949} \times 100$$

$$= 74.11\%$$

2. Another sample calculation is shown on the basis of the experimental data of Run No. 97, where the selectivity of the catalyst to formaldehyde formation remains 100% and no carbon oxides are formed.

Gas Analysis:

Peak height ratio:

$$(O_2/N_2)_h = 0.2934$$

Mole ratio:

$$(O_2/N_2)_m = 0.733\ (O_2/N_2)_h$$
$$= 0.733\ (0.2934)$$
$$= 0.2151$$

Moles of N_2 in the feed = 0.7497 moles/hr

$$F_{O_2} = 0.2151 \times 0.7497$$
$$= 0.1612 \text{ moles/hr}$$

Liquid analysis

Peak height ratio:

$$(F/\overline{W})_h = 4.329$$

$$(M/\overline{W})_h = 0.3312$$

Mole ratio:

From equation (8-6)

$$\left(\frac{W}{T_1}\right) = \frac{1}{1 + 0.231\,(F/\overline{W})_h + 0.487\,(M/\overline{W})_h}$$

$$= \frac{1}{1 + 0.231\,(4.329) + 0.487\,(0.3312)}$$

$$= 0.4627$$

$$\left(\frac{M}{T_1}\right) = 0.487\,(M/W)_h\,(W/T_1)$$

$$= 0.487\,(0.3312)\,(0.4627)$$

$$= 0.0746$$

From material balance

$$M = M_O - F_f$$

$$\overline{W} = F_f$$

$$T_1 = F_f + W + M$$

$$= 2F_f + M_O - F_f = F_f + M_O$$

$$(F_f/T_1) = \frac{F_f}{F_f + M_O} = (\overline{W}/T_1)$$

or $$F_f = \frac{M_O (\overline{W}/T_1)}{1 - (\overline{W}/T_1)}$$

$$= \frac{0.0949\ (0.4627)}{1 - 0.4627}$$

$$= 0.08172 \text{ moles/hr}$$

$$M = M_O - F_f$$

$$= 0.0949 - 0.08172$$

$$= 0.01318 \text{ moles/hr}$$

$$x = \frac{\text{moles of methanol reacted}}{\text{moles of methanol in feed}} \times 100$$

$$= \frac{0.08172}{0.0949} \times 100$$

$$= 86.11\%$$

3. Material Balance Cheek Based on Atomic Oxygen:

Component	Feed in moles/hr	Product in moles/hr
CH_3OH	0.0949	0.01318
HCHO	0	0.08172
H_2O	0	0.08172
O_2	0.3986	0.32240
Total	0.4935	0.49902

$$\% \text{ Deviation} = \frac{\text{output - input}}{\text{output}} \times 100$$

$$= \frac{0.00552}{0.49902} \times 100$$

$$= 1.05\%$$

All the deviations determined were found to be within $\pm$ 3.0%

4. Deviation between Calculated and Experimental W/F versus x Relations:

The following is a sample tabulation of the deviation between the calculated and experimental W/F versus x relations. It is based on data obtained at 375° C, with 10% methanol in air (Run No. 's 45-49).

x %	$(W/F)_{exp.}$	$(W/F)_{cal.}$	% Deviation
21.46	10.57	10.77	-1.90
31.50	15.82	16.10	-1.77
41.72	21.12	21.80	-3.13
58.49	31.70	31.95	-0.79
65.50	36.89	36.64	0.68

The percentage deviation may be defined as:

$$\% \text{ Deviation} = \frac{(W/F)_{\text{calculated}} - (W/F)_{\text{experimental}}}{(W/F)_{\text{experimental}}}$$

In general, all the deviations were found to be with in $\pm$ 4.0%, except for the last condition (Run No. 88) where, deviation was found to be -11.7%.

(F) Thermodynamic Aspects:

The values of the change in free energy, ΔG, and the equilibrium constant, K_p, of the gaseous oxidation of methanol to formaldehyde and water are given in the following table:

Table 8-F-1

The values of ΔG and K_p
for Gaseous Formaldehyde Formation
at 1 atmosphere and different temperatures

Temperature °C	-(ΔG) k cal/g. mole	K_p
25	42.900	3.4667×10^{31}
250	44.068	2.8840×10^{18}
280	44.084	2.8840×10^{17}
350	44.595	4.7860×10^{15}
450	43.125	1.8200×10^{12}

These values were calculated as functions of temperature, necessary data being either taken from literature or calculated by the group contribution method [91].

(G) External Diffusion (Drop in partial pressure)

The data for estimation of the external diffusion are obtained from Run No. 88. The conditions which apply to this evaluation are:

Temp. = 466° C

W/F = 31.7 gm.hr/moles

M% = Methanol to air ratio

= 8.0 mole %

ϕ = shape factor or sphericity

= 0.9 for irregular granules

G_m = molal mass velocity of feed based on the total cross section of the catalyst bed in moles/hr. cm^2

$$= \frac{1.1863 + 0.0949}{\frac{\pi}{4} (3/8 \times 2.54)^2}$$

= 1.8 moles/hr. cm^2

W = Weight of catalyst

= 3.008 gm

a_m = surface area of the catalyst particle per unit mass of the catalyst

= 3.87 m^2/gm

= 38700 cm^2/gm

$(F_j)_{in}$ = flow rate of component j in the feed

$(F_j)_{out}$ = flow rate of component j in the product

$(Y_j)_{in}$ = mole fraction of component j in the feed

$(Y_j)_{out}$ = mole fraction of component j in the product

Y_j = mole fraction of component j at the interface

$$\simeq \frac{(Y_j)_{in} + (Y_j)_{out}}{2}$$

r_{m_j} = molal reaction rate of component j per unit mass of catalyst

R_j = dimension less terms of component j

$$= \frac{r_{m_j}}{a_m \Phi G_m}$$

$$= \frac{r_{m_j}}{(38700)\ (0.9)\ (1.8)}$$

$$= \frac{r_{m_j}}{6.26 \times 10^4}$$

for example,

r_{m_f} = molal reaction rate of formaldehyde per unit mass of catalyst

$$= \frac{0.09388}{3.008} \quad \text{moles/gm.hr}$$

$$R_f = \frac{r_{m_f}}{6.26 \times 10^4}$$

$$= \frac{0.09388}{3.008 \times 6.26 \times 10^4}$$

$$= 4.99 \times 10^{-7}$$

$$Y_j = (0 + 0.0708)/2$$

$$= 0.0354$$

$$\frac{R_f}{Y_j} = \frac{4.99 \times 10^{-7}}{0.0354}$$

$$= 1.41 \times 10^{-5}$$

The value of $\Delta p_f/p_f$ is obtained from $\Delta p_j/p_j$ versus R_j/Y_j plot given in Figure 2 by Yoshida et al [78]. Similar procedure is adopted to find the pressure drop for other components and their values are listed in Table 8-G-1 since $\Delta p_j/p_j$ is less than 0.001, the external diffusion effects are neglected.

Table 8-G-1

Evaluation of External Diffusion

Component j	$(F_j)_{in}$ moles/hr	$(F_j)_{out}$ moles/hr	$(Y_j)_{in}$	$(Y_j)_{out}$	Y_j	R_j x 10^7	R_j/Y_j x 10^5	$\left(\frac{\Delta p_j}{p_j}\right)_{max.}$
O_2	0.2491	0.19970	0.1945	0.1506	0.1725	10.6	0.615	0.0001
N_2	0.9372	0.93720	0.7315	0.7065	0.7190	-	-	0.0001
CH_3OH	0.0949	0.00101	0.0741	0.0076	0.0408	0.054	0.0133	0.0001
HCHO	0	0.09388	0	0.0708	0.0354	4.99	1.41	0.0001
H_2O	0	0.09388	0	0.0708	0.0354	4.99	1.41	0.0001

(H) Temperature drop from catalyst particle to ambient gas stream

From Appendix (G)

$$r_{m_f} = \frac{0.09388}{3.008} \text{ moles/gm.hr}$$

$$= 0.0312 \text{ mole/gm.hr}$$

$\phi = 0.9$

$G_m = 1.8 \text{ moles/cm}^2\text{-hr}$

$a_m = 38700 \text{ cm}^2/\text{gm}$

The average specific heat of the ambient gas is calculated as follows:

Component J	Y_j	$(C_p)_j$ cal/gm.mole °C	$(C_p)_j Y_j$ cal/gm mole° C	Heat of formation H_f $\frac{KCal}{mole}$
O_2	0.1725	7.80	1.346	0
N_2	0.7190	7.26	5.220	0
CH_3OH	0.0408	16.85	0.686	-48.08
HCHO	0.0354	11.60	0.410	-28.29
H_2O	0.0354	8.78	0.311	-57.80

$$C_p = \sum_{i=1}^{5} \left((C_p)_j Y_j \right)$$

$= 7.973$ cal/gm mole °C

ΔH = molal heat of reaction of formaldehyde

$= -(57.80 + 28.29) + (48.08)$

$= -38.01$ kcal./mole

$$\mathcal{Q}_f = \frac{r_{m_f} (\Delta H)}{a_m \phi C_p G_m}$$

$$= \frac{0.0321 \times 38010}{38700 \times 0.9 \times 7.973 \times 1.8}$$

$= .00214$

Since, from Figures 3 and 4 of Yoshida et al [78] at $\mathcal{Q}_f = 0.00214$, ΔT is less than 0.1° C, the catalyst surface temperature effect can be neglected.

(I) Correlation of Initial Rate Data

Initial rates obtained by determining the slopes at x = 0 of W/F vs. x curves for various methanol to air feed ratio at temperatures 304°, 422° and 466° C are given below:

Table 8-I-1

Correlation of Initial Rate Data

Temperature ° C	Methanol to air ratio %	Initial rate r_o moles HCHO/gm catalyst hr.
304	5.0	0.352
304	6.0	0.370
304	8.0	0.397
304	9.0	0.402
304	10.0	0.408
422	5.0	0.555
422	6.0	0.600
422	8.0	0.615
422	9.0	0.620
422	10.0	0.625
466	5.0	0.850
466	6.5	0.940
466	8.0	0.955
466	9.0	0.974
466	10.0	0.990

(J) Rate Constants for various Mechanisms

The rate constants for the acceptable two-stage redox mechanism where m equalled 1.0 and n equalled 0.5 are listed in Table 5-3. The rate constants for the various other mechanism which did not fit the experimental data are given in Tables 8-J-1 to 8-J-4.

Table 8-J-1

Rate constants for m = 0.5, n = 0.0

Temp. °C	$\bar{R}$ %	k_1 X10^3	k_2 X10^2
375	5.0	3.40	6.44
	6.5	3.80	3.13
	8.0	4.23	2.31
	9.0	3.59	3.19
	10.0	3.22	4.46
	overall k values at 375° C	5.27	1.82
422	5.0	4.78	4.51
	6.5	5.24	8.60
	8.0	5.79	5.08
	9.0	5.66	5.42
	10.0	5.12	7.35
	overall k values at 422° C	7.64	3.92
466	5.0	6.09	- 8.48
	6.5	6.50	-21.98
	8.0	8.27	12.25
	9.0	9.56	7.21
	10.0	9.38	7.36

Table 8-J-2

Rate constants for m = 1.0 , n = 1.0

Temp. °C	$\bar{R}$ %	k_1 X10^3	k_2 x10^5
375	5.0	1.49	7.9
	6.5	1.74	7.2
	8.0	2.18	6.9
	9.0	1.68	7.6
	10.0	1.40	8.3
overall k values at 375° C		1.32	8.25
422	5.0	2.19	12.8
	6.5	2.25	12.6
	8.0	2.63	11.9
	9.0	2.48	12.6
	10.0	2.12	13.6
overall k values at 422° C		2.00	13.6
466	5.0	3.49	20.7
	6.5	3.79	19.5
	8.0	5.74	17.4
	9.0	4.56	18.9
	10.0	4.48	19.5
overall k values at 466° C		3.82	25.0

Table 8-J-3

Rate constants for m = 1.0 , n = 0.0

Temp. °C	$\bar{R}$ %	k_1 X10^3	k_2 X10^2
375	5.0	1.29	1.42
	6.5	1.28	1.32
	8.0	1.31	1.26
	9.0	1.06	1.39
	10.0	0.92	1.52
overall k values at 375° C		1.19	1.66
422	5.0	1.99	2.23
	6.5	2.03	2.12
	8.0	2.08	2.02
	9.0	1.99	2.09
	10.0	1.75	2.22
overall k values at 422° C		1.99	2.27
466	5.0	3.31	3.51
	6.5	3.45	3.25
	8.0	5.42	2.69
	9.0	3.60	3.09
	10.0	3.45	3.14
overall k values at 466° C		2.92	4.22

Table 8-J-4

Rate constants for m = 0.5, n = 0.5

Temp. °C	$\bar{R}$ %	k_1 X10^3	k_2 X10^3
375	5.0	3.47	4.43
	6.5	4.08	2.10
	8.0	4.80	1.55
	9.0	3.96	2.10
	10.0	3.46	2.90
	overall k values at 375°C	4.90	1.58
422	5.0	4.80	29.39
	6.5	5.25	6.76
	8.0	6.05	3.66
	9.0	5.85	4.04
	10.0	5.19	5.72
	overall k values at 422°C	6.55	3.23
466	5.0	6.16	- 7.12
	6.5	6.67	- 26.20
	8.0	8.52	8.63
	9.0	10.02	5.32
	10.0	9.85	5.46

IX. NOMENCLATURE

a_m	Catalyst surface area per unit mass, m^2/gm
C_{av}	Average specific heat, cal/gm-mole-°C
C_p	Specific heat of gas, cal/gm-mole-°C
D_{Am}	Average diffusivity of component A
D_p	Catalyst particle diameter, mm
F	Flow rate of feed, moles/hr
G	Molal velocity of flow based on the total cross-sectional area of the catalyst bed
ΔG	The change in free energy, kcal/gm-mole
H_f	Heat of formation, kcal/gm-mole
h_G	Heat transfer coefficient of the gas film
i	Component i
j	Dimensionless Chilton-Colburn factor
k	Thermal conductivity of the gas
k_G	Mass transfer coefficient of gas film
$\bar{R}$	Moles % methanol in air
p_i	Partial pressure of component i
q_m	Heat transfer due to heat of reaction per unit mass of catalyst
r	Reaction rate, moles/gm of catalyst-hr
r_o	Initial rate, moles/gm of catalyst-hr
s	Selectivity
s	Active site on catalyst
s_{ox}	Oxidized site, active site of lattice or adsorbed oxygen on catalyst

s_{red}	Reduced site of lattice oxygen or the empty site on the catalyst
t	Time
T	Temperature
T_i	Temperature of the gas-solid interface
T_l	Total liquid component flow rate, methanol, formaldehyde and water
W	Weight of catalyst, gm
$\overline{w}$	Flow rate of water
x	Conversion of methanol
y	Yield of formaldehyde

Greek Symbols

Δ	Finite increment or change of property
δ	Change in moles per mole of reactant (or product)
θ_i	Fraction of the catalyst surface that is covered by adsorbed component i
μ	Viscosity
π	Total pressure
ρ	Density
ρ_B	Bulk density of catalyst, gm/ml
$\emptyset$	Shape factor, ratio of actual external surface area available for mass and heat transfer to the total external surface area, assumed to be 0.09 for irregular granules

Superscripts

m	Reaction order with respect to methanol
n	Reaction order with respect to oxygen

Subscripts

A_i	Component A at the gas-solid surface interphase
cal	Calculated
f	Formaldehyde
f	Properties at the average condition of the gas film
exp	Experimental
g	Gaseous state
h	Height
i	Component i
in	Input
M	Methanol
M	In moles
o	Place before a symbol means in the feed
out	Output

X. REFERENCES

1. Thomos, J.M., Thomos, W.J., Introduction to the Principles of Heterogeneous Catalysis, 1967, (Academic Press, N.Y.), p. 9.

2. Smith, J.M., "Chemical Engineering Kinetics", Ist ed., p. 202, McGraw-Hill, N.Y., 1956.

3. Laidler, K.J., "Chemical Kinetics", 2nd ed., McGraw-Hill, Toronto, (1965), p. 5-28.

4. Ibid., p. 18.

5. Encyclopeadia, Kirk & Othmer, Vol. 10, p. 77.

6. Zowader, H., Chem. Eng. Progress, 45, 279-80, (1949).

7. Walker, J.F., "Formaldehyde", 3rd ed., Am. Chem. Soc. Monograph Series No. 159, Reinhold, N.Y., (1964).

8. Hofmann, A.W., Ann., 145, 357 (1868); Ber. 2, 152 (1869).

9. Loew, O.J., Prakt. Chem. (2), 33, 321-51 (1886).

10. Bugge, G., Chem. App. 18, 157-60, (1931).

11. Klar, M., and Schulze, C., German Patent 106,495, (1898).

12. Brochet, A., Compt. Rend., 119, 122 (1894), 121, 133 (1895).

13. Orlov, E.I., J. Russ. Phys.-Chem. Soc., 39, 855-68, 1023-44, 1414-39 (1907); 40, 796-9 (1908).

14. Blank, O., German Patent, 228,697 (1910).

15. LeBlanc, M., and Plaschke, E., Z. Elecktochem., 17, 45-57 (1911).

16. Kuznezow, M.J., (to Perth Amboy Chemical Works), U.S. Patent 1,067,655 (1913).

17. Thomos, M. D., J. Am. Chem. Soc., 42, 867 (1920).

18. Homer, H. W., J. Soc. Chem. Ind. (London), 60, 213-8 T (1941).

19. Schideler, P., and Richardson, R. S., (to Chem. Construction Corp.); U. S. Patent 2, 406, 908 (1946).

20. Meath, W. B., (to Allied Chem. and Dye Corp.), U. S. Patent 2, 462, 413 (1949).

21. Marullo, G., and Maffezoni, U., (to Monte Catini Soc. Gen. per l'Ind. Mineraria e Chemica), Italian Patent, 426, 333 (1947).

22. Eguchi, T., Yamamoto, T., and Yamauchi, S., U. S. Patent 2, 908, 715 (1959).

23. Polyakov, M. V., Stalya, V. V., and Vystokiy, Z. Z., Jour. Applied Chem. (U. S. S. R.), 32, 2275-83 (1959).

24. Polyakov, M. V., and Stalya, V. V., Nauchn, Osnovy Podbora i Provizv. Katalizatorov, Akad. Nank SSSR, Sibirsk Otd. 1964, 228-31.

25. Polyakov, M. V., Stalya, V. V., and Kulirich, M. G., Kinetika i Kataliz 5(5), 916-19 (1964).

26. Polyakov, M. V., Stalya, V. V., Kolotusha, B. I., and Ermenenko, N. P., Dokl. Akad. Nank SSSR, 167 (1), 132-4 (1966).

27. Punderson, J. O., (to E. I. duPont de Nemours and Co. Inc.), U. S. Patent 2, 939, 833 (1960).

28. Kushnarenko, I. P., and Afroshchenko, V. I., i Khim. Tekhnol., 8 (1), 47-54, (1969).

29. Kushnarenko, I. P., and Afroshchenko, V. I., Dokl. Vses. Nauch. Konf. Rab. Kafedr. Tekhnol. Neorg. Veshchestv, Nauch Uchrezhd. Proekt. Organ., 4th Taskent, 1964, 260-7 (1966).

30. Wolfen, V. F., (by Friedrich Wolf, Hermann Beyer, Karla Wencke and Friendric Wodtcke), German (East), 40, 953.

31. Vitvitskii, A. I., Mukhlenov, I. P., Averbukh, A. Ya., Zh. Prikl. Khim. 39 (5), 1124-30 (1966).

32. P. B. Report 73452 (Sator), 1938.

33. E. I. duPont de Nemours & Co.,
Fr. 1, 483, 218 (1967)
Fr. 1, 487, 093 (1967).

34. Shigin, E. K., and Shcherban, Khim. Prom. 43 (7), 494-500 (1967).

35. Sleeman, D. G., Chem. Engg. (N. Y.), 75 (1), 42-4, (1968).

36. VEB Chemische Maschinenbauwerke Rudisleben (by Rudolf Desiderius), Ger., 1, 259, 323 (1968).

37. Badische Anilin - Und Soda - Fabrik A. -G. Fr. 1, 588, 112 (1970).

38. Trillat, A., Bull. Soc. Chem., III, 29, 35-47, (1903).

39. Adkins, H., and Peterson, W. H., J. Am. Chem. Soc. 53, 1513 (1931).

40. Jiru, P., Wichterlova, B., Tichy, J., Proc. 3rd Cong. Catalysis (Amsterdam), North-Halland Publishing Co., Amsterdam, p. 199, (1964).

41. Wichterlova, B., Jiru, P., Chem. Prumysl, 15 (4), p. 198, (1965).

42. Allyn, C. L., Barrentine, E. M., Hodgins, T. S., Rawson, R. L., and Shelton, F. J., (to Reichhold Chemicals Inc.), U. S. Patents 2, 812, 309 (1957), and 2, 849, 492 (1958).

43. Barrentine, E. M., and Shelton, F. J., (to Reichhold Chemicals Inc.), U. S. Patent 2, 812, 308 (1957), and 2, 849, 493 (1958).

44. Hagen, G. L., Hodgins, T. S., and Warner, .O., (to Reichhold Chemicals Inc.), U.S. Patent 2,852,564 (1958).

45. Hodgins, T. S., and Shelton, F. J., (to Reichhold Chemicals Inc.), U.S. Patent 2,973,326 (1961).

46. Hodgins, T. S., Walker, R. B., and Warner, H. O., (to Reichhold Chemicals Inc.), U.S. Patent 2,812,310 (1957).

47. Montecatini Soc. Gen. (per l'Ind. Mineraria & Chimica), Australian Patent Application, 54,029 (1959), Italian Patent 589,718 (1959).

48. Mars, P., and vanKrevelen, D. W., Chem. Eng. Sci. (special supplement on proceedings of the Conference on Oxidation Process), p. 41 (1954).

49. Cotter, J. T., Dissertation, University of Rhode Island, Kingston, Rhode Island (1966).

50. Friedlander, J., and Bennett, C. O., "Symposium of reaction kinetics in product & process design", Am. Inst. Chem. Engg. and Inst. Chem. Engg., Joint meeting in London, U.K., p. 34, (1965).

51. Bliznakov, G., Jiru, P., Klissurski, D., Collection Czech. Chem. Commun. 31(7) 2995-7 (1966).

52. Dente, M., and Collina, A., Chemica e industria (Milan), 46, 752 (1964).

53. Ibid., p. 915.

54. Dente, M., Poppi, R., and Pasquon, I., Chemica e industria (Milan), 46, 1326 (1964).

55. Dente, M., Pasquon, I., Chemica e Industria (Milan), 47, (4), 359 (1967).

56. Boreskov, G. K., Kolovertnov, G. D., Kefeli, L. M., Karakchiev, L. G., and Popov, B. I., Kinetika i kataliz 7(1), 144 (1966).

57. Boreskov, G. K., Kolovertnov, G. D., Popov, B. I., Tarasove, D. V., Kinetika i kataliz, 6(6), 1052 (1965).

58. Biliznakov, G., Klissurski, D., Khim. Ind. (Sofia) 1967 (2), 58-61.

59. Bibin, V. N., Popov, B. I., Kinet. Katal. (1969), 10(6), 1326.

60. Habersberger; Karel, Jiru, Pavel, Fr. Patent 1, 526721

61. Bliznakov, G., Popov, T., and Klissurski, D., Izv. Inst. Obshta Neorga. Khim., Bulg. Akad. Nauk. 4, 83 (1966).

62. Boreskov, G. K., Popov, B. I., Bibin, V. N., Kozishnikova, E. S., Kinet. Katal. 1968, 9(4), 796.

63. Bliznakov, G., Popov, T., Klissurski, D., Nauch. Tr. Vissh. Pedagog. Inst., Plovdiv. Mat., Fiz., Khim., Biol. 1968, 6(1), 93-7.

64. Field, E., (to E. I. duPont de Nemours and Co.), U. S. Patent 2, 519, 751 (1950).

65. Klissourski, D., Bliznakov, G., Compt. Rend. Acad. Bulgare Sc. 18 (6) 549 (1965).

66. Bliznakov, G., Jiru, P., and Klissurski, D., Collection Czech. Chem. Commun. 31(7) 2995 (1966).

67. Mann, R. S., and Hahn, K. W., J. of Catalysis 15 (4), 329 (1969).

68. Bailey, G. C., and Craver, A. E., U. S. Patent 1, 383, 059 (1921).

69. Craver, A. E., (to Weiss and Daons Inc.), U. S. Patent 1, 851, 754 (1932).

70. Jaeger, A. O., (to the Seldon Co.), U. S. Patent 1, 709, 853 (1929).

71. Hahn, K. W., Ph. D. thesis, Univ. of Ottawa, Ottawa, (1968).

72. Bhattacharya, S. K., Janakiram, K., and Ganguly, M. D., J. Catalysis, 8, 128 (1967).

73. Tarama, K., Teranishi, S., Yoshida, S., and Tamura, N., Proc. 3rd Congr. Catalysis (Amsterdam), North Holland Publishing Co., Amsterdam, p. 282 (1964).

74. Kurina, L. N., Maidanovskaya, L. G., Tr. Nauch. kmf. Tomsk. Otd. Vses. khim. Obshchest., 1968 (Pub. 1969), 1947.

75. Kurina, L. N., Maidanovoskaya, I. G., Dorofeeva, L. I., Shakirova, L. I., U. S. S. R., 212, 933 (1968).

76. Hinshelwood, C. N., "The Kinetics of Chemical Change", Oxford Univ. Press, London, p. 207 (1940).

77. Chilton, T. H., and Colburn, A. P., Ind. Eng. Chem., 26, 1183 (1935).

78. Yoshida, F., Ramaswami, D., and Hougen, O. A., A. I. Ch. E. Journal, 8, 5 (1962).

79. Hougen, O. A., and Watson, K. M., "Chemical Process Principles", part III, John Wiley and Sons, New York, p. 996 (1947).

80. Morales, M., Spinn, C. W., Smith, J. M., Ind. Eng. Chem. 43, 225 (1951).

81. Schwartz, C. E., Smith, J. M., Ind. Eng. Chem., 45, 1209 (1953).

82. Smith, J. M., "Chemical Engineering Kinetics", 1st ed., McGraw-Hill, New York, p. 231-250 (1956).

83. Hougen, O. A., and Watson, K. M., "Chemical Process Principles", part III, McGraw-Hill, New York, p. 824, 834, 929 (1949).

84. Yang, K. H., and Hougen, O. A., Chem. Eng. Progr., 46, 146 (1950).

85. Shelstad, K. A., Downie, J., and Graydon, W. F., Can. J. Chem. Engg., 35, 102 (1960).

86. Downie, J., Shelstad, K. A., and Graydon, W. F., Can. J. Chem. Eng., 39, 201 (1961).

87. Ioffe, I. I., and Lyubarskii, A. G., Kinetica i Kataliz 3, 261 (1962), Abstract, J. Catalysis 1, 397 (1962).

88. Bhattacharya, S. K., and Gulati, I. B., Ind. Eng. Chem., 50, 1719 (1958).

89. Berets, D. J., and Clark, H., Advan. Catalysis, 9, 204 (1956).

90. Simard, G. L., Segel, J. F., Arnot, R. J., and Siegel, L. A., Ind. Eng. Chem., 47 1424 (1953).

91. Hougen, O. A. Watson, K. M., and Ragatz, R. A., "Chemical Process Principles", Part II, Wiley, New York, p. 1004, (1959)

All the literature in languages other than English, and the patents, were made use of through Chemical Abstracts.