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PARTIAL OXIDATION OF METHANE OVER HALOGEN MODIFIED PALLADIUM CATALYST

by

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A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirements for the
Ph.D. degree in Chemical Engineering

UNIVERSITY OF OTTAWA

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

FIGURE | PAGE

FIGURE | PAGE

FIGURE PAGE

ABSTRACT

The vapor phase air oxidation of methane to formaldehyde was investigated in an isothermal integral flow reactor at atmospheric pressure in a temperature range of 390° to 510°C. The catalyst, 0.5% palladium supported on alumina, was modified by a constant and continuous supply of small amounts of chlorine, bromine and iodine compounds.

The effect of various process variables, namely the weight ratio of halogen additive to methane, the feed ratio of air to methane, reaction temperature and the reciprocal of space velocity, on the conversion of methane and the product distribution was determined. The products and reactants were analysed by gas chromatography.

It was observed that in the presence of halogen compounds, though the overall conversion of methane decreased, the selectivity of the catalyst for formaldehyde formation significantly increased. The effect of different halogen compounds are compared and discussed. Methylene chloride, which affected in producing relatively high yields of formaldehyde, was used as a modifier for the detailed kinetic study of methane oxidation reaction. The weight ratio of modifier additive to methane in the feed mixture

at a given temperature was found to be an important variable in the selectivity of the catalyst.

It is suggested that the charged methane and oxygen are selectively adsorbed on the catalyst surface and that the partial oxidation of methane is a p-type reaction and its further oxidation to carbon dioxide is an n-type reaction under the reaction conditions. The results indicate that the promotional effect of the modifier, in the sense of increasing the catalyst selectivity, is mainly due to its successfully suppressing further oxidation of aldehyde to undesired products. The active phase of the catalyst in selective oxidation of methane was found to be palladium oxide.

Among the several mechanisms proposed for the oxidation of methane over chlorine modified palladium catalyst, the experimental data were found to be in best correlation with a mechanism involving the surface reaction between charged adsorbed methane and oxygen with surface reaction being the rate controlling step. The rate of reaction is given by the following expression:

$$r = \frac{k_S\ K_M\ P_M}{1 + K_M\ P_M + K_F\ P_F} \cdot \frac{K_O\ P_O}{1 + K_O\ P_O}$$

where k_S, K_M, K_O and K_F are temperature dependent constants.

I. INTRODUCTION

The heterogeneous catalytic oxidation of hydrocarbons is of immense technological importance. It has now been possible to obtain many valuable oxygenated carbon compounds, as well as olefins and dienes from plentiful hydrocarbons, for example: ethylene oxide and acetaldehyde from the oxidation of ethylene, acrolein from propylene, methacrolein from iso-butylene, butadiene from butene, maleic anhydride from benzene and pthalic anhydride from naphtalene. Although methane is the simplest hydrocarbon, its oxidation is very difficult. The conversion of methane to formaldehyde by direct oxidation using metal or metal oxide catalysts would be economically attractive if sufficiently high yields of formaldehyde were obtained [1].

Thermodynamically, the partial oxidation processes are usually in favor of the primary oxidative products but a major problem is that of stopping further oxidation of these products and making the reaction more selective. Success in the controlled oxidation of hydrocarbons in vapor phase to useful intermediate products is achieved mainly by varying the operating conditions, proper selection of a catalyst and modification of the catalyst with a suitable promotor. The use of severe operating conditions, such as high temperature, results in higher conversions,but it is accompanied with a decrease in the selectivity of the catalyst. Some general aspects of a catalyst and its modification are briefly mentioned in the following paragraphs.

A catalyst increases the rate of thermodynamically feasible processes only. It also facilitates the approach to equilibrium of a given chemical change. Further, for a given group of reactants there may be several reaction paths and by an 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 complex is formed by one or more of the reactants at 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 themselves. Hence the energy of activation for reaction involving chemisorbed molecules can be considerably less than that for reaction involving the molecules alone.

A variety of solids can act as heterogeneous catalysts in the partial oxidation of hydrocarbons. The most common catalysts are transition metal oxides which are usually semiconductors. Although, in general, p-type semiconductor oxides (copper oxide, nickel oxide, etc.) are among the highly active catalysts, they by themselves show little or no selectivity for a particular intermediate product. On the other hand, n-type semiconductors (molybdenum oxide, vanadium oxide, etc.) show good selectivity but have little or no activity.

Some efforts have been made in the past to achieve both high selectivity and activity in the catalyst by modifying the skeleton catalyst with different additives [3,4]. In general, the most active and selective catalysts are combinations of highly active oxides e.g., oxides of copper, nickel, cobalt, manganese, iron, chromium, tin, etc., and oxides of more negative moderating elements e.g., oxides of phosphorous, arsenic, antimony, bismuth, selenium, tellurium and halogens. The mixed oxides may form a solid solution and alter the solid structure of the catalyst. They may also affect some of the electronic properties of the solid by altering the rate of electron transfer between elements contained in the catalyst.

The surface properties of a catalyst may also be modified by a ready diffusion of certain impurities in the solids. This might create other adsorption sites with different energy and geometry characteristics at the surface of the new phase which would in turn affect catalysis. The above method is now becoming extremely effective in controlling hydrocarbon oxidation. This is confirmed by the large number of patents issued during the past 10 years on selective oxidation of organic compounds over catalysts that contain, as a rule, traces of different chemical compounds [5].

Most oxidation catalysts are semiconductors. There have been numerous attempts to correlate catalytic properties of oxides with their semi-conductivity [6-9]. One of the most widely used theories to explain the reactions on semiconductors is the Electronic Theory of Catalysis on Semiconductors. The fundamental hypothesis of the theory is that all heterogeneous catalytic reactions are either acceptor reactions (n-type) or donor reactions (p-type). An acceptor reaction is catalyzed by free electrons, and a donor reaction is catalyzed by positive holes. The activity of a semiconductor catalyst is determined by its Fermi level at the catalyst surface. The Electronic theory has been successful in explaining many empirical correlations such as the decomposition of nitrogen oxides [6,10] and oxidation of carbon monoxide over doped catalyst [11,12,13]. In the present study, the theory was used with a slight modification to investigate the oxidation of methane over a chlorine-modified palladium catalyst.

There are several methods available for studying the reaction kinetics using different types of reactors, for example, differential or integral, batch or continuous flow. There is no entirely satisfactory method by which the rate of reaction can be measured directly. In the differential method the reactor is operated with a small conversion so that the reaction rate can be made constant in a straightforward manner. The main drawback of this method is the difficulty in a precise analysis of the low concentration of product in the gas stream. On the other hand, the integral method is not restricted to a small conversion and analytical accuracy is greater. However, it is much more difficult to integrate the rate equations as there are several hidden parameters which may diminish the value of the experimental data [14].

Further, since a continuous supply of modifier is required through the catalyst bed, a batch reactor would not be suitable for catalyst modification study. Besides, from an industrial view point, one is more interested in yield and selectivity, a mixture of hydrocarbon and air over an isothermal stationary catalyst at approximately atmospheric pressure. Such studies are generally carried out in flow reactors. A fixed bed integral flow reactor, operating at atmospheric pressure is most suited for the oxidation reaction in the present study.

Most of the earlier work on the catalytic oxidation of methane reported in literature was carried out with the objective of pollution abatement and combustion elimination of process tail gases. Thus, these studies were mainly concerned to achieve total oxidation. Among the various catalysts, palladium has been reported to be one of the most active. Attempts have been made in the present study to improve the selectivity of this catalyst and to study the partial oxidation of methane.

Objectives of the Present Work

- To construct an apparatus to investigate methane oxidation over 0.5% palladium catalyst supported on alumina in the presence of halogen modifiers, and to study the promotional effects of halogen modifiers on the selectivity of the catalyst.
- To study the effect of process variables on conversion and product distribution over the most suitable modified catalyst.
- To identify the active component of the catalyst in selective oxidation.
- To propose a hypothesis which would explain the promotional effect of modifiers in methane oxidation.
- To develop a suitable rate expression which would satisfactorily represent the data.

II LITERATURE SURVEY

A. General - Oxidation of Hydrocarbons

The subject of oxidation of hydrocarbons has drawn the continuous attention of scientists and engineers since the early nineteenth century. In the beginning, most of the work was related mainly to the combustion of hydrocarbons in flames. It was then assumed that the mechanism of combustion of hydrocarbons led to their break-down into carbon and hydrogen which subsequently reacted with oxygen. Only towards the end of the last century, preliminary investigation of the gas phase slow oxidation of hydrocarbons provided information, which supported representation of their combustion in flames as successive action of oxygen on a molecule of hydrocarbon without a previous break-down of the latter into its elements. This initiated further studies on the slow oxidation of hydrocarbons which have continued to an ever-increasing extent up to the present day. There are two main reasons for this wide development of research into the slow oxidation of hydrocarbons. First, is the motivation to achieve efficient utilization of hydrocarbon fuels in the internal combustion engine, energy conservation and a control of environmental pollution, and the second is that a number of oxygen-containing products, which have valuable practical applications, are formed during the course of oxidation of hydrocarbons.

In the development of research on the gas phase oxidation of hydrocarbons, most of the work up to the late 1920's was of purely chemical, that is, related to the identification of various reaction products. The study of the kinetic mechanism of oxidation reactions in terms of the ideas of chain theory was the main topic covered in the period between the end of the twenties to the middle of the thirties. Since the mid-thirties, the precise understanding of kinetic methanism (through the establishment of the nature of all substances, stable as well as unstable, taking part in the course of the investigated transformation) has been the central problem confronting the researchers in the field of hydrocarbon oxidation. In recent years emphasis is being laid on separate quantitative studies (that is, by the establishment of values for the rate constants) of all elementary stages of the complicated process of oxidation. Another characteristic feature of this period is the intensive search for a method of controlling the gas phase oxidation of hydrocarbons for obvious economic reasons.[15]

A large number of patents and publications related to hydrocarbon oxidation are available in the literature. A comprehensive monograph, mainly on non-catalytic oxidation of hydrocarbons has been published by Shtern [15]. Some of the notable reviews which include catalytic oxidation of hydrocarbons include those published by Emmett[16] and Margolis[17].

On the oxidation of methane, several studies have involved non-catalytic systems or the use of homogeneous catalysts; however, some work has also been done on the use of heterogeneous catalysts. Studies related to the oxidation of methane are reviewed in the following sections.

B. Homogeneous Gas Phase Oxidation of Methane

It is generally understood that the homogeneous oxidation of methane proceeds by means of a free radical chain mechanism. Norrish [18] considered that the first and the only stable intermediate product was formaldehyde. The oxidation exhibits an induction period followed by a rapid exothermal reaction. The maximum concentration of formaldehyde and the maximum reaction rate are attained almost immediately after the end of the induction period and are practically unchanged during the further course of reaction [19,20]. The addition of formaldehyde either decreases or eliminates the induction period, depending upon the amount added[19,21-24]. According to Norish and Harding [23], the addition of formaldehyde, in an amount greater than its stationary concentration in a reaction without additive, caused the reaction to begin immediately without an induction period and with an increased velocity. Overall, it was clearly established that formaldehyde had an important role as an intermediate during methane oxidation. Explanation of the role of formaldehyde along with other observations such as, displacement of the maximum rate of methane oxidation [19,23,25,26], changes in the reaction orders with temperature [18,21,25,27-30], and significant differences in the magnitude of activation energies reported in different studies [23,25,27,30], were the problems which drew the attention of several researchers [14].

Based on all the experimental material available in literature relating to methane oxidation, Seminov [31], in 1958 proposed the following radical-chain scheme for this process:

(1) $CH_4 + O_2 \rightarrow \dot{C}H_3 + H\dot{O}_2$

Reaction 1 is important only in the early stages of the reaction.

(2) $\dot{C}H_3 + O_2 \rightarrow HCHO + H\dot{O}$

Formaldehyde then becomes a chain carrier by reacting with oxygen

(3) $HCHO + O_2 \rightarrow H\dot{C}O + H\dot{O}_2$

(4) $H\dot{C}O + O_2 \rightarrow CO + H\dot{O}_2$

or with $H\dot{O}$ or $H\dot{O}_2$, as follows:

(5) $HCHO + H\dot{O} \rightarrow H\dot{C}O + H_2O$

(6) $HCHO + H\dot{O}_2 \rightarrow H\dot{C}O + H_2O_2$

New chains are initiated by the attack of $H\dot{O}$ or $H\dot{O}_2$ on methane,

(7) $CH_4 + H\dot{O} \rightarrow \dot{C}H_3 + H_2O$

(8) $CH_4 + H\dot{O}_2 \rightarrow \dot{C}H_3 + H_2O_2$

Reactions of chain carriers at the wall lead to chain breaking.

(9) $H\dot{O}, H\dot{O}_2 \xrightarrow{\text{wall}}$ destruction

This mechanism accounts for the formation and destruction of formaldehyde in the reaction, and the role of formaldehyde as a chain carrier. Reactions 5 and 6, where formaldehyde is involved in radical chains, would be insignificant during the induction period when formaldehyde concentration is very low. Reactions 5 and 6 explain the effect of added formaldehyde in shortening the induction period and increasing the reaction rate.

Kinetic data obtained in the oxidation of methane in shock waves [32] indicated that reaction 3 was the rate-determining step in methane oxidation and reaction 2 in $H\dot{O}$ formation. While the mechanism provided a reasonable agreement with kinetic data, it predicted that the maximum concentration of formaldehyde should be independent of oxygen concentration. However, Magee [33] has presented data which show that maximum formaldehyde concentration is a function of oxygen concentration.

Literature dealing with the theoretical and experimental aspects of the reaction mechanism is quite comprehensive [14,31,34]. Besides providing an explanation of the reaction mechanism there is another important aspect of the chemical transformation, namely, identifying ways and means of controlling the reaction for a selective preparation of formaldehyde, which is industrially valuable.

In the hydrocarbon oxidation reactions, alcohols and acids undergo further oxidation only to a negligible extent and become end products. Thus their yields can be increased by increasing the proportion of the initial hydrocarbon. In contrast to this, formaldehyde enters readily into subsequent oxidations with the formation of water and oxides of carbon. Suppression of this further oxidation would therefore be required to increase the yield of formaldehyde in methane oxidation.

Attempts to maximize the yield of formaldehyde gave rise to a whole series of relevent experimental studies. They all reduced to an endeavour to alter the concentration of active centers, which can be achieved by many methods such as: small additions of substances capable of forming the radicals more readily that the initial reactants; addition of inert gas; variation of vessel diameter; and treatment of vessel walls. Nevertheless the results of Yenikolopyan [35] suggested that any variable that affects the reaction leading to a change in the concentration of active centers could not alter the maximum concentration of intermediate formaldehyde. This conclusion referred to the case when the intermediate product is formed and consumed by chain process. Yenikolopyan further showed that if on the other hand the intermediate product, forming a chain, was consumed by molecular process, its maximum concentration could be increased by increasing the concentration of active centers. Therefore, if it could be possible by any means (homogeneous additive, surface changes) to obtain a non-chain consumption of intermediate product, increasing the concentration of active sites may increase the yield of the intermediate product.

Bibb and Lucas [36] have demonstrated that a low concentration of nitric acid vapor acts as an effective reaction catalyst. Bone and his coworkers [19,23] found that the addition of small amounts of nitric oxide in the reaction mixture diminished the induction period of methane oxidation and a 0.32% concentration of nitric oxide completely eliminated the induction period.

Gertges et al. [37] patented a process of manufacturing formaldehyde by oxidation of methane with air or oxygen with addition of small amounts of nitric oxide in the presence of fluidized pumice at 470^{o}C. The feed contained air and methane in a ratio of 5:1. According to Mayor [38] the best results have been obtained by the use of a solid catalyst in conjuction with an oxide of nitrogen.

Levush [39] studied the oxidation of methane by atmospheric oxygen, initiated by fluorine which lowered the temperature at which methane is oxidized. However, significant yields of formaldehyde could not be obtained at low fluorine concentration because of the short chain length of the oxidation reaction at low temperatures. At higher temperatures, fluorine was intensively consumed on the reactor walls.

Vilenskii and Averbukh [40] reviewed recent Russian literature and reported that the reactor surface has a significant influence on the course of chain reactions, including partial oxidation of methane. Several investigators including them have reported that the rate of methane oxidation and the formaldehyde yield increased after treatment of silica glass and metallic reactors with acqueous potassium tetraborate solutions.

McConkey and Wilkinson [41] studied the high temperature free radical oxidation of methane with air and homogeneous initiators employing a fluidized bed as heat transfer medium. They intended to establish whether high concentration of formaldehyde in the products was possible by the introduction of selectivity into the branching-chain radical reaction through the use of suitable reacting and quenching surfaces as claimed in some of the patents[42,43]. They concluded that theoretically and experimentally it was inconceivable that free radicals could be employed to provide a high conversion to formaldehyde while further oxidation was inhibited, because of the more rapid simultaneous rate of radical attack on formaldehyde. They suggested that high yields are possible only at low methane conversions; hence appreciable concentration of formaldehyde in the effluent gases cannot be achieved.

C. Heterogeneous Catalytic Oxidation of Methane

Although methane is one of the most difficult hydrocarbons to be oxidized, several metals and metal oxides have been found to have catalytic activity for methane oxidation. In this section earlier work on the catalytic oxidation is reviewed.

1. Platinum

As early as 1825, the effect of platinum on the combustion of methane was studied by Henry[44]. According to his investigation, methane began to react with oxygen in the presence of platinum sponge at a temperature of 290°C. Later, Yant and Hawk [45] reported in 1927 that platinum had a catalytic effect at temperatures between 150 and 350°C for the oxidation of methane. The reaction mixture contained 4% methane in air and methane conversion was less than 10%. In 1961, as a part of a program for developing devices to monitor methane concentration in coal-mine atmosphere, Anderson [46] investigated activity of catalysts for the oxidation of methane in a micro-catalytic pulse reactor using oxygen as carrier gas. Platinum supported on alumina was found to have second highest activity among the thirty different catalysts tested. Davies [47] studied the oxidation of methane over heated platinum wire at temperatures around 1000°C and concluded that both methane and oxygen had to be chemisorbed for reaction to occur. This was confirmed by Lintz et al.[48]. Hiam, Wise and Chaikin [49] used a development of the heated wire technique, in which the conditions for heterogeneous thermal ignition were determined. They used ethane, propane and butane in their study and concluded that over platinum both the hydrocarbon and the oxygen were chemisorbed and that the hydrocarbon was dissociatively chemisorbed on metal sites not covered by oxygen.

2. Copper

The catalytic activity of copper oxide for methane oxidation has been studied by several researchers [50-54]. According to these studies, copper oxide shows catalytic activity at temperatures in the range of 400 - 700°C. Wheeler [55] determined the rate of oxidation of methane over copper oxide catalyst at a constant pressure and a constant volume and at temperatures between 389°C and 700°C. The activation energy measured in static experiments was 32 Kcal/g.mol,while in flow experiments it was 41 Kcal/g.mol. Branson et al. [56] studied the oxidation of methane and higher paraffins over copper oxide in the absence of oxygen, and interpreted the experimental results based on interaction of reacting gases and the constituent oxides of the catalyst. They found that the surface layer of oxygen was readily available to oxidize the hydrocarbon. The activation energy for methane oxidation was 36 Kcal/g.mol in their case.

Schonfelder [57] reported conversion of methane to formaldehyde up to 58 percent by the passage of a mixture of air, methane and steam over copper or silver at 500°C. Campbell [51] investigated the use of a number of supported metal catalysts, including copper, for methane oxidation and reported formaldehyde to be the principle intermediate product.

Huettenwerk Oberhausen [42,43] patented processes for the production of formaldehyde by the catalytic oxidation of methane and other hydrocarbons in the presence of small amounts of nitric oxide at temperatures up to $675^{o}C$. The reaction mixture was first passed through either a fixed bed or fluidized bed of pumice and then through either a metal mesh of an alloy containing 95% Pt and 5% Ir or a copper wire net before chilling it on another fluidized layer containing pumice. In the case where fluidized bed of pumice and copper wire were used, the yield increased from 16.7 gm $HCHO/m^3$ CH_4 at a reaction temperature of $470^{o}C$ to 188 gm $HCHO/m^3$ CH_4 at $685^{o}C$.

3. Cobalt oxide

Cobalt oxide has been reported [45,46,51,58-60] to be a very effective catalyst in oxidation of methane and other hydrocarbons. According to Anderson's study [46] unsupported Co_3O_4 was the most active single-component catalyst and its activity decreased when impregnated on alumina, possibly because of the formation of $CoAl_2O_4$. Co_2O_3 supported on alumina was one of the most effective catalyst as described in a study by Vendt et al.[61].

4. Hopcalite

In an extensive investigation, Lamb and coworkers[62] found that a mixture of oxides of copper, manganese, silver and cobalt was most effective in the oxidation of carbon monoxide. A commercial material Hopcalite was developed by Mine Safety Appliance Company for carbon monoxide gas masks towards the end of World War I and this was also found active for methane oxidation. Using this material, 10-60% conversion of 4% methane in air to carbon oxides and water over the temperature range of 200-350°C was obtained [45]. Hopcalite, whose exact composition has been kept a trade secret, consists of a group of compounds and mixtures which includes manganese dioxide and cuprous oxide. Catalysts of this class have a reasonably long life in the presence of dry gas, but they are rapidly poisoned by adsorbing water vapor and lose their activity by prolonged heating at temperature above 250°C due to sintering.

5. Alumino-Silicate

Recently some Russian researchers [63-66] have studied the oxidation of methane in natural gas in a fluidized bed reactor. Vilenskii et al. [63] used alumino-silicate catalyst promoted with oxides of group II metals.

The initial concentration of methane and oxygen were both 17.3% and the reactor temperature was 600^{o}C. A homogeneous initiator in trace amounts (0.2 - 0.5%) in the reactant feed stream was found to increase the yield of formaldehyde. The maximum yield of formaldehyde obtained in their study was 4.5% which compared 50% better than the best results obtained with nitrogen oxides as homogeneous catalysts. Averbukh et al. (64) reported the use of oxygen instead of air for the oxidation of methane in natural gas at temperature 700^{o}C in a fluidized bed of aluminium-silica catalyst. The maximum yield of formaldehyde was 19.4 gm. HCHO per m^3 of CH_4 passed which was no higher than the yield obtained using air. Mukhelnov et al. (65) determined optimal conditions for the oxidation of natural gas to formaldehyde in a fluidized bed of alumina-silica catalyst. They also concluded that the first stage in the oxidation of methane in natural gas in the presence of alumina-silica catalyst was the formation of formaldehyde. Zinina et al. (66) investigated the kinetics of partial oxidation of methane in a suspended layer of industrial alumino silicate catalyst. The order of reaction was found to be unity with respect to oxygen and 0.4 with respect to methane and the activation energy was 40 Kcal/mole.

6. Palladium

Palladium has been reported to be one of the most active catalysts for methane oxidation by several researchers. Anderson and coworkers [46] have concluded that the catalytic activity of metal and metal oxides decreases in the following order: Pd, Pt, Cr, Mn, Cu, Ce, Co, Fe, Ni and Ag. For catalysts supported on alumina, a similar order of effectiveness was earlier reported by Cohn and Haley [67]. Mezaki [68] used vanadia, copper chromite, cobalt, chrome alumina, hopcalite and palladium catalysts for methane oxidation and found palladium to be the most effective catalyst from the stand point of ignition temperature, stability, freedom from side reactions and good conversion.

Mezaki and Watson [69] studied the kinetics of methane oxidation over 0.5% palladium on alumina catalyst at atmospheric pressure using an integral flow reactor. The methane concentration in the feed was 1-2% and reaction temperature was varied between 320-380°C. They correlated their experimental data using Langmuir-Hinshelwood type models and indicated that the reaction rate could be controlled by a surface reaction between gaseous methane and adsorbed oxygen giving adsorbed water and adsorbed CO_2. Ahuja and Mathur [70] investigated the kinetics of methane oxidation using a palladium catalyst in a differential type reactor at pressures up to 10 atmospheres. The conversions of methane were small and limited to about 10% and temperature was varied between 300-340^{o}C. Their results indicated that the reaction rate was controlled by surface reaction in which adsorbed oxygen and adsorbed methane reacted to produce adsorbed carbon dioxide and adsorbed water.

Cullis et al. (71) studied the partial oxidation of methane using catalytic beads formed by coating alumina with a mixture of 10% Pd and 90% thoria in a microcalorimeter bead reactor and 100-120 mesh palladium sponge in a pulsed flow reactor. A 2 ml. pulse of a mixture of methane, oxygen and any additive was injected in a stream of helium (25 ml./min.) at a pressure of 35 psi for each run. The reaction was studied over a range of temperature (280-480^{o}C), methane to oxygen ratio (0.33 - 4.0) and weight of catalyst (0.09 - 2.22 g of Pd). Over the whole range of experimental conditions, products contained mainly carbon dioxide and water, and formaldehyde was found to be present in small amounts only. They also showed that, whereas the addition of higher alkanes, methanol and formaldehyde retarded overall oxidation of methane, some halogen compounds, besides reducing the rate of oxidation of methane, caused the production of isolatable quantities of formaldehyde in high selectivity. They compared the inhibiting efficiency of various halo-methanes for methane oxidation in the bead reactor, and methylene chloride was found to be the least powerful inhibitor. They briefly interpreted the action of halogen additives in terms of their ability to modify the catalyst surface and to inhibit the further oxidation of the initial products of methane oxidation. Based on the dependence of rate on reactant concentration in the uninhibited oxidation, they have suggested the rate-controlling step to be the surface reaction between methane fragments and adsorbed oxygen, the latter being present in excess.

7. Other Metals and Metal-Oxides

The oxides of transition metal such as Ni, Mn, Cr and V have been found effective for the oxidation of methane [45,45,59]. Prettre and coworkers [72] studied the high temperature (over 700°C) oxidation of methane over nickel and formulated a reaction mechanism that involved initial oxidation to carbon dioxide and water which then reacted with more methane giving carbon monoxide and hydrogen. This mechanism was supported by Peters et al. [73], and Bodrov and Apel'baum [74], who found that over a nickel catalyst at temperatures between 600 and 1000°C, methane reacted with water and carbon dioxide at about 10% of the rate of the initial methane oxidation reaction.

Andrushkevich et al. [75] studied the catalytic properties of metal oxides of period IV of the periodic table with respect to oxidation of methane. Based on 1 gm. of active metal, the catalytic activity of their oxides decreased in the following order: chromium, manganese, copper, cobalt, iron, nickel. While the most active single component was cobalt oxide, the most active supported catalyst was chromium oxide. The activation energy of the active catalyst was in the range of 15-25 Kcal/mole and the order of reaction with respect to methane was close to one. According to Kazarnovskya and Dykhno [76], the most effective catalyst for the complete combustion of 0.10 - 0.15% methane in oxygen (at 300^{o}C) was manganic ore enriched in silver. The detailed description of this catalyst was not given.

Troshenko et al. [77] studied the heterogeneous oxidation of natural gas, formaldehyde and methanol using different supported catalysts. They found the optimum amount of metal on pumice to be 2-10% and the most selective catalyst for formaldehyde formation was molybdenum dioxide. The formaldehyde selectivity order was: MoO_3, ThO_2, Nd_2O_3, Tm_2O_3, Cr_2O_3, Pt, La_2O_3, Ag_2O, V_2O_5, V_3O_8.

Firth [78] studied the complete oxidation of methane on palladium-gold alloys using a microcalorimetric method and suggested that the oxidation occurred through a series of reaction steps involving partially oxidized intermediate adsorbed on the catalyst. The slow step in the oxidation on palladium was most likely the reaction of this adsorbed intermediate and not the dissociative adsorption of methane. The reaction was found to be of first order with respect to methane.

Reviewing the literature on methane oxidation (catalytic and non-catalytic) it may be concluded that the mechanism of formaldehyde formation from methane is not well understood. Further the use of heterogeneous catalysts with some modifiers seems very promising in isolating the intermediate product, formaldehyde,and in increasing its yields.

III. EXPERIMENTAL

A. Apparatus

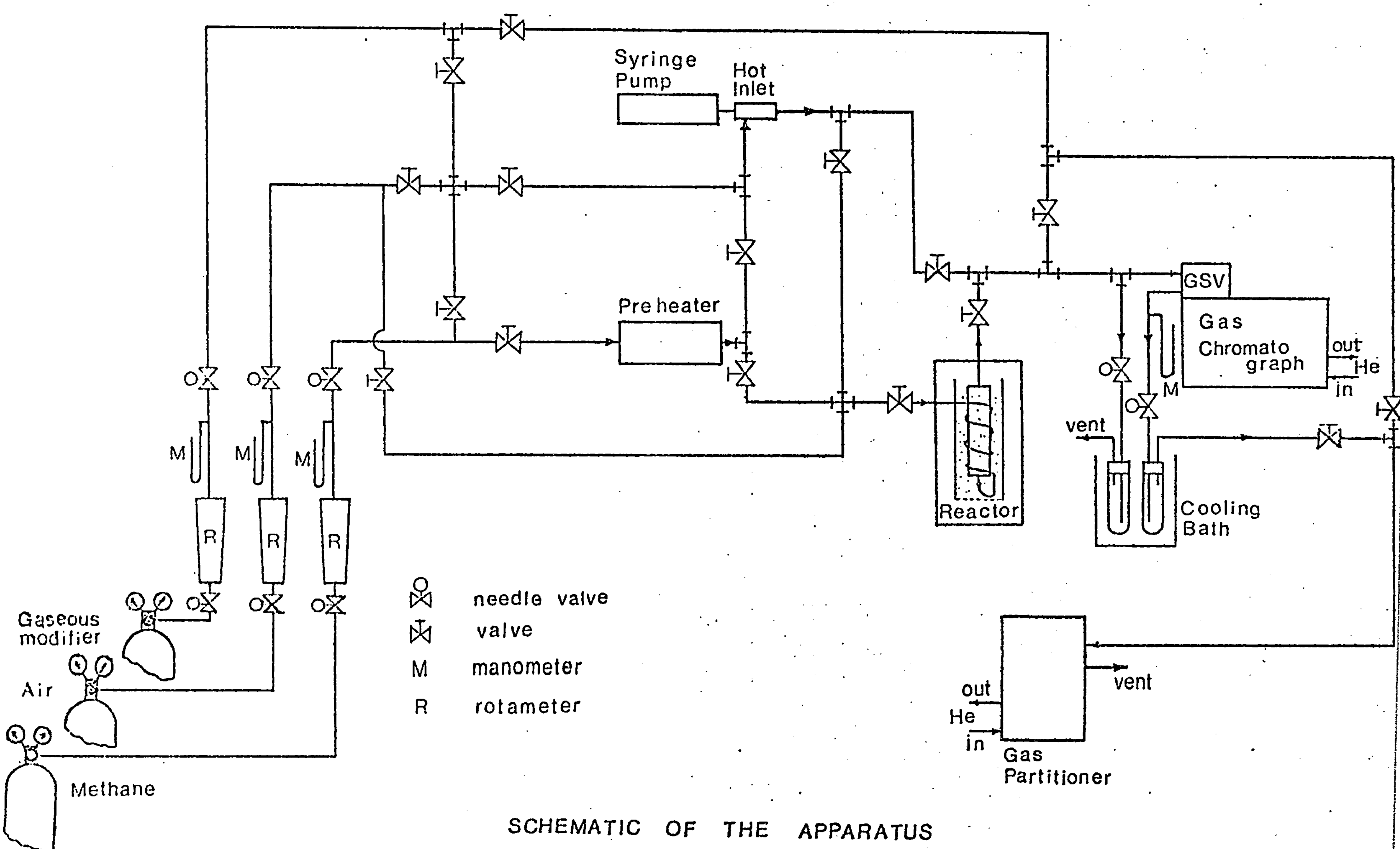
The oxidation of methane by air was investigated in a flow reactor system. The apparatus was designed to study the kinetics of oxidation reactions over a catalyst modified with a constant and continuous supply of small amounts of halogen additives. A schematic diagram of the experimental apparatus is shown in Figure 3-1.

The apparatus, constructed in the Department, was made of 316 stainless steel. It comprised of three sections: (i) Feed section, (ii) Reaction unit, and (iii) Product separation and analysis unit.

(i) Feed Section

The feed section supplied reactants, modifiers and calibrating gases in regulated amounts. It consisted of three gas streams and a liquid modifier feed system.

The reactants, air and c.p. grade methane were obtained from high pressure cylinders through a series of diaphragm type pressure regulators (Matheson of Canada, Ltd. Whitby, Ontario). Traces of moisture were removed



SCHEMATIC OF THE APPARATUS

Figure 3-1

by passing the gases through the drying tubes made of plexiglass and packed with indicating "drierite" (Calcium sulphate). The gas flow lines in this section were made of 1/8" o.d. stainless steel tubing. Fine metering valves and unidirectional check valves, supplied by Nupro Co. Cleveland, Ohio, were used for regulating the gas flow rates. All other valves and fittings were made by either Autoclave Engineering Inc., Erie, Pa., or Swagelok Valves and Fitting, Brockville, Ontario. The flow rates of each gas stream were measured by Brooks rotameters supplied by Matheson Co.. A mercury manometer was connected at the exit of each rotameter to maintain a constant pressure with the help of a needle valve.

The liquid feed system consisted of a variable speed syringe pump (Harvard Apparatus Inc., Mills, Mass.) and a hot inlet (Hamilton Co., Whitby, California). The liquid halogen modifier was introduced continuously and precisely from a gas tight syringe, fixed in the syringe pump, into the hot inlet where it was vaporized and carried away along with the incoming reactant gases. The gas tight syringe with teflon coated plunger and tip could withstand a pressure of up to 20 psig without any leakage. The syringe pump was equipped with a synchronous motor and a gear train providing a selection of twelve speeds. Reproducibility was with in 0.5%.

Flow rates of liquid discharge could further be varied by using different size of syringes. The hot inlet was made of heavy aluminium which evenly distributed the heat from a cartridge heater and eliminated cold spots. A high velocity preheated gas stream continuously washed the septum area and restricted flashback. The gas passed through a 1mm. I.D. glass vaporizer in the direction of liquid discharge from the syringe needle and provided uniform vaporisation of the liquid. The temperature of the hot inlet was maintained at 150°C by regulating the power supplied to the heater. The lines between the hot inlet and the reactor were heated by heating tapes with regulated power supply in order to prevent the possibility of condensation of the modifiers in the lines.

For the study of oxidation of formaldehyde an additional syringe pump with another vaporizer was installed prior to the entrance to reaction unit. In case of gaseous modifier, a bubble meter was used to measure the small flow rates.

The reactant stream with or without the modifier was led to the reactor through a preheating section. Lines and an on-off valve were also provided to by pass either hot inlet (vaporizer) or reactor or both and to lead the reactants or calibrating mixtures for analysis and calibration.

(ii) Reaction Unit

This unit consisted of a preheating section, a reactor, a temperature controlling device and a furnace or heating medium.

The preheater was made of a 10 feet long 1/8" O.D. 316 stainless steel tubing which was wound around the reactor. The preheated reactants with modifiers entered the reactor from the bottom of the reactor. Details of the preheating section and reactor are given in Figure 3-2. The reactor was made of 8" long 1/2" O.D. 316 stainless steel tube. A porous stainless steel plate supplied by Pall Trinity Micro Corp., Cortland, N.Y., was inserted at the bottom of the reactor tube. The grade D plate had a 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 a swagelok "T" connection (810-3-2-316) through a 1/2" to 1/4" reducer union. The side opening of the "T" acted as the exit for the reactor effluents and the upper opening of the "T" was connected to a 1/4" to 1/16" reducer through which a 1/16" O.D. stainless steel protected tube Chromel-

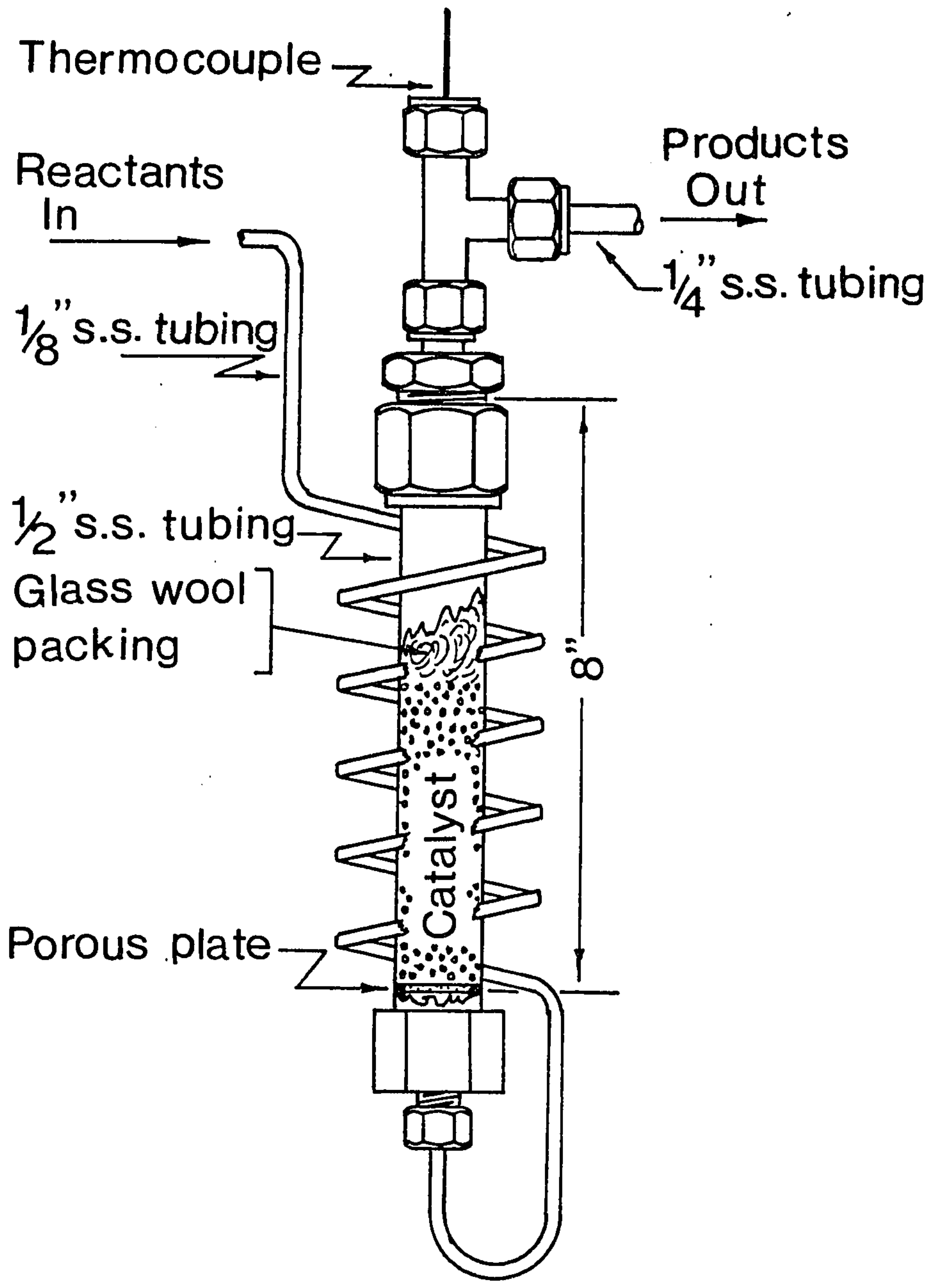


FIGURE 3-2 SCHEMATIC DIAGRAM OF REACTOR AND PREHEATER

Alumel thermocouple was inserted. The lower end of the thermocouple tube was kept just above the porous plate in contact with the catalyst. The thermocouple leads were connected with a temperature controller through a two way quick connector such that it could be used to measure the temperature during reaction with a potentiometer (Biddle Instruments, Plymouth Meeting, Pa.).

The thermocouple was supplied by Thermo-Electric Canada Ltd., Brampton, Ont.. The temperature of the reactor was controlled by a proportional temperature controller. It was a model R7350A of Honeywell Diala-Trol series and the reactor temperature could be maintained at the set point with in $\pm 1^{o}C$.

The reactor with the preheating section was kept immersed in a constant temperature fluidized bed furnace. The furnace was made from a one foot long, 5 inch O.D. and 1/4" inch thick steel cylinder with a porous stainless steel plate at its bottom. A steel funnel, 5 inch diameter at the top tapering down to 1/4 inch at the bottom, was welded to the base of the steel cylinder below the porous plate and connected to the compressed air line. Silicon carbide of 100-150 mesh particle size (supplied by Cole-Palmer Co., Chicago) was used as the heating medium of the fluidized bed and was placed in the cylinder on the top of the porous plate. The reactor was held upright in the center of the bed. During operation, sufficient air flow rate was maintained to keep the solid particles in fluidized state and to obtain a uniform temperature around the reactor. During the reaction, the temperature of the catalyst bed was measured at different positions along its length by thermocouple and temperature difference was found to be negligible ($\pm 1^{o}C$).

The furnace was equipped with two electrical heaters made of nichrome resistance wires. One was wound round the grooves of a 1 foot long and 5" I.D. ceramic cylinder which was fitted concentrically on the outer side of the 5 inch O.D. steel cylinder. This was connected to a 10 ampere powerstat 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. The other heating wire was wound around a one foot long and 2 inch I.D. ceramic cylinder. This cylinder was placed in the fluidized bed with the reactor on its inner side. Asbestos cement was used to insulate the heating wire and to keep it fixed in the grooves. The heating wire was connected to another 10 ampere powerstat through the temperature controller specified earlier. The use of two separate heaters helped in reducing the heating load in the controller circuit and provided more precise control of the reaction temperature.

The reactor and the fluidized bed vessel were further placed in an outer steel cylinder one foot in diameter, resting on an asbestos plate. Holes were provided in the center of the outer cylinder and the asbestos plate for the compressed air line. The space between the outer cylinder and the "bed" was packed with vermiculites, an insulator. The surface of the outer cylinder was wrapped with a 4" thick layer of fibre glass and asbestos cloth for further insulation.

(iii) Product Separation Unit

This unit included a gas chromatograph and a gas partitioner, each equipped with gas sampling devices for the analysis of the unreacted reactants and reaction products. A liquid trap and a drying tube were provided to condense the liquid components at ice temperature and to remove traces of moisture prior to the analysis of the gaseous components in the gas partitioner. Two chart recorders, an electronic integrator, a wet test meter and a bubble meter were also used. The reactants and products were analyzed on stream in the form of gas or vapor.

The line from the reactor exit to the gas chromatograph was heated by heating tape to prevent any possibility of condensation. This line was bifurcated; one branch was vented through a liquid trap in order to minimize back pressure in the reactor side, and the other was connected to the high temperature gas sampling valve of the gas chromatograph. The sampling valve (model 19022A) was supplied by Hewlett Packard. It provided a convenient means of introducing precise and reproducible gaseous samples into the gas chromatograph (Hewlett Packard model 5700A). The valve was made of stainless steel with a teflon rotor and had eight ports providing dual loop operation. The valve could be operated at pressures up to 200 psig. and at temperatures to 200^{o}C. The temperature was controlled within $\pm$0.5^{o}C and the pressure in the sampling valve was controlled with the help of needle valves in the exit lines.

A 5700A Hewlett Packard gas chromatograph equipped with dual column dual thermal conductivity cell detector (tungsten-rhenium) and solid state electronic temperature controlling system, was used to separate formaldehyde, water and unconsumed traces of methylene chloride. A Hewlett-Packard chart recorder (model 7127A) with 0-1 mv signal range and a 3373A electronic integrator were connected to the gas chromatograph.

The exit gases from the high temperature gas sampling valve were led to the ice-cooled liquid trap which was made of 7" x 7/8" O.D. glass test tube filled with a two-hole rubber stopper. After the heavier reaction products water and formaldehyde were condensed in the trap, the uncondensible gases were led to the drying tube. The drying tube, made of 6" x 1" O.D. plexi-glass tube with 1/8" stainless steel swagelok tube fittings, was packed with 10-20 mesh size indicating drierite. All traces of moisture from the gaseous reaction products were removed in the drying tube prior to their analysis in the Fisher Gas Partitioner. The presence of water in the gas sample deteriorates the performance of molecular sieve column rapidly.

The product stream from the drying tube was passed through the gas sampling valve built-in with the model 29 Fisher Gas Partitioner and vented. The gas sampling valve was a six-port linear type valve which provided two ports each for the sampling gas, carrier gas and the sampling loop. During its normal operation the sampling gas (product stream) was passed through the sampling loop and the other leg carried helium as the carrier gas. When the sampling valve was pushed on, the sample loop was taken out of series with the product stream and was simultaneously connected with the carrier gas which carried the contents of sample loop to the chromatographic column for the analysis.

The model 29 Fisher Gas Partitioner employed a dual-column dual-detector chromatographic system to separate and measure carbon dioxide. A constant temperature of 35^{o}C was maintained by a built-in thermal stabilizer. The partitioner was connected to a Texas Model Servo/Ritter II chart recorder (Texas Instrument Co.) and also to the Hewlett-Packard integrator (model 3373B) for peak area measurements.

B. Preparation and Properties of Catalyst

The alumina supported palladium oxide catalyst containing 0.5% palladium was prepared by impregnating [79] 20-40 mesh crushed activated alumina, supplied by Fisher Scientific Co.,with an acqueous solution of palladium ammonium chloride supplied by K and K Laboratories. The solution was first evaporated slowly at 70^{o}C to near dryness and then was dried at 100^{o}C for six hours. The temperature was raised in steps of 50^{o}C at an interval of one hour. The catalyst was heated at 550^{o}C for six hours and further calcined at 700^{o}C for four hours in a muffle furnace. The catalyst was activated at 500^{o}C in the reactor in a stream of air passing through it for 24 hours.

The initial activity of the catalyst was observed to decrease for about four hours before stabilization. It is generally attributed to water formation during the reaction which affects alumina support. Thus, the catalyst was conditioned with air-methane mixture at 500^{o}C for about 24 hours and a check for constant activity was made before taking any experimental data.

The particle diameter (D_p) was determined using a micrometer. A random sample of 25 granules was taken and the diameter of each granule was measured with a micrometer. An arithmetic average of these measurements gave the value of particle diameter as 0.027 inch. However, the average size from the screen sizes (20 and 40 Canadian Standard Sieve) was 0.0298 inch.

The particle density (ρ_p) was determined by weighing 100 granules and dividing it by the volume of 100 granules calculated on the basis of average diameter of 0.0298 inch and assuming the sphericity of the particle to be 0.9. The particle density thus determined was 1.9346 gm/cm^3.

The surface area of the catalyst was 98 m^2/gm. It was determined with the standard B.E.T. apparatus and microbalance in a laboratory of the Department of Energy, Mines and Resources, Ottawa.

The color of the fresh catalyst was light beige which turned to brown after use. The X-ray diffraction pattern showed a small amount of crystalline phase identified as palladium oxide. The X-ray diffraction studies were made in the Department of Geology at the University of Ottawa.

The activity of the catalyst was ensured periodically by repeating one of the previous runs and comparing the product distributions.

C. Experimental Procedure

(1) Check for Leakage

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

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

(ii) It was ensured that the rotameter showed no indication of gas flow through it when the valves on the downstream were closed.

(iii) It was ensured that there was no indication of a pressure drop in the system for at least two hours when the inlet and outlet valves were closed.

(2) Calibration of Equipment

The rotameters were calibrated for the volumetric flow rates of the gas streams at a constant pressure of 1400 mm Hg. The pressure in the rotameters was regulated by adjusting the fine metering valve at the exit of each rotameter. The flow rates were checked by both the bubble meter and the wet test gas meter supplied by Precision Scientific Co., Chicago. A correction for any fluctuation in the room temperature was also made and constant molar flow rates of the gas streams were thus achieved. The calibration curves for air and methane are given in Appendix (B).

The feed rates of liquid halogen modifiers and formaldehyde solution were controlled by the speed of the syringe pump. Further variation in the pump discharge rate was obtained by changing the size of the syringe. The pump discharge rates were calibrated by weighing distilled water pumped out for a known period of time at a set pump speed and syringe size. The results of calibration for the syringe pump are given in Appendix (B).

The thermocouples were calibrated by inserting them in the fluidized bed furnace and noting the temperature by an ASTM thermometer (0-400^{o}C) attached to the thermocouple. The corresponding thermocouple EMF were measured by a potentiometer. A calibration curve for the reactor thermocouple is given in Appendix (B).

The calibrations of Gas Partitioner and Gas Chromatograph were made by using synthetic mixtures of known compositions which were similar to the actual samples. The time and order of elution of the components were determined by using pure components. Mixtures of oxygen, carbon dioxide, carbon monoxide and methane with nitrogen in varying proportions were made in the feed preparation section and were passed through the Gas Partitioner for analysis bypassing the reactor. The mixture of water, methanol and formaldehyde in varying compositions were pumped through the syringe pump, vaporized in the hot inlet and mixed with the air stream. This mixture was introduced into the Gas Chromatograph through high temperature gas sampling valve at a temperature of 150^{o}C. The sample pressure was maintained at 800 mm Hg by adjusting the fine needle valves in the exit lines. Quantitative analysis of the samples in the Gas Chromatograph was made using the calibration curve of mole percent of component against its peak area. For the samples in the Gas Partitioner, the quantitative analysis was based on relative peak area ratio versus mole ratios (internal normalisation method). At lower attenuations of Gas Partitioner, calibration curve for peak height ratio versus mole ratio was also prepared for some of the runs when the area integrator could not be made available for the Partitioner. The calibration curves are given in Appendix (B).

(3) <u>Analysis Procedure</u>

(i) Gases:

The inlet feed and the product gases were analyzed for carbon dioxide, oxygen, nitrogen, methane and other hydrocarbons (if any) and carbon monoxide by introducing a 0.5 ml sample into the Fisher Gas Partition through sampling valve. The partitioner contained two gas chromatographic columns. The first was made of 6 feet long and 1/4" O.D. copper tubing and was packed with 30% DEHS (di 2-ethylhexyl sebocate) coated on celite diatomaceous silica which could separate carbon dioxide and hydrocarbons other than methane. The second column was made of 12 feet long and 3/16" O.D. copper tubing and was filled with a mixture of molecular sieve 13x and 5A in a proportion of 2 to 3 parts respectively. This could separate oxygen, nitrogen, methane and carbon monoxide. A typical analysis of the products from the Gas Partitioner is shown in Figure 3-3. Nitrogen was used as the key component for its chemical inertness.

(ii) <u>Liquid Products</u>

The hot effluent from the reactor was directly introduced in to the Hewlett-Packard Gas Chromatograph through the high temperature gas sampling valve. The temperature and pressure of the sampling gas were precisely controlled at 150°C and 800 mm Hg respectively. A gas chromatographic column packed with 15% (wt.) sucrose octa acetate coated on Columnpak T in a 15 feet long and 1/4" O.D. copper tubing was used for the product separation. The column was conditioned by heating at 195°C for one hour. During analysis the column oven temperature was maintained at 100°C. This column separated water, methanol, formaldehyde and methylene chloride very efficiently. A typical gas chromatograph is shown in Figure 3-4. The consumption of

Figure 3-3

Chromatographic Analysis

of Gaseous Components

Helium flow rate = 60 ml/min.
Helium pressure = 36 psig
Sampling loop size = 1 ml
Cell current = 150 mA
Sensitivity setting = 16
Recorder chart speed = 8 in/hr

<u>Component identification:</u>

(1) Sample injection (0 min.)
(2) Composit peak of the
mixture (1.83 min.)
(3) Carbon dioxide (2.71 min.)
(4) Oxygen (3.52 min.)
(5) Nitrogen (4.34 min.)
(6) Methane (6.49 min.)
(7) Carbon monoxide (13.65 min.)

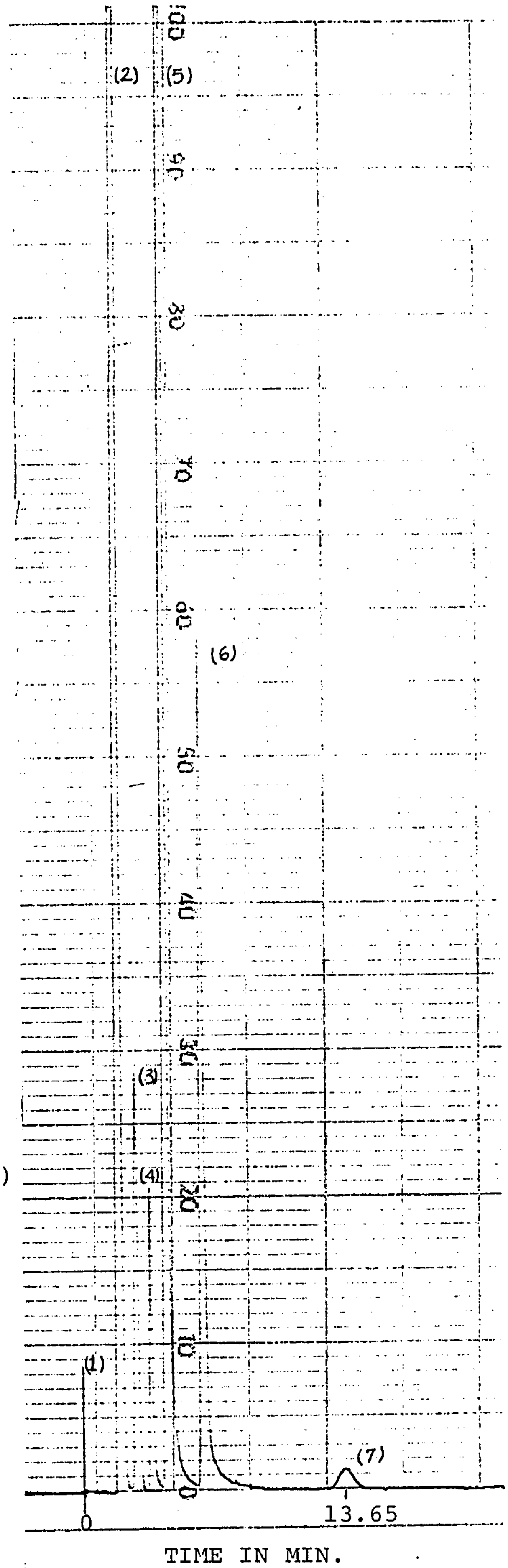
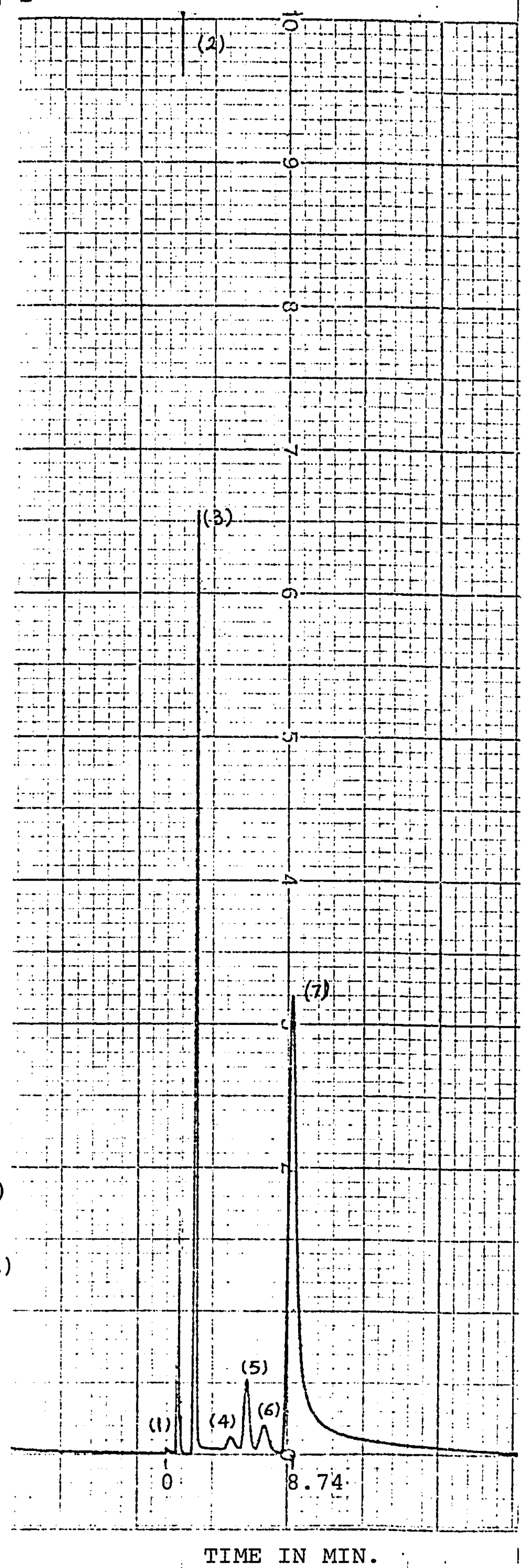


Figure 3-4
Chromatographic Analysis of Liquid Components

Helium flow rate = 75 ml/min.
Helium pressure = 44 psig
Sampling loop size = 1 ml
Detector temperature = 200°C
Detector sensitivity = 5
Detector current = 120 mA
Column temperature = 100°C
Sensitivity setting = 2
Recorder chart speed = 6 in./hr

Component identification:

(1) Sample injection (0 min.)
(2) Composite peak of mixture (0.98 min.)
(3) Formaldehyde (2.12 min.)
(4) Unknown impurity (4.53 min.)
(5) Methanol (5.55 min.)
(6) Methylene chloride (6.54 min.)
(7) Water (8.74)



methylene chloride during the reaction may have formed some hydrochloric acid which could not be detected by above gas chromatographic method.

(4) <u>Operating Procedure</u>

The details of the experimental procedures are described in two parts - first, start up and preparation and second, the actual run.

(a) Start Up

(i) Check all new connections of valves and tube fittings and tighten them properly.

(ii) Test the experimental apparatus for any leaks.

(iii) Purge the feed section and the reactor with compressed air at 20 psig.

(iv) Charge the reactor with a weighed amount of fresh catalyst and cover it with a layer of glass wool to prevent the catalyst from escaping from the reactor.

(v) Re-assemble the reactor and check for leaks. Careful attention is needed while handling the thermocouple.

(vi) Clamp the reactor to place it upright in the center of the fluidized bed furnace. Turn on the compressed air to fluidize the furnace bed. The air flow rate was adjusted to about 2 liters/min. and fluidized condition of the sand was observed visually.

(vii) Turn on the air stream from the high pressure cylinder for activating the catalyst in the reactor.

(viii) Turn on the power to the reactor heating elements through 'variac' powerstats. The power and the furnace temperature were increased in steps and approximately 24 hours were provided to initially reach thermal equilibrium from ambient temperature.

(ix) Switch on the various heating tapes for preheating the air, warming the feed lines leading to reactor and the lines between the reactor and product analysis section.

(x) Switch on power for the hot inlet. Also switch on power for the thermal stabilizer in the Gas Partitioner unit.

(xi) Turn on the helium gas for Gas Partitioner and Gas Chromatograph adjusting the rotameter settings for predetermined flow rates of 60c.c./min. and 75c.c./min. respectively.

(xii) Set the temperatures for detector, gas sampling valve, column oven and injection ports in the Gas Chromatograph at 200^o, 150^o, 100^o and 150^0C respectively.

(xiii) Set the cell current in Gas Chromatograph and Gas Partitioner at 120 mA and 150 mA respectively.

(xiv) Switch on recorders for the Gas Chromatograph and Gas Partitioner and check the stability and straightness of the baselines.

(b) Run

(i) The liquid trap was placed in the ice bath and checked for any leaks. The vents from the product analysis section were connected to laboratory gas exit line.

(ii) When the required temperature of the catalyst bed in reactor was achieved, the rotameters for air and methane were adjusted to supply the reactants, in a desired air to methane ratio, for the reaction. If the rise in reactor temperature was rapid indicating a fast reaction rate, the methane supply was immediately cut off and the reactor temperature setting was lowered by 50 to 100°C. The supply of methane was resumed when the reactor was stabilized at the lower temperature setting. After about two hours the reactor temperature was increased to the desired reaction temperature in steps of about 20-25°C every half an hour.

(iii) Once the reactor temperature and the reactants' flow rates and flow ratio attained the desired values, the modifier was introduced into the reactant feed line through the hot inlet. The amount of modifier was controlled by adjusting the speed of syringe pump or the size of syringe.

(iv) The flow rates of feed gases and modifier were maintained at their specified values for 2 hours to obtain steady state conditions at the desired reaction temperature.

(v) The samples of hot effluent gases were introduced from the reactor into the Gas Chromatograph through its high temperature gas sampling valve and the uncondensable gases were led from the ice-cooled trap into the gas partitioner via another sampling valve. No change in the compositions of consecutive product samples indicated a steady-state reaction condition.

(vi) The steady-state run was continued for a period of time during which at least two samples were analyzed.

(vii) During the run flow rates of reactants and modifier and the reaction temperature were watched for any fluctuations. Peak heights or peak areas from the integrator and chromatographs of the products were noted.

(viii) The methane and modifier supply was shut off and air flow through the catalyst bed maintained for one hour before the start of another run.

(iv) The condensates were drained from the liquid traps. If necessary, packings of the drying tubes were changed and the syringe was refilled with the modifier.

(x) Calibrations of the gas chromatographs were checked periodically to assure the stability of the columns.

D. Reactants and Chemicals

C.P. grade methane gas with a minimum purity of 99% was used in the present study. The gas was supplied from Matheson Co. in cylinder at a pressure of 2265 psig. 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 the air through a drying tube containing indicating drierite.

The chemicals which were added in the feed mixture to act as catalyst modifiers were:

- Iodomethane (Anachemia Chemical Ltd.) and diiodomethane (Eastman Organic Chemicals, N.Y.) were used as the sources of iodine modifiers.

- Dibromomethane from Eastman Kodak Co., N.Y., was used as the source of bromine modifier.

- Certified A.C.S. methylene chloride, trichloromethane and carbon tetrachloride obtained from Fisher Scientific Co., and methyl chloride obtained from Matheson Co. were used as the sources of chlorine modifier.

The chemicals used in the preparation of gas chromatographic columns were sucrose octa-acetate (Eastman Kodak Co., N.Y.), 40-60 mesh columnpak-T, and methylene chloride, both obtained from Fisher Scientific Co. Columns for the Gas Partitioner were made from 40-60 mesh molecular sieves (5A and 13x) supplied by Coast Engineering Laboratory, Redando Beach, California, and 30% DEHS on 40-60 mesh Columpak, obtained from Fisher Scientific Co.

The catalyst was prepared from palladic ammonium chloride, $Pd(NH_4)_2\ Cl_6$, obtained from K and K Laboratories Inc., Plainview, N.Y., and 8-14 activated alumina obtained from Fisher Scientific Co. (catalogue no. 7-754).

The chemicals used for the chemical analysis of formaldehyde were: sodium sulphite (B.D.H. Canada Ltd.), hydrochloric acid, phenolphthein, thymolphthalein and potassium hydroxide.

Helium used as carrier gas in the gas chromatographic analysis was supplied by Liquid Carbonic Canadian Corp. Ltd.. For calibration purposes nitrogen was supplied by Linde Specialty Gas (Union Carbide of Canada), and carbon monoxide and carbon dioxide were obtained from 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 from the product analysis. The effects of several variables, namely the ratio of halogen mofidier to methane in the feed, $\bar{Z}$, the ratio of air to methane in the feed, $\bar{R}$, reaction temperature, T, and the reciprocal of space velocity, W/F, on the conversion of methane, X, yield of formaldehyde, Y, and the selectivity, S, of the catalyst for the formation of formaldehyde were studied.

The conversion, X, is defined as the ratio of moles of methane reacted per hour to the moles of methane fed into the reactor per hour. The yield is expressed as the ratio of the moles of formaldehyde formed per hour to the methane feed rate in moles per hour. Selectivity S is defined as the ratio of the moles of formaldehyde formed per hour to the moles of methane reacted per hour.

During the experimental runs, the different feed ratio (air:methane) were obtained by adjusting the air flow rates only, while the flow rate of methane charged into the reactor was kept constant. The reciprocal of space velocity was varied by changing the feed rate and the amount of catalyst. Different amounts of halogen modifiers in the feed were obtained by varying the speed of the syringe pump and the size of the syringe.

The effect of different halogen compounds in the reaction feed mixture on the catalytic oxidation of methane is shown in Figure (4-1 to 4-5) and the results are given in Appendix C (Table A-C-4 to A-C-11). Figure (4-1) shows the effect of different chlorine compounds, namely, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, on the conversion of methane and the yield of formaldehyde under same operating conditions. The feed ratio, W/F and reaction temperature were 5.03, 38.33 gm.hr/gm mole and 475^{o}C respectively. Addition of all of the above chlorine compounds reduced the conversion of methane. Methylene chloride was observed to have the least inhibiting effect on the conversion of methane. The inhibiting effect was in the following increasing order: $CH_2Cl_2 < CHCl_3 < CH_3Cl < CCl_4$. Excepting CCl_4, all other chlorine additives showed a significant increase in the yield of formaldehyde. Methylene chloride was most effective in increasing the yield of formaldehyde.

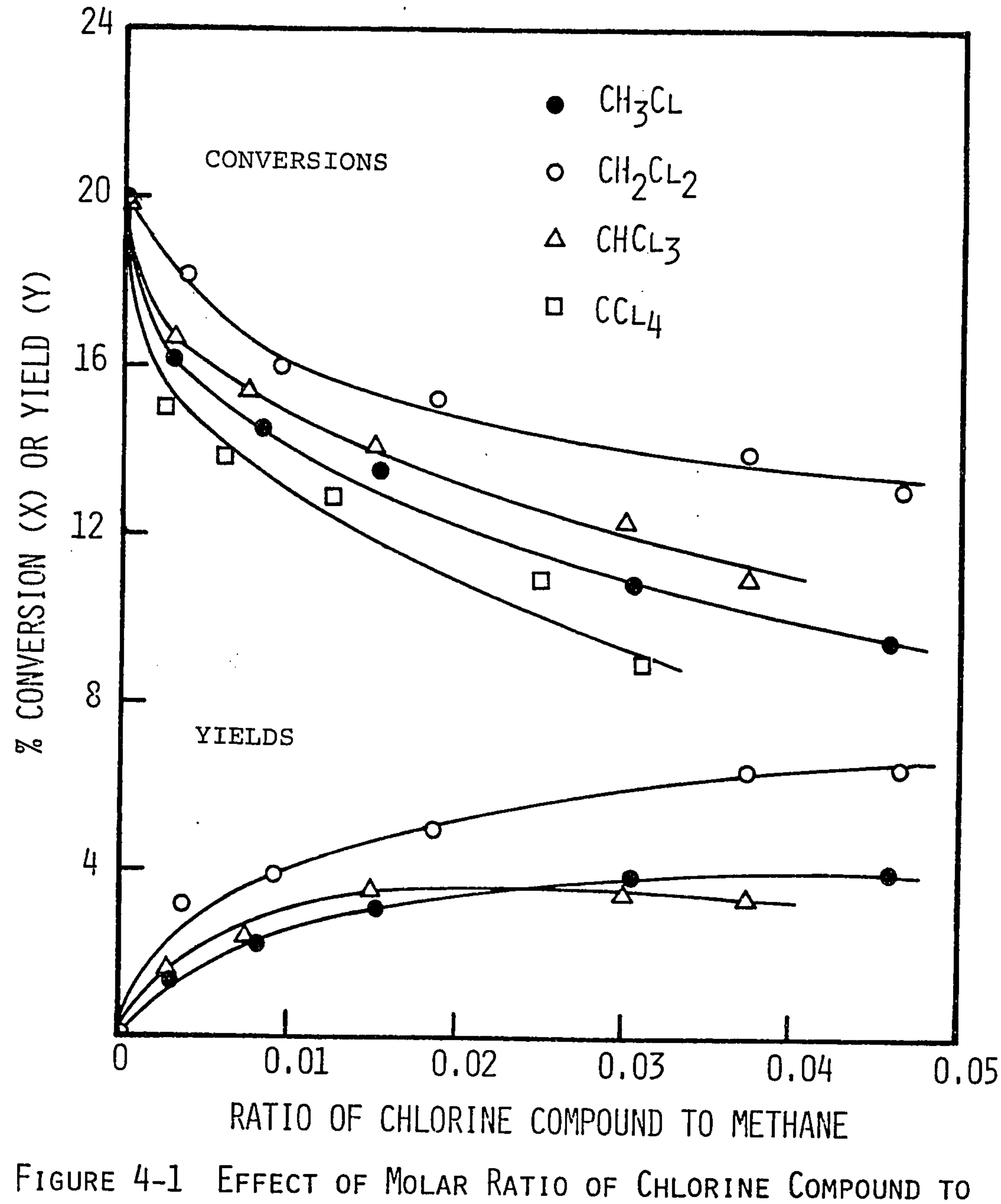


FIGURE 4-1 EFFECT OF MOLAR RATIO OF CHLORINE COMPOUND TO METHANE IN THE FEED ON CONVERSION OF METHANE AND YIELD OF FORMALDEHYDE AT 475°C.
$\bar{R}$ = 5.03 AND W/F = 38.33 GM.HR/GM MOLE

Figure (4-2) shows the effect of CH_3I and CH_2I_2 on the conversion of methane and the yield of formaldehyde at a temperature of 475°C, a feed ratio of 5.03 and a reciprocal space velocity (W/F) of 38.33 gm.hr/gm mole. Both iodine compounds were found to highly inhibit the overall methane reaction. These additives were also effective in increasing the yield of formaldehyde to a certain extent but, in general, to a much lesser degree than the chlorine additives.

Figure (4-3) shows the effect of methylene bromide on methane conversion and on yields of formaldehyde and carbon dioxide under operating conditions identical to those maintained for the studies of chlorine and iodine compounds described earlier. Addition of methylene bromide followed trends similar to chlorine and iodine additives. An increase in the amount of methylene bromide in the reaction feed mixture decreased the conversion rate of methane. The selectivity of the catalyst for formaldehyde increased with increasing amount of methylene bromide while the yield of carbon dioxide decreased. The yield of formaldehyde increased in the presence of low amounts of methylene bromide, but decreased with further increase of the modifier due to a decrease in the methane conversion rate.

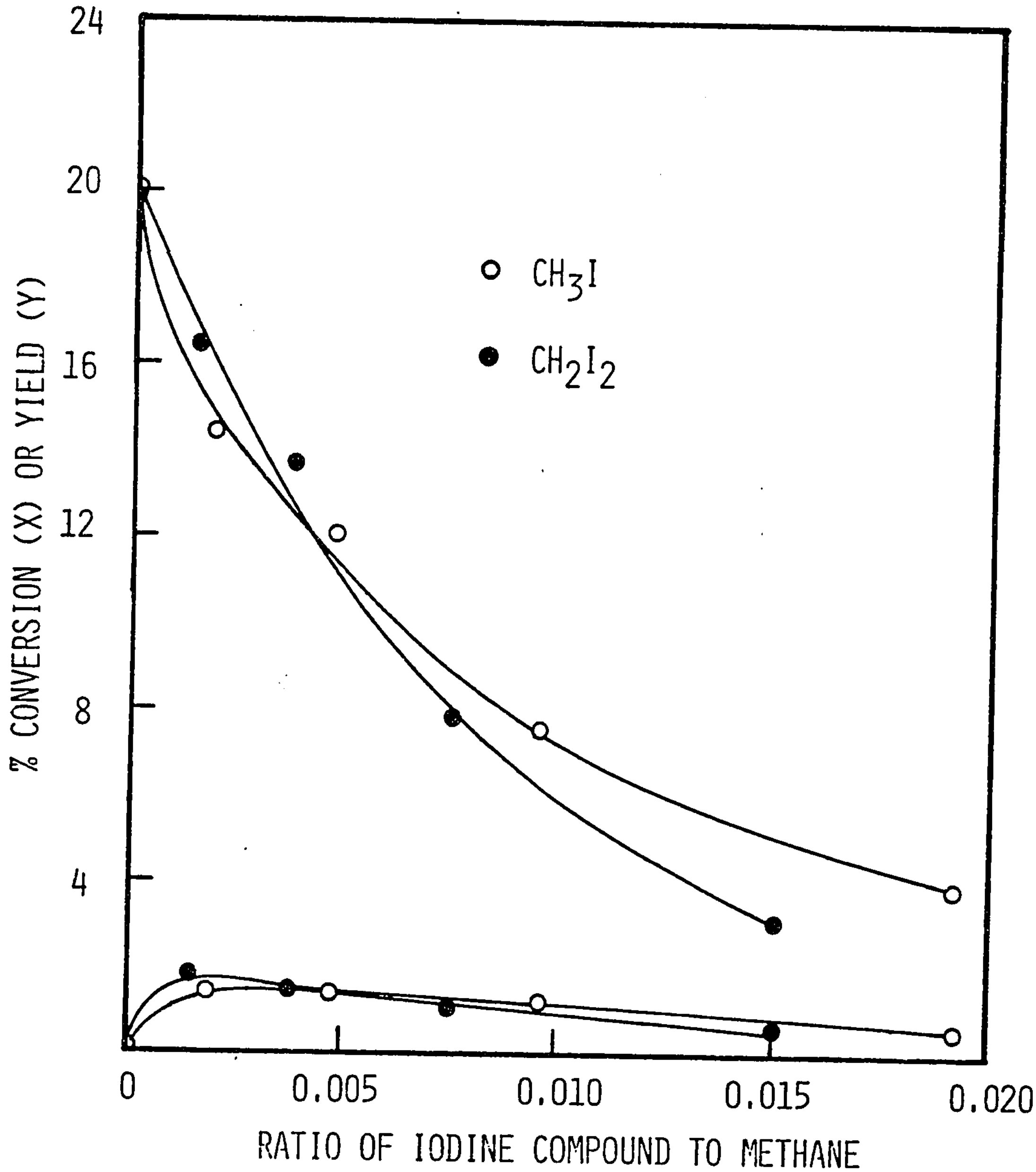


FIGURE 4-2 EFFECT OF MOLAR RATIO OF IODINE COMPOUND TO METHANE IN FEED, ON CONVERSION OF METHANE AND YIELD OF FORMALDEHYDE AT 475°C, $\bar{R}$ = 5.03 AND W/F = 38.33 GM.HR/GM MOLE

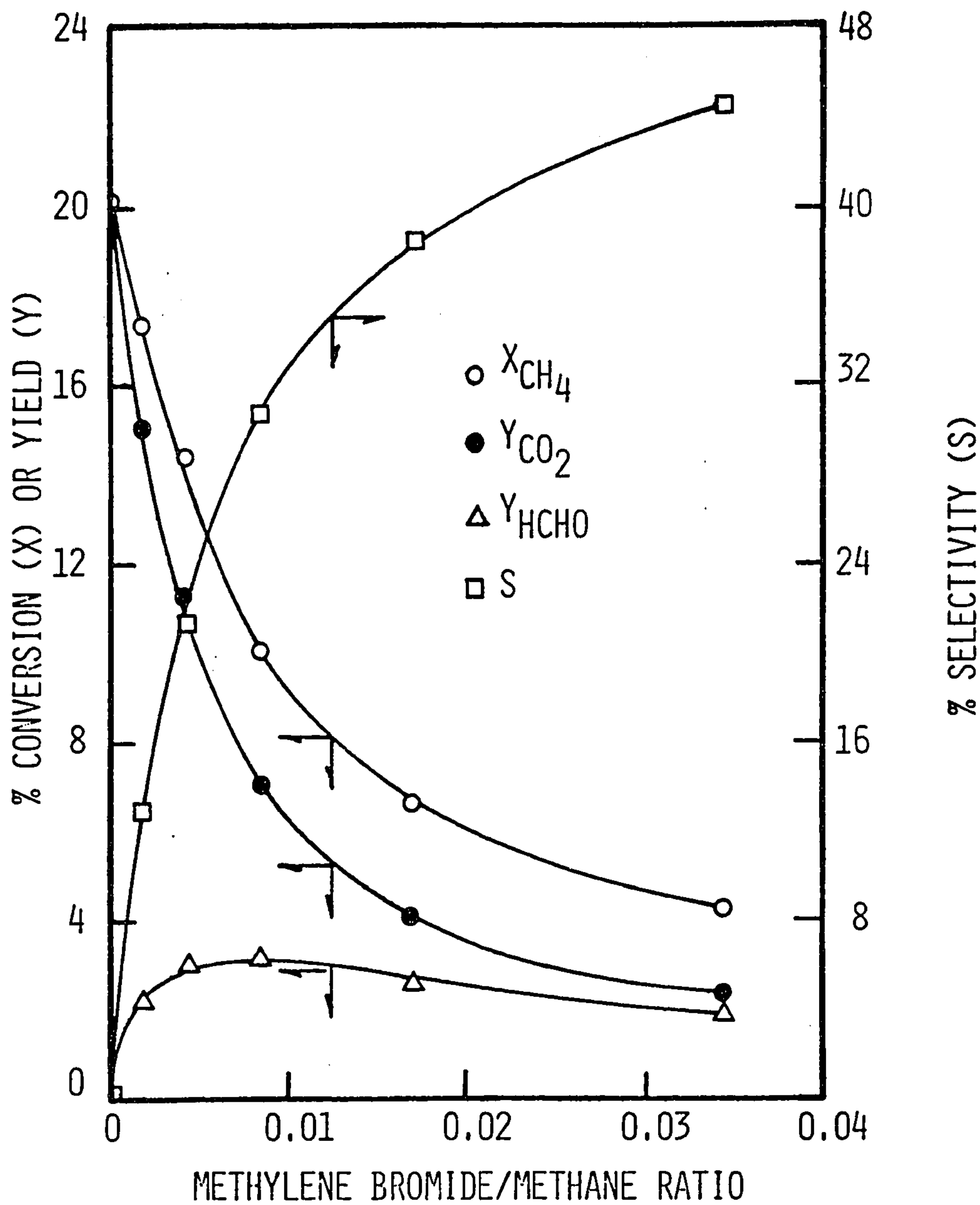


FIGURE 4-3 EFFECT OF MOLAR RATIO OF METHYLENE BROMIDE TO METHANE ON CONVERSION, SELECTIVITY AND PRODUCT YIELDS FOR OXIDATION OF METHANE AT 475°C, $\bar{R}$ = 5.03 AND W/F = 38.33 GM.HR/GM MOLE

Figure (4-4) shows the effect of reaction temperature on the methane oxidation in the presence of 0.00223 gm mole/hr. of methylene bromide. The feed ratio and reciprocal space velocity were 5.03 and 38.33 gm.hr/gm mole respectively. The conversion of methane and yield of carbon dioxide increased with an increase in the temperature. The selectivity of the catalyst for formaldehyde formation increased with temperature up to 440^{o}C but decreased with further increase in the temperature. The yield of formaldehyde increased only slightly with an increase in the temperature.

On the basis of the above preliminary study on the effect of various halogen additives, methylene chloride, which showed the least inhibiting effect on methane conversion and which made the catalyst highly selective for formaldehyde formation, was chosen for further detailed kinetic study of the partial oxidation of methane.

A typical gas chromatogram which shows the promotional effect of doping palladium catalyst in the oxidation of methane to formaldehyde is given in Figure (4-5). Chromatogram A shows the traces of formaldehyde formed in the oxidation over the unmodified catalyst. Chromatogram B shows marked increase in the selectivity for formaldehyde over the same catalyst and under identical operating conditions

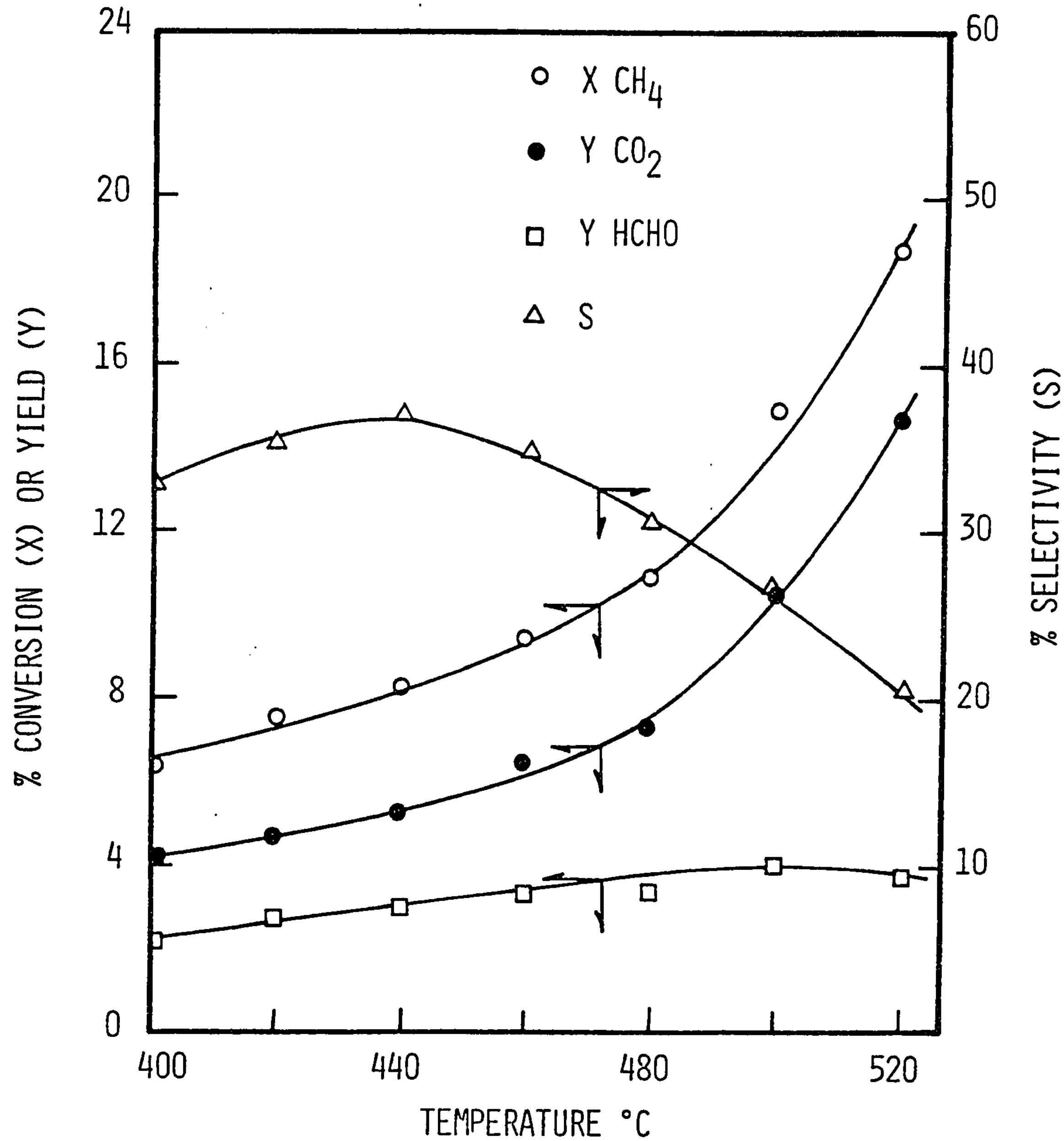
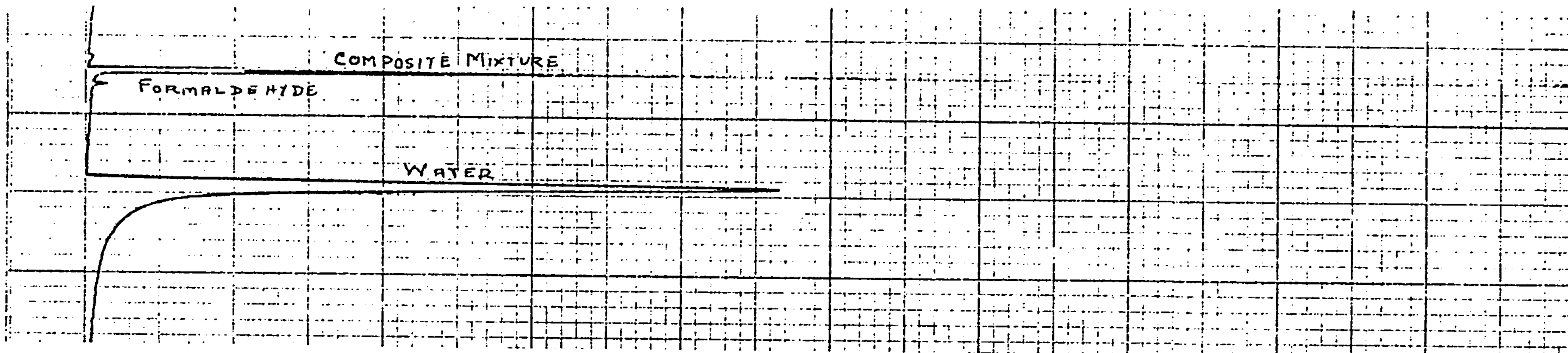
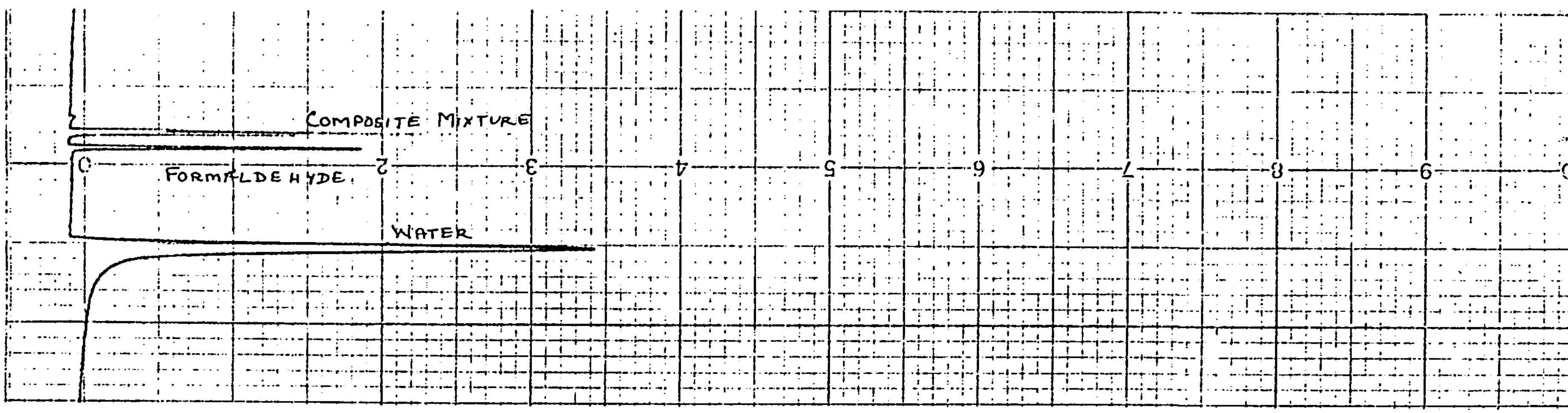


FIGURE 4-4 EFFECT OF TEMPERATURE ON CONVERSION, SELECTIVITY AND PRODUCT YIELDS FOR OXIDATION OF METHANE OVER BROMINE MODIFIED CATALYST WITH $\bar{R}$ = 5.03, W/F = 38.33 GM.HR/GM MOLE AND 0.00223 GM MOLE CH_2Br_2/HR



(A) Before adding modifier



(B) With continuous addition of modifier

Figure 4-5 Gas Chromatogram showing the Promotional Effect of Chlorine on Methane Oxidation over Palladium Catalyst but in the presence of methylene chloride in the reaction feed mixture.

Figure (4-6) shows the effect of the amount of methylene chloride in the feed on the conversion of methane, yields of formaldehyde and carbon dioxide and the selectivity of the catalyst. With an increase in the amount of methylene chloride the selectivity of catalyst for formaldehyde formation increased rapidly up to a ratio, $\bar{Z}$ equal to 0.039. Further increase in methylene chloride increased the selectivity at relatively lower rate. An increase in methylene chloride decreased the yield of carbon dioxide. The yield of formaldehyde increased fairly rapidly with an increase in $\bar{Z}$ (modifier to methane ratio) up to 0.02 beyond which the rate of increase of the yield of formaldehyde decreased. Further experimental runs for the kinetic study of methane oxidation were thus made with a constant low ratio ($\bar{Z}$ = 0.0195) of methylene chloride to methane in the reaction feed mixture. Although with this choice of a smaller amount of methylene chloride, the selectivity obtained in the catalyst was low, contamination of the products and operational difficulties due to the formation of moist chlorine were greatly reduced.

The reaction products to methylene chloride were checked by repeating some of the experimental runs

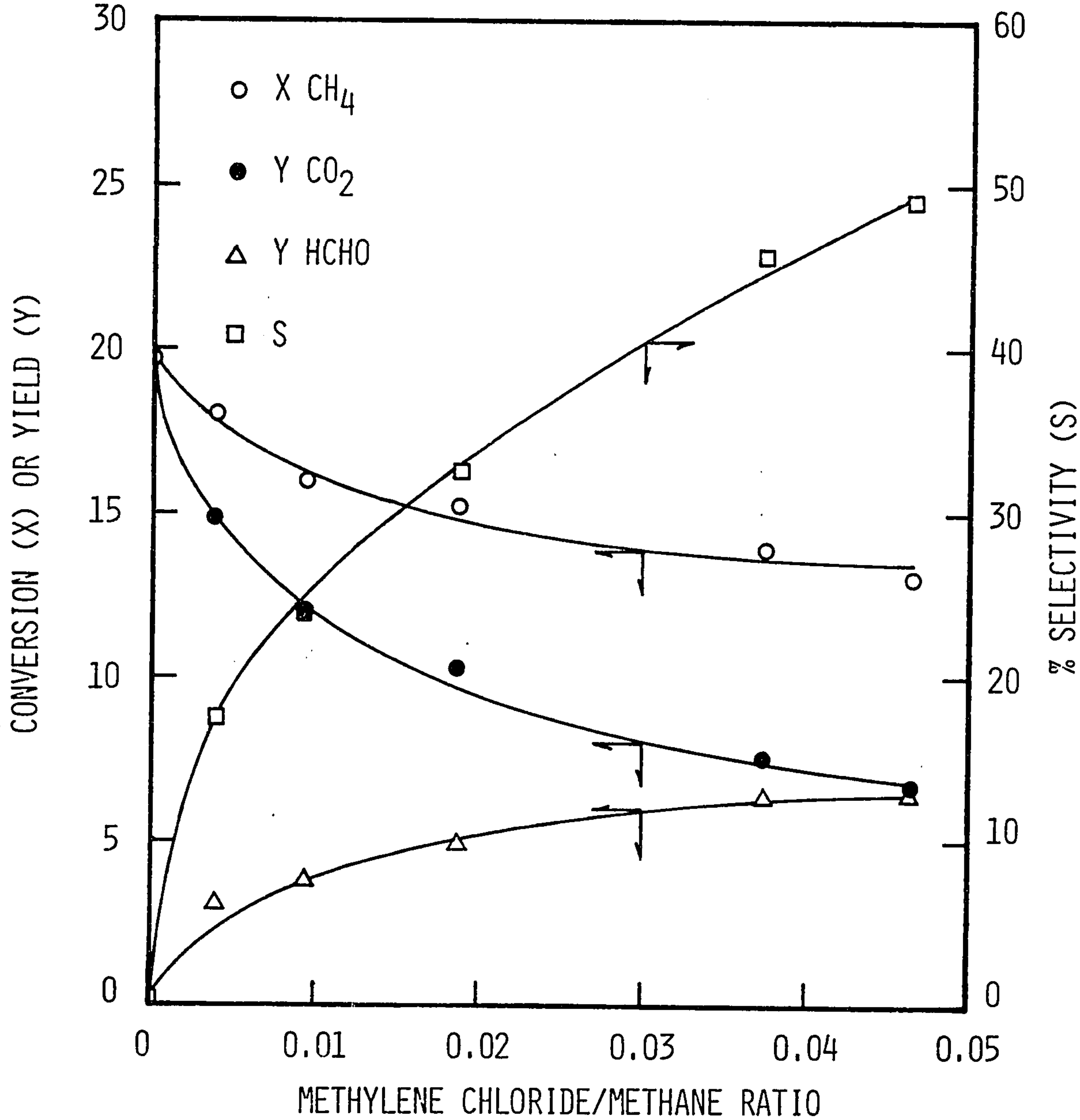


FIGURE 4-6 EFFECT OF MOLAR RATIO OF METHYLENE CHLORIDE TO METHANE ON CONVERSION, SELECTIVITY AND PRODUCT YIELDS FOR OXIDATION OF METHANE AT 475°C, $\bar{R}$ = 5.03 AND W/F = 38.33 GM.HR/GM MOLE

with methane replaced by nitrogen. No formaldehyde was detected in the product analysis and carbon dioxide was observed in stoichiometric amounts of methylene chloride decomposed. The amount of methylene chloride decomposed varied only with the temperature. However, methylene chloride added into the reaction feed mixture in small amount (0.0049 gm mole/hr.) was completely consumed in a temperature range of 390-510°C.

It was also observed in the preliminary investigations that when the supply of methylene chloride in the feed was stopped, the catalyst continued to be selective for formaldehyde formation. The selectivity of the catalyst slowly reduced and it took more than two hours to return to its initial activity and selectivity before the modifier was introduced. This implied that the modifier interacts with the catalyst surface and modifies some of the characteristics of the skeleton catalyst favoring the formaldehyde formation. It was also observed that a continuous supply of the modifier in the feed was essential to maintain a high selectivity of the catalyst for formaldehyde formation.

The effect of feed ratio (air:methane) on conversion of methane, yield of formaldehyde and selectivity of the chlorine modified catalyst is shown in Figure (4-7) for a temperature of 480°C and W/F = 49.00 gm.hr/gm mole. The air:methane ratio was varied between 2.41 and 5.28 by varying air flow rates. With an increase in the feed ratio both the conversion of methane and the yield of formaldehyde increased. However, the selectivity of the catalyst for the formation of formaldehyde remained fairly constant.

The reciprocal space velocity, W/F, was varied in the range of 12.00 to 96.00 gm.hr/gm mole by varying the weight of catalyst and the feed rates of the reactants and the modifier. The effect of reciprocal space velocity, W/F, on conversion of methane, yield of formaldehyde and catalyst selectivity at 480°C for a feed ratio of 5.28 is shown in Figure (4-8). The conversion of methane and the yield of formaldehyde both increased with an increase in W/F. The catalyst selectivity was only slightly affected by a change in the reciprocal space velocity. Experimental data for the effect of W/F on conversion of methane for some feed ratios and at different temperatures (390-510°C) are shown in figures (5-11 to 5-21). At all temperatures, conversion of methane increased with an increase in W/F. The results are given in Appendix C (Table A-C-1).

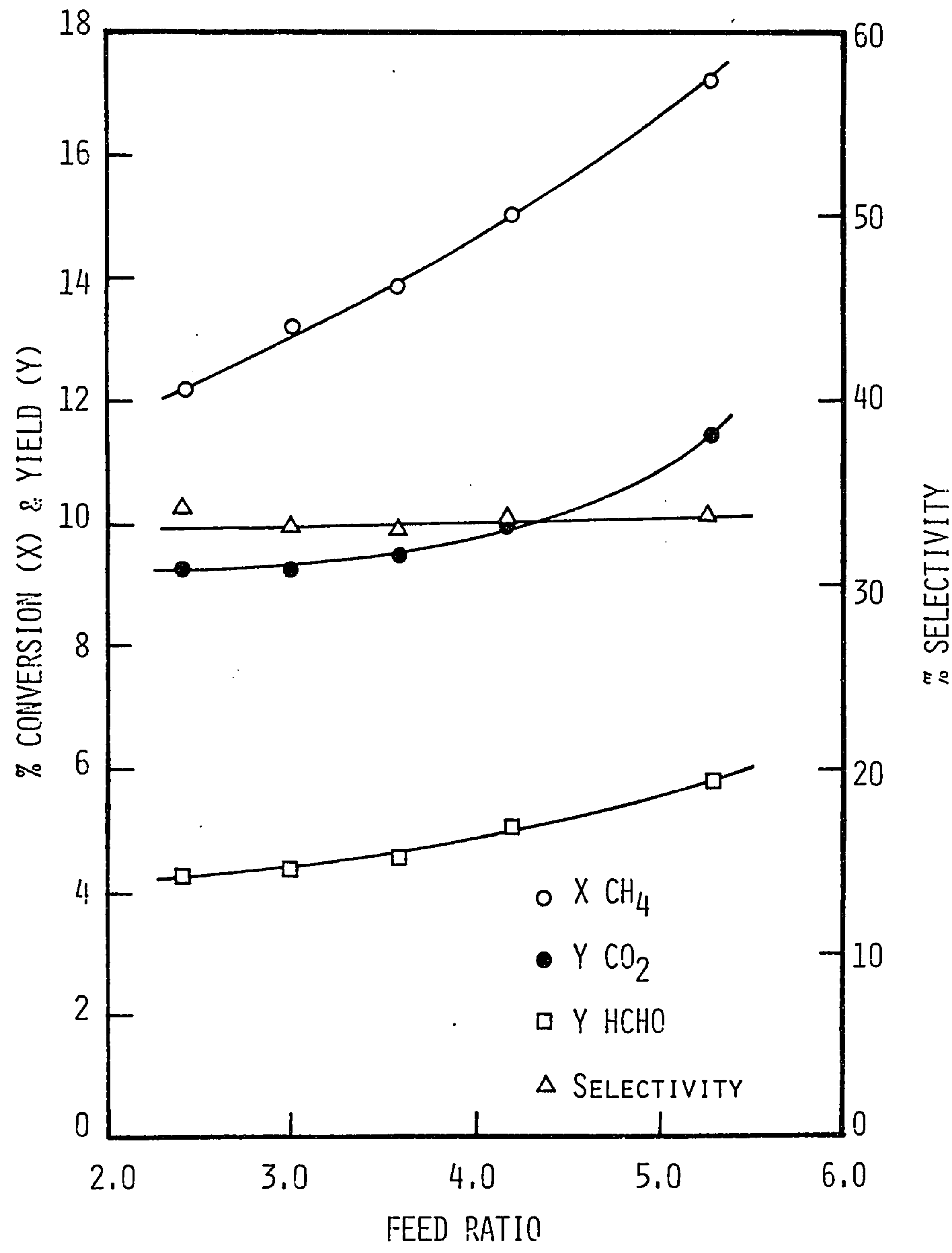


FIGURE 4-7 EFFECT OF MOLAR RATIO OF AIR TO METHANE ($\bar{R}$) ON CONVERSION OF CH_4, PRODUCT YIELDS AND CATALYST SELECTIVITY OF HCHO FORMATION AT 480°C WITH W/F = 49.00 GM.HR/GM MOLE

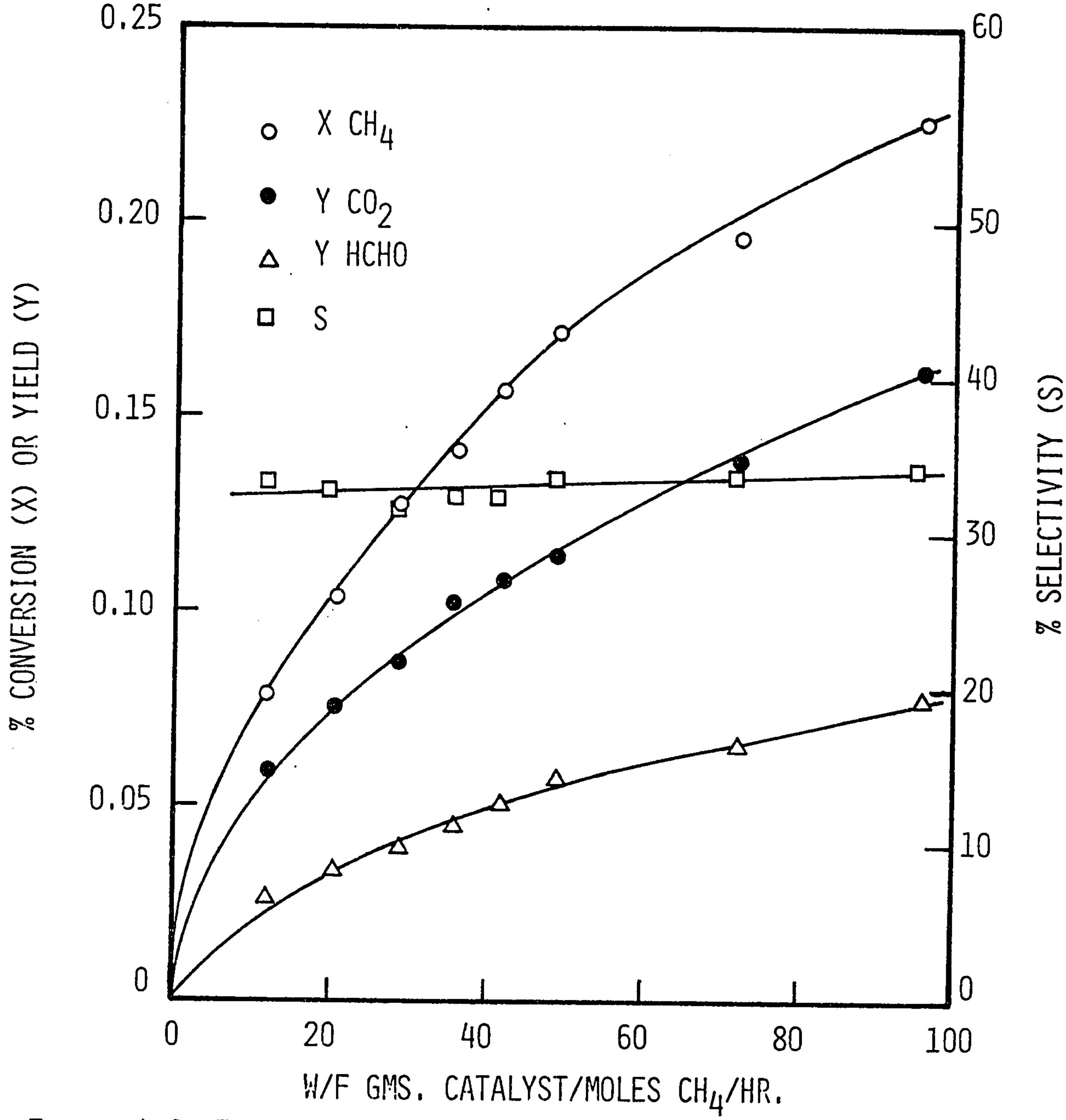


FIGURE 4-8 EFFECT OF W/F ON CONVERSION, YIELDS AND CATALYST SELECTIVITY FOR OXIDATION OF METHANE OVER CHLORINE MODIFIED PALLADIUM CATALYST AT 480°C AND $\bar{R}$ = 5.28

The effect of temperature on the conversion of methane, yield of formaldehyde and on the selectivity of the catalyst (chlorine modified) for formaldehyde formation is shown in Figure (4-9) for feed ratio and reciprocal space velocity of 5.28 and 49.00 gm.hr/gm mole respectively. The conversion of methane and the selectivity of the catalyst were observed to be sensitive to reaction temperature. The conversion of methane increased with an increase in reaction temperature. The catalyst selectivity remained unaffected at lower temperature, but at temperatures of 450^{o}C and above the selectivity of the catalyst decreased with an increase in temperature which may be attributed to the enhancement of the further oxidation of formaldehyde at higher temperatures.

The oxidation of formaldehyde, the primary product in methane oxidation, was also investigated to find whether carbon dioxide is formed from the further oxidation of intermediate formaldehyde or from the direct oxidation of methane, and to obtain some insight into the promotional effect of the chlorine modifier. The catalyst was the same as that used in methane oxidation, in which methylene chloride was used as a modifier. It was found that in the absence of the modifier, formaldehyde oxidation was quite sensitive to

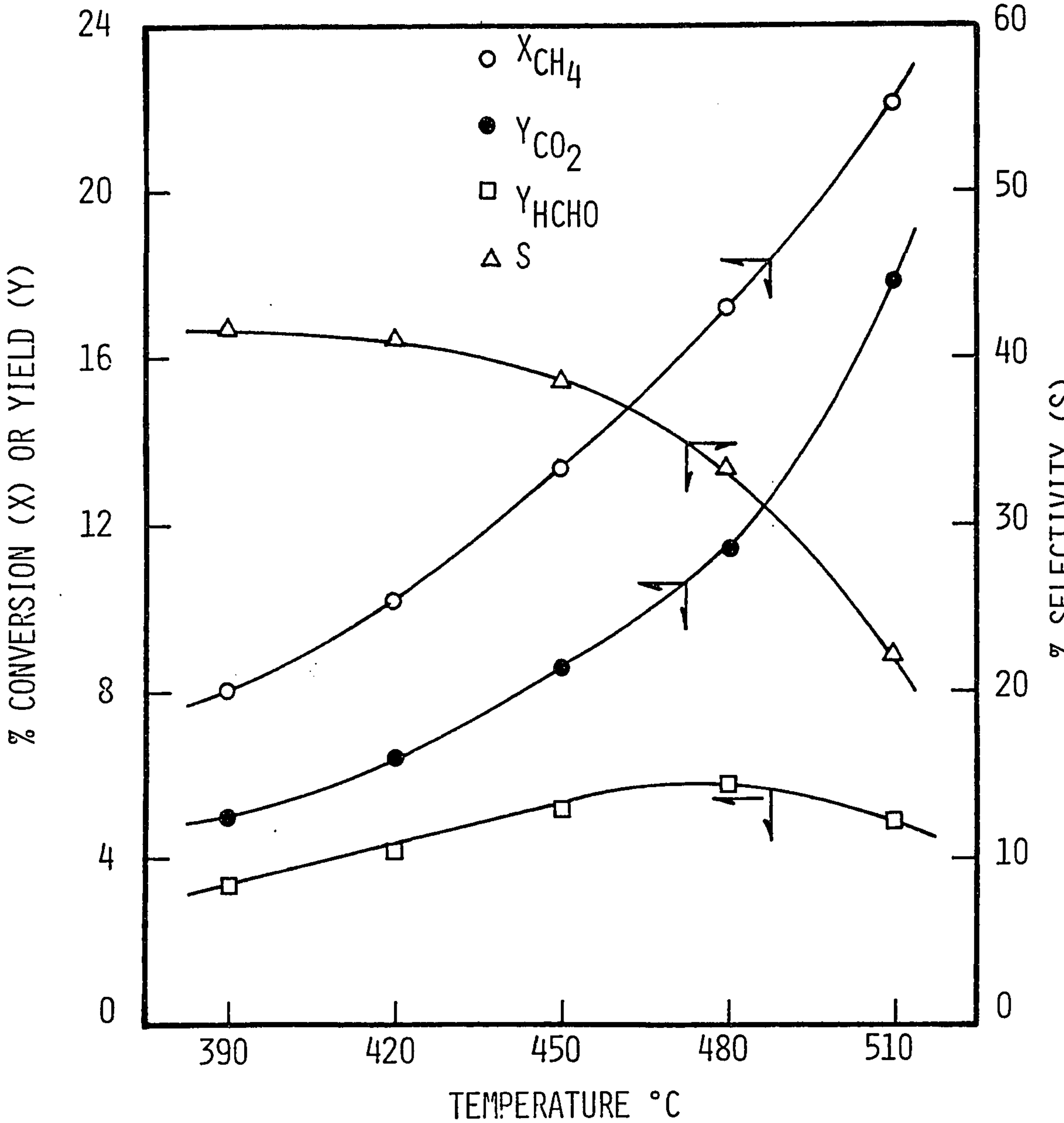


FIGURE 4-9 EFFECT OF TEMPERATURE ON CONVERSION OF METHANE, SELECTIVITY AND PRODUCT YIELDS FOR OXIDATION OF METHANE OVER CHLORINE MODIFIED CATALYST WITH $\bar{R}$ = 5.28 AND W/F = 49.00 GM.HR/GM MOLE

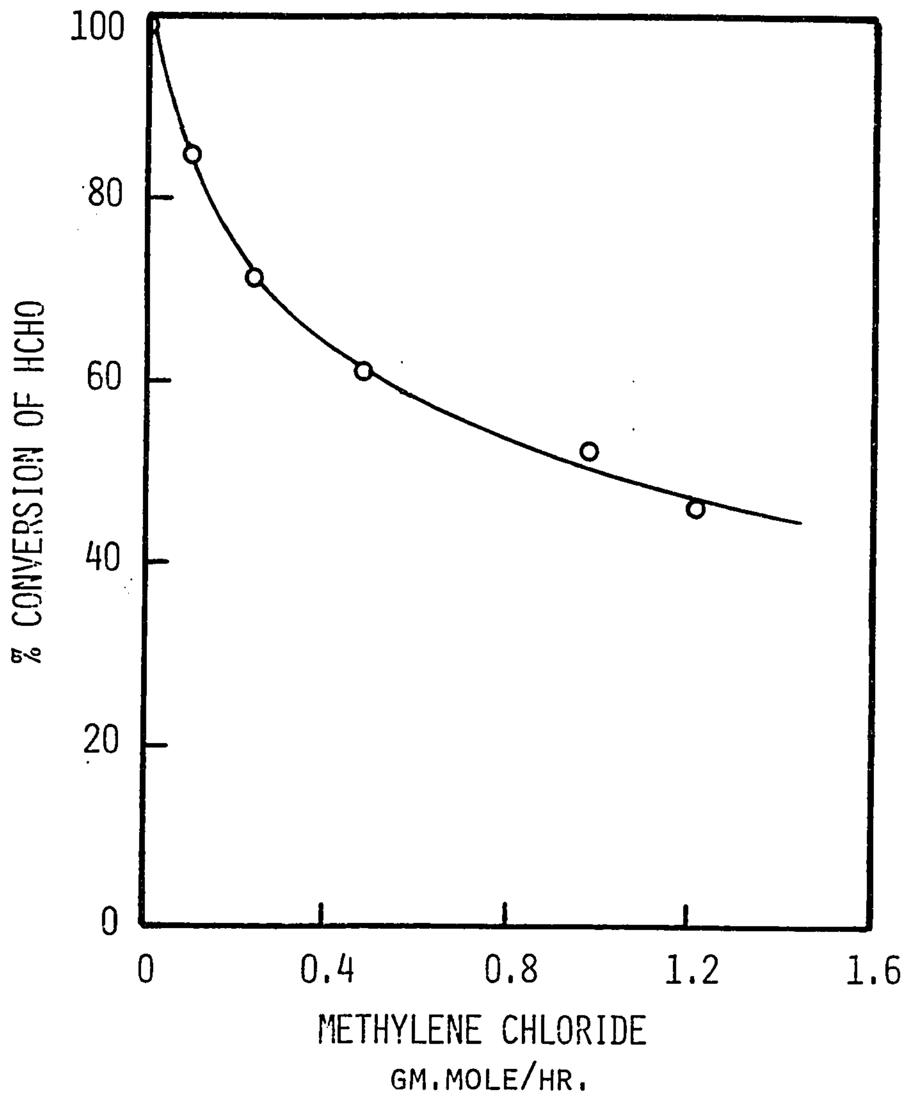
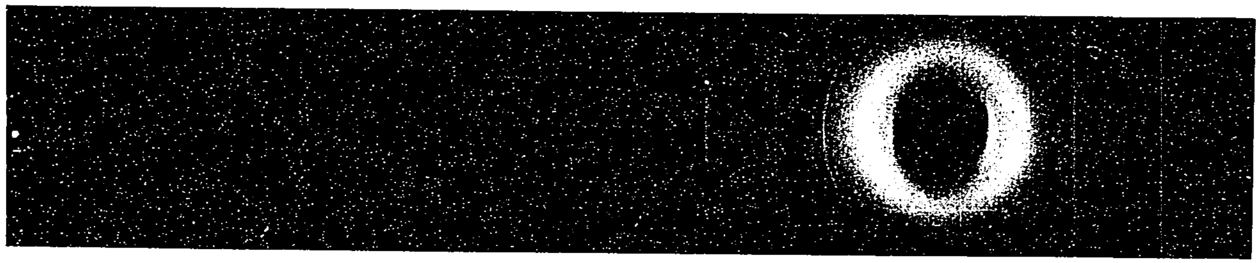


FIGURE 4-10 EFFECT OF METHYLENE CHLORIDE ON OXIDATION OF FORMALDEHYDE AT 480°C, WITH CATALYST WEIGHT = 10.05 GM, HCHO = 0.03264 GM MOLE/HR AND AIR = 1.25 GM MOLE/HR

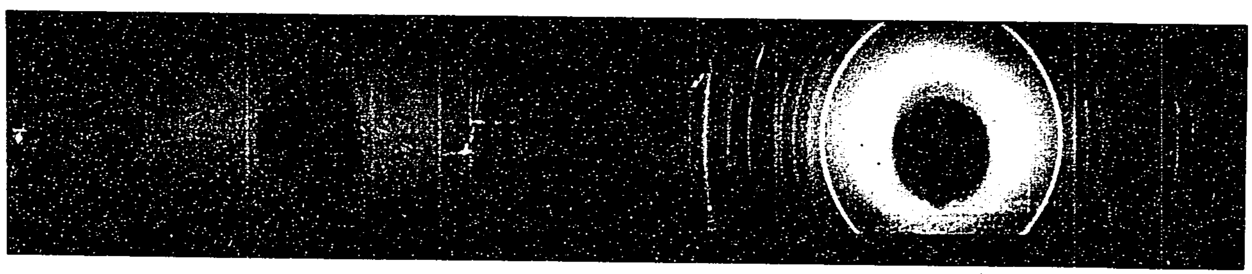
temperature. Formaldehyde completely reacted at 480°C forming carbon dioxide and water. The effect of the amount of chlorine modifier on the conversion of formaldehyde at 480°C is shown in Figure (4-10). The conversion of formaldehyde declined with an increase in chlorine modifier in the feed. This indicated that carbon dioxide originates from the further oxidation of formaldehyde.

The homogeneous oxidation of methane with air in the absence of a catalyst was also investigated during the preliminary study. Up to a reactor temperature of 525°C, no reaction products were detected.

The X-ray diffraction patterns of the catalyst were studied in the Department of Geology, University of Ottawa. Figure (4-11) shows the X-ray diffraction patterns of the 0.5% palladium catalyst supported on alumina. Picture A shows the pattern for the unmodified catalyst and picture B shows the pattern for chlorine modified catalyst. The lines corresponding to palladium metal could not be observed because of its small concentration which may have been in dispersed amorphous phase. However, it was observed that the intensity of the palladium oxide in crystalline phase was higher in the modified catalyst than that in the unmodified catalyst. This indicated that the presence of chlorine modifier favored the formation of palladium oxide.



Picture A - Unmodified Catalyst



Picture B - Modified Catalyst

Figure 4-11 X-Ray Diffraction Patterns of the Catalyst

V. KINETIC ANALYSIS

The determination of the relationship between the reaction rate and the operating variables is an important requirement in the design of a catalytic process. The reaction rate, r, can be expressed as a function of conversion. It is customary to correlate and derive rate expression in terms of partial pressure of the reactants and products based on the well-known Langmuir-Hinshelwood theory[80].

It is believed that a catalyst increases the rate of a reaction by participating in the overall reaction through intermediate reactions occuring at definite points on the catalyst surface. These points are known as active centers or active sites. On this basis different reaction mechanisms and rate equations concerning the catalytic reaction are derived.

(A) Rate Steps in Heterogeneous Catalysis

The overall catalytic process is the result of a series of steps. For porous catalysts, these steps are as follows:

(1) Transfer of the reactants from the bulk-fluid phase to external surface of the catalyst.

(2) Diffusion of the reactant molecules through the catalyst pores into the interior of the porous catalyst.

(3) Adsorption of one or more of the reactants on the catalyst surface.

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

(5) Desorption of the products from the catalyst surface.

(6) Diffusion of the product molecules from the interior of the catalyst to its surface.

(7) Transfer of the products from the external surface of the catalyst to the main fluid stream.

In the electronic theory of catalysis, the electron transfer between the reactants, products and catalyst is involved. In such cases two additional steps should be added to the above list: 3(a) charged adsoprtion of reactants on the catalyst surface (strong chemical bond, either p or n type is formed) and 5(a) discharged desorption of products on the catalyst surface.

The relative importance of these steps can vary greatly and depends on the operating conditions for the system. Each of these steps offer some resistance to the overall process. If all these steps were considered, the resulting rate equations would be very complicated. To simplify the interpretation of experimental data it is desirable to minimize the resistance offered by each of the physical step 1, 2, 6 and 7. These steps can be minimized or accounted for independently as will be described later. The chemical steps 3, 4 and 5, which lend an insight into the nature of catalytic reactions, can not be reduced by altering physical conditions and hence are the important ones to consider. Even inclusion of only these three steps results in equation 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 the rate controlling or rate determining step, while the other two are considered to be at equilibrium.

(B) Sources of Evaluation Errors and Their Elimination

In the survey of engineering kinetics, several experimental errors might be encountered. The reaction model and the resulting rate equation, therefore, might not be exactly correct. Hougen [81] stated five serious sources of error that arise in the evaluation of kinetic models and interpretation of rate data in flow reactions catalysed by solids. These are summarized as follows, arranged in order of decreasing importance:

(1) Variation in catalyst activity.

(2) Use of catalyst particles having effectiveness factor differing appreciably from unity (internal diffusion).

(3) Neglect of external resistances to mass and heat transfer.

(4) Appreciable departure from plug flow.

(5) Neglect of pressure drop due to flow.

Besides these, another source of error, that is, homogeneous reaction and catalyzed reaction by the reactor should also be considered.

In order to derive a true rate equation, the above mentioned factors are either eliminated or minimized with appropriate corrective measures. These are discussed in the following section.

(1) Variation in catalytic activity

In the present study palladium lost activity during first 24 hours when charged fresh into the reactor. This decline of activity was suspected to be caused by the adsorption of water which was produced by the oxidation reaction. However after this initial use of catalyst, the activity of the stabilized catalyst remained fairly constant. This was confirmed by repeating one of the initial runs at different times in the experimental program. The results for the stability of catalyst activity are given in Appendix C (Table A-C-3). In addition, the excellent constancy of syringe pump speed provided a precise supply of chlorine modifier in the feed.

(2) Internal diffusion and effectiveness factor

Most of the catalysts are porous, and 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 reactants into and that of product out of the pores could become an important factor in controlling reaction rate. Depending on whether the mean free path between intermolecular collisions is small or large compared with the pore radius, two kinds of diffusion in pores are possible. These are called (i) molecular diffusion, and (ii) Knudsen diffusion.

(i) <u>Molecular diffusion</u>

It predominates with all catalysts at very high pressures (>100 atm) or at atmospheric pressure with very large pores (>5000 $^{\circ}$A radius). The effect of molecular diffusion in the present study was minimized by using high velocity of gas stream passing through the catalyst bed, and its extent was evaluated by varying the feed rate while the reciprocal of space velocity was kept constant. The results are given in Appendix (F) and plotted in Figure 5-1. The constancy of conversion (negligible deviation from horizontal line) indicates that the molecular diffusion was negligible.

(ii) <u>Knudsen diffusion</u>

The Knudsen diffusivity depends on the molecular velocity and the pore radius, and is independent of pressure. Since the mean free path for gases is of the order of 1000 A$^{\circ}$ at atmospheric pressure, diffusion in micropores of a catalyst will be predominently by the Knudsen mechanism.

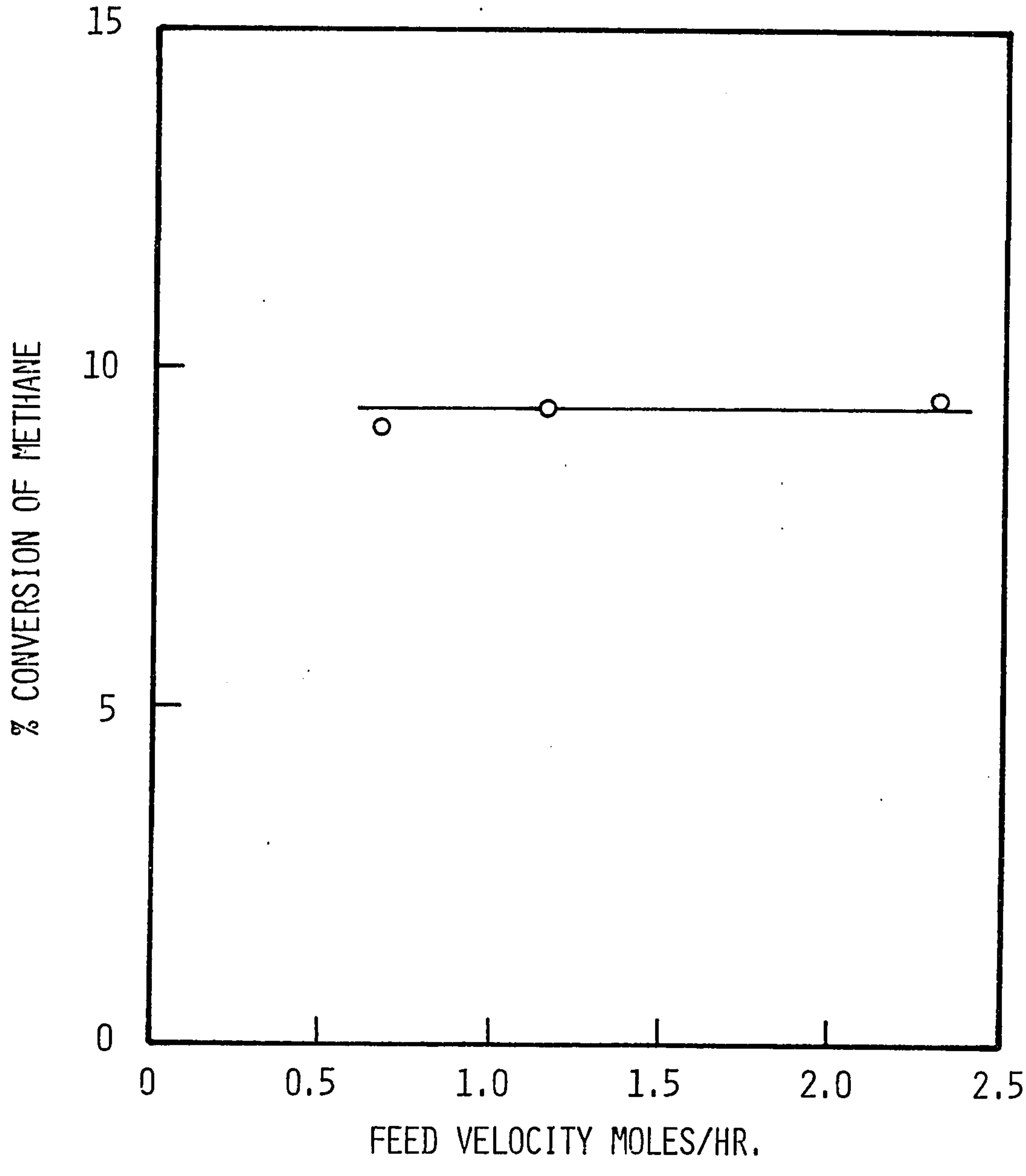


FIGURE 5-1 EFFECT OF FEED VELOCITY ON CONVERSION OF METHANE OVER CHLORINE MODIFIED CATALYST AT 475°C, W/F = 24.00 GM.HR/GM MOLE AND $\bar{R}$ = 3.61

The effective Knudsen diffusivity is given as

$$D_{K,eff} = 19,400 \; \frac{\beta^2}{\tau \; S_g \; \rho_p} \cdot \sqrt{\frac{T}{M}}$$

where β = porosity of catalyst

τ = tortuosity of catalyst

S_g = specific surface area of catalyst

ρ_p = catalyst particle density

T = absolute temperature

M = molecular weight of the gas mixture

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 the same as those at the gross exterior surface.

Although several efforts have been made to correlate effectiveness factor with the physical properties of the system, the success has not been great. Only relatively simple cases have been treated. An estimate of the effectiveness factor for the catalyst used in this study was calculated by using a modified Thiele method [82]. A value of nearly unity was obtained. The detailed calculations are shown in Appendix (F).

A common method of determining the importance of Knudsen diffusion is to examine the effect of decreased catalyst particle size on the reaction rate. If pore diffusion effects are significant, a decreased particle size results in increased reaction rate due to the shorter average pore length in the smaller particles. The catalyst used throughout this study was prepared by crushing the support to a -20 +40 mesh screen fraction. As shown in Figure 5-2, the particle size of the catalyst had no significant effect (negligible deviation from horizontal line) on the conversion rate implying that the Knudsen diffusion effect was not a rate controlling step and hence could be neglected.

(3) <u>External resistance to mass and heat transfer</u>

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

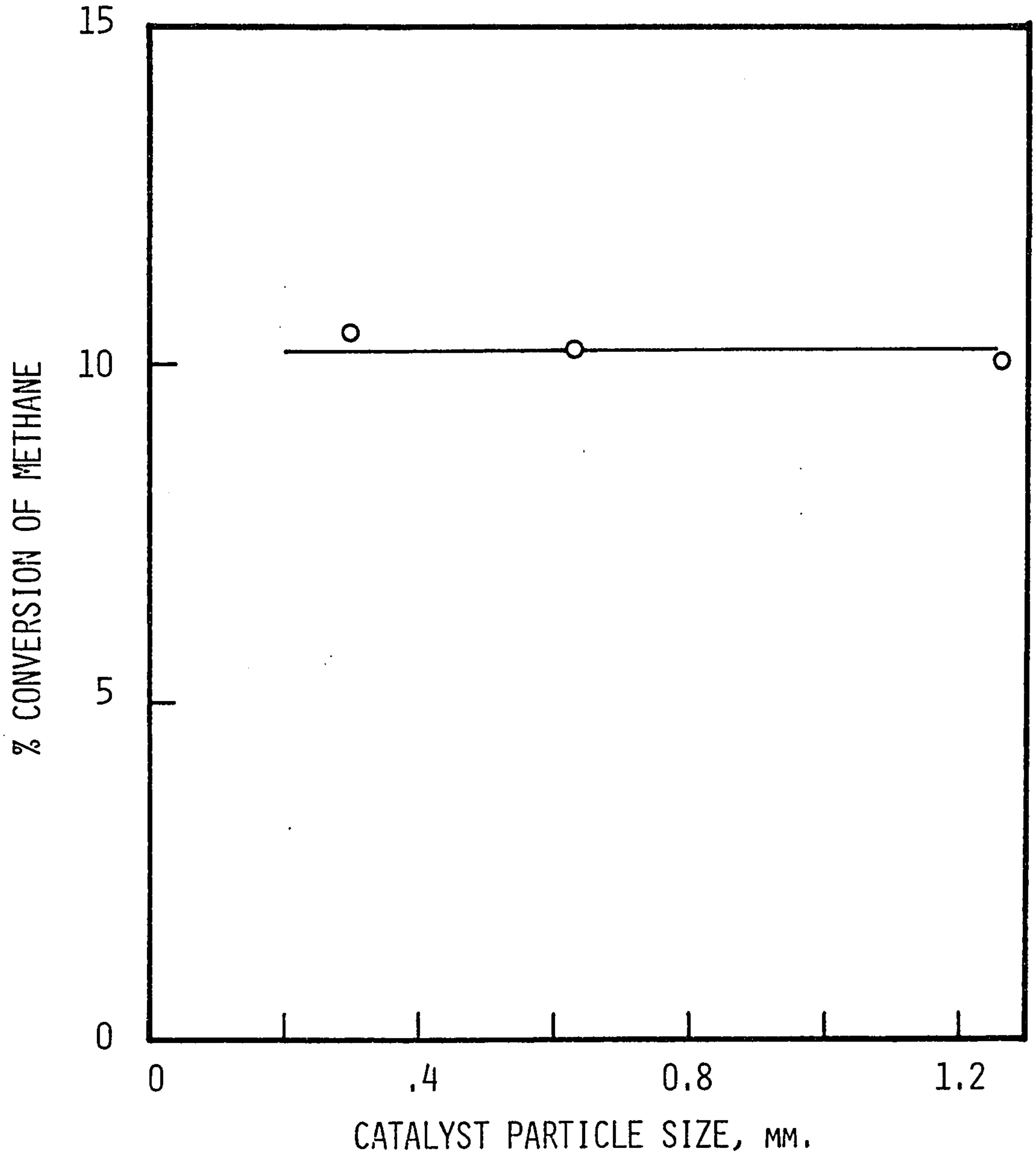


FIGURE 5-2 EFFECT OF CATALYST PARTICLE SIZE ON CONVERSION OVER CHLORINE MODIFIED CATALYST AT 450°C, $\bar{R}$ = 4.18 AND W/F = 36.06 GM.HR/GM MOLE

The rate of mass and heat transfer per unit mass are defined as

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

and

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

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 tranfer coefficient for component A.

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

a_m = external surface area of the catalyst per unit mass.

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

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 can be calculated from the dimensionless Chilton-Colburn (83) j-factors.

$$j_D = \left(\frac{k_G \; P_{f_A}}{G_m}\right) \left(\frac{\mu}{\rho \; D_{AM}}\right)_f^{2/3} \qquad (5\text{-}3)$$

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

where

P_{f_A} = film pressure factor, defined by equation (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 mass velocity of gas based on the total cross-sectional area of reactor

K = thermal conductivity of the gas

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

$$\frac{\mu}{\rho\ D_{AM}} = \text{the dimensionless Schmidt number}$$

and subscript f indicates properties at average condition for the gas film.

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

j_h and j_D can be obtained from Gamson, Thodes and Hougen's[84] equations:

$$j_h = 1.06 \left(\frac{D_p\ G_m}{\mu}\right)^{-0.41} \tag{5-5}$$

$$j_D = 0.09 \left(\frac{D_p\ G_m}{\mu}\right)^{-0.41} \tag{5-6}$$

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

j_h and j_D can be obtained by Wilke and Hougen's [85] equations:

$$j_h = 1.95 \left(\frac{D_p\ G_m}{\mu}\right)^{-0.51} \tag{5-7}$$

$$j_D = 1.82 \left(\frac{D_p\ G_m}{\mu}\right)^{-0.51} \tag{5-8}$$

where

$$\frac{D_p\ G_m}{\mu} = \text{modified Reynolds number}$$

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

π = total pressure

a_p = average surface area per particle

The term P_{f_A}, the film pressure factor for component A which accounts for the bulk flow of the fluid in equation (5-3) for the reaction

$$a\,A + b\,B = r\,R + s\,S \tag{5-9}$$

is defined as

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

where

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

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

Yoshida et al [86] have developed a simple and systematic method for evaluating the drop in pressure and temperature between the bulk-gas stream and the external catalyst particle surface. In their method, the temperature and pressure gradients were determined by using calculated values of the modified Reynolds number and dimensionless Prandtl and Schmidt numbers as follows:

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

and

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

where,

ΔT = drop in temperature across the film

ΔP_A = drop in partial pressure of component A across the gas film

$$Q = \frac{r_{m_A} \; \Delta H_A}{a_m \; \phi \; C_p \; G_m} \tag{5-14}$$

Pr = Prandtl number = $\dfrac{C_P \; \mu}{K}$

$$R = \frac{r_{m_A}}{a_m \; \phi \; G_M} \tag{5-15}$$

Sc = Schmidt numbers = $\dfrac{\mu}{\rho \; D_{AM}}$

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

The j-factors are related to the modified Reynolds numbers $(\frac{G_m}{a_V\ \phi\ \mu})$ 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 Q and ΔT have the dimensions of temperature and all other terms are dimensionless. From the data of many investigators, Yoshida et al. found that the gradients fall in a narrow band on ΔY_A vs. R or ΔT vs. Q plot indicating that the R and Q are the most significant factors in controlling the pressure and temperature gradients respectively.

Both the temperature and partial pressure drop across the gas film are proportional to $r_{m_A}\ D_p^{n+1}\ G_m^{n-1}$. Since n is either 0.51 or 0.41, it would be possible to eliminate the heat and mass transfer resistances effectively by decreasing the particle size and increasing the gas flow rates.

A sample calculation based on the method of Yoshida et al. for estimating the temperature and pressure drop from the bulk-gas stream to the surface of the catalyst is shown in Appendix (E). The highest partial pressure gradient thus calculated was found to be of the order of 0.001 and the temperature at the catalyst surface was calculated to be $1^{o}C$ higher than that of the main gas stream. Hence, these effects sould be neglected.

(4) <u>Appreciable departure from plug flow</u>

For steady and continuous plug flow the relationship between the reciprocal of space velocity, W/F and conversion is obtained by considering an elementary section of reactor containing a mass of catalyst dW in which a conversion dX is produced. Thus

$$F\,dX = r\,d\,W \tag{5-19}$$

where,

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

W = mass of catalyst in the reactor

F = feed rate, moles per unit time

X = conversion, moles per unit mole of feed

Integrating (19)

$$W/F = \int_0^x \frac{dx}{r} \tag{5-20}$$

When deriving equation (5-20), it was assumed that the gases were passing through the catalyst bed under the conditions of plug flow. The flow distribution in the packed beds were investigated by Smith et al. [87]. The flow patterns in the packed beds were affected by packing depth, the position of flow, the packing size and the tube size. According to their experimental results, the divergence from a flat profile in the plug flow increased as the packing size increased and the pipe size decreased. It was reported that the deviation from a uniform velocity profile is not very significant if the ratio of tube to catalyst pellet diameter is greater than 30. The ratio of reactor to catalyst diameter used in the present study was about 22. In addition, the use of a stainless steel porous plate, inserted at the entrance of the reactor to support the catalyst, helped in breaking any velocity pattern of the incoming gases. It therefore appeared that no appreciable error would be caused by assuming a plug flow even though it rarely exists. The results shown in Figure (5-1) where conversion of methane was not affected by the feed velocity, indicate that the assumptions of plug flow is quite reasonable.

(5) Neglect of pressure drop due to flow

In order to eliminate several sources of error discussed in this section, increasing the gas flow rate seems to be a promising approach. However, this would cause increase in the pressure drop through the catalyst bed. The difference between inlet and outlet pressure of the catalytic bed would therefore become very large. The basis of arithmetic or logarithmic mean of inlet and outlet pressures might not be correct in determining the partial pressures of the components.

The pressure drop through a packed bed is given by Ergun's equation [88] for either laminar or turbulent flow. In the present investigation the pressure drop through the catalyst bed was measured experimentally. The maximum pressure drop never exceeded 10 mm Hg. Therefore the outlet pressure of the reactor (810 mm Hg) was considered to be the reactor pressure.

(6) Homogeneous reaction and catalyzed reaction by the reactor wall

According to Bone's work [23], the induction period of methane-oxygen mixture at 420^{o}C and 1 atm is estimated to be 10-30 min. In an ordinary flow type reactor, a retention time of 10 minutes cannot be held. In this study the retention time in the heated section was less than two seconds. The wall effects and homogeneous reaction therefore may be considered negligible. This was further examined experimentally by carrying out blank tests before a series of runs was made. The air-methane mixture in varying proportion (2.4 - 5.3) with and without methylene chloride additive was passed through the empty reactor heated upto 525°C. No detectable amount of methane was oxidized under these experimental conditions.

(C) Correlation of Rate Equations

Among the various steps in heterogeneous catalytic reactions as described in section (A), the eliminates due to the physical steps (1, 2, 6 and 7) were either eliminated or minimized by appropriate selection of the physical operating conditions. The remaining chemical steps (3, 4 and 5) were examined in detail in order to determine which one of these offered a comparatively large resistance to the overall reaction. For each of the three chemical steps, namely adsorption of reactants, surface reaction and desorption of products, several mechanisms can be postulated depending on whether one or both of the reactants are adsorbed on the catalyst surface.

(1) Adsorption Isotherm

A large amount of evidence has now been accumulated which show that the catalysis by solid surfaces involves a specific chemical interaction between the surface and the reacting gas molecules, which must become adsorbed to the surface before reaction can occur [89]. In postulating a reaction mechanism for a catalytic reaction and thereby obtaining a rate expression, adsorption of at least one of the reactants is considered a necessity. A knowledge of adsorption isotherm is therefore essential. The amount of gas adsorbed after the equilibrium is established depends on various factors, including the nature of the surface and the adsorbate, the temperature and the pressure. An adsorption isotherm shows how the amount adsorbed depends upon the equilibrium pressure of the gas at constant temperature. A number of such isotherms have been suggested[90], some being empirical and others obtained theoretically. Of the theoretical equations the simplest is that due to Langmuir. It is based on the following assumptions [91]: (i) the adsorbed entities are attached on the surface of the adsorbent at definite, localized sites, (ii) each site can accomodate one and only one adsorbed entity, and (iii) the energy of the adsorbed entity is the same at all sites on the surface and is independent of the presence or absence of other adsorbed entities at the neighbouring sites.

From either a kinetic or statistical approach [92] the Langmuir isotherm can be derived as follows:

$$\theta_A = \frac{K_A \, P_A}{1 + \Sigma \, K_I \, P_I} \tag{5-21}$$

where

θ_A = the fraction of the catalyst surface covered by A

K_A = the equilibrium adsorption constant of A

P_A = the partial pressure of component A in the gas phase

K_I = the equilibrium adsorption constant of component I (including A)

P_I = the partial pressure of component I (including A) in the gas phase.

(2) Langmuir-Hinshelwood Mechanism

The derivation of the Hougen-Watson type rate equations is based on the Langmuir-Hinshelwood mechanism for catalysis and on the assumptions that only one of the reaction steps is the rate-determining step, and that the remaining are at equilibrium. According to Langmuir-Hinshelwood mechanism, the reactant or reactants are considered to be in adsorptive equilibrium with the surface, and reaction then involves the adsorbed molecules. If there is a single reactant, the surface process is a simple unimolecular change; if there are two reactants, A and B, these must be adsorbed on neighbouring surface sites for reaction to occur, and the probability that this occurs is proportional to the individual concentrations of adsorbed A and adsorbed B molecules. The Langmuir-Hinshelwood mechanism for a reaction between A and B may be formulated as follows:

$$\underset{\text{(adsorption)}}{A + B + -\overset{|}{S}- \rightleftarrows} \begin{array}{c} A \quad B \\ |\quad\ | \\ -S-S- \end{array} \rightleftarrows \begin{array}{c} A - B \\ |\quad\ | \\ -S-S- \end{array} \text{(activated complex)}$$

$$\begin{array}{c} \downarrow\uparrow \\ \begin{array}{c} |\quad\ | \\ -S-S- \end{array} + \text{products} \end{array}$$

The quantitative treatment of reactions occuring by this mechanism therefore involved obtaining an expression, using the adsorption isotherms, for the concentrations of reactant molecules on the surface, and then expressing the rate of reaction in terms of the concentration of gaseous reactants.

Another type of mechanism for surface reactions is known as Langmuir-Rideal mechanism. According to this mechanism the reaction occurs between a gas molecule and an adsorbed molecule, so that only one of the reactants has to be adsorbed. However, on the whole Langmuir-Rideal mechanisms do not appear to be as common as the Langmuir-Hinshelwood ones. In the present analysis both cases have been considered. The general development of one rate equation, the selection of a rate determining step, and correlation of the kinetic data taken in this study are described below.

As an example, a rate equation for a bimolecular reaction $A + B \rightleftarrows R + S$ is developed, since a reaction of this type has been investigated in the present study. The rate-controlling step of the reaction is assumed to be the surface reaction between adsorbed A and adsorbed B to give R and S. The forward reaction rate is proportional to the concentration of adjacently adsorbed AB pairs, C_{AB}

$$r_f = k\ C_{AB} \tag{5-22}$$

where

r_f = forward reaction rate, moles of product formed per unit time per unit mass of catalyst.

k = reaction velocity constant for surface reaction.

C_{AB} = molal concentration of adjacent A and B molecules per unit mass of catalyst.

If the surface concentration of adsorbed A is C_A and each adsorbed A is surrounded by S active sites including vacant and occupied, and coverage of sites by B is θ_B, the surface concentration of AB pairs would be

$$C_{AB} = C_A \cdot S \cdot \theta_B = C_A \cdot \frac{C_B}{L} = \frac{S}{L} C_A \cdot C_B \qquad (5\text{-}23)$$

where

L = total molal active sites per unit mass of catalyst.

Substituting equation (5-23) into equation (5-22) gives

$$r_f = \frac{kS}{L} C_A \cdot C_B = k\ S\ L \cdot \theta_A \cdot \theta_B \qquad (5\text{-}24)$$

θ_A and θ_B can be obtained by applying (5-21) to a bimolecular reaction and thus r_f will be given by

$$r_f = \frac{k\ S\ L\ K_A\ K_B\ P_A\ P_B}{(1 + K_A\ P_A + K_B\ P_B + K_R\ P_R + K_S\ P_S)^2} \qquad (5\text{-}25)$$

If the reverse reaction is included, the net forward reaction rate will become

$$r = \frac{k\ S\ L\ K_A\ K_B\ (P_A\ P_B - P_R\ P_S/K)}{(1 + K_A\ P_A + K_B\ P_B + K_R\ P_R + K_S\ P_S)^2} \tag{5-26}$$

where K = thermodynamic equilibrium constant for the overall reaction.

The initial rate, defined as the rate at zero conversion of this reaction is

$$r_o = \frac{k\ S\ L\ K_A\ K_B\ P_A\ P_B}{(1 + K_A\ P_A + K_B\ P_B)^2} \tag{5-27}$$

Rate equations similar to equation (5-26) have been systematically developed and compiled by Hougen and Watson [93] and Yang and Hougen [94] for various reaction mechanisms and with different rate controlling steps.

Following the Hougen-Watson approach, the possible reaction mechanisms for the catalytic air oxidation of methane to formaldehyde can be derived. While testing the validity of an equation for a particular mechanism the following assumptions were made: (i) the term $(P_F)(P_W)/K$ was omitted since the oxidation process is thermodynamically irreversible ($K > 10$) and (ii) the adsorption term for nitrogen

(K_N P_N) was not included in the rate equation because the chemisorption of nitrogen on palladium catalyst is considered to be negligible. The rate equations derived using Hougen-Watson approach are listed in Table (1). The subscripts M, F and O used in these equations represent methane, formaldehyde and oxygen respectively.

(3) Mechanisms Based on Two Types of Active Sites

In the case of adsorption of a mixture of gases, Langmuir isotherm predicts that the addition of one gas to a second will always decrease the amount adsorbed of the latter. However, several cases of adsorption are known in which the reverse behavior is observed that is, where the second gas increases the adsorption of the first gas [95]. Some observations were also found on chemisorption [96] in which marked enhancement of adsorption of a gas from mixture over that of the pure gas at the same partial pressure was reported. Adsorption of this kind corresponds mathematically to having a negative adsorption coefficient in the denominator of the extended Langmuir equation. For example, when the adsorption of A is increased in presence of B, the amount of A adsorbed is given by an expression of the form

TABLE 1

RATE EQUATIONS DERIVED USING HOUGEN-WATSON METHOD

(ONE TYPE OF ACTIVE SITE)

No.	Rate Controlling Step	Mechanism	Rate Equation
1	Adsorption of Methane	Surface Reaction Between Adsorbed Methane and Oxygen	$r = \frac{k_s P_M}{1 + K_O P_O + K_F P_F}$
2	Adsorption of Methane	Surface Reaction Between Adsorbed Methane and O_2 in Gas Phase	$r = \frac{k_s P_M}{1 + K_F P_F}$
3	Adsorption of Oxygen	Surface Reaction Between Adsorbed Methane and Oxygen	$r = \frac{k_s P_O}{1 + K_M P_M + K_F P_F}$
4	Adsorption of Oxygen	Surface Reaction Between Adsorbed Oxygen and Methane in Gas Phase	$r = \frac{k_s P_O}{1 + K_F P_F}$
5	Desorption of Formaldehyde	Surface Reaction Between Adsorbed Methane and Oxygen	$r = \frac{K'_d \left(\frac{K P_M P_O}{P_W} - P_F\right)}{1 + K_M P_M + K_O P_O + K K_F \frac{P_F P_O}{P_W}}$

No.	Rate Controlling Step	Mechanism	Rate Equation
6	Desorption of formaldehyde	Surface reaction between adsorbed methane and oxygen in gas phase	$r = \dfrac{K'_d \left(\dfrac{K P_M P_O}{P_W} - P_F\right)}{1 + K_M P_M + K K_F \dfrac{P_M P_O}{P_W}}$
7	Desorption of formaldehyde	Surface reaction between adsorbed oxygen and methane in gas phase	$r = \dfrac{K'_d \left(\dfrac{K P_M P_O}{P_W} - P_F\right)}{1 + K_O P_O + K K_F \dfrac{P_M P_O}{P_W}}$
8	Surface reaction	Surface reaction between adsorbed methane and oxygen	$r = \dfrac{k_s K_M P_M K_O P_O}{(1 + K_M P_M + K_O P_O + K_F P_F)^2}$
9	Surface reaction	Surface reaction between adsorbed methane and oxygen in gas phase	$r = \dfrac{k_s K_M P_M P_O}{1 + K_M P_M + K_F P_F}$
10	Surface reaction	Surface reaction between adsorbed oxygen and methane in gas phase	$r = \dfrac{k_s K_O P_O P_M}{1 + K_O P_O + K_F P_F}$

$$\theta_A = \frac{K_A \; P_A}{1 + K_A \; P_A - K_B \; P_B} \tag{5-28}$$

In the usual application of Langmuir-Hinshelwood approach this kind of experimental results will be considered physically impossible and any reaction mechanism which leads to a negative adsorption coefficient will be discarded.

In order to overcome this difficulty and to explain the catalyst modification, a concept of two types of active sites is introduced.

Let

$$\theta = \theta^{(I)} + \theta^{(II)} \tag{5-29}$$

then for component A

$$\theta_A = \theta_A^{(I)} + \theta_A^{(II)}$$

$$= \frac{K_A^{(I)} P_A}{1 + \Sigma \; K_I^{(I)} \; P_I} + \frac{K_A^{(II)} P_A}{1 + \Sigma \; K_I^{(II)} \; P_I} \tag{5-30}$$

and

$$\theta_B = \theta_B^{(I)} + \theta_B^{(II)}$$

$$= \frac{K_B^{(I)} P_B}{1 + \Sigma \; K_I^{(I)} P_I} + \frac{K_B^{(II)} P_B}{1 + \Sigma \; K_I^{(II)} P_I} \tag{5-31}$$

The superscript (I) and (II) refer to the type (I) and type (II) active sites respectively. With the above approach, the difficulty of having negative adsorption coefficient in the Langmuir isotherm is resolved since the adsorption is not restricted to competition for active sites.

This concept may be applied to the catalytic oxidation of hydrocarbons where free electrons and positive holes on the catalyst surface can be treated as the two different types of active sites. Further if the hydrocarbon and oxygen molecules are selectively adsorbed, the equilibrium fraction covered by oxygen and methane hydrocarbons would be

$$\theta_O = \frac{K_O \; P_O}{1 + K_O \; P_O} \tag{5-32}$$

and

$$\theta_M = \frac{K_M \; P_M}{1 + K_M \; P_M + K_F \; P_F} \tag{5-33}$$

Methane and formaldehyde are positively charged adsorbed and competive for active sites (holes) and oxygen is negatively charged adsorbed.

As an illustration of this approach, a rate equation is developed for a bimolecular reaction $A + B \rightleftarrows R + S$ and the rate-controlling step of the reaction is assumed to be the irreversible charged adsorption of A and B, while surface reaction and discharged desorption of products are at equilibrium.

$$A + \square \xrightarrow{k_1} A^+ — \odot \qquad (5\text{-}34)$$

$$B + \odot \xrightarrow{k_2} B^- — \square \qquad (5\text{-}35)$$

Where $\square$ and $\odot$ represent positive holes and free electrons on the catalyst surface respectively.

The rate of process given by equation (5-34) is

$$r_1 = k_1 P_A \theta_{\square} \qquad (5\text{-}36)$$

and the rate of process given by equation (5-35) is

$$r_2 = k_2 P_B \theta_{\odot} \qquad (5\text{-}37)$$

Where $\theta_{\square}$ and $\theta_{\circ}$ represent the fraction of active sites being positive holes and free electron respectively.

At steady state $r_1 = r_2 = r$ (5-38)

also,

$$\theta_{\odot} = 1 - \theta_{\square} \qquad (5\text{-}39)$$

from equations (5-36), (5-37), (5-38) and (5-39).

$$\theta_{\square} = \frac{k_2\ P_B}{k_1\ P_A + k_2\ P_B} \tag{5-40}$$

and

$$r = k_1\ P_A\ \theta_{\square} = \frac{k_1\ P_A}{1 + (\frac{k_1}{k_2})\ (\frac{P_A}{P_B})} \tag{5-41}$$

Reaction rate equations based on the two types of active sites approach are listed in Table (2).

(4) <u>Correlation of Initial Rate Data</u>

The initial rate of reaction is defined as the rate of reaction at zero time or at zero space velocity in the case of flow reactor. Its value is determined by plotting the experimental data (conversion versus W/F) and finding the slope of the curve when space velocity (W/F) equals zero. The initial rate approach is frequently used to simplify the kinetic studies. Yang and Hougen [94] have considered a number of reactions and mechanisms and have examined the results when adsorption, desorption or surface reaction controls the rate. They have presented tables for the estimation of the most plausible reaction mechanisms

TABLE 2

RATE EQUATIONS DERIVED FROM MODIFIED LANGMUIR-HINSHELWOOD MECHANISM

(TWO TYPES OF ACTIVE SITES)

No.	Rate Controlling Step	Mechanism	Rate Equation
11	Surface Reaction	Surface reaction between charged adsorbed methane and oxygen	$r = \frac{k_s K_M P_M}{1 + K_M P_M + K_F P_F} \cdot \frac{K_O P_O}{1 + K_O P_O}$
12	Irreversible charged adsorption of oxygen and methane	Surface reaction between charged adsorbed methane and oxygen	$r = \frac{K_M P_M}{1 + (\frac{K_M}{K_O})(\frac{P_M}{P_O})}$
13	Irreversible charged adsorption of oxygen and methane	Surface reaction between charged adsorbed methane and oxygen, oxygen is dissociated	$r = \frac{K_M P_M}{1 + (\frac{K_M}{K_O})(\frac{P_M}{P_O^{\frac{1}{2}}})}$

from the shape of rate curves when plotted against such variables as pressure, feed composition, temperature or conversion. Using this method, it is possible to reduce the number of reaction mechanisms and further 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 pressures of the products are neglected. However, a 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 at x = 0 i.e. $[dx \mid d(W/F)]\ x = 0$, from the equations which fitted experimental data (x Vs. W/F) for various air: methane ratios in the feed. The initial rates, thus obtained, are plotted against the partial pressure of methane in the feed as shown in Figure 5.3 . The values for initial rates at various feed ratios and temperatures are given in Appendix G . The shape of rate curves were compared with the corresponding charts of Yang and Hougen [94] and it was concluded that desorption of product was definitely not rate controlling. Mechanisms 5, 6 and 7 in Table (1) were therefore discarded.

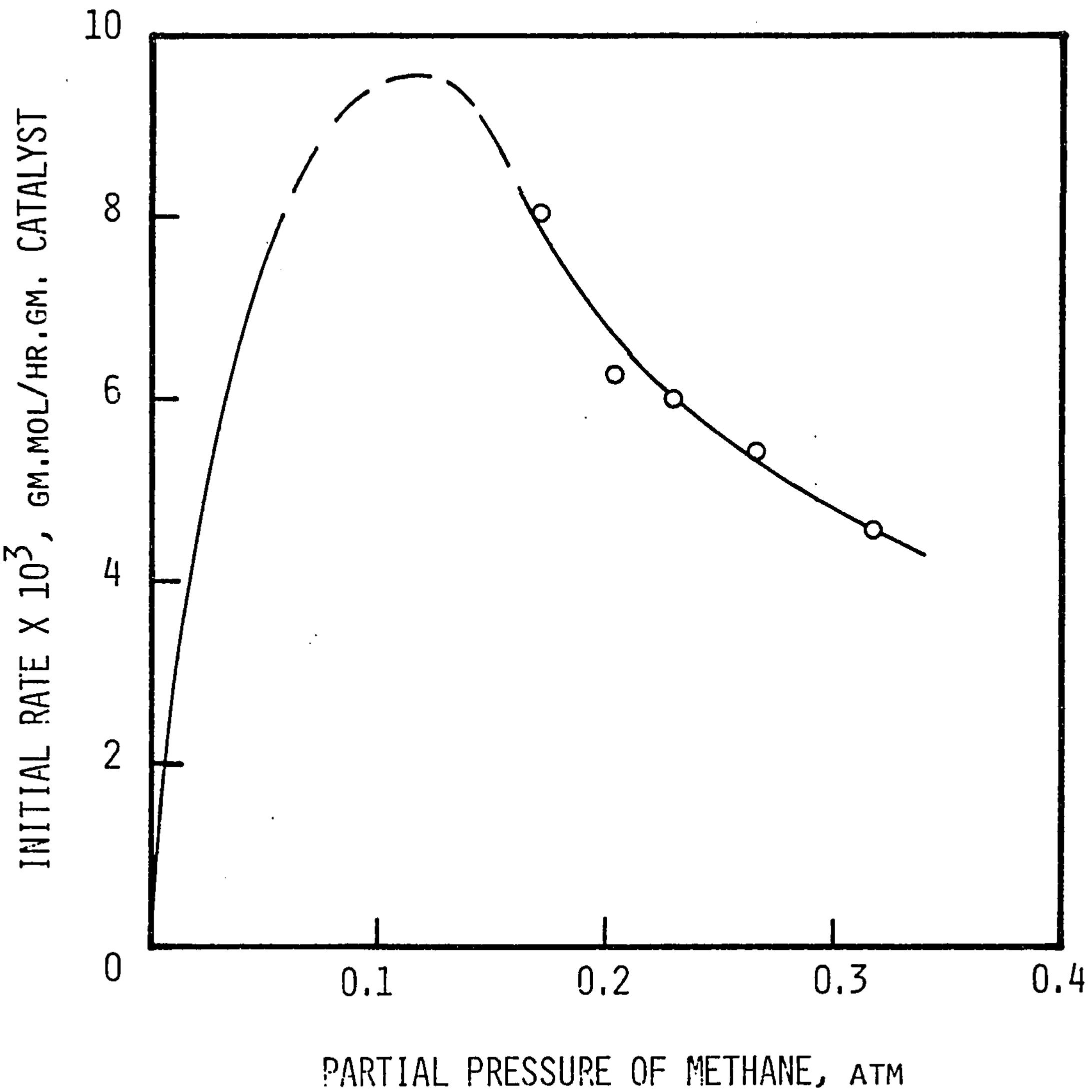


FIGURE 5-3 INITIAL REACTION RATES VERSUS PARTIAL PRESSURE OF METHANE IN FEED AT 450°C

(5) Correlation of Conversion Data

In several studies [18,31,41,51,65] on the oxidation of methane, it has been postulated that the total oxidation product carbon dioxide comes mainly from the consecutive oxidation of formaldehyde which is an intermediate product. The results of Cullis et al [71] for the oxidation of methane on palladium catalyst and the experimental results in the present study on the oxidation of formaldehyde in presence of halogen additive are also in conformity with consecutive reaction shceme for methane oxidation. On the basis that the oxidation of methane with air over a palladium catalyst is a consecutive reaction, all the components of the reaction can be expressed in terms of the conversion of methane (X). In the following steps:

$$\text{Step I :} \quad CH_4 + O_2 \rightleftarrows HCHO + H_2O \tag{5-42}$$

$$\text{Step II:} \quad HCHO + O_2 \rightleftarrows CO_2 + H_2O \tag{5-43}$$

let, X = moles of methane reacted per hour by reaction (5-42)/ moles of methane fed per hour

Z = moles of formaldehyde reacted per hour by reaction (5-43) /moles of methane fed per hour

Y = moles of formaldehyde produced per hour from the overall reaction/moles of methane fed per hour

$= X - Z$

or $$Z = X - Y \tag{5-44}$$

Values of Z and X for different feed ratios at various temperatures (Table A-C-1 in Appendix C) were plotted as show in the figures 5.4 to 5.8. From these plots, the relationship between Z and X was obtained in the following form:

$$Z = m\,X \tag{5-45}$$

The values of m for different temperatures are given in Table (3).

Table 3

Temperature ^{o}C	390	420	450	480	510
m	0.579	0.579	0.605	0.670	0.780

The partial pressure of each component was expressed as described below:

Let

oN_M = moles of methane in the feed

oN_O = moles of oxygen in the feed

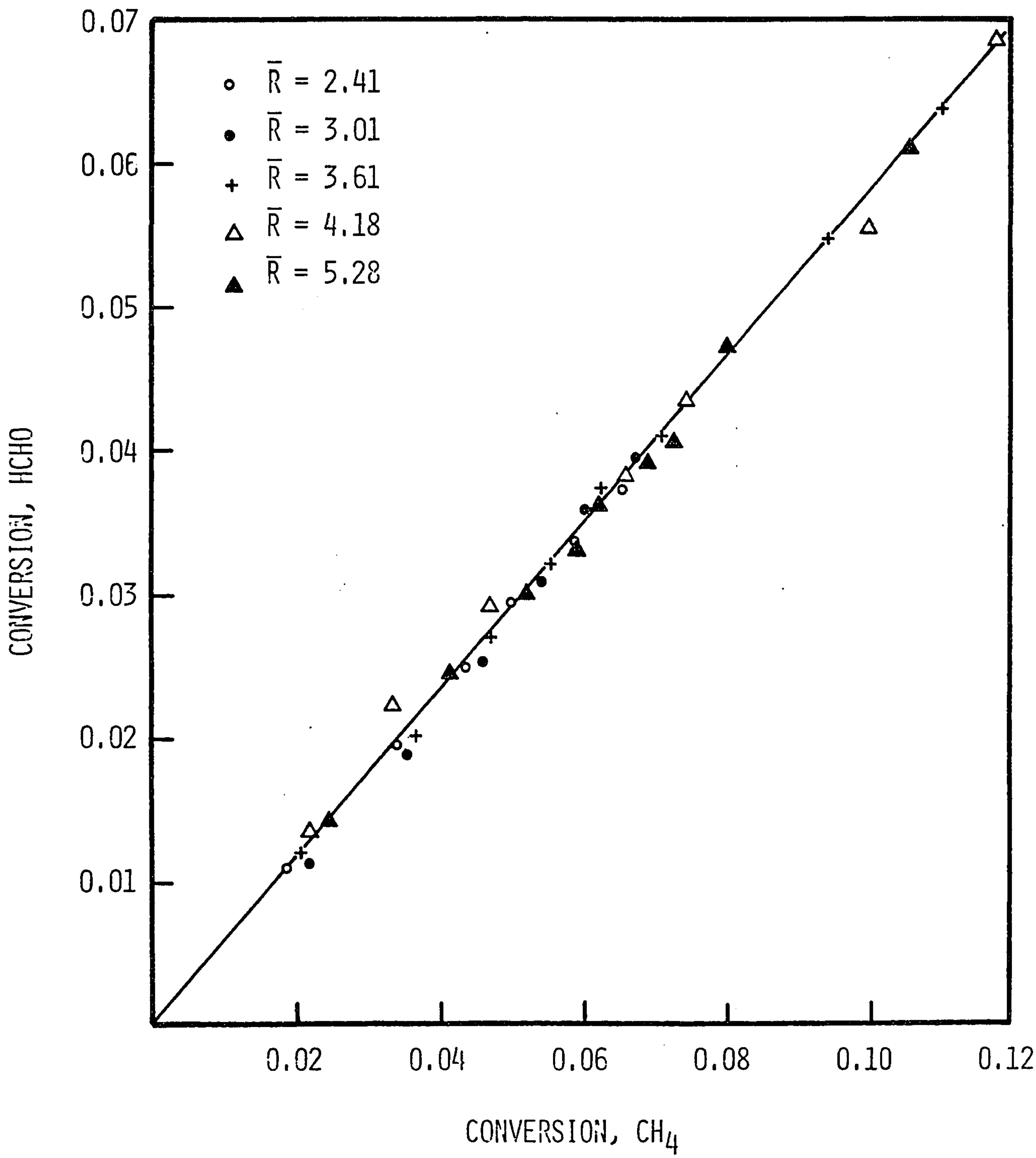


FIGURE 5-4 CONVERSION OF HCHO BY STEP II VERSUS CONVERSION OF CH_4 BY STEP I AT 390°C

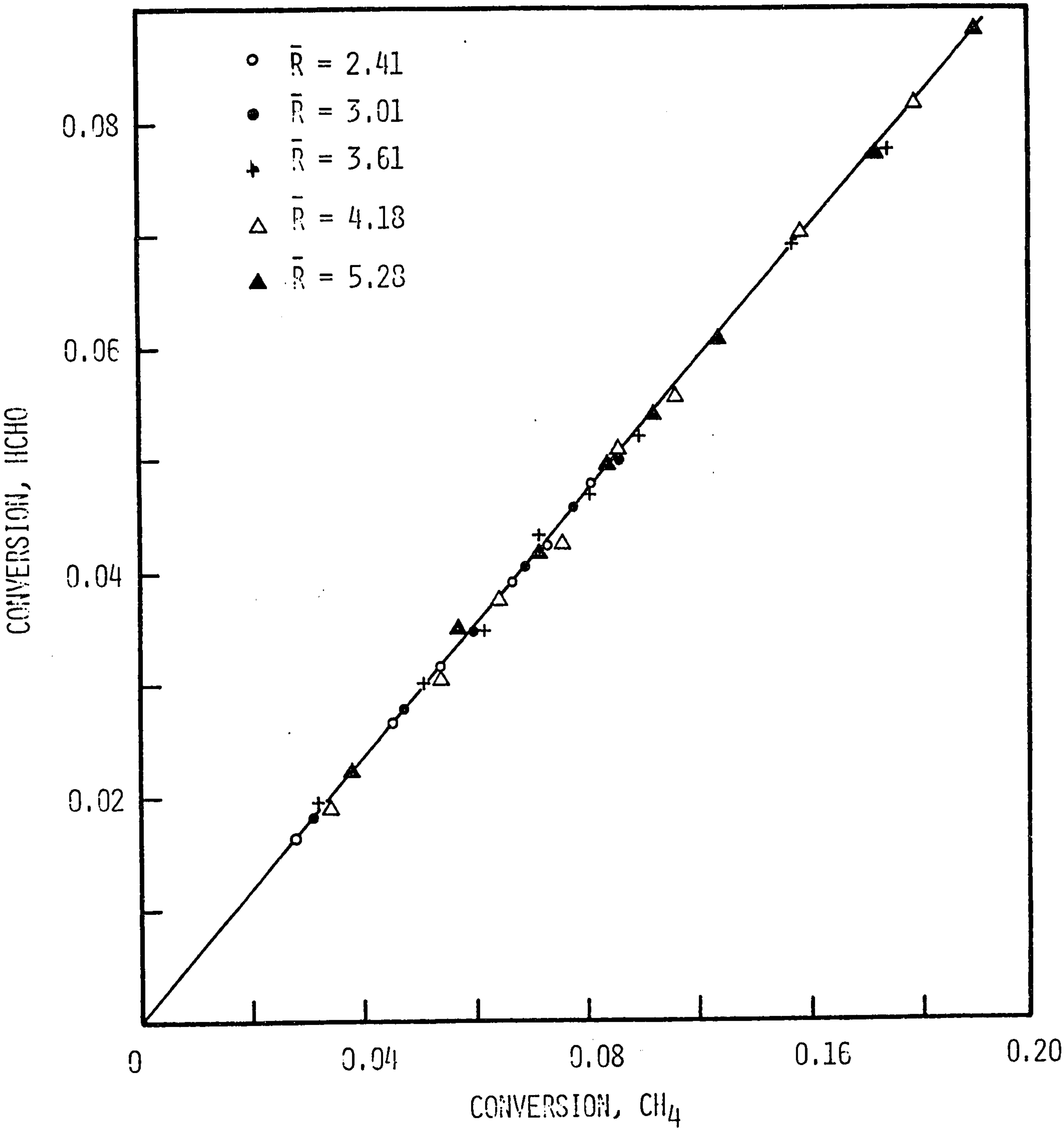


FIGURE 5-5 CONVERSION OF HCHO BY STEP II VERSUS CONVERSION OF CH_4 BY STEP I AT 420°C

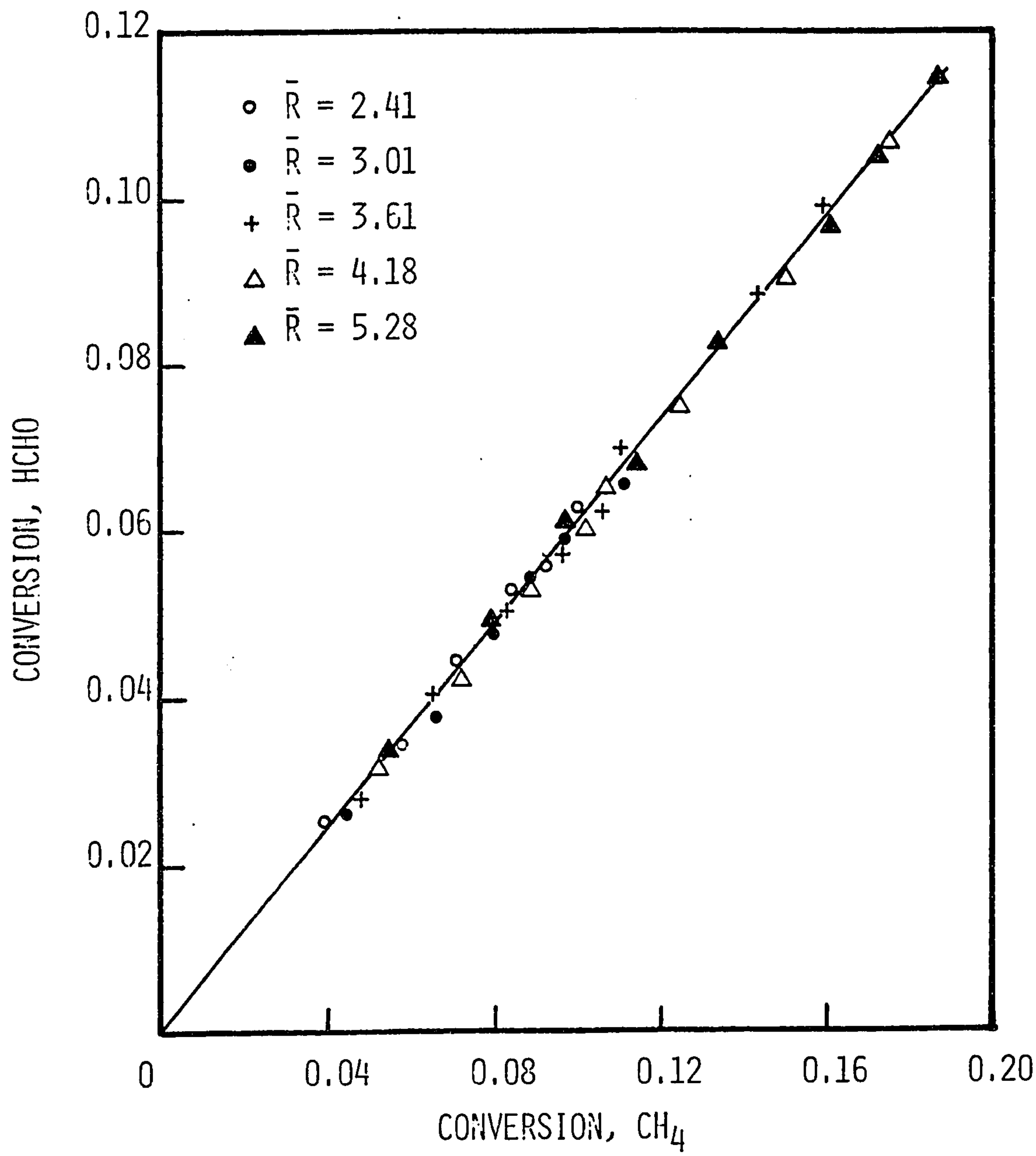


FIGURE 5-6 CONVERSION OF HCHO BY STEP II VERSUS CONVERSION OF CH_4 BY STEP I AT 450°C

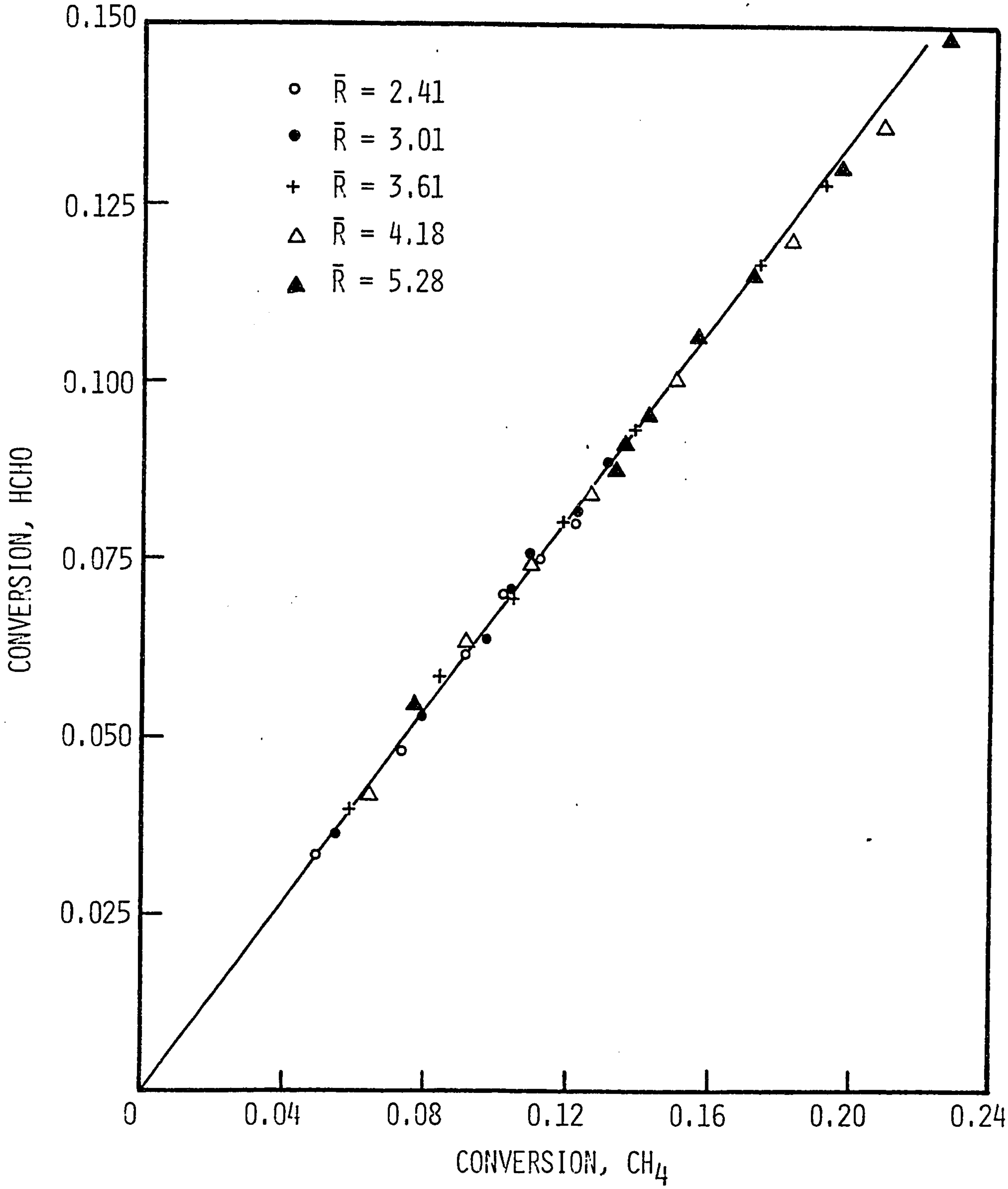


FIGURE 5-7 CONVERSION OF HCHO BY STEP II VERSUS CONVERSION OF CH_4 BY STEP I AT 480°C

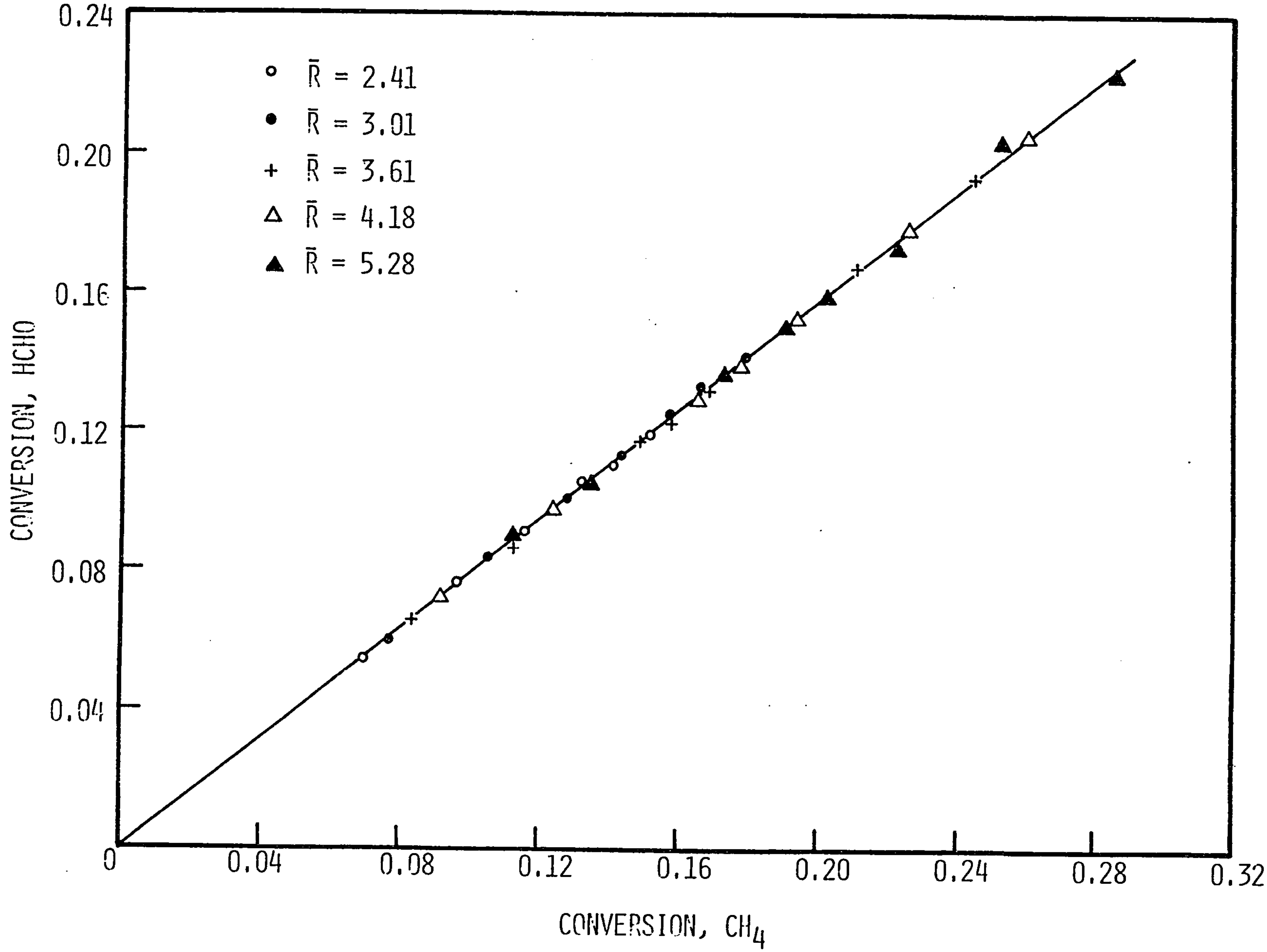


FIGURE 5-8 CONVERSION OF HCHO BY STEP II VERSUS CONVERSION OF CH_4 BY STEP I AT 510°C

Then, for any conversion, X

$$N_M = \text{moles of methane in the product}$$
$$= oN_M\ (1 - X)$$
$$N_F = \text{moles of formaldehyde in the product}$$
$$= oN_M\ (X - Z) = oN_M\ (1 - m)\ X$$
$$N_W = \text{moles of water in the product}$$
$$= oN_M\ (X + Z) = oN_M\ (1 + m)\ X$$
$$N_C = \text{moles of carbon dioxide in the product}$$
$$= oN_M\ Z = oN_M\ m\ X$$
$$N_O = \text{moles of oxygen in the product}$$
$$= oN_O - oN_M\ (X + Z) = oN_O - oN_M\ (1 + m)\ X$$
$$N_N = \text{moles of nitrogen in the product}$$
$$= \text{moles of nitrogen in the feed} = oN_N$$

Further the following relations were assumed to simplify some of the bulky mathematical groups:

$$oN_M \cdot (P_T/oN_T) = a \qquad (5\text{-}46)$$

$$(1 - m)\ oN_M \cdot (P_T/oN_T) = b \qquad (5\text{-}47)$$

$$m\ oN_M \cdot (P_T/oN_T) = c \qquad (5\text{-}48)$$

$$oN_O \cdot (P_T/oN_T) = d \qquad (5\text{-}49)$$

$$(1 + m)\ oN_M \cdot (P_T/oN_T) = e \qquad (5\text{-}50)$$

Where oN_T = total number of moles in the feed

and P_T = reaction pressure (810 mm Hg in the present case)

The partial pressure of each component in the rate equation can be expressed in terms of conversion. Thus for any conversion, X;

$$P_M = a\ (1 - X) \tag{5-51}$$

$$P_O = d - e\ X \tag{5-52}$$

$$P_F = b\ X \tag{5-53}$$

$$P_W = e\ X \tag{5-54}$$

$$P_C = c\ X \tag{5-55}$$

The values of partial pressure in terms of conversion were substituted in the rate equations and the equations were integrated. These integrated rate equations of the possible mechanisms (no.1-4 and 8-13 in tables 1 & 2) are given in table 4.

A non-linear regression technique, developed by Marquart [97] which is based on the least square method, was used to test the validity of these integrated rate equations. A fortran program, "Least-Square Estimation of Nonlinear Parameters" using above method was made available through the Computer Science Department. Equations which gave negative coefficients were rejected. It was found that

TABLE 4

INTEGRATED RATE EQUATIONS

MECHANISM	
1	$W/F = \left(\frac{1}{k_s}\right) \frac{K_O\ (e-d) - K_F b - 1}{a} \ln\ (1-x) + \frac{K_O e - K_F b}{a}\ x$
2	$W/F = \left(\frac{-1}{k_s}\right) \frac{(1 + K_F b)}{a} \ln\ (1-x) + \frac{K_F b}{a}\ x$
3	$W/F = \left(\frac{1}{k_s}\right) \frac{(K_M a - K_F b)}{e}\ x - \frac{(e + K_M a\ (e-d) + K_F b\ d)}{e^2} \ln\ (1-ex/d)$
4	$W/F = \left(\frac{-1}{k_s}\right) \frac{(e + K_F b\ d)}{e^2} \ln\ (1-ex/d) + \frac{K_F b}{e}\ x$
8	$W/F = \left(\frac{1}{K_O k_s}\right) \left(\frac{K_M a}{e} - \frac{2K_F b}{e} + \frac{K_F^2\ b^2}{K_M\ a\ e}\right) x + \frac{K_F^2\ b^2}{e^2} \ln\ (1-x)$ $- \left(\frac{K_M a\ (e-d)}{e^2} + \frac{K_F^2\ b^2\ d^2}{K_M a\ e^2 (e-d)} - \frac{2K_F b\ d}{e^2}\right) \ln(1-ex/d)$

...CONTINUATION...

MECHANISM

9 $$W/F = \left(\frac{1}{k_s}\right) \frac{1 + K_F b}{K_M a(e-d)} \ln (1-x) - \left(\frac{1 + K_F b}{K_M a(e-d)} + \frac{1}{e} - \frac{K_F b}{K_M a\ e}\right) \ln(1-ex/d)$$

10 $$W/F = \left(\frac{1}{k_s}\right) \left(\frac{1 + K_F b}{K_O a(e-d)} - \frac{1}{a}\right) \ln(1-x) - \left(\frac{1+K_F b}{K_O a(e-d)} - \frac{K_M b}{K_O a\ e}\right) \ln(1-ex/d)$$

11 $$W/F = \left(\frac{1}{k_s}\right) \left(\frac{1}{K_O K_M a(e-d)} + \frac{K_F b\ d}{K_O K_M a\ e(d-e)} - \frac{1}{K_O e}\right) \ln(1-ex/d) + \left(1 - \frac{K_F b}{K_M a}\right) x$$

$$- \left(\frac{1}{K_O K_M a(d-e)} + \frac{1}{K_M a} + \frac{K_F b}{K_O K_M a(d-e)} + \frac{K_F b}{K_M a}\right) \ln(1-x)$$

12 $$W/F = \frac{1}{K_M a} \ln(1-x) - \frac{1}{K_O e} \ln(1-ex/d)$$

13 $$W/F = - \frac{1}{K_M a} \ln(1-x) - \frac{1}{K_O e} \sqrt{d-ex} + \frac{1}{K_O e} \sqrt{d}$$

the mechanism no.11 in Table (4) fitted the experimental data best. The rate equation based on this mechanism can be expressed as

$$r = \frac{k_S\ K_M\ P_M}{1 + K_M\ P_M + K_F\ P_F} \cdot \frac{K_O\ P_O}{1 + K_O\ P_O} \qquad (5\text{-}56)$$

The values of k_S, K_M, K_F and K_O between temperatures 390 and 510°C are listed below in Table (5).

TABLE 5

Temperature Effect on Rate Constant and Equilibrium Constants

Temperature °C	$^{\circ}$K	1/T x 10^3	k_S x 10^1	K_M x 10^{-3}	K_F x 10^{-2}	K_O
390	663	1.508	0.1303	5.1282	2.2664	1.1453
420	693	1.443	0.2780	3.7974	1.2034	0.8300
450	723	1.383	0.4171	3.1138	0.7728	0.7884
480	753	1.328	0.7007	1.9122	0.4528	0.5754
510	783	1.277	1.1254	1.5312	0.3090	0.5072

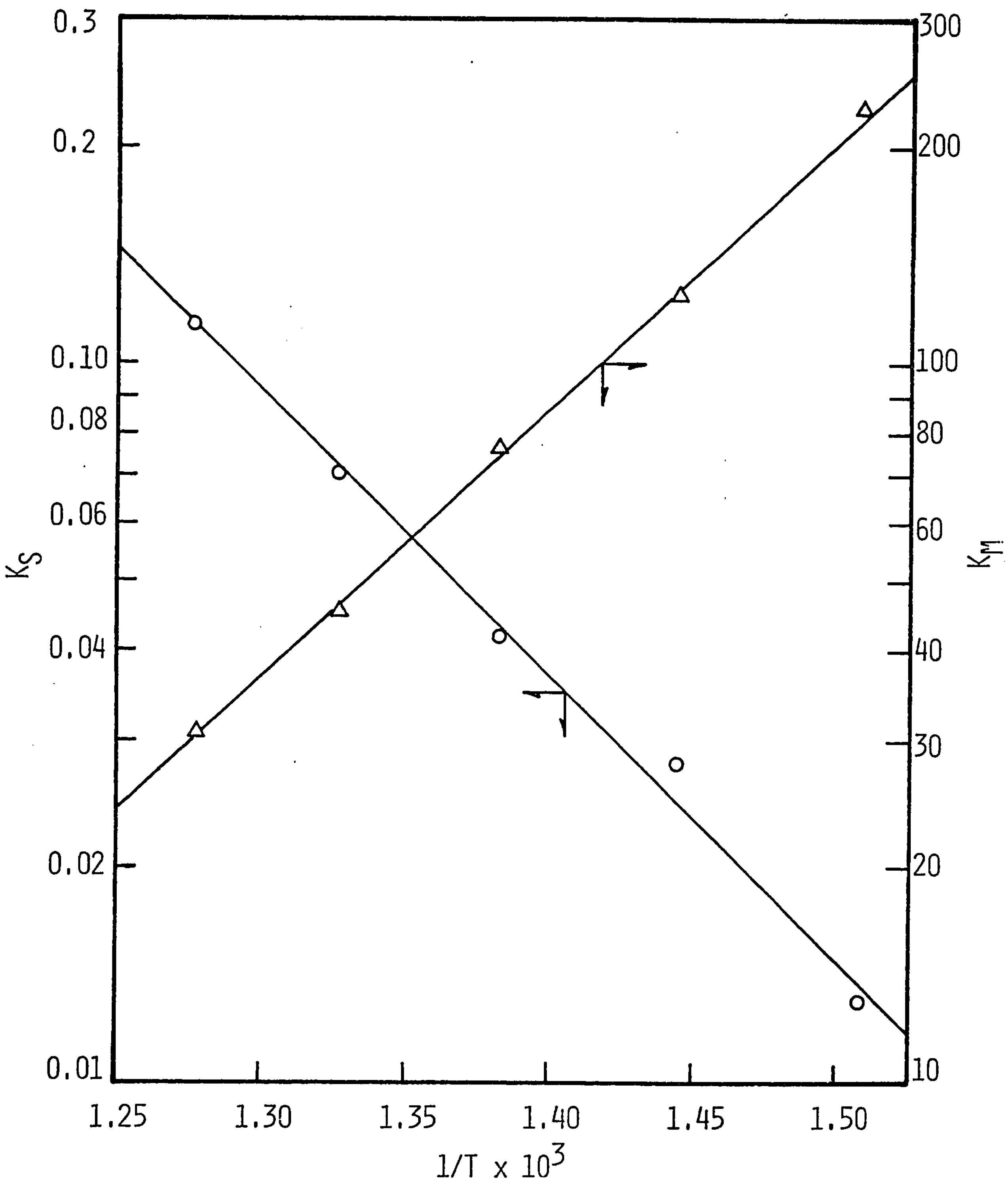


FIGURE 5-9 EFFECT OF TEMPERATURE ON K_S AND K_M

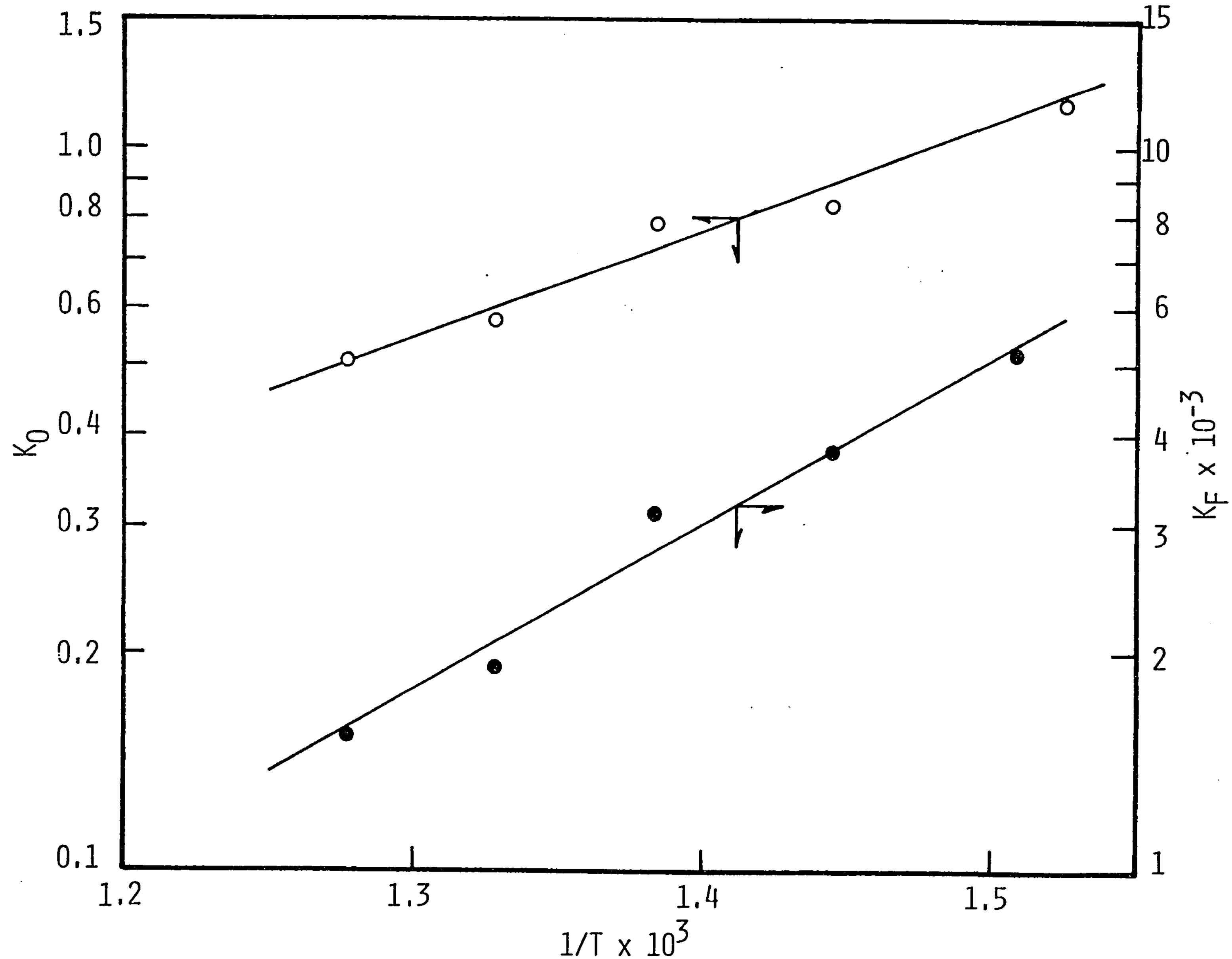


FIGURE 5-10 EFFECT OF TEMPERATURE ON K_F AND K_0

(6) Temperature Effect on Rate Constants

The temperature dependence of k_s, K_M, K_F and K_O are shown in Figures 5-9 & 5-10. The mathematical expressions describing the temperature dependence of k_s, K_M, K_F and K_O are given in the following equations:

$$\ln k_s = -3.946 \times 10^3 (\frac{1}{T}) + 4.092 \tag{5-57}$$

$$\ln K_M = 2.326 \times 10^3 (\frac{1}{T}) + 0.222 \tag{5-58}$$

$$\ln K_F = 3.715 \times 10^3 (\frac{1}{T}) - 3.264 \tag{5-59}$$

$$\ln K_O = 1.502 \times 10^3 (\frac{1}{T}) - 2.217 \tag{5-60}$$

These constants appear to follow the Arrhenius behavior in the temperature range studied.

The values of K's obtained from Table (5) were substituted into equation 11 of Table (4) to determine the W/F versus X relation. Figures (5-11 to 5-21) show the comparison between experimental and predicted values of this relation. The solid lines in these figures refer to the curves predicted by substituting the estimated values of K's in the relations; whereas the circles represent the experimental data. Deviations between calculated and experimental values of W/F have been given in Appendix H. The maximum deviation was 15.7%.

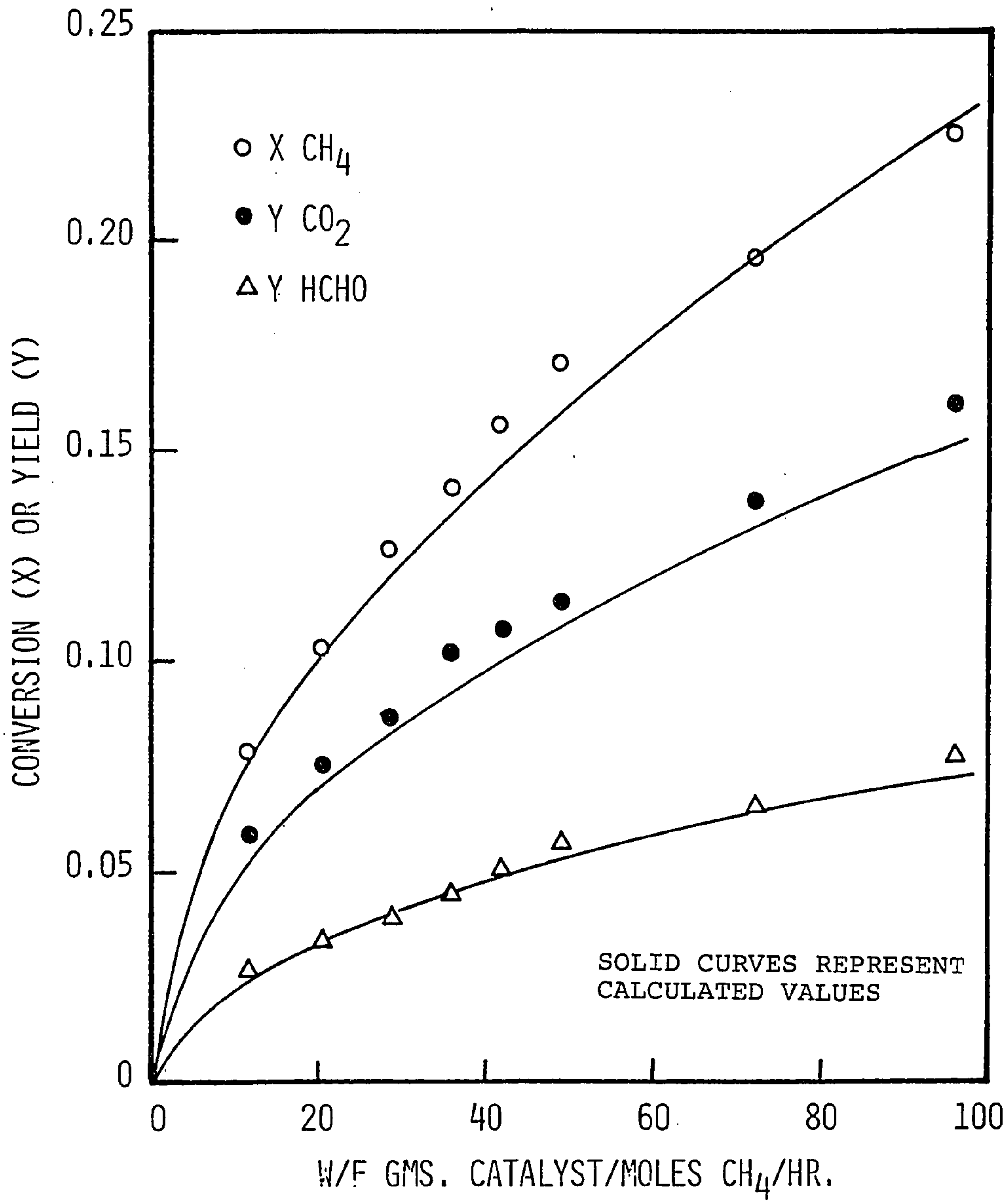


FIGURE 5-11 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 480°C AND $\bar{R}$ = 5.28

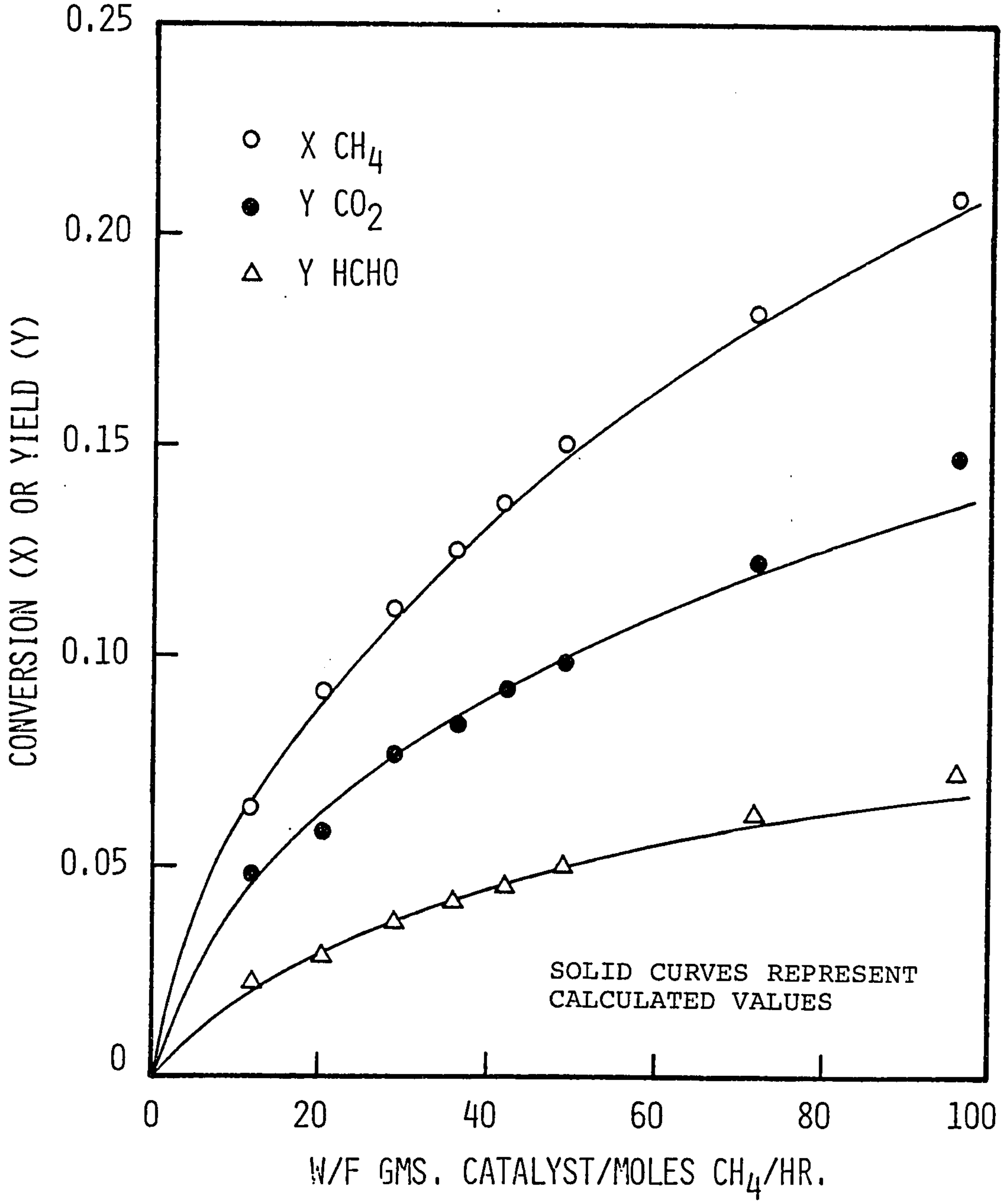


FIGURE 5-12 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 480°C AND $\bar{R}$ = 4.18

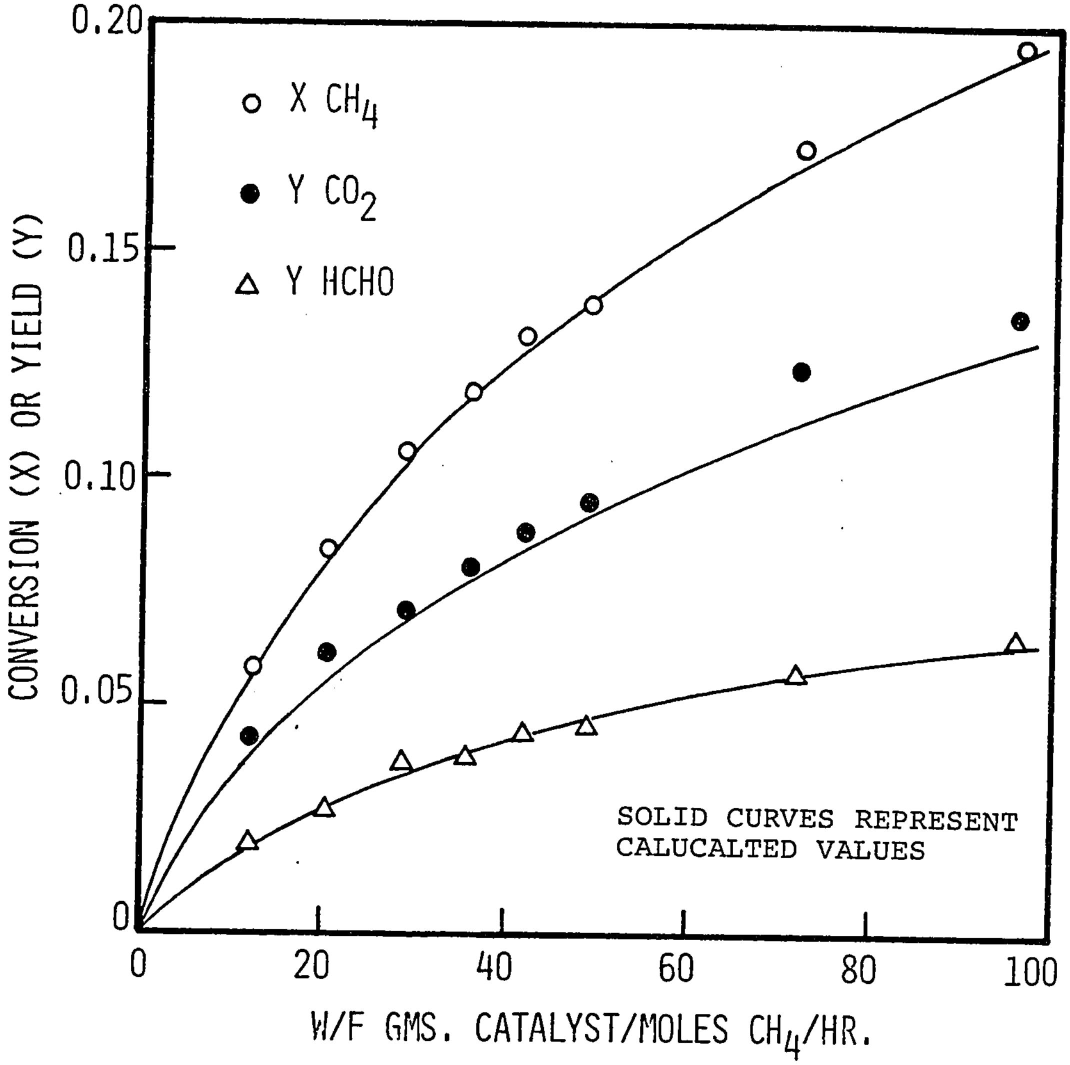


FIGURE 5-13 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 480°C AND $\bar{R}$ = 3.61

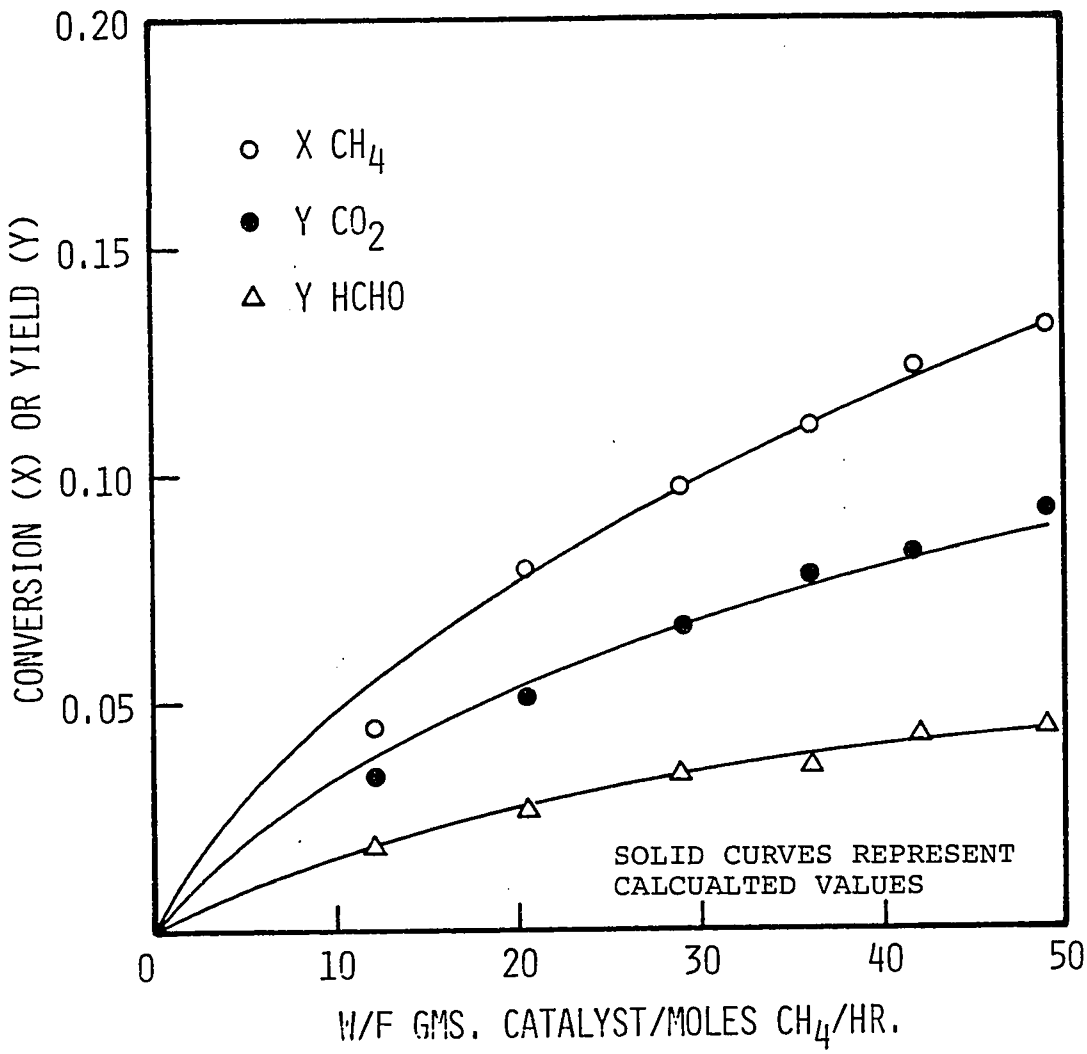


FIGURE 5-14 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 480°C AND $\bar{R}$ = 3.01

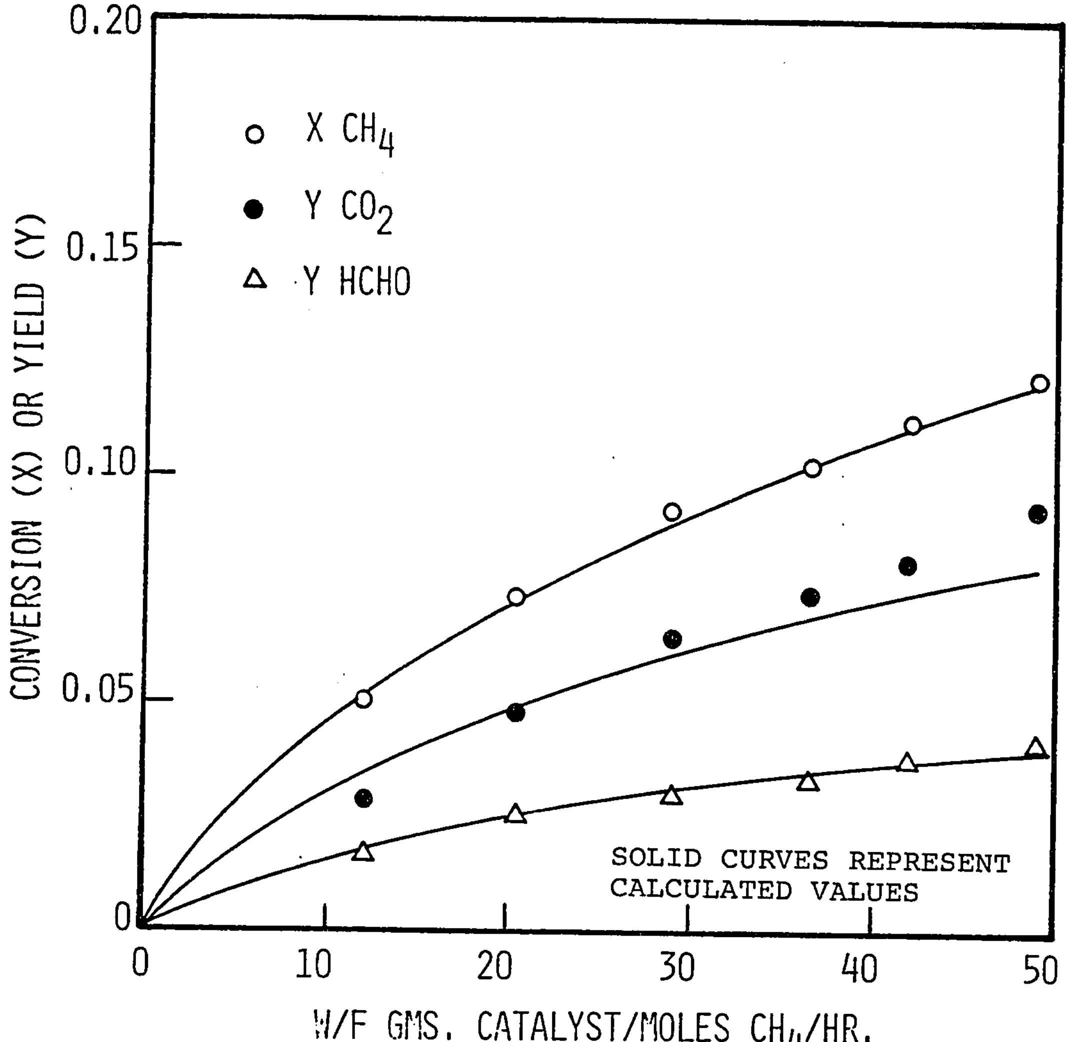


FIGURE 5-15 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 480°C AND $\bar{R}$ = 2.41

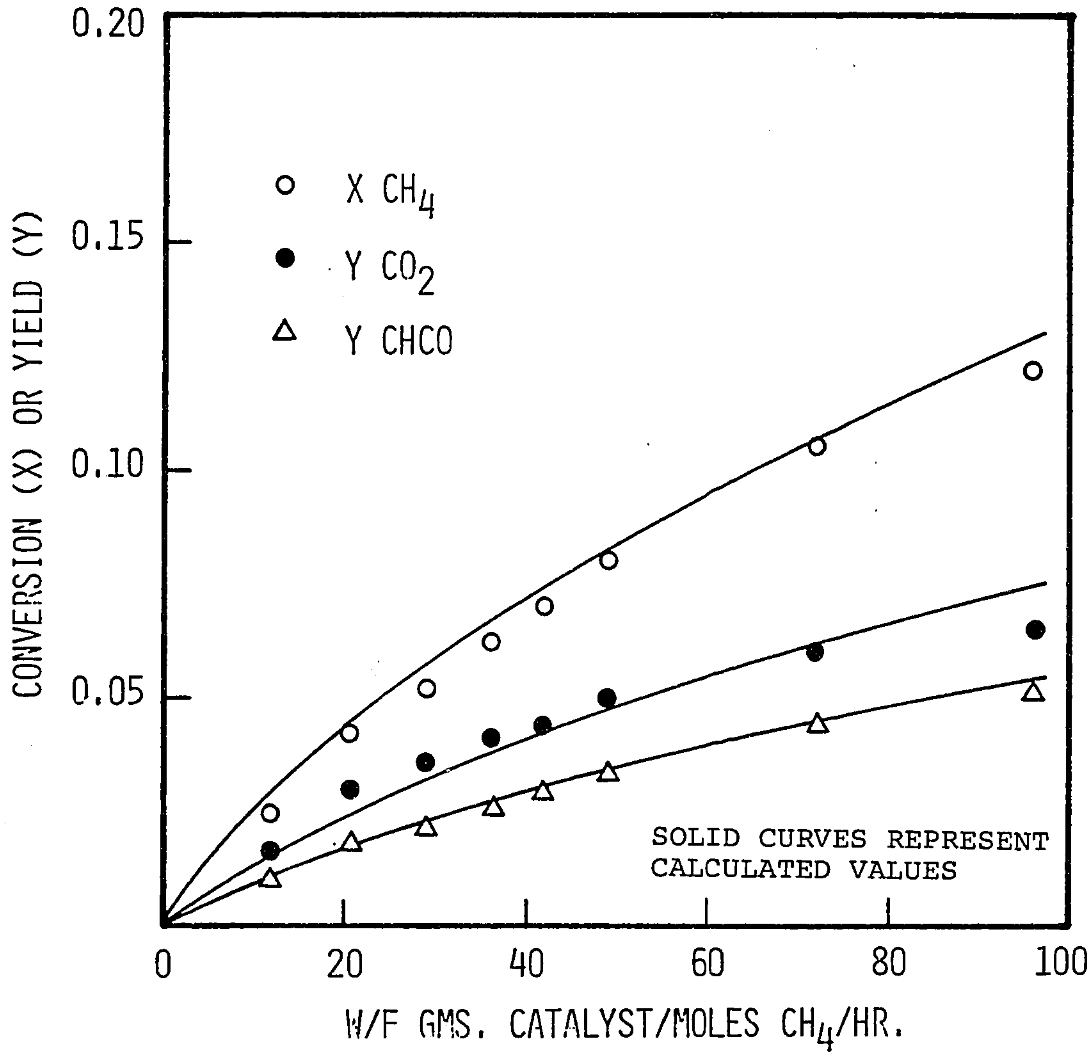


FIGURE 5-16 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 390°C AND $\bar{R}$ = 5.28

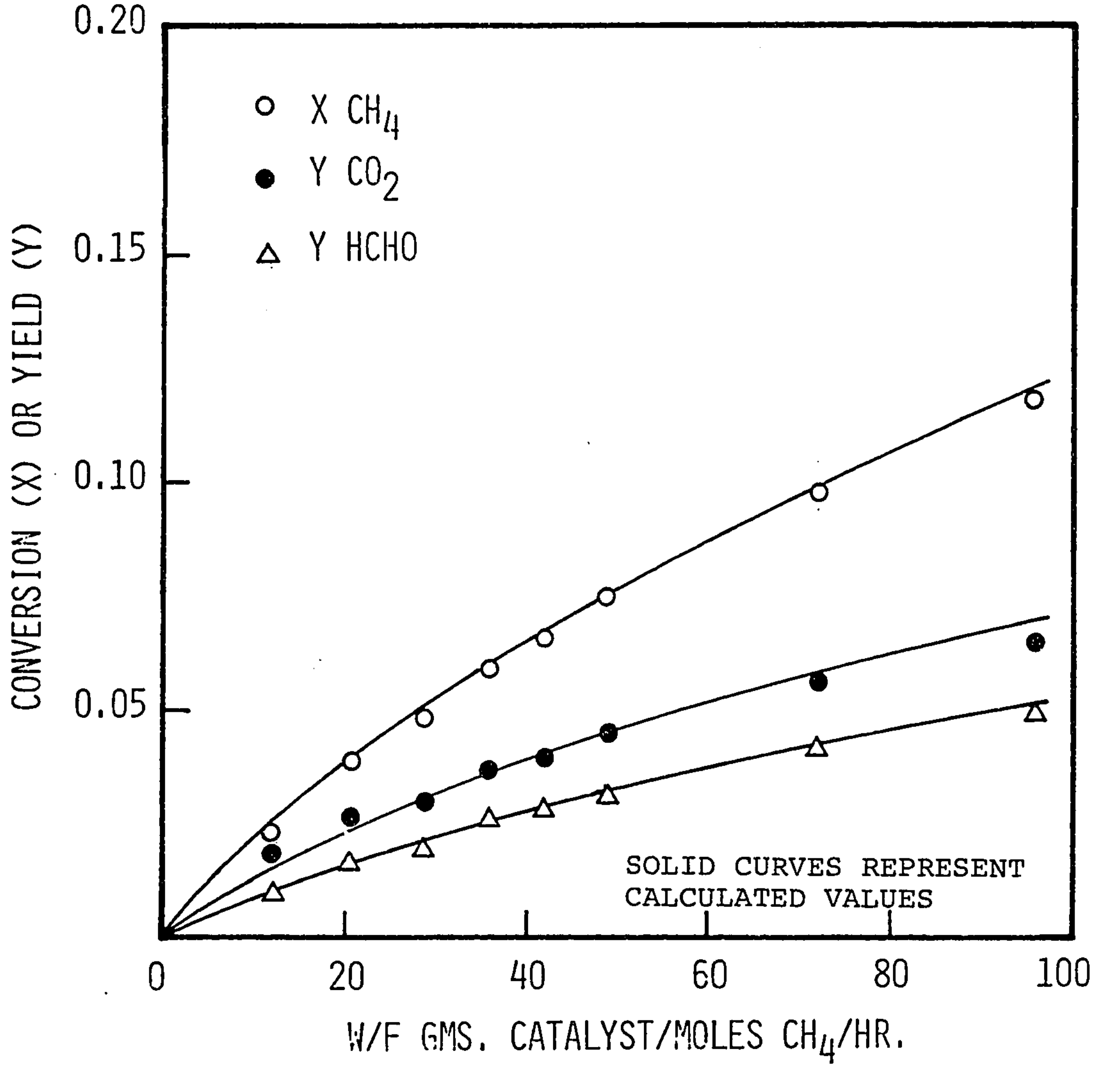


FIGURE 5-17 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 390°C AND $\bar{R}$ = 4.18

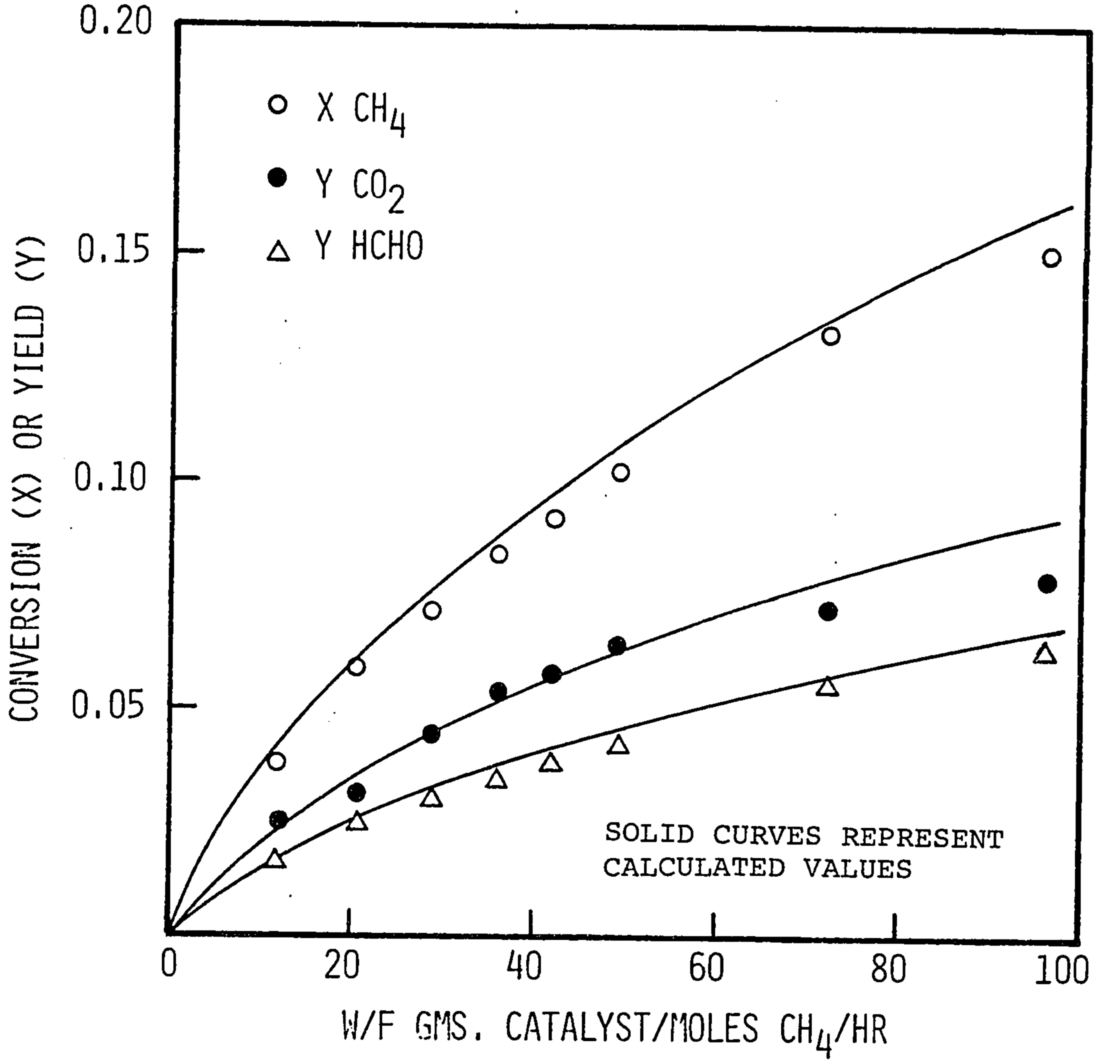


FIGURE 5-18 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 420°C AND $\bar{R}$ = 5.28

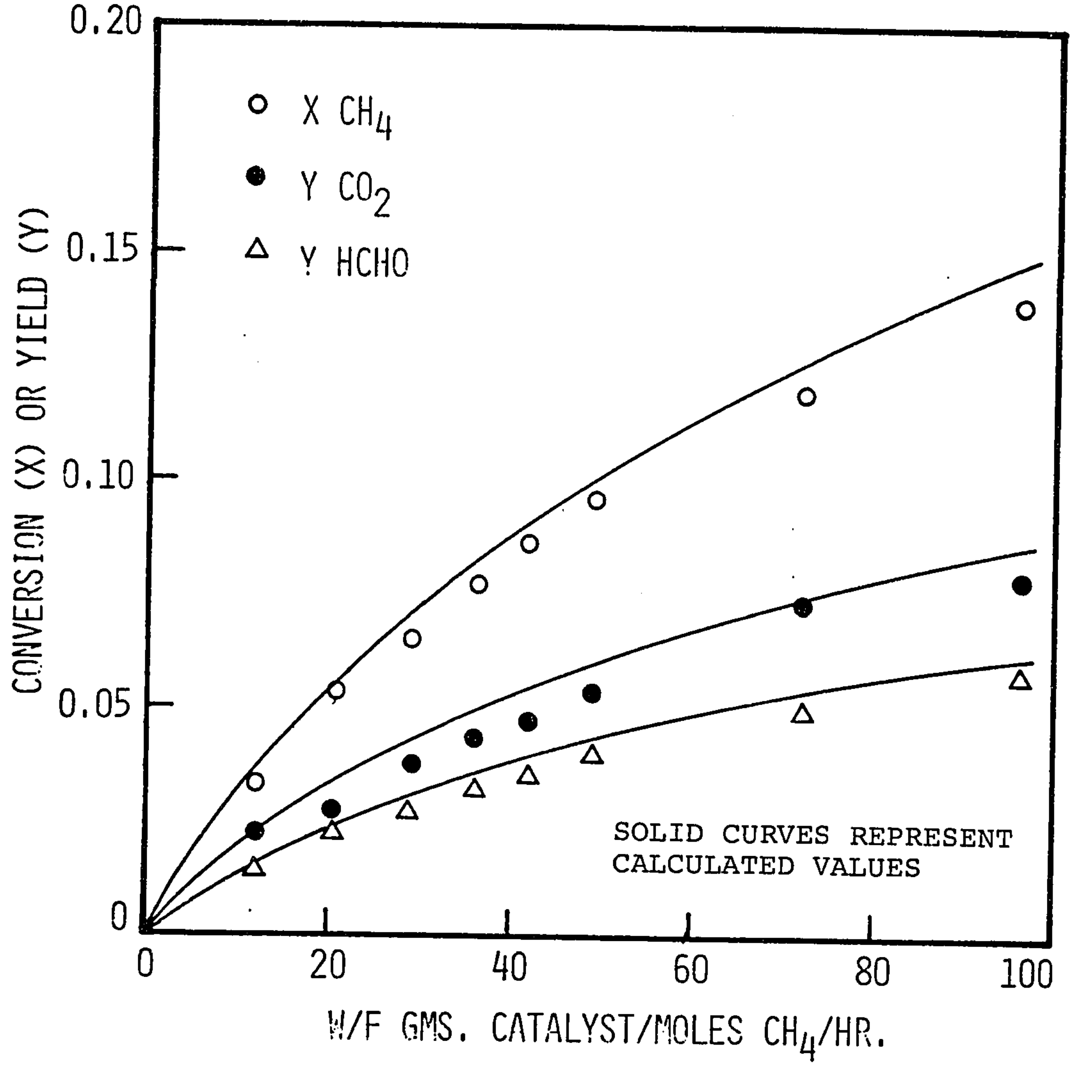


FIGURE 5 19 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 420°C AND $\bar{R}$ = 4.18

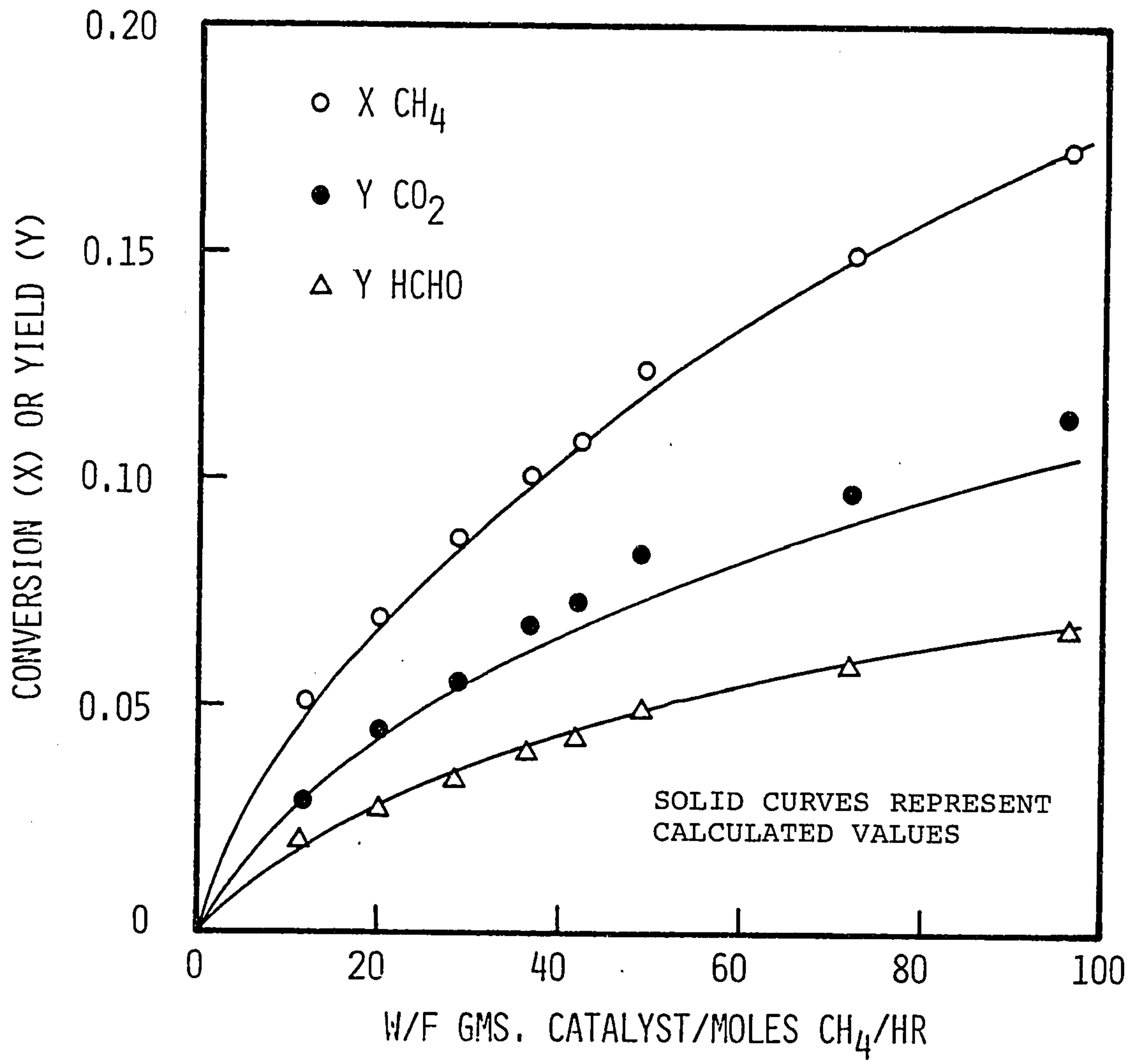


FIGURE 5-20 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 450°C AND $\bar{R}$ = 4.18

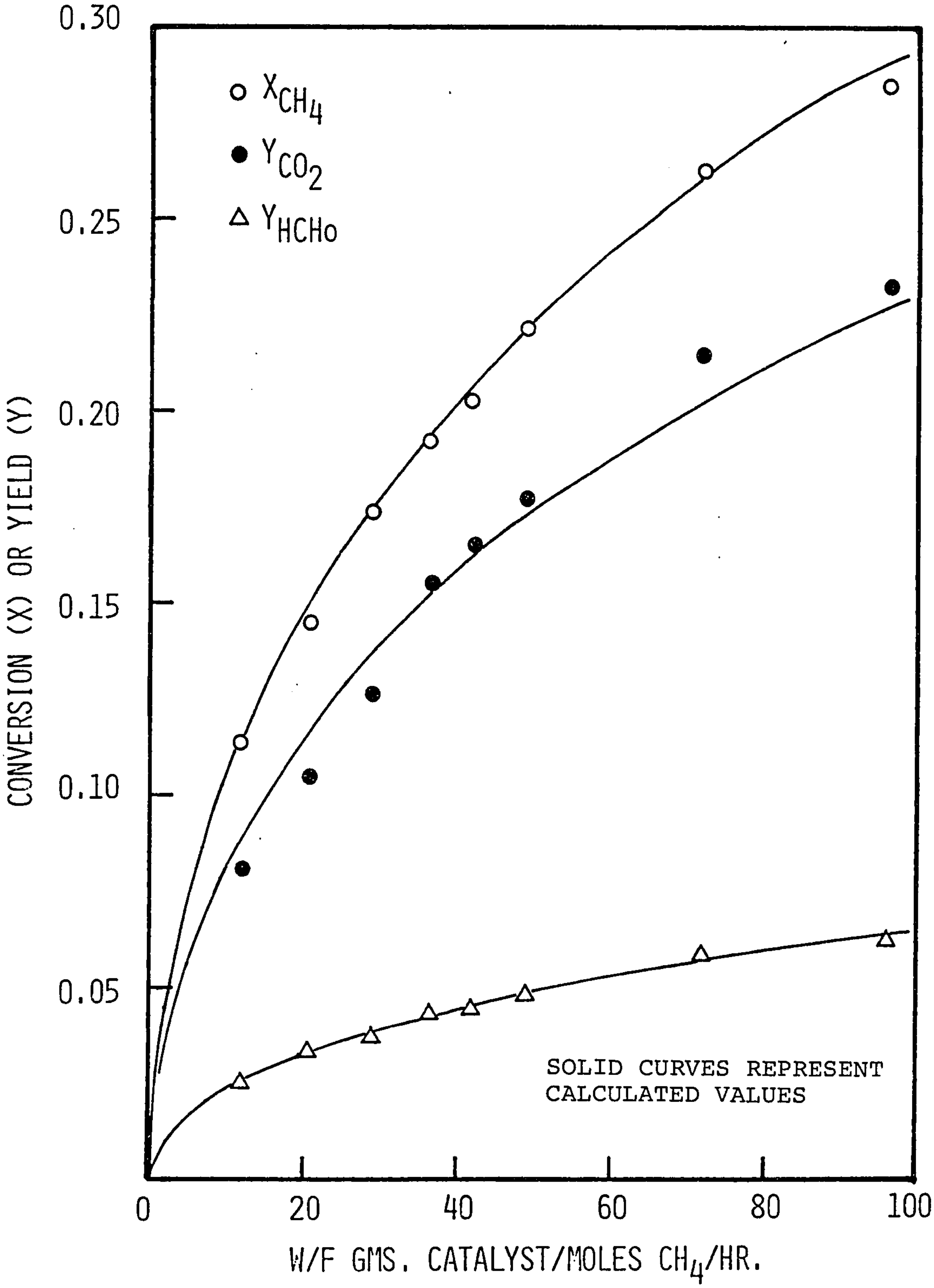


FIGURE 5-21 EFFECT OF W/F ON CONVERSION OF CH_4 AND YIELDS OF CO_2 AND HCHO AT 510°C AND $\bar{R}$ = 5.28

The values of adsoprtion equilibrium constants for each components were further tested to verify their compliance with Boudart's rule [124] for entropies of adsorption as follows:

	Rule	Methane	Formaldehyde	Oxygen
I	$\Delta S_a^\circ < 0$	$0.441 \nless 0$	$-6.486 < 0$	$-4.405 < 0$
II	$\lvert\Delta S_a^\circ\rvert < S_g^\circ$	$0.441 < 44.50$	$6.486 < 52.26$	$4.41 < 49.00$
III	$\lvert\Delta S_a^\circ\rvert > 10$	$0.441 \ngtr 10$	$6.486 \ngtr 10$	$4.405 \ngtr 10$
IV	$-\Delta S_a^\circ <$ $(12.2 - 0.0014\Delta H_a^\circ)$	$-0.44 < 18.67$ $(\Delta H_a^\circ = -4621.8)$	$6.48 < 22.53$ $(\Delta H_a^\circ = -7381.7)$	$4.40 < 16.38$ $(\Delta H_a^\circ = -2984.5)$

The values of standard enthalpy of adsorption (ΔH_a°) and standard entropy of adsoprtion (ΔS_a°) for methane were obtained by re-writing equation 5-58 in the following form and by comparing the corresponding terms:

$$K = e^{\Delta S_a^\circ/R} \cdot e^{-\Delta H_a^\circ/RT}$$

Similarly, the values of ΔS_a° and ΔH_a° for formaldehyde and oxygen were obtained from equations 5-59 and 5-60 respectively. The values of standard entropy S_g° were obtained from literature [125].

In the above table the values of standard entropy change are consistent with rules II and IV. The positive value of ΔS_a^o for methane violates rules I, which indicates that the adsoprtion of methane deviates from ideal Langmuir adsorption behaviour. In the survey of 129 cases made by Boudart [124] et al., 41 cases have reported positive values of ΔS_a^o. As regards the third rule, Boudard has considered it to be a general guide line and which may not be always valid. Further, it is worth mentioning here that the above value of entropy changes include the effect of methylene chloride which was continuously added into the reaction feed mixture of air and methane. And from the present study it was not possible to obtain true values of entropy change for each component isolated from the effect of methylene chloride. However, within reasonable approximation, the values of adsorption equilibrium constants are found to comply with Boudart's rules.

VI. DISCUSSION

In the catalytic oxidation of methane, formaldehyde is generally obtained in traces only. The oxidation of methane usually results in its complete conversion to carbon dioxide and water, which in principle, may take place either directly or via the formation of molecular intermediate such as formaldehyde. In order to isolate this intermediate compound in appreciable quantities, the direct route for complete oxidation and further oxidation of the intermediate products should be suppressed [98].

Recently, the use of halogen modifiers along with the reaction mixture over the catalyst has been reported in literature to be very successful in increasing the selectivity of conversion of the initial hydrocarbon to its partial oxidation products [17,99-102]. Since methane requires severe reaction conditions for its oxidation where formaldehyde would be unstable, the use of a high activity catalyst along with halogen modifiers appeared to be most suited in obtaining formaldehyde in high yields. Hence, palladium, a catalyst reported to be the most active for methane oxidation, was chosen for the present study.

Various halomethanes were used as modifiers in the present study. All of them inhibited overall methane conversion, but, with the exception of CCl_4, were found very effective in increasing the yield of formaldehyde as shown in Figure 4-1. Among the four chloromethanes, methylene chloride was found to inhibit methane oxidation reaction the least. The inhibiting effect was observed to be in the following increasing order: $CH_2Cl_2 < CH_3Cl < CHCl_3 < CCl_4$. This suggests that inhibition is not only dependent on number of chlorine atoms per molecule, it also depends on the stability of the particular chloromethane. The shifted position of chloromethane in the sequence may be explained by the higher reactivity of this compound [103], which results in a higher coverage of the catalyst.

As observed from Figures 4-2, 4-3 and 4-6, the inhibiting effect of the three dihalomethanes studied was in the following increasing order:

$$CH_2Cl_2 < CH_2Br_2 < CH_2I_2$$

The relative reactivity of the three dihalomethanes may explain the above observed sequence of inhibiting effect. For example, the carbon-halogen bond strengths for chlorine, bromine and iodine are 66.5, 54.0 and 45.5 Kcal/mole respectively.

These observations are in agreement with those reported in literature (71) for cases where a microcalorimeter bead reactor was used.

Methylene chloride, being least inhibiting and also being capable of markedly increasing the selectivity of the catalyst for formaldehyde formation, became the obvious choice for studying in further detail the kinetics of partial oxidation of methane. That formaldehyde is produced only from methane and not from the added methylene chloride is evident from the following preliminary observations:

(i) Yield of formaldehyde was higher than that possible from the added methylene chloride;

(ii) Even after the addition of methylene chloride was stopped, formaldehyde formation continued in high yields for over two hours;

(iii) In the absence of methane in the feed, that is, when the feed contained only air and a small amount of methylene chloride, the chromatographic analysis of the products did not show any trace of formaldehyde. The analysis showed only the formation of carbon dioxide and traces of water.

The methylene chloride, added in small amounts (0.0049 gm mol/hr), was completely consumed. The study of the decomposition of methylene chloride was not a part of the present work. However, some insight into this may be obtained from a recent study by Bond et al.[104] who have reported that chlorinated hydrocarbons are converted to carbon dioxide and hydrogen chloride over Pt/γ - Al_2O_3 catalysts at about 450°C. The conversions exceeded 95% and were independent of partial pressure of chlorinated hydrocarbons. The effect of temperatures, in the range of 420°C to 500°C, on the conversion was also reported to be very small. Considering the general similarity in the catalytic behaviors of platinum and palladium, it may be suggested that methylene chloride might have been converted to carbon dioxide and hydrogen chloride. The presence of hydrogen chloride in the products could not be detected by the analytical technique employed in the present study.

Further, it was observed that in the oxidation of methane, as long as the weight ratio of modifier (i.e., methylene chloride) to methane in the feed was kept constant, a change in the air to methane ratio in the feed (Figure 4-7) or in the reciprocal space velocity (Figure 4-8) did not affect the selectivity of the catalyst for formaldehyde formation.

However, at a given temperature a change in the modifier to methane ratio in the feed significantly affected the selectivity of the catalyst (Figure 4-6). Change in temperature affected the selectivity, only slightly, up to 450°C. Above this, further increase in temperature may have enhanced the rate of further oxidation of intermediate formaldehyde and thus decreased the yield of formaldehyde as observed in Figure 4-9. The weight ratio of modifier to methane in the feed was, thus, an important variable in optimizing the production of formaldehyde.

In the past, several attempts have been made to maximize the yield of formaldehyde during methane oxidation. Among these, high temperature partial oxidation of methane, principally in static systems, has been studied exhaustively[15,31]. Even with the use of homogeneous catalysts of initiators such as nitrogen oxides, the maximum conversion to formaldehyde has been reported only up to 3% of the methane present[105]. Vilenskii et al.[63] reported a yield of formaldehyde of up to 4.5% in a fluidized bed reactor at 600°C using aluminosilicate catalyst promoted with oxides of II group metals and in the presence of 0.5% homogeneous initiator in the reaction feed mixture. Based on experimental results and theoretical grounds, McConkey and Wilkinson[41] have reported that it is inconceivable that free radicals can be employed in a high conversion of methane to formaldehyde while further oxidation is inhibited. However the use of a halogen modifier in the present research, resulted in a significant increase in the selectivity of the catalyst for formaldehyde formation, and a high yield (up to 8%) of formaldehyde was obtained. This, as well as the observation that the catalyst continued to be selective for a long period (over 2 hours) after the supply of modifier was stopped, indicate that the function of the modifier involves a modification in some of the surface properties of the catalyst rather than simply in catalyst poisoning.

Cullis et al.[71] have studied the partial oxidation of methane in a pulsed flow microreactor. They have suggested that non-halogenated additives inhibit methane oxidation simply by competing successfully with methane for surface sites. The formation of formaldehyde in high yields in the presence of halogen additives was interpreted as indicative of formaldehyde being an important intermediate in methane oxidation. Noting the analogy with other catalytic insertion reaction, studied by Orchin[106], Cullis et al. proposed that an intermediate precursor of formaldehyde was a complex CH_2O, formed by the interaction of linearly bonded methylene radicals with some oxygen containing species. They also proposed that the effect of halogen modifier was to restrict further interaction of this complex species with oxygen, thus inhibiting the direct oxidation of methane to carbon oxides and water. Although, they have suggested that the modifiers act in modifying the surface properties of the catalyst, no mention has been made of the mechanism by which the surface properties are changed in the presence of the modifier. Also, they have not studied the kinetics of methane oxidation in the presence of modifiers.

Due to lack of experimental information regarding the nature of elementary steps in the catalytic oxidation of methane, it is rather difficult to establish the true mechanism of heterogeneous catalytic reaction. As regards the adsorbed methane species, Kemball [107] has suggested that chemisorption of methane over palladium involves dissociation to adsorbed methyl or methylene groups. On the other hand Margolis [17] has suggested that over semiconductor oxides, rapid non-dissociated adsorption to form chemisorbed species of the type RH^+ can occur on both p-type and n-type semiconductors, as indicated by changes in the conductivity of their oxide layers. According to Trapnell [108], the chemisorption of hydrocarbons on the transitional metals, Ti, Ta, Cr, Mo, W, Rh and Pd, is initially very rapid, giving weakly adsorbed radicals, but this process stops far short of a monolayer coverage. In the case of chemisorption of alkanes on metal oxides, Trapnell [109] has suggested that the surface radicals are attached to the metal atoms in the same way as with metals.

Oxygen is known to be chemisorbed strongly on palladium catalyst [78]. For transition metal oxides of the first series, oxygen is said to be adsorbed as the ionic species O^{2-} and O^{-} [110], with O^{2-} ion being more stable than O^{-}. The second transition series are in general characterised by a higher degree of covalent contribution to the bonds formed in the oxides and other similar compounds [111], which may result in a less polar surface species of chemisorbed oxygen. The presence of diatomic oxygen species (O_2^-) on silver has been reported by Sachtler et al. [112]. Thus, although the exact nature of the adsorbed species of the reactants has not been established, it is generally agreed that the chemisorbed species of methane and oxygen carry a positive and a negative charge respectively [17].

Further, as mentioned in the chapter on Literature Survey, many researchers have regarded the formaldehyde formation as the main intermediate step in methane oxidation. The rate mechanisms suggested by Mezaki and Watson, and Ahuja and Mathur assume that the methane oxidation to carbon dioxide and water is a single reaction, which seems improbable. More realistically, it may be taken as representing a series of fast elementary steps leading to total oxidation products. Cullis et al. have also emphasized that the formation of a formaldehyde complex is the first step in methane oxidation. Hence, based on observations reported in the literature, and from the results obtained in the present study during the oxidation of formaldehyde over chlorine modified and unmodified palladium catalyst, it may be concluded that carbon dioxide mostly originates from the further oxidation of aldehyde.

The experimental data obtained in the present work has been correlated in conjunction with the Electronic Theory of Catalysis to seek a satisfactory reaction mechanism. The following assumptions have been made in arriving at a mechanism for the oxidation reaction:

(i) The catalyst surface consists of two types of active sites, presumably free electrons and positive holes, on which oxygen and methane are selectively chemisorbed.

(ii) The surface defects produced in the catalyst by the presence of modifier affect both the charge transfer rate between reactants, and the equilibrium surface concentration of charged species.

(iii) Surface reaction between charged reactants on the catalyst are responsible for the formation of primary and final oxidation products.

It may be noted that these assumptions do not exclude either the possible presence of adsorbed species in a neutral form such as radicals, or the homogeneous oxidation of aldehyde.

In a recent study using E.S.R. techniques, Mann et al.[113] have reported that palladium-alumina catalyst possesses both acceptor as well as donor characteristics. However, the acceptor property was observed in larger intensity. Thus palladium-alumina catalyst is treated as a p-type (acceptor) catalyst. Further, chemisorption on metals and semiconductors is accompanied by electron transfer between the adsorbed molecule and the catalyst. As discussed earlier, the adsorption of oxygen moelcules usually results in a negative charge on the surface, while a positive charge is observed for hydrocarbons irrespective of their structure[17]. The formation of formaldehyde by the partial oxidation of methane is visualized as taking place according to the following scheme.

Reaction I - Partial Oxidation

$$CH_4(g) \rightleftarrows CH_4(s) \overset{\dot{p}L}{\rightleftarrows} CH_4^+(s) \qquad (6\text{-}1)$$

$$O_2(g) \rightleftarrows O_2(s) \overset{\dot{e}L}{\rightleftarrows} O_2^- \overset{\dot{e}L}{\rightleftarrows} 2O^-(s) \qquad (6\text{-}2)$$

$$CH_4^+(s) + 2O^-(s) \overset{2\dot{p}L}{\rightleftarrows} \text{activated complex} \rightleftarrows HCHO^+(s) + H_2O(s) \qquad (6\text{-}3)$$

$$HCHO^+(s) \overset{\dot{e}L}{\rightleftarrows} HCHO(s) \rightleftarrows HCHO(g) \qquad (6\text{-}4)$$

$$H_2O^+(s) \overset{\dot{e}L}{\rightleftarrows} H_2O(s) \rightleftarrows H_2O(g) \qquad (6\text{-}5)$$

Overall reaction: $CH_4 + O_2 \rightleftarrows HCHO + H_2O$ (6-6)

Reaction II - Further Oxidation

$$HCHO^+(s) + 2O^-(s) \rightleftarrows \text{activated complex} \rightleftarrows CO_2(s) + H_2O^+(s) \qquad (6\text{-}7)$$

$$CO_2(s) \rightleftarrows CO_2(g) \qquad (6\text{-}8)$$

$$H_2O^+(s) \overset{\dot{e}L}{\rightleftarrows} H_2O(s) \rightleftarrows H_2O(g) \qquad (6\text{-}9)$$

Overall reaction: $HCHO + O_2 \rightleftarrows CO_2 + H_2O$ (6-10)

Reaction III - Direct Oxidation

$$CH_4^+(s) + 4O^-(s) \rightleftarrows \text{activated complex} \rightleftarrows CO_2(s) + 2H_2O^+(s) \qquad (6\text{-}11)$$

$$CO_2(s) \rightleftarrows CO_2(g) \tag{6-12}$$

$$H_2O^+(s) \overset{\dot{e}L}{\rightleftarrows} H_2O(s) \rightleftarrows H_2O(g) \tag{6-13}$$

$$\text{Overall reaction: } CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O \tag{6-14}$$

In the above $\dot{e}L$ and $\dot{p}L$ represent free electrons and positive holes on the catalyst surface respectively, and (s) and (g) indicate surface and gaseous species. The sign of electrical charge on each adsorbed species is determined from work function measurements reported in the literature [114-115] assuming that all charged species are bound to the surface.

Extending the definition [116] of p-type and n-type reaction to the charged adsorption process, it may be concluded that only step (1) is a p-type and this would be accelerated by an increase in the concentration of positive holes. On the other hand, all other steps which are n-type would be accelerated by an increase in the concentration of free electrons. The type of overall reaction is determined not only by the individual sorption step but also by whether sorption or surface reaction is a controlling step.

Reaction I, II and III can also be expressed in terms of "Power Rate Law" as follows:

$$r_1 = k_1(C_{CH_4}+)^{m_1} \cdot (C_O-)^{n_1} - k_1'(C_{A+})^{m_1'} \cdot (C_{H_2O}+)^{n_1'} \quad (6\text{-}15)$$

$$r_2 = k_2(C_A+)^{m_2} \cdot (C_O-)^{n_2} - k_2'(C_{CO_2})^{m_2'} \cdot (C_{H_2O}+)^{n_2'} \quad (6\text{-}16)$$

$$r_3 = k_3(C_{CH_4}+)^{m_3} \cdot (C_O-)^{n_3} - k_3'(C_{CO_2})^{m_3'} \cdot (C_{H_2O}+)^{n_3'} \quad (6\text{-}17)$$

where, $C_{CH_4^+}$, C_{O^-}, C_{A^+} and $C_{H_2O^+}$ are the surface concentrations of charged methane, oxygen, formadelhyde and water species respectively. Since, thermodynamically these oxidation reactions are highly irreversible, the backward reactions may be neglected and the reaction rate would be as follows:

$$r_1 = k_1(C_{CH_4}+)^{m_1} \cdot (C_O-)^{n_1} \quad (6\text{-}18)$$

$$r_2 = k_2(C_A+)^{m_2} \cdot (C_O-)^{n_2} \quad (6\text{-}19)$$

$$r_3 = k_3(C_{CH_4}+)^{m_3} \cdot (C_O-)^{n_3} \quad (6\text{-}20)$$

Although quantitative determination of these surface concentrations is difficult, some satisfactory explanation of qualitative nature can be obtained in respect of the activity and selectivity of the catalyst in the presence of a modifier.

In the absence of a modifier, the activity and the selectivity of the catalyst depend on the concentration of charged adsorbed methane, oxygen and aldehyde ions which are in turn dependent on the operating conditions and intrinsic properties of the catalyst. The addition, in small amounts, of a halogen modifier which is known to be a good electron acceptor, increases the surface concentration of positively charged species (CH_4^+ , C_A^+) and decreases the surface concentration of negatively charged oxygen species, so that

$$\frac{dC_{O^-}}{dZ} < 0, \quad \frac{dC_{CH_4^+}}{dZ} > 0 \quad \text{and} \quad \frac{dC_{A^+}}{dZ} > 0 \tag{6-21}$$

where Z represent the amount of modifier in the feed.

As mentioned earlier, the final product, carbon dioxide is formed because of the further oxidation of aldehyde in which case $r_2 >> r_3$. The conversion of methane would depend on reaction rate r_1 and the yield for aldehyde would be determined by rates r_1 and r_2. The decrease in concentration of adsorbed oxygen, C_{O^-}, in the presence of chlorine ions would cause both rate r_1 and rate r_2 to decrease so that

$$\frac{dr_1}{dZ} < 0 \quad \text{and} \quad \frac{dr_2}{dZ} < 0 \tag{6-22}$$

As a result, the conversion of methane will be decreased. Again, the increase of $C_{CH_4}+$ and C_A+ should result in increasing the methane conversion (step I) rate r_1 and aldehyde conversion (step II) rate r_2. But, keeping in view that step I is a p-type reaction and step II is an n-type reaction, increase in r_2 will be relatively less favored as compared to the increase in r_1. This would cause an increased yield of formaldehyde. The selectivity of the catalyst, that is the moles of formaldehyde formed per mole of methane reacted, would thus be increased with increasing amount of modifier. However, the yield of formaldehyde will decrease with increasing amount of modifier beyond a certain optimum due to decrease in conversion of methane through step I, as observed in Figure 4-6.

The action of chlorine modifier may also be explained in terms of the catalyst work function. The chemisorption of methylene chloride is known to occur by dissociation and the electronegative chlorine atoms are thought to be adsorbed as chloride ions [117]. Doping the catalyst with electron acceptors (i.e. chlorine) increases the catalyst work function [99] and this is accompanied by certain changes in the nature and relative surface concentrations of the reacting species. On the undoped palladium oxide, chemisorbed oxygen is thought to be present as negatively charged ions and methane as relatively weakly charged positive species. An increase in the catalyst work function would be expected to produce stronger methane chemisorption with a more polar bond (positive charge on the adsorbate), and a weaker, less polar chemisorption of oxygen. The resulting changes in the relative surface coverages are then expected to increase the probability of partial oxidation. However such changes in the work function would also be expected to result in stronger chemisorption of formaldehyde which would tend to decrease the formaldehyde yield.

Doping of the catalyst with oxygen ions, as for thoroughly pre-oxidized catalyst, should have the same effect as that of CI^- ions. This would explain relatively higher yields of formaldehyde over freshly activated catalyst as compared to those over equilibrium catalysts (i.e. with stabilized activity). The activity of the freshly activated (in a current of air) catalyst is usually high at the begining of its use. The activity of the catalyst decreases with time up to the first 20 hours of use after which a constant activity is obtained. This is usually attributed to the inhibiting effect of water formed during the reaction.

The oxidation of methane over palladium oxide catalyst may also involve the participation of lattice oxygen. The equilibrium reaction is represented by:

$$4PdO(s) + CH_4(g) \rightleftarrows CO_2(g) + 2H_2O(g) + 4Pd(s) \quad (6\text{-}23)$$

$$\Delta F = -133.8 \text{ k cal/mole}$$

which shows that methane should reduce palladium oxide to the metal. However, with short contact times, equilibrium (i.e. complete oxidation of methane) may not be attained, and under these conditions the degree of oxidation of the catalyst would depend on the relative rates of the oxidation of methane and of palladium. Bransom et al.[56] have reported that in the oxidation of alkanes (including methane) by cuprous oxide, there is a fast initial stage where lattice oxygen at or near the surface is readily available to oxidize the hydrocarbon. This is followed by a slower stage where the rate is limited by the diffusion of Cu^+ ions into the lattice.

Several researchers [118-119] have reported that in the case of metals there is a definite relationship between the stability of the metal oxide (formed during the reaction) and its effectiveness as a total oxidation catalyst. Metals forming the most stable oxides are the least active catalysts. Furthermore, for a given heterogeneous surface coverage of chemisorbed oxygen on an oxide or metal catalyst, the most weakly bound oxygen is preferentially used in air oxidation reaction[120].

In the case of the oxidation of methane over palladium catalysts there will be competition between methane and palladium for the available oxygen and thus the equilibrium between the metal and metal oxide will depend on reaction conditions.

According to a recent review of catalytic hydrocarbon oxidation by Margolis [5], the existence of diatomic O_2^- ions, of atomic O^- ions and of regular ions in the lattice of O^{2-} in oxide systems is beyond doubt. Kazanskii et al.[121], who extensively studied the reoxidation of oxides, have reported O^- to be highly reactive so that it gets consumed in the reaction even before converting to the regular lattice ion. Sachtler et al.[112] identified the oxygen species on silver using infrared techniques and concluded that the presence of diatomic oxygen (O_2^-) species on silver was responsible for the selective oxidation of ethylene to ethylene oxide. Chlorine was found to inhibit dissociative adsorption of oxygen (O^-) and to favor adsorption of diatomic O_2^- species on silver. The increased selectivity of the catalyst for formaldehyde formation and increased palladium oxide content in the catalyst, noted in the present study on methane oxidation over a palladium catalyst, may also be explained as due to selective adsorption of diatomic oxygen (O_2^-) species (or inhibition of dissociative adsorption of oxygen, O^-) in the presence of chlorine modifier.

It is known that larger work function of a metal oxide (relative to that of a metal), in general, tends to favor partial oxidation. As mentioned earlier, chlorine modifier too favors partial oxidation by increasing the work function of the catalyst. It may therefore be suggested that the action of chlorine modifier is to provide a selective adsorption of oxygen species which helps in maintaining a higher proportion of palladium oxide phase in the catalyst. This would explain the larger intensity of palladium oxide phase detected in X-ray diffraction pattern of the used catalyst as compared to that obtained with the catalyst before it is doped with chlorine modifier. It may therefore be concluded that the active phase of the catalyst used in the present study is palladium oxide and that, without a modifier, it would be difficult to maintain a high proportion of this active oxide phase in the catalyst.

VII. CONCLUSIONS AND RECOMMENDATIONS

The catalytic oxidation of methane over halogen modified palladium catalyst was investigated in an isothermal integral flow reactor between 390 and 510°C with air to methane feed ratio 2.41 - 5.28 and reciprocal space velocity up to 96.0 gm.hr/gm mole in order to establish the conditions for maximum conversion and yield, to derive a suitable rate equation and to identify a possible reaction mechanism.

The experimental method used in this study enabled a precise continuous addition of modifiers in small amounts to the catalyst. An accurate analysis was made feasible by the use of gas chromatographic techniques coupled with on-line heated gas sampling valve and an electronic area integrator.

Based on experimental results, the following conclusions were drawn:

(i) All halogen modifiers decreased the conversion of methane but were effective in enhancing the selectivity of palladium catalyst towards formaldehyde formation.

(ii) The inhibiting effect of the modifiers on the conversion of methane was dependent on the reactivity of halogen and the number of halogen atoms in the halo-compound. Methylene chloride was found to have the least inhibiting effect on methane oxidation.

(iii) A continuous supply of a constant amount of modifier to the catalyst was essential for maintaining a high selectivity of the catalyst for the aldehyde.

(iv) The molar ratio of modifier to methane in the feed ($\bar{Z}$) was an important factor in the selective oxidation. The selectivity of the catalyst increased with a higher amount of modifier, but the yield of formaldehyde decreased with an increase in $\bar{Z}$ above the optimum value of nearly 0.02.

(v) The modified oxidation process proved more suitable for oxidation under rigorous conditions (such as, increased feed ratio, contact time or reaction temperature) since a high selectivity (about 35%) along with a relatively high conversion could be maintained for formaldehyde formation.

(vi) The maximum yield of formaldehyde (7.7%) was obtained at 480^{o}C, with an air to methane ratio of 5.28 and a reciprocal space velocity of 96.00 gm.hr/gm.mole, and with a chlorine modified palladium catalyst. The conversion of methane was 22.6% with a catalyst selectivity of 34%.

(vii) Electronic factors governing the rates of reaction at the catalyst surface were found to be very important. It was suggested that the chemisorption of reactants, oxygen and methane was preferential on the catalyst surface, the partial oxidation of methane was a p-type reaction, and the further oxidation of methane to carbon dioxide was an n-type reaction under optimum conditions.

(viii) The active component of the palladium catalyst supported on alumina appeared to be palladium oxide.

(ix) The Hougen-Watson approach based on the modified Langmuir-Hinshelwood mechanism was used for the kinetic analysis of data. Using a non-linear regression method, the most satisfactory rate equation correlating the data was found to be

$$r = \frac{k_s K_M P_M}{1 + K_M P_M + K_F P_F} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

where K_M, K_F, K_O and k_s are temperature dependent constants. In the temperature range of 390 to 510^{o}C, the value of k_s increased with an increase in temperature whereas those of K_M, K_F and K_O decreased. This rate equation corresponded to a reaction mechanism where the surface reaction between the charged adsorbed methane and oxygen was a rate controlling step.

It is recommended that:

(i) In order to obtain a better understanding of catalyst modification, the changes in catalytic properties such as, work function, electrical conductivity for example, taking place during the adsorption of reactants on the catalyst surface with or without the presence of a modifier, should be studied.

(ii) E.S.R. studies of the palladium catalyst in vacuum and in the presence of methane, oxygen and chlorine modifier (individually or together) at high temperature and also at liquid nitrogen temperature might also provide information on the nature of adsorbed species and of intermediate complex formation at various stages of the reaction.

(iii) Further work on oxidation of methane over other p-type and n-type oxide catalysts in the presence of different modifiers should be studied in order to test the present postulations and to obtain higher yields of formaldehyde.

VIII. APPENDIX

APPENDIX A

Thermodynamic Aspects of Oxidation of Methane

Thermodynamic Aspects:

The value of change in Gibb's Free Energy, ΔF^{o}, and the equilibrium constant, K, of the gaseous oxidation of methane to formaldehyde are given in the following table.

Table A-A-1

The Values of ΔF^{o} and K for Gaseous Formaldehyde Formation at 1 atm and Different Temperature

Temperature ^{o}K	$- F^{o}$ Kcal/gm mole	K
25	68.759	2.67×10^{50}
500	69.302	1.96×10^{30}
600	69.538	2.13×10^{25}
650	69.642	2.60×10^{23}
700	69.735	5.91×10^{21}
750	69.816	2.19×10^{20}
800	69.884	1.23×10^{19}
850	69.939	9.60×10^{17}

The above values were calculated as functions of temperature necessary data being collected from the literature [122,123]. Since the values of K are bery large, the process can be considered highly irreversible.

APPENDIX B

Calibration of Equipment

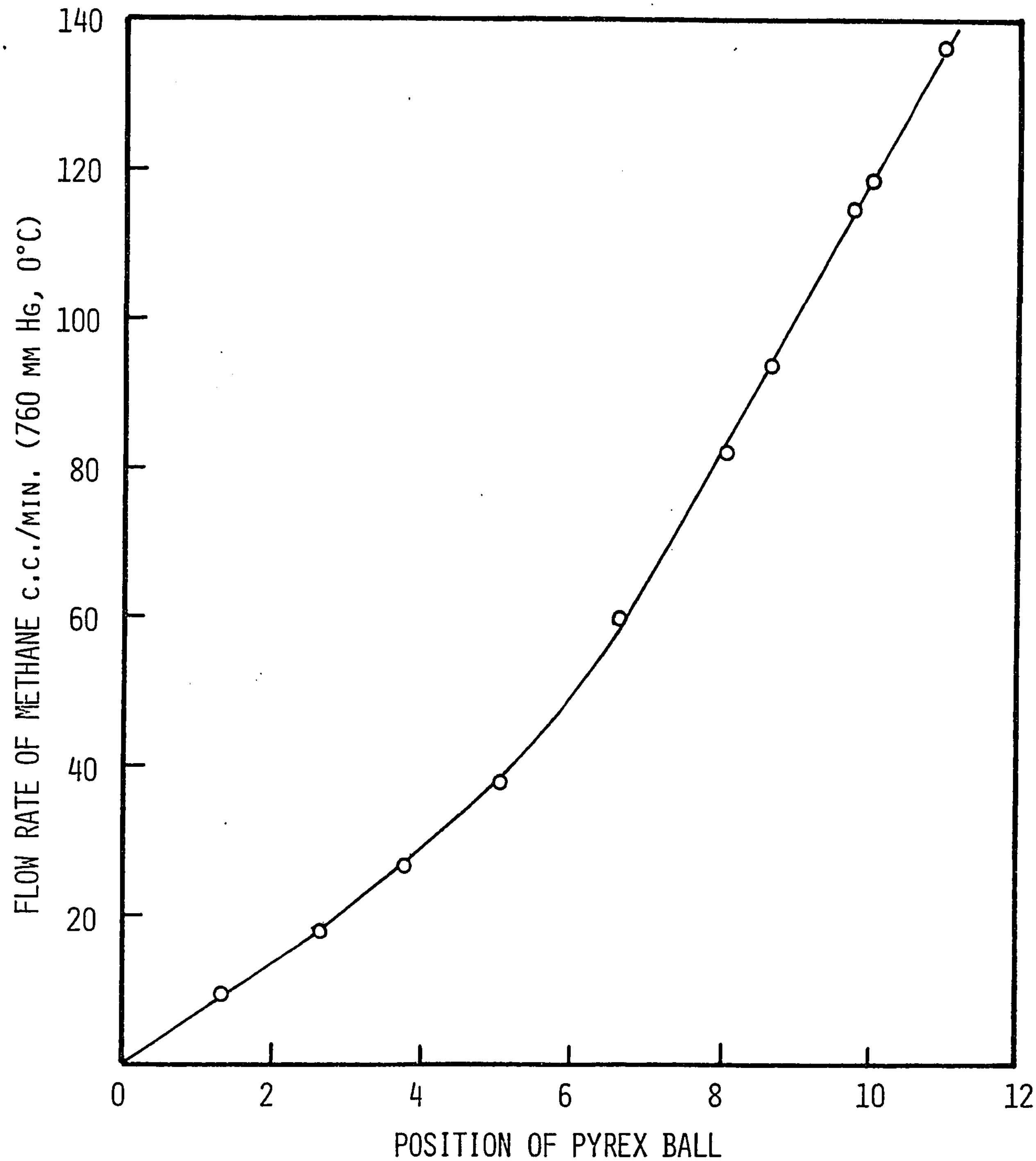


FIGURE A-B-1 CALIBRATION OF ROTAMETER FOR METHANE

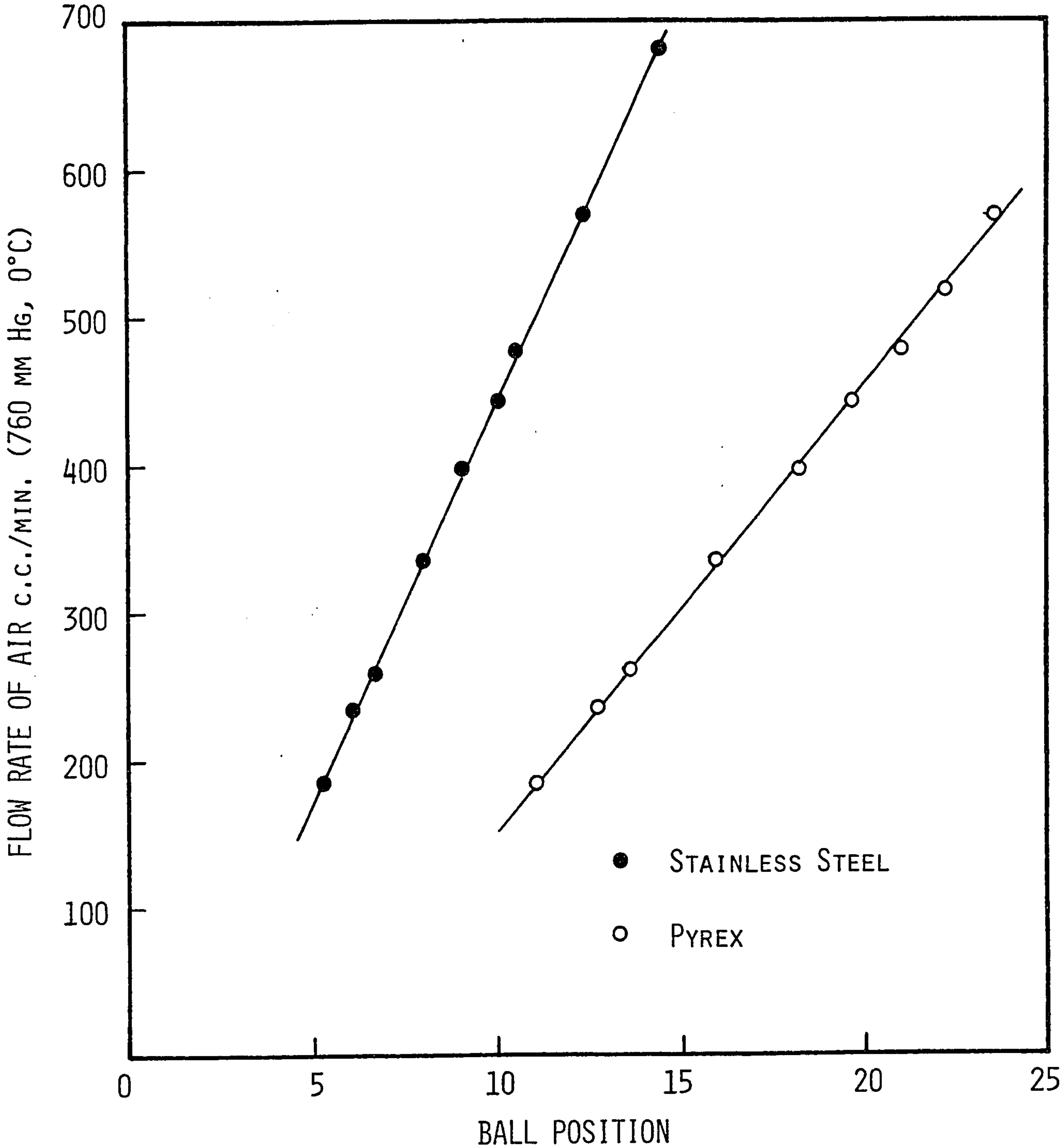


FIGURE A-B-2 CALIBRATION OF ROTAMETER FOR AIR

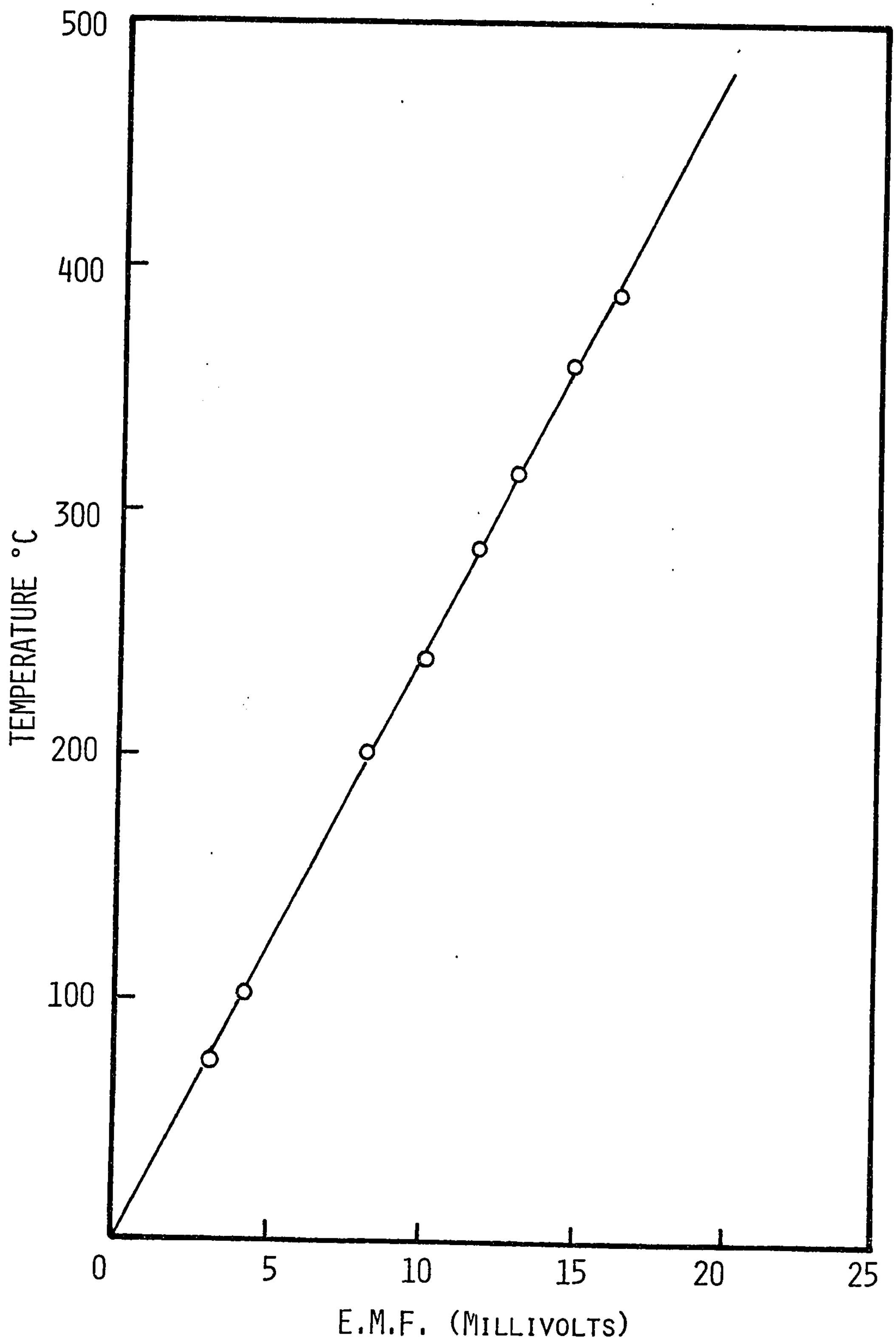


FIGURE A-B-3 CALIBRATION OF CHROMEL-ALUMEL THERMOCOUPLE

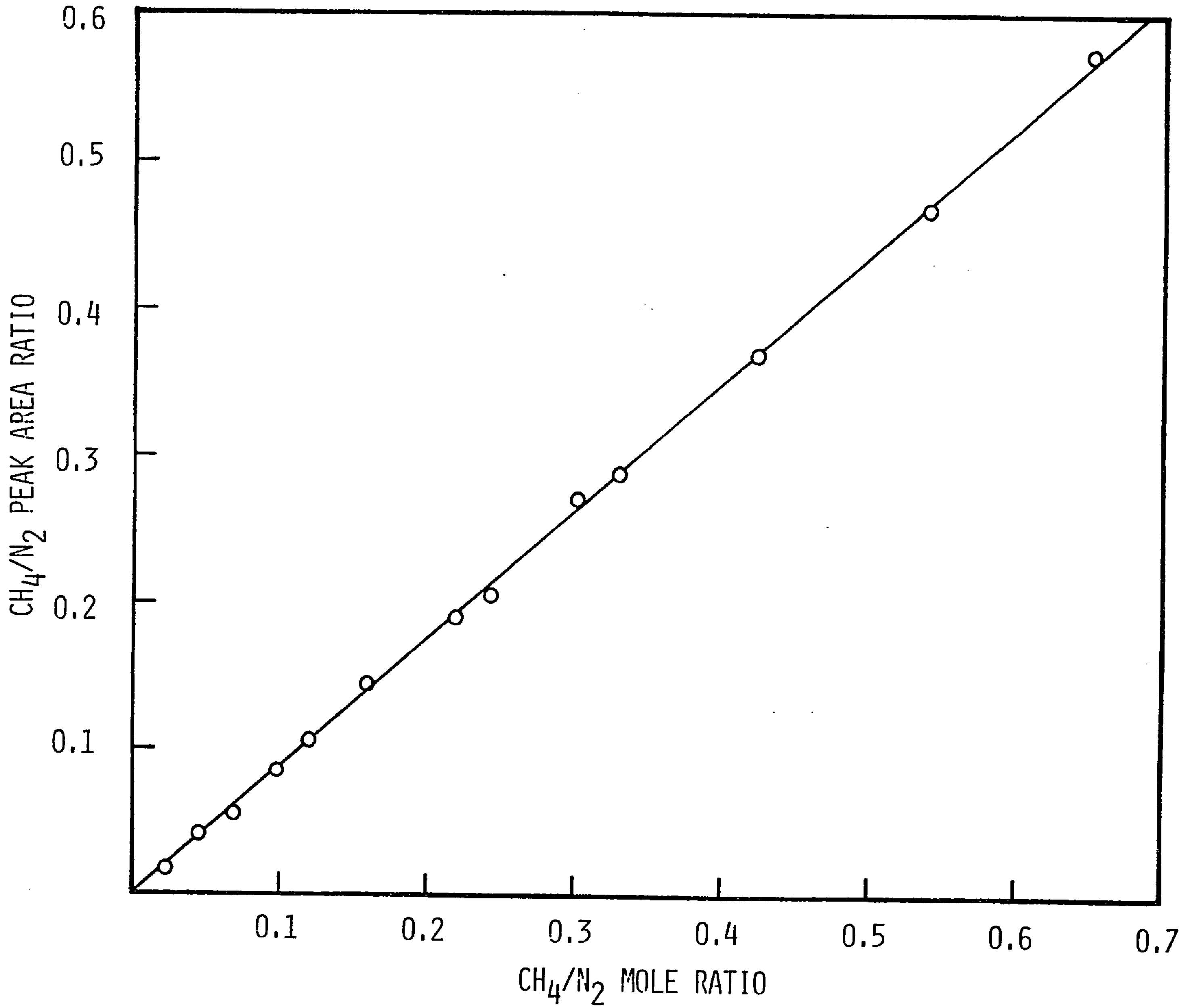


FIGURE A-B-4 CALIBRATION FOR METHANE ANALYSIS IN FISHER GAS PARTITIONER

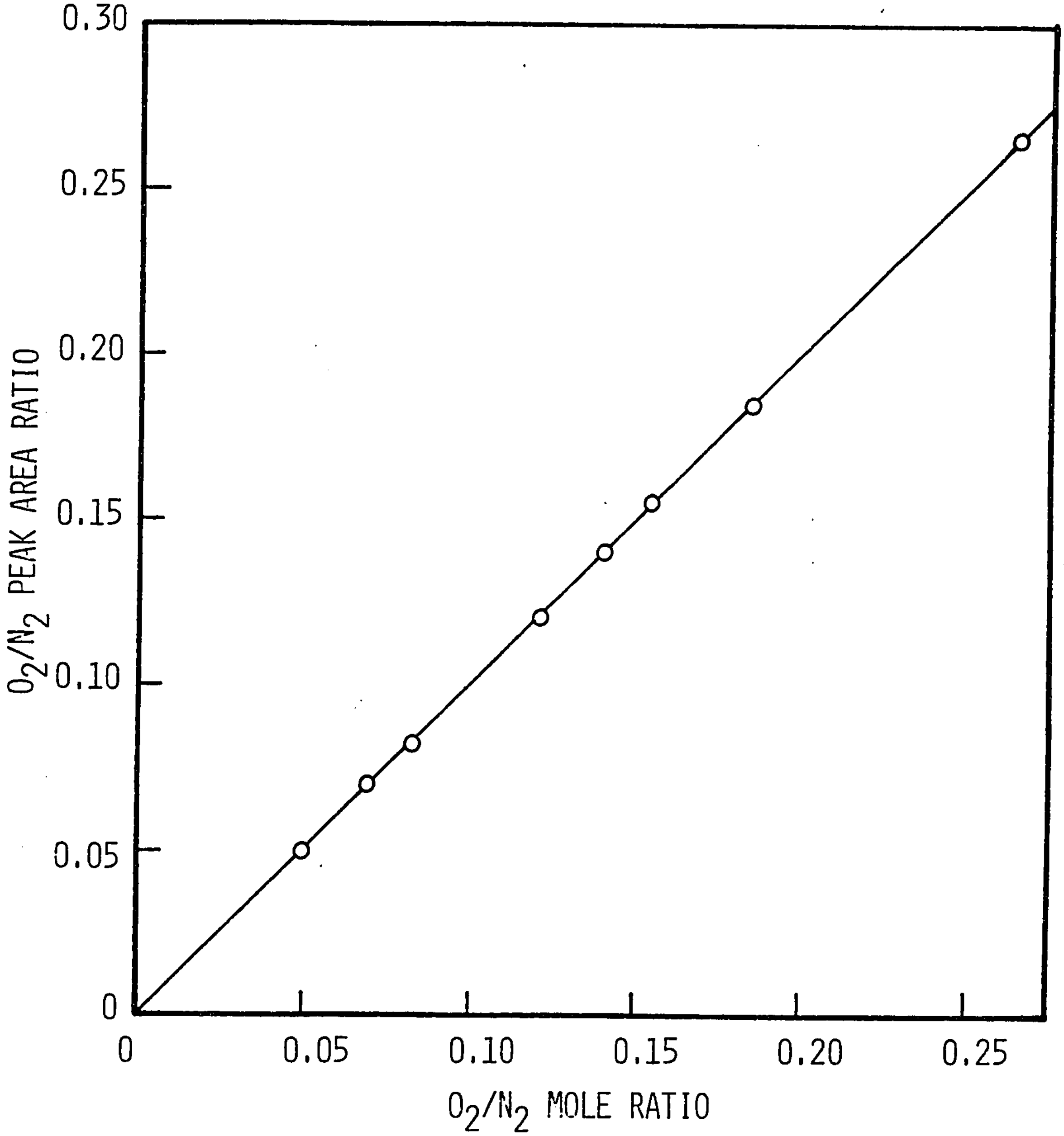


FIGURE A-B-5 CALIBRATION FOR OXYGEN ANALYSIS IN FISHER GAS PARTITIONER

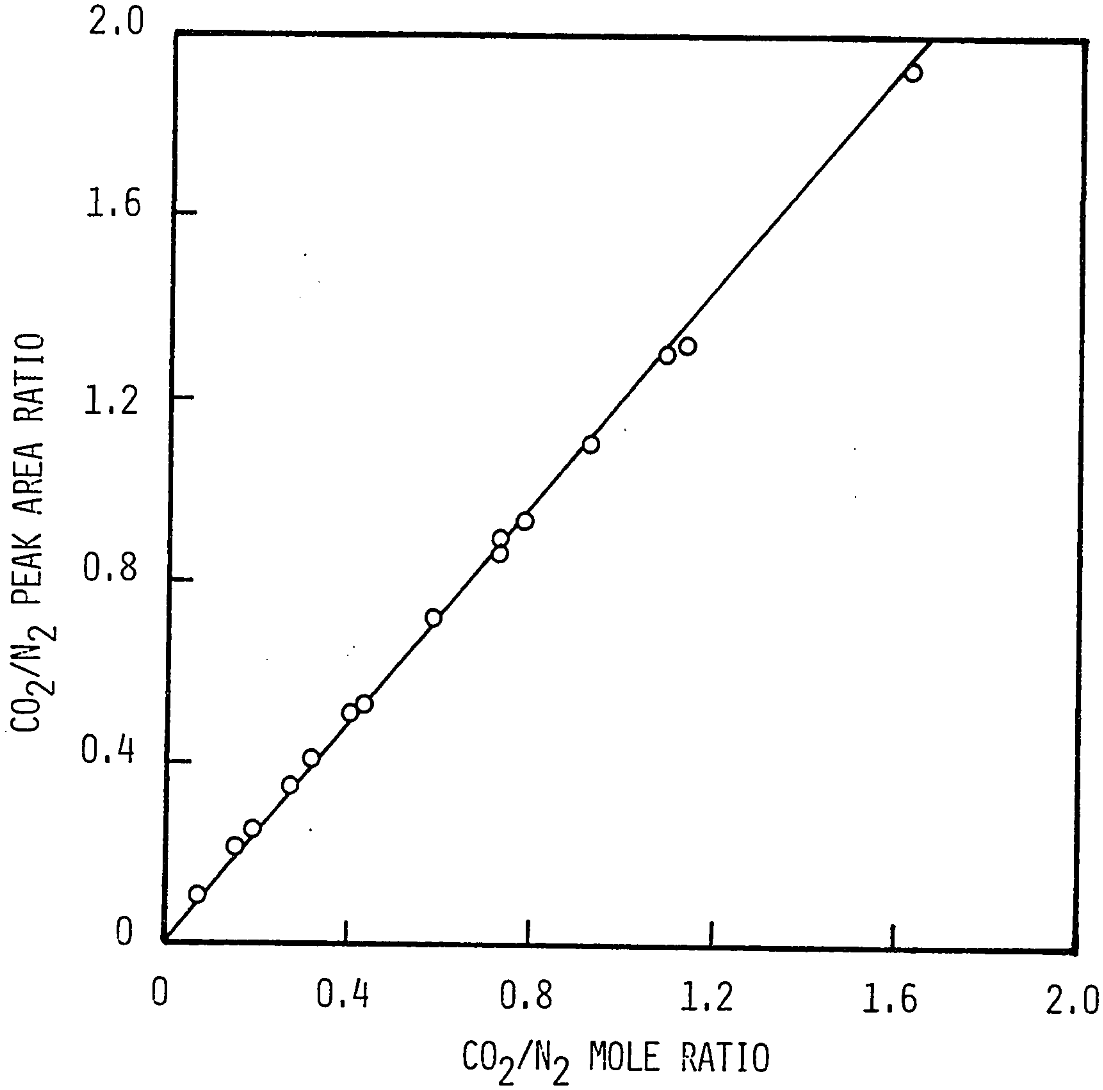


FIGURE A-B-6 CALIBRATION FOR CARBON DIOXIDE ANALYSIS IN FISHER GAS PARTITIONER

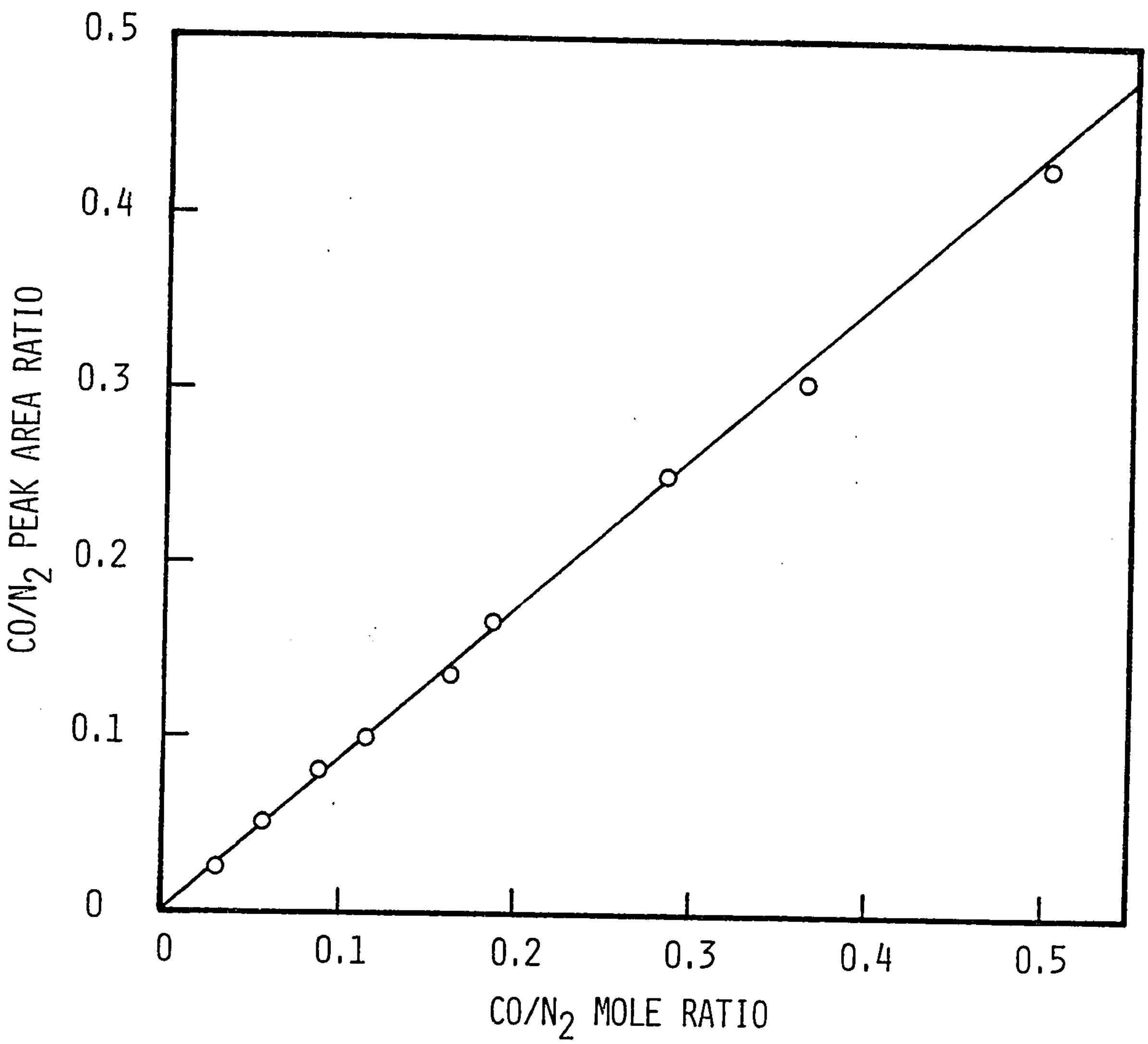


FIGURE A-B-7 CALIBRATION FOR CARBON MONOXIDE ANALYSIS IN FISHER GAS PARTITIONER

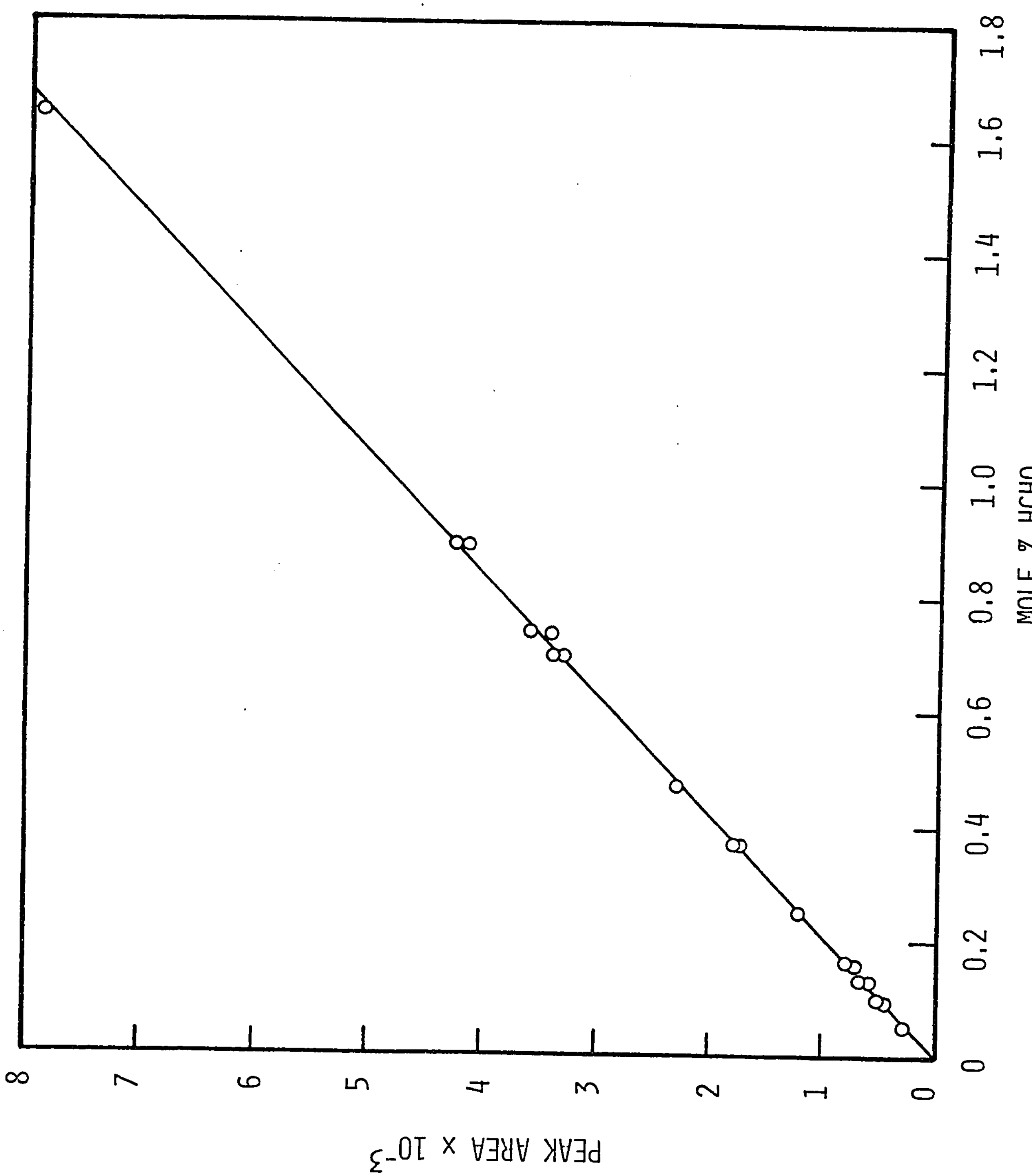


FIGURE A-B-8 CALIBRATION FOR FORMALDEHYDE ANALYSIS IN GAS CHROMATOGRAPH

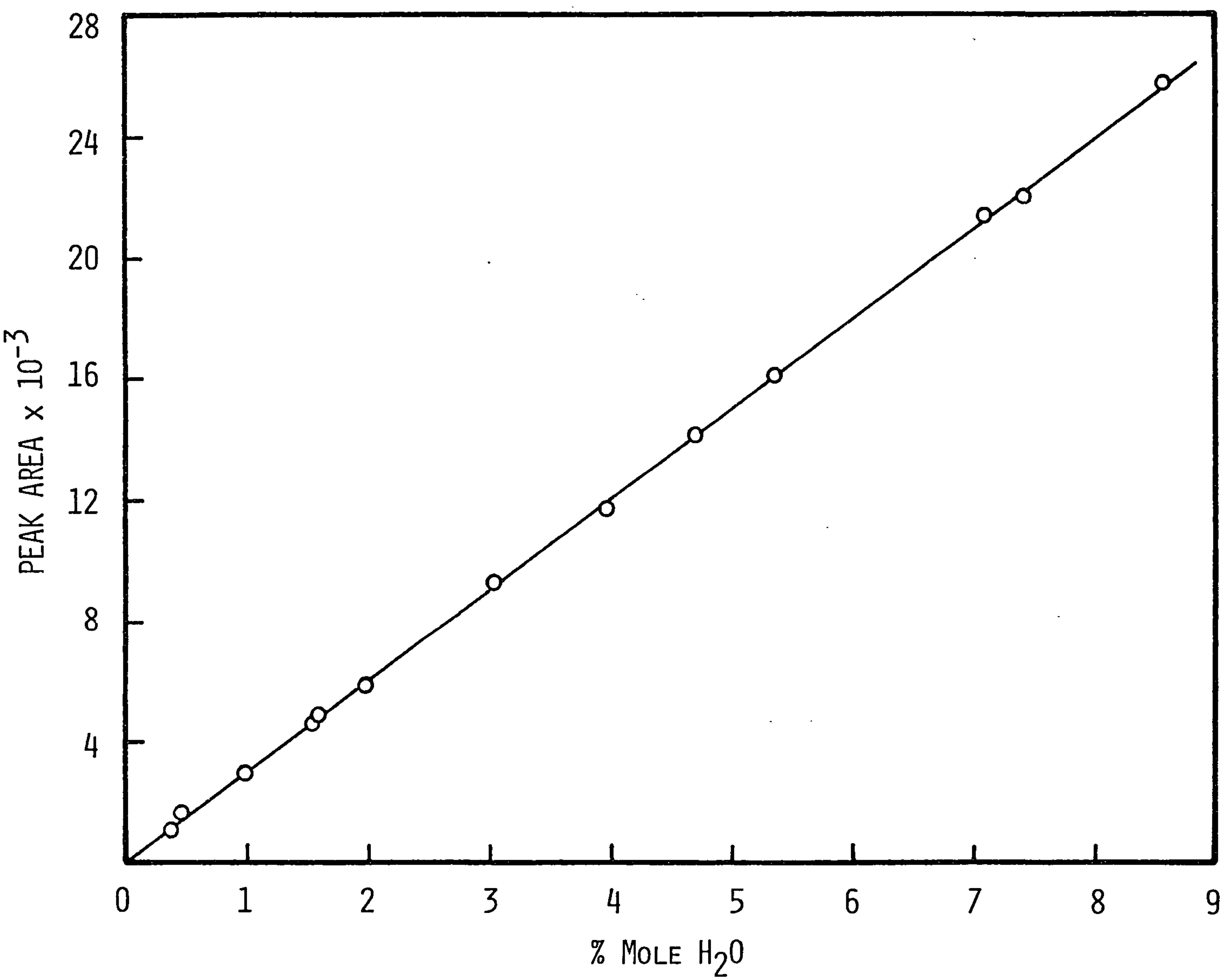


FIGURE A-B-9 CALIBRATION FOR ANALYSIS OF WATER IN GAS CHROMATOGRAPH

Calibration of Syringe Pump:

Table A-B-1

Pump Speed Setting	Liquid Discharge Rate ml/hr for Syringe Size	
	5 ml	2 ml
8	1.5726	0.7890
9	0.6346	0.3156
10	0.3167	0.1578
11	0.1571	0.0789
12	0.0634	0.0316

Specific gravity of methylene chloride at 24°C = 1.315

APPENDIX C

Tabulated Experimental Data

TABLE A-C-1

Effect of W/F on Conversion, Yields and Selectivity for Oxidation of Methane over Chlorine Modified Palladium Catalyst

Temperature: 390°C $\bar{R}$: 2.41 $\bar{Z}$: 0.0195

Run No.	W/F gm.hr/mole	Feed moles/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
101	12.00	0.2504	1.1264	0.4770	0.0192	0.0084	0.0127
102	20.45	0.2504	0.1264	0.4770	0.0345	0.0152	0.0217
103	28.83	0.2504	0.1264	0.4770	0.0439	0.0191	0.0313
104	36.06	0.2504	0.1264	0.4770	0.0501	0.0210	0.0339
105	41.81	0.2504	0.1264	0.4770	0.0590	0.0256	0.0366
106	49.00	0.2504	0.1264	0.4770	0.0655	0.0282	0.0429

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
101	0.2456	0.1091	0.4770	0.2103	0.1385	0.0808	43.75
102	0.2418	0.0999	0.4770	0.3806	0.1681	0.1034	44.06
103	0.2394	0.0995	0.4770	0.4784	0.2412	0.1275	43.51
104	0.2379	0.0948	0.4770	0.5259	0.2589	0.1339	41.92
105	0.2356	0.0931	0.4770	0.6411	0.3063	0.1407	43.39
106	0.2340	0.8854	0.4770	0.7061	0.3245	0.1565	43.05

TABLE A-C-1 (continued)

Temp. = 390°C $\bar{R}$ = 3.01 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
107	12.00	0.2504	0.1579	0.5958	0.0205	0.0090	0.0095
108	20.45	0.2504	0.1579	0.5958	0.0348	0.0155	0.0211
109	28.83	0.2504	0.1579	0.5958	0.0455	0.0200	0.0295
110	36.06	0.2504	0.1579	0.5958	0.0542	0.0228	0.0334
111	41.81	0.2504	0.1579	0.5958	0.0610	0.0255	0.0333
112	49.00	0.2504	0.1579	0.5958	0.0690	0.0301	0.0376

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
107	0.2453	0.1426	0.5958	0.2253	0.1122	0.0728	43.90
108	0.2417	0.1406	0.5958	0.3882	0.2184	0.1018	44.56
109	0.2390	0.1316	0.5958	0.5007	0.2539	0.1228	43.94
110	0.2368	0.1297	0.5958	0.5709	0.2939	0.1326	42.07
111	0.2351	0.1306	0.5958	0.6386	0.3245	0.1324	41.81
112	0.2331	0.1295	0.5958	0.7537	0.3531	0.1432	43.61

TABLE A-C-1 (continued)

Temp. = 390°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
113	12.00	0.2504	0.1894	0.7146	0.0208	0.0091	0.0154
114	20.45	0.2504	0.1894	0.7146	0.0362	0.0160	0.0243
115	28.83	0.2504	0.1894	0.7146	0.0475	0.0204	0.0302
116	36.06	0.2504	0.1894	0.7146	0.0565	0.0244	0.0369
117	41.81	0.2504	0.1894	0.7146	0.0630	0.0260	0.0394
118	49.00	0.2504	0.1894	0.7146	0.0716	0.0302	0.0462
119	72.00	0.1242	0.0939	0.3544	0.0944	0.0397	0.0529
120	96.00	0.1242	0.0939	0.3544	0.1105	0.0467	0.0602

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	%S
113	0.2452	0.1711	0.7146	0.2280	0.1187	0.0875	43.79
114	0.2413	0.1636	0.7146	0.4007	0.2100	0.1098	44.21
115	0.2385	0.1626	0.7146	0.5108	0.2553	0.1246	42.94
116	0.2363	0.1618	0.7146	0.6110	0.2841	0.1413	43.19
117	0.2346	0.1504	0.7146	0.6511	0.2837	0.1477	41.26
118	0.2325	0.1679	0.7146	0.7563	0.3008	0.1647	42.18
119	0.1125	0.0640	0.3544	0.4930	0.2329	0.0900	42.07
120	0.1105	0.0622	0.3544	0.5801	0.2621	0.0991	42.26

TABLE A-C-1 (continued)

Temp. = 390°C $\bar{R}$ = 4.18 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
121	12.00	0.2504	0.2193	0.8274	0.0230	0.0098	0.0188
122	20.45	0.2504	0.2193	0.8274	0.03881	0.0165	0.0273
123	28.83	0.2504	0.2193	0.8274	0.0485	0.0198	0.0304
124	36.06	0.2504	0.2193	0.8274	0.0592	0.0261	0.0371
125	41.81	0.2504	0.2193	0.8274	0.0660	0.0282	0.0394
126	49.00	0.2504	0.2193	0.8274	0.0744	0.0312	0.0455
127	72.00	0.1242	0.1088	0.4104	0.0986	0.0419	0.0533
128	96.00	0.1242	0.1088	0.4104	0.1180	0.0495	0.0625

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	%S
121	0.2446	0.2007	0.8274	0.2454	0.1877	0.0960	42.63
122	0.2407	0.1987	0.8274	0.4133	0.2273	0.1174	42.52
123	0.2388	0.1976	0.8274	0.4956	0.2559	0.1250	40.82
124	0.2356	0.1907	0.8274	0.6534	0.2585	0.1419	44.08
125	0.2339	0.1900	0.8274	0.7060	0.2656	0.1477	42.73
126	0.2318	0.1867	0.8274	0.7811	0.3177	0.1629	41.94
127	0.1119	0.0793	0.4104	0.5204	0.2475	0.0905	42.50
128	0.1095	0.0777	0.4104	0.6147	0.2800	0.1019	41.95

TABLE A-C-1 (continued)

Temp. = 390°C $\bar{R}$ = 5.28 $\bar{Z}$ = 1.095

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
129	12.00	0.2504	0.2770	1.0451	0.0243	0.0102	0.0169
130	20.45	0.2504	0.2770	1.0451	0.0425	0.0181	0.0298
131	28.83	0.2504	0.2770	1.0451	0.0520	0.0218	0.0358
132	36.06	0.2504	0.2770	1.0451	0.0621	0.0260	0.0410
133	41.81	0.2504	0.2770	1.0451	0.0705	0.0294	0.0441
134	49.00	0.2504	0.2770	1.0451	0.0802	0.0335	0.0501
135	72.00	0.1242	0.1374	0.5184	0.1056	0.0444	0.0599
136	96.00	0.1242	0.1374	0.5184	0.1219	0.0515	0.0649

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
129	0.2443	0.2570	1.0451	0.2555	0.1669	0.0944	41.91
130	0.2398	0.2505	1.0451	0.4527	0.2434	0.1238	42.55
131	0.2374	0.2480	1.0451	0.5459	0.3055	0.1387	41.95
132	0.2348	0.2439	1.0451	0.6511	0.3426	0.1517	41.88
133	0.2327	0.2427	1.0451	0.7361	0.3708	0.1592	41.71
134	0.2303	0.2394	1.0451	0.8389	0.3935	0.1745	41.77
135	0.1111	0.1056	0.5184	0.5514	0.2499	0.0987	41.70
136	0.1091	0.1039	0.5184	0.6395	0.2854	0.1049	42.26

TABLE A-C-1 (continued)

Temp. = 420°C $\bar{R}$ = 2.41 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
137	12.00	0.2504	0.1264	0.4770	0.0279	0.0117	0.0138
138	20.45	0.2504	0.1264	0.4770	0.0451	0.0187	0.0257
139	28.83	0.2504	0.1264	0.4770	0.0540	0.0225	0.0324
140	36.06	0.2504	0.1264	0.4770	0.0665	0.0275	0.0401
141	41.81	0.2504	0.1264	0.4770	0.0723	0.0302	0.0404
142	49.00	0.2504	0.1264	0.4770	0.0808	0.0333	0.0414

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
137	0.2434	0.9994	0.4770	0.2930	0.1792	0.0836	41.92
138	0.2391	0.9951	0.4770	0.4683	0.2513	0.1134	41.46
139	0.2369	0.9627	0.4770	0.5630	0.2880	0.1301	41.67
140	0.2337	0.9145	0.4770	0.6886	0.3014	0.1494	41.35
141	0.2323	0.9078	0.4770	0.7561	0.3123	0.1501	41.76
142	0.2302	0.8601	0.4770	0.8335	0.3444	0.1527	41.22

TABLE A-C-1 (continued)

Temp. = 420°C $\bar{R}$ = 3.01 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
143	12.00	0.2504	0.1579	0.5958	0.0311	0.0129	0.0162
144	20.45	0.2504	0.1579	0.5958	0.0477	0.0195	0.0322
145	28.83	0.2504	0.1579	0.5958	0.0596	0.0250	0.0419
146	36.06	0.2504	0.1579	0.5958	0.0690	0.0290	0.0465
147	41.81	0.2504	0.1579	0.5958	0.0778	0.0324	0.0492
148	49.00	0.2504	0.1579	0.5958	0.0866	0.0365	0.0557

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
143	0.2426	0.1371	0.5958	0.3233	0.1860	0.0895	41.93
144	0.2385	0.1254	0.5958	0.4880	0.2595	0.1296	40.88
145	0.2355	0.1218	0.5958	0.6258	0.3050	0.1538	41.93
146	0.2331	0.1178	0.5958	0.7260	0.3592	0.1655	41.02
147	0.2309	0.1149	0.5958	0.8115	0.3812	0.1722	41.65
148	0.2287	0.1080	0.5958	0.9144	0.4345	0.1885	42.16

TABLE A-C-1 (continued)

Temp. = 420°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
149	12.00	0.2504	0.1894	0.7146	0.0328	0.0139	0.0213
150	20.45	0.2504	0.1894	0.7146	0.0506	0.0210	0.0332
151	28.83	0.2504	0.1894	0.7146	0.0626	0.0283	0.0384
152	36.06	0.2504	0.1894	0.7146	0.0727	0.0305	0.0474
153	41.81	0.2504	0.1894	0.7146	0.0810	0.0341	0.0534
154	49.00	0.2504	0.1894	0.7146	0.0903	0.0384	0.0605
155	72.00	0.1242	0.0939	0.3544	0.1180	0.0493	0.0733
156	96.00	0.1242	0.0939	0.3544	0.1342	0.0565	0.0759

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
149	0.2422	0.1641	0.7146	0.3480	0.1679	0.1023	42.39
150	0.2377	0.1557	0.7146	0.5257	0.2837	0.1321	41.45
151	0.2347	0.1531	0.7146	0.7084	0.3477	0.1451	45.20
152	0.2322	0.1491	0.7146	0.7636	0.3632	0.1677	41.95
153	0.2301	0.1424	0.7146	0.8538	0.3891	0.1827	42.09
154	0.2278	0.1407	0.7146	0.9614	0.4364	0.2006	42.52
155	0.1095	0.0635	0.3544	0.6122	0.2723	0.1153	41.78
156	0.1075	0.0610	0.3544	0.7017	0.3034	0.1186	42.10

TABLE A-C-1 (continued)

Temp. = 420°C $\bar{R}$ = 4.18 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
157	12.00	0.2504	0.2193	0.8274	0.0330	0.0138	0.0223
158	20.45	0.2504	0.2193	0.8274	0.0535	0.0228	0.0257
159	28.83	0.2504	0.2193	0.8274	0.0645	0.0270	0.0371
160	36.06	0.2504	0.2193	0.8274	0.0770	0.0327	0.0435
161	41.81	0.2504	0.2193	0.8274	0.08611	0.0355	0.0471
162	49.00	0.2504	0.2193	0.8274	0.0959	0.0406	0.0540
163	72.00	0.1242	0.1088	0.4104	0.1195	0.0494	0.0735
164	96.00	0.1242	0.1088	0.4104	0.1390	0.0578	0.0798

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
157	0.2421	0.1881	0.8274	0.3453	0.2059	0.1048	41.78
158	0.2370	0.1821	0.8274	0.5707	0.2950	0.1134	42.60
159	0.2342	0.1689	0.8274	0.6758	0.3349	0.1419	41.84
160	0.2311	0.1699	0.8274	0.8186	0.3925	0.1579	42.45
161	0.2288	0.1673	0.8274	0.8887	0.4267	0.1670	41.22
162	0.2264	0.1658	0.8274	1.0165	0.4670	0.1843	42.33
163	0.1094	0.0789	0.4104	0.6134	0.2848	0.1156	41.33
164	0.1069	0.0770	0.4104	0.7179	0.3217	0.1234	41.59

TABLE A-C-1 (continued)

Temp. = 420°C $\bar{R}$ = 5.28 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
165	12.00	0.2504	0.2770	1.0451	0.0385	0.0162	0.0251
166	20.45	0.2504	0.2770	1.0451	0.0589	0.0245	0.0407
167	28.83	0.2504	0.2770	1.0451	0.0715	0.0298	0.0444
168	36.06	0.2504	0.2770	1.0451	0.0837	0.0346	0.0543
169	41.81	0.2504	0.2770	1.0451	0.0918	0.0382	0.0585
170	49.00	0.2504	0.2770	1.0451	0.1022	0.0421	0.0645
171	72.00	0.1242	0.1374	0.5184	0.1325	0.0558	0.0722
172	96.00	0.1242	0.1374	0.5184	0.1503	0.0627	0.0818

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
165	0.2408	0.2657	1.0451	0.4054	0.2277	0.1119	42.05
166	0.2357	0.2386	1.0451	0.6140	0.3066	0.1510	41.60
167	0.2325	0.2407	1.0451	0.7460	0.3964	0.1602	41.67
168	0.2294	0.2408	1.0451	0.8661	0.4095	0.1850	41.31
169	0.2274	0.2215	1.0451	0.9564	0.4437	0.1955	41.62
170	0.2248	0.2095	1.0451	0.1054	0.4925	0.2104	41.18
171	0.1077	0.1067	0.5184	0.6931	0.2998	0.1140	42.12
172	0.1055	0.1002	0.5184	0.7786	0.2961	0.1259	41.70

TABLE A-C-1 (continued)

Temp. = 450°C $\bar{R}$ = 2.41 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
173	12.00	0.2504	0.1264	0.4770	0.04119	0.0163	0.0232
174	20.45	0.2504	0.1264	0.4770	0.0576	0.0232	0.0367
175	28.83	0.2504	0.1264	0.4770	0.0720	0.0280	0.0461
176	36.06	0.2504	0.1264	0.4770	0.0853	0.0330	0.0542
177	41.81	0.2504	0.1264	0.4770	0.0921	0.0368	0.0609
178	49.00	0.2504	0.1264	0.4770	0.1015	0.0395	0.0675

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
173	0.2401	0.1044	0.4770	0.4081	0.2351	0.1071	39.57
174	0.2360	0.0961	0.4770	0.5807	0.2907	0.1409	40.27
175	0.2324	0.0941	0.4770	0.7010	0.3135	0.1644	38.88
176	0.2290	0.0806	0.4770	0.8261	0.3738	0.1847	38.68
177	0.2273	0.0774	0.4770	0.9214	0.4535	0.2015	39.96
178	0.2250	0.0719	0.4770	0.9889	0.4887	0.2179	38.91

TABLE A-C-1 (continued)

Temp. = 450°C $\bar{R}$ = 3.01 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
179	12.00	0.2504	0.1579	0.5958	0.0442	0.0175	0.0280
180	20.45	0.2504	0.1579	0.5958	0.0625	0.0246	0.0393
181	28.83	0.2504	0.1579	0.5958	0.0792	0.0315	0.0503
182	36.06	0.2504	0.1579	0.5958	0.0886	0.0342	0.0548
183	41.81	0.2504	0.1579	0.5958	0.0970	0.0380	0.0603
184	49.00	0.2504	0.1579	0.5958	0.1083	0.0422	0.0644

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
179	0.2393	0.1417	0.5958	0.4380	0.2411	0.1192	39.61
180	0.2347	0.1321	0.5958	0.6159	0.3243	0.1474	39.36
181	0.2306	0.1198	0.5958	0.7879	0.3843	0.1750	39.73
182	0.2282	0.1174	0.5958	0.8564	0.4395	0.1862	39.59
183	0.2261	0.1073	0.5958	0.9514	0.4579	0.2000	39.17
184	0.2233	0.1027	0.5958	1.0565	0.4592	0.2103	38.97

TABLE A-C-1 (continued)

Temp. = 450°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
185	12.00	0.2504	0.1894	0.7146	0.0460	0.0182	0.0258
186	20.45	0.2504	0.1894	0.7146	0.0662	0.0265	0.0446
187	28.83	0.2504	0.1894	0.7146	0.0835	0.0332	0.0541
188	36.06	0.2504	0.1894	0.7146	0.0947	0.0376	0.0574
189	41.81	0.2504	0.1894	0.7146	0.1031	0.0414	0.0648
190	49.00	0.2504	0.1894	0.7146	0.1150	0.0459	0.0714
191	72.00	0.1242	0.0939	0.3544	0.1431	0.0555	0.0869
192	96.00	0.1242	0.0939	0.3544	0.1614	0.0630	0.1034

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
185	0.2389	0.1567	0.7146	0.4557	0.2528	0.1137	39.56
186	0.2338	0.1531	0.7146	0.6635	0.3520	0.1606	40.03
187	0.2295	0.1499	0.7146	0.8314	0.4189	0.1845	39.76
188	0.2267	0.1462	0.7146	0.9415	0.4614	0.1927	39.71
189	0.2246	0.1437	0.7146	1.0368	0.4847	0.2113	40.16
190	0.2216	0.1417	0.7146	1.1490	0.5487	0.2278	39.91
191	0.1064	0.0576	0.3544	0.6892	0.3321	0.1322	38.78
192	0.1041	0.0550	0.3544	0.7824	0.3757	0.1527	39.03

TABLE A-C-1 (continued)

Temp. = 450°C $\bar{R}$ = 4.18 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
193	12.00	0.2504	0.2193	0.8274	0.0514	0.0200	0.0289
194	20.45	0.2504	0.2193	0.8274	0.06971	0.0275	0.0450
195	28.83	0.2504	0.2193	0.8274	0.0871	0.0343	0.0556
196	36.06	0.2504	0.2193	0.8274	0.1003	0.0397	0.0680
197	41.81	0.2504	0.2193	0.8274	0.1080	0.0430	0.0722
198	49.00	0.2504	0.2193	0.8274	0.1242	0.0490	0.0838
199	72.00	0.1242	0.1088	0.4104	0.1492	0.0586	0.0977
200	96.00	0.1242	0.1088	0.4104	0.1728	0.0666	0.1114

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
193	0.2375	0.1846	0.8274	0.5008	0.2839	0.1213	38.90
194	0.2329	0.1839	0.8274	0.6886	0.3495	0.1616	39.45
195	0.2286	0.1857	0.8274	0.8589	0.4298	0.1881	39.39
196	0.2253	0.1832	0.8274	0.9940	0.4875	0.2193	39.58
197	0.2233	0.1802	0.8274	1.0765	0.5173	0.2298	39.81
198	0.2193	0.1526	0.8274	1.2265	0.5834	0.2588	39.46
199	0.1057	0.0727	0.4104	0.7278	0.3417	0.1456	39.28
200	0.1027	0.0649	0.4104	0.8272	0.3890	0.1627	38.54

TABLE A-C-1 (continued)

Temp. = 450°C $\bar{R}$ = 5.28 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr CH_4	Feed mole/hr O_2	Feed mole/hr N_2	Conversion X_{CH_4}	Yield Y_{HCHO}	Yield Y_{CO_2}
201	12.00	0.2504	0.2770	1.0451	0.0539	0.0211	0.0381
202	20.45	0.2504	0.2770	1.0451	0.0802	0.0314	0.0561
203	28.83	0.2504	0.2770	1.0451	0.0985	0.0380	0.0675
204	36.06	0.2504	0.2770	1.0451	0.1112	0.0430	0.0714
205	41.81	0.2504	0.2770	1.0451	0.1210	0.0463	0.0765
206	49.00	0.2504	0.2770	1.0451	0.1341	0.0519	0.0819
207	72.00	0.1242	0.1374	0.5184	0.1589	0.0625	0.1015
208	96.00	0.1242	0.1374	0.5184	0.1866	0.0725	0.1114

Run No.	Products moles/hr CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	Selectivity %S
201	0.2369	0.2604	1.0451	0.5284	0.3251	0.1443	39.16
202	0.2303	0.2498	1.0451	0.7864	0.3999	0.1894	39.15
203	0.2257	0.2251	1.0451	0.9510	0.4205	0.2180	38.58
204	0.2226	0.2188	1.0451	1.0760	0.4725	0.2277	38.671
205	0.2201	0.2178	1.0451	1.1604	0.4908	0.2406	38.31
206	0.2168	0.2145	1.0451	1.2990	0.5541	0.2541	38.70
207	0.1045	0.1090	0.5184	0.7762	0.3761	0.1504	39.33
208	0.1010	0.0964	0.5184	0.9006	0.3978	0.1627	38.85

TABLE A-C-1 (continued)

Temp. = 480°C $\bar{R}$ = 2.41 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
209	12.00	0.2504	0.1264	0.4770	0.0503	0.0174	0.0293
210	20.45	0.2504	0.1264	0.4770	0.0738	0.0259	0.0488
211	28.83	0.2504	0.1264	0.4770	0.0919	0.0304	0.0649
212	36.06	0.2504	0.1264	0.4770	0.1025	0.0327	0.0747
213	41.81	0.2504	0.1264	0.4770	0.1123	0.0379	0.0811
214	49.00	0.2504	0.1264	0.4770	0.1219	0.0418	0.0929

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
209	0.2378	0.9226	0.4770	0.4357	0.2806	0.1224	34.60
210	0.2319	0.8478	0.4770	0.6484	0.3732	0.1712	35.09
211	0.2274	0.8209	0.4770	0.7612	0.4590	0.2114	33.08
212	0.2247	0.7738	0.4770	0.8187	0.5063	0.2360	31.90
213	0.2223	0.7499	0.4770	0.9489	0.5684	0.2521	33.75
214	0.2199	0.7121	0.4770	1.0465	0.6125	0.2817	34.29

TABLE A-C-1 (continued)

Temp. = 480°C $\bar{R}$ = 3.01 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
215	12.00	0.2504	0.1579	0.5958	0.0546	0.0186	0.0340
216	20.45	0.2504	0.1579	0.5958	0.0791	0.0266	0.0514
217	28.83	0.2504	0.1579	0.5958	0.0972	0.0338	0.0669
218	36.06	0.2504	0.1579	0.5958	0.1101	0.0356	0.0778
219	41.81	0.2504	0.1579	0.5958	0.1234	0.0419	0.0822
220	49.00	0.2504	0.1579	0.5958	0.1318	0.0435	0.0917

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
215	0.2367	0.1267	0.5958	0.4657	0.3062	0.1341	34.06
216	0.2306	0.1117	0.5958	0.6661	0.4229	0.1777	33.63
217	0.2261	0.1067	0.5958	0.8463	0.4819	0.2165	34.77
218	0.2228	0.1062	0.5958	0.8913	0.5355	0.2438	32.33
219	0.2195	0.1027	0.5958	1.0495	0.5386	0.2548	33.95
220	0.2174	0.09903	0.5958	1.0890	0.5491	0.2786	33.00

TABLE A-C-1 (continued)

Temp. = 480°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
221	12.00	0.2504	0.1894	0.7146	0.0587	0.0195	0.0433
222	20.45	0.2504	0.1894	0.7146	0.0842	0.0263	0.0609
223	28.83	0.2504	0.1894	0.7146	0.1061	0.0374	0.0711
224	36.06	0.2504	0.1894	0.7146	0.1192	0.0391	0.0803
225	41.81	0.2504	0.1894	0.7146	0.1315	0.0445	0.0887
226	49.00	0.2504	0.1894	0.7146	0.1385	0.0455	0.0939
227	72.00	0.1242	0.0939	0.3544	0.1732	0.0571	0.1245
228	96.00	0.1242	0.0939	0.3544	0.1925	0.0650	0.1362

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
221	0.2357	0.1518	0.7146	0.4882	0.2690	0.1574	33.22
222	0.2293	0.1396	0.7146	0.6586	0.4267	0.2014	31.24
223	0.2238	0.1375	0.7146	0.9363	0.5284	0.2272	35.25
224	0.2205	0.1367	0.7146	0.9192	0.5829	0.2501	32.80
225	0.2175	0.1359	0.7146	1.1145	0.6546	0.2711	33.84
226	0.2157	0.1305	0.7146	1.1390	0.6827	0.2841	32.85
227	0.1027	0.0523	0.3544	0.7091	0.3605	0.1789	32.97
228	0.1003	0.0670	0.3544	0.8073	0.4577	0.1935	33.25

TABLE A-C-1 (continued)

Temp. = 480°C $\bar{R}$ = 4.18 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
229	12.00	0.2504	0.2193	0.8274	0.0640	0.0224	0.0478
230	20.45	0.2504	0.2193	0.8274	0.0914	0.0280	0.0581
231	28.83	0.2504	0.2193	0.8274	0.1109	0.0370	0.0763
232	36.06	0.2504	0.2193	0.8274	0.1252	0.0415	0.0818
233	41.81	0.2504	0.2193	0.8274	0.1360	0.0451	0.0923
234	49.00	0.2504	0.2193	0.8274	0.1501	0.0502	0.1082
235	72.00	0.1242	0.1088	0.4104	0.1815	0.0625	0.1229
236	96.00	0.1242	0.1088	0.4104	0.2080	0.0723	0.1468

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
229	0.2344	0.1771	0.8274	0.5606	0.3476	0.1687	34.99
230	0.2275	0.1631	0.8274	0.7009	0.4932	0.1946	30.63
231	0.2226	0.1637	0.8274	0.9264	0.5335	0.2401	33.36
232	0.2190	0.1632	0.8274	1.0390	0.5370	0.2538	33.14
233	0.2163	0.1592	0.8274	1.1292	0.5777	0.2801	33.16
234	0.2128	0.1551	0.8274	1.2567	0.6228	0.3200	33.43
235	0.1017	0.0711	0.4104	0.7761	0.3629	0.1769	34.43
236	0.0984	0.0589	0.4104	0.8978	0.4239	0.2066	34.76

TABLE A-C-1 (continued)

Temp. = 480°C $\bar{R}$ = 5.28 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
237	12.00	0.2504	0.2770	1.0451	0.0792	0.0263	0.0593
238	20.45	0.2504	0.2770	1.0451	0.1037	0.0340	0.0757
239	28.83	0.2504	0.2770	1.0451	0.1273	0.0398	0.0860
240	36.06	0.2504	0.2770	1.0451	0.1414	0.0460	0.1018
241	41.81	0.2504	0.2770	1.0451	0.1561	0.0503	0.1079
242	49.00	0.2504	0.2770	1.0451	0.1720	0.0576	0.1079
243	72.00	0.1242	0.1374	0.5184	0.1960	0.0660	0.1305
244	96.00	0.1242	0.1374	0.5184	0.2258	0.0773	0.1622

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	%S
237	0.2306	0.2418	1.0451	0.6584	0.4116	0.1974	33.19
238	0.2244	0.2346	1.0451	0.8510	0.5318	0.2385	32.776
239	0.2185	0.2273	1.0451	0.9964	0.6347	0.2647	31.26
240	0.2150	0.2191	1.0451	1.1510	0.6898	0.3039	32.53
241	0.2113	0.2128	1.0451	1.2586	0.7619	0.3192	32.20
242	0.2073	0.1886	1.0451	1.4422	0.8086	0.3347	33.49
243	0.0999	0.0881	0.5184	0.8196	0.4523	0.1963	33.67
244	0.0962	0.0810	0.5184	0.9601	0.5186	0.2257	34.23

TABLE A-C-1 (continued)

Temp. = 510°C $\bar{R}$ = 2.41 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
245	12.00	0.2504	0.1264	0.4770	0.0697	0.0156	0.0566
246	20.45	0.2504	0.1264	0.4770	0.0974	0.0217	0.0794
247	28.83	0.2504	0.1264	0.4770	0.1163	0.0255	0.0941
248	36.06	0.2504	0.1264	0.4770	0.1332	0.0282	0.0994
249	41.81	0.2504	0.1264	0.4770	0.1417	0.0320	0.1038
250	49.00	0.2504	0.1264	0.4770	0.1522	0.0334	0.1101

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
245	0.2329	0.9045	0.4770	0.3905	0.3750	0.1907	23.04
246	0.2260	0.7220	0.4770	0.5433	0.5141	0.2478	22.28
247	0.2213	0.6271	0.4770	0.6385	0.5912	0.2846	21.92
248	0.2170	0.5642	0.4770	0.7060	0.6195	0.2978	21.17
249	0.2149	0.5305	0.4770	0.8011	0.6388	0.3089	22.58
250	0.2123	0.4901	0.4770	0.8362	0.7592	0.3248	21.94

TABLE A-C-1 (continued)

Temp. = 510°C $\bar{R}$ = 3.01 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
251	12.00	0.2504	0.1579	0.5958	0.0766	0.0169	0.0634
252	20.45	0.2504	0.1579	0.5958	0.1057	0.0242	0.0863
253	28.83	0.2504	0.1579	0.5958	0.1283	0.0275	0.1092
254	36.06	0.2504	0.1579	0.5958	0.1447	0.0320	0.1115
255	41.81	0.2504	0.1579	0.5958	0.1580	0.0341	0.1148
256	49.00	0.2504	0.1579	0.5958	0.1669	0.0350	0.1249

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	
251	0.2312	0.1198	0.5958	0.4230	0.4073	0.2078	22.65
252	0.2239	0.1019	0.5958	0.6058	0.5586	0.2651	22.89
253	0.2183	0.08842	0.5958	0.6885	0.6624	0.3223	21.43
254	0.2142	0.08163	0.5958	0.8012	0.7102	0.3282	22.11
255	0.2108	0.07925	0.5958	0.8537	0.7132	0.3365	21.58
256	0.2086	0.07870	0.5958	0.8763	0.7394	0.3618	20.97

TABLE A-C-1 (continued)

Temp. = 510°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
257	12.00	0.2504	0.1894	0.7146	0.0831	0.0184	0.0579
258	20.45	0.2504	0.1894	0.7146	0.1143	0.0265	0.0935
259	28.83	0.2504	0.1894	0.7146	0.1381	0.0295	0.1146
260	36.06	0.2504	0.1894	0.7146	0.1573	0.0346	0.1222
261	41.81	0.2504	0.1894	0.7146	0.1679	0.0370	0.1327
262	49.00	0.2504	0.1894	0.7146	0.1791	0.0376	0.1432
263	72.00	0.1242	0.0939	0.3544	0.2114	0.0441	0.1748
264	96.00	0.1242	0.0939	0.3544	0.2446	0.0515	0.2061

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
257	0.2296	0.1363	0.7146	0.4607	0.4512	0.1940	22.14
258	0.2218	0.1245	0.7146	0.6634	0.5977	0.2832	23.18
259	0.2158	0.1239	0.7146	0.7386	0.6901	0.3360	21.36
260	0.2110	0.1109	0.7146	0.8663	0.7053	0.3550	22.00
261	0.2084	0.1104	0.7146	0.9264	0.7618	0.3813	22.04
262	0.2055	0.1028	0.7146	0.9414	0.8089	0.4076	20.99
263	0.0979	0.0404	0.3544	0.5477	0.5238	0.2414	20.86
264	0.0938	0.0381	0.3544	0.6395	0.5383	0.2802	21.05

TABLE A-C-1 (continued)

Temp. = 510°C $\bar{R}$ = 4.18 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr CH_4	Feed mole/hr O_2	Feed mole/hr N_2	Conversion X_{CH_4}	Yield Y_{HCHO}	Yield Y_{CO_2}
265	12.00	0.2504	0.2193	0.8274	0.0924	0.0205	0.0719
266	20.45	0.2504	0.2193	0.8274	0.1240	0.0273	0.1085
267	28.83	0.2504	0.2193	0.8274	0.1492	0.0322	0.1258
268	36.06	0.2504	0.2193	0.8274	0.1672	0.0377	0.1323
269	41.81	0.2504	0.2193	0.8274	0.1785	0.0408	0.1475
270	49.00	0.2504	0.2193	0.8274	0.1945	0.0422	0.1595
271	72.00	0.1242	0.1088	0.4104	0.2268	0.0478	0.1802
272	96.00	0.1242	0.1088	0.4104	0.2590	0.0543	0.2128

Run No.	Products moles/hr CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	Selectivity %S
265	0.2273	0.1807	0.8274	0.5134	0.4963	0.2290	22.19
266	0.2193	0.1632	0.8274	0.6831	0.6499	0.3206	22.00
267	0.2130	0.1516	0.8274	0.8063	0.7856	0.3640	21.58
268	0.2085	0.1425	0.8274	0.9440	0.8017	0.3802	22.55
269	0.2057	0.1261	0.8274	1.0220	0.8096	0.4185	22.86
270	0.2017	0.1185	0.8274	1.0560	0.8560	0.4485	21.70
271	0.0960	0.0515	0.4104	0.5937	0.5646	0.2481	21.08
272	0.0920	0.0523	0.4104	0.6743	0.6182	0.2886	21.44

TABLE A-C-1 (continued)

Temp. = 510°C $\bar{R}$ = 5.28 $\bar{Z}$ = 0.0195

Run No.	W/F gm.hr/mole	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
273	12.00	0.2504	0.2770	1.0451	0.1145	0.0258	0.0802
274	20.45	0.2504	0.2770	1.0451	0.1443	0.0328	0.1047
275	28.83	0.2504	0.2770	1.0451	0.1735	0.0377	0.1262
276	36.06	0.2504	0.2770	1.0451	0.1920	0.0435	0.1552
277	41.81	0.2504	0.2770	1.0451	0.2027	0.0445	0.1644
278	49.00	0.2504	0.2770	1.0451	0.2212	0.0486	0.1777
279	72.00	0.2504	0.1374	0.5184	0.2619	0.0594	0.2143
280	96.00	0.2504	0.1374	0.5184	0.2845	0.0624	0.2319

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
273	0.2217	0.2220	1.0451	0.6462	0.5774	0.2498	22.54
274	0.2143	0.1951	1.0451	0.8214	0.7540	0.3111	22.74
275	0.2070	0.1906	1.0451	0.9441	0.8823	0.3650	21.73
276	0.2023	0.1895	1.0451	1.0890	0.9438	0.4375	22.66
277	0.1996	0.1803	1.0451	1.1145	1.0201	0.4607	21.96
278	0.1950	0.1763	1.0451	1.2175	1.1002	0.4940	21.97
279	0.0917	0.0776	0.5184	0.7378	0.5641	0.2904	22.68
280	0.0889	0.0735	0.5184	0.7750	0.6220	0.3123	21.93

TABLE A-C-2

Stability of the Chlorine Modified Palladium Catalyst

for Methane Oxidation

Temp. = 480°C $\overline{R}$ = 3.61 $\overline{Z}$ = 0.0195

Run No.	W/F	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
226	49.0	0.2504	0.1894	0.7146	0.1385	0.0455	0.0939
226a	49.0	0.2504	0.1894	0.7146	0.1406	0.0464	0.0943
226b	49.0	0.2504	0.1894	0.7146	0.1398	0.0469	0.0868
226c	49.0	0.2504	0.1894	0.7146	0.1376	0.0458	0.0948

Run No.	Products mole/hr						Time after Initial Steady-State Hrs.
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
226	0.2157	0.1305	0.7146	1.1390	0.6827	0.2841	2
226a	0.2152	0.1284	0.7146	1.1621	0.7165	0.2852	24
226b	0.2154	0.1294	0.7146	1.1744	0.6714	0.2664	48
226c	0.2159	0.1242	0.7146	1.1469	0.6908	0.2864	72

TABLE A-C-3

Experimental Data for Oxidation of Formaldehyde Over

Chlorine Modified Palladium Catalyst

Temp.= 480°C W = 10.05 gm

Run No.	Feed moles/hr					Conversion
	CH_2Cl_2	HCHO x 10	H_2O	O_2	N_2	HCHO
281	0.0	0.3264	0.1370	0.2619	0.9881	1.000
282	0.0010	0.3264	0.1370	0.2619	0.9881	0.8441
283	0.0024	0.3264	0.1370	0.2619	0.9881	0.7125
284	0.0049	0.3264	0.1370	0.2619	0.9881	0.6107
285	0.0098	0.3264	0.1370	0.2619	0.9881	0.5206
286	0.0122	0.3264	0.1370	0.2619	0.9881	0.4612

Run No.	Products moles/hr					
	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	CO x 10^2
281	0.2309	0.9881	-	1.6736	0.3382	-
282	0.2352	0.9881	0.5089	1.6242	0.2932	-
283	0.2381	0.9881	0.9383	1.6337	0.2619	-
284	0.2332	0.9881	1.2707	1.6382	0.2414	-
285	0.2316	0.9881	1.5648	1.6557	0.2598	-
286	0.2311	0.9881	1.7590	1.6183	0.2635	0.2410

TABLE A-C-4

Experimental Data for Oxidation of Methane Over Palladium Catalyst

Modified with Methylene Chloride

Temp. = 450°C $\bar{R}$ = 4.18 W/F = 36.06 gm.hr/gm mole

Run No.	$\bar{Z}$	Feed mole/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
196a	0.0	0.2504	0.2193	0.8274	0.1282	-	0.1323
196b	0.0097	0.2504	0.2193	0.8274	0.1107	0.0332	0.0807
196	0.0195	0.2504	0.2193	0.8274	0.1003	0.0397	0.0680
196c	0.0391	0.2504	0.2193	0.8274	0.0863	0.0474	0.0377

Run No.	Products moles/hr						Selectivity %S
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
196a	0.2183	0.1574	0.8274	-	0.6521	0.3312	-
196b	0.2268	0.1681	0.8274	0.8315	0.5479	0.2264	30.00
196	0.2253	0.1832	0.8274	0.9940	0.4875	0.2193	39.58
196c	0.2288	0.1653	0.8274	1.1870	0.5184	0.1925	54.92

TABLE A-C-4 (cont'd)

Experimental Data for Oxidation of Methane Over Palladium Catalyst

Modified with Methylene Chloride

Temp. = 475°C $\bar{R}$ = 5.03 W/F = 38.33 gm.hr/gm mole

Run No.	Feed moles/hr				Conversion	Yield	
	CH_2Cl_2	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
301	0.0	0.2614	0.2755	1.0394	0.1975	-	0.1975
302	0.0001	0.2614	0.2755	1.0394	0.1811	0.0317	0.1494
303	0.0024	0.2614	0.2755	1.0394	0.1592	0.0385	0.1207
304	0.0049	0.2614	0.2755	1.0394	0.1522	0.0496	0.1026
305	0.0098	0.2614	0.2755	1.0394	0.1390	0.0636	0.0754
306	0.0122	0.2614	0.2755	1.0394	0.1307	0.0642	0.0665

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10	%S
301	0.2098	0.1762	1.0394	-	0.9915	0.0535	-
302	0.2141	0.1843	1.0394	0.8287	0.8707	0.3875	17.50
303	0.2198	0.1915	1.0394	1.0066	0.8214	0.3524	24.18
304	0.2216	0.1932	1.0394	1.2968	0.7949	0.3271	32.72
305	0.2251	0.1929	1.0394	1.6630	0.7707	0.2814	45.75
306	0.2272	0.1997	1.0394	1.6785	0.7628	0.2555	49.12

TABLE A-C-5

Experimental Data for Oxidation of Methane Over Palladium Catalyst Modified with Methyl Chloride

Temp. = 475°C $\bar{R}$ = 5.03 W/F = 38.33 gm.hr/gm mole

Run No.	Feed mole/hr				Conversion	Yield
	CH_3Cl	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}
310	0.0	0.2614	0.2755	1.0394	0.2003	-
311	0.0008	0.2614	0.2755	1.0394	0.1614	0.0128
312	0.0022	0.2614	0.2755	1.0394	0.1447	0.0224
313	0.0040	0.2614	0.2755	1.0394	0.1352	0.0305
314	0.0080	0.2614	0.2755	1.0394	0.1079	0.0381
315	0.0120	0.2614	0.2755	1.0394	0.0945	0.0398

Run No.	Products moles/hr					
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$
310	0.2090	0.1657	1.0394	-	1.0172	0.5328
311	0.2192	0.1928	1.0394	0.3346	0.8063	0.4164
312	0.2236	0.1943	1.0394	0.5856	0.7619	0.3517
313	0.2260	0.1957	1.0394	0.7973	0.7271	0.3337
314	0.2332	0.2075	1.0394	0.9962	0.6545	0.2724
315	0.2367	0.2116	1.0394	1.0407	0.6102	0.2377

TABLE A-C-6

Experimental Data for Oxidation of Methane Over Palladium Catalyst

Modified with Tri-chloro Methane

Temp. = 475°C $\bar{R}$ = 5.03 W/F = 38.33 gm.hr/gm mole

Run No.	Feed mole/hr				Conversion	Yield
	$CH\ Cl_3$	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}
320	0.0	0.2614	0.2755	1.0394	0.1987	-
321	0.0008	0.2614	0.2755	1.0394	0.1661	0.0161
322	0.0019	0.2614	0.2755	1.0394	0.1542	0.0237
323	0.0039	0.2614	0.2755	1.0394	0.1403	0.0353
324	0.0079	0.2614	0.2755	1.0394	0.1230	0.0342
325	0.0098	0.2614	0.2755	1.0394	0.1092	0.0337

Run No.	Products moles/hr						
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	$CO \times 10^2$
320	0.2095	0.1666	1.0394	-	1.0158	0.5494	-
321	0.2180	0.2242	1.0394	0.4210	0.8623	0.4191	-
322	0.2211	0.1980	1.0394	0.6196	0.8042	0.3911	-
323	0.2247	0.1963	1.0394	0.9228	0.7115	0.2896	-
324	0.2292	0.2097	1.0394	0.8948	0.5669	0.2187	0.2087
325	0.2328	0.2388	1.0394	0.8809	0.5404	0.2322	0.4162

TABLE A-C-7

Experimental Data for Oxidation of Methane over Palladium Catalyst

Modified with Carbon Tetra-Chloride

Temp. = 475^{o}C $\bar{R}$ = 5.03   W/F = 38.33 gm.hr/gm mole

Run No.	Feed moles/hr				Conversion
	CCl_4	CH_4	O_2	N_2	X_{CH_4}
330	0.0	0.2614	0.2755	1.0394	0.1969
331	0.0007	0.2614	0.2755	1.0394	0.1497
332	0.0016	0.2614	0.2755	1.0394	0.1380
333	0.0033	0.2614	0.2755	1.0394	0.1291
334	0.0065	0.2614	0.2755	1.0394	0.1083
335	0.0081	0.2614	0.7712	1.0394	0.0890

Run No.	Products moles/hr					
	CH_4	O_2	N_2	H_2O x 10	CO_2 x 10	CO_2x10^2
330	0.2099	0.1625	0.1394	1.1281	0.5297	-
331	0.2223	0.1902	1.0394	0.8259	0.4132	-
332	0.2253	0.2104	1.0394	0.7874	0.3686	-
333	0.2276	0.2147	1.0394	0.7392	0.3825	-
334	0.2331	0.2228	1.0394	0.5605	0.2617	0.4245
335	0.2381	0.2253	1.0394	0.4144	0.2014	0.5640

TABLE A-C-8

Experimental Data for Oxidation of Methane over Palladium Catalyst

Modified with Methyl Iodide

Temp. = 475^{o}C $\bar{R}$ = 5.03   W/F = 38.33 gm.hr/gm mole

Run No.	Feed moles/hr				Conversion	Yield
	CH_3I	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}
340	0.0	0.2614	0.2755	1.0394	0.2004	-
341	0.0005	0.2614	0.2755	1.0394	0.1438	0.0140
342	0.0012	0.2614	0.2755	1.0394	0.1210	0.0142
343	0.0025	0.2614	0.2755	1.0394	0.0752	0.0129
344	0.0050	0.2614	0.2755	1.0394	0.0383	0.0050

Run No.	Products moles/hr					
	CH_4	O_2	N_2	HCHO x 10^2	H_2O x 10	CO_2 x 10
340	0.2080	0.1678	1.0394	-	1.0177	0.5384
341	0.2238	0.2003	1.0394	0.3665	0.6961	0.3323
342	0.2298	0.2065	1.0394	0.3717	0.6771	0.3017
343	0.2417	0.2409	1.0394	0.3372	0.4416	0.1778
344	0.2514	0.2449	1.0394	0.1308	0.3152	0.1161

TABLE A-C-9

Experimental Data for Oxidation of Methane over Palladium Catalyst

Modified with Methylene Iodide

Temp. = 475°C $\bar{R}$ = 5.03 W/F = 38.33 gm.hr/gm mole

Run No.	Feed moles/hr				Conversion	Yield
	CH_2I_2	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}
350	0.0	0.2614	0.2755	1.0394	0.2015	-
351	0.0004	0.2614	0.2755	1.0394	0.1642	0.0184
352	0.0010	0.2614	0.2755	1.0394	0.1371	0.0147
353	0.0020	0.2614	0.2755	1.0394	0.0783	0.0103
354	0.0039	0.2614	0.2755	1.0394	0.0314	0.0065

Run No.	Products moles/hr					
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$
350	0.2087	0.1747	1.0394	-	1.0834	0.5117
351	0.2185	0.1946	1.0394	0.4810	0.8922	0.3971
352	0.2256	0.2142	1.0394	0.3843	0.6548	0.3187
353	0.2409	0.2285	1.0394	0.2692	0.4527	0.2004
354	0.2532	0.2543	1.0394	0.1699	0.2166	0.1038

TABLE A-C-10

Experimental Data for Oxidation of Methane Over Palladium Catalyst

Modified with Methylene Bromide

Temp. = 475°C $\bar{R}$ = 5.03 W/F = 38.33 gm.hr/gm mole

Run No.	Feed mole/hr				Conversion	Yield	
	CH_2Br_2	CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
360	0.0	0.2614	0.2755	1.0394	0.2018	-	0.2018
361	0.0004	0.2614	0.2755	1.0394	0.1730	0.0224	0.1506
362	0.0011	0.2614	0.2755	1.0394	0.1435	0.0306	0.1129
363	0.0022	0.2614	0.2755	1.0394	0.1008	0.0310	0.0698
364	0.0045	0.2614	0.2755	1.0394	0.0662	0.0255	0.0407
365	0.0090	0.2614	0.2755	1.0394	0.0421	0.0187	0.0234

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
360	0.2086	0.1732	1.0394	-	1.0435	0.5199	-
361	0.2162	0.1955	1.0394	0.5855	0.8403	0.3857	12.95
362	0.2239	0.1994	1.0394	0.7999	0.6992	0.2996	21.32
363	0.2350	0.2208	1.0394	0.8107	0.5407	0.2148	30.75
364	0.2441	0.2396	1.0394	0.6666	0.3952	0.1544	38.52
365	0.2478	0.2417	1.0394	0.4899	0.2880	0.1355	44.42

TABLE A-C-11

Experimental Data for Effect of Temperature on Oxidation of Methane Over Palladium Catalyst Modified with Methylene Bromide

W/F = 38.33 gm.hr/gm mole $\bar{R} = 5.03$ $\bar{Z} = 0.0085$

Run No.	Temp. °C	Feed moles/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
370	400	0.2614	0.2755	1.0394	0.0631	0.0208	0.0403
371	420	0.2614	0.2755	1.0394	0.0759	0.0268	0.0514
372	440	0.2614	0.2755	1.0394	0.0822	0.0305	0.0552
373	460	0.2614	0.2755	1.0394	0.0948	0.0309	0.0618
374	480	0.2614	0.2755	1.0394	0.1089	0.0308	0.0742
375	500	0.2614	0.2755	1.0394	0.1485	0.0397	0.1126
376	520	0.2614	0.2755	1.0394	0.1877	0.0388	0.1475

Run No.	Products moles/hr						Selectivity
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	%S
370	0.2449	0.2507	1.0394	0.5450	0.3251	0.1278	33.04
371	0.2416	0.2435	1.0394	0.7003	0.3953	0.1567	35.30
372	0.2399	0.2264	1.0396	0.7973	0.4287	0.1665	37.10
373	0.2366	0.2373	1.0394	0.8090	0.4741	0.1841	32.65
374	0.2329	0.2279	1.0394	0.8052	0.4973	0.2164	28.28
375	0.2226	0.1932	1.0394	1.3724	0.7341	0.3168	26.72
376	0.2123	0.1811	1.0394	1.0319	0.8889	0.4079	20.65

APPENDIX D

Sample Calculation and Material Balance

Sample Calculation:

A sample calculation for the experimental result of run No.234 is described below:

(1) Moles in:

Moles of CH_4/hr

$$= \frac{5609.0 \text{ cc/hr}}{22400 \text{ cc/gm mole}} = 0.2504 \text{ gm mole/hr}$$

Moles of O_2/hr

$$= \frac{23446.0 \text{ cc/hr} \times 0.2095}{22400 \text{ cc/gm mole}} = 0.2193 \text{ gm mole/hr}$$

Moles of N_2/hr

$$= \frac{23446.0 \text{ cc/hr} \times 0.7905}{22400 \text{ cc/gm mole}} = 0.8274 \text{ gm mole/hr}$$

Moles of CH_2Cl_2

$$= \frac{0.3167 \text{ cc/hr} \times 1.315 \text{ gm/cc}}{85.0 \text{ gm/gm mole}} = 0.0049 \text{ gm mole/hr}$$

Total moles in = 0.2504 + 0.2193 + 0.8274 + 0.0049

= 1.3020 gm mole/hr

(2) Moles out:

Analysis

(A) From Fisher Gas Partitioner

Component	Peak Area	Area Ratio $\frac{\text{Component}}{N_2}$	Calibration Factor $\frac{\text{Area Ratio}}{\text{Mole Ratio}}$	Mole Ratio $\frac{\text{Component}}{N_2}$
CO_2	1144	0.0460	1.1891	0.03868
O_2	4663	0.1875	1.0000	0.18749
N_2	2487 x 10	1.0000	--	--
CH_4	5569	0.2239	0.8705	0.25723

(B) From H-P Gas Chromatograph

Component	Peak Area	Calibration Factor Area/(mole % Component)	mole %
HCHO	4604	4770	0.96520
H_2O	1423 x 10	2975	4.78319

The molar flow rates of non-condensable gaseous components in the product stream (analysed from Fisher Gas Partitioner) were calculated on the basis of input rate of nitrogen in the feed. The molar flow rates of liquid components analysed from H-P Gas Chromatograph were calculated on the basis of total molar flow rate of the reactants and modifier in the feed.

Moles N_2/hr	=	0.8274 gm mole/hr		
Moles CO_2/hr	=	0.03868 x 0.8274	=	0.03200 gm mole/hr
Moles O_2/hr	=	0.18749 x 0.8274	=	0.15512 gm mole/hr
Moles CH_4/hr	=	0.25723 x 0.8274	=	0.21283 gm mole/hr
Moles HCHO/hr	=	$\frac{0.96520}{100}$ x 1.302	=	0.01257 gm mole/hr
Moles H_2O/hr	=	$\frac{4.78319}{100}$ x 1.302	=	0.06228 gm mole/hr

$$\text{Conversion of } CH_4 = \frac{0.2504 - 0.2128}{0.2504} = 0.1501$$

$$\text{Yield of } CO_2 = \frac{0.0320 - 0.0049}{0.2504} = 0.1082$$

$$\text{Yield of HCHO} = \frac{0.01257}{0.2504} = 0.0502$$

$$\begin{array}{l}\text{Selectivity of}\\ \text{HCHO formation}\end{array} = \frac{0.01257}{0.2504 - 0.2128} \times 100 = 33.43\%$$

Material Balance

(a) Based on atomic oxygen

Component	in feed moles/hr	in product moles/hr
O_2	0.43860	0.31024
CO_2		0.06400
HCHO		0.01257
H_2O		0.06228
Total	0.43860	0.44909

$$\% \text{ deviation} = \frac{0.43860 - 0.44909}{0.43860} \times 100 = -2.38\%$$

(b) Based on atomic hydrogen

Component	in feed moles/hr	in product moles/hr
CH_4	1.0016	0.84932
HCHO		0.02514
H_2O		0.12456
CH_2Cl_2	0.0098	
TOTAL	1.0114	0.99902

$$\% \text{ deviation} = \frac{1.0114 - 0.99902}{1.0114} \times 100$$

$$= 1.22\%$$

(c) Based on atomic carbon

Component	in feed moles/hr	in product moles/hr
CH_4	0.2504	0.21283
CO_2		0.03200
HCHO		0.01257
CH_2Cl_2	0.0049	
TOTAL	0.2553	0.25740

$$\% \text{ deviation} = \frac{0.2553 - 0.2574}{0.2553} \times 100$$

$$= -0.82\%$$

APPENDIX E

External Resistance to Mass and Heat Transfer

(1) Drop in Partial Pressure from Catalyst Particle to Ambient Gas Stream

The data for estimation of external diffusion are taken from run No.242 with the following conditions:

Temperature = 480°C

W/F = 49.00 gm.hr/gm mole

$\bar{R}$ = 5.28

W = 12.27 gm.

The composition of inlet and outlet streams:

Component	Inlet		Outlet	
	gm moles/hr	Mole Fraction	gm mole/hr	Mole Fraction
CH_4	0.2504	0.1592	0.2073	0.1321
HCHO			0.0144	0.0092
H_2O			0.0809	0.0515
CO_2			0.0335	0.0213
O_2	0.2770	0.1762	0.1886	0.1201
N_2	1.0451	0.6646	1.0451	0.6657
TOTAL	1.5725	1.000	1.5698	0.9999

The drop in partial pressure for each component was estimated using the method of Yoshida et al. in the following way:

(i) Calculation of dimensionless term R_j

$$R_j = \frac{r_{m_j}}{a_m \ \phi \ G_m}$$

Where

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

$= \frac{\text{(moles in - moles out) per hour of component j}}{\text{wt. of catalyst}}$

a_m = specific surface area of catalyst

$= 98.0 \times 10^4 \ cm^2/gm$

ϕ = shape factor

= 0.9 for irregular grannules

G_m = molar mass velocity based on total cross-sectional area of catalyst bed in moles/hr.cm^2

$$= \frac{1.5725}{\frac{\pi}{4}(2.54 \times 0.375)^2}$$

$= 2.2068$ moles/hr.cm^2

$a_m \ \phi G_m = 98.0 \times 10^4 \times 0.9 \times 2.2068$

$= 19.4640 \times 10^5$

(ii) Calculation of partial pressure drop $\Delta p_j/p_j$

y_j = mole fraction of component j at the interface

$\doteqdot [(y_j)_{in} + (y_j)_{out}]/2$

The factor R_j/y_j is calculated for each component and the corresponding value of $\Delta p_j/p_j$ versus R_j/y_j plot given in Figure 2 of Reference No.86 (Yoshida et al.). These values are listed below:

Component	y_j	$r_{m_j} \times 10^2$	$R_j \times 10^8$	$(R_j/y_j) \times 10^6$	$(\Delta p_j/p_j)_{max}$
CH_4	0.1457	0.3513	0.1805	0.0123	<0.0001
HCHO	0.0046	0.1174	0.0603	0.1311	<0.0001
H_2O	0.0258	0.6593	0.3387	0.1312	<0.0001
CO_2	0.0106	0.2730	0.1402	0.1323	<0.0001
O_2	0.1481	0.7204	0.3701	0.0250	<0.0001
N_2	0.6652				

Since the $\Delta p_j/p_j$ is less than 0.0001 for all the components, the external diffusion effect can be neglected.

(2) Temperature Drop from Catalyst Particle to Ambient Gas Stream

A simplified method described by Yoshida et al.[86] has been used to calculate the temperature drop from catalyst particle to ambient gas stream during reaction, in the following way:

$$Q = \frac{r_{m_A}}{a_m} \frac{\Delta H_A}{\phi C_p G_m}$$

where

ΔH_A = molar heat of reaction of component A

and, C_p = molar heat capacity at constant pressure of the gas stream which is calculated as follow:

Component j	Average Mole Fraction y_j	$(C_p)_j$ at 480°C	$(C_p)_j\ y_j$
CH_4	0.1457	14.530	2.1170
HCHO	0.0046	12.944	0.0595
H_2O	0.0258	9.147	0.2360
CO_2	0.0106	12.032	0.1275
O_2	0.1481	7.960	1.1789
N_2	0.6652	7.465	4.9657

$$C_p = \Sigma_j (C_p)_j \cdot y_j$$

$$= 8.685 \ \text{cal/gm mole} \ ^{\circ}C$$

$$G_m = 2.2068 \ \text{gm mole/hr.cm}^2$$

$$\phi = 0.9$$

$$a_m = 98.0 \times 10^4 \ \text{cm}^2/\text{gm}$$

$$r_{m_{CH_4}} = 0.3513 \times 10^{-2} \ \text{moles/hr.gm catalyst}$$

$$\Delta H_{CH_4} \ \text{at } 480^{\circ}C = -196,470 \ \text{cal/gm mole}$$

$$Q = \frac{0.3513 \times 10^{-2} \times 19.6470 \times 10^4}{98.0 \times 10^4 \times 0.9 \times 8.685 \times 2.2068}$$

$$= 0.4083 \times 10^{-4}$$

The value of ΔT corresponding to the above value of Q, obtained from ΔT vs Q plot given in Figure 4 of reference 86 (Yoshida et al.), was less than $0.1^{\circ}C$ and thus the catalyst surface temperature effect can be neglected.

APPENDIX F

Effect of Internal Diffusion

Internal Diffusion

a) Molecular Diffusion (Effect of Feed Velocity on Conversion)

The experimental results for molecular diffusion are given in table A-F-1. The constancy of conversion with varying feed velocity indicates that molecular diffusion is not important in the catalytic oxidation of methane.

b) Knudsen Diffusion and Effectiveness Factor

An estimate of Knudsen diffusion and effectiveness factor for the γ-alumina supported palladium catalyst used in the present study is calculated (for Run 242) by modified Thiele method which is given as follows:

Temperature = $480^{\circ}C$

$\bar{R}$ = 5.28

W/F = 49.00 gm.hr/gm mole

W = 12.27 gm.

(i) Calculation for average molecular weight of gas mixture:

Component	Mole Fraction Input	Mole Fraction Output	Average Mole Fraction (N_{av})	n_{av} x mol.wt.
CH_4	0.1592	0.1321	0.1457	2.3312
HCHO		0.0092	0.0046	0.1380
H_2O		0.0515	0.0258	0.4644
CO_2		0.0213	0.0106	0.4664
O_2	0.1762	0.1201	0.1481	4.7392
N_2	0.6646	0.6657	0.6652	18.6256
				26.7648

$$M_{av} = \Sigma\ M \times n_{av} = 26.7648$$

(ii) Calculation of Knudsen diffusion coefficent, $D_{K,eff.}$:

$$D_{K,eff} = 19400 \frac{\beta^2}{\tau\ Sg\ \rho_p} \sqrt{T/M}$$

where

T = reaction temperature = 753^oK

β = porosity of catalyst = 0.40

τ = tortuosity = 5

Sg = catalyst surface area = $98 \times 10^4\ cm^2/gm$

ρ_p = particle density = 1.9346 gm/c.c.

M = average molecular weight = 26.7648

The tortuosity is an empirical factor related to pore geometry and its value must be estimated. The value of tortuosity is conservatively estimated to be about 5 for a 0.5% palladium catalyst supported on γ-alumina

$$D_{K,eff} = 19,400 \frac{(0.4)^2}{5 \times 98 \times 10^4 \times 1.9346} \sqrt{\frac{753}{26.765}}$$

$$= 1.7368 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

(iii) Calculation of reaction (diffusion) rate

$$r = \frac{0.2504 - 0.2073}{12.27} = 0.00351 \text{ gm mole/gm.hr}$$

$$= \frac{0.00351 \times 1.9346}{3600} = 1.886 \times 10^{-6} \text{ gm mole/sec./c.c. of catalyst}$$

(iv) Calculation of reaction concentration, C:

Average mole fraction of methane = 0.1457

$$\therefore C = \frac{0.1457 \text{ mole of } CH_4}{1 \text{ mole of reaction mixture}}$$

$$= \frac{0.1457}{22400 \times \frac{760}{810} \times \frac{753}{273}} \text{ gm mole/cm}^3 \text{ at reaction conditions}$$

$$= 0.2513 \times 10^{-5} \text{ gm mole/c.c.}$$

(v) Calculation of dimensionless modulus, Φ:

$$\Phi = \frac{R^2 \; r}{D_{K,eff} \cdot C}$$

R = radius of catalyst particle in cm.

= 0.03152 cm

$$\Phi = \frac{(0.03152)^2 \times 1.886 \times 10^{-6}}{1.7368 \times 10^{-3} \times 0.2513 \times 10^{-5}}$$

= 0.4293

(vi) Calculation of Effectiveness Factor, E:

The value of E corresponding to the above value of Φ was obtained to be close to unity from either Figure 3.4, 3.5, 3.6 or 3.7 of reference 82 (Shatterfield).

The experimental and calculated results show that the pore diffusion resistance was negligible.

TABLE A-F-1

Experimental Data for External Diffusion

(Effect of Feed Velocity on Oxidation of Methane over Chlorine Modified Catalyst)

Temp.= 475°C $\bar{R}$ = 3.61 $\bar{Z}$ = 0.0195

Run No.	W/F	Feed moles/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
400	24.00	0.1242	0.0939	0.3544	0.0912	0.0312	0.0657
401	24.00	0.2504	0.1894	0.7146	0.0938	0.0338	0.0762
402	24.00	0.5018	0.3795	1.4320	0.0952	0.0333	0.0747

Run No.	Products moles/hr						Feed Velocity moles/hr
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
400	0.1129	0.0765	0.3544	0.3875	0.2052	0.0815	0.5725
401	0.2269	0.1574	0.7146	0.8464	0.5082	0.1907	1.1544
402	0.4540	0.2729	1.4320	1.6695	0.9314	0.3747	2.3133

TABLE A-F-2

Experimental Data for Knudsen Diffusion

with Chlorine Modified Palladium Catalyst

Temp.= $450^{o}C$ $\bar{R} = 4.18$ $\bar{Z} = 0.0195$

Run No.	W/F	Feed moles/hr			Conversion	Yield	
		CH_4	O_2	N_2	X_{CH_4}	Y_{HCHO}	Y_{CO_2}
196	36.06	0.2504	0.2193	0.8274	0.1003	0.0397	0.0680
196d	36.06	0.2504	0.2193	0.8274	0.1021	0.0410	0.0651
196e	36.06	0.2504	0.2193	0.8274	0.1046	0.0405	0.0673

Run No.	Products moles/hr						Particle Size mm.
	CH_4	O_2	N_2	$HCHO \times 10^2$	$H_2O \times 10$	$CO_2 \times 10$	
196	0.2253	0.1832	0.8274	0.9940	0.4875	0.2193	0.63
196d	0.2248	0.1765	0.8274	1.0257	0.0484	0.2121	1.26
196e	0.2242	0.1734	0.8274	1.0146	0.0502	0.2175	0.30

APPENDIX G

Initial Reaction Rate Data

TABLE A-G-1

Initial Reaction Rate Data at Various Temperatures

Air:Methane Feed Ratio $\bar{R}$	Partial Pressure of Methane p_{CH_4} atm.	Initial Reaction Rate (mole/hr.gm catalyst) at Temperature				
		$390^{o}C$	$420^{o}C$	$450^{o}C$	$480^{o}C$	$510^{o}C$
2.41	0.3126	0.1914×10^{-2}	0.2882×10^{-2}	0.4582×10^{-2}	0.6643×10^{-2}	0.1004×10^{-1}
3.01	0.2658	0.1973×10^{-2}	0.3207×10^{-2}	0.5382×10^{-2}	0.6760×10^{-2}	0.1120×10^{-1}
3.61	0.2312	0.2229×10^{-2}	0.3469×10^{-2}	0.6025×10^{-2}	0.9275×10^{-2}	0.1179×10^{-1}
4.18	0.2058	0.2242×10^{-2}	0.3949×10^{-2}	0.6280×10^{-2}	0.9003×10^{-2}	0.1605×10^{-1}
5.28	0.1698	0.2607×10^{-2}	0.4411×10^{-2}	0.8031×10^{-2}	0.1603×10^{-1}	0.4671×10^{-1}

APPENDIX H

Calculated Values of Reciprocal Space Velocity, W/F

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 390.00

AIR TO METHANE RATIO IN THE FEED = 2.41

AVERAGE RATE CONSTANTS:

KS = 0.01303

KF =5128.19922

KM = 226.64000

KO = 1.14534

A = 0.3126 B = 0.1316 C = 0.1810 D = 0.1582 E = 0.4936

EXPERIMENTAL VALUES W/F	CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
49.0000	0.0655	47.4566	3.1498
41.8100	0.0590	41.1478	1.5838
36.0600	0.0501	33.1589	8.0451
28.8300	0.0439	28.0115	2.8390
20.4500	0.0345	20.8201	-1.8100
12.0000	0.0192	10.5722	11.8984

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 390.00

AIR TO METHANE RATIO IN THE FEED = 3.01

AVERAGE RATE CONSTANTS:

KS = 0.01303

KF =5128.19922

KM = 226.64000

KO = 1.14534

A = 0.2658 B = 0.1119 C = 0.1539 D = 0.1680 E = 0.4198

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
49.0000	0.0690	47.0005	4.0805
41.8100	0.0610	39.7805	4.8541
36.0600	0.0542	34.0531	5.5654
28.8300	0.0455	27.2458	5.4950
20.4500	0.0348	19.6293	4.0134
12.0000	0.0205	10.6610	11.1587

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 390.00

AIR TO METHANE RATIO IN THE FEED = 3.61

AVERAGE RATE CONSTANTS:

KS = 0.01303

KF =5128.19922

KM = 226.64000

KO = 1.14534

A = 0.2312 B = 0.0974 C = 0.1339 D = 0.1753 E = 0.3651

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.1105	87.4551	8.9010
72.0000	0.0944	68.9173	4.2815
49.0000	0.0716	46.5308	5.0391
41.8100	0.0630	39.1541	6.3524
36.0600	0.0565	33.9382	5.8840
28.8300	0.0475	27.2031	5.6431
20.4500	0.0362	19.5084	4.6044
12.0000	0.0208	10.2979	14.1845

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 390.00

AIR TO METHANE RATIO IN THE FEED = 4.18

AVERAGE RATE CONSTANTS:

KS = 0.01303

KF =5128.19922

KM = 226.64000

KO = 1.14534

A = 0.2058 B = 0.0866 C = 0.1192 D = 0.1806 E = 0.3249

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.1180	91.6482	4.5332
72.0000	0.0986	69.7576	3.1144
49.0000	0.0744	46.7150	4.6632
41.8100	0.0660	39.7219	4.9942
36.0600	0.0592	34.4147	4.5625
28.8300	0.0485	26.6760	7.4712
20.4500	0.0388	20.2774	0.8440
12.0000	0.0230	11.0365	8.0290

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 390.00

AIR TO METHANE RATIO IN THE FEED = 5.28

AVERAGE RATE CONSTANTS:

KS = 0.01303

KF =5128.19922

KM = 226.64000

KO = 1.14534

A = 0.1697 B = 0.0715 C = 0.0983 D = 0.1882 E = 0.2680

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.1219	87.3530	9.0073
72.0000	0.1056	70.1446	2.5770
49.0000	0.0802	47.1476	3.7803
41.8100	0.0705	39.4990	5.5274
36.0600	0.0621	33.3480	7.5207
28.8300	0.0520	26.5103	8.0460
20.4500	0.0425	20.6113	-0.7886
12.0000	0.0243	10.6738	11.0513

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 420.00

AIR TO METHANE RATIO IN THE FEED = 2.41

AVERAGE RATE CONSTANTS:

KS = 0.02780

KF =3797.39990

KM = 120.34000

KO = 0.82998

A = 0.3126 B = 0.1316 C = 0.1810 D = 0.1582 E = 0.4936

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
49.0000	0.0808	44.0505	10.1009
41.8100	0.0723	37.1199	11.2176
36.0600	0.0665	32.7614	9.1477
28.8300	0.0540	24.3121	15.6706
20.4500	0.0451	19.0229	6.9784
12.0000	0.0279	10.3402	13.8319

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 420.00

AIR TO METHANE RATIO IN THE FEED = 3.01

AVERAGE RATE CONSTANTS:

KS = 0.02780

KF =3797.39990

KM = 120.34000

KO = 0.82998

A = 0.2658 B = 0.1119 C = 0.1539 D = 0.1680 E = 0.4198

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
49.0000	0.0866	44.5081	9.1672
41.8100	0.0778	37.7480	9.7154
36.0600	0.0690	31.5775	12.4306
28.8300	0.0596	25.5966	11.2152
20.4500	0.0477	18.8673	7.7394
12.0000	0.0311	10.9214	8.9885

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,
AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 420.00

AIR TO METHANE RATIO IN THE FEED = 3.61

AVERAGE RATE CONSTANTS:

KS = 0.02780

KF =3797.39990

KM = 120.34000

KO = 0.82998

A = 0.2312 B = 0.0974 C = 0.1339 D = 0.1753 E = 0.3651

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.1342	85.1221	11.3311
72.0000	0.1180	68.0691	5.4596
49.0000	0.0903	44.0519	10.0982
41.8100	0.0810	37.2818	10.8305
36.0600	0.0727	31.7376	11.9866
28.8300	0.0626	25.5894	11.2405
20.4500	0.0506	19.0873	6.6637
12.0000	0.0328	10.9253	8.9557

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 420.00

AIR TO METHANE RATIO IN THE FEED = 4.18

AVERAGE RATE CONSTANTS:

KS = 0.02780

KF =3797.39990

KM = 120.34000

KO = 0.82998

A = 0.2058 B = 0.0866 C = 0.1192 D = 0.1806 E = 0.3249

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.1390	84.4628	12.0179
72.0000	0.1195	65.0389	9.6682
49.0000	0.0959	45.4420	7.2612
41.8100	0.0861	38.4388	8.0630
36.0600	0.0770	32.4859	9.9114
28.8300	0.0645	25.1223	12.8606
20.4500	0.0535	19.3766	5.2489
12.0000	0.0330	10.3637	13.6355

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 420.00

AIR TO METHANE RATIO IN THE FEED = 5.28

AVERAGE RATE CONSTANTS:

KS = 0.02780

KF =3797.39990

KM = 120.34000

KO = 0.82998

A = 0.1697 B = 0.0715 C = 0.0983 D = 0.1882 E = 0.2680

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.1503	85.0303	11.4268
72.0000	0.1325	67.9767	5.5879
49.0000	0.1022	43.9783	10.2484
41.8100	0.0918	37.0672	11.3438
36.0600	0.0837	32.1180	10.9318
28.8300	0.0715	25.3454	12.0866
20.4500	0.0589	19.1687	6.2656
12.0000	0.0385	10.8096	9.9201

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 450.00

AIR TO METHANE RATIO IN THE FEED = 2.41

AVERAGE RATE CONSTANTS:

KS = 0.04171

KF =3113.79980

KM = 77.27800

KO = 0.78836

A = 0.3126 B = 0.1235 C = 0.1891 D = 0.1582 E = 0.5017

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
49.0000	0.1015	48.1555	1.7235
41.8100	0.0921	40.6736	2.7179
36.0600	0.0853	35.7509	0.8570
28.8300	0.0720	27.2030	5.6433
20.4500	0.0576	19.3956	5.1558
12.0000	0.0412	12.1106	-0.9217

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 450.00

AIR TO METHANE RATIO IN THE FEED = 3.01

AVERAGE RATE CONSTANTS:

KS = 0.04171

KF =3113.79980

KM = 77.27800

KO = 0.78836

A = 0.2658 B = 0.1050 C = 0.1608 D = 0.1680 E = 0.4267

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
49.0000	0.1083	48.0590	1.9204
41.8100	0.0970	39.7689	4.8819
36.0600	0.0886	34.2135	5.1207
28.8300	0.0792	28.5657	0.9167
20.4500	0.0625	19.8910	2.7336
12.0000	0.0442	12.1783	-1.4860

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 450.00

AIR TO METHANE RATIO IN THE FEED = 3.61

AVERAGE RATE CONSTANTS:

KS = 0.04171

KF =3113.79980

KM = 77.27800

KO = 0.78836

A = 0.2312 B = 0.0913 C = 0.1399 D = 0.1753 E = 0.3711

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.1614	91.8271	4.3467
72.0000	0.1431	72.6973	-0.9685
49.0000	0.1150	48.8086	0.3906
41.8100	0.1031	40.4347	3.2894
36.0600	0.0947	35.0816	2.7131
28.8300	0.0835	28.6147	0.7467
20.4500	0.0662	20.0157	2.1238
12.0000	0.0460	11.9044	0.7966

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 450.00

AIR TO METHANE RATIO IN THE FEED = 4.18

AVERAGE RATE CONSTANTS:

KS = 0.04171

KF =3113.79980

KM = 77.27800

KO = 0.78836

A = 0.2058 B = 0.0813 C = 0.1245 D = 0.1806 E = 0.3303

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.1728	96.6872	-0.7158
72.0000	0.1492	72.6361	-0.8834
49.0000	0.1242	51.8505	-5.8173
41.8100	0.1080	40.6308	2.8204
36.0600	0.1003	35.8592	0.5569
28.8300	0.0871	28.4611	1.2795
20.4500	0.0697	20.1116	1.6545
12.0000	0.0514	12.8989	-7.4912

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 450.00

AIR TO METHANE RATIO IN THE FEED = 5.28

AVERAGE RATE CONSTANTS:

KS = 0.04171

KF =3113.79980

KM = 77.27800

KO = 0.78836

A = 0.1697 B = 0.0670 C = 0.1027 D = 0.1882 E = 0.2724

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.1866	96.3603	-0.3753
72.0000	0.1589	69.9832	2.8011
49.0000	0.1341	50.7662	-3.6045
41.8100	0.1210	42.1084	-0.7137
36.0600	0.1112	36.2533	-0.5360
28.8300	0.0985	29.4111	-2.0158
20.4500	0.0802	20.9365	-2.3789
12.0000	0.0539	11.3653	5.2891

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 480.00

AIR TO METHANE RATIO IN THE FEED = 2.41

AVERAGE RATE CONSTANTS:

KS = 0.07007

KF =1912.19995

KM = 45.27599

KO = 0.57538

A = 0.3126 B = 0.1032 C = 0.2094 D = 0.1582 E = 0.5221

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
49.0000	0.1219	49.4723	-0.9638
41.8100	0.1123	42.3819	-1.3679
36.0600	0.1025	35.9169	0.3967
28.8300	0.0919	29.7106	-3.0544
20.4500	0.0738	20.7618	-1.5248
12.0000	0.0503	11.7540	2.0496

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 480.00

AIR TO METHANE RATIO IN THE FEED = 3.01

AVERAGE RATE CONSTANTS:

KS = 0.07007

KF =1912.19995

KM = 45.27599

KO = 0.57538

A = 0.2658 B = 0.0877 C = 0.1781 D = 0.1680 E = 0.4439

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
49.0000	0.1318	49.5153	-1.0515
41.8100	0.1234	43.7768	-4.7041
36.0600	0.1101	35.6379	1.1706
28.8600	0.0972	28.7458	0.3956
20.4500	0.0791	20.5449	-0.4641
12.0000	0.0546	11.8017	1.6521

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 480.00

AIR TO METHANE RATIO IN THE FEED = 3.61

AVERAGE RATE CONSTANTS:

KS = 0.07007

KF =1912.19995

KM = 45.27599

KO = 0.57538

A = 0.2312   B = 0.0763   C = 0.1549   D = 0.1753   E = 0.3862

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.1925	94.1964	1.8787
72.0000	0.1732	75.2407	-4.5010
49.0000	0.1385	48.3748	1.2759
41.8100	0.1315	43.9078	-5.0175
36.0600	0.1192	36.7317	-1.8627
28.8300	0.1061	29.9607	-3.9220
20.4500	0.0842	20.4359	0.0690
12.0000	0.0587	11.8108	1.5765

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 480.00

AIR TO METHANE RATIO IN THE FEED = 4.18

AVERAGE RATE CONSTANTS:

KS = 0.07007

KF =1912.19995

KM = 45.27599

KO = 0.57538

A = 0.2058 B = 0.0679 C = 0.1379 D = 0.1806 E = 0.3437

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.2080	99.5984	-3.7483
72.0000	0.1815	74.4330	-3.3792
49.0000	0.1501	50.9267	-3.9319
41.8100	0.1360	42.2505	-1.0535
36.0600	0.1252	36.2984	-0.6611
28.8300	0.1109	29.2673	-1.5169
20.4500	0.0914	21.1007	-3.1818
12.0000	0.0640	12.0729	-0.6076

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 480.00

AIR TO METHANE RATIO IN THE FEED = 5.28

AVERAGE RATE CONSTANTS:

KS = 0.07007

KF =1912.19995

KM = 45.27599

KO = 0.57538

A = 0.1697 B = 0.0560 C = 0.1137 D = 0.1882 E = 0.2835

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.2258	96.0316	-0.0329
72.0000	0.1960	70.2257	2.4643
49.0000	0.1720	53.3001	-8.7756
41.8100	0.1561	43.7401	-4.6163
36.0600	0.1414	35.9593	0.2793
28.8300	0.1273	29.3759	-1.8937
20.4500	0.1037	20.1105	1.6602
12.0000	0.0792	12.5762	-4.8020

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 510.00

AIR TO METHANE RATIO IN THE FEED = 2.41

AVERAGE RATE CONSTANTS:

KS = 0.11254

KF =1531.19995

KM = 30.90199

KO = 0.50722

A = 0.3126 B = 0.0688 C = 0.2438 D = 0.1582 E = 0.5564

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
49.0000	0.1522	47.9551	2.1324
41.8100	0.1417	41.1482	1.5829
36.0600	0.1332	36.2511	-0.5298
28.8300	0.1163	27.8892	3.2631
20.4500	0.0974	20.3228	0.6219
12.0000	0.0697	11.8748	1.0429

CALCULATED VALUES OF RECIPROCAL VELOCITY, W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 510.00

AIR TO METHANE RATIO IN THE FEED = 3.01

AVERAGE RATE CONSTANTS:

KS = 0.11254

KF =1531.19995

KM = 30.90199

KO = 0.50722

A = 0.2658 B = 0.0585 C = 0.2074 D = 0.1680 E = 0.4732

EXPERIMENTAL VALUES W/F	EXPERIMENTAL VALUES CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
49.0000	0.1669	47.8075	2.4336
41.8100	0.1580	42.6184	-1.9336
36.0600	0.1447	35.6990	1.0012
28.8300	0.1283	28.3664	1.6079
20.4500	0.1057	20.0832	1.7937
12.0000	0.0766	11.9309	0.5755

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 510.00

AIR TO METHANE RATIO IN THE FEED = 3.61

AVERAGE RATE CONSTANTS:

KS = 0.11254

KF =1531.19995

KM = 30.90199

KO = 0.50722

A = 0.2312 B = 0.0509 C = 0.1804 D = 0.1753 F = 0.4116

EXPERIMENTAL VALUES W/F	CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.2446	97.8475	-1.9245
72.0000	0.2114	68.4633	4.9121
49.0000	0.1791	47.4291	3.2058
41.8100	0.1679	41.4726	0.8069
36.0600	0.1573	36.3700	-0.8598
28.8300	0.1381	28.3027	1.8290
20.4500	0.1143	20.1148	1.6392
12.0000	0.0831	11.8838	0.9686

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPFRATURE = 510.00

AIR TO METHANE RATIO IN THE FEED = 4.18

AVERAGE RATE CONSTANTS:

KS = 0.11254

KF =1531.19995

KM = 30.90199

KO = 0.50722

A = 0.2058 B = 0.0453 C = 0.1605 D = 0.1806 E = 0.3663

EXPERIMENTAL VALUES		CALCULATED VALUES	PERCENT
W/F	CONVERSION	W/F	DEVIATION
96.0000	0.2590	96.2937	-0.3060
72.0000	0.2268	69.7214	3.1647
49.0000	0.1945	49.4081	-0.8329
41.8100	0.1785	41.2116	1.4313
36.0600	0.1672	36.0568	0.0089
28.8300	0.1492	28.8123	0.0613
20.4500	0.1240	20.4194	0.1494
12.0000	0.0924	12.3217	-2.6806

CALCULATED VALUES OF RECIPROCAL VELOCITY,W/F,

AND PERCENTAGE DEVIATION FROM THEIR CORRESPONDING EXPERIMENTAL VALUES

REACTION TEMPERATURE = 510.00

AIR TO METHANE RATIO IN THE FEED = 5.28

AVERAGE RATE CONSTANTS:

KS = 0.11254

KF =1531.19995

KM = 30.90199

KO = 0.50722

A = 0.1697 B = 0.0373 C = 0.1324 D = 0.1882 E = 0.3021

EXPERIMENTAL VALUES W/F	CONVERSION	CALCULATED VALUES W/F	PERCENT DEVIATION
96.0000	0.2845	91.5538	4.6315
72.0000	0.2619	74.1629	-3.0040
49.0000	0.2212	49.3983	-0.8129
41.8100	0.2027	40.4510	3.2505
36.0600	0.1920	35.8397	0.6109
28.8300	0.1735	28.7500	0.2775
20.4500	0.1443	19.5802	4.2534
12.0000	0.1145	12.4138	-3.4481

IX. NOMENCLATURE

A	Component A
a_m	External particle surface area per unit mass , m^2/gm
a_v	External particle surface area per unit volume, $m^2/$ c.c.
a	${}_oN_M \cdot (P_T/{}_oN_T)$
B	Component B
b	$(1 - m) \cdot {}_oN_M \cdot (P_T/{}_oN_T)$
C_p	Specific heat of gas, cal/gm mole ^oC
C_{av}	Average specific heat of gas, cal/gm mole ^oC
C	Molal concentration of adsorbed reactants or products
c	$m \cdot {}_oN_M \cdot (P_T/{}_oN_T)$
D_p	Diameter of particle, cm
$D_{K,eff.}$	Effective Knudsen diffusion coefficient
D_{AM}	Average diffusivity of component A
d	${}_oN_O \cdot (P_T/{}_oN_T)$
E	Effectiveness factor of catalyst
e	$(1 + m) \cdot {}_oN_M \cdot (P_T/N_T)$
eL or ⊙	Free electrons
F	Flow rate of feed, gm moles/hr
G	Molar velocity of gas flow based on the total cross-sectional area of the catalyst bed.
ΔG	Change in Gibb's free energy
ΔH_A	Heat of reaction per mole of A reacted
h_G	Heat transfer coefficient of the gas film

I	Component I
j_d	Chilton-Colburn mass-transfer factor
j_h	Chilton-Colburn heat-transfer factor
K	Thermodynamic equilibrium constant
K	Adsorption equilibrium constant (with subscript A,B,...)
k	Thermal conductivity of the gas
k_G	Mass transfer coefficient of the gas film
k_c	Thermal conductivity of the catalyst
k_s	Reaction rate constant combined with surface parameters
k	Reaction rate constant (with subscript 1,2)
L	Molar concentration of active sites per unit mass
M	Molecular weight
M_m	Mean molecular weight
m	Slope of Z vs. X plot
P	Partial pressure
P_i	Partial pressure in the gas-solid interface
P_f	Film pressure factor
Pr	Prandtl number, $\frac{C_p \mu}{k}$
pL or $\square$	Positive holes
Q	$\frac{r_{m_A} \quad \Delta H_A}{a_m \; C_p \; G_m}$
q_m	Heat transfer rate per unit mass of catalyst
R	Component R
$\bar{R}$	Air to methane mole ratio in the feed
R	$\frac{r_{m_A}}{a_m \; \phi \; G_m}$

Re	Reynolds number $\frac{D_p G}{\mu}$ or $\frac{G_m}{a_v \phi \mu}$
r	Reaction rate (with subscript 1, 2 and 3) gm moles/hr.gm of catalyst
r_o	Initial rate, gm mole/hr.gm of catalyst
S	Component S
S	Selectivity of the catalyst for formaldehyde formation
s	Active sites on the catalyst surface
Sc	Schmidt number $= \frac{\mu}{\rho D_{AM}}$
S_g	Specific surface area of catalyst
T	Temperature
T_i	Temperature of the gas-solid interface
W	Wight of catalyst, gm.
X	Conversion of methane
Y	Yield
$\bar{Z}$	Mole ratio of modifier to methane in the feed
Z	Conversion of formaldehyde

Greek Symbols

β	Porosity of catalyst
Δ	Finite increment or change of property
θ	Fractional coverage of catalyst surface by a certain component
μ	Viscosity
π	Total pressure
ρ	Density of gas
ρ_P	Density of the catalyst particle

ϕ	Shape factor, ratio of actual external surface area available for mass and heat transfer to the total external surface area, assumed to be 0.90 for irregular granules.
Φ	Dimensionless Modulus for Effectiveness Factor
τ	Tortuosity of catalyst

Superscripts

I	Type (I) active sites
II	Type (II) active sites
m,m'	Reaction order (with subscript 1,2,...)
n,n'	Reaction order (with subscript 1,2,...)

Subscripts

A^+	Charged adsorbed aldehyde
CH_4^+	Charged adsorbed methane
C	Carbon dioxide
cal	Calculated
F	Formaldehyde
f	Properties at the average condition of the gas film
I	Component I
i	Properties at the gas-solid surface interphase
in	Input
M	Methane
O	Oxygen
o	Placed before a symbol means in the feed
O^-	Charged adsorbed oxygen
out	Output

X. BIBLIOGRAPHY

1. Thomas, J.M. and Thomas, W.J., "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, London, p.383 (1967).
2. Smith, J.M., "Chemical Engineering Kinetic", 2nd Edn. McGraw Hill Book Co., N.Y., p.283 (1970).
3. Mann, R.S. and Dosi, M.K., J. Catal., 28, 282 (1973).
4. Mann, R.S., Jain, S.K. and Dosi, M.K., J. Appl. Chem. Biotechnol., 27, 198 (1977).
5. Margolis, L.Ya, Catalysis Reviews, 8, 241 (1974).
6. Boudart, M., J.A.C.S. 72, 1040 (1950).
7. Dowden, D.A., J. Chem. Soci., 242 (1950).
8. Paravano, G. and Boudart, M., Advances in Catalysis, I, 1, (1955).
9. Wolkenstein, Th., "The Electronic Theory of Catalysis on Semiconductors", p.126, Pergamon, N.Y. (1963).
10. Dell, R.M., Stone, F.S. and Tiley, P.F., Trans. Farad. Soc., 49, 201, (1953).
11. Dry, M.E. and Stone, F.S., Disc. Farad. Soc., 28, 192 (1959).
12. Paravano, G., J.A.C.S., 75, 1448 (1953).
13. Schwab, G.M., "Semiconductor Surface Physics", Univ. of Pennsylvania Press, p.283 (1957).

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

15. Shtern, V.Ya , "The Gas Phase Oxidation of Hydrocarbons", McMillan Co., N.Y. (1964).

16. Emmett, P.H., Catalysis, Vol. VII, Reinhold Pub. Corp., N.Y., p.183 (1960).

17. Margolis, L.Ya, Advances in Catalysis & Relat. Subj. 14, 429 (1963).

18. Norish, R.G.W., Cinētique et mécanisme de rēactions d'inflammation et de combustion en phase gazeuse, Paris, 16 (1948).

19. Bone, W.A. and Gardner, J.B., Proc. Roy. Soc., A154, 297 (1936).

20. Karmilova, L.V., Yenikolopyan, N.S. and Nalbandyan, A.B., Zh. ftz, khim., 31, 857 (1957); 34, 990 (1960); 35, 1046 (1961); 34, 1176 (1960).

21. Norish, R.G.W. and Foord, S.G., Proc. Roy. Soc., A157, 503 (1936).

22. Vanpée, M. and Gaard, F., Fuel, 34, 433 (1955).

23. Bone, M.A. and Allum, R.E., Proc. Roy. Soc., A134, 578 (1932).

24. Norish, R.G.W., Disc. Farad. Soc., No.10, 269 (1951).

25. Fort, R. and Hinshelwood, C.N., Proc. Roy. Soc., A129, 284 (1930).

26. Slotin, L. and Style, D.W.G., Trans. Farad. Soc., 35, 420 (1939).

27. Vanpée, M., Ann. Min. Belg., 47, 1053 (1948).

28. Van Meersche, M., Ann. Min. Belg., 44 (1949).

29. Hoare, D.E. and Walsh, A.D., Fifth Symp. on Combustion, N.Y., 467-474 (1955).

30. Nemeth, A. and Sawyer, R.F., J. Phy. Chem., 73, No.7, 2421 (1969).

31. Semenov, N.N., "Some Problems of Chemical Kinetics and Reactivity", Pergamon Press, London (1959).

32. Miyama, H. and Takeyama, T., J. Chem. Phys., 40, 2049 (1964).

33. Magee, E.M., J. Am. Chem. Soc., 81, 278 (1959).

34. Lewis, B. and von Elbe, G., "Combustion, Flames and Explosions of Gases", Academic Press, Inc., N.Y., p.94-116 (1951).

35. Yenikolopyan, N.S., Korolev, G.V. and Sarushkina, G.P., Zh, Fiz, Khim., 31, 865 (1957).

36. Bibb, C.H. and Lucas, H.J., Ind. Eng. Chem., 21, 633 (1929).

37. Gertges, H., Heinze, H.O. and Brocke, W., (Bergbau, A.G. Neue Hoffnung) German patent 1,050,752 (1959), Brit. patent 880,873 (1961).

38. Mayor, Y., Rev. Chim. Ind. (Paris), 46, 34 (1937).

39. Levush, S.S., Kinet. Katal. 14, No.6, 1366 (1969).

40. Vilenskii, A.R. and Averbukh, A. Ya, J. Appl. Chem. of U.S.S.R. 43, No.8, 1854 (1970).

41. McConkey, B.H. and Wilkinson, P.R., I. & E.C. Proc. Des. and Dev., 6, No.4, 436 (1967).

42. Huettenwerke Oberhausen, A.G., Brit. Patents 880,873 (1961); 913,581 (1962); 926,889 (1963).

43. Brocke, W., Gertges, H. and Heinze, O., (Huettenwerk Oberhausen A.G.) Ger. 181,292 (1964).

44. Henry, G., Phil. Mag., 65, 269 (1825).

45. Yant, W.P. and Hawk, C.O., J. Am. Chem. Soc., 49, 1454 (1927).

46. Anderson, R.B., Stein, K.C., Feenan, J.J. and Hofer, L.J.E., I. and E.C. 53, 809 (1961).

47. Davies, W., Phil. Mag. 21, 513 (1936).

48. Lintz, H.G., Pentenero, A. and LeGoff, P., J. Chim. Phys. 59, 933 (1962).

49. Hiam, L., Wise, H. and Chaikin, S., J. Catalysis, 10, 272 (1968).

50. Bancroft, W.F., J. Phy. Chem., 21, 644 (1917).

51. Campbell, J.R. and Thomas, G., J. Soc. Chem. Ind., 49, 432 (1930).

52. Arneil, A., J. Soc. Chem. Ind., 53, 899 (1934).

53. Brükner, H. et al., Gas u. Wasserfach., 82, 189 (1939).

54. Araki, S., Japan Analyst, 2, 365 (1953).

55. Wheeler, T.S., Rec. Trav. Chim., 50, 874 (1931).

56. Bransom, S., Hanlon, L. and Smyth, B., Trans. Faraday Soc., 52, 672 (1956).

57. Schonfelder, R.J., J. Soc. Chem. Ind., 48, 93T (1929).

58. Sachachner, H., Cobalt, No.9, 12 (1960).

59. Thompson, G.P., et a., Air Pollution Control Assoc., 10, 275 (1960).

60. Belgium Patent, 573509, Dec.31 (1958).

61. Vendt, V.P., et al., Zavodskaya Lab., 24, 915 (1958).

62. Lamb, A.B., Bray, W.C. and Frazer, J.C.D., I. and E.C., 12, 213 (1920).

63. Vilenskii, A.R., Mukhlenov, I.P., Averbukh, A.Ya and Kholodnov, V.A., J. App. Chem. U.S.S.R., 46, No.9, 2086 (1973).

64. Averbukh, A. Ya and Vitvitskii, A.I., J. App. Chem. U.S.S.R., 48, No.6, 1408 (1970).

65. Mukhlenov, I.P., Vitvitskii, A.I. and Averbukh, A. Ya, J. App. Chem. U.S.S.R. 42, No.8, 1775 (1969).

66. Zinina, E.M. and Averbukh, A.Ya, J. App. Chem. U.S.S.R., 42, No.1, 234 (1969).

67. Cohn, J.G.E. and Haley, A.J., Can. Patent 597,459 (1960).

68. Mazaki, R., "Kinetics of the Catalytic Oxidation of Methane", Ph.D. Thesis, Univ. of Wisconsin, Madison, Wis. (1963).

69. Mezaki, R. and Watson, C.C., I. and E.C. Proc. Des. and Dev. 5, 62 (1966).

70. Ahuja, O.P. and Mathur, G.P., Can. J. Chem. Eng., 45, 367 (1967).

71. Cullis, C.F., Keen, D.E. and Trimm, D.L., J. of Catalysis, 19, 378 (1970).

72. Prettre, M., Eichner, Ch. and Perrin, M., Trans. Faraday Soc., 42, 335 (1966).

73. Peters, K., Rudolf, M. and Voetter, H., Brennstoff Chem., 36, 257 (1955).

74. Bodrov, I.S. and Apel'baum, L.O., Kinetics and Catalysis, 9, 326 (1967).

75. Andrushkevich, T.V., Papovskii and Boreskov, G.K., Kinetika i Kataliz, 6, No.5, 860 (1965).

76. Kazarnovskya, L.K. and Dykhno, N.M., Kislorod, 12, No.28 (1959).

77. Troschenko, V.I.A., Garyra, N.A. and Shchenkoy, Z.M., Dokl. Ves. Nauch. Korf. Rab. Kafedv. Teckhnol. Neary. Veschestr. Nauch. Vchrezhd. Prockt, Organ., 252 (1964).

78. Firth, J.F., Trans. Faraday Soc., 62, 2566 (1966).

79. Emmett, P.H., Catalysis, Vol.1, Reinhold Publishing Corp., N.Y., p.339 (1954).

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

81. Hougen, O.A., Ind. Eng. Chem., 53, 509 (1961).

82. Shatterfield, Charles N., "Mass Transfer in Heterogeneous Catalysis", M.I.T. Press Massachussets, p.141, (1970).

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

84. Gramson, B.W., Thodos, G. and Hougen, O.A., Trans. Am. Inst. Chem. Eng., 39, 1 (1943).

85. Wilke, C.R. and Hougen, O.A., Trans. Am. Inst. Chem. Eng., 61, 445 (1945).

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

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

88. Ergun, A., Chem. Eng. Prog., 48, 89 (1952).

89. Laidler, K.J., "Chemical Kinetics", 2nd Edn. McGraw Hill, p.257 (1965).

90. Emmett, P.H., Catalysis, Vol.I, Reinhold Publishing Corp., N.Y., p.88 (1754).

91. Thomas, J.M. and Thomas W.J., "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, p.34 (1967).

92. Hayward, D.O. and Trapnell, B.M.W., "Chemisorption", Butterworths, London, p.161 (1964).

93. Hougen, O.A. and Watson, K.M., "Chemical Process Principles", Part III, John Wiley and Sons, N.Y. (1947).

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

95. Brunauer, S., "The Adsorption of Gases and Vapors", Vol.I, chap.XIV, Princeton Univ. Press, Princeton (1943).

96. Ghosh, J.C., Shastri, M.V.C. and Kini, K.A., Ind. Eng. Chem., 44, 2463 (1952).

97. Marquart, D.W., J. of Society for Industrial and Applied Mathematics, vol.II, 431 (1963).

98. Dowden, D.A., Proc. Int. Cong. Catal., 4th Moscow Prepr. 62, 1120 (1968).

99. Enikeev, E.K., Isaev, O.V. and Margolis, L.Ya, Kinet. Katal., 1, 402 (1960).

100. Mann, R.S. and Yao, K.C., DECHEMA, 68, 329 (1971).

101. Mann, R.S., Yao, K.C. and Dosi, M.K., J. Appl. Chem. Biotechnol., 22, 915 (1972).

102. Mann, R.S. and Dosi, M.K., ACHEMA - Congress, Frankfurt, Germany, June, 1976.

103. Finar, I.L., "Organic Chemistry", Longmans, 1, 91 (1954).

104. Bond, G.C. and Sadeghi, N., J. App. Chem. Biotechnol., 25, 241 (1975).

105. Anisonyan, A.A., Gudkov, S.F., Ivanov, A.K., Enikolopyan, N.S., Markevich, A.M. and Nalbandyan, A.B., "Conversion of Natural Gas", Tr. Vses. Nauchn. - Issled. Inst. Priordn. Gazov, 3, (11), 130 (1958).

106. Orchin, M., Advan. Catal. Relat. Subj., 16, 21 (1966).

107. Kemball, C., Advac. Catal, Relat. Subj., 11, 223 (1959).

108. Trapnell, B.M.W., Trans. Faraday Soc., 52, 1618 (1956).

109. Hayward, D.O. and Trapnell, B.M.W., "Chemisorption", Butterworths, p.278 (1964).

110. Stone, F.S., Adv. Catalysis, 13, 1 (1962).

111. Klier, K., J. Catalysis, 7, 14 (1967).

112. Kilty, P.A., Rol, N.C. and Sachtler, W.M.H., Proc. Fifth Int. Cong. Catalysis, North Holland, Amsterdam, Prept. 64, (1972).

113. Bodrikov, I., Khulbe, K.C. and Mann, R.S., J. Catalysis, 43, 339 (1976).

114. Margolis, L. Ya, Enikeev, E.Kh., Isaev, O.V., Krylova, A.V. and Kushnerov, M. Ya, Kinetics and Catalysis, 3, 153 (1962).

115. Garner, W.E., Stone, F.S. and Tilley, P.F., Proc. Roy. Soc., (London), A211, 472 (1952).

116. Wolkenstein, Th., Advances in Catalysis, Vol. XII, Academic Press, Inc. N.Y., p.189 (1960).

117. Anderson, J.R. and McConkey, B.H., J. Catalysis, 11, 54 (1968).

118. Sasonov, B.A., Popovskii, V.V. and Boreskov, G.K., Kinetics and Catalysis, 9, 255 (1968).

119. Moro-Oka, Y., Morikawa, Y. and Ozaki, A., J. Catalysis, 7, 23 (1967).

120. Barry, T.I. and Stone, F.S., Proc. Roy. Soc., A255, 124 (1960).

121. Kon, M.Ya, Shvets, V.A. and Kazanskii, Kinet. Katal., 13, 635 (1972).

122. Smith, J.M. and Van Ness, H.C., "Introduction to Chemical Engineering Thermodynamics", 2nd Edn., McGraw Hill (1959).

123. Walker, J.F., "Formaldehyde", Reinhold Publishing Co., N.Y., p.40 (1964).

124. Boudart, M., Mears, D.E. and Vannice, M.A., "Compte-rendu XXXVIe Congrès International de Chimie industrielle", Industrie Chimique Belge, 32 (special issue), Part I, 281 (1967).

125. Handbook of Chemistry and Physics, CRC Press, Ohio, 53rd Edition, D72 (1972-73).