VAPOUR PHASE CATALYTIC OXIDATION
OF
2-METHYLPROPENE OVER BISMUTH MOLYBDATE CATALYSTS

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The vapor phase air oxidation of 2-methylpropene to methacrolein was investigated in an isothermal integral flow reactor at 1.15 atmospheric pressure, in the temperature range 390°C - 560°C. Bismuth molybdate supported on zirconium oxide, an n-type catalyst was used.

The effect of various process variables, namely the feed ratio of oxygen to 2-methylpropene, reaction temperature, and the reciprocal of space velocity on the conversion of olefin and the product distribution was investigated.

It was observed that an increase in the conversion of 2-methylpropene was always accompanied with a decrease in the selectivity. In most cases the selectivity for methacrolein increased with the increasing feed ratio of oxygen to 2-methylpropene (0.6 to 2.0). Relatively lower temperature was found to favor the selectivity of methacrolein. Though the conversion of 2-methylpropene, the yield of methacrolein and carbon dioxide increased rapidly at longer contact time, it was hardly affected in the range of shorter contact time.

Out of the several models proposed for the oxidation of 2-methylpropene over bismuth molybdate catalyst. The most suitable one appear to be the one in which the rate determining step

is the surface reaction between adsorbed olefin and oxygen on different active sites, the rate of reaction can expressed by the equation

$$r = \frac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

where K_S, K_H, K_O and K_M are temperature dependent constants.

I. INTRODUCTION

The controlled oxidation of olefins and dienes to useful intermediate products has attracted wide attention recently. It has now been possible to obtain many valuable hydrocarbons, such as the oxidation of ethene to acetaldehyde, ethene to ethylene oxide, propene to acrolein, 2-methylpropene to methacrolein, butene to butadiene, benzene to maleic anhydride and so on.

Thermodynamically , these partial oxidation processes are usually quite in favor of the primary oxidative products. Yet the major problem is that of stopping the further oxidation of these products, and making the reaction more selective. Usually the oxidation giving the intermediate products is accompanied by a series of consecutive or parallel reactions leading to a complete oxidation.

The conversion and yield of the reaction depend on the relative values of reaction rate constants which could be easily altered by the presence of a catalyst. From an industrial viewpoint, one is more interested in obtaining a maximum space-time yield and to develop a catalyst which could give both a high selectivity and conversion for the particular oxidation process.

Success in the controlled oxidation of olefins in the vapor phase to useful intermediate products is mainly achieved by varying the operating conditions, proper selection of catalyst and modifying it with a suitable promotor. The operating variable, for us to control the reaction are namely, feed composition, reaction temperature, pressure and contact time (such techniques as photoexcitation and radiation bombardment may be helpful but are of limited applicability for processing on a large scale). Though the conversion in olefin oxidation can be increased by using severe operating conditions, i.e, higher reaction temperature, feed ratio (oxygen / olefin) and contact time it has been observed that the selectivity of the bismuth molybdate catalyst for methacrolein production always decreases with increasing conversion as required for a consecutive reaction. Similar results have been reported for propene oxidation over copper oxide catalyst (1, 44, 51).

Many solids can act as heterogeneous catalysts for the partial oxidation of hydrocarbons. The most common catalysts are transition metal oxides which are usually semiconductors. Copper oxide and molybdenum oxide catalysts are used more often than the others. According to Adams (2) the reaction mechanism of catalytic oxidation over the two catalysts are the same. Nevertheless, the kinetics are quite different.

Although several methods are available for measuring the reaction kinetics, using different types of reactor; differential, or integral, batch or continuous flow, yet there is no entirely satisfactory method by which the reaction can be measured directly.

The differential method consists in operating the reactor with a small conversion so that the reaction rate may be assumed constant. Rate determinations in a differential reactor can be made in a straightforward manner, however, the main drawback is the diffculty in a precise analysis because of the low concentration of products in the gas stream. On the other hand, the integral method is not restricted to a small conversion and the analytical accuracy is greater.

From an industrial view point, one is more interested in yield and selectivity, using a mixture of olefin and air over a heated stationary catalyst at approximately atmospheric pressure. A fixed bed integral flow reactor, operating at near atmospheric pressure is most suitable for studying oxidation reactions.

It was therefore decided to study the reaction of 2-methyl-propene and air over a bismuth molybdate catalyst, and to determine the rate controlling step for the reaction and derive a rate equation, which may satisfactory explain the kinetics of the reaction.

The Objects of the Present Work

(1) To design and set up the apparatus to study the effect of process variables on the conversion and product distribtuion for the 2-methylpropene oxidation over bismuth molybdate catalyst.

(2) To propose a hypothesis which might explain the reaction kinetics.

(3) To develop a suitable rate expression which might satisfactorily represent the data useful for reactor design.

II. LITERATURE SURVEY

The oxidation of olefin to unsaturated carbonyl compounds is of great industrial importance, many attempts have been made in the past to achieve high selectivity and activity of the catalyst by trying different catalysts, by varying catalysis compositions, and by modifying the skelton catalyst with different additives. Unfortunately most of the work available in literature is covered in the patents, details are not available. Especially very little scientific literature is available on the kinetics and mechanism of the reaction. The major reasons for this lack of information are due to the large exothermity of the reaction, the changing character of the catalyst, and the pronounced inhibition of the reaction by the products.

The present survey is limited to the studies concerning the heterogeneous catalytic oxidation of propene and 2-methylpropene to corresponding unsaturated aldehydes, since both reactions are generally carried out over the same type of catalyst and the same mechanisms appear to be involved.

A survey of the patents and the published literature pertaining to the partial oxidation of propene and 2-methylpropene is presented together, though the present studies deal largely with the oxidation of 2-methypropene to methacrolein.

A summary of the published literature on the two distinctive kind of catalysts (bismuth molybdate and copper oxide) and their modifiers is presented in this chapter, Emphasis is placed on the reaction kinetics; evidence regarding the influence of catalyst composition, the reaction mechanism and the yield of corresponding unsaturated aldehydes. Also included is the oxidation of olefins over some other metal oxide catalysts.

(1) Bismuth molybdate and its modifiers;

Though Janner (70) used a catalyst containing bismuth and molybdenum for the oxidation of acetylene, in early 1931, only recently similar catalysts were employed for oxidation of mono-olefins. Sometimes bismuth phosphomolybdate catalysts has been mentioned.

Serban (66) investigated the oxidation reaction of propylene, by using various compositions of catalysts mixtures. Best results were reported in the presence of water vapor with the catalysts haveing the following composition: Bi_2O_3 19.6 %, MoO_3 12.6 %, P_2O_5 2.9 %, Silica gel 64.9 %. The increase in the oxygen to propylene ratio favored the oxidation of propylene for the production of acrolein, CO_2 and acids, up to a certain maximum, beyond which, the selectivity with respect to acrolein formation decreased. No acrolein formed at temperature below 380°C , From 380°C and up to 490 C., The acrolein production increased to a maximum value.

The total conversion of propylene increased with the temperature, and reached 90 % at 500°C .

Veatch et al. (72) reported a catalyst with composition $Bi_9Mo_{12}O_{52}$, either supported on silica gel or unsupported, to give high conversions of propene, and high specificity to acrolein. The reaction was studied at high temperatures between 350° and 500°C., using an equal weight of the active phase and support (silica gel), and a reactant ratio of propene : air : steam of 1 : 5 : 6.3 . The presence of steam was found to be beneficial and the optimum specificity was 60 % at about 375°C . The maximum propene conversion was 55 % . A variation in the air-propene feed ratio between 3 and 12, only slightly affect the selectivity to acrolein at temperatures higher than 450°C, the propene conversion declined.

Batist and co-workers(6) studied the bismuth molybdate catalyst having different Bi : Mo ratios for olefin oxidation in order to find the reasons for the markedly distinct behavior of the catalysts relative to bismuth and molybdenum oxide. The most active region was found to be 40-70 atomic % bismuth. Some irregularities were noted, depending on the preparations and heat treatment of the catalysts. Maximum activity was found to be Bi : Mo = 1 provided that catalyst was not heated over 500°C.

Margolis and co-workers(54) reported that the best selectivity was obtained for a mixed bismuth-molybdenum oxide catalyst that contained about 30 atomic % bismuth. The electronic work function was found to be a maximum at about this concentration.

Keulks and co-workers (31,32) found the oxidation of propylene to acrolein over bismuth molybdate catalysts was first order in propylene and zero order in oxygen. Between the temperature range of 400°C - 460°C they found the activation energy was 29 Kcal per mole. The reaction also yielded, in addition to acrolein, considerable amounts of carbon monoxide, carbon dioxide and water, and trace amount of ethylene, formaldehyde and acetaldehyde.

Adams and co-workers (4) investigated the oxidation of butylenes and propylene over bismuth molybdate catalysts. The reactions were found to be quite selective, the main side reaction being the total combustion to carbon dioxide. 2-methylpropene gave methacralein with 80 % selectivity. There was a pronounced effect of temperature on the selectivity and a maximum value was observed in the region of 450°C to 550°C. It was found that in the oxidation of propene and 2-methylpropene, there was no effect of steam addition on the activity or selectivity. The kinetics of the oxidation of propene and of the butenes over bismuth molybdate have been also investigated by the Adam's group. The reaction was found to be first order with respect to olefins and independent of oxygen and products. Relative reactivities of olefins were determined by feeding a mixture of the olefin to be tested with 1-butene as a reference (relative reactivity per molecule : propene 0.11,2-methylpropene 0.5, 1-butene 0.11, 2-methylpropene 0.5, 1-butene 1.00). The rate of oxidation was found to be a strong function of the olefin structure, being inversely related to the strength of the allylic C-H bond.

Uckijima and Oda (71) also found that the oxidation of propene and 2-methylpropene to corresponding unsaturated aldehydes was first order in olefin and independent of oxygen over bismuth molybdate catalyst. They concluded that the same mechanism was involved in the formation of the aldehydes. However, 2-methylpropene was more readily oxidized than propene. The ratio of the two oxidation rate constants ($K_{methacrolein}$ / $K_{acrolein}$) at 450°C was found to be 4.5 / 13.2. Though the oxidation of propene was significantly affected by the addition of a phosphorous promoter to the bismuth molybdate, the oxidation of 2-methylpropene was hardly influenced by the addition of the promoter. The apparent activation energy for propene and 2-methylpropene oxidation was found to be about 14 and 28 Kcal / G-mole respectively. Evidence on the mechanism of oxidation over bismuth molybdate has been mainly from kinetics and tracer experiments carried out by several groups of investigators. Adams and Jennings (4) oxidized several deuterated propenes to acroleins and in the presence of ammonia to acrylonitriles. The isotopic compositions of the products were in good agreement with those obtained over cuprous oxide, indicating that the same mechanisms was inherent with both catalysts.

Sachtler (64) , and Sachetler and de Boer (65) also found evidence regarding the existence of a symmetric intermediate from the oxidation of propene containing radioactive carbon over bismuth molybdate. When C^{14} was at either end of the propene molecule, half of it was found in the carbonyl group of the product acrolein. However , when it was in the middle carbon, no C^{14} was found in the carbonyl group.

McCain, Gough and Godin (57) found the similar results by using a bismuth phosphomolybdate supported on silica for propene oxidation .

Kutseva and Margolis (39) investigated the oxidation of propene over oxide of vanadium and molybdenum and their mixtures, either alone or in the presence of additives. An approximately 50-fold excess of propene, relative to oxygen was used. The reaction was found to be first and zero order with respect to oxygen and propene respectively. In each case, the selectivity to oxygen was less than 30 % . Though the selectivity with vanadium oxide was poorer to that with molybdenum oxide, its activity was much greater. Saturated aldehydes, carbonylic acids and carbon monoxide were formed in quantities comparable to those of acrolein and carbon dioxide.

Gorokhovatskii et al. (24) investigated the influence of supports, (porous glass, silion carbide and alumina) on the catalytic oxidation of olefins. Pore structure and chemical composition were found to influence the oxidation. The increase in the surface area or decrease in the pore size of the supports was accompanied by a decrease in the specifity.

Kitahara and Moriya (34) investigated the catalytic oxidation of 2-methylpropene to methacrolein over various metal oxides and their mixtures, and found vanadium oxide-molybdenum oxide -phosphorous oxides supported on an alumina sponge was the most effective catalyst for oxidation. The effects of various types of supports, grain size of Al-sponge, feed ratio of oxygen to 2-methylpropene, space velocity and the promotional effect of steam was studied. Several undesirable by-products, i.e., ketones and acids besides methacrolein were obtained in the liquid products.

In a study directed primarily at the synthesis of methacronitrile, Brill and Finley (13) oxidized 2-methypropene using oxygen / 2-methylpropene ratio of 2 in a tube coated with α-alumium and molybdenum oxide and obtained a 40 % selectivity to methacrolein at a conversion 34 %. Beside methacrolein, carbon dioxide and carbon monoxide were formed.

Zhizneuskii et al. (81) studied the oxidation of 2-methylpropene over iron-molybdenum-tellurium catalyst of composition in the range 21 -62 % iron, 20 -50 % molybdenum and 0 - 40 % tellurium between 360°C and 420°C, while an increase in the percentage of tellurium (up to 30 %) was found to increase the selectivity, an increase in molybdenum up to 22-35 % increased the specific activity. The best result were obtained with the catalyst containing iron : tellurium : molybdenum in an ratio of 1 : 0.85 : 1. They reported that the formation of carbon dioxide was mainly due to a parallel oxidation of 2-methylpropene. An increase in the contact time was found to have no effect on selectivity for methacrolein. The activation energies were 32, 39 and 45 Kcals for methacrolein, carbon dioxide and carbon monoxide respectively.

(2) Copper oxide and its modifiers:

Isaev and Margolis (28) made a kinetic study of the air oxidation of propene at atomosheric pressure in a dynamic unit. The copper-catalyzed reaction yielded acrolein, carbon dioxide, water and a small quantity of acetaldehyde. Propene oxidation rate was proportional to oxygen concentration and was independent of propene concentration. Apparent activation energies of 30 and 23-25 kcalgram was obtained for carbon dioxide formation over a silite supported copper catalyst and a pumice supported catalyst respectively. The acrolein oxidation rate was proportional to oxygen concentration and independent of acrolein concentration.

It has been suggested that the presence of propene reduced considerably the acrolein oxidation rate.

The oxidation of 2-methylpropene with oxygen over a 0.1 - 1.5 % copper oxide (70 % cuprous oxide - 30 % cupric oxide) catalyst supported on silite was investigated by Popova, Mil'man and Latysheva (61, 62) at 350 C - 370 C. Using a 2-methylpropene-oxygen ratio of 5.6 over a wide range of space velocities, 3.8 % of 2-methylpropene was converted to carbonyl compounds, 82.5 % of which was methacrolein, 7.2 % propionaldehyde, 6.2 % acetaldehyde and 4.1 % acrolein.

The oxidation of propene to acrolein on pumice supported copper oxide catalyst was investigated by Enikeev et al. (20) from experimental data on oxygen and propene adsorption, and results obtained while investigating the nature of the intermediates by an isotope method, a stage scheme for the oxidation of propene to acrolein was proposed, oxygen in either atomic or molecular form was first adsorbed on the surface of the catalyst. Next propene was adsorbed with its methyl group on the adsorbed oxygen without the rupture of the C = C bond and the formation of a hydroperoxide. The hydroperoxide decomposed into acrolein and water. The adsorbed acrolein interacted with oxygen from the gas phase giving a charged intermediary complex, which decomposed into carbon dioxide, water and a hydrocarbon radical adsorbed on the surface. The latter reacted again with oxygen. By analogy it was postulated that propene was adsorbed on the cuprous oxide surface with the rupture of $C = C$ bond and be converted into a radical, which would react with adsorbed oxygen. The intermediary complex thus formed then decomposed into carbon dioxide, water and a hydrocarbon radical with a smaller number of carbon and hydregen atoms. The surface of cuprous oxide was charged, when oxygen, propene and acrolein were adsorbed. This change in the work function caused by the adsorption enabled them to determine the sign of the charge on the adsorbed molecules, and then it is suggested that whereas propene and acrolein, like most of the organic substances were electron donors on the cuprous oxide surface and oxygen was an electron acceptor.Water, while lowering the work function insignificantly, was found also to be an electron donor.

Further study of the effect of steam on the oxidation of propene was made by Gorokhoratskii and Popova (24) over a copper oxide catalyst of low concentration, supported on silicon carbide, using steam up to 60 % of the feed, they found that the rates for acrolein and carbon dioxide production could be expressed as

$$\text{Acrolein Production Rate} = \frac{K_1 \,(O_2)^{0.8} (C_3H_6)(1 + (H_2O))^{0.5}}{(1 + b(C_3H_4O))(1 + b_1(H_2O))}$$

Carbon dioxide production Rate

$$= \frac{K_2(O_2)(C_3H_6)}{(1 + b''(C_3H_6O)) \; (1 + b_2(H_2O))}$$

At high steam concentration, the rate was approximately first order in propene and in oxygen as well.

The air oxidation of propene to acrolein over a cement pasted copper oxide catalyst in a continuously stirred reactor was studied by Lakshmanan and Rouleau(41) at temperature range 375°-450°C. The rate controlling step was the surface reaction between adsorbed propene, a vacant site and oxygen in the gas phase. The following rate expression was proposed

$$\text{Acrolein Production Rate} = \frac{k_s K_1 (C_3H_6) (O_2)}{(1 + k_1 (C_3H_6) + k_2 (C_3H_4O))^2}$$

Billingsley and Holland(9) presented a very different picture of propene oxidation kinetics over a copper oxide catalyst. The reaction was studied in a differential reactor at 240°C. The reaction was found to be limited by mass transfer of the oxygen. The following rate equations were proposed:

$$\text{Acrolein Production Rate} = \frac{0.72\ k (C_3H_6) (O_2)}{0.72 (C_3H_6) + 4.5 (O_2)}$$

Carbon Dioxide Production Rate

$$= \frac{3\ k (O_2)^2}{0.72 (C_3H_6) + 4.5 (O_2)}$$

The catalyst, a coprecipitated copper oxide-alumina was calcined at 800°C and was therefore quite different from the copper oxide deposited on inert supports having low surface area used by most of workers.

Dowden and Coldwell(17) investigated the effect of reactant ratio, contact time and temperature on the conversion and yield of 2-methylpropene oxidation. A conversion of 17 % per pass with a 95 % yield of methacrolein was obtained at 400°C on passing 100 liter/hr of a mixture of 85 % air and 15 % by volume of 2-methylpropene through a flow reactor packed with 30 ml. of a silite supported copper catalyst.

Popova and Milman(61,62) studied the kinetics of 2-methylpropene oxidation to methacrolein in a conventional flow reactor. They reported the rates of methacrolein and carbon dioxide formation were first and zero order with respect to oxygen and olefin respectively. The same orders has veen reported by Mann and Rouleau (45) for the overall oxidation in a static system between 360°C and 400°C

Mann and Rouleau(46,47) also published data on kinetics of oxidation of 2-methylpropene to methacrolein over a copper oxide catalyst supported on pumice in a flow system, and obtained the following rate equation:

$$\text{Rate} = \frac{a\ K_1\ (C_4H_8)\ (O_2)}{1 + K_1\ (C_4H_8) + K_2\ (C_4H_6O)}$$

It has been suggested that the rate controlling step was the surface reaction between adsorbed 2-methylpropene and gases oxygen or weakly adsorbed oxygen.

Hearne and Adams(26) studied the oxidation of several olefins over copper oxide catalyst. The reaction was not necessary a direct substitution in allylic position but involved a hydrogen elimination from the allyl position and a shift of the double bond, since methyl vinyl ketones and not crotonaldehyde was made from both butene-1 and butene-2.

Voge, Wagner and Stevenson(73) used carbon 14 tracer technique to investigate the mechanism of propene oxidation. It has been observed that half of the heavy carbon in the acrolein product was in the carbonyl group and the isomerization of the unreacted propene was negligible. It has been suggested that the only plausible mechanism seemed to be the initial removal of a hydrogen atom from the methyl group to form an allyl intermediate which subsequently reacted at either end with equal probability. It has also been pointed out that carbon dioxide was largely formed from complete oxidation of acrolein. Adams and Jennings(2,3) confirmed and extented this scheme.The oxidation of propene labelled with deuterium in various positions over two catalysts cuprous oxide and bismuth molybdate to acrolein and in the presence of ammonia to acrylonitrile has been reported. The mechanism of propene oxidation was found to be the same over both catalysts.

The catalytic oxidation of 2-methylpropene over selenium dioxide and sulfur dioxide modified copper oxide catalysts has been studied by many investigators and according to Mann and Yao(48,49) the presence of an optimum amount of those oxides increased the selectivity of the catalyst for methacrolein very much. It has been suggested (51) that by controlling the distribution of positive holes and free electrons on the catalyst surface with a controlled valency state of the skeleton catalyst, a high selectivity in the partial oxidation products could be expected. It has been postulated that the partial oxidation of 2-methylpropene to methacrolein is a p-type reaction (reaction rate was accelerated with the increase in positive hole concentrations on the catalyst surface) and its further oxidation to carbon dioxide was an n-type reaction (reaction rate was accelerated with the increase in concentration of free electrons on the catalyst surface) under optimum conditions. They also reported(51,52,53) the effect of modifiers such as sulfur, bromine, chlorine and iodine on the vapor phase air oxidation of propene and 2-methylpropene to acrolein and methacrolein. It has been reported with the presence of small amounts of these modifiers, the selectivity for unsaturated aldehydes increased very substantially. The promotional effects of different modifiers are compared and discussed. It was observed that the weight ratio of modifier to olefin in the feed is the most important variable in the selective oxidation of olefin, and that its optimum value is in the range of 0.0005 to 0.0015 for the oxidation of 2-methylpropene. They suggested the rate determing step is the surface reaction between adsorbed olefin and oxygen on different active sites. The rate of reaction was expressed as

$$r = \frac{K_s K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

Where K_S, K_H, and K_M are temperature dependent constants.

III. EXPERIMENTAL

The partial oxidation of 2-methylpropene was investigated in a flow system. A schematic diagram of the experimental apparatus used in the study of the reaction is shown in Figure 1.

A. Reactants and Chemicals

1. 2-methylpropene:

C.P. grade 2-methylpropene (Matheson of Canada Ltd.) with a minimum purity of 99.0 % was used in this investigation. The gas was received in cyclinders containing 126 lbs. of liquid 2-methylpropene at a pressure of 24.3 p.s.i.g. (70°F). Analysis of 2-methylpropene by the gas chromatograph showed that the presence of impurities were in such minor quantities, that they did not interfere with the experimental accuracy.

2. Air:

The air used was supplied by the Linde Co. in compressed cylinders at a pressure of 2500 p.s.i.g. Analysis of air by the gas chromatograph showed that it contained 20.95 % oxygen, 0.05 % carbon dioxide and 79 % nitrogen.

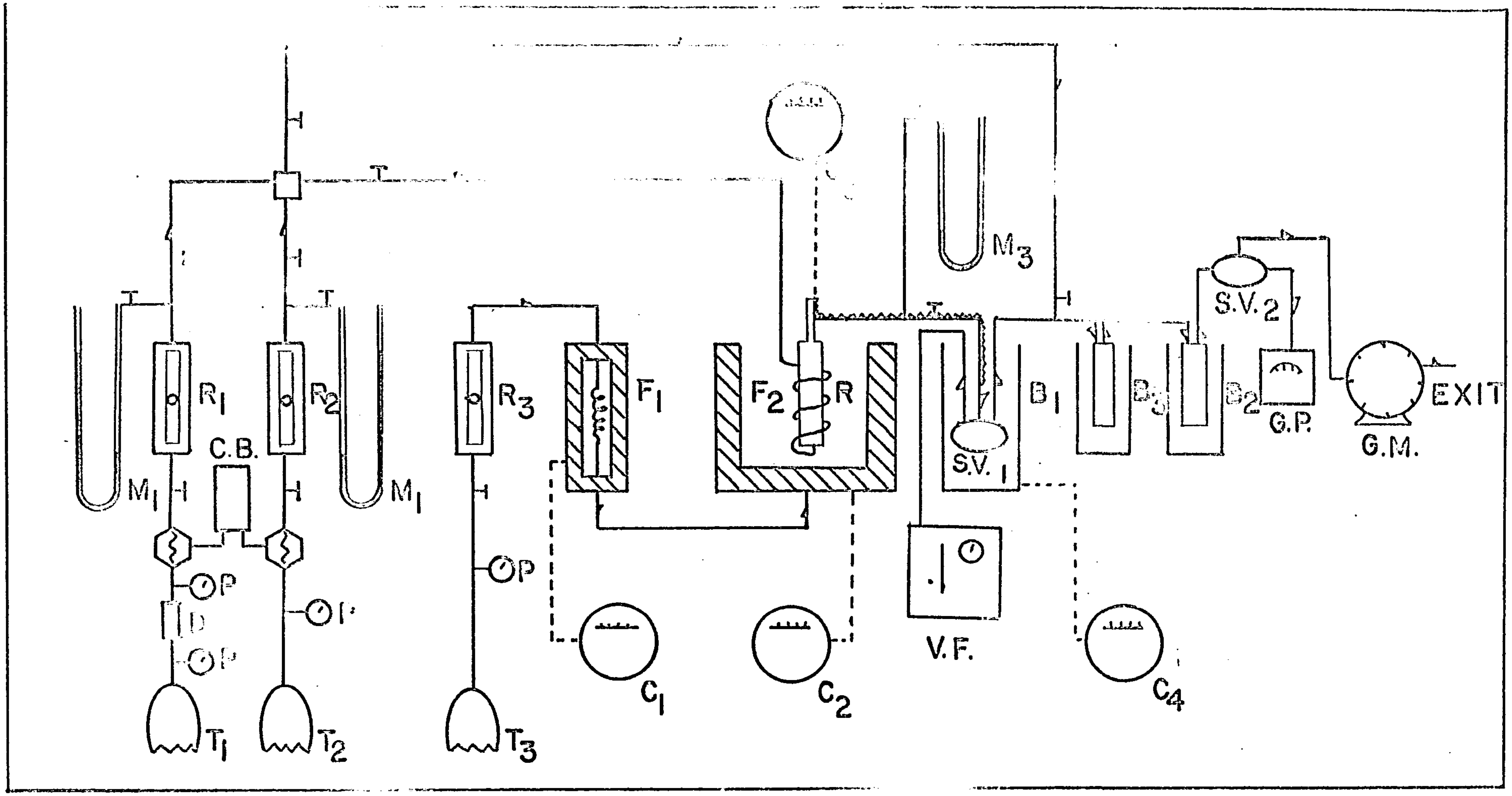


Figure III-1 Schematic Diagram of the Apparatus

Where	B_1	: oil bath	D	: drying tube	G.P.	: gas partitioner	SV_1, SV_2	: sampling-valves
	B_2, B_3	: ice bath	F_1, F_2	: furnace	M_1-M_3	: manometer	T_1, T_3	: air tank
	C_1-C_4	: temp. controller	P	: pressure controller	R	: reactor	T_2	: C_4H_8 tank
	C.B.	: water bath	G.M.	: gas test meter	R_1-R_3	: rotameter	V.F.	: vapour-fractometer

3. Helium:

Helium with a minimum purity of 99.99 % was used, supplied by Canadain Liquid Air Ltd. Gas chromatographic analysis showed no significant impurity.

4. Chemicals:

Bismuth citrate

$BiC_6H_5O_7 \cdot H_2O$, K & K Laboratories Inc., Lot No. 12307.

Molybdic anhydrate

MoO_3, Fisher Scientific Co., Catalogue No. A-174, Lot No. 791663.

Zirconium oxide

ZrO_2, Fisher Scientific Co., Catalogue No. Z-87, Lot No. 771142.

Cupric nitrate

$Cu(NO_3)_2 \cdot 3H_2O$, Fisher Scientific Co., Catalogue No. C-467, Lot No. 292266.

Ammonium Hydroxide

NH_4OH (28 % to 30 % of NH_3), McArthur Chemical Co. Ltd.

Methacrolein

C_4H_6O, reagent grade, K & K Laboratories Inc., Lot No. 3903. The gas chromatograph showed that it contained 98 % minimum methacrolein with acrolein as the main impurity.

B. Preparation of the catalysts

Bismuth molybdate catalysts were prepared by impregnation of inert supports of zirconium oxide with aqeous solutions of bismuth and molybdenum salts of hydroxypolycarboxylic acid with small amount of copper nitrate.

200 gms. of bismuth citrate was dissolved in 160 gms. of concentrated aqeous solution of NH_3, which was then diluted to 1000 ml. and was labeled as solution A. 85.2 gms. of molybdic acid was dissolved in 80 gms. of concentrated aqeous solution of NH_3, which was then diluted to 500 ml. and was labeled as solution B.

Zirconium oxide was cleaned by boiling with concentrated hydrochloric acid for half an hour and washed with warm distilled water until the addition of silver nitrate solution did not give any precipitate. It was then dried in an oven at 150°C for 10 hours.

Solutions A and B in a 2:1 ratio were mixed and a small amount of $Cu(NO_3)_2$ was added to the mixture. This was then poured onto zirconium oxide (particle size 20-40 mesh). For every 100 ml.

of mixture solution of A and B. 0.8 gms. of copper nitrate was added and 50 gms of zirconium oxide was used. Water was evaporated in vacuum on a steam bath the solid was calcinated at 450° C for 6 hours in a muffle furnace.

Catalysts was charged into the reactor and activated by passing air over it for 24 hours at 450°C.

C. Experimental Apparatus

The experimental equipment, made of 316 stainless steel throughout, was designed to investigate the kinetics of catalytic partial oxidation of olefins to corresponding aldehydes. A schematic diagram of this apparatus is given in Figure 1. The apparatus itself may be divided into three main sections: (1) Feed, (2) Reactor Assembly, and (3) Product Analysis.

(1) Feed Section

All tubing in this section were 1/8 inches in O.D. and made of 316 stainless steel. All pressure fittings, valves, used in this section were made of 316 stainless steel and were supplied by Autoclave Engineering Inc., Erie, Pa. (unless otherwise specified), They were capable to withstand pressures of 5000 lbs./sq.in.

The reactants, dry air and chemically pure 2-methylpropene were obtained from high pressure cyclinders, through high pressure diaphram type regulators (Matheson, one stage, model 1P for 2-methylpropene, and Matheson, two stage, model 8C for air) and their pressures reduced to 20 lbs./sq.in. gauge. The air was subsequently passed through a drying tube where trace amounts of moisture were removed.

Prior to the gases passing through the Brooks rotameters, both gas lines were immersed in a circulatory constant temperature bath (Precision Scientific Co., Chicago). Two Matheson flowmeters with needle valve (model series No, 622P5V, tube size 601,602 for air and 2-methylpropene respectively) and fine metering valves (Nupro Co., Cleveland, Ohio) were used for controlling and measuring the flow rates of 2-methylpropene and air. Each flowmeter was connected with a mercury mamometer at its' outlet so that the pressure effect on the gas flow rates could be corrected.

Air and 2-methylpropene were mixed before entering into preheater, in this section, a 5 ft. length, 1/8 in.O.D. 316 stainless steel tubing were wound around the reactor and immersed in a fluidized sand bath, where the temperature of the mixed gases was raised to reaction temperature, details of which are given in Figure 2.

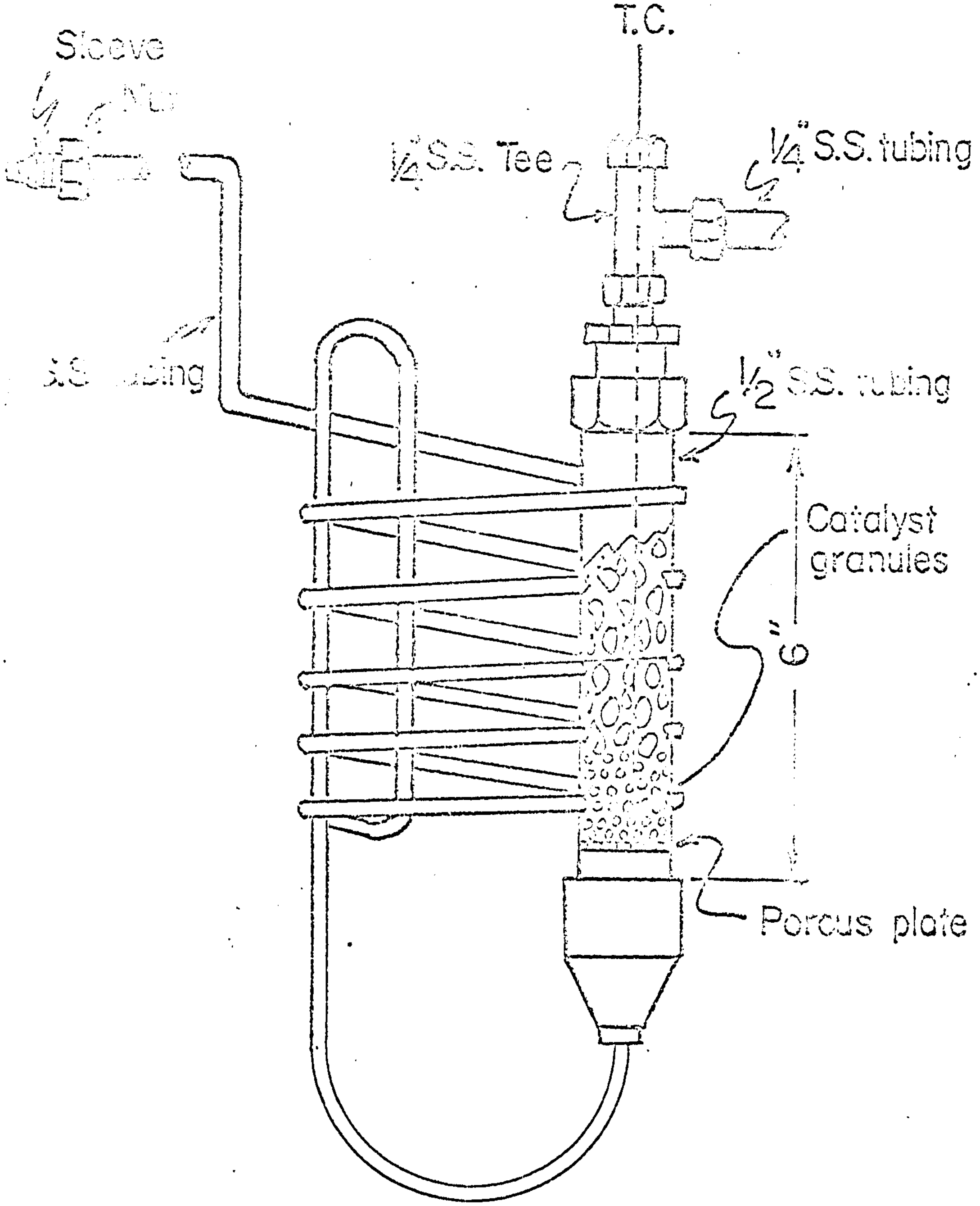


Figure III-2 Reac[illegible]d Preheater

(2) Reactor Assembly

The reactor was made from a 6 in. long, 1/2 in. O.D. 304 stainless steel tubing (Figure 2). A porous stainless steel plate (grade D plate with a mean pore size of 65 microns, a normal thickness of 1/16 in., and which produced a pressure drop of approximately 0.1 p.s.i.g. per 180 cfm / sq. ft. of air, supplied by Pall Trinity Micro Corporation, Cortland, New York) was installed at the bottom fo the tube. This served as a support for the catalyst. A Swagelok reducer was used below the porous plate and attached to the air-2-methylpropene preheater from feed section.

The top of the reactor was fitted with a Swagelok "T" connection. A stainless steel tubing, 1/16 in. O.D. containing two chromel-alumel thermocouples was inserted through this connection to a level just above the top of the porous plate. Where the first thermocouple in protection tube was connected with the temperature controller C_1 for controlling the catalyst bed temperature, the second was connected to a potentiometer (Honeywell, model 2745) for measuring the temperature during the reaction. The thermocouples were supplied by Honeywell Controls Ltd., Montreal, P.Q.

The temperature of the reactor was controlled by a Fisher electronic pyrometer controller (model OVA 536), by connection with transducers such as thermocouples that generated a millvolt signal. The controller measured the output of a thermocouple positioned in the reactor and provided relay contact closure to maintain the reaction temperature to within ± 2°C.

The fluidized bed furnace was made from a 2 feet long, 4 in. O. D. and 1/4 in. thick brass cylinder with a porous stainless steel plate inserted at the bottom. Two independent Ceram-A-Flex beaded heating wires (Chemical Rubber Co., Cleveland, Ohio) with resistances of 30. and of 25 ohms respectively were wrapped around the shell side of the brass cyclinder. The 25 ohms wire was connected to powerstat then to temperature controller C_1. The wire with 30 ohms was connected to a powerstat only and the powerstat was set in such a way as to produce sufficient heat to overcome the heat losses to surroundings. The shell side of the brass cyclinder was pasted with a 1 in. thick layer asbestos cement.

Sand was used as the heating medium for the fluidized bed and was placed inside the brass cyclinder on top of the porous plate. Where the reactor was held upright in the center of the bed, the sand was almost completly filled to the top.

Compressed air was used to fluidize the sand, which was first passed through a filter to remove oil and moisture, and then the pressure was adjusted to 30 p.s.i.g. by a pressure regulator (Bink M.F.G.Co., Chicago, U.S.A.) . Before it was introduced into the fluidized bed, a Brooks flowmeter and a valve were used to measure and control the compressed air flowrate. With the help of an electric furnace and a temperature controller C_2 (Honeywell, model 2745) The temperature of the compressed air was raised to about 10° less than the desired reaction temperature.

The reactor and the fluidized bed were then placed in the center of another aluminium cycliner, which was one foot in diameter, and rested on a piece of asbestos board, in the center of which a hole had been drilled for the compressed air line. The space between the aluminium cycliner and brass cycliner was packed with fiber glass wool for insulation.

(3) Product Analysis

This section consisted of two ice traps, a drying tube, two gas chromatographs with two sampling devices for analyzing the unreacted reactants and reaction products, two chart recorders for recording gas chromatographs, a constant temperature oil bath and a wet test meter were used. The reactants and products were analyzed on stream in the form of gas or vapour.

From the reactor all the gas line was made out of 1/4 in. O.D. 316 stainless steel tubing. The line in between the liquid sampling valve and the reactor was wrapped with heating tapes controlled by temperature controller No. 3 (Yellow Springs thermistor temperature controller model 63, having a temperature deviation of ± 0.05°C) The sensing element probe was placed in the line just before the liquid sampling valve.

The high temperature sampling valve supplied by Perkin-Elmer Corp., New Jersey, was made of stainless steel with a teflon rotor which can stand a temperature up to 200°C and a 50 p.s.i.g. pressure without any leakage. The bath oil was heated by an immersion heater (Fisher, Catalogue No. 11-463-1804) with a Variac powerstat. A constant bath temperature was maintained by temperature controller C_4 (Yellow Springs Thermistor Temperature Controller model 71) with a temperature deviation ± 0.01°C. The liquid bath, 10" x 10" O.D. (Pyrex-Corning Glass Works, Corning, New Jersey) was well insulated with asbestos cement and glass wool to reduce the heat losses to the suroundings. The temperature of the sampling gases, were maintained at 100° C . The pressure was controlled at 874 mm Hg by adjusting the needle valve in the exit line.

The Perkin-Elmer model 154-D Vapour fractometer equipped with thermal conductivity cell detector (consisting of matched thermistors), D.C. power supply and electronic temperature controlling system was used to separate acrolein, methacrolein, and water.

A Philips chart recorder Pr2216, with various multi-range unit was connected to the vapour fractometer to record the peak composition of the effluent stream.

The exit gas from the high temperature sampling valve was led to the condenser, then ice-cooled traps, where the heavier reaction products, water and small amount of methacrolein were condensed in the traps. The uncondensable gases were led to the drying tube.

The drying tube, made of a 4 in. x 1 in. O.D. pyrex was packed 10-20 mesh indicating drierite (Calcium sulfate anhydrous), two pieces of stainless steel gauge wire of 100 mesh were placed at either end to prevent the small Drierite particles from escaping into the gas stream. Before the uncondensable gases entered into the Fisher gas partitioner for analysis, at the condenser and by drying tube, all traces of moisture from the gaseous reaction products, which could damage the column were removed.

The product stream was led to the Fisher gas partitioner. through a six-way linear gas sampling valve (Aerograph Co.), the sampling gas then passed through the sampling loop (0.25 ml.) and vented.

A stream of the carrier gas, (helium) passed through the other leg of the sampling valve on its way to the separating columns in the gas partitioner.

When the sampling valve was turned on, the sampling loop was taken out of series with the product stream, and was simutaneously connected with the carrier gas. It was then possible to flush reproducible sample volumes into the separating columns of the gas partitioner.

The Fisher Gas Partitioner (model 25V) with a dual columns and dual detectors could separate oxygen, nitrogen, methane, propane 2-methylpropene, carbon dioxide and carbon monoxide. A constant temperature of 40° C was maintained by the Fisher thermal stablizer (model 27).

A zero suppressor (Fisher Scientific Co.) 0-10 mv. was connected to the gas partitioner and the chart recorder (Texas Instrument Inc., Texas model servo/ritter II), to suppress any signal to recorder, which may exceed 1 mv.

D. Experimental Procedure

(1) Leakage Check and Calibration

Leakage check, calibrations of chromatograph columns and of gases flow rates were carried out perodically to assure experimental accuracy.

a) Leakage Test

Leakage test for the experimental apparatus were carried out at 50 p.s.i.g. with every accessible connection part tested with Snoop.

With the inlet valves, down stream valves of the manometers, and outlet valves were closed, there was no indication of pressure drop in the entire system or isolated sections.

There was no indication of gas flow through flowmeters, on closing the manometer branch valves and the outlet valves.

b) Calibration of Equipments

Rotameters

Flow rates of the gas streams were measured by calibrated rotameters. The temperature of the inlet gases were maintained at 25° C . by a circulatory constant temperature bath. The pressure was maintained at 1010 mm Hg. by the manual adjustment of the fine metering valves on the exit side of the rotameters. The volumetric flow rates were checked by both the soap bubble method and wet test meter. The operating temperature and pressures remained constant throughout the whole experiment (both calibration and experimental runs). Calibration curves for the flow rates of air and olefin are given in Appendix A.

Thermocouples

The thermocouples were calibrated by inserting them into the fluidized furnace and an ASTM thermometer was attached to it. A calibration curve of temperature against thermocouple indicating temperature, which was measureed by a potentiometer is given in Appendix A.

Chromatograph Columns

Synthetic mixtures, similar to the actual samples, were used to calibrate the gas partitioner and the vapour fractometer, with the time and order of elution of the components based on previous injections of the pure components.

The gas samples were separated by the Fisher gas partitioner. A synthetic mixture of both gases was prepared from the feed section through the bypass of the reactor. Mixtures of oxygen, carbon dioxide, 2-methylpropene and carbon monooxide with nitrogen in a varying proportions were accordingly made for separation on the gas partitioner. The sampling gases were maintained at 25° C by connecting it with the circulatory constant temperature controller from the feed section. Mixtures of water, acrolein and methacrolein of known composition were injected into the Perkin-Elmer Model 154-D vapour fractometer. The calibration curves, both for the gas partitioner and vapour fractometer, are given in Appendix A
The widths of each of the component peaks in the samples tested were found to be nearly unchanged. A quantitative analysis could therefore be based on either peak height or the relative peak hight ratio versus percentage composition or mole ratios.

The peak height ratio method (internal normalization method) was chosen due to its simplicity and greater accuracy over [illegible] method of measuring the areas under the peaks with an integrator, since the variations due to the differences in each sample, especially when the sample quantites were very small, were negligable.

The density of acrolein, methacrolein and water at 20°C. (room temperature at time of calibration) were determind by using the psychometer. The calibrations are given in Appendix B.

(2) Analysis Procedure

a) Acids

The total acid content was obtained by titration of the condensate from the traps with 0.055 N potassium hydroxide solution. Phenolphthalein was used as the indicator for the titration. The total acid was found to be too low to effect the material balance. Therefore, it was not included in the analysis of the products.

b) Aldehydes and Water

The hot effluent from the reactor was directly introduced into the Perkin-Elmer vapor fractometer through a high temperature sampling valve. The temperature and presure of the sample gas were well controlled.

The column used for the separation was 6 ft. long 15 % by weight of carbon-wax 1500 (supplied by Gas Chromotographic Specialities, Brockville, Ont.) coated on columnpak T (Teflon Powder). Methyl chloride was used as the solvent. Though the column could separate acetone, acetaldehyde, propionaldehyde,butyraldehyde, crotonaldehyde, acrolein, methacrolein and water, yet only acrolein, methacrolein and water were observed in the product stream. A typical chromatograph obtained from Vapor Fractometer is shown in Figure. III-3.

c) Gases

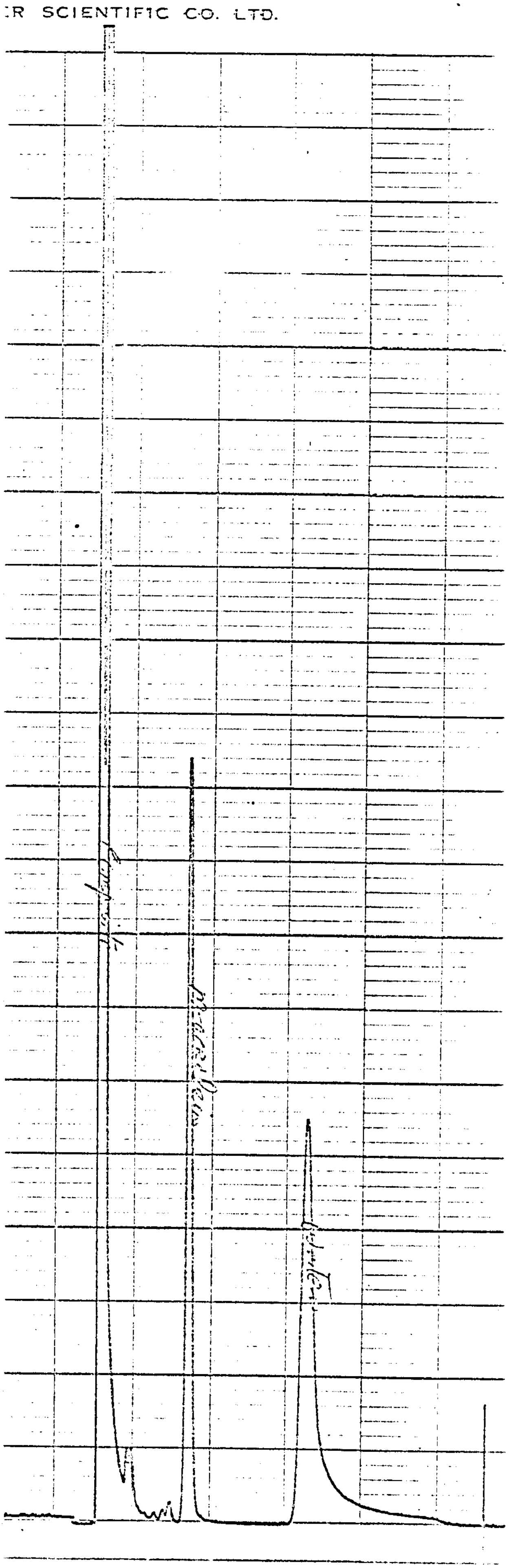
The inlet feed and the product gases were analyzed for carbon dioxide, oxygen, nitrogen, propene, 2-methylpropene and carbon monoxide by periodic injection of 0.25 ml. sample into the Fisher Gas Partitioner containing two $\frac{1}{4}$ in. O.D. copper tubing column joined in series.

The first column was packed with a 6 ft long, 30% HMPA (hexamethylphosphoramide) coated on celite diatomaceous silica followed by a foot long 30% DEHS (di-2, ethylhexyl sebacate) coated on celite diatomaceous silica which could separate carbon dioxide, propene and 2-methylpropene. The second column was packed with a 7 ft long molecular sieve

Figure III-3

Typical Chromatograph From

Vapour Fractometer



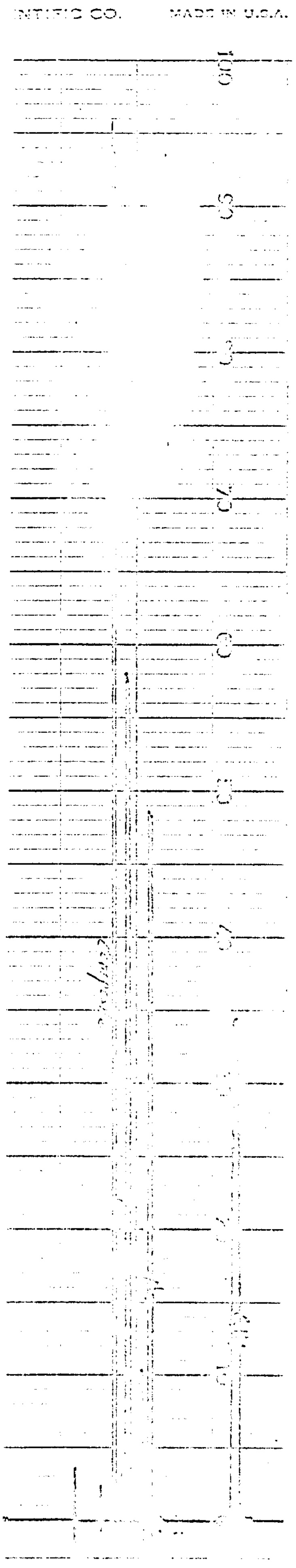


Figure III-4

Typical Chromatograph From

Gas Partitioner

5A followed by a 5 ft long uncoated celite diatomaceous silica and was used to separate oxygen, nitrogen and carbon monoxide. A typical analysis of the products form the Gas Partitioner is shown in Figure 4. Nitrogen gas was used as the key component for its chemical inertness.

(3) Operating Procedure

Details of the experimental procedure for making a run with a specified weight of fresh catalyst are described in this section.

a) Start up

i) Test the system for any leaks by pressuring the system with air to 50 p.s.i.g.

ii) Purge the feed line and reactor with compressed air at 20 p.s.i.g.

iii) Turn the helium gas streams,and the temperature controllers for the gas partitioner and vapor fractometer on.

iv) Switch on the detectors and recorders for gas chromatographs.

v) Compressed air for fludized bed was turned at 30 p.s.i.g. Flow rates depended on the reaction temperature.

vi) Charge the reactor with the desired weight of fresh catalyst and cover it with a layer of glass wool to prevent the catalyst escape from the reactor.

vii)Switch on the varous "Variac" powerstats and the temperature controllers for

1) The inlet gases.

2) Fluidized bed furnace.

3) Furnace for compressed air, used in fludidized bed.

4) Reactor.

5) Sampling gas for vapor fractometer.

6) Turn on the air stream for the activation of the catalyst and later the oxidation of olefins.

b) Run

i) When the required temperature was attained, olefin was added to the feed stream and the flow rates of olefin and air were adjusted so as to give the desired total flow rate and molecular ratios of oxygen to olefin in the feed.

ii) Maintain the feed gases at their specified flow rates for 2 hours to obtain steady state conditions at the particular temperature desired.

iii) Place the traps in position, and continue the run for another hour, while maintaining the required feed ratio and reaction temperature constant.

iv) Introduce the hot effluent gases from the reactor into the vapor fractometer via the high temperature sampling valve and the uncondensable gases from the ice-cooled traps into the gas partitioner via another sampling valve, until both samples in the two gas chromatographs show no change in composition therby indicating that a steady state has been reached.

V) Continue the steady state run for another hour during which time at least two samples would be analyzed.

Vi) Shut off the olefin feed and keep air flowing through the catalyst bed for another hour, before the start of another run.

Vii) Drain the condensates from both traps.

Viii) Periodically the gas chromatograph calibrations and flow rates of gases were checked to assure the stablity of the columns and of the system.

IV RESULTS

The experimental data were obtained by means of an isothermal fixed bed reactor at 1.15 atmospheric pressure. Steady state was not only realized from the operating conditions but also from the product analysis. The effects of various variables, namely oxygen to olefin ratio in feed R , reaction temperature, T and the reciprocal of space products, W / F , on the conversion of olefins, X , yield of various product, Y , carbon dioxide, water and aldhydes and also the selectivity, S , of the catalyst for methacrolein formation were investigated.

Conversion (X) is defined as the moles of 2-methylpropene reacted per hour to the moles of 2-methylpropene feed per hour, the yield (Y) is defines as the moles of various products formed per hour to the moles of 2-methylpropene feed per hour. The ratio of the moles of methacrolein produced per hour to the moles of 2-methylpropene reacted per hour has been defined as selectivity (S) .

Throughout the experiments, the rate of olefins charged into the reactor was maintained constant, different feed ratios were obtained by adjusting the air flow rate. The reciprocal of space velocity was varied by changing the amount of catalyst.

The effect of feed ratio (oxygen / 2-methylpropene), reaction temperature on the conversion, selectivity for oxidation of 2-methylpropene over bismuth molybdate catalyst at temperature range of 360°-560°C, oxygen to 2-methylpropene ratio of 0.8995 -2.4000 are shown in Figure IV-1 , and experimental data are given in Appendix D, while the selectivity for methacrolein decreased with decreased oxygen to 2-methylpropene ratios, it increased at lower temperature.

The effect of the reciprocal of space velocity on the conversion, yield and selectivity for the oxidation of 2-methylpropene at various feed ratios and temperature is given in Figure V-8,9,10,11 and the data are tabulated in Appendix D. The conversion of 2-methylpropene and the yield of methacrolein and carbon dioxide increased rapidly at longer contact time. However it was affected little for short contact time.

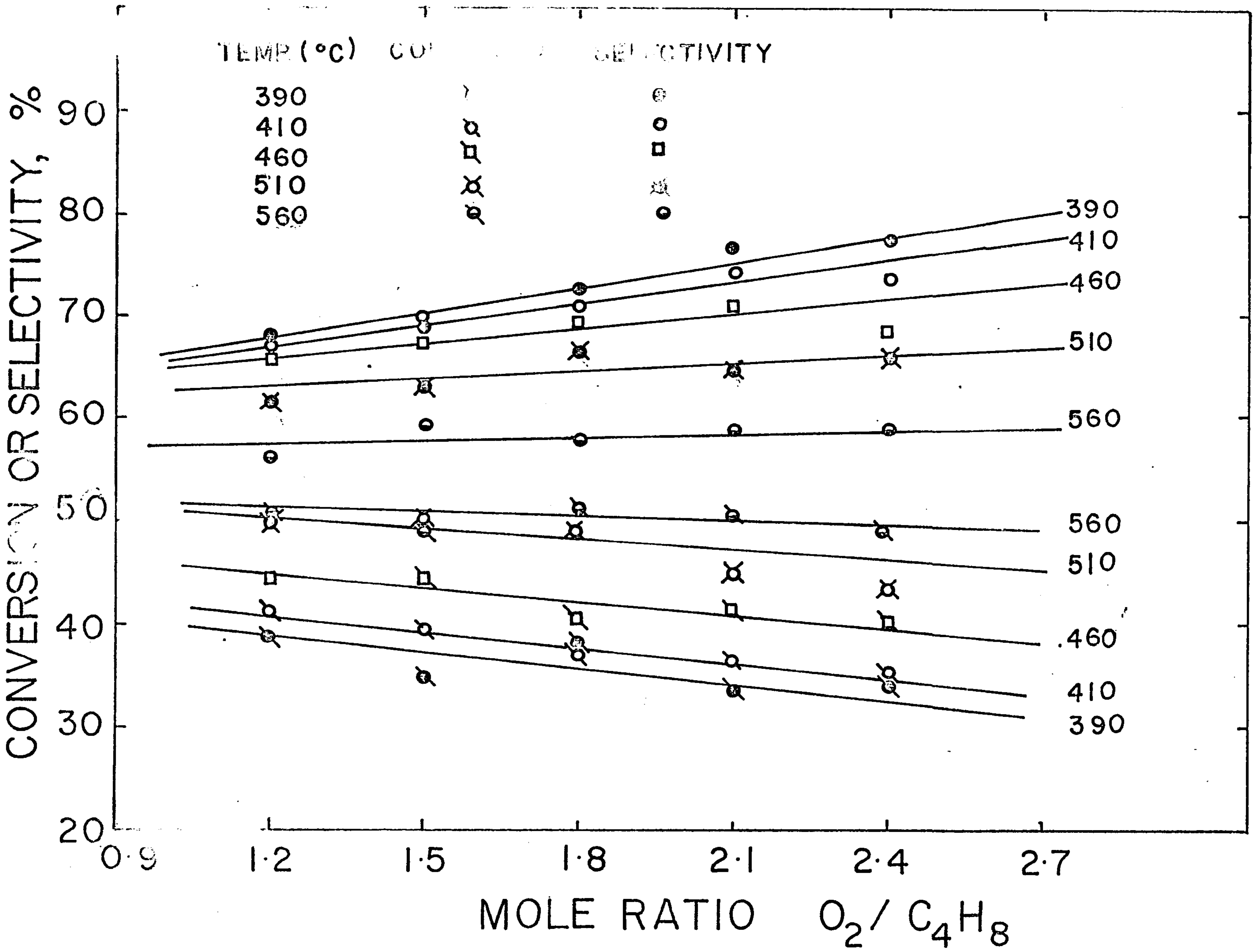


Figure IV - 1 Conversion or Selectivity Versus Mole Ratio (O_2/C_4H_8) in Feed for W/F = 3.75

V KINETIC ANALYSIS OF DATA

It is generally believed that in the course of catalytic reaction a catalyst must participate in intermediate steps in such a manner as to facilitate the over-all course of the reaction. In terms of absolute reaction rates the function of the catalyst is to reduce the positive free-energy change accompanying the formation of the activiated complex. This may be brought about by the substitution of a sequence of steps. Each having a low free energy of activation for a single step involving a high free energy of activation in the uncatalysed reaction. Catalysts may also function through forming definite intermediate compounds with the reactants. The high degree of specificity of chemical combination is then in agreement with the selectvity exhibited by catalysts in accelerating certain reactions in preference to others. For solid catalysts, which function through the occurrence of intermediate reaction at definite points on their surface. Those points are known as active centres or active sites.

To design or to analyse a catalytic flow process, the pertinent problem is the relationship between the reaction rate and operating variables. The Hougen-Watson type rate equations represent a methodical and systematic way of describing this relationship. The reaction rate, r, can be expressed as a function of conversion.

In order to correlate the experimental data directly it is customary to apply the Langmuir-Hinshelwood Theory to derive a rate expression in terms of partial pressures of reactants and products.

A. Rate Steps in Heterogenous Catalysis

Chemical reactions involving a fluid-solid system, that is, reaction in which the reactants and products are fluids and the catalyst a porous solid, involve the following seven successive steps:

(1) Diffusion of the reactant molecules from the main gas stream to the 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 gas stream.

In the electronic theory of catalysis, the electron transfers between the reactants, products and catalyst are involved. Hence two additional steps should be added to the list in such cases, i.e.

(3a) Charged adsorption of reactants on the catalyst surface (strong chemical bond, either p or n type is formed).

(5a) Discharged desorption of products on the catalyst surface.

It is evident that the rates of these steps are dependent on the operating conditions for the system. Each of these steps offers some resistance to the overall process. If all these resistances were considered, the resulting rate equations could be very complicated. Steps 1, 2, 6 and 7 are physical process which can be minimized or accounted independently as will be described later. The chemical steps 3,4,and 5 that lend insight into the nature of catalytic reactions which can not be reduced by altering physical conditions and hence are the most important ones to consider. The inclusion of 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. Exterior Heat and Mass Transfer Effects

In correlating the experimental data for the rate equations of solid surface catalyzed reactions, the partial pressures and temperatures should be the values at gas-solid interface. These interfacial partial pressures can be significantly different from those in the ambient stream due to the resistance in the gas film to the diffusion of reactants towards, and of products away from the exterior catalyst surface. Similarly, temperature differences could exist between the exterior catalyst surface and the ambient stream due to the release of large amounts of heat of reaction in highly exothermic reactions at the catalyst surface.

It is desirable, in an experimental packed-bed reactor, to establish very large heat and mass transfer coefficient such that the conditions at the surface of the catalyst particle are very close to those measured in the ambient stream. It is then simplified the procedure to correlate the experimental data for reaction rate equations. An estimation of the temperature and pressure drop from the bulk gas stream to the surface of the catalyst by using the method of Yoshilu et al. (79) for the experimental data is given in appendix F. The highest partial pressure gradients, calculated was found to be of the order of 0.05 and the temperature at the catalyst surface was calculated to be 5^{o} C. higher than that of the main gas stream. Hence, these effects could be neglected.

C. Internal Diffusions

Two kinds of diffusion in pores are possible, bulk diffusion (molecular diffusion) and Knudson diffusion depending on whether the mean free path between intermolecular collisions is small or large compared with the pore radius.

(1) Molecular diffusion:

It will predominate with all catalysts at very high pressure ($>$ 100 atm) or at atmospheric pressure with catalysts having very large pores ($>$ 5000 Å radius). The effect of molecular diffusion in this investigation was minimized by passing the gas stream at high velocity through the catalyst bed, and the extent was evaluated by varying the feed rate while the reciprocal of space velocity was kept constant. The results are given in Appendix and represented in Figure V-1 . The constancy of conversion indicates that molecular diffusion was negligable.

(2) Knudson diffusion:

It occurs in small catalyst pores, i.e. at atmospheric pressure, when the mean pore radius is $<$ 200 Å .

A common experimental method of determining the importance of Knudson 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

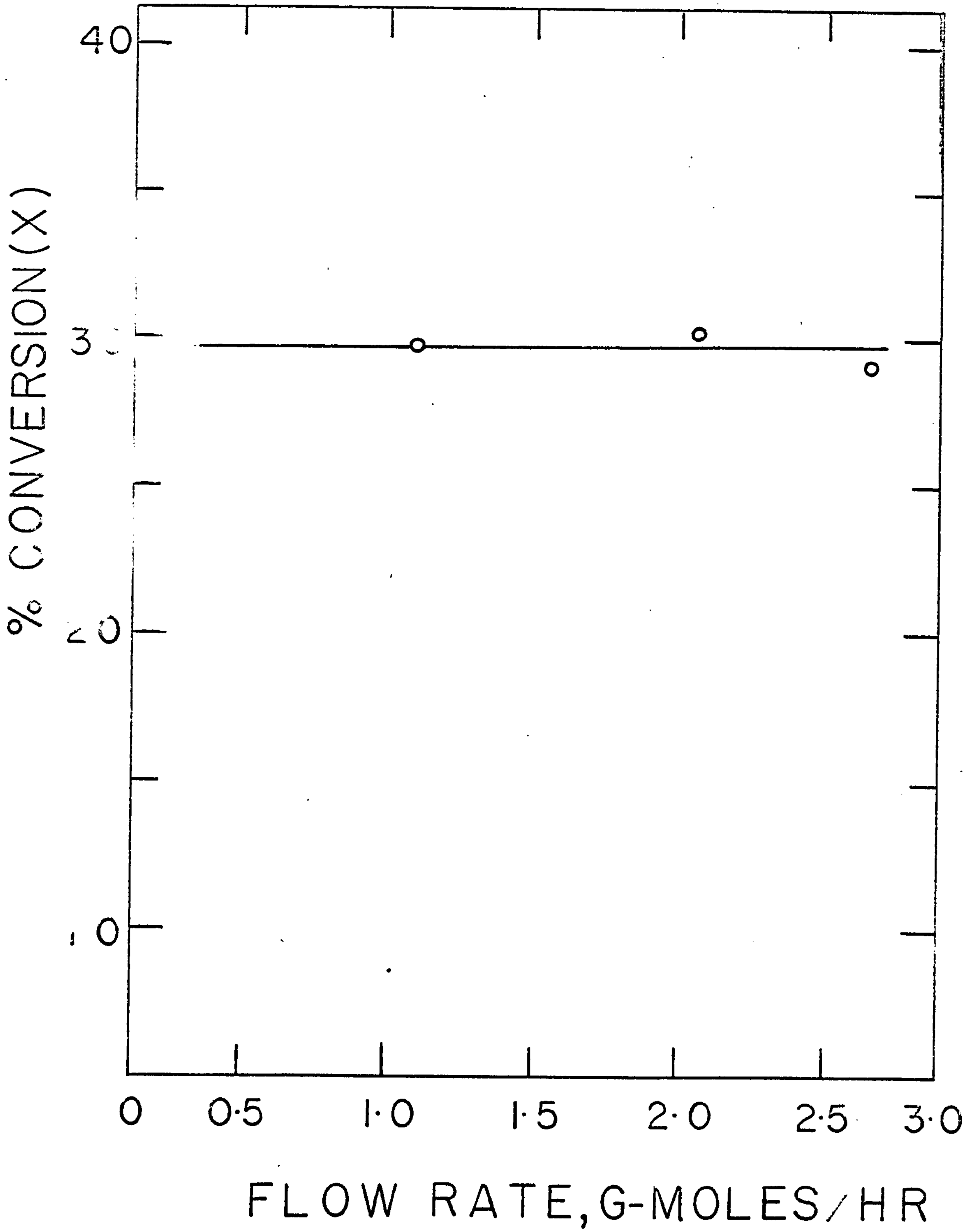


Figure V-1 Effect of Feed Velocity on Conversion for Oxidation of 2-methylpropene particle. The catalyst used throughout this study was prepared by crushing the support and consisted of a 20 to 30 mesh screen fraction. The average diameter of the particle was 0.58 mm. The catalyst selected for evaluating the magnitude of Knudson diffusion consisted of H 40 to 60 mesh screen fraction with an average diameter of 0.31 mm. As shown in table 5-1 , the particle size of catalyst did not significant effect the conversion rate, thereby implying that the Knudson type diffusional effect was not rate-determining and hence could be negleted.

D. Correlation of Rate Equations:

Since mass transfer of reactants or products between the gas stream and the catalyst external surface, diffusion of reactant molecules or product molecules to or from the interior of catalyst pores are not rate controlling, it is left for consideration only the possibility of the adsorption of the reactants, desorption of the products and surface reaction as rate controlling. These are all chemical processes, and are examined in detail in order to determine which one offered the greatest resistance to the overall reaction. For each of the three chemical steps, several mechanisms can be postulated depending on whether one or both of the reacting substances are adsorbed on the catalyst surface.

TABLE 5-1

Experimental Data For Knudson Diffusion With Bismuth Molybdate Catalyst

Run. No.	R	W/F	C_4H_8(in)	O_2 (in)	N_2 (in)
212	1.5014	1.25	o.1105	0.1659	0.6260
212 a	1.5014	1.25	0.1105	0.1659	0.6260

Run No.	C_4H_8 (out)	O_2 (out)	CO_2 (out)	N_2 (out)	H_2O (out)
212	0.0734	0.0931	0.0285	0.6260	0.0574
212a	0.0744	0.0928	0.0269	0.6260	0.0596

Run No.	C_4H_6O (out)	Selectivity	Conversion	Catalyst size
212	0.0299	80.59 %	33.57 %	0.58
212a	0.0303	83.93 %	32.66 %	0.31

(1) Langmuir Isotherm:

While postulating a reaction mechanism for a catalytic reaction mechanism for a catalytic reaction and thereby to obtain a rate expression, adsorption of at least one of the reactants is considered a necessity. Hence a brief description of adsorption isotherms is presented. There are three well known theoretical isotherms, namely, Langmuir, Freundlich and Temkin. Each is characterized by certain assumptions, in particular as to the manner in which the differential heat of adsorption varies with the adsorbed amount, and each is applicable to certain experimental systems. The Langmuir isotherm was chosen mainly because of its simplicity and widely proved applicabilities in the interpretation of adsorption behavior and surface catalysis. Certain idealized conditions are taken as a basis for this development, namely

(i) All the active sites available for the chemisorption behave similarly.

(ii) The energy of an adsorbed particle is the same at any site on the surface and is independent of the presence or absence of nearly adsorbed molecules.

Consider a surface reaction of gaseous reactants, apparently the process of chemisorption involves a reaction between the adsorbate say "g", and active positions on the surface, say " a ". Accordingly the process can be represented by a chemical-type reaction equation, thus

$$g + a' \underset{K_2}{\overset{K_1}{\rightleftharpoons}} g\,a' \qquad (5\text{-}1)$$

It is assumed that the rate of adsorption r_1 of a particular substance at any time is proportional to its partial pressure p and to the fraction 1 - q of surface remaining uncovered at that time. Thus

$$r_1' = K_1 \, p \, (1 - q) \qquad (5\text{-}2)$$

On the other hand, the rate of desorption is proportional only to the fraction q of surface covered, i.e.

$$r_{-1}' = K_{-1} \, q \qquad (5\text{-}3)$$

At equilibrium the rates of adsorption and desorption are equal. Therefore

$$K_1 \, p \, (1 - q) = K_{-1} \, q \qquad (5\text{-}4)$$

$$q = K p \; / \; 1 + K p \qquad (5\text{-}5)$$

where $K = K_1 / K_{-1}$ is an equilibrium constant for adsorption.

Extension to more complex cases. For example, consider the reversible reaction taking place in the presence of a chemically inert material I, with all five substances adsorbed:

$$A + B \rightleftharpoons R + S \qquad (5\text{-}6)$$

The expression for the various q are

$$q_a = \frac{K_a P_a}{1 + K_a P_a + K_b P_b + K_r P_r + K_s P_s + K_I P_I} \qquad (5-7)$$

$$q_b = \frac{K_b P_b}{1 + K_a P_a + K_b P_b + K_r P_r + K_s P_s + K_I P_I} \qquad (5-8)$$

generally

$$q_a = \frac{K_a P_a}{1 + \sum K_i P_i} \qquad (5-9)$$

Where q_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

Based on the Langmuir-Hinshelwood theory of catalysis, assuming that only one of the reaction steps is the rate determining step, the rest of the steps are at equilibrium, the Hougen-Watson type equations can be derived. 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.

As a specific example, a rate equation is developed for the reaction

$$A + B \rightleftharpoons R + S \qquad (5-6)$$

The rate controlling step of the reaction is the surface reaction between adsorbed A and adsorbed B to give R and S. Since in a Hougen-Watson rate equation only one of the successive steps is considered rate-controlling, the adsorption and adsorption stages in this case are assumed to be at equilibrium. The forward reaction rate is proportional to the concentration of adjacently adsorbed AB pairs, C_{AB} :

$$r_f = K' C_{AB} \qquad (5-10)$$

Where r_f = forward reaction rate, moles product formed per unit time per unit catalyst

K' = reaction velocity constant for the surface reaction

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

Since the surface concentration of adsorbed A is C_A and each adsorbed A is surrounded by s active sites including vacant and occupied, also, on the average, coverage of sites by B is q_B, the surface concentration of AB pairs is

$$C_{AB} = C_A \, s \, q_B = C_A \, s \, C_B / L = s \, C_A \, C_B / L \qquad (5-11)$$

Where C_B is the surface concentration of adsorbed B

L is the concentration of active sites, i.e. the number of active sites per unit mass of catalyst divided by the Avogardro number.

$$q_a = C_A / L \tag{5-12}$$

Substituting equation (5-11) into equation (5-10) gives

$$r_f = k' s\, C_A\, C_B / L$$

Substituting for C_A from equation (5-12) and a similar one for C_B, gives

$$r_f = \frac{k' s\, L\, K_A\, K_B\, P_A\, P_B}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \tag{5-13}$$

If the reverse reaction is included, the net forward reaction rate is:

$$r = \frac{k' s\, L\, K_A\, K_B\, (P_A P_B - P_R P_S / K)}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \tag{5-14}$$

Where K = thermodynamic equilibrium constant for the overall reaction

The initial rate of a differential reaction where conversion is extremely small, P_R and P_s are negligible , it then can be written as

$$r_o = \frac{k\, s\, L\, K_A\, K_B\, P_A\, P_B}{(1 + K_A P_A + K_B P_B)^2} \qquad (5\text{-}15)$$

(3) Yang-Hougen Approach

Equation of the type

$$r = \frac{k'\, s\, L\, K_A\, K_B\, (P_A P_B - P_R P_S / K)}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \qquad (5\text{-}14)$$

have been systematically developed and compiled for various adsorption mechanisms and controlling steps. The various terms in equations of this type have been identified by Yang and Hougen (80) by comparison with the fundamental form

$$r = \frac{(\text{Kinetic terms})\,(\text{driving force})}{(\text{adsorption terms})^n}$$

Based on their study, and to apply to our particular investigation, those terms are summarized herewith for the reaction of type

$$A + B \rightleftharpoons R + S$$

and for the following rate-controlling mechanisms.

Rate-Controlling Mechanism:

(i) Reaction between molecularly adsorbed reactants and products without dissociation of any component upon adsorption

a. Adsorption of A controlling

b. Adsorption of B controlling

c. Desorption of R controlling

d. Surface reaction controlling

(ii) Reactant B is not adsorbed, A,R, and S are molecularly adsorbed

e. Adsorption of A controlling

f. Desorption of R controlling

g. Surface reaction controlling

(iii) Reactant A is not adsorbed, B,R, and S are molecularly adsorbed.

h. Impact of A controlling

i. Desorption of R controlling (or S)

j. Adsorption of B controlling

Driving Potential Term

The driving potential in any rate equation fulfills the condition of becoming zero at conditions of equilibrium where the equilibrium constant K is related to the appropriate activity ratio for the overall reaction. In the case of $A + B \rightleftharpoons R + S$ the driving potential is zero where

$$z_A z_B = z_R z_S / K \quad \text{or} \quad K = z_R z_S / z_A z_B$$

Where z stands for activity for component A, B, R, and S according to subscript A, B, R and S.

In accordance with the definition of the equilibrium constant for the over-all reaction. Those driving potentials are summarized in Table 2 for the reaction of $A + B \rightleftharpoons R + S$ and various mechanisoms.

TABLE 5-2 DRIVING POTENTIAL TERMS

REACTION	$A + B \rightleftharpoons R + S$
Adsorption of A controlling	$z_A - z_R z_S / K z_B$
Adsorption of B controlling	$z_B - z_R z_S / K z_A$
Desorption of R controlling	$z_A z_B / z_S - z_R / K$
Surface reaction controlling	$z_A z_B - z_R z_S / K$
Impact of a controlling	$z_A z_B - z_R z_S / K$

Kinetic Term

The designation, ' kinetic term', includes all factors which appear in the numerator of the reaction rate equation other than the driving potential such as L, the total of active sites; the effectiveness factor E; appropriate kinetic constants for adsorption controlling, K_A and K_B; for desorption controlling, K_R and K_S; for surface reaction controlling k_s; The factor s represents the number of adjacent active sites. Values of L and s will usually not be known and will be included in a characteristic constant for a specific catalyst. Overall equilibrium and adsorption equilibrium constants of the reactants A and B may also appear in the kinetic term. Factors in the kinetic term are tabulated in Table 5-3

TABLE 5-3 KINETIC TERMS

REACTION	$A + B \rightleftharpoons R + S$
Adsorption of A controlling	$E\ L\ K_A$
Adsorption of B controlling	$E\ L\ K_B$
Desorption of R controlling	$E\ L\ K_R\ K$
Impact of A controlling	$E\ L\ K_A\ K_B$
Surface reaction controlling without dissociation	$E\ L\ K_s\ S\ K_A\ K_B$
Surface reaction controlling, B not adsorbed	$E\ L\ K_s\ S\ K_A$

Adsorption Term

Where all reactants, products, and inerts are adsorbed under equilibrium conditions and without dissociation, the adsorption term is

$$(1 + K_A z_A + K_B z_B + K_R z_R + K_S z_S + K_I z_I)^n$$

Under other conditions the replacements shown in Table 5-4 should be made

TABLE 5-4 REPLACEMENTS IN THE GENERAL ADSORPTION

$$(1 + K_A z_A + K_B z_B + K_R z_R + K_S z_S + K_I z_I)^n$$

REACTION $A + B \rightleftharpoons R + S$

Adsorption of A is rate controlling replace $K_A z_A$ by	$K_A z_R z_S / K z_B$
Adsorption of B is rate controlling replace $K_B z_B$ by	$K_B z_R z_S / K z_A$
Desorption of R is rate controlling replace $K_R z_R$ by	$K K_R z_B z_R / z_A$
Where A is not adsorbed replace $K_A z_A$ by	0

Similar replacement for other components which are not adsorbed, could also be made.

The exponent n of the adsorption term is equal to 1 where the reaction involves only one site, equal to 2 when reaction involves two adjacent sites, and is equal to 3 when the reaction involves three adjacent sites. The exponents take the values shown in Table 5-5

TABLE 5-5 EXPONENTS OF ADSORPTION TERMS

REACTION $A + B \rightleftharpoons R + S$

Adsorption of A controlling without dissociation	n = 1
Desorption of R controlling	n = 1
Impact of A without dissociation	n = 2
Surface reaction controlling	
no dissociation of A	n = 2
no dissociation of A (B not adsorbed)	n = 2

Hougen and Watson(27) has derived a few reaction mechanisms for the reaction $A + B \rightleftharpoons R + S$, by following their approach the possible reaction mechanisms for the catalytic air oxidation of

2-methylpropene to methacrolein are derived. While testing the validity of an equation for a particular mechanism the following assumptions are made (i) Since the oxidation process is highly thermodynamically irreversible ($K > 10$), the term (P_M)(P_W)/K was omitted, (ii) the adsorption term for nitrogen (K_NP_N) was not included in the rate equations. Since according to Dowden(17) the chemisorption of nitrogen on bismuth molybdate catalyst is negligible.

The rate equations derived ,using Hougen-Watson approach are listed in Table 5-6. Where the subscript H,M and O represent 2-methylpropene, methacrolein and oxygen respectivity.

(4) Modified Langmuir-Hinshelwood Mechanism

According to Langmuir equation, the adsorption of a mixture of gases takes place in such an order that the addition of one gas to a second gas will always decrease the amount adsorbed of the later. Anyhow exactly the opposite behavior is observed for numerous cases of physical adsorpton, i.e., where the second gas increased the adsorption of the first gas(14) . Some observations were also found on chemisorptoion(22), in which marked enhancement of adsorption of a gas from mixtures, over that of the pure gas at the same partial pressure was reported. Adsorption of this kind corresponds mathematically to have a negative adsorption coefficient in the

TABLE 5-6

Rate Equations Derived From Hougen-Watson method

(One Type of Active Site)

No.	Mechanism	Rate-Controlling Step	Rate Equation
1	Surface reaction between molecularly adsorbed 2-methylpropene and oxygen without dissociation of any component upon adsorption	Adsorption of 2-methylpropene controlling	$r = \dfrac{K_s\ P_H}{1 + K_O\ P_O + K_M\ P_M}$
2		Adsorption of oxygen controlling	$r = \dfrac{K_s\ P_O}{1 + K_H\ P_H + K_M\ P_M}$
3	〃	Desorption of methacrolein controlling	$r = \dfrac{K_d'\ (\ K\ P_H\ P_O\ /\ P_W - P_W\ )}{1 + K_H\ P_H + K_O\ P_O + K\ K_M\ P_M\ P_O\ /\ P_W}$
4	〃	Surface reaction controlling	$r = \dfrac{K_s\ K_H\ P_H\ K_O\ P_O}{(\ 1 + K_H\ P_H + K_O\ P_O + K_M\ P_M\ )^2}$

... continuation...

No.	Mechanism	Rate-Controlling Step	Rate Equation
5	Surface reaction between molecularly adsorbed 2-methylpropene and oxygen in gas phase, which is not adsorbed	Adsorption of 2-methylpropene controlling	$r = \dfrac{K_s P_H}{1 + K_M P_M}$
6		Desorption of methacrolein controlling	$r = \dfrac{K_d' (K P_M P_O / P_W - P_M)}{1 + K_H P_H + K K_M P_H P_O / P_W}$
7		Surface reaction controlling	$r = \dfrac{K_s K_H P_H P_O}{1 + K_H P_H + K_M P_M}$

... continuation...

No.	Mechanism	Rate-Controlling Step	Rate Equation
8	Surface reaction between molecularly adsorbed oxygen and 2-methylpropene in gas phase which is not adsorbed	Adsorption of oxygen controlling	$r = \dfrac{K_s P_O}{1 + K_M P_M}$
9		Desorption of methacrolein controlling	$r = \dfrac{K_d' (K P_H P_O / P_W - P_M)}{1 + K_O P_O + K K_M P_H P_O / P_W}$
10	"	Surface reaction controlling	$r = \dfrac{K_s K_O P_O P_H}{1 + K_O P_O + K_M P_M}$

denominator of the extended Langmuir equation. For example, when the adsorption of A is increased in the presence of B, the amount of A adsorbed is given by an expression of the form

$$q_A = \frac{K_A P_A}{1 + K_A P_A - K_B P_B} \qquad (5\text{-}16)$$

This is considered to be physically impossible in the usual application of Langmuir-Hinshelwood, as any reaction mechanism which lead to a negative adsorption coefficent is automatically discarded.

To overcome the difficulty of this kind we use the concept of two types of active sites and apply to the catalytic oxidation of 2-methylpropene on bismuth molybdate catalyst. Where free electrons and positive holes on the catalyst surface can be treated as the two different types of active sites. Furthermore, if one assumes for simplicity that oxygen and 2-methylpropene are to be selectively adsorbed, then the equilibrium fractions covered by oxygen and 2-methylpropene would be

$$q_O = \frac{K_O P_O}{1 + K_O P_O} \qquad (5\text{-}17)$$

$$q_H = \frac{K_H P_H}{1 + K_H P_H + K_M P_M} \qquad (5\text{-}18)$$

2-Methylpropene and methacrolein are positively charged adsorbed and competive for active sites (holes). Oxygen is negatively charged adsorbed.

To illustrate this approach, a rate equation is developed for a bimolecular reaction $A + B \rightleftharpoons R + S$ 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.

$$A + \square \xrightarrow{k_1} A^{+}-\ominus \tag{5-19}$$

$$B + \ominus \xrightarrow{k_2} B^{-}-\square \tag{5-20}$$

where $\square$ and $\ominus$ represent positive holes and free electrons on the catalyst surface respectively.

The rate of precess given by equation (5-19) is

$$r_1 = k_1 P_A q_{\square} \tag{5-21}$$

and the rate of process given by equation (5-20) is

$$r_2 = k_2 P_B q_o \tag{5-22}$$

Where $q_{\square}$ and q_o represent the fraction of active site being positive hole and free electron respectively.

At steady state

$$r_1 = r_2 = r \tag{5-23}$$

also $$q_o = 1 - q_{\blacksquare} \qquad (5\text{-}24)$$

Substituting equations (5-21), (5-24) and (5-23) into equation (5-22) give

$$q = \frac{k_2 \; P_B}{k_1 \; P_A + k_2 \; P_B} \qquad (5\text{-}25)$$

and $$r = k_1 P_A q = \frac{k_1 \; P_A}{1 + (k_1 / k_2) (P_A / P_B)} \qquad (5\text{-}26)$$

Reaction rate equations based on the two types of active sites approach are listed in Table 5-7.

E. Correlation of Initial Rate Data

In a steady-state flow system, the relationship between space velocity or its reciprocal, the time factor W/F, and conversion is obtained by consideration of an elementary section of reactor containing a mass of catalyst dW in which a conversion dX is produced. Then a material balance gives

$$r \, dW = F \, dX \qquad (5\text{-}27)$$

Where r = reaction rate, moles 2-methylpropene reacted / (mass of catalyst) (hour)

W = mass of catalyst in reactor, gms.

F = moles of 2-methylpropene fed to the reactor

X = moles of 2-methylpropene reacted / moles of 2-methylpropene fed.

TABLE 5-7

Rate Equations Deriived From Modified Langmuir-Hinshelwood Mechanism

(Two type of Active Sites)

No.	Mechanism	Rate-Controlling Step	Rate Equation
11	Surface reaction between charged adsorbed 2-methylpropene and oxygen	Surface reaction controlling	$r = \frac{K_s\ K_H\ P_H}{1 + K_H\ P_H + K_M\ P_M} \ \frac{K_O\ P_O}{1 + K_O\ P_O}$
12	Surface reaction between charged adsorbed 2-methylpropene and oxygen	Irreversible charged adsorption of oxygen and 2-methylpropene	$r = \frac{K_H\ P_H}{1 + (K_H/K_O) (P_H/P_O)}$
13	Surface reaction between charged adsorbed 2-methylpropene and oxygen, oxygen is dissociated	Irreversible charged adsorption of oxygen and 2-methylpropene	$r = \frac{K_H\ P_H}{1 + (K_H/K_O) (P_H/P_O^{\frac{1}{2}})}$

Integration yields

$$W / F = \int_0^x \frac{dx}{r} \qquad (5\text{-}28)$$

When integrating equation (5-28), one must make the assumption that the gases are passing through the catalyst bed under conditions of plug flow, that is, the velocity profile across the width of the reactor is flat. This can be verified in large reactors by inserting pitot tubes inside the reactor and then establishing the velocity profile. However, in small reactors such as the one used in this kinetic study ($\frac{1}{2}$ inches in diameter), the use of pitot tubes was not considered very practical, hence the velocity profile was not determined. However, a porous stainless steel plate was inserted at the entrance of the reactor ao as to brake the velocity pattern of the incoming gases and create conditions approaching plug flow in the catalyst bed. It appears that no appreciable errors were produced due to this assumption as the composition of the products did not change very much with velocity (see Figure V-1) If the assumption of plug flow had not been justified, large variations in product composition would have been observed since the velocity profile is a function of velocity.

Yang and Hougen (80), who considered several reactions, have shown that by considering the effect of pressure on initial rate

($x = 0$) it is possible to reduce the number of reaction mechanism, and finally to test some of them for their suitability in representing the data.

Briefly, this method involves the plotting of the experimental data (conversion versus W / F), and determining the slope of the curve as W / F approaches to zero. The rate of reaction at zero conversion is defined as the initial rate.

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

The initial rates were obtained by finding the slopes of the curves at $x = 0$ and $W / F = 0$. The initial rates were determined for a series of reactant ratios and plotted in Figure V-2,6 against the partial pressure of 2-methylpropene in the feed. From the charts of Yang and Hougen (80), which show the effect of feed composition upon initial rates for various mechanisms, and the information derived from Figure V-2,3,4,5, it was concluded that desorption of product was definitely not rate controlling. Mechanisms 3, 6 and 9 were therefore discarded.

F. Correlation of Conversion Data

By means of an isotope method, Vogue, Wagner and Stevenson (73)

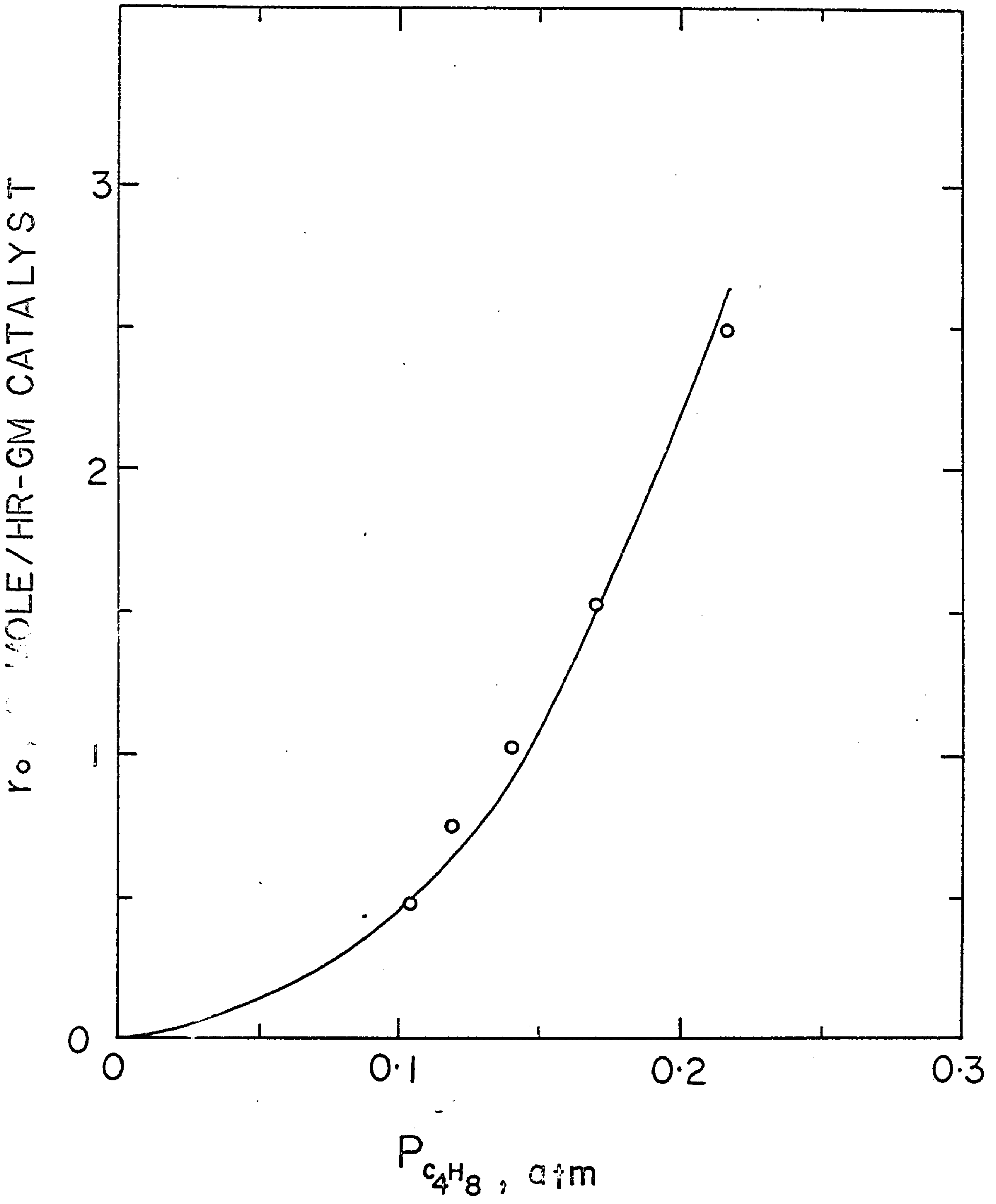


Figure V-2 Initial Rates (r_o) Versus $P_{C_4H_8}$ in Feed at 390°C.

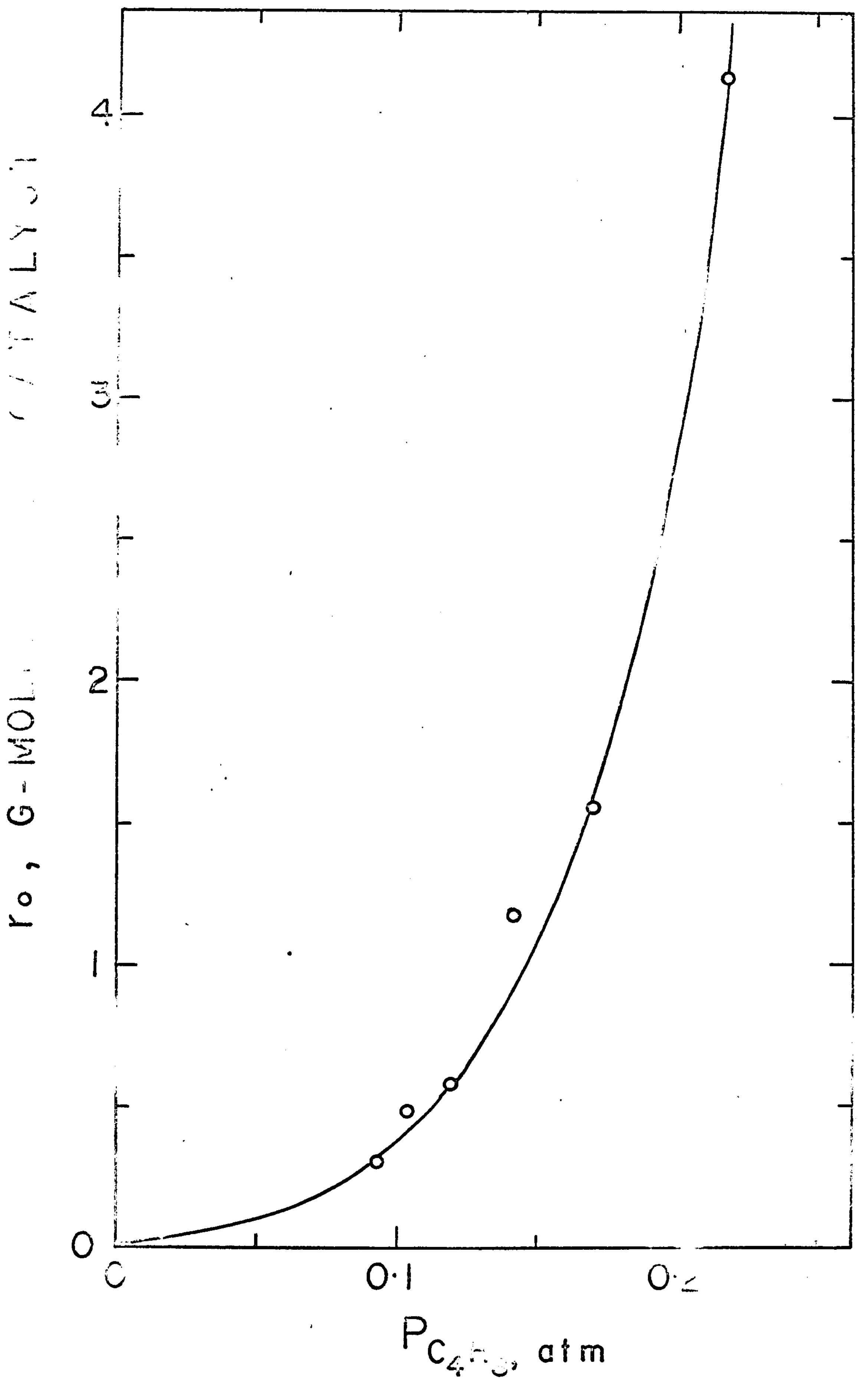


Figure V-3 Initial Rates (r) Versus P in Feed at 410°C

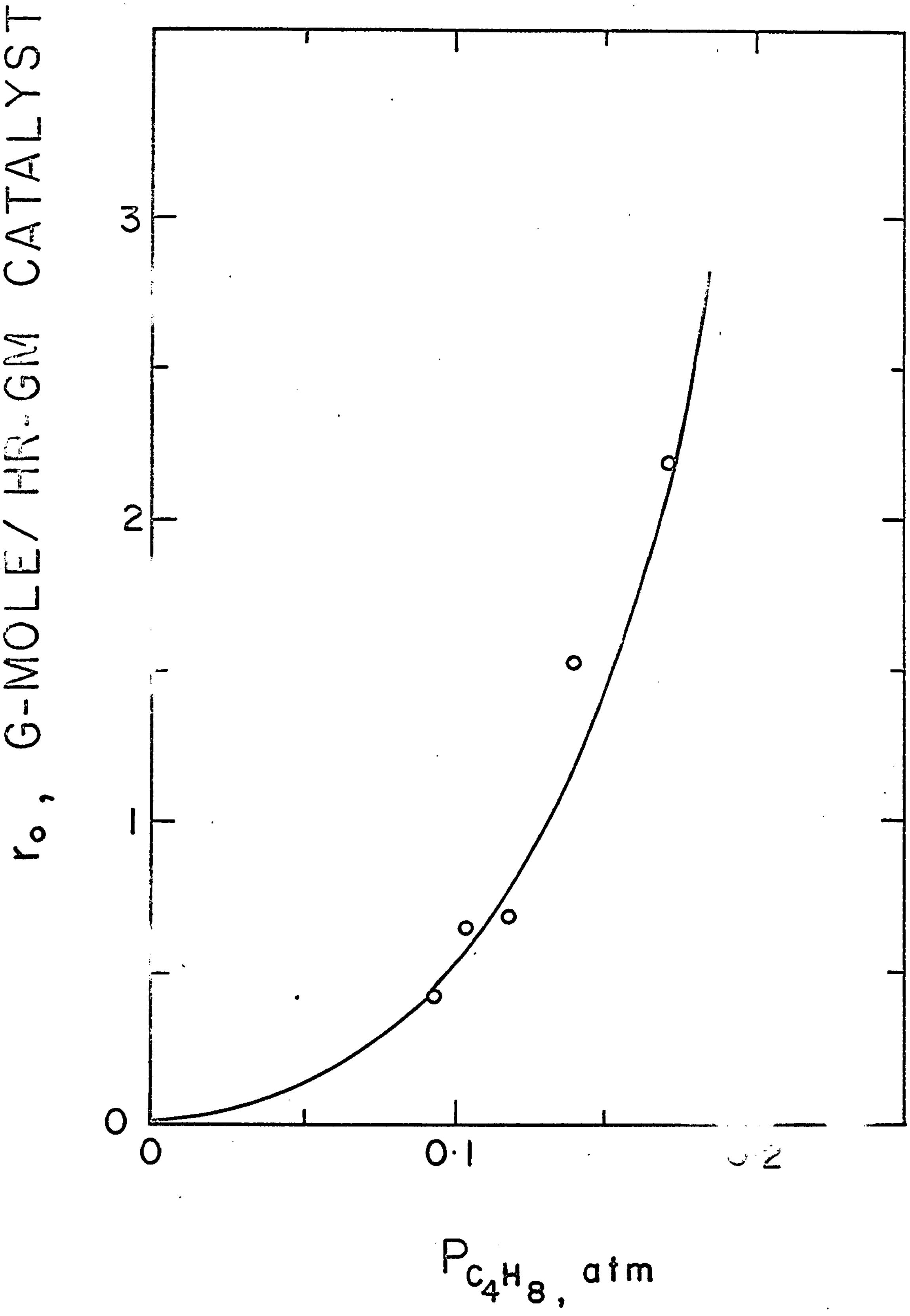


Figure V-4 Initial Rates (r_o) Versus $P_{C_4H_8}$ in Feed at 460°C

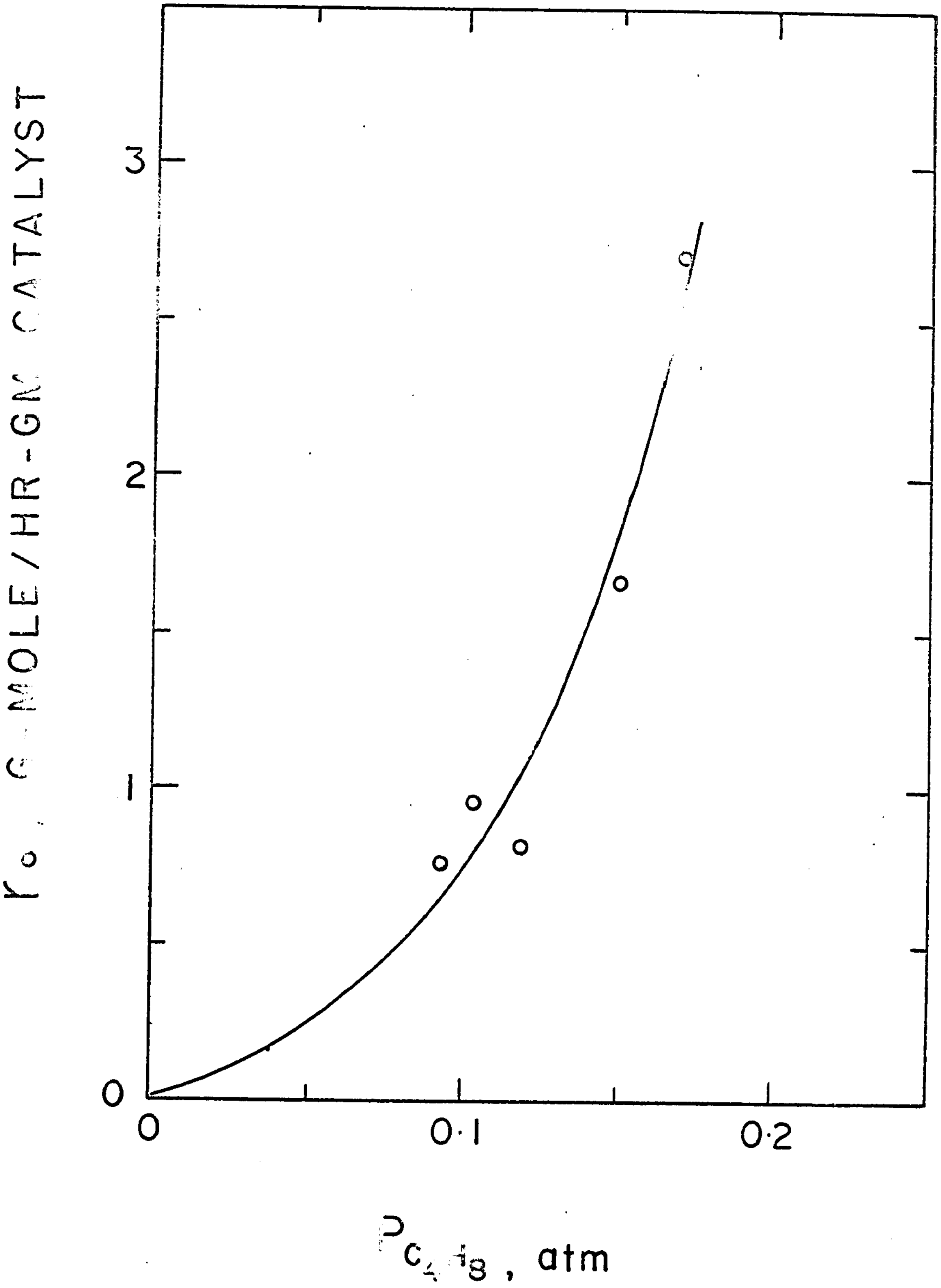


Figure V-5 Initial Rates (r_o) Versus $P_{C_4H_8}$ in Feed 0°C

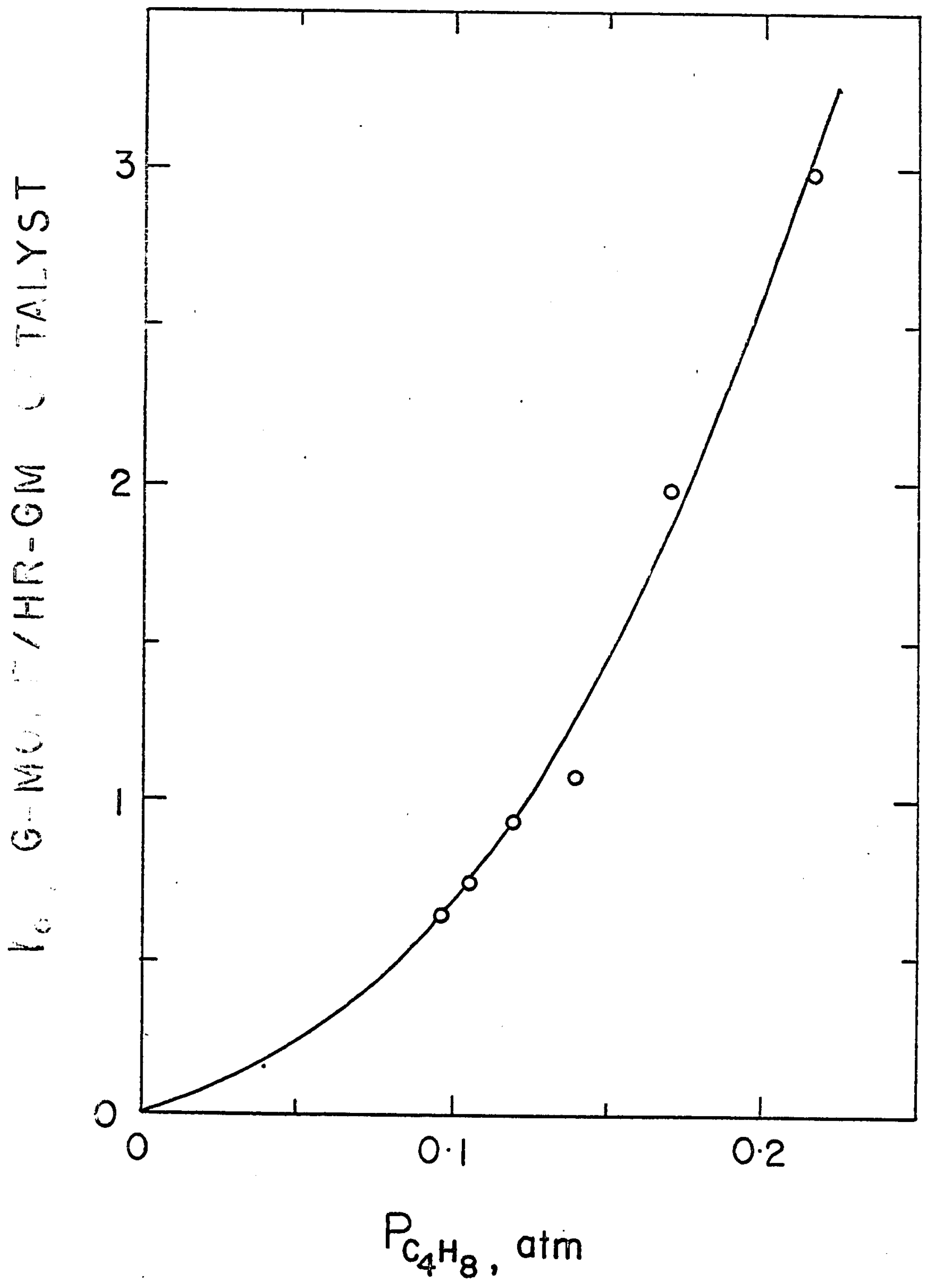


Figure V-6 Initial Rates (r_o) Versus $P_{C_4H_8}$ in Feed at 56 were able to establish that the carbon dioxide in the oxidation of propylene to acrolein came mainly from the complete oxidation of acrolein. Similarly, carbon dioxide from the oxidation of isobutylene to methacrolein could be considered as coming mainly from the complete oxidation of methacrolein. Experimental evidence seems to support this view. Selectivity was found to decrease with the conversion of isobutylene increased. On the basis that the oxidation of 2-methylpropene with air over a bismuth molybdate catalyst is a consecutive reaction, a scheme has been developed to express all the components of the reaction in terms of the conversion of 2-methylpropene (X). For the following consecutive reaction:

$$C_4H_8 + O_2 \rightleftharpoons C_4H_6O + H_2O \qquad (5\text{-}29)$$

$$C_4H_6O + 5O_2 \rightleftharpoons 4CO_2 + 3H_2O \qquad (5\text{-}30)$$

Let X = moles of 2-methylpropene reacting per hour by reaction / moles of 2-methylpropene fed per hour.

Z' = moles of methacrolein reacting per hour by reaction / moles of 2-methylpropene fed per hour.

Since carbon dioxide comes solely from oxidation of methacrolein (equation 5-30), then

$$Z' = \frac{1}{4} X_{CO_2} \qquad (5\text{-}31)$$

Where X_{CO_2} = moles of carbon dioxide produced per hour / moles of 2-methylpropene fed per hour.

Values of X and $\frac{1}{4} X_{CO_2}$ for different feed ratios at various temperature (Experimental data, in Appendix D) were plotted as shown in Figure V-7, and the following equation was derived

$$Z' = 0.202 X \qquad (5-32)$$

Having obtained a relationship between X and Z' , it is possible to express the partial pressure of each component as a function of X only. This is illustrated below:

Let $(N_{C_4H_8})^o$ = moles of 2-methylpropene in the feed

and $(N_{O_2})^o$ = moles of oxygen in the feed

then for any conversion , X

$N_{C_4H_8}$ = moles of 2-methylpropene in the product

$= (N_{C_4H_8})^o (1 - X)$

$N_{C_4H_6O}$ = moles of methacrolein in the product.

$= (N_{C_4H_8})^o (X - Z)$

$= 0.798 (N_{C_4H_8})^o X$

N_{H_2O} = moles of water in the product

$= (N_{C_4H_8})^o (X + 3Z)$

$= 1.606 (N_{C_4H_8})^o X$

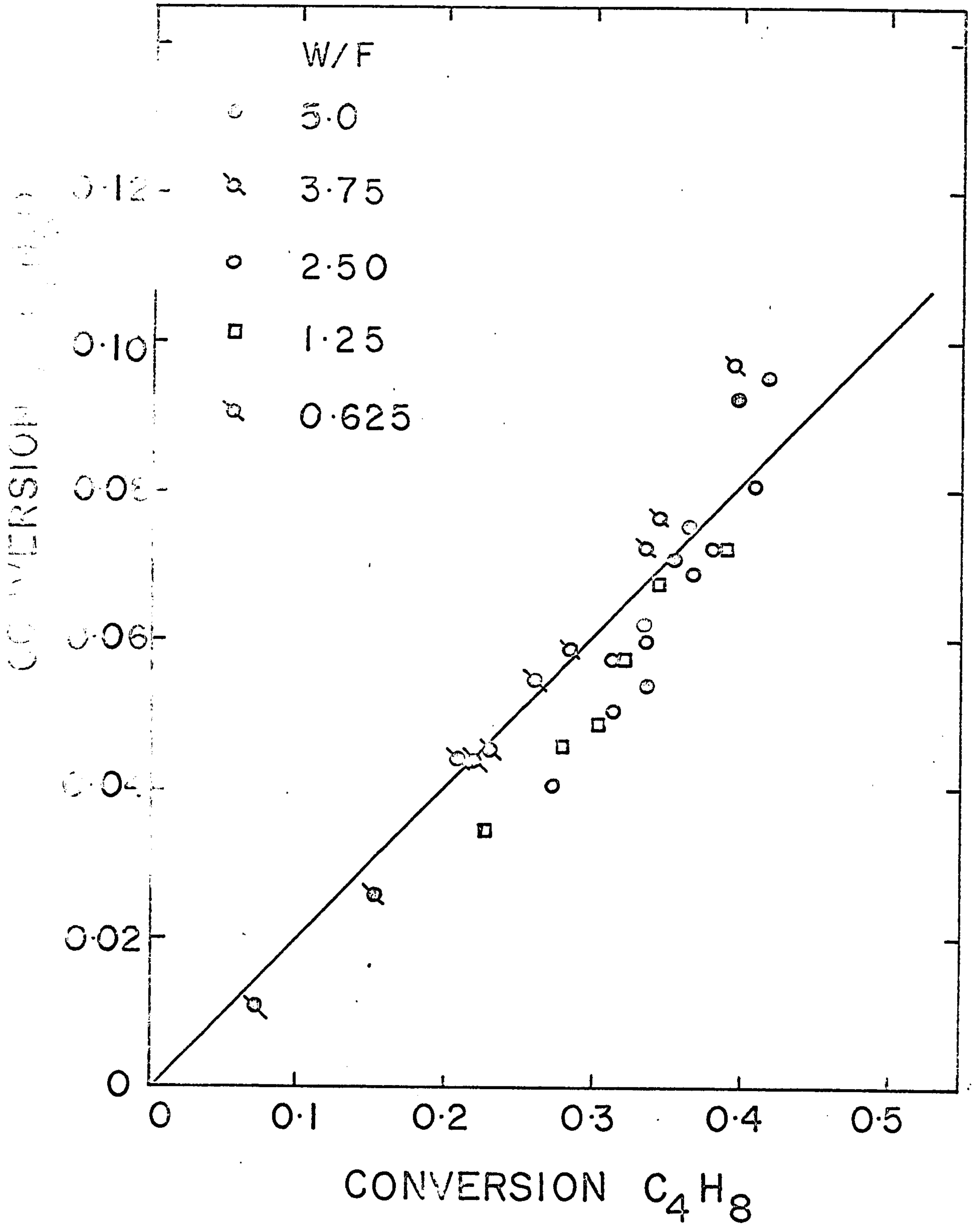


Figure V-7 Conversion of 2-methylpropene Versus Conversion of Methacrolein at 390°C

N_{CO_2} = moles of carbon dioxide in the product

$= (N_{C_4H_8})^o \, 4Z$

$= 0.808 \, (N_{C_4H_8})^o \, X$

N_{O_2} = moles of oxygen in the product.

$= (N_{O_2})^o - (N_{C_4H_8})^o \, (X + 5Z)$

$= (N_{O_2})^o - 2.010 \, (N_{C_4H_8})^o$

N_{N_2} = moles of nitrogen in the product.

$= (N_{N_2})^o$

= moles of nitrogen in the feed.

Since the total number of moles (N_T) did not vary by more than 5 % it was assumed constant and the total number of moles in the feed (N_T)^o was used. Now if one lets

$$(N_{C_4H_8})^o \, (P_T / (N_T)^o) = a \qquad (5\text{-}33)$$

$$0.798 \, (N_{C_4H_8})^o \, (P_T / (N_T)^o) = b \qquad (5\text{-}34)$$

$$0.808 \, (N_{C_4H_8})^o \, (P_T / (N_T)^o) = c \qquad (5\text{-}35)$$

$$(N_{O_2})^o \, (P_T / (N_T)^o) = d \qquad (5\text{-}36)$$

$$2.010 \, (N_{C_4H_8})^o \, (P_T / (N_T)^o) = e \qquad (5\text{-}37)$$

and P_T = Reaction pressure (874 mm Hg or 1.15 atm in this case) then the partial pressure of each component in the rate equation can be expressed in terms of conversion. Thus for any conversion X;

$$P_{C_4H_8} = a (1 - X) \tag{5-38}$$

$$P_{O_2} = d - e X \tag{5-39}$$

$$P_M = b X \tag{5-40}$$

$$P_W = c X \tag{5-41}$$

The values of the partial pressures were substituted in the rate equations and the equations were integrated. These integrated rate equations of the possible mechanisms are given in Table 5-8. Finally, a non-linear regression technique, developed by Marquart (55,56) which is based on the least square method was used to test the validity of these integrated rate equations. It was found that reaction mechanism of surface reaction between charged adsorbed 2-methylpropene and oxygen, with surface reaction as rate-controlling step fitted the experimental data best. The rate equation based on this mechanism can be expressed as

$$r = \frac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \; \frac{K_O P_O}{1 + K_O P_O}$$

TABLE 5-8

Mechanism	Integrated Rate Equation
1	$\frac{W}{F} = \left(\frac{1}{K_s} \right) \left[\frac{K_O (e - d) - K_M b - 1}{a} \ln (1 - X) + \frac{K_O e - K_M b}{a} X \right]$
2	$\frac{W}{F} = \left(\frac{-1}{K_s} \right) \left[\frac{(1 + K_M b)}{a} \ln (1 - X) + \frac{K_M B}{a} X \right]$
4	$\frac{W}{F} = \left(\frac{1}{K_s} \right) \left[\frac{(K_H a - K_M b)}{e} X - \frac{(e + K_H a (e - d) + K_M b d)}{e^2} \ln (1 - e X / d) \right]$
5	$\frac{W}{F} = \left(\frac{-1}{K_s} \right) \left[\frac{(e + K_M b d)}{e^2} \ln (1 - e X / d) + \frac{K_M b}{e} X \right]$

...continuation...

Mechanism

7

$$\frac{W}{F} = \left(\frac{1}{K_o\,K_s}\right)\left[\left(\frac{K_H\,a}{e} - \frac{2\,K_M\,b}{e} + \frac{K_M^2\,b^2}{K_H\,a\,e}\right)X + \frac{K_M^2\,b^2}{e^2}\ln(1-X) - \left(\frac{K_H\,a\,(e-d)}{e^2} + \frac{K_M^2\,b^2\,d^2}{K_H\,a\,e^2\,(e-d)} - \frac{2\,K_M\,b\,d}{e^2}\right)\ln(1 - e\,X/d)\right]$$

8

$$\frac{W}{F} = \left(\frac{1}{K_s}\right)\left[\frac{1+K_M\,b}{K_H\,a\,(e-d)}\ln(1-X) - \left(\frac{1+K_M\,b}{K_H\,a\,(e-d)} + \frac{1}{e} - \frac{K_M\,b}{K_H\,a\,e}\right)\ln\left(1 - \frac{e\,X}{d}\right)\right]$$

10

$$\frac{W}{F} = \left(\frac{1}{K_s}\right)\left[\left(\frac{1+K_M\,b}{K_o\,a\,(e-d)} - \frac{1}{a}\right)\ln(1-X) - \left(\frac{1+K_M\,b}{K_o\,a\,(e-d)} - \frac{K_M\,b}{K_o\,a\,e}\right)\ln\left(1 - \frac{eX}{d}\right)\right]$$

...continuation...

Mechanism

11
$$\frac{W}{F} = \left(\frac{1}{K_s}\right)\Bigg[\left(\frac{1}{K_o K_H a (e - d)} + \frac{K_M b d}{K_o K_H a e (d - e)} - \frac{1}{K_o e}\right) \ln \left(1 - \frac{e X}{d} \right)$$
$$+ \left(1 - \frac{K_M b}{K_H a} \right) X - \left(\frac{1}{K_o K_H a (d - e)} + \frac{1}{K_H a} + \frac{K_M b}{K_o K_H a (d - e)} + \frac{K_M b}{K_H a} \right) \ln (1 - X)\Bigg]$$

12
$$\frac{W}{F} = - \frac{1}{K_H a} \ln (1 - X) - \frac{1}{K_o e} \ln \left(1 - \frac{e X}{d} \right)$$

13
$$\frac{W}{F} = - \frac{1}{K_H a} \ln (1 - X) - \frac{1}{K_o e} (d - e X)^{\frac{1}{2}} + \frac{1}{K_o e} (d)^{\frac{1}{2}}$$

TABLE 5-9

Temperature Effect On Rate Constants

^oK	$\frac{1}{T} \times 10^3$	K_{O_2}	$K_{C_4H_8}$	$K_{C_4H_6O}$	K_s
663	1.508	1.4	482.4	1522.6	12.9
683	1.464	1.7	437.6	1481.2	14.7
733	1.364	1.3	422.8	1291.7	19.2
783	1.277	0.9	411.3	1000.9	28.9
833	1.200	1.6	394 5	821.2	31.4

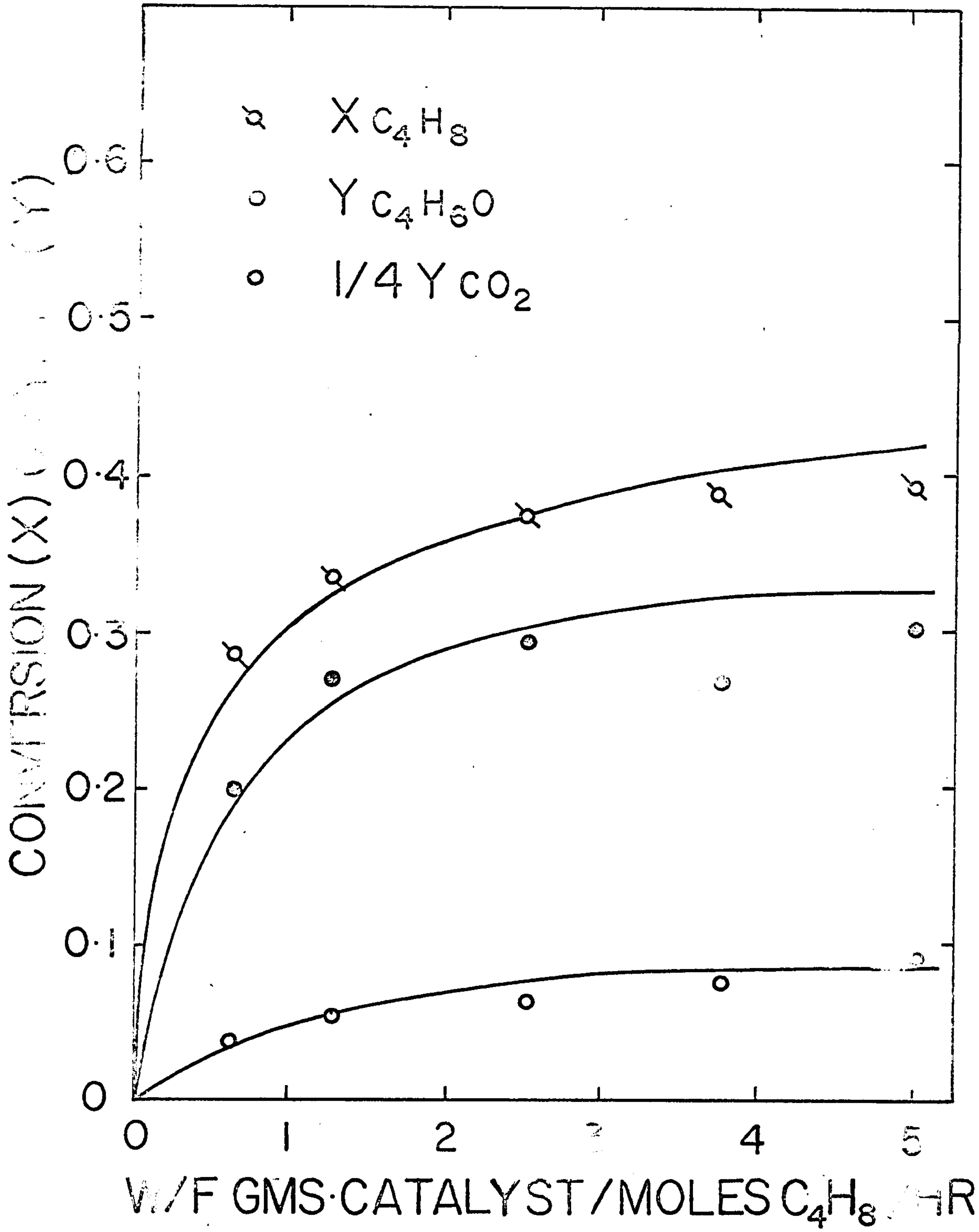
The values of K_S, K_H and K_o between 390°C and 560°C are given in Table 5-9. The conversion curves calculated from mechanism 11 for a reactant ratio of 1.2 are compared with the experimental data at temperature of 390, 410, 460 and 510°C in Figure V-8,9,10,11 respectively by solid lines. The dependence of K_H, K_M with temperature is shown in Figure V-12 The mathematical expressions describing the temperature dependence of K_H and K_M are given in the equations (5-42) to (5-45). These constants appear to follow the Arrhenius behavior in the temperature range studied.

$$\ln K_{C_4H_8} = 5.18 + \frac{17.79 \times 10^3}{T} \tag{5-42}$$

$$\ln K_{C_4H_6O} = 4.30 + \frac{24.47 \times 10^3}{T} \tag{5-43}$$

$$\ln K_{O_2} = 0.75 + \frac{3.64 \times 10^3}{T} \tag{5-44}$$

$$\ln K_S = 7.44 - \frac{7.32 \times 10^3}{T} \tag{5-45}$$



igure V-8 W/F Effect on Conversion and Yield for Oxidatio

2-methylpropene over Bismuth Molybdate catalyst at

390° C, R = 1.1991

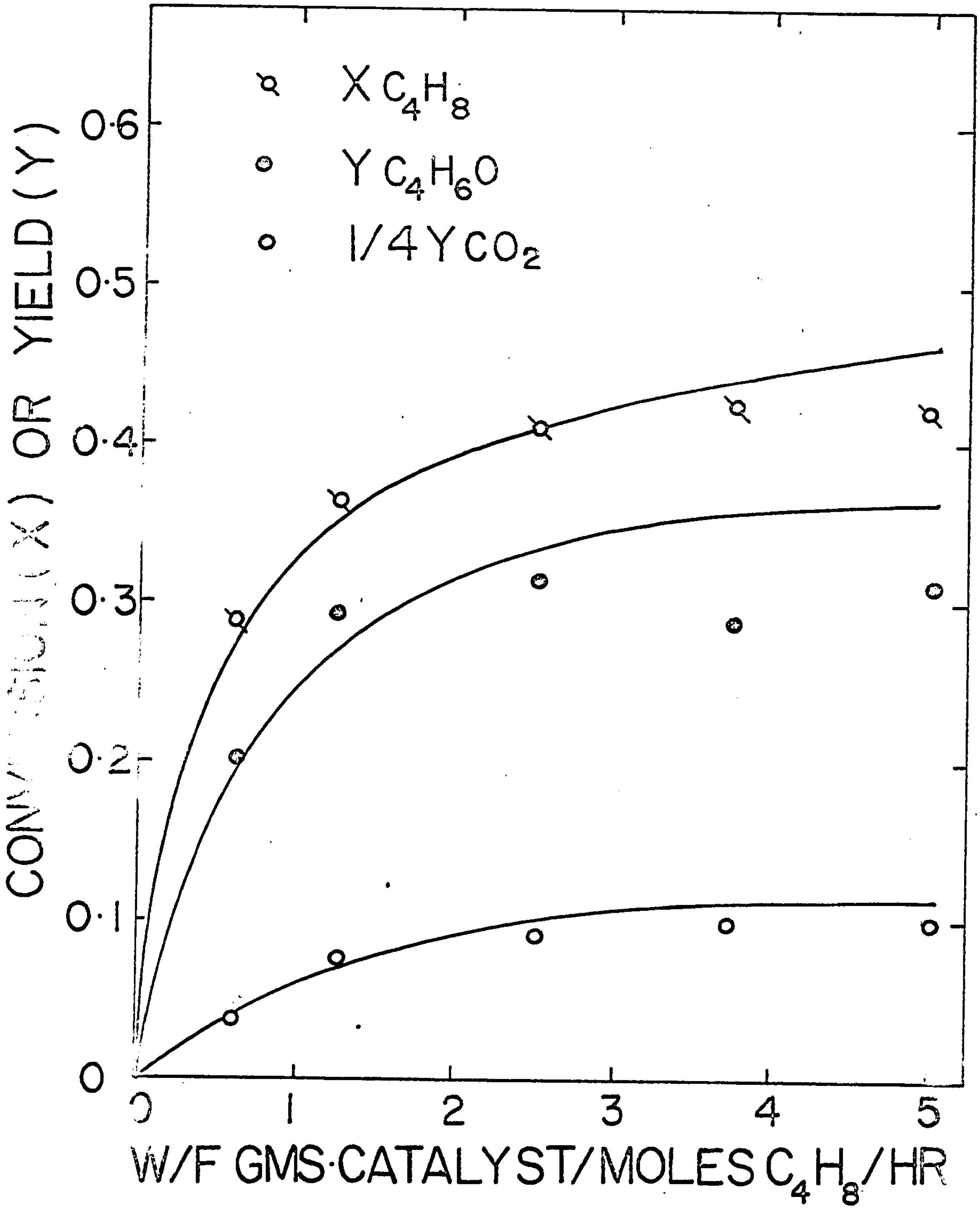


Figure V-9 W/F Effect on Conversion and Yields for oxidation 2-methylpropene over Bismuth Molybdate Catalyst a. 410° C. R = 1.1991

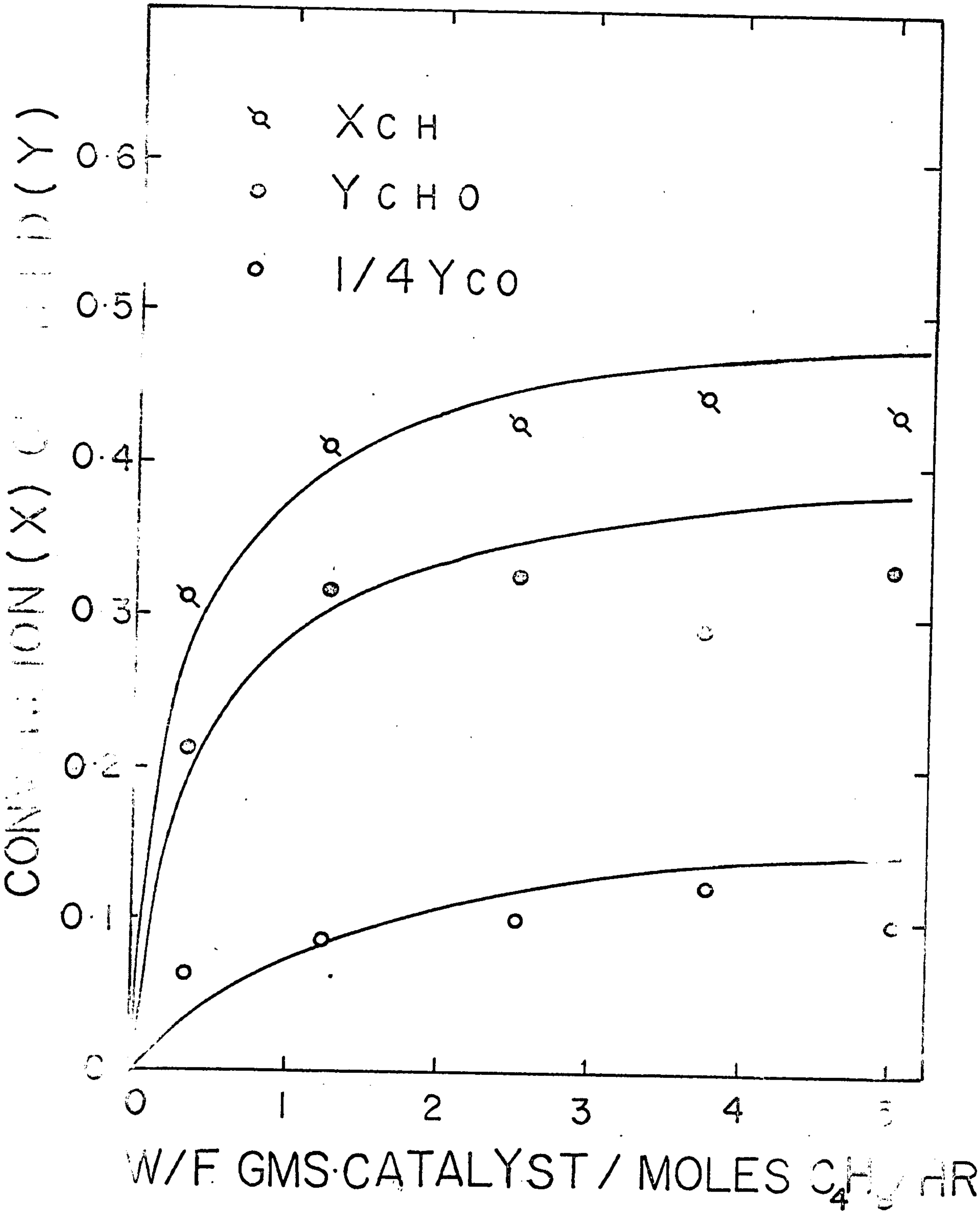


Figure V-10 W/F Effect on Conversion and Yields for oxidation of 2-methylpropene over Bismuth molybdate catalyst at 460° C, R = 1.19

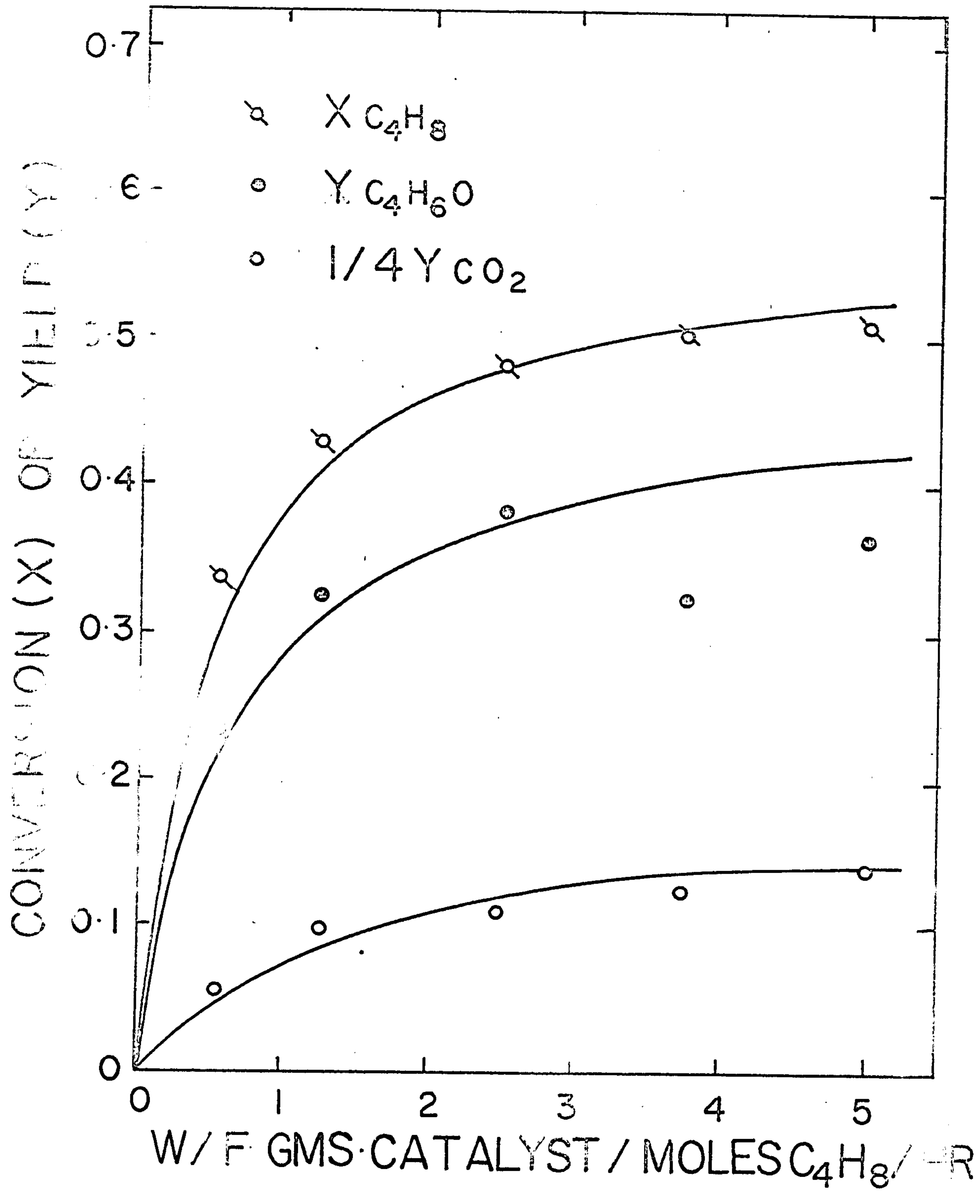
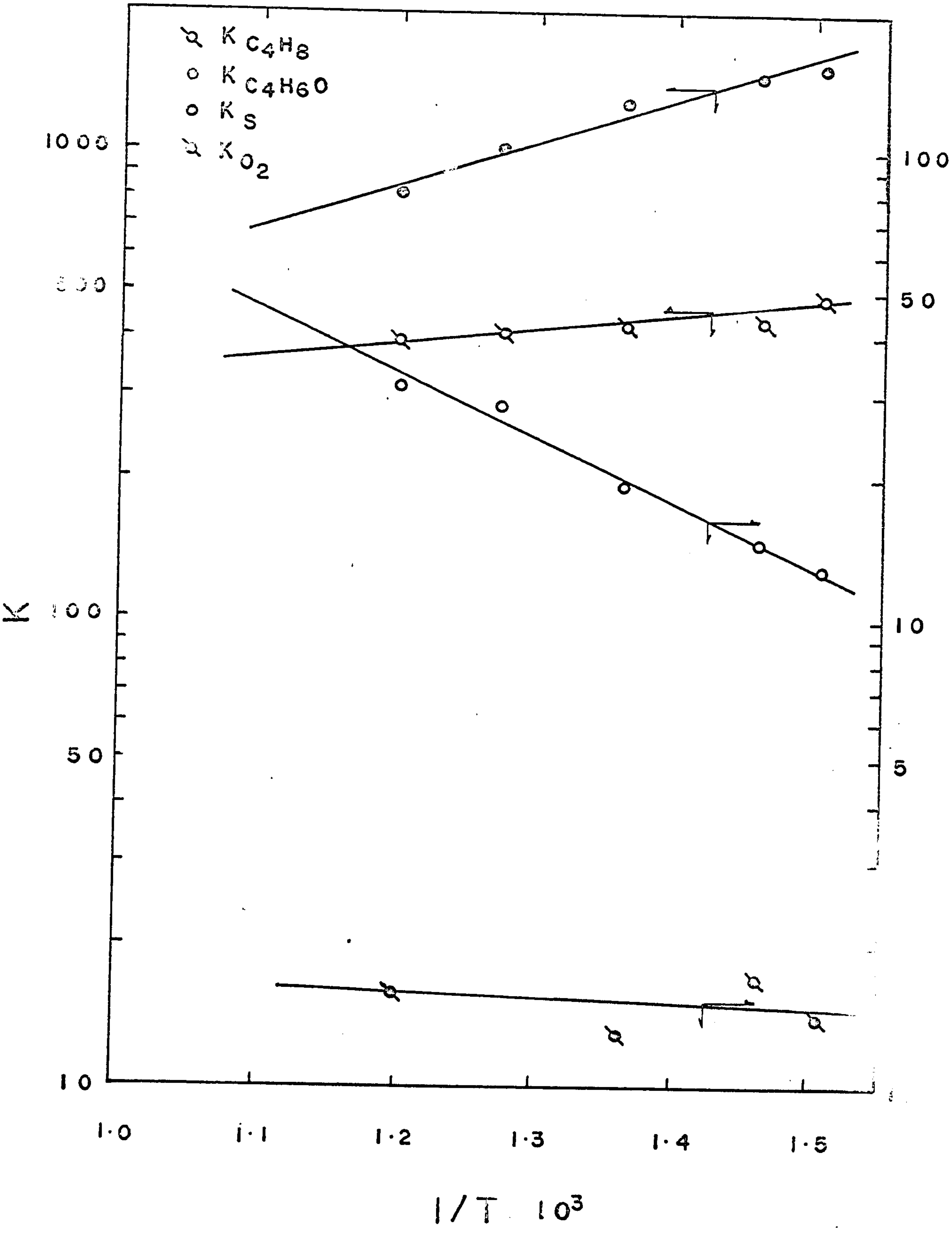


Figure V-11 W/F Effect on Conversion and Yield for Oxidation of 2-methylpropene over Bismuth Molybdate Catalyst at 510° C, R = 1.1991



F ure V-12 Temperature Effect on $K_{C_4H_8}$, $K_{C_4H_6O}$, K_s and K_{O_2}

VI DISCUSSION

It is observed that the yield of methacrolein in the catalytic oxidation of 2-methylpropene over bismuth molybdate catalyst is generally limited, as an increase in the 2-methylpropene conversion is always accompanied with a decrease in the selectivity. Similar results were reported in the literature for the oxidation of propene over bismuth molybdate catalyst (4) and for the oxidation of 2-methylpropene and propene over copper oxide (44,51).

The results obtained suggest that carbon dioxide originates mostly from the further oxidation of methacrolein which is in agreement with the observations of other investigators (73).

Mann and Yao (49) treated the free electrons or positive holes on the surface as one of the reactants or products and proposed that a surface reaction between charged adsorbed particles, both reactants and products, was the essential step. Based on this theory, the heterogeneous catalytic reactions traditionally are described as taking place through the following steps:

(1) Diffusion (external and internal) of reactants and products.

(2) Adsorption and desorption of reactants and products (physical adsorption and weak chemisorption).

(3) Surface reaction.

Which can be modified to take place as follows:

1) Electron transfer from on to the reactants (strong chemical bond formation).
2) Homogeneous reaction (formation of activated complex and rearrangement of the charged particles on the surface).
3) Electron transfer from on to the products.

The formation of methacrolein by the partial oxidation of 2-methylpropene, based on the above modification, can be visualized to take place according to the following scheme.

Reaction I : <u>Partial Oxidation</u>

$$C_4H_8\ (g) \rightleftharpoons (\ C_4H_8\ )^* + pL \rightleftharpoons (\ C_4H_8^+\ )^* \qquad (6\text{-}1)\ \ \text{p-type}$$

$$O_2\ (g) \rightleftharpoons (\ O_2\ )^* + 2\ eL \rightleftharpoons (\ 2\ O^-\ )^* \qquad (6\text{-}2)\ \ \text{n-type}$$

$$(\ C_4H_8^+\ )^* + (\ 2\ O^-\ )^* \overset{\text{activated complex}}{\rightleftharpoons} (\ C_4H_6O^+)^* + (H_2O^+)^* \qquad (6\text{-}3)$$

$$(\ C_4H_6O^+\ )^* + eL \rightleftharpoons (\ C_4H_6O\ )^* \rightleftharpoons C_4H_6O\ (g) \qquad (6\text{-}4)\ \ \text{n-type}$$

$$(\ H_2O^+\ )^* + eL \rightleftharpoons (\ H_2O\ )^* \rightleftharpoons H_2O\ (g) \qquad (6\text{-}5)\ \ \text{n-type}$$

Over-all reaction:

$$C_4H_8 + O_2 \rightleftharpoons C_4H_6O + H_2O \qquad (6\text{-}6)$$

Reaction II. Further Oxidation

$$(C_4H_6O^+)^* + (10\ O^-)^* \underset{}{\overset{\text{activated complex}}{\rightleftharpoons}} (4\ CO_2^+)^* + (3\ H_2O^+)^* \qquad (6\text{-}7)$$

$$(CO_2^+)^* + eL \rightleftharpoons (CO_2)^* \rightleftharpoons CO_2\ (g) \qquad (6\text{-}8)$$

$$(H_2O^+)^* + eL \rightleftharpoons (H_2O)^* \rightleftharpoons H_2O\ (g) \qquad (6\text{-}9)$$

Overall reaction:

$$C_4H_6O + 5\ O_2 \rightleftharpoons 4\ CO_2 + 3\ H_2O \qquad (6\text{-}10)$$

Reaction III. Complete Oxidation

$$(C_4H_8^+)^* + (12\ O^-)^* \overset{\text{activated complex}}{\rightleftharpoons} (4\ CO_2^+)^* + (4\ H_2O^+)^* \qquad (6\text{-}11)$$

$$(CO_2^+)^* + eL \rightleftharpoons (CO_2)^* \rightleftharpoons CO_2\ (g) \qquad (6\text{-}12)$$

$$(H_2O^+)^* + eL \rightleftharpoons (H_2O)^* \rightleftharpoons H_2O\ (g) \qquad (6\text{-}13)$$

overall reaction:

$$C_4H_8 + 6\ O_2 \rightleftharpoons 4\ CO_2 + 4\ H_2O \qquad (6\text{-}14)$$

Each step in the above reaction may contribute a certain resistance. The over-all rate is usually determined by the so-called rate-controlling step.

Reactions I, II and III can be also expressed in terms of " Power Rate Law " (49) as following:

$$r_1 = k_1 (C_{C_4H_8^+})^{m1} (C_{O_2^-})^{n1} - k_1' (C_{C_4H_6O^+})^{m2'} (C_{H_2O^+})^{n1'} \qquad \ldots (6\text{-}15)$$

$$r_2 = k_2 (C_{C_4H_6O^+})^{m2} (C_{O_2^-})^{n2} - k_2' (C_{CO_2^+})^{m2'} (C_{H_2O^+})^{n2'} \qquad \ldots (6\text{-}16)$$

$$r_3 = k_3 (C_{C_4H_8^+})^{m3} (C_{O_2^-})^{n3} - k_3 (C_{CO_2^+})^{m3'} (C_{H_2O^+})^{n3'} \qquad \ldots (6\text{-}17)$$

Where $C_{C_4H_8^+}$, $C_{O_2^-}$, $C_{C_4H_6O^+}$ and $C_{H_2O^+}$ are the surface concentration of the charged olefin, oxygen, aldehyde and water species respectively. Since thermodynamically these oxidation reactions are highly irreversible, the backward reaction can be neglected and the reaction rates r_1 , r_2 and r_3 would be $k_1 (C_{C_4H_8^+})^{m1} (C_{O_2^-})^{n1}$, $k_2 (C_{C_4H_6O^+})^{m2} (C_{O_2^-})^{n2}$ and $k_3 (C_{C_4H_8^+})^{m3} (C_{O_2^-})^{n3}$ respectively.

Based on the foregoing argument, a theoretical interpretation of the mechanism, in which the rate-controlling step in the reaction between charged adsorbed 2-methylpropene and oxygen, can be discussed.

When 2-methylpropene (a donor type gas) is adsorbed on the surface of bismuth molybdate (a n-type semiconductor), because of the electropositive nature of 2-methylpropene, electrons from it flow to the catalyst surface, and pass through the acceptor level. Since the acceptance of these electrons is unlimited, an inundation boundary layer is formed. Chemisorption of 2-methylpropene on the surface is fast and proceeds easily, forming nearly a complete monolayer of it on the surface. On the other hand, when oxygen (an acceptor-type gas) is adsorbed on the surface, because of its electronegative nature, electrons flow from the catalyst to it and are removed from the valence bond, creating free holes. Since the supply of these electrons is limited, an exhaustion boundary layer is formed. And the chemisorption of oxygen ceases at low coverage and far from equilibrium. The adsorption of oxygen on the surface of the catalyst is thus relatively much slower than the adsorption of 2-methylpropene on it, which can, therefore, be considered as a next slower step than the surface reaction.

Because the existing 2-methylpropene ions on the catalyst surface do not hinder the further charged adsorption of 2-methylpropene, since less energy is required for the charged adsorption, the surface coverage of 2-methylpropene is extensive. Therefore, at any time, the surface concentration of adsorbed 2-methylpropene $C_{C_4H_8^+}$ is strongly dependent on the number of molecules in the gas phase, $P_{C_4H_8}$. Hence the reaction being nearly first order with respect to 2-methylpropene , as suggested by equation (6-15) is quite understandable.

On the other hand, because of the ablity of giving electrons of n-type catalyst is limited, the charged adsorption of oxygen is hindered by the existing oxygen ions, and require much more energy. It is for these reasons that the surface covered by the adsorbed charged oxygen is always low, and far from equilibrium. Therefore, at any time, the surface concentration of adsorbed oxygen ion, $C_{O_2^-}$ is strongly dependent on the surface defect and is relatively immaterial to the number of molecules of oxygen in the gas phase. Hence the reaction rate being zero order with respect to oxygen is understandable.

VII CONCLUSIONS AND RECOMMENDATIONS

The catalytic oxidation of 2-methylpropene was investigated over bismuth molybdate catalysts in an isothermal integral flow reactor between 390°C and 560°C with feed ratio (O_2 / 2-methylpropene) 0.6 - 2.1 and reciprocal of space velocity up to 5.0 gm-hr / gm-mole in order to establish the conditions for maximum conversion and yield to derive a suitable rate equation and propose a possible reaction mechanism.

Based on the experimental results, the following conclusions were drawn:

(1) Electronic factors governing the rate of reaction at the surface of the catalyst are unquestionably important. It has been suggested that the chemisorption of reactants, oxygen and olefin is preferrential on the catalyst surface and that the partial oxidation of olefin is a p-type reaction, and its further oxidation to carbon dioxide is an n-type reaction under optimum conditions.

(2)The Hougen-Waston approach based on the modified Langmuir-Hinshelwood Mechanism was used for the kinetic analysis of the data. The most satisfactory rate equation correlating the data has been found as :

$$r = \frac{K_s K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

Where K_M, K_H , K_O and K_s are temperature dependent constant. Which is similar with the rate equation derived by Mann & Yao (51) for the oxidation of 2-methylpropene over modified copper oxide catalyst. This is in agreement with Adams (2) who has suggested that the reaction mechanism of catalytic oxidation over the two catalysts are the same.

It is recommended that:

(1) Further work on the oxidation of olefin over n-type and p-type oxides in the presence and absence of different types of modifiers be studied, in order to test the present postulations.

(2) In order to obtain a better understanding in catalyst modification, the changes in catalytic properties (i.e., electrical conductivity, work function, etc.) during the adsorption of reactants on the catalyst surface in the presence and absence of a modifier should be studied.

VIII NOMENCLATURE

A	Component A
a_m	Specific surface area
a'	Active position on the catalyst surface
a	$(N_{C_4H_8})^{o}(P_T/(N_T)^{o})$
B	Component B
b	$0.798\,(N_{C_4H_8})^{o}(P_T/(N_T)^{o})$
C_p	Specific heat of gas, cal / gm-mole-°C
C	Molal concentration of adsorbed reactants or products
c	$0.808\,(N_{C_4H_8})^{o}(P_T/(N_T)^{o})$
d	$(N_{O_2})^{o}(P_T/(N_T)^{o})$
D_p	Diameter of particle, cm.
d_p	Density of particle, gm. / cc.
E	Effectiveness factor
e	$2.010\,(N_{C_4H_8})^{o}(P_T/(N_T)^{o})$
eL or o	Free electrons
ΔF	The change in Gibb's free energy
F	Flow rate of feed, gm-moles / hr.
G_m	Molal velocity of gas flow based on the total cross-sectional area of the catalyst bed.

g	Component g
ΔH_A	Heat of reaction per mole of A reacted
I	Component I
K'_d	Reaction velocity constant for desorption controlling
K_i, k_i	Adsorption equilibrium constant of component i
K_s, k'	Reaction velocity constant for the surface reaction
k	Reaction rate constant (with subscripts 1,2)
L	Molal concentration of active sites per unit mass
M	Molecular weight
n	Constant
P_i	Partial pressure of component i
pL or	Positive holes
Q	$(r_{mA} \ H_A) / (a_m C_P G_m)$
q	Fraction of coverage catalyst surface by a certain component
R	Component R
R	Oxygen to 2-methylpropene ratio in feed
$\bar{R}$	$r_A / (a_m G_m)$
r'_1, r'_{-1}	Rate of adsorption, desorption respectively
r	Reaction rate (with subscript) gm-mole / hr-gm of catalyst
r_{ma}	Molal reaction rate of component A per unit mass of catalyst surface
r_o	Initial rate, gm-mole / hr. gm of catalyst

S	Component S
S	Selectivity
s	The number of adjacent active sites
T	Temperature
W	Weight of catalyst
X	Conversion
Y	Yield
Y_j	Average mole fraction
y_{in}	Mole fraction of components in feed.
y_{out}	Mole fraction of components in products
Z_i	Activities of components i.
Z'	Moles of methacrolein reacting per hr / moles of C_4H_8 fed / hr

Greek Symbols

π	Total Pressure
ρ	Density of gas
ϕ	Shape factor, ratio of actual external surface area available for mass and heat transfer to the total external surface area, it is assumed to be 0.9 for irregular granules

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....)
o	Placed after a symbol means in feed

Subscripts

$C_4H_6O^+$	Charged adsorbed methacrolein
$C_4H_8^+$	Charged adsorbed 2-methylpropene
CO_2^+	Charged adsorbed carbon dioxide
f	Forward reaction rate moles product formed per unit time per unit catalyst
H_2O^+	Charged adsorbed H_2O
H	2-methylpropene
O	Oxygen
O_2^-	Charged adsorbed oxygen

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APPENDIX

Appendix A

Calibration of Equipment

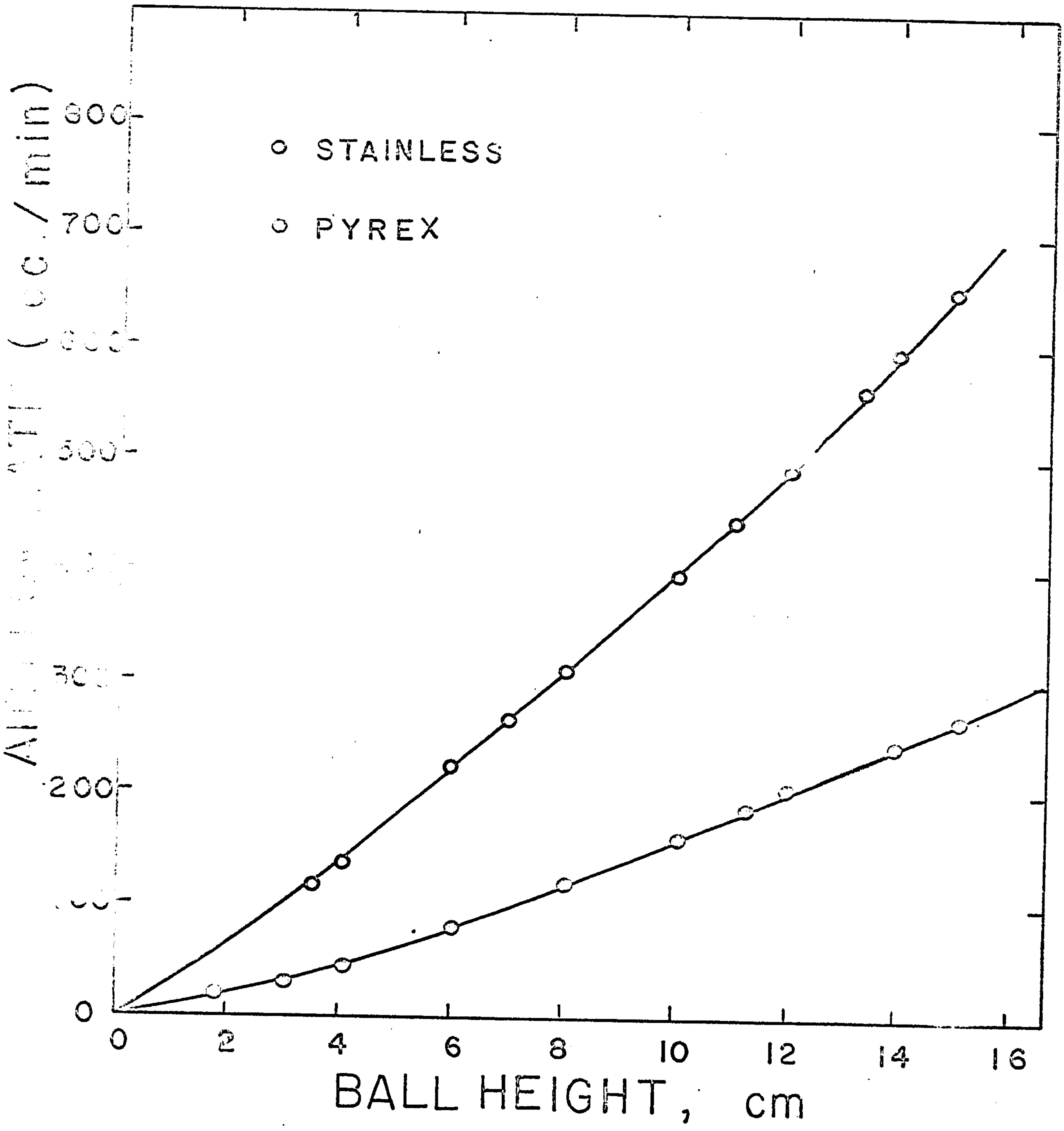

Figure X-1 Rotameter Calibration for Air

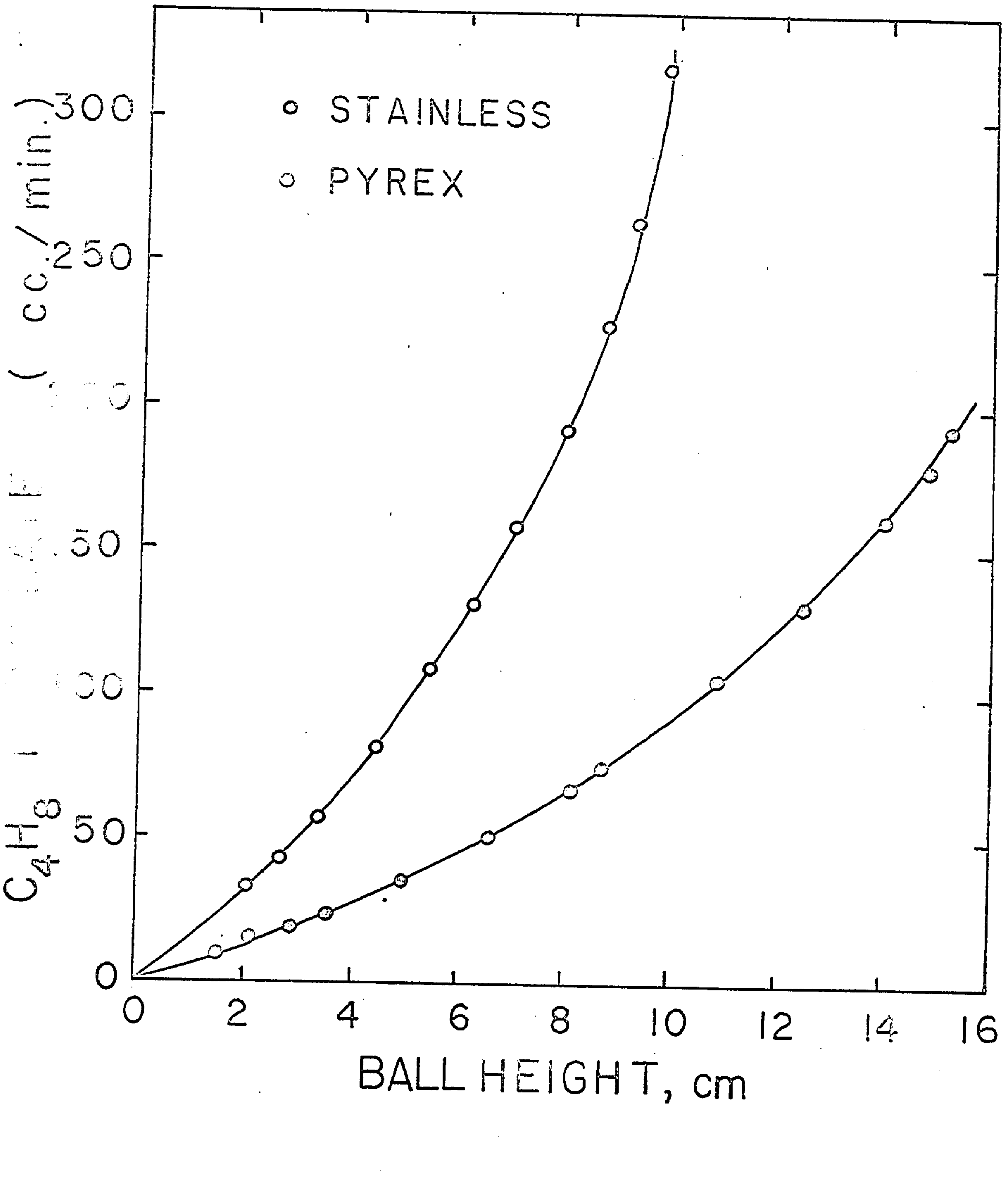

Figure X-2 Rotameter Calibration for 2-methylpropene

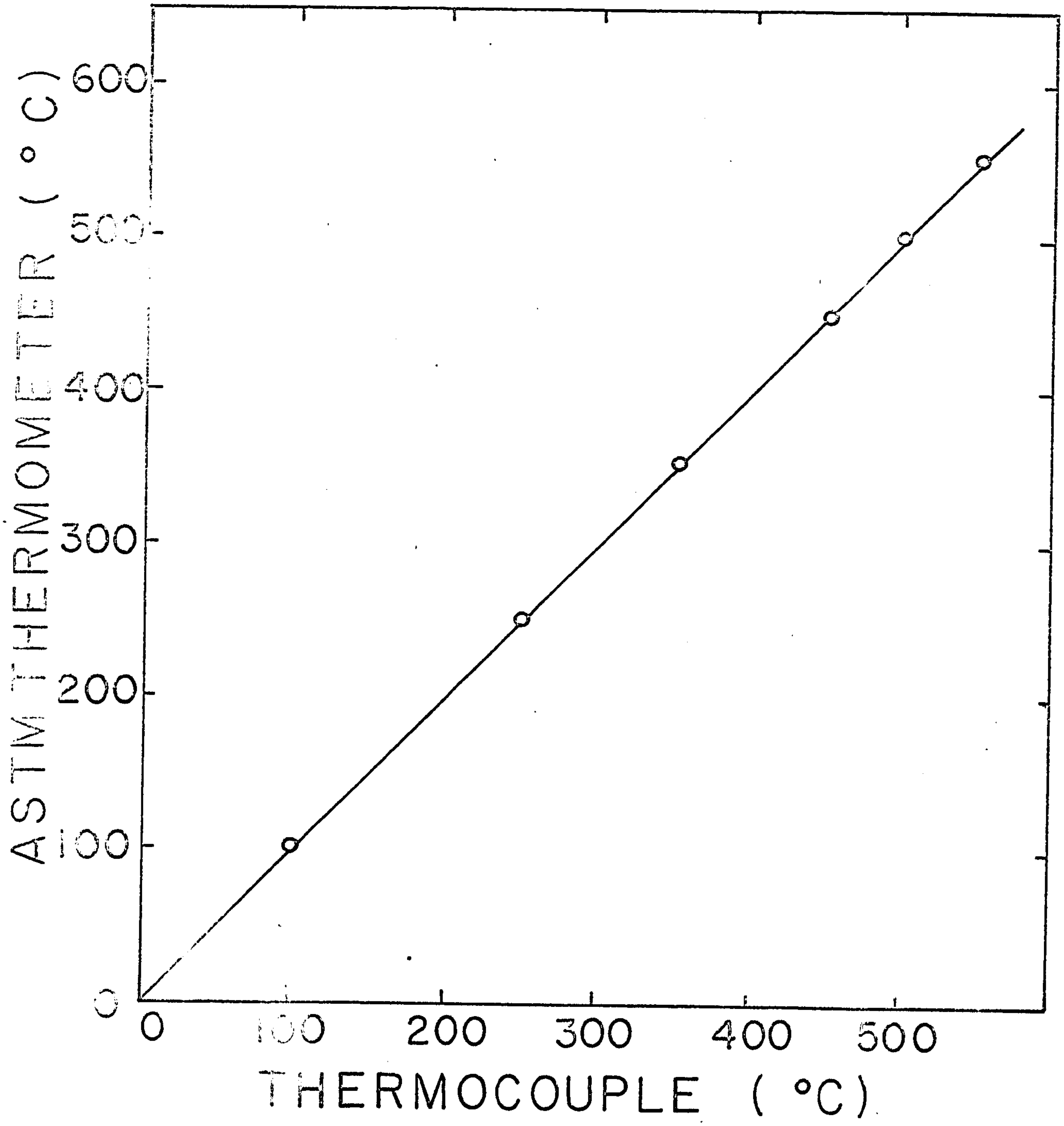

Figure X-3 Calibration of Thermocouples

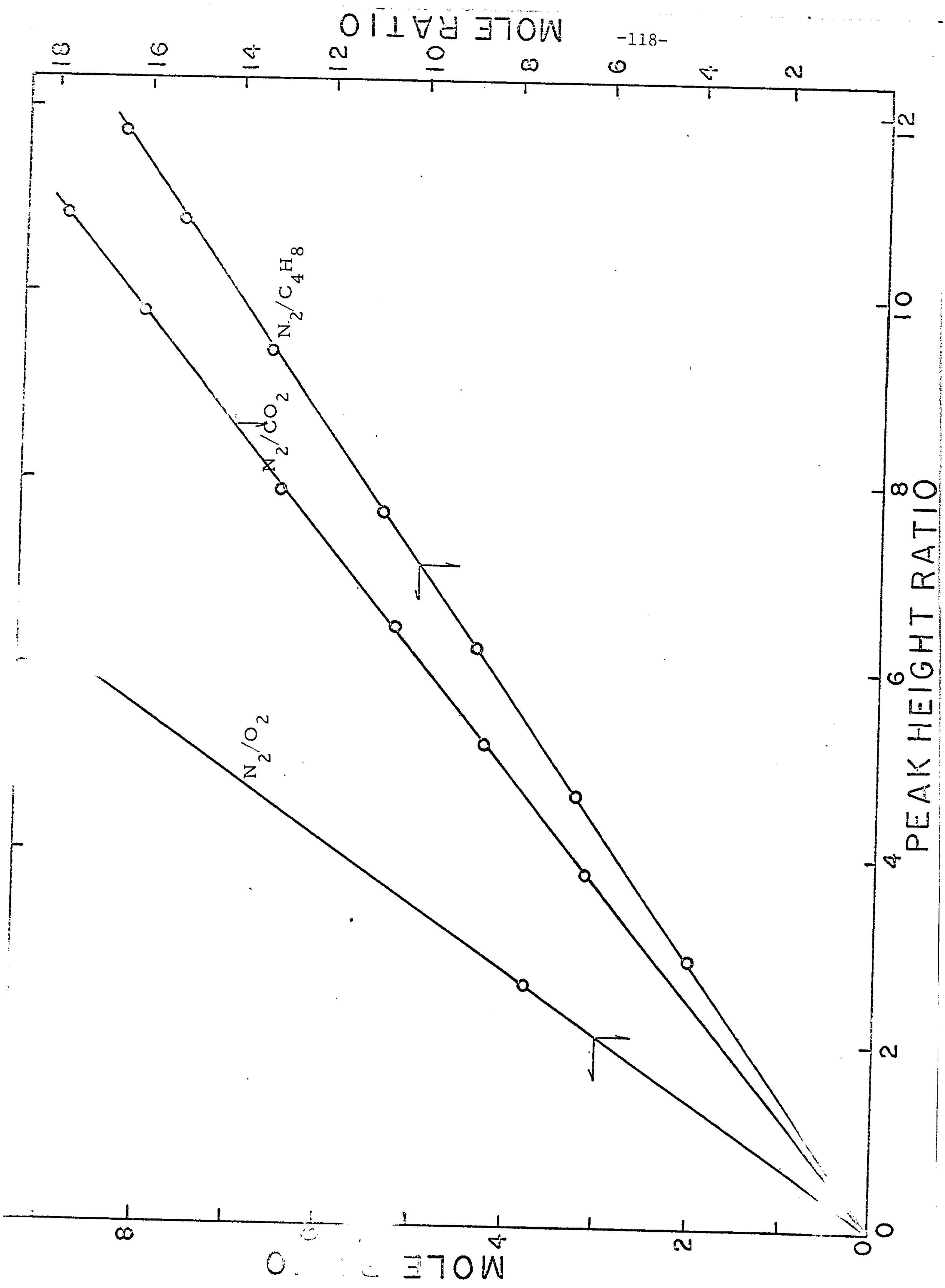

Figure [illegible] Calibration of Fisher Gas Partitioner

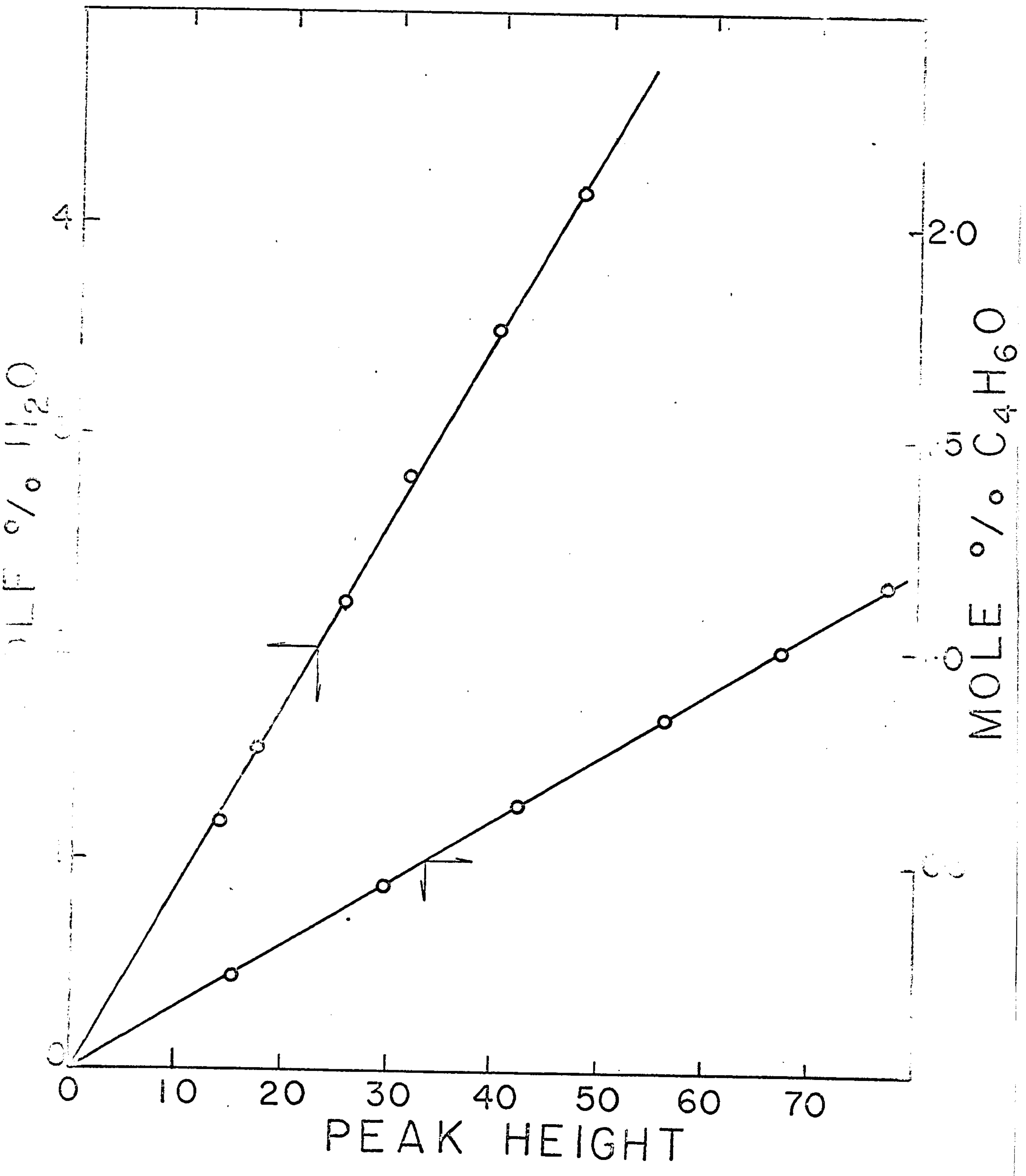

Figure X-5 Calibration of Perkin-Elmer Vapor Fractometer

Appendix B

Properties of Methacrolein and Bismuth Molybdate

Properties of the Catalyst:

Only those properties of the catalyst (particle diameter, particle density) which have a direct bearing on the rate of catalytic oxidation of 2-methylpropene were determined.

Properties of The Zirconium Oxide Supported Bismuth Molybdate

Particle diameter (D_p)	= 0.0313 inches
Particle density (d_p)	= 46.3 lbs./ft^3

The particle diameter (D_p) was determined by measurement with a micrometer of a random sample of 30 granules. An arithemetic average of these values gave the value of particle diameter as 0.0313 inches

The particle density (d_p) was determined by measuring the weight and volume occupied by 100 granules. Since the granules were relatively small. The sphericity was taken as 0.8. and the density was calculated as 46.3 lb / ft^3.

It was found that the surface area of the particle was less than 1 m^2 / gm. And it was too low for accurate measurement. The surface area value was assumed to be 0.6 m^2 / gm, based on the average values collected in literature (47,48) for the particle granules having similar mesh size (20-40).

Density of Properties of Methacrolein

Temperature 25 °C

Weight of Pycnometer(dry) = 28.21504 gms.

Weight of Pycnometer with Water = 38.00233 gms.

Weight of Water at 25 °C = 9.78729 gms.

Density of Water at 25 °C = 0.99707 gm / c.c.

Volume of Pycnometer = 9.81605 c.c.

Weight of Pycnometer with Methacrolein = 37.52959 gms.

Weight of Methacrolein = 9.31455 gms.

Density of Methacrolein at 25 °C = 0.94891 gm / c.c.

Appendix C

Sample Calculation and Material Balance

Sample Calculation:

This calculation is based on the experimental data of Run No. 163.

1) Moles in Feed

moles C_4H_8 / hr.

$$= \frac{45.03 \text{ cc./min. x } 60 \text{ min/ hr x } 273^{\circ}\text{K}}{22400 \text{ cc/g-mole x } 298^{\circ}\text{K}} = 0.1105 \text{ g-mole/hr}$$

moles N_2 / hr

$$= \frac{451.29 \text{ cc. / min. x } 0.7905 \text{ x } 60 \text{ min / hr x } 273^{\circ}\text{K}}{22400 \text{ cc/g-mole x } 298^{\circ}\text{K}} = 0.8754 \text{ g-mole/hr}$$

moles O_2 / hr

$$= \frac{451.29 \text{ cc/min x } 0.2095 \text{ x } 60 \text{ min / hr x } 273^{\circ}\text{K}}{22400 \text{ cc/g-mole x } 298^{\circ}\text{K}} = 0.2320 \text{ g-mole/hr}$$

2) Moles in Products

a) Analysis from Chromatograph

Gas Partitioner	Component	Peak height	Peak height ratio (N_2/ Component)
	CO_2	9.5	28.110
	O_2	84.8	3.157
	N_2	268	1.0
	C_4H_8	19.9	13.465

Vapor Fractometer	Component	Peak height	Peak height ratio C_4H_6O / H_2O
	C_4H_6O	31.8	2.190
	H_2O	14.5	1.0

b) Calculations

Because the moles of nitrogen in the feed and in the effluent stream were the same, the effluent rates were computed on the basis of the nitrogen fed and on the peak height ratios of nitrogen to the reaction products.

From calibration curve

$$\text{Slope}_{C_4H_8} = 0.709$$

$$\text{Slope}_{CO_2} = 1.597$$

$$\text{Slope}_{O_2} = 1.458$$

moles C_4H_8 / hr $= 0.8754 / (0.709 \times 13.465) = 0.0917$ g-mole/hr

moles O_2 / hr $= 0.8754 / (1.458 \times 3.157) = 0.1902$ g-mole/hr

moles CO_2/ hr $= 0.8754 / (1.597 \times 28.110) = 0.0195$ g-mole/hr

moles N_2 / hr $= 0.8754$ g-moles / hr

From Calibration Curve

$$\text{Ratio of slope} = \frac{\text{Slope of } C_4H_6O}{\text{Slope of } H_2O} = 0.2012$$

$$W_{C_4H_6O} \,/\, W_{H_2O} \simeq 2.190 \times 0.2012 \times 71.091 \,/\, 18.015 \simeq 1.739 \qquad (1)$$

$$\begin{aligned} W_{C_4H_6O} + W_{H_2O} &= 71.091\ (N_{C_4H_6O}) + 18.015\ (N_{H_2O}) \\ &= 31.998\ (N_{O_2})_o + 56.108\ (N_{C_4H_8})_o - 31.998\ (N_{O_2}) \\ &\quad - 56.108\ (N_{C_4H_8}) - 44.009\ (N_{CO_2}) \\ &\simeq 31.998\ (0.2320 - 0.1902) + 56.108\ (0.1105 - 0 \\ &\quad - 0.0917) - 44.009\ (0.0195) \\ &\simeq 1.534 \qquad (2) \end{aligned}$$

W_{H_2O} = 0.560

$W_{C_4H_6O}$ = 0.9739

Moles H_2O $\simeq$ 0.0311 g-moles / hr

Moles C_4H_6O $\simeq$ 0.0137 g-moles / hr

Conversion $\simeq$ 17.01 %

Selectivity $\simeq$ 70.21 %

Yield CO_2 = 0.1764

Yield C_4H_6O = 0.1194

Material Balance

This calculation is based on atomic elements present in feed and in products as well, data are obtained from experimental run No. 163.

Atomic elements feed in :

C $= 0.1105 \times 4 = 0.4420$

H $= 0.1105 \times 8 = 0.8840$

O $= 0.2320 \times 2 = 0.4640$

Atomic elements in products:

C $= 0.0917 \times 4 - 0.0137 \times 4 - 0.0195$

$= 0.4411$

H $= 0.0137 \times 6 - 0.0311 \times 2 - 0.0917 \times 8$

$= 0.8780$

O $= 0.1902 \times 2 - 0.0195 \times 2 - 0.0137$

$= 0.4331$

% Deviation:

C $= (0.4420 - 0.4411) / 0.4420 \simeq 0.20 \%$

$H = (0.8840 - 0.8780) / 0.8840 = 0.67 \%$

$O = (0.4640 - 0.4331) / 0.4640 = 6.66 \%$

Appendix D

Experimental Data

Temperature 390°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
132	0.6250	2.7001	0.1105	0.2904	1.1028
133	0.6250	2.4000	0.1105	0.2652	0.9801
134	0.6250	2.0995	0.1105	0.2320	0.8574
135	0.6250	1.7991	0.1105	0.1988	0.7501
136	0.6250	1.5014	0.1105	0.1659	0.6260

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
132	0.1023	0.2740	1.1028	0.0070	0.0117	0.0047
133	0.0978	0.2222	0.9801	0.0085	0.0252	0.0148
134	0.0938	0.2001	0.8574	0.0137	0.0250	0.0095
135	0.0883	0.1516	0.7501	0.0168	0.0329	0.0167
136	0.0865	0.1159	0.6260	0.0186	0.0414	0.0176

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\,Y_{CO_2}$
132	85.37	7.42	0.0633	0.0106
133	66.93	11.49	0.0769	0.0334
134	82.04	15.11	0.1239	0.0214
135	75.68	20.09	0.1520	0.0377
136	77.50	21.72	0.1683	0.0398

Temperature 390°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
137	0.6250	1.1991	0.1105	0.1325	0.5028
138	0.6250	0.8995	0.1105	0.0994	0.3750
139	0.6250	0.6000	0.1105	0.0663	0.2501
216	1.2500	2.0995	0.1105	0.2320	0.8754
217	1.2500	1.7991	0.1105	0.1998	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
137	0.0766	0.0531	0.5028	0.0230	0.0679	0.0173
138	0.0821	0.0893	0.3751	0.0216	0.0469	0.0214
139	0.0853	0.0139	0.2501	0.0195	0.0417	0.0208
216	0.0854	0.1909	0.8754	0.0213	0.0351	0.0149
217	0.0799	0.1001	0.7501	0.0251	0.0449	0.0202

Run No.	% selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
137	72.10	28.87	0.2081	0.0392
138	76.06	25.70	0.1954	0.0484
139	77.38	22.81	0.1764	0.0470
216	84.86	22.71	0.1927	0.0337
217	82.03	27.69	0.2271	0.0457

Temperature 390°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
218	1.2500	1.5014	0.1105	0.1659	0.6260
219	1.2500	1.1991	0.1105	0.1325	0.5028
220	1.2500	0.8995	0.1105	0.0994	0.3751
221	1.2500	0.6000	0.1105	0.0633	0.2501
252	2.5000	2.0995	0.1105	0.2320	0.8754

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
218	0.0769	0.1009	0.6260	0.0277	0.0509	0.0217
219	0.0726	0.0561	0.5028	0.0322	0.0605	0.0298
220	0.0714	0.0204	0.3751	0.0306	0.0625	0.0319
221	0.0749	/	0.2501	0.0282	0.0529	0.0254
252	0.0772	0.1683	0.8754	0.0271	0.0492	0.0221

Run No.	%Selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
218	82.44	30.41	0.2506	0.0490
219	76.68	34.30	0.2733	0.0674
220	78.26	35.38	0.2769	0.0721
221	79.21	32.22	0.2552	0.0574
252	81.38	30.14	0.2452	0.0500

Temperature 390°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
255	2.5000	1.7991	0.1105	0.1988	0.7501
256	2.5000	1.5014	0.1105	0.1659	0.6260
257	2.5000	1.1991	0.1105	0.1325	0.5028
258	2.5000	0.8995	0.1105	0.0994	0.3751
259	2.5000	0.6000	0.1105	0.0663	0.2501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
255	0.0732	0.1258	0.7501	0.0301	0.0576	0.0263
256	0.0698	0.0841	0.6260	0.0321	0.0648	0.0305
257	0.0684	0.0621	0.5028	0.0329	0.0681	0.0319
258	0.0654	0.0061	0.3751	0.0348	0.0747	0.0358
259	0.0758	/	0.2501	0.0278	0.0544	0.0253

Run No.	%Selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
255	80.70	33.76	0.2723	0.0595
256	78.62	36.83	0.2904	0.0690
257	78.15	38.09	0.2977	0.0721
258	77.16	40.81	0.3149	0.0809
259	80.12	31.42	0.2515	0.0572

Temperature 390^{o}C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
260	2.5000	0.4633	0.1105	0.0512	0.2083
101	3.7500	2.4000	0.1105	0.2652	0.9801
102	3.7500	2.0995	0.1105	0.2320	0.8574
103	3.7500	1.7991	0.1105	0.1988	0.7501
104	3.7500	1.5014	0.1105	0.1659	0.6260

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
260	0.0802	/	0.2083	0.0251	0.0449	0.0178
101	0.0727	0.1798	0.9801	0.0293	0.0629	0.0339
102	0.0735	0.1492	0.8575	0.0284	0.0618	0.0322
103	0.0680	0.0943	0.7501	0.0309	0.0769	0.0429
104	0.0719	0.0701	0.6260	0.0266	0.0701	0.0472

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
260	82.84	27.42	0.2271	0.0402
101	77.51	34.21	0.2651	0.0766
102	76.77	33.48	0.2570	0.0728
103	72.70	38.46	0.2796	0.0970
104	68.91	34.93	0.2407	0.1067

Temperature 390^{o}C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
105	3.7500	1.1991	0.1105	0.1325	0.5028
106	3.7500	0.8995	0.1105	0.0994	0.3751
107	3.7500	0.6000	0.1105	0.0663	0.2501
186	5.0000	2.0995	0.1105	0.2320	0.8754
187	5.0000	1.7991	0.1105	0.1988	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
105	0.0674	0.0219	0.5028	0.0294	0.0811	0.0341
106	0.0676	0.0012	0.3751	0.0315	0.0770	0.0439
107	0.0791	/	0.2501	0.0247	0.0475	0.0261
186	0.0731	0.1608	0.8754	0.0305	0.0574	0.0270
187	0.0715	0.1193	0.7501	0.0308	0.0619	0.0314

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
105	68.21	39.00	0.2660	0.0723
106	73.43	38.82	0.2850	0.0993
107	78.59	28.42	0.2235	0.0590
186	81.55	33.85	0.2760	0.0610
187	78.97	35.29	0.2787	0.0710

Temperature 390°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
187	5.0000	1.5014	0.1105	0.1659	0.6260
188	5.0000	1.1991	0.1105	0.1325	0.5028
189	5.0000	0.8995	0.1105	0.0994	0.3751
190	5.0000	0.6000	0.1105	0.0663	0.2501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
187	0.0703	0.0814	0.6260	0.0315	0.0659	0.0335
188	0.0666	0.0361	0.5028	0.0335	0.0748	0.0409
189	0.0643	0.0013	0.3751	0.0349	0.0756	0.0421
190	0.0734	/	0.2501	0.0305	0.0512	0.0236

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
187	78.36	36.38	0.2805	0.0757
188	76.31	39.72	0.3031	0.0925
189	75.54	41.81	0.3158	0.0952
190	82.21	33.57	0.2760	0.0533

Temperature 410°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
161	0.6250	2.7001	0.1105	0.2984	1.1028
162	0.6250	2.4000	0.1105	0.2652	0.9801
163	0.6250	2.0995	0.1105	0.2320	0.8574
164	0.6250	1.7991	0.1105	0.1988	0.7501
165	0.6250	1.5014	0.1105	0.1659	0.6260
166	0.6250	1.1991	0.1105	0.1325	0.5028
167	0.6250	0.8995	0.1105	0.0984	0.3751

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
161	0.1002	0.2751	1.1028	0.0082	0,0159	0.0084
162	0.0952	0.2320	0.9801	0.0116	0.0261	0.0139
163	0.0917	0.1902	0.8574	0.0137	0.0311	0.0195
164	0.0873	0.1458	0.7501	0.0171	0.0401	0.0231
165	0.0808	0.1004	0.6260	0.0232	0.0491	0.0281
166	0.0783	0.0507	0.5028	0.0225	0.0601	0.0184
167	0.0820	0.0346	0.3751	0.0217	0.0483	0.0259

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
161	79.61	9.32	0.0742	0.0190
162	75.82	13.25	0.1049	0.0314
163	70.21	17.01	0.1194	0.0441
164	73.73	21.00	0.1547	0.0522
165	78.11	26.88	0.2099	0.0635
166	69.88	29.14	0.2036	0.0434
167	76.68	25.61	0.1963	0.0585

Temperature 410°C

Run No.	W / F	R	Feed moles/ hr C_4H_8	O_2	N_2
209	1.2500	2.4000	0.1105	0.2652	0.9801
210	1.2500	2.0995	0.1105	0.2320	0.8754
211	1.2500	1.7991	0.1105	0.1988	0.7501
212	1.2500	1.5014	0.1105	0.1659	0.6260
213	1.2500	1.1991	0.1105	0.1325	0.5028
214	1.2500	0.8995	0.1105	0.0994	0.3751

Run No.	Products moles / hr C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
209	0.0835	0.0200	0.9801	0.0226	0.0398	0.0174
210	0.0815	0.1749	0.8754	0.0242	0.0421	0.0179
211	0.0773	0.1348	0.7501	0.0272	0.0509	0.0241
212	0.0734	0.0631	0.6260	0.0299	0.0574	0.0285
213	0.0698	0.0503	0.5028	0.0323	0.0651	0.0325
214	0.0758	0.0458	0.3751	0.0281	0.0517	0.0217

Run No.	%Selectivity $S_{C_4H_6O}$	%Conversion $X_{C_4H_8}$	Yield $Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
209	83.70	24.43	0.2045	0.0393
210	83.45	26.24	0.2190	0.0404
211	81.68	30.14	0.2461	0.0545
212	80.59	33.57	0.2705	0.0644
213	79.36	36.83	0.2923	0.0735
214	80.98	31.40	0.2542	0.0490

Temperature 410°C

Run No.	W / F	R	Feed Moles / hr		
			C_4H_8	O_2	N_2
234	2.5000	2.0995	0.1105	0.2320	0.8754
235	2.5000	1.7991	0.1105	0.1988	0.7501
236	2.5000	1.5014	0.1105	0.1659	0.6260
237	2.5000	1.1991	0.1105	0.1325	0.5028
238	2.5000	0.8995	0.1105	0.0994	0.3751
239	2.5000	0.6000	0.1105	0.0663	0.2501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
234	0.0776	0.1791	0.8754	0.0263	0.0531	0.0284
235	0.0769	0.1288	0.7501	0.0268	0.0543	0.0255
236	0.0671	0.0783	0.6260	0.0343	0.0689	0.0194
237	0.0649	0.0202	0.5028	0.0319	0.0743	0.0249
238	0.0676	0.0061	0.3751	0.0334	0.0722	0.0223
239	0.0770	0.0031	0.2501	0.0243	0.0508	0.0140

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
234	79.33	29.77	0.2380	0.0599
235	79.17	30.41	0.2425	0.0606
236	79.72	38.28	0.2832	0.0708
237	76.54	41.27	0.3701	0.0925
238	76.46	38.82	0.3628	0.0907
239	72.50	30.32	0.2199	0.0549

Temperature 410°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
120	3.7500	2.4000	0.1105	0.2652	0.9801
121	3.7500	2.0995	0.1105	0.2320	0.8574
122	3.7500	1.7991	0.1105	0.1988	0.7501
123	3.7500	1.5014	0.1105	0.1659	0.6260
124	3.7500	1.1991	0.1105	0.1325	0.5028
125	3.7500	0.8995	0.1105	0.0994	0.3751

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
120	0.0712	0.1744	0.9801	0.0290	0.0701	0.0409
121	0.0700	0.1408	0.8574	0.0301	0.0696	0.0412
122	0.0686	0.1108	0.7501	0.0298	0.0763	0.0337
123	0.0665	0.0633	0.6260	0.0304	0.0830	0.0455
124	0.0638	0.0451	0.5028	0.0315	0.0525	0.0452
125	0.0737	0.0111	0.3751	0.274	0.0613	0.0332

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
120	73.79	35.57	0.2959	0.0925
121	74,32	36.65	0.3095	0.0932
122	71.12	37.92	0.3058	0.0762
123	69.09	39.82	0.3248	0.1029
124	67.45	42.26	0.2833	0.1022
125	74.46	33.30	0.2470	0.0764

Temperature 410°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
174	5.0000	2.0995	0.1105	0.2320	0.8754
175	5.0000	1.7991	0.1105	0.1988	0.7501
176	5.0000	1.5014	0.1105	0.1659	0.6260
177	5.0000	1.1991	0.1105	0.1325	0.5028
178	5.0000	0.8995	0.1105	0.0994	0.3751
179	5.0000	0.6000	0.1105	0.0663	0.2501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
174	0.0690	0.1454	0.8754	0.0327	0.0664	0.0348
175	0.0659	0.1014	0.7501	0.0342	0.0732	0.0407
176	0.0660	0.0690	0.6260	0.0338	0.0704	0.0412
177	0.0638	0.0543	0.5028	0.0344	0.0749	0.0421
178	0.0727	0.0203	0.3751	0.0304	0.0604	0.0299
179	0.0771	0.0034	0.2501	0.0273	0.0505	0.0237

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
174	78.80	35.56	0.2624	0.0783
175	76.68	40.36	0.2723	0.0920
176	75.96	40.27	0.2696	0.0932
177	75.38	42.26	0.3120	0.0952
178	79.89	34.21	0.02850	0.0976
179	81.74	30.23	0.2479	0.0536

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
147	0.6250	2.7001	0.1105	0.2984	1.1028
148	0.6250	2.4000	0.1105	0.2652	0.9801
149	0.6250	2.0995	0.1105	0.2320	0.8574
150	0.6250	1.7991	0.1105	0.1988	0.7501
151	0.6250	1.5014	0.1105	0.1659	0.6260

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
147	0.0942	0.2621	1.1028	0.0123	0.0281	0.0152
148	0.0918	0.2213	0.9801	0.0137	0.0335	0.0199
149	0.0884	0.1766	0.8574	0.0153	0.0411	0.0261
150	0.0869	0.1432	0.7501	0.0172	0.0421	0.0257
151	0.0765	0.0832	0.6260	0.0242	0.0631	0.0384

Run No.	% Selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
147	75.46	14.75	0.1113	0.0343
148	73.26	16.92	0.1239	0.0450
149	69.23	20.00	0.1384	0.0590
150	72.88	21.38	0.1556	0.0581
151	71.18	30.77	0.7190	0.0868

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
152	0.6250	1.1991	0.1105	0.1325	0.5028
153	0.6250	0.8995	0.1105	0.0994	0.3751
222	1.2500	2.4000	0.1105	0.2652	0.9801
223	1.2500	2.0995	0.1105	0.2320	0.8754
224	1.2500	1.7991	0.1105	0.1988	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
152	0.0759	0.0469	0.5028	0.0240	0.0661	0.0312
153	0.0735	0.0031	0.3751	0.0250	0.0728	0.0472
222	0.0796	0.2040	0.9801	0.0254	0.0461	0.0214
223	0.0745	0.1618	0.8754	0.0288	0.0561	0.0263
224	0.0732	0.1253	0.7501	0.0298	0.0589	0.0268

Run No.	%Selectivity	%Conversion	Yield	
,	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
152	69.36	31.31	0.2171	0.0709
153	67.57	33.48	0.2262	0.1067
222	82.20	27.96	0.2298	0.0484
223	80.00	32.58	0.2606	0.0595
224	79.89	33.76	0.2696	0.0606

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
225	1.2500	1.5014	0.1105	0.1659	0.6260
226	1.2500	1.1991	0.1105	0.1325	0.5028
227	1.2500	0.8995	0.1105	0.0994	0.3751
228	2.5000	2.0995	0.1105	0.2320	0.8754
229	2.5000	1.7991	0.1105	0.1988	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
225	0.0687	0.0974	0.6260	0.0330	0.0674	0.0349
226	0.0649	0.0357	0.5028	0.0354	0.0750	0.0401
227	0.0641	/	0.3751	0.0339	0.0769	0.0431
228	0.0685	0.1403	0.8754	0.0325	0.0681	0.0376
229	0.0718	0.1153	0.7501	0.0302	0.0629	0.0331

Run No.	% Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
225	78.94	37.83	0.2986	0.0789
226	77.63	41.27	0.3203	0.0907
227	73.06	41.99	0.3067	0.0975
228	77.38	38.00	0.2941	0.0857
229	78.03	35.02	0.2733	0.0748

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
230	2.5000	1.5014	0.1105	0.1659	0.6260
231	2.5000	1.1991	0.1105	0.1325	0.5028
232	2.5000	0.8995	0.1105	0.0994	0.3751
233	2.5000	0.6000	0.1105	0.0663	0.2501
108	3.7500	2.4000	0.1105	0.2652	0.9801

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
230	0.0634	0.0642	0.6260	0.0361	0.0775	0.0437
231	0.0630	0.0301	0.5028	0.0361	0.0801	0.0441
232	0.0662	0.0059	0.3751	0.0340	0.0743	0.0392
233	0.0768	/	0.2501	0.0241	0.0642	0.0284
108	0.0660	0.1547	0.9801	0.0305	0.0866	0.0518

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
230	76.64	42.62	0.3266	0.0988
231	76.00	42.99	0.3257	0.0997
232	76.75	40.09	0.3076	0.0866
233	80.00	30.49	0.2570	0.0541
108	68.54	40.27	0.2760	0.1171

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
109	3.7500	2.0995	0.1105	0.2320	0.8574
110	3.7500	1.7991	0.1105	0.1988	0.7501
111	3.7500	1.5014	0.1105	0.1659	0.6260
112	3.7500	1.1991	0.1105	0.1325	0.5028
113	3.7500	0.8995	0.1105	0.0994	0.3751

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
109	0.0643	0.1193	0.8574	0.0328	0.0851	0.0509
110	0.0656	0.0851	0.7501	0.0312	0.0848	0.0540
111	0.0613	0.0362	0.6260	0.0334	0.0964	0.0625
112	0.0616	0.0025	0.5028	0.0321	0.0990	0.0644
113	0.0694	/	0.3751	0.0288	0.0751	0.0469

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
109	70.99	41.81	0.2968	0.1151
110	69.49	40.63	0.2823	0.1221
111	67.89	44.52	0.3022	0.1414
112	65.64	44.25	0.2904	0.1457
113	70.07	37.19	0.2626	0.1061

Temperature 460°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
180	5.0000	2.0995	0.1105	0.2320	0.8754
181	5.0000	1.7991	0.1105	0.1988	0.7501
182	5.0000	1.5014	0.1105	0.1659	0.6260
183	5.0000	1.1991	0.1105	0.1325	0.5028
184	5.0000	0.8995	0.1105	0.0994	0.3751
185	5.0000	0.6000	0.1105	0.0664	0.2501

Run No.	Products Moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
180	0.0638	0.1274	0.8754	0.0346	0.0816	0.0458
181	0.0628	0.0908	0.7501	0.0352	0.0834	0.0483
182	0.0616	0.0561	0.6260	0.0371	0.0839	0.0463
183	0.0620	0.0283	0.5028	0.0370	0.0825	0.0443
184	0.0641	0.0161	0.3751	0.0312	0.0641	0.0336
185	0.0750	/	0.2501	0.0264	0.0542	0.0251

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\, Y_{CO_2}$
180	74.52	42.26	0.3131	0.1036
181	73.79	43.17	0.3185	0.1092
182	75.87	44.25	0.3357	0.1047
183	76.29	43.89	0.3348	0.1002
184	77.81	41.99	0.2823	0.0760
185	78.34	32.13	0.2389	0.0567

Temperature 510°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
140	0.6250	2.7001	0.1105	0.2984	1.1028
141	0.6250	2.4000	0.1105	0.2652	0.9801
142	0.6250	2.0995	0.1105	0.2320	0.8574
143	0.6250	1.7991	0.1105	0.1988	0.7501
144	0.6250	1.5014	0.1105	0.1659	0.6260
145	0.6250	1.1991	0.1105	0.1325	0.5028

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
140	0.0856	0.2413	1.1028	0.0193	0.0404	0.0257
141	0.0843	0.2001	0.9801	0.0183	0.0499	0.0309
142	0.0797	0.1489	0.8574	0.0201	0.0621	0.0201
143	0.0833	0.1319	0.7501	0.0192	0.0509	0.0314
144	0.0756	0.0814	0.6260	0.0244	0.0647	0.0398
145	0.0732	0.0321	0.5028	0.0258	0.0721	0.0458

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
140	77.51	22.53	0.1746	0.0581
141	69.85	23.71	0.1656	0.0699
142	65.26	27.87	0.1819	0.0914
143	70.58	24.62	0.1737	0.0710
144	69.91	31.58	0.2208	0.0900
145	69.71	33.76	0.2334	0.1036

Temperature 510°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
146	0.6250	0.8995	0.1105	0.0994	0.3751
197	1.2500	2.4000	0.1105	0.2652	0.9801
198	1.2500	2.0995	0.1105	0.2320	0.8754
199	1.2500	1.7991	0.1105	0.1988	0.7501
200	1.2500	1.5014	0.1105	0.1659	0.6260
201	1.2500	1.1991	0.1105	0.1325	0.5028

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
146	0.0769	0.0011	0.2501	0.0273	0.0523	0.0249
197	0.0724	0.1868	0.9801	0.0300	0.0618	0.0321
198	0.0697	0.1483	0.8754	0.0316	0.0654	0.0348
199	0.0693	0.1129	0.7501	0.0322	0.0668	0.0351
200	0.0642	0.0685	0.6260	0.0362	0.0749	0.0404
201	0.0627	0.0281	0.5028	0.0366	0.0806	0.0448

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\,Y_{CO_2}$
146	81.25	30.41	0.2162	0.0563
197	78.74	34.48	0.2714	0.0726
198	77.45	36.92	0.2859	0.0787
199	78.16	37.29	0.2914	0.0794
200	78.19	41.90	0.3276	0.0914
201	76.57	43.26	0.3312	0.1013

Temperature 510°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
202	1.2500	0.8995	0.1105	0.0994	0.3751
246	2.5000	2.0995	0.1105	0.2320	0.8754
247	2.5000	1.7991	0.1105	0.1988	0.7501
248	2.5000	1.5014	0.1105	0.1659	0.6260
249	2.5000	1.1991	0.1105	0.1325	0.5028
250	2.5000	0.8995	0.1105	0.0994	0.3751

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
202	0.0754	0.0058	0.3751	0.0347	0.0744	0.0382
246	0.0657	0.1372	0.8754	0.0344	0.0709	0.0408
247	0.0629	0.0967	0.7501	0.0364	0.0810	0.0431
248	0.0591	0.0541	0.6260	0.0391	0.0873	0.0482
249	0.0571	0.0142	0.5028	0.0402	0.0927	0.0518
250	0.0707	0.0011	0.3751	0.0281	0.0738	0.0458

Run No.	% Selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
202	77.28	30.89	0.3140	0.0864
246	76.78	40.54	0.3113	0.0923
247	76.47	43.05	0.3294	0.0975
248	76.07	46.52	0.3538	0.1090
249	75.28	48.33	0.3638	0.1171
250	70.60	36.02	0.3285	0.1036

Temperature 510°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
251	2.5	0.6000	0.1105	0.0663	0.2501
126	3.750	2.4000	0.1105	0.2652	0.9801
127	3.750	2.0995	0.1105	0.2320	0.8574
128	3.750	1.7991	0.1105	0.1988	0.7501
129	3.750	1.5014	0.1105	0.1659	0.6260
130	3.750	1.1991	0.1105	0.1325	0.5028

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
251	0.0735	/	0.2501	0.0300	0.0547	0.0238
126	0.0626	0.1348	0.9801	0.0313	0.0969	0.0653
127	0.0611	0.0957	0.8574	0.0319	0.1011	0.0684
128	0.0562	0.0533	0.7501	0.0360	0.1092	0.0728
129	0.0564	0.0162	0.6260	0.0345	0.1123	0.0753
130	0.0559	0.0098	0.5028	0.0340	0.0918	0.0594

Run No.	%Selectivity	% Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
251	83.32	33.48	0.2714	0.0538
126	65.34	43.35	0.2832	0.1477
127	64.57	44.71	0.2886	0.1547
128	66.30	49.14	0.3257	0.1647
129	63.77	48.96	0.3122	0.1701
130	72.49	49.43	0.3076	0.1343

Temperature 510°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
131	3.750	0.8995	0.1105	0.0944	0.3751
192	5.000	2.0995	0.1105	0.2320	0.8754
193	5.000	1.7991	0.1105	0.1988	0.2501
194	5.000	1.5014	0.1105	0.1659	0.6260
195	5.000	1.1991	0.1105	0.1325	0.5028
196	5.000	0.8995	0.1105	0.0994	0.3751

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
131	0.0656	0.0058	0.3751	0.0347	0.0744	0.0382
192	0.0593	0.1068	0.8754	0.0371	0.0931	0.0562
193	0.0573	0.0709	0.7501	0.0383	0.0980	0.0581
194	0.0579	0.0369	0.6260	0.0372	0.0969	0.0609
195	0.0538	0.0042	0.5028	0.0408	0.0965	0.0616
196	0.0638	0.0018	0.3751	0.0363	0.0713	0.0402

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
131	77.28	40.63	0.2542	0.0864
192	72.46	46.33	0.3357	0.1271
193	71.99	48.14	0.3466	0.1314
194	70.72	47.60	0.3366	0.1378
195	68.29	51.24	0.3694	0.1393
196	77.23	42.25	0.3285	0.0911

Temperature 560°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
154	0.6250	2.7001	0.1105	0.2984	1.1028
155	0.6250	2.4000	0.1105	0.2652	0.9801
156	0.6250	2.0995	0.1105	0.2320	0.8574
157	0.6250	1.7991	0.1105	0.1988	0.7501
158	0.6250	1.5014	0.1105	0.1659	0.6260

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
154	0.0779	0.2143	1.1028	0.0222	0.0635	0.0409
155	0.0776	0.1797	0.9801	0.0220	0.0609	0.0433
156	0.0749	0.1303	0.8574	0.0229	0.0737	0.0498
157	0.0748	0.1101	0.7501	0.0247	0.0671	0.0416
158	0.0745	0.0948	0.6260	0.0247	0.0681	0.0438

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
154	68.10	29.50	0.2009	0.0925
155	66.87	29.77	0.1990	0.0979
156	64.33	32.22	0.2072	0.1126
157	69.19	32.31	0.2235	0.0941
158	68.61	32.58	0.2235	0.0990

Temperature 560°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
159	0.6250	1.1991	0.1105	0.1325	0.5028
160	0.6250	0.8995	0.1105	0.0994	0.3751
203	1.2500	2.4000	0.1105	0.2652	0.9801
204	1.2500	2.0995	0.1105	0.2320	0.8754
205	1.2500	1.7991	0.1105	0.1988	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
159	0.0724	0.0304	0.5028	0.0256	0.0754	0.0482
160	0.0764	0.0064	0.3751	0.0233	0.0693	0.0466
203	0.0702	0.1804	0.9801	0.0314	0.0669	0.0352
204	0.0668	0.1281	0.8754	0.0335	0.0738	0.0401
205	0.0643	0.1001	0.7501	0.0352	0.0783	0.0418

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
159	67.19	34.48	0.2316	0.1090
160	65.39	30.86	0.2018	0.1054
203	77.92	36.47	0.2841	0.0796
204	76.66	39.55	0.3031	0.0907
205	76.19	41.81	0.3185	0.0945

Temperature 560°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
206	1.2500	1.5014	0.1105	0.1659	0.6260
207	1.2500	1.1991	0.1105	0.1325	0.5028
208	1.2500	0.8995	0.1105	0.0994	0.3751
240	2.5000	2.0995	0.1105	0.2320	0.8754
241	2.5000	1.7991	0.1105	0.1988	0.7501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
206	0.0634	0.0544	0.6260	0.0349	0.0834	0.0472
207	0.0594	0.0143	0.5028	0.0370	0.0900	0.0531
208	0.0688	0.0011	0.3751	0.0321	0.0691	0.0321
240	0.0592	0.1103	0.8754	0.0386	0.0879	0.0502
241	0.0613	0.1105	0.7501	0.0376	0.0833	0.0454

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\,Y_{CO_2}$
206	74.10	42.62	0.3158	0.1067
207	72.41	46.24	0.3348	0.1201
208	76.98	37.74	0.2904	0.0832
240	75.24	46.43	0.3493	0.1135
241	76.42	44.52	0.3402	0.1027

Temperature 560°C

Run No.	W / F	R	Feed moles/hr		
			C_4H_8	O_2	N_2
242	2.5000	1.5014	0.1105	0.1659	0.6260
243	2.5000	1.1991	0.1105	0.1325	0.5028
244	2.5000	0.8995	0.1105	0.0994	0.3751
245	2.5000	0.6000	0.1105	0.0663	0.2501
114	3.750	2.4000	0.1105	0.2652	0.9801

Run No.	Products mole / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
242	0.0577	0.0469	0.6260	0.0392	0.0924	0.0521
243	0.0572	0.0098	0.5028	0.0391	0.0951	0.0549
244	0.0656	0.0071	0.3751	0.0352	0.0737	0.0368
245	0.0740	/	0.2501	0.0306	0.0538	0.0234
114	0.0561	0.0988	0.9801	0.0320	0.1211	0.0893

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
242	74.24	47.78	0.3547	0.1178
243	73.35	48.24	0.3538	0.1242
244	78.39	40.63	0.3185	0.0832
245	83.83	33.03	0.2769	0.0529
114	58.82	49.23	0.2895	0.2020

Temperature 560°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
115	3.7500	2.0995	0.1105	0.2320	0.8574
116	3.7500	1.7991	0.1105	0.1988	0.7501
117	3.7500	1.5014	0.1105	0.1659	0.6260
118	3.7500	1.1991	0.1105	0.1325	0.5028
119	3.7500	0.8995	0.1105	0.0994	0.3750

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
115	0.0544	0.0608	0.8574	0.0329	0.1240	0.0923
116	0.0539	0.0226	0.7501	0.0327	0.1266	0.0955
117	0.0565	0.0039	0.6260	0.0322	0.1188	0.0865
118	0.0543	0.0011	0.5028	0.0313	0.1182	0.0675
119	0.0683	/	0.3750	0.0293	0.0782	0.0491

Run No.	%Selectivity	%Conversity	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
115	58.65	50.77	0.2977	0.2088
116	57.77	51.22	0.2959	0.2160
117	59.63	48.69	0.2914	0.1954
118	55.69	50.86	0.2832	0.1527
119	69.43	38.19	0.2651	0.1110

Temperature 560°C

Run No.	W / F	R	Feed moles/ hr		
			C_4H_8	O_2	N_2
168	5.0000	2.0995	0.1105	0.2320	0.8754
169	5.0000	1.7991	0.1105	0.1988	0.7501
170	5.0000	1.5014	0.1105	0.1659	0.6260
171	5.0000	1.1991	0.1105	0.1325	0.5028
172	5.0000	0.8995	0.1105	0.0994	0.3751
173	5.0000	0.6000	0.1105	0.0663	0.2501

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
168	0.0493	0.0807	0.8754	0.0429	0.1143	0.0718
169	0.0482	0.0513	0.7501	0.0418	0.1133	0.0690
170	0.0481	0.0038	0.6260	0.0419	0.1209	0.0804
171	0.0546	0.0011	0.5028	0.0403	0.0909	0.0501
172	0.0661	/	0.3751	0.0338	0.0735	0.0419
173	0.0749	/	0.2501	0.0279	0.0569	0.0288

Run No.	%Selectivity	%Conversion	Yield	
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$Y_{C_4H_6O}$	$\frac{1}{4}\ Y_{CO_2}$
168	70.10	55.38	0.3882	0.1624
169	67.09	56.38	0.3782	0.1561
170	67.14	56.47	0.3791	0.1819
171	72.35	50.41	0.3647	0.1133
172	76.13	40.18	0.3058	0.0947
173	78.30	32.22	0.2524	0.0651

Appendix E

Thermodynamic Aspects of Oxidation of 2-methylpropene

The values of the change of Gibb's free energy, ΔF^{o}, and the equilibrium constant, K, of the gaseous oxidation of 2-methyl-propene to methacrolein were collected from literature(47,48), which were reported being calculated as function of temperature.

The Values of ΔF^{o} and K for gaseous Methacrolein Formation at 1 atm And Different Temperatures

Temperature °C	$-\Delta F^{o}$ K_{cal}/gm-mole	K
204	96.30	1.32×10^{44}
260	98.46	2.34×10^{40}
316	100.67	2.24×10^{37}
371	103.14	1.00×10^{35}
427	105.13	6.61×10^{32}

Appendix F

External Resistance to Mass and Heat Transfer:

A) Drop in Partial Pressure

B) Temperature Drop From Catalyst Particle to Ambient Gas Stream.

Experimental Data on External Diffusion

The data for estimation of the external resistances to mass and heat transfer are obtained from experimental run 176 . The reaction conditions are :

Temperature = 410°C.
W/F = 5.0
R = 1.5014
Weight of Catalyst = 0.5525 gms.

COMPOSITION	FEED		PRODUCTS	
	Flow Rate g-mole/ hr.	Mole Fraction	Flow Rate g-mole/hr.	Mole Fraction
O_2	0.1659	0.1838	0.0690	0.0762
N_2	0.6260	0.6938	0.6260	0.6906
C_4H_8	0.1105	0.1224	0.0660	0.0728
CO_2	0	0	0.0412	0.0445
C_4H_6O	0	0	0.0338	0.0373
H_2O	0	0	0.0704	0.0776
Total	0.9024	1.000	0.9064	1.000

a). Estimation of Partial Pressure Drop For Each Component

Partial pressure drops from Yoshida, Ramaswami and Hougen's plot (79) of $\Delta P_j/P_j$ vs. $\bar{R}/y_j$ were calculated as the following:

$$\bar{R} = r_{mA} / a_m \phi G_m$$

O_2 $$r_{ma} = \frac{0.1659 - 0.0690}{0.5525} = 0.1754$$ moles/gm-catalyst

C_4H_8 $$r_{ma} = \frac{0.1105 - 0.0660}{0.5525} = 0.0805$$ "

CO_2 $$r_{ma} = \frac{0.0412}{0.5525} = 0.0746$$ "

C_4H_6O $$r_{ma} = \frac{0.0338}{0.5525} = 0.0612$$ "

H_2O $$r_{ma} = \frac{0.0704}{0.5525} = 0.1274$$ "

$$G_m = 0.9024 \Big/ \left(\left(\frac{\pi}{4}\right) \times (2.54 \times 0.430)^2 \right)$$

$$= 0.963 \quad \text{g-mole/hr-cm}^2$$

O_2 $$\bar{R} = \frac{0.1754}{6000 \times 0.9 \times 0.963} = 0.3373 \times 10^{-4}$$

C_4H_8 $$\bar{R} = \frac{0.0805}{6000 \times 0.9 \times 0.963} = 0.1548 \times 10^{-4}$$

CO_2 $$\bar{R} = \frac{0.0746}{6000 \times 0.9 \times 0.963} = 0.1435 \times 10^{-4}$$

C_4H_6O $$\bar{R} = \frac{0.0612}{6000 \times 0.9 \times 0.963} = 0.1177 \times 10^{-4}$$

H_2O $$\bar{R} = \frac{0.1274}{6000 \times 0.9 \times 0.963} = 0.2450 \times 10^{-4}$$

	y_i	$\bar{R}/y_i$
O_2	0.13	2.5946×10^{-4}
C_4H_{10}	0.0976	1.5861×10^{-4}
CO_2	0.0727	6.3216×10^{-4}
C_4H_6O	0.0186	6.3280×10^{-4}
H_2O	0.0318	7.2485×10^{-4}

Where r_{mA} : Molal reaction rate of component A per unit mass of catalyst particle

a_m : Specific surface area of catalyst

ϕ : Shape factor

G_m : Molal mass velocity of gas based on total cross section of catalyst bed.

Hence

$$r_{mA} = \frac{0.1105 - 0.0660}{0.5525} = 0.0805 \text{ moles / gm-catalyst}$$

$$a_m = 0.6 \text{ m}^2\text{/ gm.}$$

$$\phi = 0.9 \text{ (irregular gransles)}$$

$$G_m = 0.9024 / ((\pi / 4)x(2.54 \times 0.430)^2)$$

$$= 0.963 \text{ g-mole / hr-cm}^2$$

$$\bar{R} = 0.0805 / (6000 \times 0.9 \times 0.963)$$

$$= 0.3190 \times 10^{-4}$$

$$y_j = (y_{in} + y_{out}) / 2$$

Where y_j : average mole fraction

y_{in} : Feed mole fraction

y_{out} : Products mole fraction

COMPONENT	$\bar{R}$	y_j	$\bar{R}/y_j$	$(\Delta P_j / P_j)_{max}$
O_2	0.3290×10^{-4}	0.1300	2.5355×10^{-4}	0.05
N_2	/	0.6900	/	/
C_4H_8	0.1306×10^{-4}	0.0976	1.3403×10^{-4}	0.05
CO_2	0.1578×10^{-4}	0.0227	6.9600×10^{-4}	0.05
C_4H_6O	0.1291×10^{-4}	0.0186	6.9498×10^{-4}	0.05
H_2O	0.2691×10^{-4}	0.0338	7.9670×10^{-4}	0.05

b) Estimation of Temperature Drop From The Bulk Gas Phase To The Surface of The Catalyst From Experimental Run 176 .

Using the method of Yoshida, Ramaswami and Hougen(79) Q was obtained from the following expression:

$$Q = \frac{r_{mA} \quad H_A}{a_m \quad \phi \quad C_p \quad G_m}$$

where C_p = molal heat capacity

H_A = molal heat of reaction of component A.

The temperature drop, T, corresponding to the value of Q was obtained from T vs. Q charts.

COMPONENT	C_{pi} Cal / g-mole °C
O_2	7.41
N_2	7.11
C_4H_8	37.80
CO_2	11.5
H_2O	8.39
C_4H_6O	48.76

$C_p = Y_j\ C_i - 11.0027$

$H_A = 260{,}000$ Cal / g mole

$$Q = \frac{0.0805 \times 260000}{6000 \times 0.9 \times 11.0027 \times 0.9631}$$

$= 0.3630$

Temperature 410°C

External Diffusion: Effect of Feed Velocity on Oxidation of 2-methylpropene

Run No.	W / F	R	Feed Moles / hr		
			C_4H_8	O_2	N_2
234	2.5	2.0995	0.1105	0.2320	0.8754
253	2.5	2.0995	0.1876	0.3940	1.4850
254	2.5	2.0995	0.2412	0.5065	1.9200

Run No.	Products moles / hr					
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2
234	0.0776	0.1791	0.8754	0.0263	0.0531	0.0284
253	0.1310	0.2887	1.4850	0.0467	0.0849	0.0391
254	0.1718	0.3541	1.9200	0.0545	0.1074	0.0573

Run No.	% Selectivity	% Conversion	Total g-moles in feed / hr
	$S_{C_4H_6O}$	$X_{C_4H_8}$	$N_{C_4H_8} - N_{O_2} - N_{N_2}$
234	79.94	29.77	1.2179
253	82.51	30.18	2.0666
254	78.53	28.77	2.6675

Appendix G

Correlation of Initial Rate Data

Correlation of Initial Rate Data

Temperature °C	R	$(P_{C_4H_8})_o$, atm	r_o, g-mole/hr-gm
390	0.8995	0.1889	2.4812
390	1.1991	0.1482	1.5261
390	1.5014	0.1225	1.0377
390	1.7991	0.1043	0.7694
390	2.0995	0.0907	0.4079
390	2.4000	0.0815	0.3256
410	0.8995	0.1889	4.1468
410	1.1991	0.1482	1.5535
410	1.5014	0.1225	1.1930

...continuation...

Temperature ^{o}C	R	$(P_{C_4H_8})_o$,atm	r_o, g-mole/hr-gm
410	1.7991	0.1043	0.5882
410	2.0995	0.0907	0.4947
410	2.4000	0.0815	0.3256
460	1.1991	0.1482	2.1853
460	1.5014	0.1225	1.5268
460	1.7991	0.1043	0.6526
460	2.0995	0.0907	0.6452
460	2.4000	0.0815	0.4327
510	1.1991	0.1482	2.7141

...continuation...

Temperature ^{o}C	R	$(P_{C_4H_8})_o$,atm	r_0, g-mole/hr-gm
510	1.5014	0.1225	1.6684
510	1.7991	0.1043	0.8059
510	2.0995	0.0907	0.9668
510	2.4000	0.0815	0.7626
560	0.8995	0.1889	2.9985
560	1.1991	0.1482	1.9898
560	1.5014	0.1221	1.0714
560	1.7991	0.1043	0.9334
560	2.0995	0.0907	0.7483
560	2.4000	0.0815	0.6491